

RADIATION CHEMISTRY

THE RADIATION-INDUCED OXIDATION OF METHANOL
AND AQUEOUS 2-PROPANOL BY NITROUS OXIDE IN
ALKALINE SOLUTIONS

A thesis submitted to the Faculty
of Graduate Studies and Research, University
of Manitoba, in partial fulfillment of the
requirements for the degree of
MASTER OF SCIENCE

by

George Peter WOLLNER, B.Sc. (Hons.)

Winnipeg, Manitoba

August, 1971

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ACKNOWLEDGEMENTS

I especially wish to thank my supervisor, Dr. C.E. Burchill, for his guidance, helpful suggestions, and friendship during the course of my work.

I am grateful to Dr. J.B. Westmore and Mr. D.C.K. Lin who aided in the interpretation of mass spectral data. The assistance of other members of the Department of Chemistry of the University of Manitoba is appreciated.

I would also like to thank Miss M.F. Harvey for her patient typing of this work.

I am indebted to the University of Manitoba for financial assistance in the form of a demonstratorship and a Graduate Fellowship.

George P. Wollner

ABSTRACT

The radiation-induced oxidation of methanol and aqueous 2-propanol by nitrous oxide in alkaline solutions has been investigated extensively. A sigmoidal increase in product yields with increasing base concentration was observed.

At pH > 12.5 high acetone yields from 2-propanol indicate a chain reaction. A mechanism is proposed which includes H atom abstraction by O^- from both the α and the β carbons of 2-propanol, with 85% α attack calculated. Chain propagation occurs by the reaction of the 2-propanol radical anion $(CH_3)_2\dot{C}O^-$ with N_2O , with a rate constant calculated to be $(3.81 \pm 0.35) \times 10^4 M^{-1} s^{-1}$, and by conversion of the β 2-propanol radical $(CH_3CHOH\dot{C}H_2)$ to the α radical $((CH_3)_2\dot{C}OH)$ as the rate-determining step with a calculated rate constant of $431 \pm 27 M^{-1} s^{-1}$.

In contrast to 2-propanol, the results obtained are rationalized adequately by a reaction scheme employing a single radical species from methanol. The proposed mechanism involves rate-determining chain propagation by the reaction of the methanol radical anion $\dot{C}H_2O^-$ with N_2O with a calculated rate constant of $386 \pm 11 M^{-1} s^{-1}$ in alkaline pure methanol. The decrease in yields in going from methanol to water as solvent is construed as a decrease in the rate of the propagating reaction.

The proposed mechanisms are supported by the results obtained using selectively deuterated alcohols. Primary kinetic isotope effects are measured for H atom abstractions by O^- from both the α and the β positions of 2-propanol, giving calculated values of $k_{\alpha(H)}/k_{\alpha(D)} = 1.35 \pm 0.10$ and $k_{\beta(H)}/k_{\beta(D)} = 3.26 \pm 0.23$, and for the radical conversion reaction which involves H atom transfer, giving a value of $k_{(H)}/k_{(D)} = 10.7 \pm 5.6$. On substitution of CD_3OH for CH_3OH , no primary kinetic isotope effect is apparent.

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1. INTRODUCTION

Chemical reactions initiated by ionizing radiation comprise the subject of radiation chemistry. General discussions concerning the many aspects of radiation chemistry are given by Spinks and Woods (1), Allen (2), Vereshchinskii and Pikaev (3), and Swallow (4). The high energy radiation involved may be either corpuscular, such as fast neutrons, protons, α -particles, and β -particles, or electromagnetic, such as x-rays and γ -rays; the latter type of radiation from a Co^{60} source was utilized exclusively in the work presented here.

1.1 The Effects of Electromagnetic Ionizing Radiation on Matter

When electromagnetic ionizing radiation penetrates matter, three processes may occur as the photons lose their energy to the material absorber, namely Compton scattering, photoelectric absorption, and pair production.

The photoelectric effect occurs when the electron cloud of an atom absorbs an incident photon with the emission of an electron, usually from an inner shell, which carries away the energy of the photon less the electronic binding energy. For low energy radiation and elements of high atomic number this process predominates.

The Compton effect results from the scattering of an incident photon due to an inelastic collision with an electron which is subsequently ejected from an atom, the energy of the electron being the difference between the energies of the scattered and incident photons. This process is important at medium energies (several KeV to 2 MeV) and for elements of low atomic number. The predominant process when Co^{60} γ -rays, having energies of 1.17 MeV and 1.33 MeV, interact with water and aqueous systems and other

absorbers of low atomic number is Compton scattering.

Pair production entails the disappearance of a photon and the appearance of an electron and a positron which eventually annihilate each other to form two or three low energy photons. This process is only possible at photon energies exceeding 1.02 MeV and is of importance only at energies above 10 MeV. Hence pair production is insignificant in considering the effects of Co^{60} γ -rays.

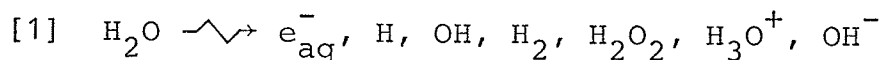
Electrons with various kinetic energies of large magnitude resulting from the photoelectric and Compton effect cause excitation and ionization of molecules leading to chemical reactions. These high energy electrons traverse the irradiated medium, slowly losing energy by interacting with the molecules of the medium to produce outer electrons either excited to higher energy levels or ejected from their atoms leaving behind positive ions.

The rate of energy loss from charged species such as electrons is known as the linear energy transfer (LET). The LET depends on the initial electron energy. As energy is dissipated along the track, the LET increases; the production of secondary electrons, with energies of at least 100 eV accounts for approximately half of the dissipated energy and forms branches from the main track known as δ -rays.

Energy losses averaging 40 eV account for the remainder of the events, producing "spurs", which in the first 10^{-16} seconds may be pictured as a cluster of excited molecules, electrons, and positive ions having a diameter of 10 to 20 Å. Although in closer proximity towards the end of the track where the electron energy is least, random distribution of the spurs along the electron track occurs. Consequent processes, dependent upon the particular absorbing medium involved, capture the attention of radiation chemists.

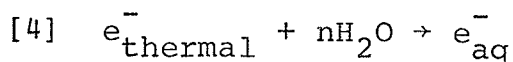
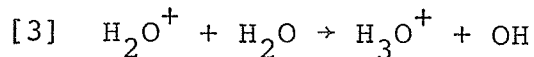
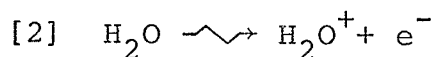
1.2 Primary Yields in Aqueous Radiation Chemistry

The primary products in the γ -radiolysis of aqueous systems existing after 10^{-8} seconds at the termination of spur reactions may be summarized by reaction 1.

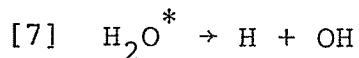
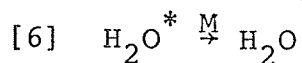
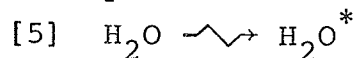


A brief outline of the origin of these products now follows.

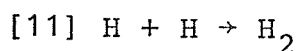
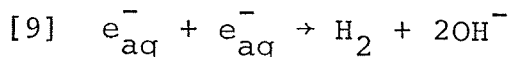
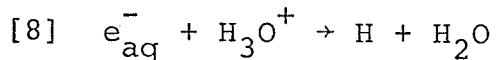
A characteristic process of radiolysis is ionization, occurring in 10^{-16} seconds, followed by solvent interaction to yield OH radicals and moderation of the approximately 40 eV electrons (e^-) to sub-excitation energies, and then to thermal energies in about 10^{-13} seconds; finally hydration of the electrons occurs in about 10^{-11} seconds.

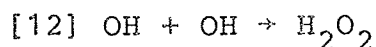


Alternately, water may be excited and either quenched or decomposed to H and OH radicals in about 10^{-13} seconds.



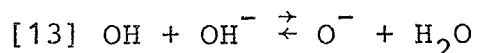
Secondary spur reactions lead to all the other products indicated in equation 1.



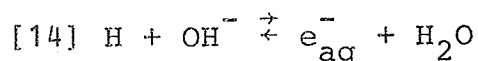


Afterwards these species diffuse into the bulk solution where interaction with additional solutes may occur. The hydrogen atom is capable of behaving as either a reducing or an oxidizing agent, e_{aq}^- generally behaves as a reducing agent, while OH acts always as an oxidizing agent. Reactions of e_{aq}^- and other primary species are detailed by Hart and Anbar (5).

In alkaline solutions OH radicals can be present as the basic form O^- with $k_{13} = 10^8 \text{ M}^{-1} \text{ s}^{-1}$ (6) and $\text{pK}_{13} = 11.9 \pm 0.2$ (6).



Although OH and O^- react differently in electron abstraction reactions, both are reported by Rabani (7) to be about equally efficient in hydrogen atom abstractions. Hydrogen atoms from the radiolysis of water are converted into hydrated electrons in alkaline solutions with $k_{14} = (1.8 \pm 0.6) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ (8) and $\text{pK} = 9.6$ (9).



The radiation chemical yield or G-value of any species is defined as the number of molecules, ions, or radicals formed or converted per 100 eV of absorbed energy. The symbol G_x refers to the primary yield of a reactive intermediate; the symbol $G(X)$ denotes the yield of a permanent experimentally determined product. The units of G-values are conventionally omitted.

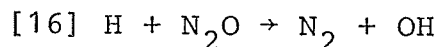
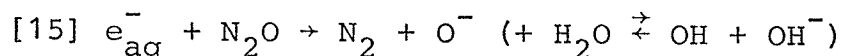
Product yields may vary with pH as a result of the acid-base equilibria of some radicals. For instance, in strongly acidic media few e_{aq}^- can diffuse far from their origins before reacting with H_3O^+ , and the chemistry involves H and OH. In strongly alkaline solution where H is changed to e_{aq}^- and OH ionizes, the chemistry involves e_{aq}^- and O^- .

All species are likely to contribute to reactions at intermediate pH's.

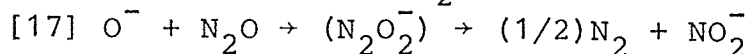
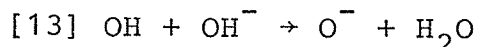
A great deal of effort has been devoted to the radiation chemistry of acidic and neutral aqueous solutions but comparatively little has been done with alkaline solutions. A brief survey of the pertinent work that has been performed using principally nitrous oxide as an electron scavenger is now presented.

1.3 Radiation Chemistry of Aqueous Systems containing Nitrous Oxide and Alkali

Dainton and Peterson (10) have shown that nitrous oxide readily scavenges and reacts with hydrated electrons with $k_{15} = 5.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (11) but reacts comparatively ineffectively with H atoms with $k_{16} \leq 10^5 \text{ M}^{-1} \text{ s}^{-1}$ (11).



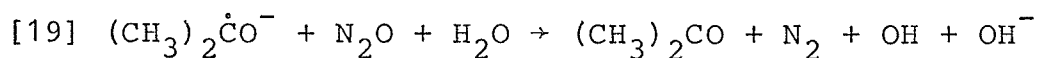
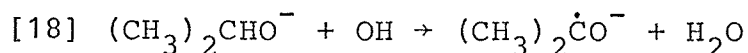
As they increased the pH of a γ -irradiated aqueous solution of 0.014 M N_2O from 0.1 to 4, they found that $G(\text{N}_2)$ rose sigmoidally from 0.75 to 3.1 and remained constant up to pH 11.2 where $G(\text{N}_2)$ increased sharply by about one unit. This step at pH 11.2 in the plot of $G(\text{N}_2)$ vs. pH was attributed to the ionic dissociation of the hydroxyl radical followed by reaction 17.



However, no evidence in support of reaction 17 exists.

Scholes, Simic, and Weiss (12) have determined the yields of products from linear yield-dose plots as a function of solute concentration and pH in aqueous solutions of various aliphatic alcohols irradiated by Co^{60} γ -rays. Their results indicated a high specificity

of nitrous oxide towards e_{aq}^- and demonstrated the existence and reactions of two reducing species. They found that in alkaline solutions of 1.6×10^{-2} M nitrous oxide and 2-propanol a radiation-induced chain reaction leading to high yields of acetone and nitrogen was exhibited; at pH 13 a value of $G(N_2) \approx 50$ was obtained. They assumed that the 2-propanol radical anion was formed and could interact with nitrous oxide to give an oxidizing radical.



The disproportionation of two alcohol radicals to give acetone and 2-propanol was then responsible for chain termination.

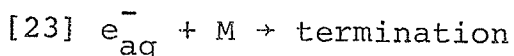
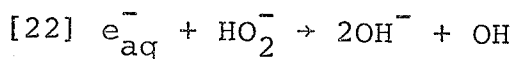
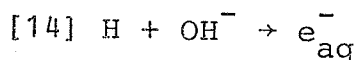
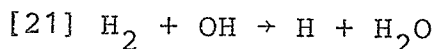
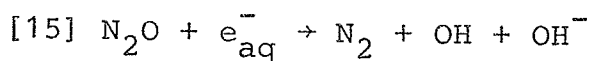
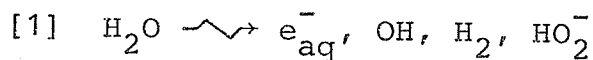
Using 2.5 MeV electrons for irradiation, Allan and Beck (13) measured product yields from deaerated aqueous solutions of 2-propanol containing nitrous oxide and found that the high yields of nitrogen indicated a chain reaction in alkaline solutions. At pH ≈ 5 for 10^{-2} M 2-propanol solutions containing 10^{-2} M N_2O , $G(N_2)$ was measured to be 2.98 while in the presence of 0.1 N NaOH (pH ≈ 13) $G(N_2)$ was found to be 10.6. The high yields of nitrogen were attributed to the interaction of nitrous oxide with the radical produced from the 2-propanol anion. They postulated the same reactions 18 and 19 proposed by Scholes, Simic, and Weiss (12). The $G(N_2)$ values obtained by Allan and Beck do not satisfy the simple kinetic relationship 20 derivable from the above two reactions 18 and 19 and from the bimolecular termination of $(CH_3)_2\dot{C}O^-$.

$$[20] \quad G(N_2) = G(e_{aq}^-) + \frac{k_{18}[N_2O] \cdot \sqrt{G_{e_{aq}^-} + G_{OH}}}{\sqrt{2k_t \cdot D}}$$

where D is the dose rate. This discrepancy was attributed to the fact that only 87% of the 10^{-2} M 2-propanol was present as the 2-propanol anion at pH 13 as found by Wells (14). More recently however, Murto (15) has shown that

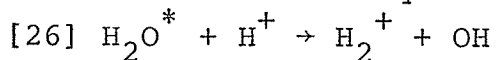
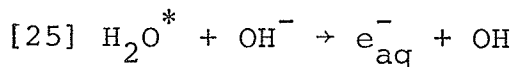
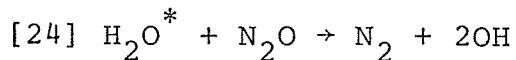
the pK of 2-propanol is 17.1 so that reactions involving the 2-propanol anion are improbable at pH 13.

Studying mixtures of N_2O and H_2 , Cheek and Swinnerton (16) found that nitrous oxide oxidized H_2 by a radiation-induced chain reaction which proceeded moderately at neutral pH and quite efficiently but with strong pH dependence above pH 12; no chain reaction was observed in strongly acid solution. The mechanism proposed in strongly alkaline solution included reactions 15, 21, and 14 which constituted a chain sequence in which the oxidation of H_2 by nitrous oxide was greatly enhanced as the pH became sufficiently high for reaction 14 to compete effectively for H atoms. Chain termination was considered to be brought about by impurities.

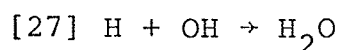
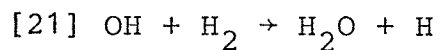
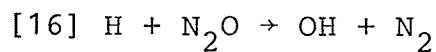


The terminating reactions with impurities, predominating over radical-radical combination, were said to account for the fact that their yields in neutral and alkaline solutions were unaffected by variation in the dose rate. They offered an alternate interpretation to Dainton and Peterson (10) of the sigmoid increase in $G(N_2)$ at high pH in irradiated nitrous oxide solutions, suggesting that oxygen produced in the radiolysis of nitrous oxide solutions prevented the net reaction between N_2O and H_2 in neutral solution but allowed G_{H_2} to contribute to $G(N_2)$ in strongly alkaline solution, thus accounting in part for the observed increase in $G(N_2)$ at high pH.

Buxton and Dainton (17) found that increasing the pH of γ -irradiated aqueous solutions of potassium iodide containing nitrous oxide increased $G(N_2)$ from 0.25 at pH 0.1 to 3.2 at pH 4; $G(N_2)$ remained constant at 3.2 up to pH 10.8 where it increased to 4 at pH 14. $G(I_2)$ decreased from 1 at pH 0.1, passed through a minimum of 0.65 at pH 1.1, increased to a constant value of 2.3 over the range $4 < \text{pH} < 11$, and finally increased to 3.8 at pH 14. These results were interpreted on the basis that $G_{e_{aq}^-}$ and G_H remained constant over the entire pH range, that excited water molecules were formed which could react with N_2O via reaction 24, with OH^- via reaction 25, with H^+ via reaction 26, and that O^- , OH , and H_2^+ oxidized iodide ions whereas H reduced I_3^- .

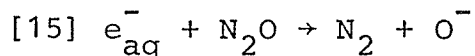
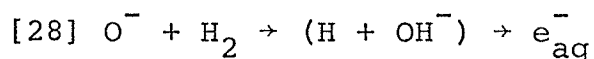
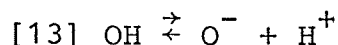


Dainton and Walker (18) found that irradiation of aqueous solutions containing N_2O and H_2 induced a short chain reaction at $\text{pH} < 10$ with $G(N_2)$ increasing with increasing H_2 or N_2O concentration, but essentially independent of pH. Chain propagation was thought to be by reactions 16 and 21 with termination in ~ 0.1 msec by cross-termination reaction 27 within the same track or spur.



Between pH 10 and 13 $G(N_2)$ rose from approximately 15 to 60 but above pH 13 was again independent of pH and also of dose rate and nitrous oxide concentration, but proportional to H_2 concentration. The pH effect was attributed by them

to reaction 13 followed by reaction 28 with reaction 15 being the non-rate-determining propagation step; termination occurred by mutual interaction of O^- radicals within the same track.



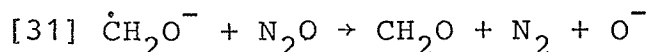
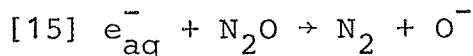
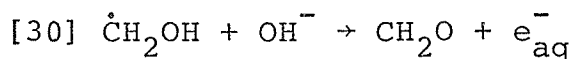
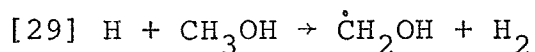
At pH 13.9, $G(N_2)$ was found to be independent of nitrous oxide pressure within the range 295 to 400 mm Hg although proportional to nitrous oxide concentration at natural pH. These results indicated that while H_2 was involved in a rate-determining process at both high and low pH, nitrous oxide was only involved in rate determination at $pH < 10$ and not at $pH \geq 13$.

These findings were contrary to those of Cheek and Swinnerton (16) who did not observe any chain reaction in the pH range 10.5 to 12, any chain reaction at pH 1, and a chain length independent of pH at $pH > 13$, and whose mechanism predicted that $G(N_2)$ should depend upon nitrous oxide concentration but not on H_2 concentration. No evidence was presented concerning the lack of nitrous oxide concentration dependence, and their data indicated dependence on H_2 , as found also by Dainton and Walker (18).

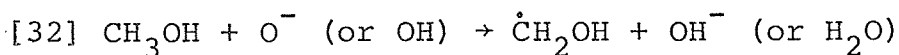
Dainton and Rumfeldt (19) γ -irradiated aqueous alkaline solutions ($pH > 10.4$) of sodium tellurite containing nitrous oxide and measured $G(H_2)$, $G(N_2)$, $G(H_2O_2)$ and $G(Te^{VI})$ at different doses. Their results indicated that an increase in pH in the range 11 to 14 did not change $G(H_2)$ or $G(H_2O_2)$ but caused all other reducing and oxidizing radical yields to increase by one unit.

Dainton and Fowles (20) recorded quantum yields of N_2 and H_2 for the photolysis at 1849 Å of aqueous alkaline solutions 0.02 M in methanol and containing

nitrous oxide in sufficient concentration to scavenge all e_{aq}^- . A chain mechanism was indicated. The hydrogen yields were found to increase with increase in NaOH concentration while the nitrogen yields passed through a maximum at $[OH^-] \approx 10^{-3}$ M. The increase in rate of N_2 production as the OH^- concentration was increased above 10^{-4} M, observed only with methanol present, was attributed to a chain oxidation of methanol similar to that reported for 2-propanol by Scholes, Simic, and Weiss (12) and by Allan and Beck (13). The radical $\dot{C}H_2OH$, formed by hydrogen atom abstraction from methanol, was said either to lose a hydrogen atom to OH^- forming e_{aq}^- (via reaction 30) which then reacted with nitrous oxide according to equation 15, or to lose a proton leaving the radical anion $\dot{C}H_2O^-$ which could react with nitrous oxide via equation 31.



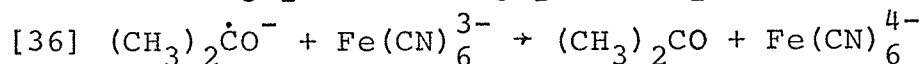
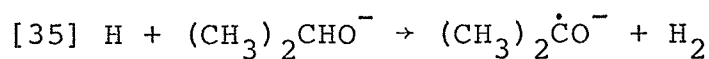
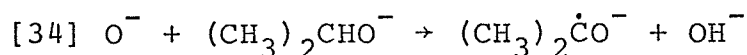
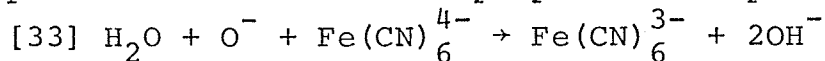
In either event the O^- ions or the OH radicals formed by protonation of O^- were said to propagate the chain by reacting with methanol according to reaction 32.



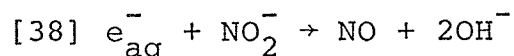
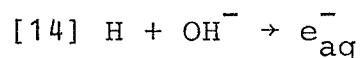
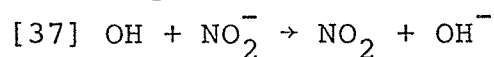
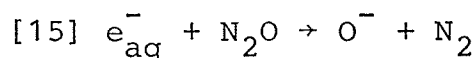
The cause of the maximum in the rate of formation of N_2 at pH 11 and the subsequent diminution in rate at higher pH was unknown, but perhaps due to carbonate impurity in the alkali. The mechanism given was considered to be incomplete.

Dainton, Gibbs, and Smithies (21) x-irradiated deaerated solutions of several solutes containing nitrous oxide. In solutions of 2-propanol and nitrous oxide at pH 13 high yields of N_2 were formed by a chain process,

$G(N_2)$ increasing with increasing 2-propanol and nitrous oxide concentration. The results at 0.1 M 2-propanol and 0.015 M nitrous oxide agreed well with others (12, 13). In aqueous solutions of 0.1 M $Fe(CN)_6^{4-}$ and concentrations of 2-propanol in the range 0.19 to 0.93 M at pH 13 the following reactions involving conversion of OH to O^- and partial ionization of 2-propanol were postulated.



Alkaline solutions of nitrite ions were irradiated in the presence of nitrous oxide and the following mechanism proposed at pH > 12.

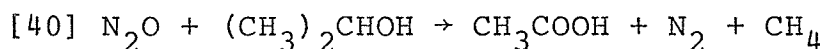
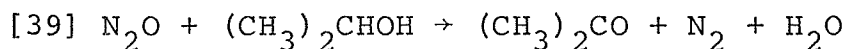


$G(N_2)$ increased with increasing pH. They found that in solutions of ferrocyanide ions, $G(Fe^{III})$ increased with increasing pH in the range 11 to 13.5 and with increasing ferrocyanide ion concentration in the range 5×10^{-4} to 10^{-1} M.

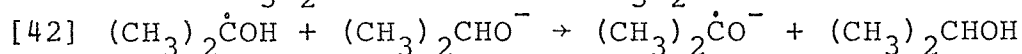
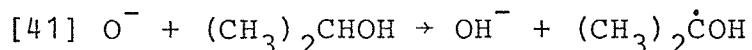
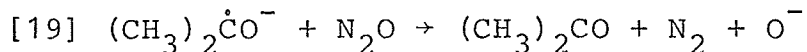
Dainton and Rumfeldt (22) γ -irradiated aqueous solutions of $Ir^{III} + Ir^{IV} + N_2O$ and $Pt^{II} + N_2O$. They found that the yields of reducing and oxidizing radicals increased with increasing pH in the alkaline pH range. A linear plot of $1/G(N_2)$ vs. $1/[N_2O]$ gave an intercept such that $G^\infty(N_2)$ was calculated to be 3.50 ± 0.2 . A postirradiation reaction involving nitrous oxide and producing N_2 , with the "excess" amount of N_2 being proportional to irradiation time, was reported; suppression

of this effect was possible by preventing the entrance of daylight into the reaction vessel.

Sherman (23) has studied the Co^{60} γ -radiolysis of 2-propanol solutions of KOH and nitrous oxide and identified nitrogen, methane, acetone and potassium acetate as products. Substitution of potassium 2-propoxide or NaOH for KOH had no effect on the nature and yields of the products. The yields were found to be independent of base concentration when $[\text{KOH}] > 2 \times 10^{-2}$ M but were proportional to the concentration of nitrous oxide. The high limiting value of $G(\text{N}_2) = 3.5 \times 10^3$ at $[\text{N}_2\text{O}] = 5 \times 10^{-2}$ M and a dose rate of 7.2×10^{16} $\text{eV l}^{-1} \text{min}^{-1}$, and the high yields in general, indicated a chain mechanism. The yields of nitrogen and acetone were always of the same order of magnitude while the ratio of $G(\text{N}_2)$ to $G(\text{CH}_4)$ remained essentially constant at 14 ± 2 . These observations suggested that nitrogen and acetone had their origins in a common intermediate while the minor product methane, and presumably potassium acetate, were formed by a side reaction according to the stoichiometry of reactions 39 and 40.



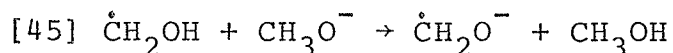
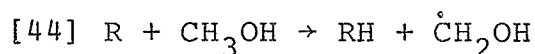
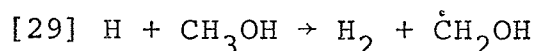
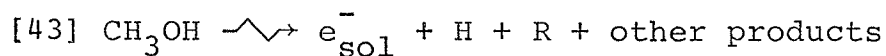
The chain reaction was not observed under acid or neutral conditions so that an anionic chain carrier, $(\text{CH}_3)_2\dot{\text{C}}\text{O}^-$, was suggested in strongly alkaline solutions. The following propagating reactions were proposed to account for the formation of nitrogen and acetone.



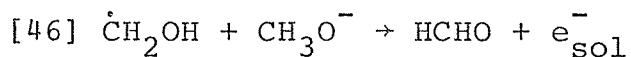
Bimolecular termination was indicated by the observed

dependence of the yields on the reciprocal of the square root of the dose rate. Acetone in small initial concentrations was reported to retard and inhibit the chain. Postirradiation yields were noted; the yields of gaseous products when the irradiated sample was plunged into liquid air immediately after removal from the radiation source and kept frozen until analysis were considerably less than those obtained from a solution allowed to stand at room temperature prior to freezing for product analysis.

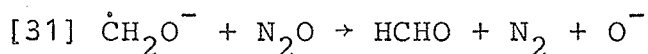
The γ -radiolysis of methanol solutions containing nitrous oxide and potassium hydroxide was also investigated by Sherman (24). The yields of the three products N_2 , H_2 , and CH_4 were found to increase markedly with increasing base concentration up to a limit indicating the occurrence of a chain mechanism in alkaline solution involving the anionic species $\dot{C}H_2O^-$. Dependence upon the reciprocal of the square-root of the dose rate indicated bimolecular termination. Reaction 43, with R being any species capable of undergoing a hydrogen abstraction reaction with the solvent, was proposed to initiate the chain.



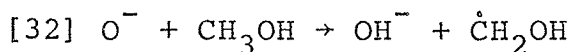
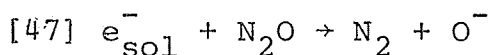
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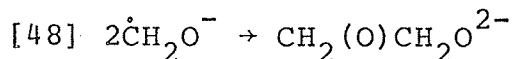
Chain propagation involved N_2O , $\dot{\text{C}}\text{H}_2\text{O}^-$, and O^- .



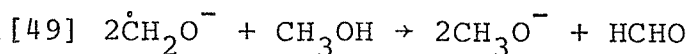
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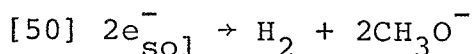
Termination occurred according to the following reactions.



and/or



and/or



Reaction 50 is most unlikely in view of the relatively large nitrous oxide concentration which causes reaction 47 involving e_{sol}^- and N_2O to be preferable. A chain propagation step analogous to reaction 31 was previously proposed by Scholes, Simic, and Weiss (12). Dainton and Fowles (20) also wrote reaction 31 as a propagating step in their study of the light-induced chain oxidation of methanol by nitrous oxide in alkaline aqueous solutions.

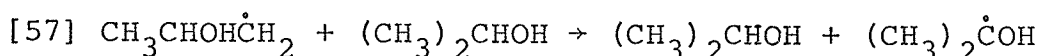
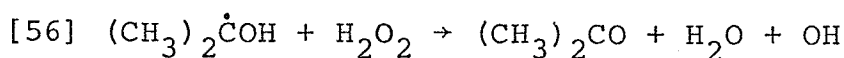
The review just presented has served to underline several points. In general, the systems that have been investigated demonstrate increased radical yields with increase of solute concentration and at $\text{pH} > 11$. Certain chain reactions which proceed strongly in alkaline solution proceed only slowly or not at all in neutral or acid solutions. Systems containing nitrous oxide generally indicate higher radical yields at high pH than those which do not contain this solute. Although there is general agreement qualitatively, there are conflicts in quantitative results and the mechanisms presented are controversial and in need of clarification, particularly concerning the nature of the intermediates and the roles they play in alkaline systems.

1.4 Scope and Purpose of this Work

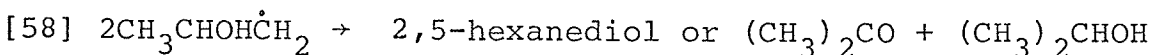
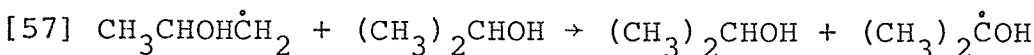
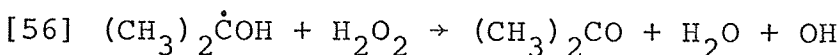
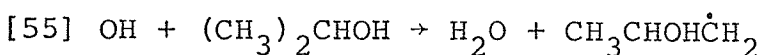
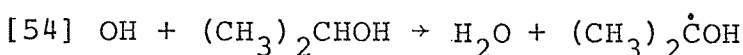
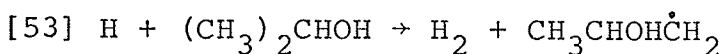
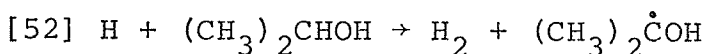
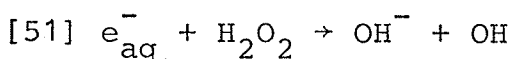
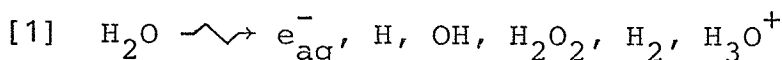
Previous work in this laboratory (25, 26, 27) has dealt with the radiation chemistry of deaerated neutral aqueous solutions of alcohols using hydrogen

peroxide as an oxidant.

Burchill and Ginns (25) found that 2-propanol was oxidized to acetone and hydrogen peroxide was reduced in stoichiometrically equivalent high yields under γ -irradiation. To explain the results, a mechanism was invoked with initiation by hydrogen atom abstraction to form either $\text{CH}_3\text{CHOH}\dot{\text{C}}\text{H}_2$, which could abstract the α hydrogen from the parent alcohol as in reaction 57, or $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$ which could react with H_2O_2 in the chain propagating reaction 56.



Their complete reaction scheme is summarized below together with expressions for $G(\text{acetone})$ and $G(-\text{H}_2\text{O}_2)$.



$$[59] G(\text{acetone}) = \left[G_{\text{H}} \left\{ \frac{k_{52}}{k_{55}} \left(\frac{k_{54} + k_{55}}{k_{52} + k_{53}} \right) \right\} + \frac{k_{54}}{k_{55}} (G_{e_{\text{aq}}^-} + G_{\text{OH}}) \right] + \left(1 + \frac{k_{54}}{k_{55}} \right) k_{57} \sqrt{\frac{G_{\text{R}}}{2k_{58} \cdot D}} [(\text{CH}_3)_2\text{CHOH}]$$

where $G_{\text{R}} = G_{e_{\text{aq}}^-} + G_{\text{H}} + G_{\text{OH}}$ and D is the dose rate in units of $6.023 \times 10^{25} \text{ eV l}^{-1} \text{ s}^{-1}$.

$$[60] \quad G(-H_2O_2) = G(\text{acetone}) + G_{e_{aq}} - G_{H_2O_2}$$

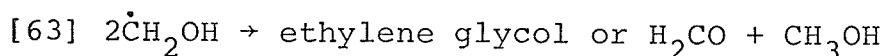
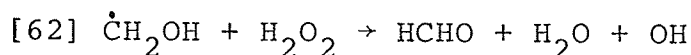
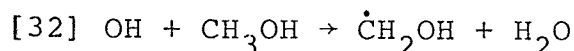
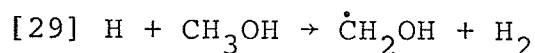
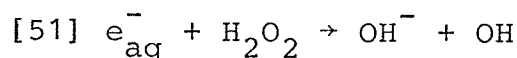
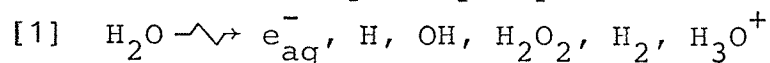
The mechanism predicted a linear dependence of the yields on 2-propanol concentration and on the reciprocal of the square-root of the dose rate, no dependence on hydrogen peroxide concentration, and a non-zero intercept at zero alcohol concentration. The experimental results conformed to these mechanistic predictions in alcohol concentrations up to 1.0 M and H_2O_2 concentrations in the range 10^{-2} to 10^{-3} M, except that though the yields decreased with increasing dose rate, they were not the predicted linear function of $1/\sqrt{D}$. A competing reaction such as that of H_2O_2 with the radical $CH_3CHOH\dot{C}H_2$ was suggested.

As the concentration of 2-propanol was increased above 1.0 M, $G(\text{acetone})$ increased more slowly, levelled off at 3.7 M, and above 4.0 M decreased to a limit of $G(\text{acetone}) = 16 \pm 1$ in pure 2-propanol. At a constant concentration of 0.52 M 2-propanol, $G(-H_2O_2)$ was found to become dependent on hydrogen peroxide concentration below 10^{-3} M and essentially first-order in hydrogen peroxide below 10^{-4} M. This was interpreted as an indication of reaction 56 becoming sufficiently slow to be rate-determining.

The radiation-induced oxidations of neutral aqueous solutions of ethanol and methanol by hydrogen peroxide were investigated by Burchill and Ginns (26) to test the generality of the mechanism proposed for 2-propanol. As expected, the results with ethanol were analogous to those with 2-propanol while methanol offered a contrast; the yields from methanol depended linearly on the concentration of hydrogen peroxide, were independent of methanol concentration up to 2.0 M, and depended linearly on the reciprocal of the square-root of the dose rate (equation 61).

A simple reaction mechanism involving the

formation of a single radical, $\dot{\text{C}}\text{H}_2\text{OH}$, from methanol was proposed which adequately explained the results obtained.



$$[61] \quad \frac{-d[\text{H}_2\text{O}_2]}{dt} = \left\{ G_{e_{\text{aq}}^-} - G_{\text{H}_2\text{O}_2} \right\} D + k_{62} \sqrt{\frac{(G_{e_{\text{aq}}^-} + G_{\text{H}} + G_{\text{OH}}) \cdot D}{2k_{63}}} [\text{H}_2\text{O}_2]$$

Strong support for the proposed mechanism came from kinetic isotope studies by Burchill and Thompson (27). Using selectively deuterated alcohols, they unequivocally demonstrated the occurrence of hydrogen abstraction from both the α and the β positions of 2-propanol and ethanol in the radiation-induced chain oxidation of these alcohols. No primary kinetic isotope effect was discernable upon substitution of CD_3OH for CH_3OH .

An extension of the study of the radiation-induced oxidation of alcohols into alkaline solutions seemed appropriate. An endeavour has been made to clarify the radiation chemistry of the alkaline aqueous 2-propanol and methanol systems oxidized by nitrous oxide, hydrogen peroxide being unstable above pH 11. Primary kinetic isotope effects were studied to confirm the experimental findings. In light of the experimental evidence, mechanisms are set forth employing reasonable assumptions and evaluated as to their applicabilities. A comparison of the numerical results obtained in alkaline solution to those obtained previously in neutral solution is presented in the final section.

2. EXPERIMENTAL

2.1 Materials

Triply distilled water, used in the preparation of all irradiated solutions, was produced from distilled water from the tap by further distillation from alkaline potassium permanganate and then from acidic potassium dichromate through 60 cm columns in an all Pyrex glass system as described by Hickling (28).

2-propanol (Fisher Certified Reagent) was used without further purification in the preparation of stock solutions.

Methanol (Fisher Certified Reagent and Matheson, Coleman and Bell) was used as received for stock solution preparations.

Sodium hydroxide (Fisher Certified Reagent) was used to make basic solutions for irradiation and analysis.

Potassium hydroxide (Fisher Certified Reagent), assumed to contain 15% water, was used to make basic solutions of high methanol concentration.

Sodium methoxide (Anachemia Chemicals Ltd.) was used to make alkaline one solution containing pure methanol.

Borax (sodium borate) (Shawinigan Chemicals) was used to prepare solutions buffered to pH 9.2.

Sodium carbonate (Anachemia Chemicals Ltd.) was added to one solution to check the effects of carbonate impurity present in NaOH and KOH.

Acetone (Baker Analyzed Reagent, Spectrophotometric) was doubly distilled and used in calibration and inhibition studies.

Formaldehyde (U.S.P. 40% W/V) was used as received for calibration. The concentration of formaldehyde was verified by the method of Donnally (29).

Salicylaldehyde (Fisher Certified Reagent) was used as received in the analysis for acetone.

Chromotropic acid (Eastman Organic Chemicals) was used as received in formaldehyde analysis.

Ferrous ammonium sulfate, $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$, (Fisher Certified Reagent) was used as received in dosimetry.

Sulfuric acid (Baker Analyzed Reagent, Spectrophotometric) was used as received in the analysis of formaldehyde and in dosimetry.

Nitrous oxide (Matheson, Anaesthetic Grade) was freed from carbonates by passage through a column of KOH pellets and from non-condensable gases by three cycles of freezing-pumping-thawing before addition to samples on a vacuum line.

1,1,1,3,3,3-d₆-2-propanol ($(\text{CD}_3)_2\text{CHOH}$), 2-d₁-2-propanol ($(\text{CH}_3)_2\text{CDOH}$), d₃-methanol (CD_3OH), and deuterium oxide (Merck, Sharp and Dohme), guaranteed to be of 99% isotopic purity, were used as received to prepare solutions containing deuterated alcohols.

O-deutero-2-propanol ($(\text{CH}_3)_2\text{CHOD}$) was prepared by dissolving $(\text{CH}_3)_2\text{CHOH}$ in deuterium oxide.

2.2 Irradiation and Dosimetry

All irradiations were performed on a Co^{60} Gammacell 220 installed by Atomic Energy of Canada Ltd. (AECL). This source emits γ -rays of average energy 1.25 MeV. Samples were placed into the cylindrical chamber of 8 inch height and 6 inch diameter. The dose received by samples being irradiated was a function of position inside the chamber as indicated by the isodose curves provided by AECL. Attenuation of the dose rate to a nominal 45, 30, and 10% was attained by the placement of lead shields provided with the Gammacell inside the sample chamber.

Dose rates were determined by the Fricke dosimeter employing an aerated solution of 10^{-3} M ferrous ammonium sulfate in 0.4 M sulfuric acid. 10 ml aliquots of the dosimeter solution were irradiated for various times. Fe^{2+} was oxidized to Fe^{3+} and its concentration measured at room temperature relative to a reagent blank at $\lambda = 304$ nm on a Carl Zeiss PMQ II spectrophotometer; $G(\text{Fe}^{3+}) = 15.6$ (30) and an extinction coefficient $\epsilon = 2201 \text{ M}^{-1} \text{ cm}^{-1}$ were assumed. The dose rates were checked periodically but in general a monthly correction was applied to the dose rate according to the decay characteristics of Co^{60} . Table 2.1 lists the dose rates determined experimentally. The dose rates were also determined at various positions inside the chamber and were found to agree with the isodose chart, emphasizing the necessity for reproducible positioning of samples.

TABLE 2.1

Dose rates determined by Fricke dosimetry.

Nominal Attenuation (%)	Dose Rate ($\text{eV l}^{-1} \text{ s}^{-1}$)
Unattenuated	1.16×10^{19}
45	4.56×10^{18}
30	3.12×10^{18}
10	1.02×10^{18}

Compton scattering being the prime mode of absorption of γ -radiation, the actual dose absorbed by a solution was taken to be proportional to its electron density. Sample calculations of true absorbed dose rates calculated from the dose rate measured by the Fricke dosimeter are given by Hickling (28).

2.3 Apparatus and Sample Preparation

All glassware was cleaned carefully with either

permanganic or chromic acid, rinsed with water, allowed to stand with concentrated nitric acid containing a small amount of hydrogen peroxide, thoroughly rinsed with distilled water and then triply distilled water, and allowed to dry. Whenever possible, stock solutions were prepared using fresh triply distilled water, degassed, irradiated, and analyzed on the same day. Generally, solutions were prepared in volumetric flasks by pipetting in the appropriate amount of alcohol and weighing in the base. Sodium hydroxide was used to make alkaline 2-propanol solutions and methanol solutions up to 0.2 mole fraction methanol; owing to the limited solubility of NaOH, solutions concentrated in methanol were made basic with potassium hydroxide. Alkaline solutions were unbuffered except solutions of pH 9.2 which were prepared by using a borax buffer. All pH's of solutions were calculated from the mass of base added and checked on a Coleman Metrion Model 28 AC pH meter equipped with a glass electrode. Calculated and measured pH's were found to agree within ± 0.2 pH units at $\text{pH} > 12$ and within ± 0.1 pH units at $\text{pH} \leq 12$.

Aliquots of the stock solution were pipetted into irradiation bulbs to be described below and degassed on a vacuum line using four freeze-pump-thaw cycles. All vacuum seals were made with Apiezon N grease. Either a carbon dioxide/acetone slurry or a liquid nitrogen bath was used to freeze the samples. Nitrous oxide was introduced into the samples by either equilibration at 26°C or freezing with liquid nitrogen. Pressures were measured by means of a mercury manometer. Appendix II details the calculation of nitrous oxide concentrations.

Irradiation bulbs were of two types depending upon the nitrous oxide plus vapour pressures within. At pressures below one atmosphere, demountable Pyrex irradiation bulbs and taps as described by Hickling (28) were used. This type of bulb, into which 10 ml of stock solution was

pipetted, was used in all work with methanol and in low pressure work with 2-propanol. At pressures above one atmosphere, 25 ml bulbs with constrictions were used into which nitrous oxide was frozen from a 200 ml bulb on the vacuum line containing nitrous oxide to a measured pressure. After freezing, these bulbs, containing 5 ml of stock 2-propanol solutions, were permanently sealed by closing off their constrictions.

Samples were reproducibly positioned in the Gammacell chamber using holders described by Hickling (28) and irradiated for specific times controlled by the automatic timer of the Gammacell. All irradiations were performed at the ambient temperature of the Gammacell. No attempt was made to thermostat the samples inside the chamber since irradiation times were usually brief and the liquid surface undisturbed while being irradiated.

To conserve deuterated methanol, KOH was added directly to 5 g of CD_3OH in a sample bulb which was then degassed, equilibrated with nitrous oxide, irradiated, and analyzed by withdrawal of a 200 μl sample. This same solution was subsequently degassed, equilibrated, irradiated, and analyzed by the same procedure repeated four times to obtain a yield-dose plot.

2.4 Analyses

Product analyses were performed spectrophotometrically at room temperature on a Carl Zeiss PMQ II spectrophotometer using unthermostated 1.000 cm cells.

Acetone was analyzed by the salicylaldehyde method of Berntsson (31). 1 ml NaOH (212.5 g/500 ml), 1 ml sample, 250 μl salicylaldehyde, and 10 ml NaOH were sequentially pipetted into a 25 ml volumetric flask subsequently filled to the mark with triply distilled water. The samples were shaken, allowed to develop colour

for two hours, and their absorbances measured at $\lambda = 474$ nm relative to a reagent blank. A calibration using various aliquots of acetone gave an extinction coefficient $\epsilon = 1.78 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$. This value agrees favourably with the values found by Ginns (32) and Hickling (28). Fig. 2.1 shows the Beer-Lambert plot for acetone and the linear concentration range.

Formaldehyde was determined by a minor modification of the chromotropic acid method of Bricker and Johnson (33). 500 μl sample, 250 μl chromotropic acid, and 3 ml concentrated sulfuric acid were carefully pipetted into test-tubes which were stoppered and placed into a beaker of boiling water for 30 minutes. The samples were then cooled, diluted to twice their volumes, cooled again, and transferred quantitatively into 25 ml volumetric flasks which were subsequently filled to the mark with triply distilled water. The absorbances of the samples were read against a reagent blank at $\lambda = 570$ nm. Various aliquots of a stock formaldehyde solution were used for calibration, linear over the concentration range shown in Fig. 2.2. From this Beer-Lambert plot $\epsilon = 1.51 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ was calculated in good agreement with the values determined by others (32, 34).

Mass spectrometric analysis for methane was accomplished on a Hitachi Perkin Elmer RMU-6D mass spectrometer.

FIG. 2.1

Beer-Lambert relationship for
acetone. Salicylaldehyde method.

$$\lambda = 474 \text{ nm}$$

FIG. 2.1

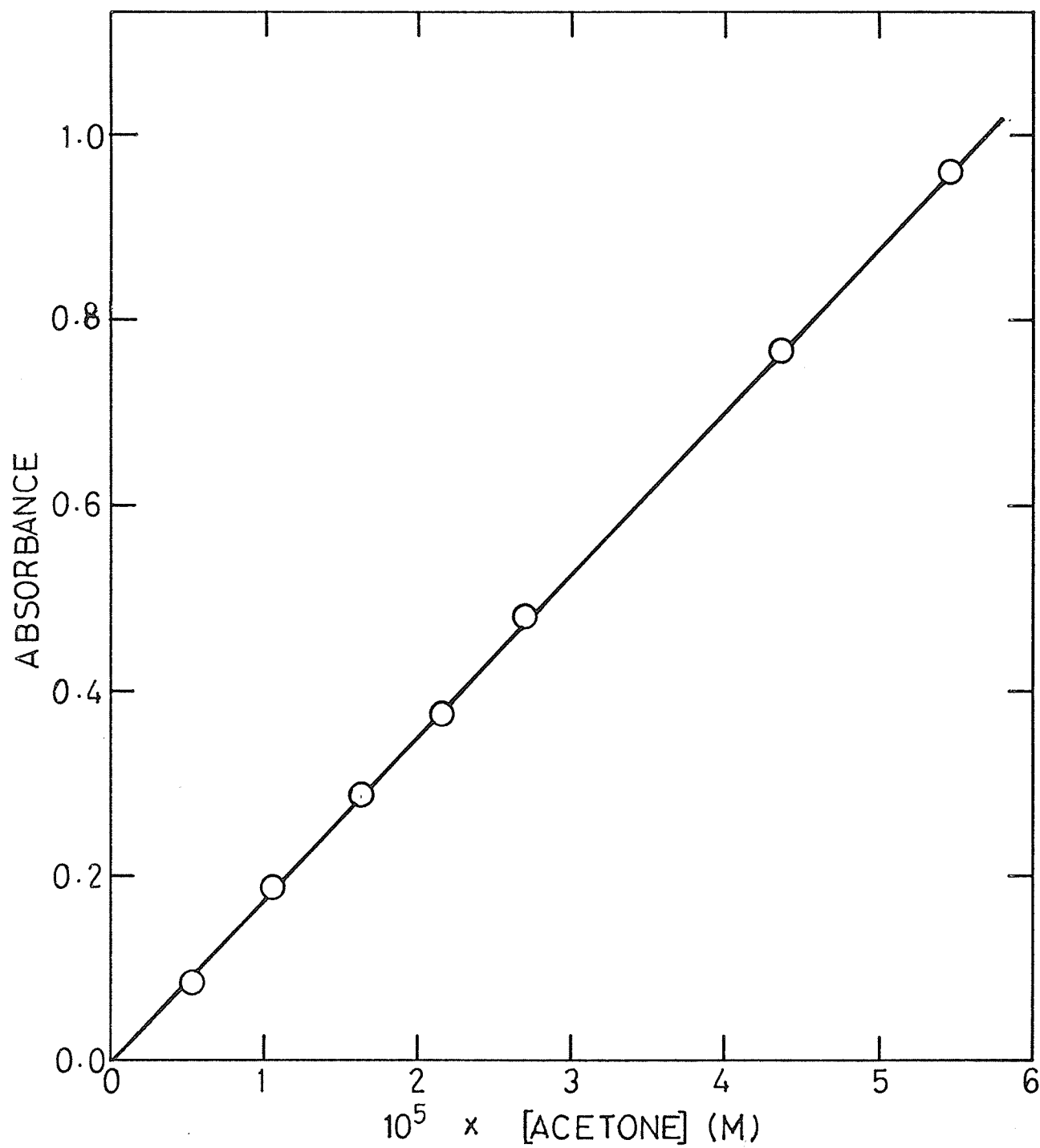
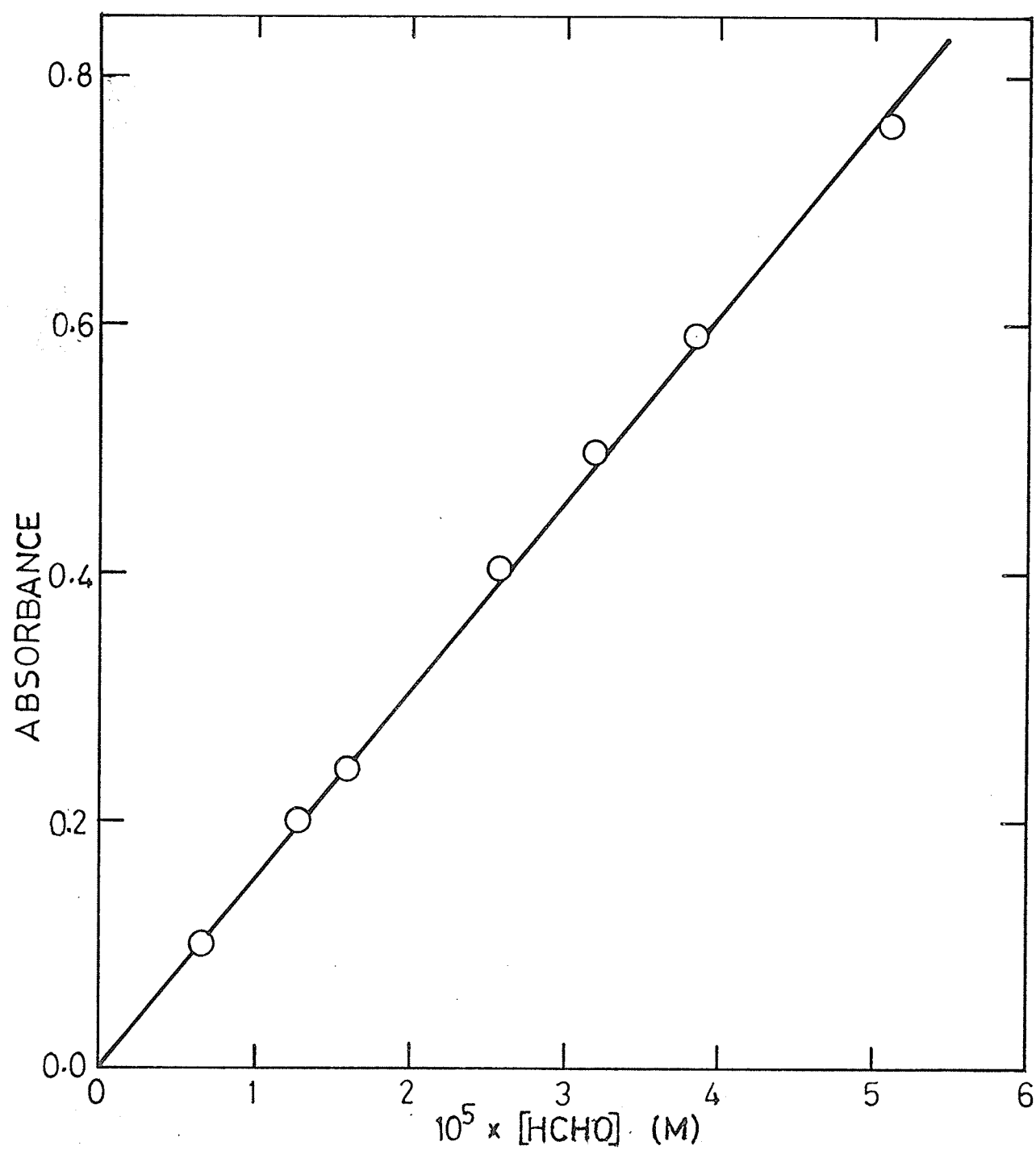


FIG. 2.2

Beer-Lambert relationship for
formaldehyde. Chromotropic acid
method.

$$\lambda = 570 \text{ nm}$$

FIG. 2.2



3. RESULTS AND DISCUSSION: 2-PROPANOL

Alkaline aqueous solutions of 2-propanol using nitrous oxide as an oxidant were irradiated and analyzed for acetone formation. The effects of varying the pH, the dose rate, and the nitrous oxide and alcohol concentrations were extensively investigated. Selectively deuterated 2-propanols were checked for their effect on the acetone yields. Mechanisms are presented and evaluated.

3.1 Acetone Yields

Initial acetone yields were found to be linear with dose allowing $G(\text{acetone})$ values to be calculated with an estimated accuracy of $\pm 3\%$. Typical yield-dose plots are depicted in Fig. 3.1. A few $G(\text{acetone})$ values in Fig. 3.2 were obtained from single points assuming linearity of their yield-dose plots together with values obtained by full yield-dose plots using at least four points. All other $G(\text{acetone})$ values were obtained from complete yield-dose plots. Deliberate addition of carbonate showed that the amount of carbonate impurity present in the bases used had no significant effect on the product yields. Uncertainties quoted in slopes and intercepts are based on standard deviations or scatter of points from best-fit lines of regression; quoted limits of quantities are then derived solely on the basis of propagation of these uncertainties.

At constant pH and alcohol concentration, the acetone yields were found to depend markedly on the nitrous oxide concentration below 9×10^{-2} M in nitrous oxide; above this concentration the acetone yields were essentially independent of nitrous oxide concentration. Table 3.1 and Fig. 3.2 demonstrate this fact at pH 13.5 and 0.105 M 2-propanol.

FIG. 3.1

Initial acetone formation from the
radiation-induced oxidation of
alkaline aqueous 2-propanol by N_2O .

pH 13.5

$[N_2O] = 0.104 \text{ M}$

(O) $[(CH_3)_2CHOH] = 5.23 \times 10^{-3} \text{ M}$

(Φ) $[(CH_3)_2CHOH] = 5.23 \times 10^{-2} \text{ M}$

(Θ) $[(CD_3)_2CHOH] = 1.05 \times 10^{-1} \text{ M}$

(⊕) $[(CH_3)_2CDOH] = 1.05 \times 10^{-1} \text{ M}$

FIG. 3.1

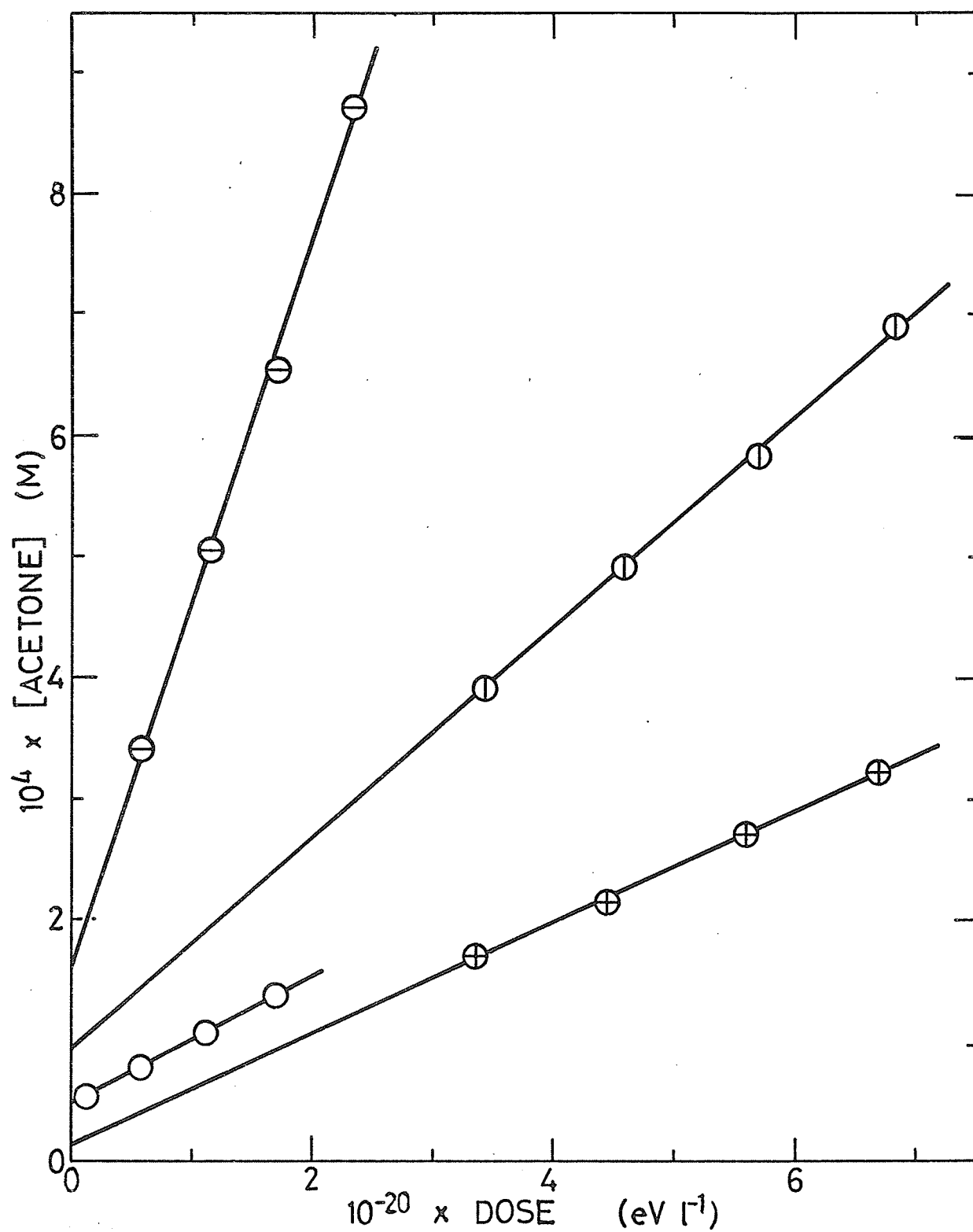


FIG. 3.2

Variation of G(acetone) with $[N_2O]$ (M).

$[(CH_3)_2CHOH] = 0.105 \text{ M}$

pH 13.5

Av. dose rate = $1.13 \times 10^{19} \text{ eV l}^{-1} \text{ s}^{-1}$

(O) Calculated from a yield-dose plot.

(⊙) Calculated from a single point.

FIG. 3.2

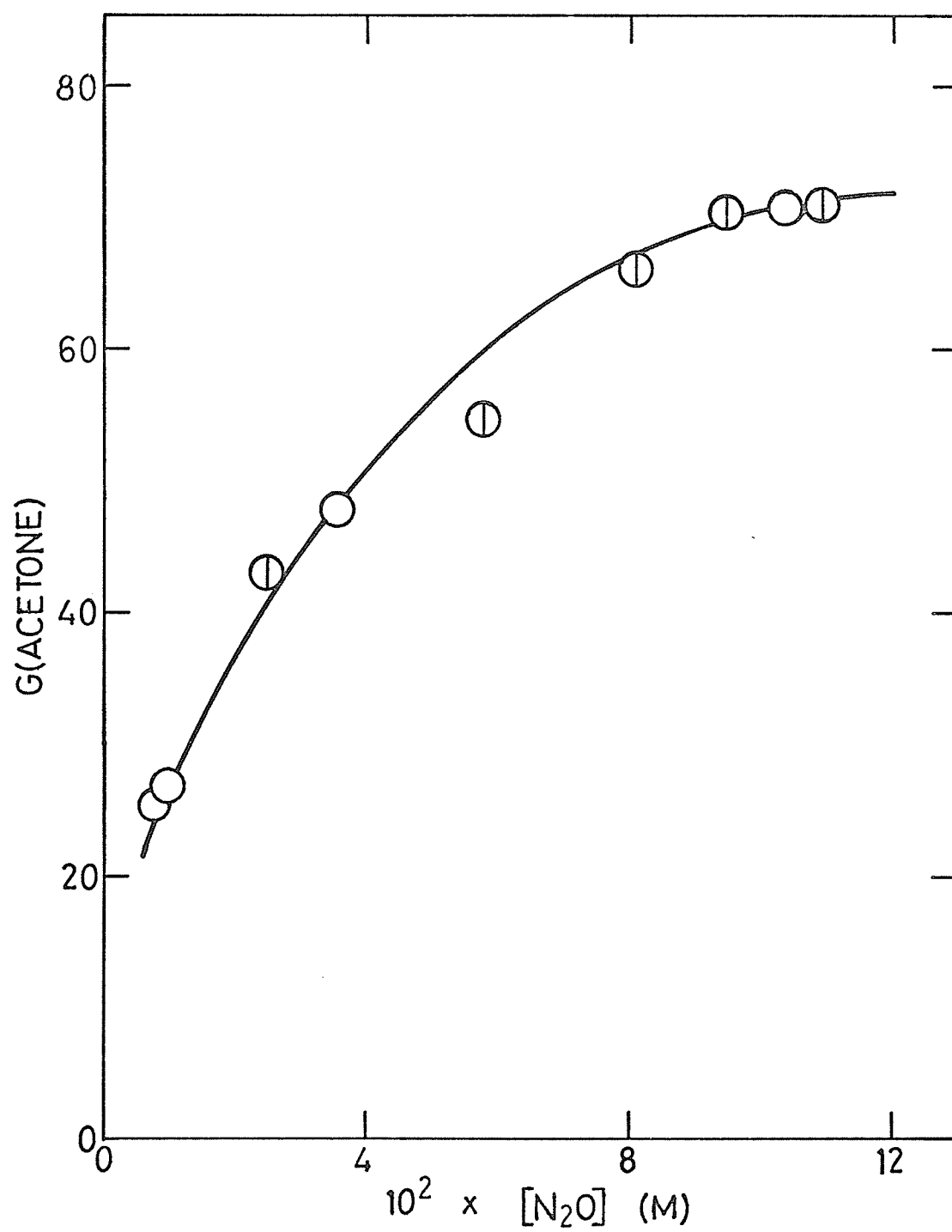


TABLE 3.1

Variation of G(acetone) with N_2O concentration. [2-propanol] = 0.105 M. pH 13.5.

P_{N_2O} (cm Hg)	$10^2 \times [N_2O]$ (M)	G(acetone)
29.0	0.742	25.2
37.5	0.960	26.7
107	2.45	43.1
154	3.52	47.9
252	5.76	54.5
350	8.01	65.9
414	9.47	70.3
453	10.4	70.6
475	10.9	70.9

At a constant 2-propanol concentration of 0.105 M, the yields were found to vary with pH as shown in Table 3.2 and Fig. 3.3. This pH dependence was found both in the region where the yields were independent of nitrous oxide concentration and in the region where they were dependent on nitrous oxide concentration. The yields were essentially independent of base concentration above pH 12.5.

All work with 2-propanol mentioned hereafter was confined to a nitrous oxide concentration of 0.104 M (453 cm Hg N_2O pressure) and a pH of 13.5. Here the yields were independent of both pH and nitrous oxide concentration within experimental error.

A linear dependence of G(acetone) on 2-propanol concentration in the range 1.05×10^{-3} M to 2.09×10^{-1} M was found as depicted in Fig. 3.4 and Table 3.3. The best-fit line gave a slope of $359 \pm 10 \text{ M}^{-1}$ and an ordinate intercept, corresponding to zero alcohol concentration, $G^\circ(\text{acetone}) = 32.0 \pm 1.0$.

FIG. 3.3

Variation of $G(\text{acetone})$ with pH.

$$[(\text{CH}_3)_2\text{CHOH}] = 0.105 \text{ M}$$

$$(\text{O}) \quad [\text{N}_2\text{O}] = 1.04 \times 10^{-1} \text{ M}$$

$$(\ominus) \quad [\text{N}_2\text{O}] = 7.42 \times 10^{-3} \text{ M}$$

$$\text{Av. dose rate} = 1.13 \times 10^{19} \text{ eV l}^{-1} \text{ s}^{-1}$$

FIG. 3.3

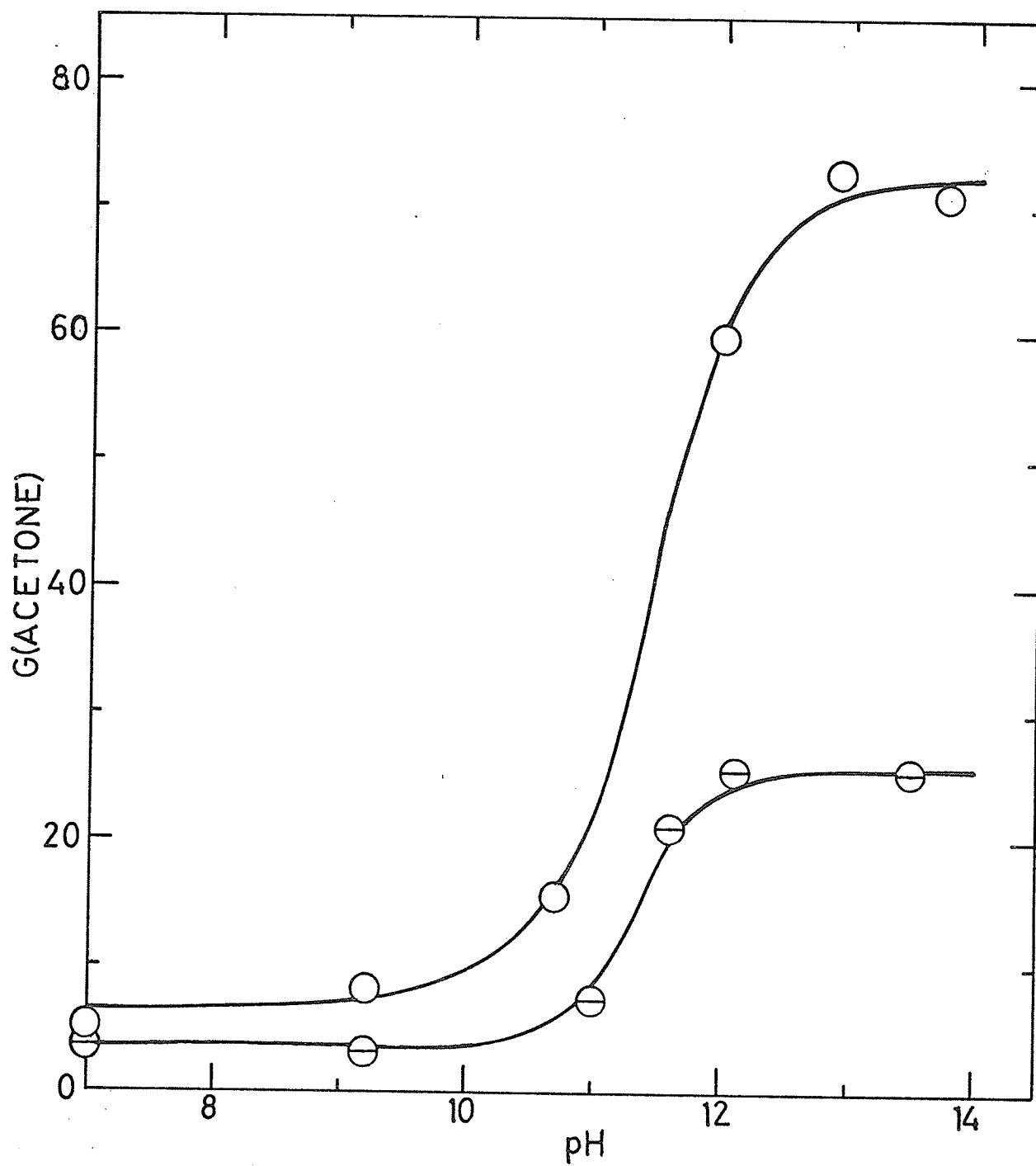


FIG. 3.4

Variation of G(acetone) with [2-propanol] (M).

pH 13.5

$[N_2O] = 0.104 \text{ M}$

(O) $(CH_3)_2CHOH$

(\ominus) $(CD_3)_2CHOH$

(\oplus) $(CH_3)_2CDOH$

Av. dose rate = $1.12 \times 10^{19} \text{ eV l}^{-1} \text{ s}^{-1}$

FIG. 3.4

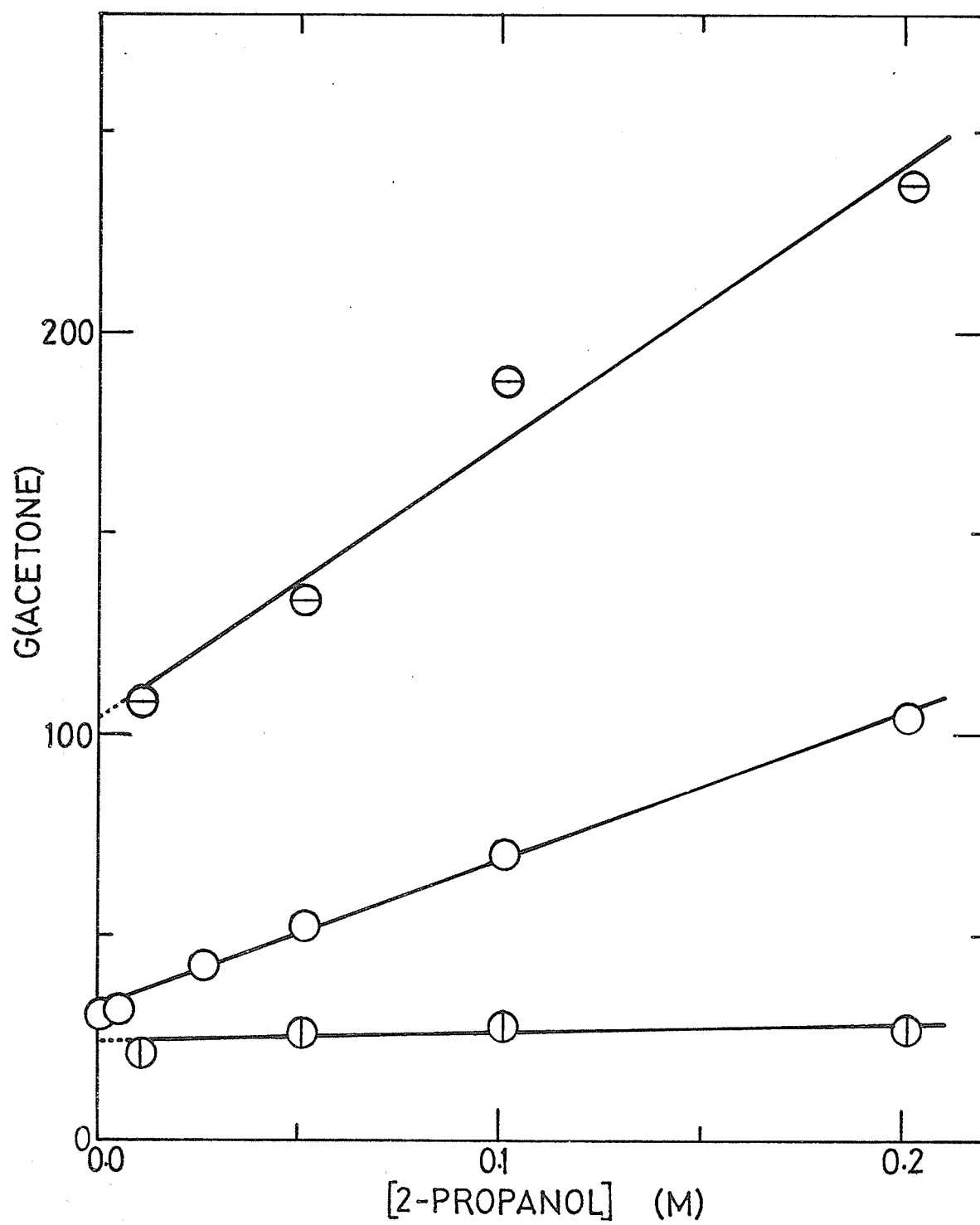


TABLE 3.2

Variation of G(acetone) with pH. [2-propanol] = 0.105 M.

pH	G(acetone) [N ₂ O] = 7.42 x 10 ⁻² M	G(acetone) [N ₂ O] = 0.104 M
7.0	3.37	5.25
9.2	3.16	8.26
10.7		15.5
11.0	7.23	
11.6	20.9	
12.0		59.5
12.1	25.4	
12.9		72.6
13.5	25.2	70.6

TABLE 3.3

Variation of G(acetone) with 2-propanol concentration.

[N₂O] = 0.104 M. pH 13.5.

[2-propanol] (M)	G(acetone) (CH ₃) ₂ CHOH	G(acetone) (CD ₃) ₂ CHOH	G(acetone) (CH ₃) ₂ CDOH
0.00105	30.4		
0.00523	32.0		
0.0105		108	21.3
0.0261	43.4		
0.0523	52.9	134	27.3
0.105	70.6	188	28.1
0.209	106	237	27.9

The acetone yields were found to vary linearly with the reciprocal of the square-root of the dose rate. At an alcohol concentration of 5.23×10^{-2} M, Fig. 3.5 and Table 3.4 demonstrate the variation of G(acetone)

FIG. 3.5

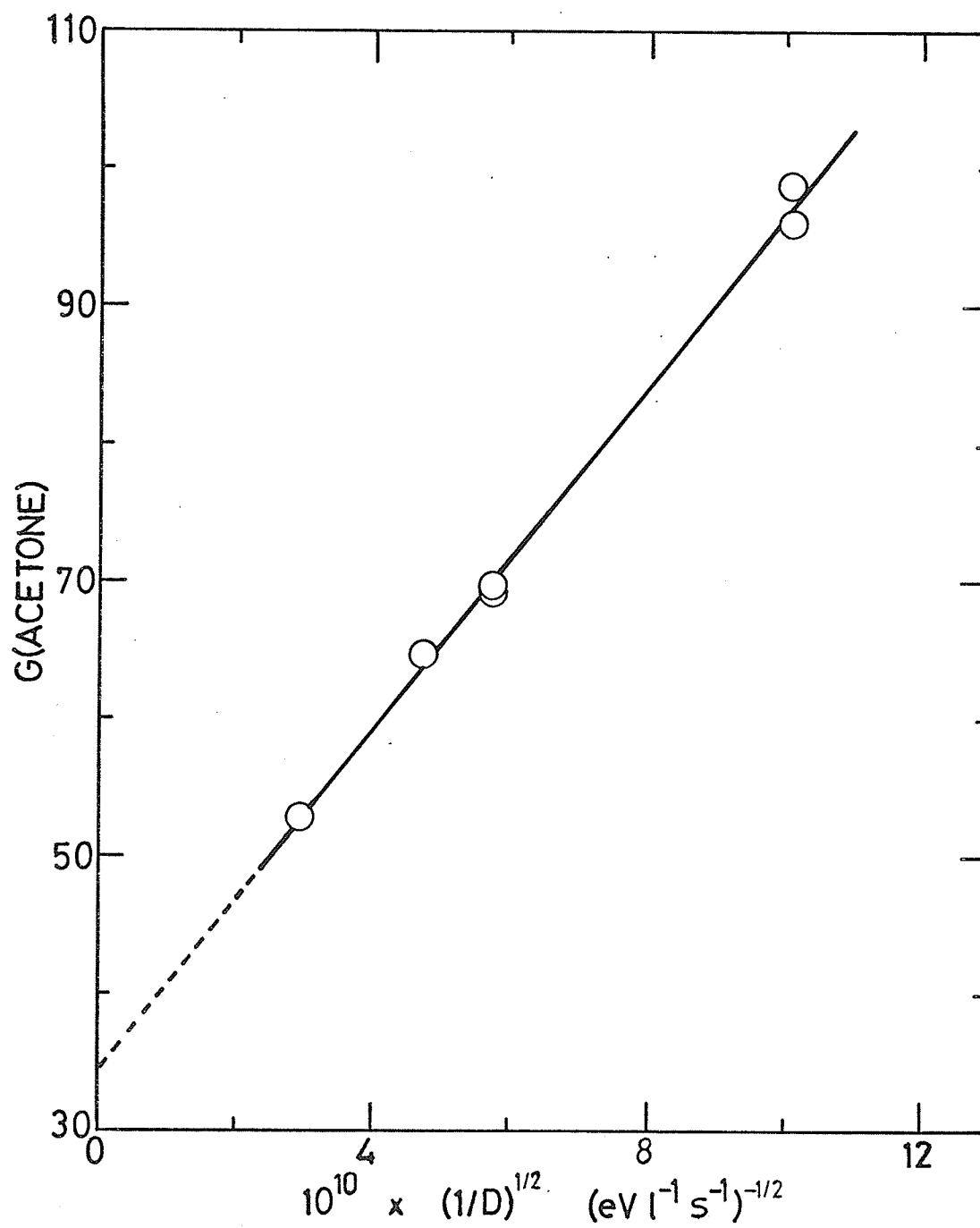
Variation of $G(\text{acetone})$ with $1/\sqrt{D}$
where D is the dose rate.

$$[(\text{CH}_3)_2\text{CHOH}] = 5.23 \times 10^{-2} \text{ M}$$

pH 13.5

$$[\text{N}_2\text{O}] = 0.104 \text{ M}$$

FIG. 3.5



found for dose rates (Fricke dosimeter) in the range 1.16×10^{19} to $1.02 \times 10^{18} \text{ eV l}^{-1} \text{ s}^{-1}$. Extrapolation of the best-fit straight line to infinite dose rate gave a slope of $(6.23 \pm 0.18) \times 10^{10} (\text{eV l}^{-1} \text{ s}^{-1})^{1/2}$ and an ordinate intercept of 34.2 ± 1.2 .

TABLE 3.4

Variation of $G(\text{acetone})$ with $1/\sqrt{D}$ where D is the dose rate. $[2\text{-propanol}] = 5.23 \times 10^{-2} \text{ M}$. pH 13.5.

Nominal Attenuation of D (%)	$10^{10} \times 1/\sqrt{D}$ ($\text{eV l}^{-1} \text{ s}^{-1}$) $^{-1/2}$	$G(\text{acetone})$
Unattenuated	2.97	52.9
45	4.73	64.8
30	5.73	69.0
30	5.73	69.1
10	10.1	95.8
10	10.1	98.7

3.2 Acetone Yields from Selectively Deuterated 2-propanols

All work was again performed using conditions for which the acetone yields were independent of both pH (pH > 12.5) and nitrous oxide concentration ($[\text{N}_2\text{O}] > 9 \times 10^{-2} \text{ M}$).

Relative to $(\text{CH}_3)_2\text{CHOH}$, deuteration of 2-propanol in the β position ($(\text{CD}_3)_2\text{CHOH}$) increased the yields markedly for a given 2-propanol concentration as shown in Table 3.3 and Fig. 3.4. A linear dependence of the yields on the concentration of the β -deuterated alcohol was found, giving a line with a slope of $664 \pm 57 \text{ M}^{-1}$, and an ordinate intercept $G^\circ(\text{acetone}) = 104 \pm 7$ upon extrapolation to zero alcohol concentration.

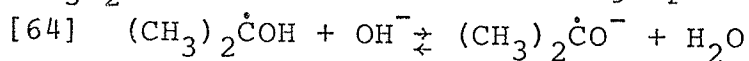
Deuteration of 2-propanol in the α position ($(\text{CH}_3)_2\text{CDOH}$) had the opposite effect. The yields for a

given alcohol concentration decreased as shown in Table 3.3. Fig. 3.4 depicts the lower slope of $26.3 \pm 13.6 \text{ M}^{-1}$ and extrapolation to an intercept of $G^\circ(\text{acetone}) = 23.6 \pm 1.6$ in the linear variation of $G(\text{acetone})$ with $[(\text{CH}_3)_2\text{CDOH}]$.

Deuteration of 2-propanol in the hydroxy group $(\text{CH}_3)_2\text{CHOD}$ gave $G(\text{acetone}) = 67.0$ at an alcohol concentration of 0.105 M. This value is relatively close to the value of $G(\text{acetone}) = 70.6$ obtained for the analogous undeuterated 2-propanol.

3.3 Mechanisms and Discussion

The pH dependence of the acetone yields is attributed to an equilibrium 64 between the 2-propanol radical $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$, being the dominant species in neutral and slightly alkaline solutions, and the radical anion $(\text{CH}_3)_2\dot{\text{C}}\text{O}^-$, being dominant at high pH.



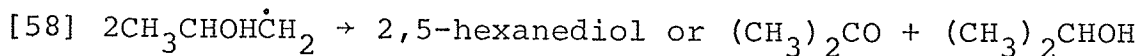
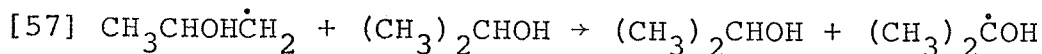
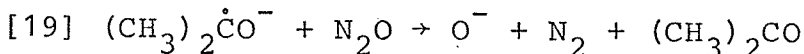
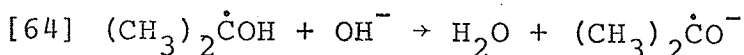
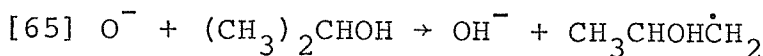
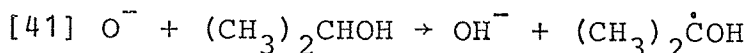
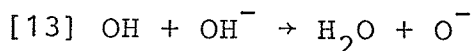
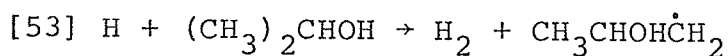
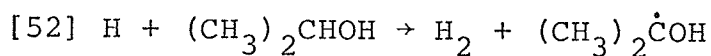
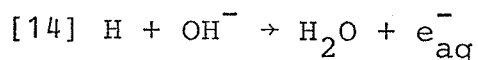
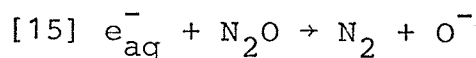
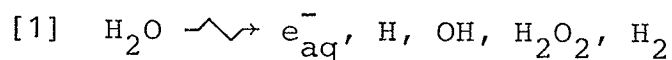
Employing steady irradiation with a 2.8 MeV electron beam, ESR experiments by Eiben and Fessenden (35) have demonstrated the existence of $(\text{CH}_3)_2\dot{\text{C}}\text{O}^-$ and its formation from $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$ between pH 11 and 12. With N_2O -saturated neutral and basic solutions of 2-propanol, their spectra indicated a significant decrease in hyperfine constant and increase of g-factor upon dissociation via reaction 64. Their spectra in neutral solution were like those found earlier by Livingston and Zeldes (36) for aqueous solution in which the spectrum exhibited a splitting by the hydroxyl proton. At higher pH values where appreciable concentrations of both undissociated and dissociated radicals were present, the spectrum was found to represent a weighted average over the two forms due to the rapid equilibrium dynamics. Simic, Neta, and Hayon (37) observed the dissociation of α -hydroxyalkyl radicals, including that from aqueous 2-

propanol saturated with nitrous oxide, in detailed pulse radiolysis studies. In comparison to the undissociated form, larger extinction coefficients and lower decay rate constants were exhibited by the dissociated form of the transients. $\lambda_{\text{max}} < 210 \text{ nm}$ at pH 6 and $\lambda_{\text{max}} < 230 \text{ nm}$ at pH 13.3 were found for 2-propanol. The lower decay rate constants of the transients found in alkaline solutions are consistent with the expected lower decay rate for charged species and provide strong evidence in support of the dissociation of the radical. Their results excluded the radical $\text{CH}_3\text{CHOH}\dot{\text{C}}\text{H}_2$ or the alkoxy radical $(\text{CH}_3)_2\text{CH}\dot{\text{O}}$, and confirmed that only the radical $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$ dissociated to form its anion. In the pulse radiolysis of aqueous alcohol solutions, Asmus et al. (38) observed a pH dependence of the transient absorption spectra; they attributed this alteration to the dissociation of the transient radicals. Since the anion always absorbed more strongly in the UV than the undissociated radical, the equilibrium was discerned easily and pK values could be calculated. For the 2-propanol radical $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$, pK = 12.2 was reported.

The point of inflection of a plot of $G(\text{acetone})$ vs. pH gives the pK of the 2-propanol radical $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$; from Fig. 3.3 the pK is taken to be 11.4 ± 0.3 at $[\text{N}_2\text{O}] = 1.04 \times 10^{-1} \text{ M}$ and 11.3 ± 0.3 at $[\text{N}_2\text{O}] = 7.42 \times 10^{-2} \text{ M}$. These values are only in fair agreement with that of Asmus et al. but in both cases, kinetic rather than equilibrium considerations may determine the point of inflection.

Large acetone yields independent of pH in strongly alkaline solution (pH > 12.5) indicate a chain mechanism involving the radical anion. A mechanism similar to that proposed by Burchill and Ginns (25) is now outlined and considered in the light of the experimental evidence gathered. It must be noted that in addition to the assumption of pH independence, the following mechanism also

assumes no dependence on nitrous oxide concentration; hence this mechanism is applicable only at $\text{pH} > 12.5$ and $[\text{N}_2\text{O}] > 9 \times 10^{-2} \text{ M}$. A mechanism will be suggested in a later section to account for the nitrous oxide concentration dependence of the yields at lower nitrous oxide concentrations. The γ -radiation is assumed to interact specifically with the solvent water as indicated by reaction 1.



At $\text{pH} > 12.5$ reaction 64 may be considered to be stoichiometric. Reactions 15 and 13 yielding O^- , the basic form of OH , and reaction 14, conversion of H to e_{aq}^- , are known to occur in alkaline media. Nitrous oxide does not react with uncharged species (39, 40) such as 2-propanol at high pH but does react with e_{aq}^- via reaction 15 and with the radical anion $(\text{CH}_3)_2\dot{\text{C}}\text{O}^-$ via reaction 19 to produce O^- and the products nitrogen and acetone.

Chain initiation occurs by reaction of H with 2-propanol and O^- with 2-propanol. Abstractions of hydrogen from both the α and β positions of 2-propanol are

proposed. Burchill and Ginns (25) have cited evidence for such reactions as well as for the radical conversion reaction 57, taken to be the rate controlling propagation step.

Chain termination by the bimolecular combination 58 of two $\text{CH}_3\text{CHOH}\dot{\text{C}}\text{H}_2$ radicals is indicated by the mechanism. The chain length is then determined by the competition between the radical terminating reaction 58 and the reaction 57 of that radical with the alcohol, with no dependence on nitrous oxide concentration. Such a lack of dependence of nitrous oxide concentration was assumed at the outset and will be shown to follow from this mechanism in the derivation of the expression for $G(\text{acetone})$.

Since $k_{14}[\text{OH}^-] \gg (k_{52} + k_{53})[(\text{CH}_3)_2\text{CHOH}]$ (11), $k_{14}[\text{OH}^-] \gg (k_{53} - k_{53}k_{41}/k_{65})G_H[(\text{CH}_3)_2\text{CHOH}]$ and $(k_{52} - k_{53}k_{41}/k_{65})G_H[(\text{CH}_3)_2\text{CHOH}](k_{14}[\text{OH}^-])^{-1} \ll 1$, and if the usual steady-state assumptions are made, for small $[(\text{CH}_3)_2\text{CHOH}]$ and large $[\text{OH}^-]$ equation 66 is derived for $G(\text{acetone})$ from the preceeding mechanism.

$$[66] \quad G(\text{acetone}) = \left(\frac{k_{41}}{k_{65}}\right)G_R + \left(1 + \frac{k_{41}}{k_{65}}\right)k_{57}\sqrt{\frac{G_R}{2k_{58}D}}[(\text{CH}_3)_2\text{CHOH}]$$

where D is the dose rate in units of $6.023 \times 10^{25} \text{ eV l}^{-1} \text{ s}^{-1}$ and $G_R = G_{e_{\text{aq}}}^- + G_H + G_{\text{OH}}$. Equation 66 predicts that

$G(\text{acetone})$ will vary linearly with 2-propanol concentration and with the reciprocal of the square-root of the dose rate; the first term, $k_{41}/k_{65}G_R$, represents an alcohol independent chain term.

The small but not negligible $G(\text{acetone})$ values obtained in neutral solution (Table 3.2 and Fig. 3.3), in excess of the amount ($G(\text{acetone}) \sim 3$) formed by the disproportionation of two $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$ radicals by non-chain processes, may be attributed to a slow reaction of nitrous oxide with the undissociated 2-propanol radical. Obviously

such a reaction is insignificant in strongly alkaline solution compared with the reaction of nitrous oxide with the 2-propanol radical anion which leads to large yields.

The slope and intercept of the experimentally determined linear plot of $G(\text{acetone})$ vs. $[2\text{-propanol}]$ (Fig. 3.4) allow calculation of the ratio of the rates of reaction of O^- with 2-propanol to form either the α or β radical and the rate of the chain propagating reaction 57. Assuming $G_R = 5.9$ (41) independent of pH and $2k_{58} = 2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ being typical of the bimolecular termination rate of simple organic radicals (37), $k_{57} = 445 \pm 18 \text{ M}^{-1} \text{ s}^{-1}$ and $k_{\alpha}/k_{\beta} = k_{41}/k_{65} = 5.43 \pm 0.17$ are calculated. This ratio corresponds to 84% attack of O^- at the α position of 2-propanol.

The mechanistic prediction of linear dependence on the reciprocal of the square-root of the dose rate has been realized experimentally as Fig. 3.5 indicates. The slope and intercept of this plot of $G(\text{acetone})$ vs. $1/\sqrt{D}$ allow another calculation of k_{α}/k_{β} and k_{57} . The values determined in this way are $k_{57} = 416 \pm 19 \text{ M}^{-1} \text{ s}^{-1}$ and $k_{\alpha}/k_{\beta} = 5.80 \pm 0.21$, corresponding to 85% attack of O^- at the α position. These values agree closely with those obtained from the linear variation of the yields with 2-propanol concentration and lend support to the validity of the mechanism. The significant dose rate effect in itself confirms the predicted occurrence of bimolecular termination. In addition, the large intercept values, $G^0(\text{acetone})$, bear witness to an alcohol independent chain term embodied in the mechanism.

Using the mean of the two values determined for $k_{41}/k_{65} = k_{\alpha}/k_{\beta} = 5.62 \pm 0.27$ and $k_{41} + k_{65} = 1.05 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (42), values for k_{41} and k_{65} are calculated to be $(8.92 \pm 0.43) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ and $(1.59 \pm 0.08) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$

respectively.

A normal primary kinetic isotope effect would be expected to arise from reactions 53 and 65 upon substitution of $(\text{CD}_3)_2\text{CHOH}$ for $(\text{CH}_3)_2\text{CHOH}$ if these reactions are actually hydrogen atom transfer reactions. An increase in both the slope and the intercept of a plot of $G(\text{acetone})$ vs. [2-propanol] is then predicted by equation 66. Substitution of $(\text{CH}_3)_2\text{CDOH}$ for $(\text{CH}_3)_2\text{CHOH}$ should result in reactions 52, 41, and 57 showing a primary kinetic isotope effect. Equation 66 now predicts the opposite effect: a decrease in both the slope and the intercept of a plot of $G(\text{acetone})$ vs. [2-propanol]. According to the proposed mechanism, substitution of $(\text{CH}_3)_2\text{CHOD}$ for $(\text{CH}_3)_2\text{CHOH}$ should have virtually no effect on the product yields.

That these predictions have largely been realized experimentally confirms the applicability of the mechanism, demonstrating the non-specificity of hydrogen atom abstraction from 2-propanol and the involvement of the β position as indicated by the magnified chain yields from $(\text{CD}_3)_2\text{CHOH}$. In a similar fashion to undeuterated 2-propanol, values for the rate of radical conversion (reaction 57) and for the ratio of α to β abstraction may be calculated for the deuterated alcohols. From the slopes and intercepts of the linear plots of $G(\text{acetone})$ vs. [2-propanol] for the respective alcohols as shown in Fig. 3.4, $k_{57} = 280 \pm 30 \text{ M}^{-1} \text{ s}^{-1}$ and $k_\alpha/k_\beta = 17.7 \pm 1.2$, or 94% α attack, for $(\text{CD}_3)_2\text{CHOH}$ while $k_{57} = 41.5 \pm 13.7 \text{ M}^{-1} \text{ s}^{-1}$ and $k_\alpha/k_\beta = 4.01 \pm 0.28$, or 80% α attack, for $(\text{CH}_3)_2\text{CDOH}$ were calculated.

The values enumerated in Table 3.5 allow quantitative estimation of the primary kinetic isotope effects for reactions 41, 65, and 57. Neglecting secondary isotope effects, from equation 66 it follows that the ratio of the intercept of $(\text{CH}_3)_2\text{CHOH}$ to that of $(\text{CH}_3)_2\text{CDOH}$ will give $k_{41(\text{H})}/k_{41(\text{D})}$, while the ratio of the intercept of

$(\text{CD}_3)_2\text{CHOH}$ to that of $(\text{CH}_3)_2\text{CHOH}$ will be $k_{65(\text{H})}/k_{65(\text{D})}$. The ratio of k_{57} determined for $(\text{CH}_3)_2\text{CHOH}$ to k_{57} found for $(\text{CH}_3)_2\text{CDOH}$ will give $k_{57(\text{H})}/k_{57(\text{D})}$. The values thus obtained are gathered in Table 3.6.

TABLE 3.5

Slopes and intercepts ($G^\circ(\text{acetone})$) calculated for the lines of Fig. 3.4. k_{57} and $k_{41}/k_{65} = k_\alpha/k_\beta$ calculated from these slopes and intercepts.

Alcohol	$G^\circ(\text{acetone})$	Slope (M^{-1})	k_{57} ($\text{M}^{-1} \text{s}^{-1}$)	k_α/k_β
$(\text{CH}_3)_2\text{CHOH}$	32.0 ± 1.0	359 ± 10	445 ± 18	5.43 ± 0.17
$(\text{CD}_3)_2\text{CHOH}$	104 ± 7	664 ± 57	280 ± 30	17.7 ± 1.2
$(\text{CH}_3)_2\text{CDOH}$	23.6 ± 1.6	26.3 ± 13.6	41.5 ± 21.7	4.01 ± 0.28

TABLE 3.6

Rate constant ratios for hydrogen atom abstraction reactions from 2-propanol obtained from primary kinetic isotope effects.

Ratio	Rate Constant Ratio
$\frac{\text{Intc. } ((\text{CH}_3)_2\text{CHOH})}{\text{Intc. } ((\text{CH}_3)_2\text{CDOH})}$	$\frac{k_{41(\text{H})}}{k_{41(\text{D})}} = 1.35 \pm 0.10$
$\frac{k_{57} ((\text{CH}_3)_2\text{CHOH})}{k_{57} ((\text{CH}_3)_2\text{CDOH})}$	$\frac{k_{57(\text{H})}}{k_{57(\text{D})}} = 10.7 \pm 5.6$
$\frac{\text{Intc. } ((\text{CD}_3)_2\text{CHOH})}{\text{Intc. } ((\text{CH}_3)_2\text{CHOH})}$	$\frac{k_{65(\text{H})}}{k_{65(\text{D})}} = 3.26 \pm 0.23$

Although the mechanism predicts that k_{57} determined from $(\text{CD}_3)_2\text{CHOH}$ should be equal to that from $(\text{CH}_3)_2\text{CHOH}$, this was not found experimentally as is evident from Table 3.5. It would appear that the radical conversion reaction 57 slows down when $(\text{CD}_3)_2\text{CHOH}$ is substituted for $(\text{CH}_3)_2\text{CHOH}$; no explanation is evident for this diminution in rate nor does the proposed mechanism take account of this experimental finding.

It should be mentioned that a postirradiation effect that resulted in the formation of increasing amounts of additional acetone with increasing time after irradiation was noticed. However this effect did not alter the acetone yields calculated from yield-dose plots since the amount of acetone formed after irradiation was apparently independent of the dose received by the sample. This fact accounts for the positive intercepts of Fig. 3.1. It was thus necessary to calibrate simultaneously the few $G(\text{acetone})$ values obtained from single points relative to full yield-dose plots. Dainton and Rumfeldt (22) and Sherman (23) have reported similar post-irradiation product yields but their measured $G(\text{N}_2)$ values increased with increasing time after irradiation, possibly due to the fact that their yields were determined in any one experiment on the basis of a single point.

As mentioned previously, Sherman (23) has reported methane as a product of the γ -radiolysis of alkaline pure 2-propanol and nitrous oxide. To check for methane, several samples containing 0.105 M 2-propanol and 0.104 M nitrous oxide at pH 13.5 were irradiated to large doses and analyzed by mass spectrometry. Any methane present was below the level of detectability of the mass spectrometer. It was concluded that γ -radiolysis of alkaline aqueous 2-propanol and nitrous oxide did not yield methane as a significant product.

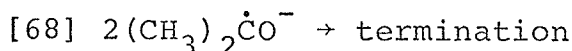
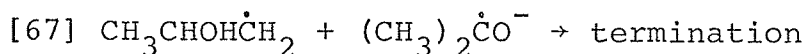
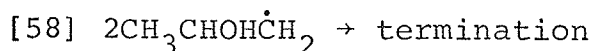
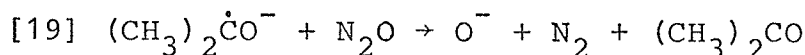
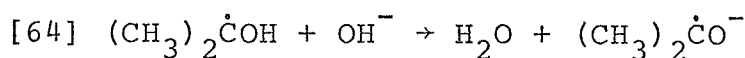
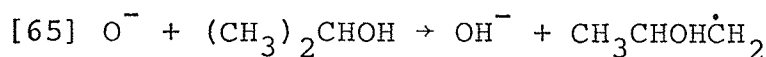
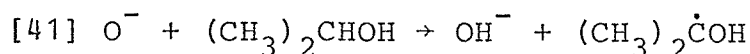
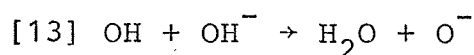
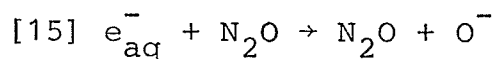
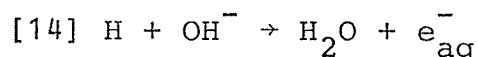
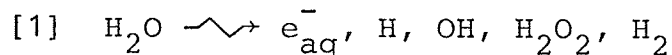
Sherman (23) has also reported that addition of small amounts of acetone prior to irradiation of alkaline pure 2-propanol and nitrous oxide resulted in chain retardation and inhibition. Initial addition of 8.10×10^{-4} M acetone to a solution 0.105 M in 2-propanol and 0.104 M in nitrous oxide at pH 13.5, comparable to the concentration of acetone anticipated as a product yield from reaction, gave $G(\text{acetone}) = 72.1$ upon irradiation. Irradiation of a similar solution with no acetone added initially gave $G(\text{acetone}) = 70.6$, the same value within experimental error as that with acetone added initially, indicating no retardation or inhibition of the chain sequence by acetone, as expected from the proposed mechanism. It may be mentioned that the acetone yields obtained by Sherman with no initial addition of acetone showed no chain retardation or inhibition although the quantity of acetone formed was comparable to the amount which was said to give inhibition.

The mechanism put forward previously employs a single termination reaction 58 involving bimolecular combination of $\text{CH}_3\text{CHOH}\dot{\text{C}}\text{H}_2$ leading to a prediction of no dependence on nitrous oxide concentration. The experimental results imply that this prediction does hold but only at nitrous oxide concentrations exceeding 9×10^{-2} M.

Chain termination involving the $(\text{CH}_3)_2\dot{\text{C}}\text{O}^-$ radical would be in competition with the chain propagating reaction 19 and would lead to some dependence of chain length on nitrous oxide concentration. Since this is observed experimentally (Fig. 3.2), it must be concluded that the $(\text{CH}_3)_2\dot{\text{C}}\text{O}^-$ radical does indeed play a role in the termination process by cross termination 67 with $\text{CH}_3\text{CHOH}\dot{\text{C}}\text{H}_2$ radicals and/or by bimolecular combination 68. To this end, the mechanism proposed may be extended to include three terminating processes as outlined below. Stoichiometric formation of $(\text{CH}_3)_2\dot{\text{C}}\text{O}^-$ from $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$ and OH^- and pH > 12.5

are again assumed. It is also assumed that reactions 14, 15, and 13 are sufficiently rapid to be stoichiometric so that the rate of primary O^- generation is given by

$(G_{e_{aq}^-} + G_H + G_{OH}) \cdot D = G_R \cdot D$. Hence reactions 52 and 53 involving hydrogen atom abstraction from 2-propanol by primary hydrogen atoms are omitted.



Equation 69 for $G(\text{acetone})$ is derived from this mechanism assuming normal steady-state conditions, primary O^- generation given by $G_R \cdot D$ and $2k_{58} = k_{67} = 2k_{68} = k_t$. The latter assumption gives a simple algebraic solution.

$$[69] \quad G(\text{acetone}) = \frac{k_{19} \left(\frac{k_{41} \cdot G_R}{k_{41} + k_{65}} + k_{57} \sqrt{\frac{G_R}{k_t \cdot D}} [(CH_3)_2CHOH] \right) [N_2O]}{\frac{k_{65} \cdot k_{19} [N_2O] + k_{57} [(CH_3)_2CHOH] + \sqrt{G_R \cdot D \cdot k_t}}{k_{41} + k_{65}}}$$

Rearrangement leads to equation 70.

$$[70] \quad \frac{1}{G(\text{acetone})} = \frac{k_{65}/(k_{41} + k_{65})}{\frac{k_{41} \cdot G_R}{k_{41} + k_{65}} + k_{57} \sqrt{\frac{G_R}{k_t \cdot D}} [(\text{CH}_3)_2\text{CHOH}]} + \frac{\sqrt{G_R \cdot D \cdot k_t} + k_{19} [(\text{CH}_3)_2\text{CHOH}]}{k_{19} \left(\frac{k_{41} \cdot G_R}{k_{41} + k_{65}} + k_{57} \sqrt{\frac{G_R}{k_t \cdot D}} [(\text{CH}_3)_2\text{CHOH}] \right)} \cdot \frac{1}{[\text{N}_2\text{O}]}$$

Equation 70 predicts that $1/G(\text{acetone})$ will vary linearly with $1/[\text{N}_2\text{O}]$. It is noteworthy that equation 69 reduces to equation 66 at high $[\text{N}_2\text{O}]$ since then $k_{65}/(k_{41} + k_{65})k_{19} \times [\text{N}_2\text{O}] \gg k_{57}[(\text{CH}_3)_2\text{CHOH}] + (G_R \cdot D \cdot k_t)^{1/2}$.

A plot of $1/G(\text{acetone})$ vs. $1/[\text{N}_2\text{O}]$ using the values in Table 3.1 is shown in Fig. 3.6. It can be seen that the plot is only roughly linear; evidently the three terminating reactions do not have a simple algebraic relationship among themselves as assumed. The slope and intercept of the best-fit straight line through the points in Fig. 3.6 allow a rough estimate of the rate of the chain propagating reaction 19; k_{19} is given by equation 71 and is calculated to be $(3.81 \pm 0.35) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ assuming $G_R = 5.9$ and $k_t = 2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.

$$[71] \quad k_{19} = \frac{\text{Intc.}}{\text{Slope}} \left\{ 1 + \frac{k_{41}}{k_{65}} \right\} \left\{ (G_R \cdot D \cdot k_t)^{1/2} + k_{57} [(\text{CH}_3)_2\text{CHOH}] \right\}$$

At high nitrous oxide concentrations ($[\text{N}_2\text{O}] > 9 \times 10^{-2} \text{ M}$) the terminating reaction 58 involving only $\text{CH}_3\text{CHOH}\dot{\text{C}}\text{H}_2$ radicals would be expected to predominate since the concentration of $(\text{CH}_3)_2\dot{\text{C}}\text{O}^-$ may be shown to be less than one-fifth that of $\text{CH}_3\text{CHOH}\dot{\text{C}}\text{H}_2$ making cross-termination via reaction 67 relatively unimportant and termination by bi-molecular combination 68 of $(\text{CH}_3)_2\dot{\text{C}}\text{O}^-$ radicals insignificant being in at least a ratio of 1:25 with bimolecular combination of $\text{CH}_3\text{CHOH}\dot{\text{C}}\text{H}_2$ radicals. It may be noted that the ratio $k_\alpha/k_\beta = 5.62 \pm 0.27$

FIG. 3.6

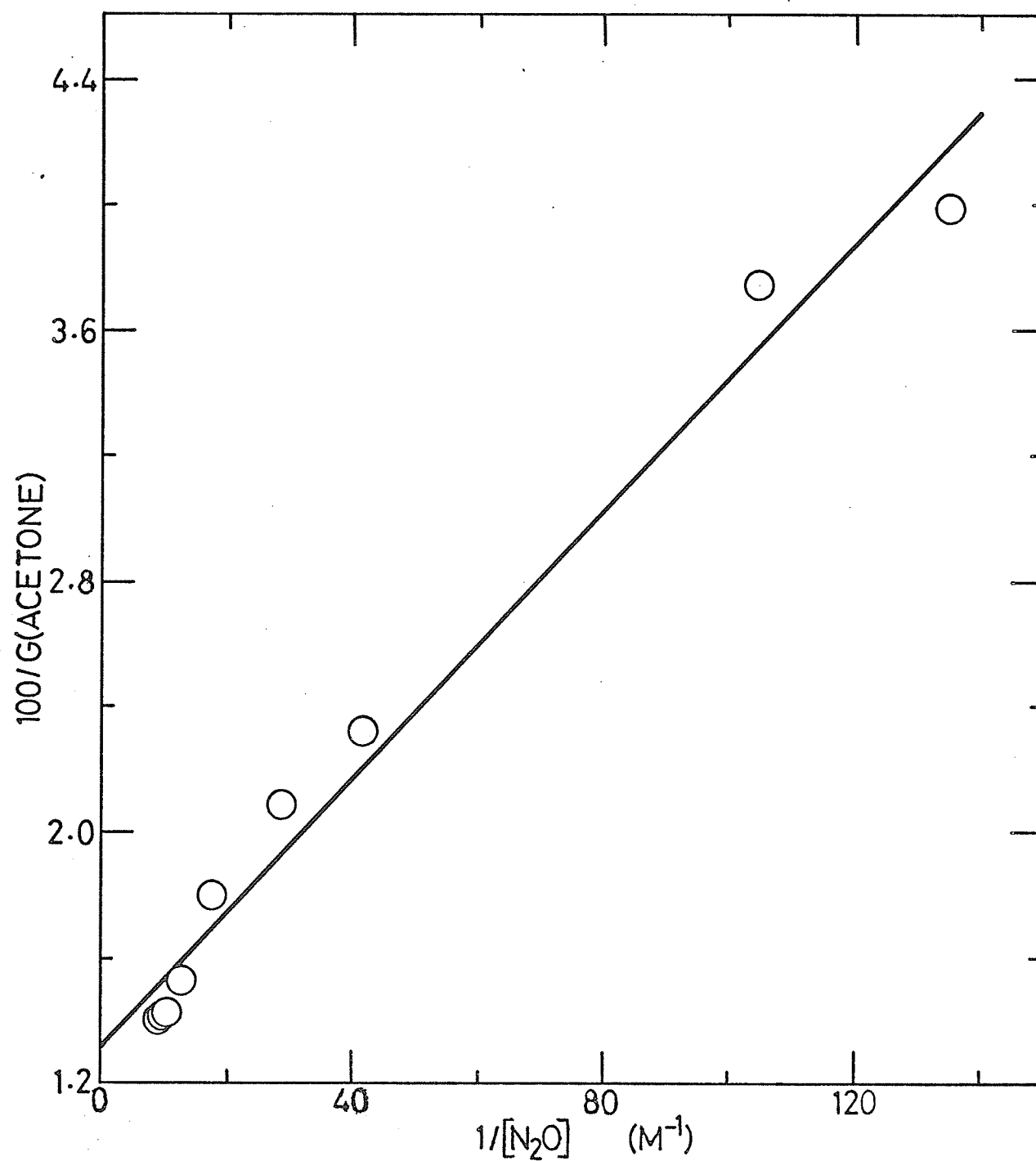
Variation of $1/G(\text{acetone})$ with $1/[N_2O]$
(M^{-1}).

$[(CH_3)_2CHOH] = 0.105 \text{ M}$

pH 13.5

Av. dose rate = $1.13 \times 10^{19} \text{ eV l}^{-1} \text{ s}^{-1}$

FIG. 3.6



(mean value) must be regarded as a lower limit since the nitrous oxide concentration of 0.104 M at which the determination was made, though high, was not infinite.

4. RESULTS AND DISCUSSION: METHANOL

Alkaline solutions of methanol and nitrous oxide were investigated to compare the mechanism proposed for 2-propanol with a system where only one radical species, namely $\dot{\text{C}}\text{H}_2\text{OH}$, is expected to be formed from the parent alcohol. The effects of varying the methanol and nitrous oxide concentrations, pH, and dose rate were examined together with the effects of deuteration.

4.1 Formaldehyde Yields

Solutions were irradiated to different doses to enable measurement of formaldehyde yields. The yield-dose plots for initial formaldehyde formation were linear, enabling calculation of accurate $G(\text{HCHO})$ values ($\pm 3\%$). Typical plots are shown in Fig. 4.1. Some values in Figs. 4.2 and 4.3 were obtained from single points while others were from full yield-dose plots. No postirradiation effects occurred with methanol as evidenced by the zero intercepts in Fig. 4.1. The single points were found to give reliable yields, fitting in with the yields obtained using full yield-dose plots. The procedure for error analysis used previously was followed.

$G(\text{HCHO})$ was found to increase with increasing methanol concentration as shown in Table 4.1. Pure methanol was used in all subsequent investigations. As shown in Table 4.2 and Fig. 4.2, $G(\text{HCHO})$ increased with increasing base concentration up to 0.1 M where the yields became relatively independent of alkalinity. $G(\text{HCHO})$ increased linearly with increasing nitrous oxide concentration in the region where the yields were independent of base concentration, giving a line with a slope of $629 \pm 16 \text{ M}^{-1}$, and increased non-linearly with nitrous oxide concentration at $[\text{KOH}] = 2.75 \times 10^{-2} \text{ M}$ as depicted in Fig. 4.3 and Table 4.3. An inverse square-root dependence on the dose rate,

FIG. 4.1

Initial formaldehyde formation from
the radiation-induced oxidation of
alkaline methanol by N_2O .

$$[\text{N}_2\text{O}] = 2.95 \times 10^{-2} \text{ M}$$

$$[\text{OH}^-] = 0.120 \text{ M}$$

(○)	Mole fraction CH_3OH	= 0.0469
(⊖)	"	= 0.221
(⊖)	"	= 0.608
(⊕)	"	= 1.00

FIG. 4.1

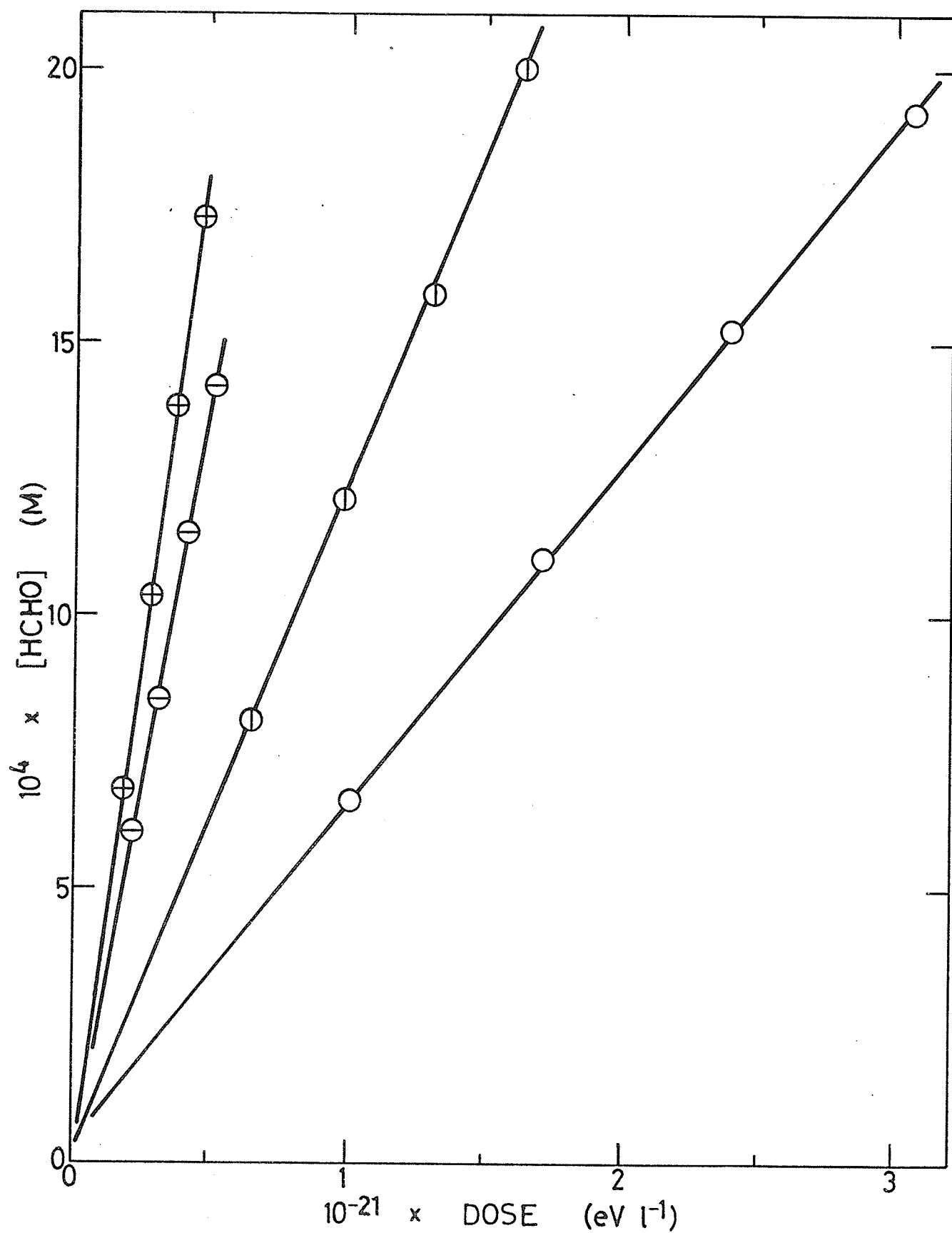


FIG. 4.2

Variation of $G(\text{HCHO})$ with $\log [\text{OH}^-]$.

Pure CH_3OH

$[\text{N}_2\text{O}] = 2.95 \times 10^{-2} \text{ M}$

Av. dose rate = $9.19 \times 10^{18} \text{ eV l}^{-1} \text{ s}^{-1}$

FIG. 4.2

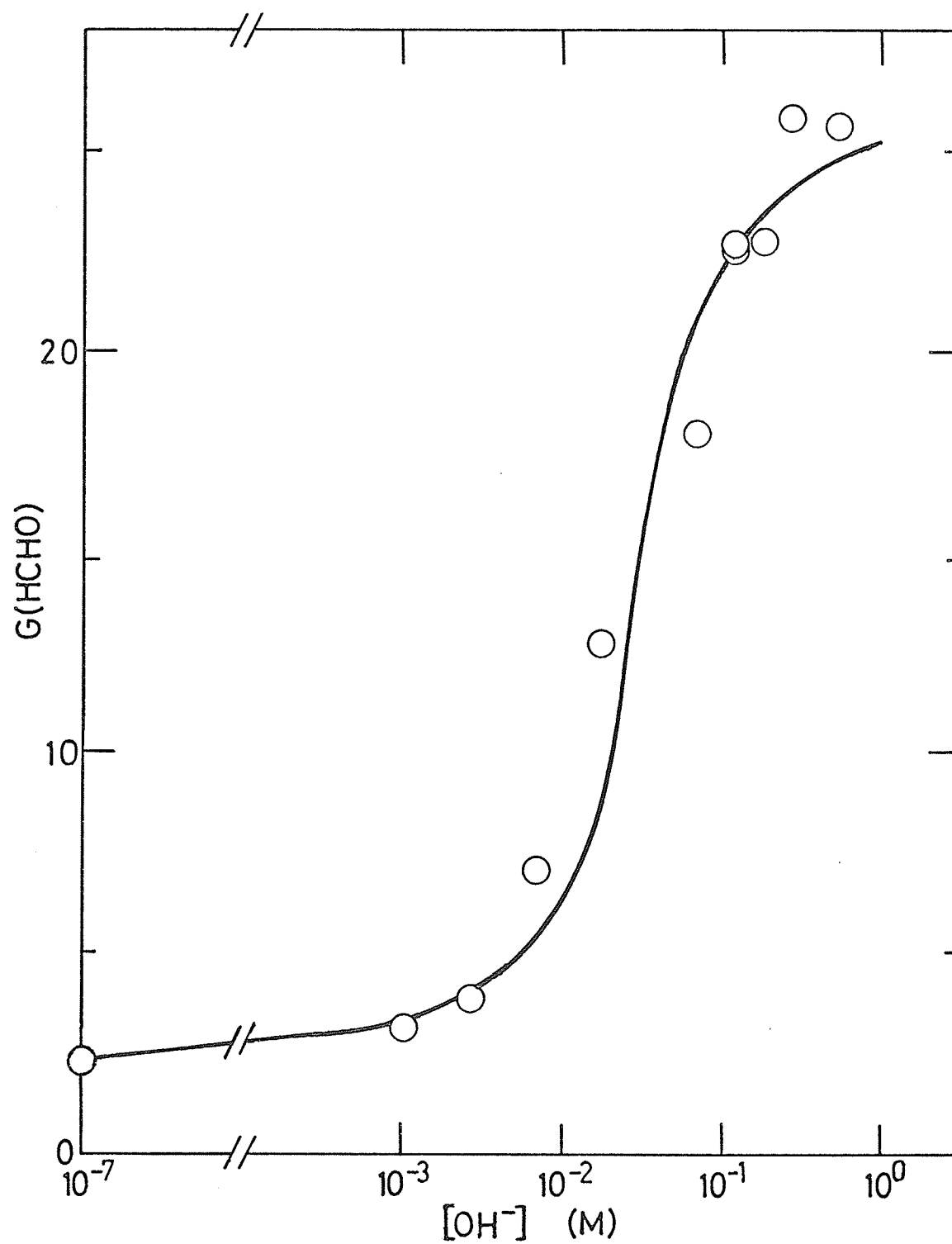


TABLE 4.1

Variation of $G(\text{HCHO})$ and k_{31} with mole fraction methanol ($X_{\text{CH}_3\text{OH}}$). All $G(\text{HCHO})$ values corrected to $[\text{N}_2\text{O}] = 2.95 \times 10^{-2}$ M assuming $G(\text{HCHO}) \propto [\text{N}_2\text{O}]$. $[\text{OH}^-] = 0.120$ M.

Base	$X_{\text{CH}_3\text{OH}}$	$G(\text{HCHO})$	$k_{31} (\pm 3\%)$ ($\text{M}^{-1} \text{s}^{-1}$)
NaOH	0.00179	8.32	153
"	0.0182	9.72	178
"	0.0469	11.3	206
"	0.0985	11.7	212
"	0.221	14.6	261
KOH	0.221	14.4	256
"	0.380	16.5	290
"	0.680	20.2	345
"	1.00	22.7	372
"	1.00	22.3	365
NaOCH_3	1.00	20.7	339

TABLE 4.2

Variation of $G(\text{HCHO})$ with base concentration. Pure CH_3OH . $[\text{N}_2\text{O}] = 2.95 \times 10^{-2}$ M.

$[\text{KOH}]$ (M)	$G(\text{HCHO})$	$[\text{KOH}]$ (M)	$G(\text{HCHO})$
0.00	2.35	0.120	22.7
0.00106	3.14	0.120	22.3
0.00269	3.90	0.173	22.8
0.00694	7.08	0.263	25.9
0.0265	12.8	0.510	25.7
0.0673	19.0		

FIG. 4.3

Variation of $G(\text{HCHO})$ with $[\text{N}_2\text{O}]$ (M).

Pure CH_3OH

(○) $[\text{OH}^-] = 2.75 \times 10^{-2} \text{ M}$

(⊖) $[\text{OH}^-] = 1.20 \times 10^{-1} \text{ M}$

Av. dose rate = $9.01 \times 10^{18} \text{ eV l}^{-1} \text{ s}^{-1}$

FIG. 4.3

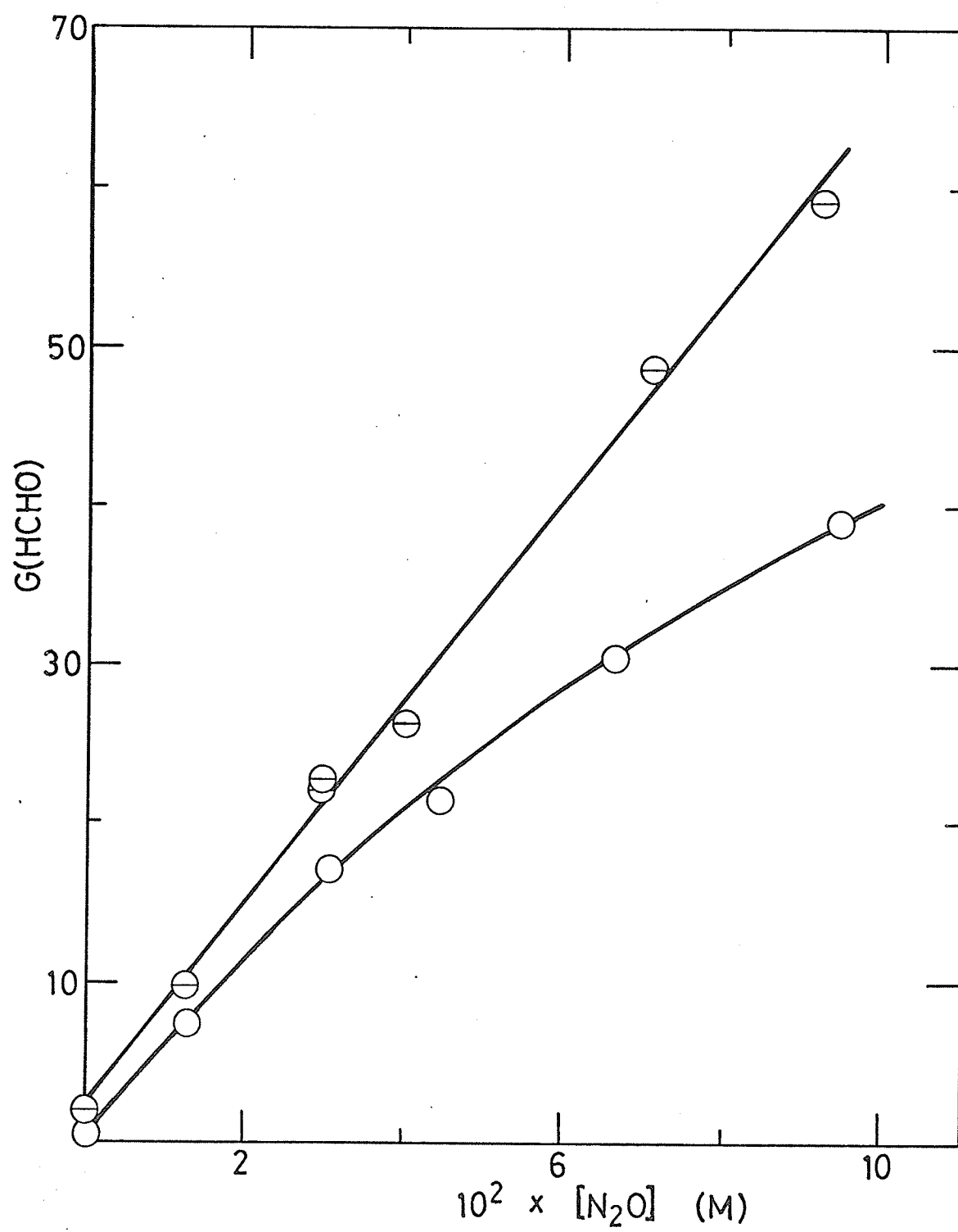


FIG. 4.4

Variation of $G(\text{HCHO})$ with $1/\sqrt{D}$
where D is the dose rate.

Pure CH_3OH

$[\text{OH}^-] = 0.120 \text{ M}$

$[\text{N}_2\text{O}] = 2.95 \times 10^{-2} \text{ M}$

FIG. 4.4

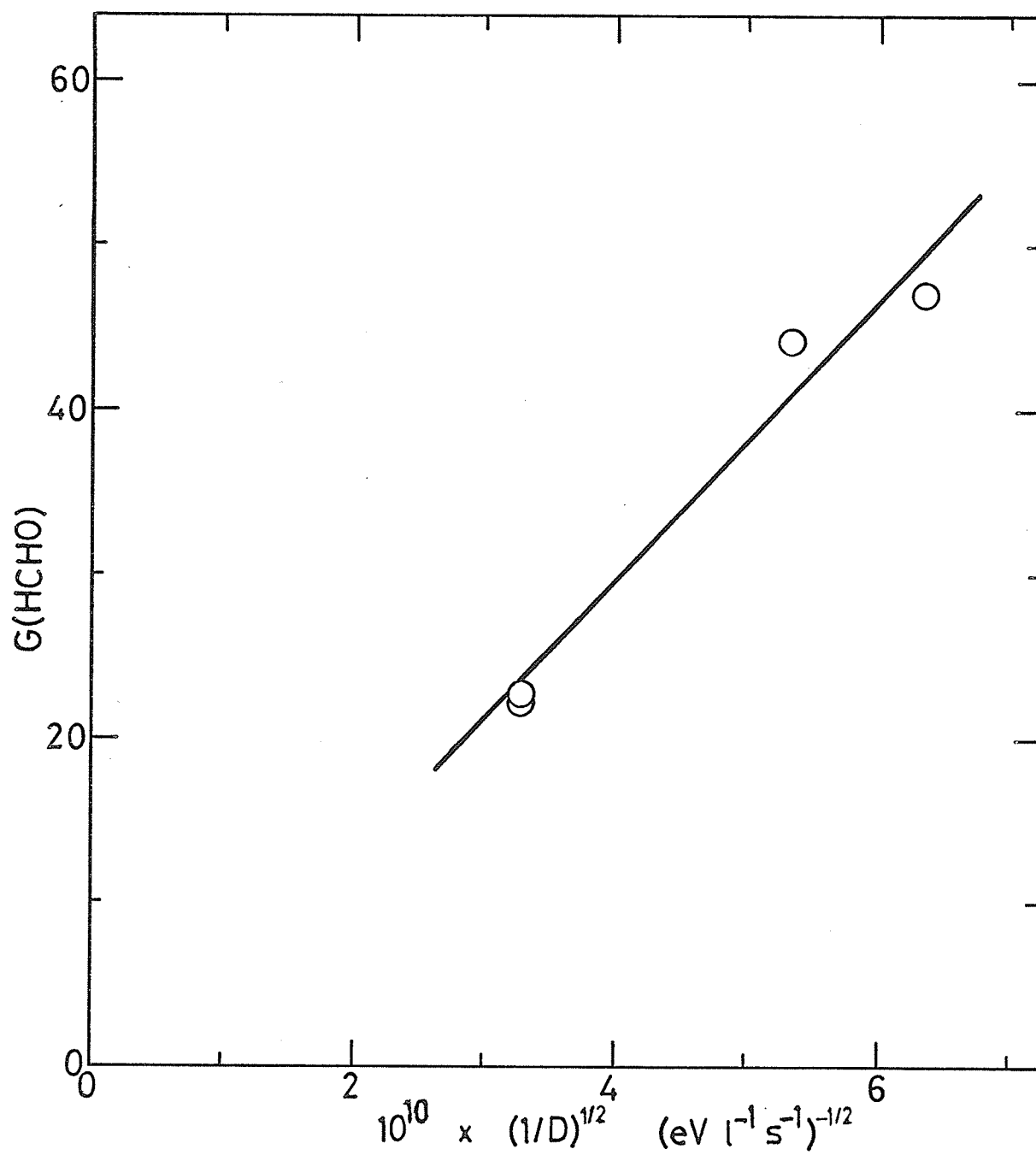


TABLE 4.3

Variation of $G(\text{HCHO})$ and k_{72} with nitrous oxide concentration or nitrous oxide pressure ($P_{\text{N}_2\text{O}}$). Pure CH_3OH .

[KOH] (M)	$P_{\text{N}_2\text{O}}$ (cm Hg)	$10^2 \times [\text{N}_2\text{O}]$ (M)	$G(\text{HCHO})$	$10^{-3} \times k_{72}$ ($\text{M}^{-1} \text{s}^{-1}$)
2.75×10^{-2}	0.0	0.00	0.496	
"	8.3	1.28	7.49	3.05 ± 0.12
"	20.0	3.08	17.1	3.06 ± 0.12
"	29.1	4.48	21.5	2.34 ± 0.09
"	42.9	6.61	30.5	2.52 ± 0.10
"	61.3	9.44	39.0	2.40 ± 0.10
1.20×10^{-1}	0.0	0.00	1.40	
"	8.6	1.23	9.81	
"	19.5	2.95	22.3	
"	19.5	2.95	22.7	
"	26.5	4.00	26.8	
"	46.9	7.08	48.8	
"	61.4	9.27	59.2	

TABLE 4.4

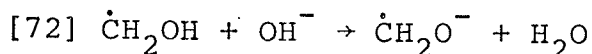
Variation of $G(\text{HCHO})$ with $1/\sqrt{D}$ where D is the dose rate.
 $[\text{OH}^-] = 0.120 \text{ M}$. $[\text{N}_2\text{O}] = 2.95 \times 10^{-2} \text{ M}$.

Nominal Attenuation (%)	$10^{10} \times 1/\sqrt{D}$ ($\text{eV l}^{-1} \text{s}^{-1}$) $^{-1/2}$	$G(\text{HCHO})$
Unattenuated	3.29	22.3
"	3.29	22.7
45	5.34	44.3
30	6.36	47.0

giving a line of slope $(8.59 \pm 0.09) \times 10^{10} \text{ (eV l}^{-1} \text{ s}^{-1})^{1/2}$, in the range 1.16×10^{19} to $3.12 \times 10^{18} \text{ eV l}^{-1} \text{ s}^{-1}$ was found as shown in Table 4.4 and Fig. 4.4. Substitution of CD_3OH for CH_3OH with $[\text{KOH}] = 0.120 \text{ M}$ and $[\text{N}_2\text{O}] = 2.95 \times 10^{-2} \text{ M}$ gave $G(\text{formaldehyde}) = 28.4$, somewhat higher than the yield obtained for the undeuterated alcohol.

4.2 Mechanisms and Discussion

By analogy with 2-propanol, the dependence of the formaldehyde yields on the base concentration is attributed to the formation of the radical anion $\dot{\text{C}}\text{H}_2\text{O}^-$ at high base concentration, with the uncharged radical $\dot{\text{C}}\text{H}_2\text{OH}$ from methanol being dominant at low base concentration. Avery, Remko, and Smaller (43) observed the ESR spectrum of $\dot{\text{C}}\text{H}_2\text{O}^-$ produced by pulsed electron irradiation of a flowing 1 M solution of methanol in water at pH 12 and 12°C. More recently Eiben and Fessenden (35) observed the formation of $\dot{\text{C}}\text{H}_2\text{O}^-$ via reaction 72 from ESR studies employing steady 2.8 MeV electron irradiation of N_2O -saturated 0.1 M aqueous methanol solutions at various pH's.

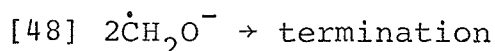
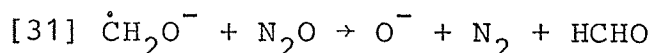
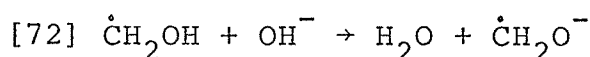
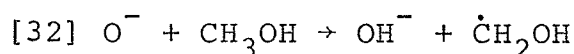
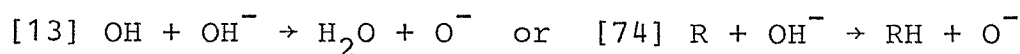
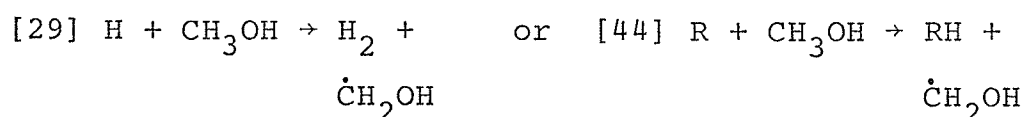
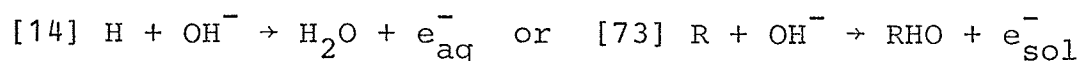
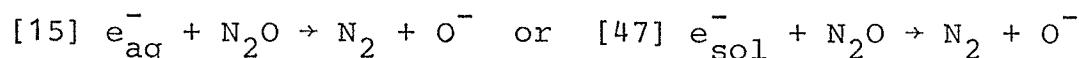
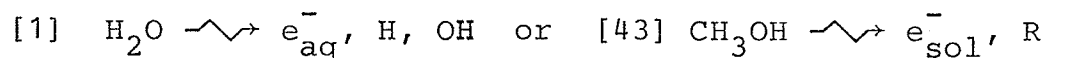


An increase of g-factor and decrease in hyperfine constant were evident upon dissociation. In neutral solution the spectra resembled those found by Livingston and Zeldes (36) who attributed them to the undissociated form of the radical. Simic, Neta, and Hayon (37) observed dissociation of $\dot{\text{C}}\text{H}_2\text{OH}$ by pulse radiolysis, giving results similar to those found for the 2-propanol radical $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$.

The point of inflection of Fig. 4.2 gives 12.4 ± 0.4 as the pK of the methanol radical in pure methanolic solution. The pK of the methanol radical in aqueous solution was reported by Asmus et al. (38) to be 10.7. The pK of weak acids such as the hydroxymethyl radical is known to increase with decrease in dielectric constant (44). The

increase in pK of the methanol radical in going from aqueous to pure methanolic solution is attributable to the simultaneous decrease in dielectric constant, the dielectric constant of water being 78.36 while that of methanol is 32.63.

Where the formaldehyde yields are high, indicating a significant chain reaction, and independent of base concentration ($[\text{OH}^-] > 0.1 \text{ M}$), the following mechanism is proposed. The formation of the methanol radical anion is assumed to be stoichiometric. It is also assumed that the γ -radiation interacts primarily with the solvent water in aqueous solutions via reaction 1 or with methanol in methanolic solutions via reaction 43; R is any species capable of hydrogen atom abstraction from the solvent.



Equation 75 is derived for $G(\text{HCHO})$ from this mechanism with the usual steady-state assumptions.

$$[75] \quad G(\text{HCHO}) = k_{31} \sqrt{\frac{G_{\text{R}}}{2k_{48} \cdot D}} [\text{N}_2\text{O}]$$

where D is the dose rate in units of $6.023 \times 10^{25} \text{ eV l}^{-1} \text{ s}^{-1}$ and $G_{\text{R}} = G_{\text{e}_{\text{aq}}^-} + G_{\text{H}} + G_{\text{OH}}$ (or analogous primary yields in

methanol solution).

In contrast to 2-propanol, the mechanism for methanol predicts a linear dependence of the formaldehyde yields on nitrous oxide concentration and no dependence on methanol concentration. A linear dependence of the yields on the reciprocal of the square-root of the dose rate is forecast as in the case of 2-propanol.

The experimental results are in good agreement with these predictions. Since the primary yields in methanolic solutions ($G_R \sim 6$) are similar to those in aqueous solutions (1, 45), the increase of $G(\text{HCHO})$ with increasing mole fraction methanol may simply reflect an increase in the rate of the chain propagating reaction 31 as shown in Fig. 4.5 and tabulated in Table 4.1; values of k_{31} were calculated from equation 75 assuming $2k_{48} = 0.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (37) and $G_R = 5.9$ (41), independent of base concentration. As shown in Fig. 4.4 and Table 4.4, $G(\text{HCHO})$ varies directly with the reciprocal of the square-root of the dose rate. From this line of essentially zero intercept as predicted from the proposed mechanism, a value of $k_{31} = 464 \pm 5 \text{ M}^{-1} \text{ s}^{-1}$ is calculated from the slope. Fig. 4.3 and Table 4.3 show that at $[\text{OH}^-] = 0.120 \text{ M}$ $G(\text{HCHO})$ is linearly dependent on nitrous oxide concentration with a small intercept corresponding to formaldehyde formation independent of nitrous oxide but nearly zero as predicted by the mechanism. A value of $k_{31} = 309 \pm 8 \text{ M}^{-1} \text{ s}^{-1}$ was determined from the slope. The mean value of k_{31} is then $386 \pm 11 \text{ M}^{-1} \text{ s}^{-1}$.

At $[\text{OH}^-] = 2.75 \times 10^{-2} \text{ M}$ in pure methanol, $G(\text{HCHO})$ increases non-linearly with increasing nitrous oxide concentration as shown in Fig. 4.3 and Table 4.3. At this particular base concentration, the formation of the radical anion, existing significantly in both the dissociated and the undissociated forms, is non-stoichiometric. Additional terminating reactions involving the undissociated form of

FIG. 4.5

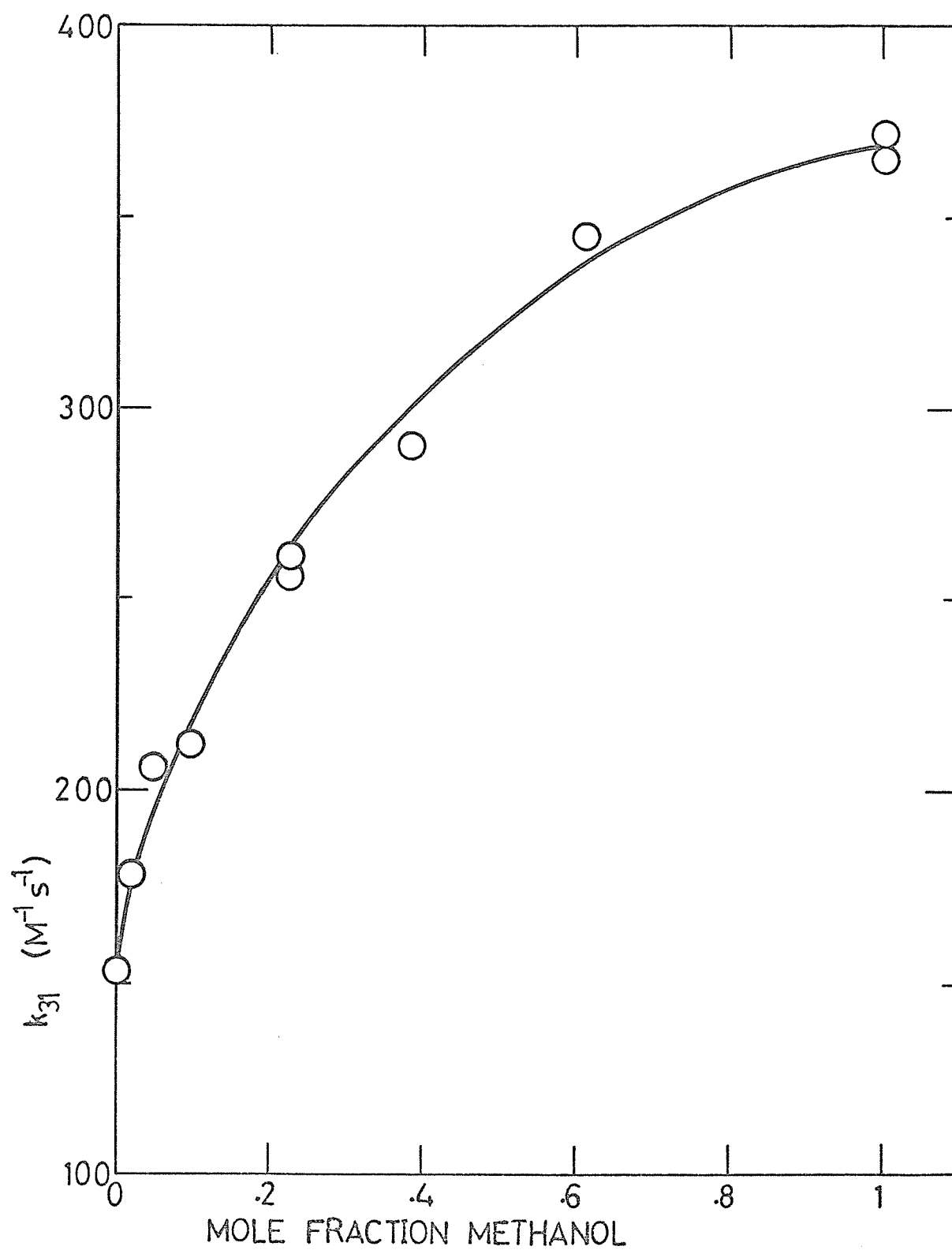
Variation of k_{31} with mole fraction
 CH_3OH .

$$[\text{OH}^-] = 0.120 \text{ M}$$

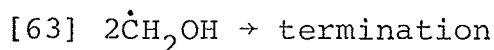
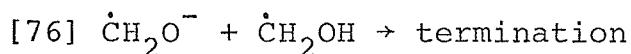
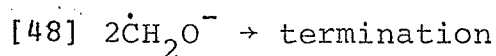
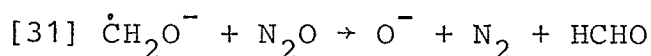
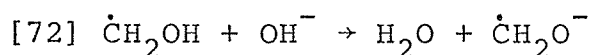
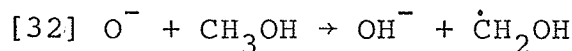
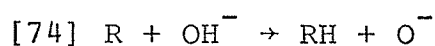
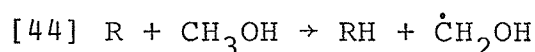
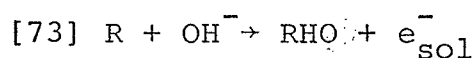
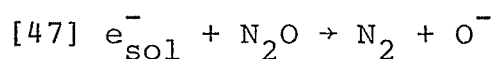
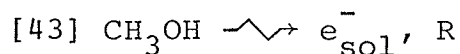
$$[\text{N}_2\text{O}] = 2.95 \times 10^{-2} \text{ M}$$

$$\text{Av. dose rate} = 1.06 \times 10^{19} \text{ eV l}^{-1} \text{ s}^{-1}$$

FIG. 4.5



the radical $\dot{\text{C}}\text{H}_2\text{OH}$ are possible now besides bimolecular termination 48 of the dissociated radical $\dot{\text{C}}\text{H}_2\text{O}^-$. Extension of the previously proposed mechanism, applicable only at $[\text{OH}^-] > 0.1 \text{ M}$, to include cross termination 76 by the dissociated and undissociated forms of the radical and bimolecular termination 63 by the undissociated form of the radical, gives a chain mechanism applicable at $[\text{OH}^-] \leq 0.1 \text{ M}$. This mechanism is summarized below for methanolic solutions.



Employing the usual steady-state assumptions and assuming $2k_{48} = k_{76} = 2k_{63} = k_t$ in order to obtain a simple algebraic solution, equation 77 may be derived from the above mechanism.

$$[77] G(\text{HCHO}) = \frac{k_{31} k_{72} \sqrt{\frac{G_R}{k_t \cdot D}} [\text{OH}^-] \cdot [\text{N}_2\text{O}]}{k_{72} [\text{OH}^-] + k_{31} [\text{N}_2\text{O}] + \sqrt{G_R \cdot k_t \cdot D}}$$

where D is the dose rate in units of $6.023 \times 10^{25} \text{ eV l}^{-1} \text{ s}^{-1}$ and G_R is the yield of primary species in methanolic solution. Equation 77 predicts a non-linear variation of $G(\text{HCHO})$ with nitrous oxide and base concentrations at $[\text{OH}^-] \leq 0.1 \text{ M}$ as observed experimentally. It may be noted

that at high base concentration $k_{72}[\text{OH}^-] \gg k_{31}[\text{N}_2\text{O}] + (G_R \cdot k_t \cdot D)^{1/2}$ and equation 77 reduces to equation 75, valid at $[\text{OH}^-] > 0.1 \text{ M}$.

As a further test of the validity of equation 77, k_{72} values were computed at $[\text{OH}^-] = 2.75 \times 10^{-2} \text{ M}$ using each value of $[\text{N}_2\text{O}]$ and $G(\text{HCHO})$ given in Table 4.3. The mean value is $k_{72} = (2.68 \pm 0.24) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$. The comparative similarity of the individual k_{72} values (listed in Table 4.3) attests to the applicability of the proposed mechanism in a region where the yields are dependent on both nitrous oxide and base concentrations. At $[\text{OH}^-] = 0.1 \text{ M}$ and $[\text{N}_2\text{O}] = 2.95 \times 10^{-2} \text{ M}$, the values $k_{72}[\text{OH}^-] = 268$, $k_{31}[\text{N}_2\text{O}] = 11$, and $(G_R \cdot k_t \cdot D)^{1/2} = 28$ are calculated so that the simplification of equation 77 to equation 75 at $[\text{OH}^-] > 0.1 \text{ M}$ is indeed justified.

No primary kinetic isotope effect would be expected on the basis of the proposed mechanism on substitution of CD_3OH for CH_3OH . Assuming that hydrogen atom transfer from a C-H bond occurs in neither reaction 31 nor 48, the formaldehyde yields from CH_3OH and CD_3OH should be identical as predicted by equation 75. As mentioned previously, the formaldehyde yield from CD_3OH exceeded that of CH_3OH , being respectively 28.4 and 22.5 (mean value). However, if disproportionation contributes to the terminating reaction 48, the value of k_{48} will decrease and $G(\text{formaldehyde})$ will increase. Therefore these values are regarded as an indication of no significant kinetic isotope effect. Hence reaction 31 is not involved in C-H bond-breaking as a rate determining process in accord with the mechanism.

On the basis of pulse radiolysis of alkaline ethanol solutions Fletcher, Richards, and Seddon (46) have proposed a mechanism which predicts that $G(\text{HCHO})$ should vary linearly with methoxide concentration and should be independent of nitrous oxide concentration in alkaline methanol solutions

containing nitrous oxide. Their mechanism was said to fit more closely the methoxide concentration dependence observed by Sherman (23). A pure methanol solution 0.120 M in sodium methoxide and 2.95×10^{-2} M in nitrous oxide was therefore irradiated and gave $G(\text{HCHO}) = 20.7$, slightly lower than the value obtained using KOH as shown in Table 4.1 but still comparable. Hence the yields using any of NaOH, KOH, or NaOCH_3 were considered essentially independent of base concentration above 0.1 M. From Figure 2 given by Sherman (47) it is apparent that the nitrogen yields showed a similar effect to that of the formaldehyde yields in the present work: a lack of dependence on base concentration above approximately 0.1 M in base with dependence on base concentration below 0.1 M. A lack of dependence on nitrous oxide concentration was observed neither in the present work nor in the work of Sherman (23). As mentioned previously, quite definite linear dependence of $G(\text{HCHO})$ on nitrous oxide concentration was found at $[\text{OH}^-] = 0.120 \text{ M}$; at $[\text{OH}^-] = 2.75 \times 10^{-2} \text{ M}$, where the yields were still base concentration dependent, $G(\text{HCHO})$ increased non-linearly but significantly with increasing nitrous oxide concentration up to $[\text{N}_2\text{O}] = 9.44 \times 10^{-2} \text{ M}$.

The reaction scheme proposed by Fletcher, Richards, and Seddon is inconsistent with these observations. Based on the assumption that the equilibrium between ethanol and ethoxide is not rapidly attained, they postulated a single terminating reaction involving bimolecular combination of two undissociated radicals in alkaline solution, in competition with hydrogen abstraction from the ethoxide ion $\text{CH}_3\text{CH}_2\text{O}^-$ by the radical $\text{CH}_3\dot{\text{C}}\text{HOH}$ as the rate-determining propagating step. Propagation of the chain by reaction of N_2O with $\text{CH}_3\dot{\text{C}}\text{HO}^-$ was proposed but was assumed to be sufficiently rapid not to be involved in determining the chain length. They assumed that their mechanism could be

generalized to other alcohols. This was not the case for methanol nor for 2-propanol. It is proposed that the mechanisms presented in the present work suitably rationalize the experimental findings. For alkaline methanol, equation 77 at $[\text{OH}^-] \leq 0.1 \text{ M}$ and equation 75 at $[\text{OH}^-] > 0.1 \text{ M}$ provide a better rationalization of Sherman's results than the equation derived by Fletcher, Richards, and Seddon. In addition, the reaction scheme proposed by Fletcher, Richards, and Seddon implies a decrease in yields upon substitution of CD_3OH for CH_3OH since hydrogen abstraction from the methyl group is contained within their mechanism. If there were any kinetic isotope effect at all in the present work, it served to increase the yields upon deuteration of the methyl group of methanol.

5. CONCLUSION

5.1 Summary

A qualitative summary of the essential experimental findings relating to the predictions of the proposed mechanisms for alkaline aqueous 2-propanol and methanol solutions containing nitrous oxide is presented below.

G(acetone) from 2-propanol:

- (a) increased sigmoidally with increasing pH, becoming independent of pH at $\text{pH} > 12.5$.
- (b) increased linearly, with a non-zero intercept, with increasing [2-propanol].
- (c) increased linearly, with a non-zero intercept, with increasing $1/\sqrt{D}$.
- (d) was independent of $[\text{N}_2\text{O}]$ at $[\text{N}_2\text{O}] > 9 \times 10^{-2} \text{ M}$.
- (e) increased non-linearly with increasing $[\text{N}_2\text{O}]$ at $[\text{N}_2\text{O}] \leq 9 \times 10^{-2} \text{ M}$; $1/G(\text{acetone})$ varied approximately linearly with $1/[\text{N}_2\text{O}]$.
- (f) increased upon substitution of $(\text{CD}_3)_2\text{CHOH}$ for $(\text{CH}_3)_2\text{CHOH}$.
- (g) decreased upon substitution of $(\text{CH}_3)_2\text{CDOH}$ for $(\text{CH}_3)_2\text{CHOH}$.
- (h) was unchanged upon substitution of $(\text{CH}_3)_2\text{CHOD}$ for $(\text{CH}_3)_2\text{CHOH}$.

G(HCHO) from methanol:

- (a) increased sigmoidally with increasing $[\text{OH}^-]$, becoming independent of $[\text{OH}^-]$ at $[\text{OH}^-] > 0.1 \text{ M}$.
- (b) increased non-linearly with increasing $[\text{CH}_3\text{OH}]$.
- (c) increased linearly, with essentially zero intercept, with increasing $1/\sqrt{D}$.
- (d) increased linearly, with essentially zero intercept, with increasing $[\text{N}_2\text{O}]$ at $[\text{OH}^-] > 0.1 \text{ M}$.

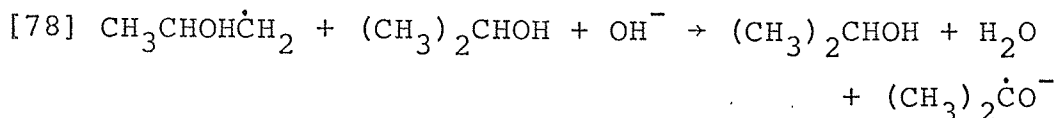
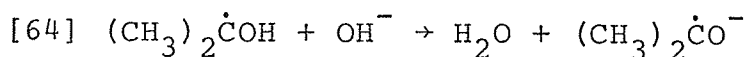
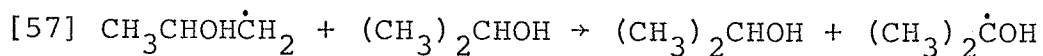
- (e) increased non-linearly with increasing $[N_2O]$ at $[OH^-] \leq 0.1$ M.
- (f) was essentially unchanged upon substitution of CD_3OH for CH_3OH .

Notably two qualitative features listed above were not observed in the neutral aqueous 2-propanol and methanol systems containing hydrogen peroxide (25, 26, 27). In neutral solutions of aqueous 2-propanol containing hydrogen peroxide a non-linear increase with increasing $1/\sqrt{D}$ up to a limit was found as mentioned earlier (Section 1.4). The yields in neutral solutions of methanol containing hydrogen peroxide decreased with increasing methanol concentration above 2.0 M methanol although they were independent of methanol concentration below 2.0 M. This decrease in yields was attributed to a decrease in the rate constant for the propagating reaction 62 caused by the decrease in the dielectric constant of the solution with increasing methanol concentration, resulting in an increase of the activation energy of formation of the polar transition state (48). In the alkaline system, the propagating reaction 31 does not involve the reaction of two uncharged dipoles, $\dot{C}H_2OH + H_2O_2$, as in the neutral system (reaction 62) but rather the reaction of a charged species, $\dot{C}H_2O^-$, with a dipole, N_2O , and k_{31} increases with increasing methanol concentration since the primary yields remain approximately constant. The rate-determining step, to which the energy of activation refers, in reactions between anions and polar molecules is the escape of the ion from its solvation sheath (49). The work done in the reorganization of solvent molecules which solvate the ion accounts for most of the energy of activation. The magnitude of this work term is determined by the intrinsic properties of the ion and the solvent, but is to some extent modified by the presence of the polar molecule with which the ion reacts after or during its escape from the solvation

shell. The role of the solvent water is thus in any case a strongly retarding one on the rate of a reaction such as 31 relative to methanol.

A comparison of the rate constants and rate constant ratios for hydrogen atom abstraction and propagating reactions determined for alkaline aqueous 2-propanol and methanol containing N_2O with those determined previously in this laboratory for analogous neutral systems containing H_2O_2 is given in Table 5.1. Wherever two methods of calculation of a single quantity were made in the present work, the mean value is given in the table. Reference may be made to Appendix I for the reactions corresponding to the rate constants.

Certain quantitative distinctions are worthy of comment. The rate of the radical conversion reaction 57 in the alkaline aqueous 2-propanol + N_2O system is about 8.5 times faster than that in the neutral aqueous 2-propanol + H_2O_2 system. If the overall reaction, reaction 57 and reaction 64, can be regarded as a concerted reaction 78, i.e. a base-catalyzed reaction, the greater solvation energy of the radical anion will make the total energy of the anion in solution less than that of the neutral radical.



If this difference in the energy of the product is reflected in a decrease in the activation energy for the hydrogen atom transfer reaction, the conversion reaction in alkaline solution might well have a greater rate constant.

The rate constant for the chain propagating reaction 19 in alkaline solution is approximately an order of magnitude less than the analogous rate constant for the

TABLE 5.1

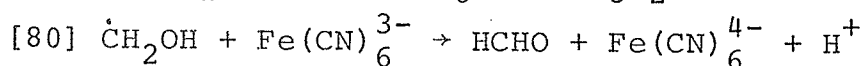
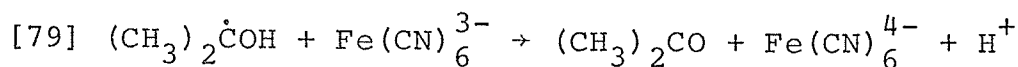
Rate constants and rate constant ratios: a comparison of alkaline aqueous 2-propanol and methanol containing N_2O with neutral aqueous 2-propanol and aqueous methanol containing H_2O_2 (26, 27, 50).

Alkaline Aqueous 2-propanol + N_2O			Neutral Aqueous 2-propanol + H_2O_2		
$k_{57} (M^{-1} s^{-1})$	$= 431 \pm 27$	(a)	$k_{57} (M^{-1} s^{-1})$	$= 51 \pm 2$	(a)
$k_{41} (M^{-1} s^{-1})$	$= (8.92 \pm 0.43) \times 10^8$	(b)	$k_{54} (M^{-1} s^{-1})$	$= 1.2 \times 10^9$	(c)
$k_{65} (M^{-1} s^{-1})$	$= (1.59 \pm 0.08) \times 10^8$	(b)	$k_{55} (M^{-1} s^{-1})$	$= 2.3 \times 10^8$	(c)
$k_{19} (M^{-1} s^{-1})$	$= (3.81 \pm 0.35) \times 10^4$		$k_{56} (M^{-1} s^{-1})$	$= (4.8 \pm 0.3) \times 10^5$	
k_{41}/k_{65}	$= 5.62 \pm 0.27$		k_{54}/k_{55}	$= 5.2 \pm 0.1$	
$k_{41}(H)/k_{41}(D)$	$= 1.35 \pm 0.10$		$k_{54}(H)/k_{54}(D)$	$= 1.38 \pm 0.05$	
$k_{65}(H)/k_{65}(D)$	$= 3.26 \pm 0.23$		$k_{55}(H)/k_{55}(D)$	$= 2.15 \pm 0.16$	
$k_{57}(H)/k_{57}(D)$	$= 10.7 \pm 5.6$		$k_{57}(H)/k_{57}(D)$	$= 7.3 \pm 1.5$	
Alkaline Methanol + N_2O			Neutral Aqueous Methanol + H_2O_2		
$k_{31} (M^{-1} s^{-1})$	$= 386 \pm 11$	(d)	$k_{62} (M^{-1} s^{-1})$	$= (4.0 \pm 0.4) \times 10^4$	(e)
Assuming $(M^{-1} s^{-1})$: (a) $2k_{58} = 2 \times 10^9$ (37); (b) $k_{41} + k_{65} = 1.05 \times 10^9$ (42); (c)					
$k_{54} + k_{55} = 1.4 \times 10^9$ (11); (d) $2k_{48} = 0.9 \times 10^9$ (37); (e) $2k_{63} = 2.4 \times 10^9$ (37).					

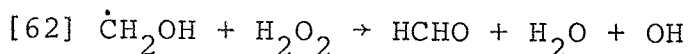
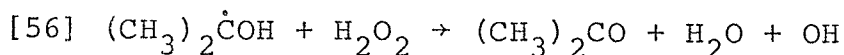
chain propagating reaction 56 in neutral solution. This difference reflects the difference in the rates of the rate-determining propagating reaction 57 between the alkaline and neutral systems.

The values of k_α/k_β in both systems are very close indicating that O^- (85% α attack) and OH (84% α attack) have approximately the same reactivities in hydrogen atom abstractions from 2-propanol. Adams and Willson (51) found that 95% α position attack by OH on 2-propanol occurred in the rapid bleaching of ferricyanide relative to methanol having 100% α attack. An error of approximately $\pm 5\%$ was involved in this determination so their value may be an upper limit to k_α/k_β .

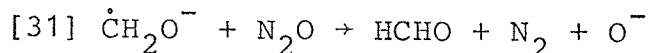
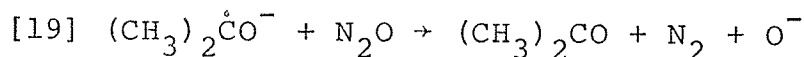
Adams and Willson (51) determined that $k_{79} = 4.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and $k_{80} = 4.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ so that $k_{79} > k_{80}$ for the following reactions with ferricyanide.



Burchill and Jones (50) found that $k_{56} = 4.8 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ while Burchill and Ginns (26) found that $k_{62} = 4.0 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ so that $k_{56} \gg k_{62}$.



In the present work the values $k_{19} = 3.81 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ and $k_{31} = 386 \text{ M}^{-1} \text{ s}^{-1}$ were determined so that $k_{19} \gg k_{31}$.



Thus the α radical (or radical anion) derived from methanol is always observed to react more slowly as a reductant than the α radical (or radical anion) derived from 2-propanol and this differential increases as the intrinsic rate of the

reaction decreases.

The kinetic isotope effects had similar trends in both the alkaline aqueous 2-propanol + N_2O system and the neutral aqueous 2-propanol + H_2O_2 system. However, the decrease in the rate constant for the radical conversion reaction 57 by a factor ~ 1.5 upon substitution of $(CD_3)_2CHOH$ for $(CH_3)_2CHOH$ found in the alkaline system was not observed in the neutral system. As stated previously, no explanation for the decrease in k_{57} in the alkaline system is evident. In the alkaline system it may be seen that $k_{41(H)}/k_{41(D)} < k_{65(H)}/k_{65(D)} < k_{57(H)}/k_{57(D)}$ which is the reverse order of the magnitudes of the intrinsic rate constants: $k_{41} > k_{65} > k_{57}$. This is the expected trend for such a series of hydrogen atom abstraction reactions. Burchill and Thompson (27) have observed the same ordering in neutral solution. They also found that the chain oxidation of neutral aqueous methanol + H_2O_2 showed no primary kinetic isotope effect on substitution of CD_3OH , as was found for alkaline methanol + N_2O in the present work.

5.2 Further Work Suggested

The work done on aqueous alkaline 2-propanol and nitrous oxide solutions could be extended from 0.209 M to higher alcohol concentrations to determine the ultimate range of applicability of the proposed mechanism. It was noticed, however, that at 0.209 M in the deuterated and undeuterated 2-propanols the yields were slightly lower than anticipated. This may be an indication that $G(\text{acetone})$ does not vary linearly with alcohol concentration exceeding 0.209 M. A similar effect was observed by Burchill and Ginns (25) in neutral hydrogen peroxide and concentrated 2-propanol solutions. As demonstrated herein, a plot of $1/G(\text{acetone})$ vs. $1/[N_2O]$ can yield an estimate for k_{19} , the propagating reaction rate constant. This suggests the possibility of

determining whether k_{19} increases with increasing 2-propanol concentration as the analogous rate constant k_{31} does for methanol.

The radiation chemistry of alkaline aqueous (and concentrated) solutions of ethanol containing nitrous oxide could be investigated. This system is expected to be completely analogous to the 2-propanol system. Previous work (25, 26, 27) in this laboratory has shown this to be the case with ethanol and 2-propanol in neutral solutions containing hydrogen peroxide. Such a study might be able to sort out the controversy in the mechanisms proposed by Fletcher, Richards, and Seddon (46) and by Simic, Neta, and Hayon (37) (and those given in the present work), and provide an answer to the question of whether a single mechanism can apply to ethanol in the entire range from water to alcohol as solvent.

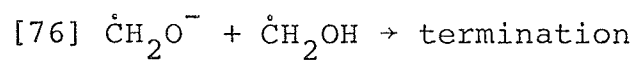
As an extension of a recent ESR study by Burchill and Jones (50), using in-cavity UV photolysis to measure the ratio $[(CH_3)_2\dot{C}OH]/[CH_3CHOH\dot{C}H_2]$ and k_{56} (assuming a value for k_α/k_β from previous radiation chemical work (25)) for 2-propanol and hydrogen peroxide in neutral solution, this ratio and k_{19} could be measured for 2-propanol and nitrous oxide in alkaline solution. Such a determination could perhaps be done by using in-cavity electron beam irradiation and by introducing nitrous oxide into the sample to a pressure exceeding 5.5 atmospheres. The results of the present work seem self-consistent, and this further work would provide a valuable test of the proposed mechanism.

APPENDIX I: LIST OF REACTIONS AND EQUATIONS

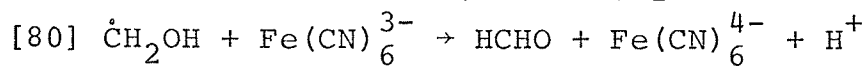
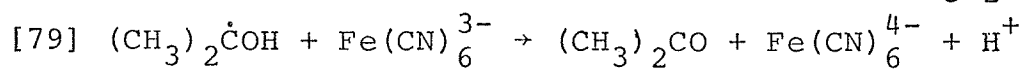
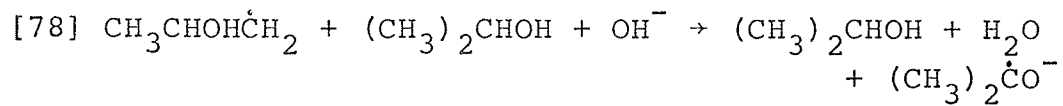
- [1] $\text{H}_2\text{O} \xrightarrow{\sim} \text{e}_{\text{aq}}^-, \text{H}, \text{OH}, \text{H}_2, \text{H}_2\text{O}_2, \text{H}_3\text{O}^+, \text{OH}^-$
- [2] $\text{H}_2\text{O} \xrightarrow{\sim} \text{H}_2\text{O}^+ + \text{e}^-$
- [3] $\text{H}_2\text{O}^+ + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{OH}$
- [4] $\text{e}_{\text{thermal}}^- + n\text{H}_2\text{O} \rightarrow \text{e}_{\text{aq}}^-$
- [5] $\text{H}_2\text{O} \xrightarrow{\sim} \text{H}_2\text{O}^*$
- [6] $\text{H}_2\text{O}^* \xrightarrow{\text{M}} \text{H}_2\text{O}$
- [7] $\text{H}_2\text{O}^* \rightarrow \text{H} + \text{OH}$
- [8] $\text{e}_{\text{aq}}^- + \text{H}_3\text{O}^+ \rightarrow \text{H} + \text{H}_2\text{O}$
- [9] $\text{e}_{\text{aq}}^- + \text{e}_{\text{aq}}^- \rightarrow \text{H}_2 + 2\text{OH}^-$
- [10] $\text{e}_{\text{aq}}^- + \text{H} \rightarrow \text{H}_2 + \text{OH}^-$
- [11] $\text{H} + \text{H} \rightarrow \text{H}_2$
- [12] $\text{OH} + \text{OH} \rightarrow \text{H}_2\text{O}_2$
- [13] $\text{OH} + \text{OH}^- \rightarrow \text{O}^- + \text{H}_2\text{O}$
- [14] $\text{H} + \text{OH}^- \rightarrow \text{e}_{\text{aq}}^- + \text{H}_2\text{O}$
- [15] $\text{e}_{\text{aq}}^- + \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O}^- (+ \text{H}_2\text{O} \rightleftharpoons \text{OH} + \text{OH}^-)$
- [16] $\text{H} + \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{OH}$
- [17] $\text{O}^- + \text{N}_2\text{O} \rightarrow (\text{N}_2\text{O}_2^-) \rightarrow (1/2)\text{N}_2 + \text{NO}_2^-$
- [18] $\text{OH} + (\text{CH}_3)_2\text{CHO}^- \rightarrow (\text{CH}_3)_2\dot{\text{C}}\text{O}^- + \text{H}_2\text{O}$
- [19] $(\text{CH}_3)_2\dot{\text{C}}\text{O}^- + \text{N}_2\text{O} \rightarrow (\text{CH}_3)_2\text{CO} + \text{N}_2 + \text{O}^- (+ \text{H}_2\text{O} \rightleftharpoons \text{OH} + \text{OH}^-)$
- [20] $\text{G}(\text{N}_2)$: refer to p.6
- [21] $\text{H}_2 + \text{OH} \rightarrow \text{H} + \text{H}_2\text{O}$
- [22] $\text{e}_{\text{aq}}^- + \text{HO}_2^- \rightarrow 2\text{OH}^- + \text{OH}$
- [23] $\text{e}_{\text{aq}}^- + \text{M} \rightarrow \text{termination}$
- [24] $\text{H}_2\text{O}^* + \text{N}_2\text{O} \rightarrow \text{N}_2 + 2\text{OH}$

- [25] $\text{H}_2\text{O}^* + \text{OH}^- \rightarrow \text{e}_{\text{aq}}^- + \text{OH}$
- [26] $\text{H}_2\text{O}^* + \text{H}^+ \rightarrow \text{H}_2^+ + \text{OH}$
- [27] $\text{H} + \text{OH} \rightarrow \text{H}_2\text{O}$
- [28] $\text{O}^- + \text{H}_2 \rightarrow (\text{H} + \text{OH}^-) \rightarrow \text{e}_{\text{aq}}^- + \text{H}_2\text{O}$
- [29] $\text{H} + \text{CH}_3\text{OH} \rightarrow \dot{\text{C}}\text{H}_2\text{OH} + \text{H}_2$
- [30] $\dot{\text{C}}\text{H}_2\text{OH} + \text{OH}^- \rightarrow \text{HCHO} + \text{e}_{\text{aq}}^-$
- [31] $\dot{\text{C}}\text{H}_2\text{O}^- + \text{N}_2\text{O} \rightarrow \text{HCHO} + \text{N}_2 + \text{O}^-$
- [32] $\text{CH}_3\text{OH} + \text{O}^- \text{ (or OH)} \rightarrow \dot{\text{C}}\text{H}_2\text{OH} + \text{OH}^- \text{ (or H}_2\text{O)}$
- [33] $\text{H}_2\text{O} + \text{O}^- + \text{Fe}(\text{CN})_6^{4-} \rightarrow \text{Fe}(\text{CN})_6^{3-} + 2\text{OH}^-$
- [34] $\text{O}^- + (\text{CH}_3)_2\text{CHO}^- \rightarrow (\text{CH}_3)_2\dot{\text{C}}\text{O}^- + \text{OH}^-$
- [35] $\text{H} + (\text{CH}_3)_2\text{CHO}^- \rightarrow (\text{CH}_3)_2\dot{\text{C}}\text{O}^- + \text{H}_2$
- [36] $(\text{CH}_3)_2\dot{\text{C}}\text{O}^- + \text{Fe}(\text{CN})_6^{3-} \rightarrow (\text{CH}_3)_2\text{CO} + \text{Fe}(\text{CN})_6^{4-}$
- [37] $\text{OH} + \text{NO}_2^- \rightarrow \text{NO}_2 + \text{OH}^-$
- [38] $\text{e}_{\text{aq}}^- + \text{NO}_2^- \rightarrow \text{NO} + 2\text{OH}^-$
- [39] $\text{N}_2\text{O} + (\text{CH}_3)_2\text{CHOH} \rightarrow (\text{CH}_3)_2\text{CO} + \text{N}_2 + \text{H}_2\text{O}$
- [40] $\text{N}_2\text{O} + (\text{CH}_3)_2\text{CHOH} \rightarrow \text{CH}_3\text{COOH} + \text{N}_2 + \text{CH}_4$
- [41] $\text{O}^- + (\text{CH}_3)_2\text{CHOH} \rightarrow (\text{CH}_3)_2\dot{\text{C}}\text{OH} + \text{OH}^-$
- [42] $(\text{CH}_3)_2\dot{\text{C}}\text{OH} + (\text{CH}_3)_2\text{CHO}^- \rightarrow (\text{CH}_3)_2\dot{\text{C}}\text{O}^- + (\text{CH}_3)_2\text{CHOH}$
- [43] $\text{CH}_3\text{OH} \xrightarrow{\sim} \text{e}_{\text{sol}}^- + \text{H} + \text{R} + \text{other products}$
- [44] $\text{R} + \text{CH}_3\text{OH} \rightarrow \text{RH} + \dot{\text{C}}\text{H}_2\text{OH}$
- [45] $\dot{\text{C}}\text{H}_2\text{OH} + \text{CH}_3\text{O}^- \rightarrow \dot{\text{C}}\text{H}_2\text{O}^- + \text{CH}_3\text{OH}$
- [46] $\dot{\text{C}}\text{H}_2\text{OH} + \text{CH}_3\text{O}^- \rightarrow \text{HCHO} + \text{e}_{\text{sol}}^-$
- [47] $\text{e}_{\text{sol}}^- + \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O}^-$
- [48] $2\dot{\text{C}}\text{H}_2\text{O}^- \rightarrow \text{termination}$
- [49] $2\dot{\text{C}}\text{H}_2\text{O}^- + \text{CH}_3\text{OH} \rightarrow 2\text{CH}_3\text{O}^- + \text{HCHO}$
- [50] $2\text{e}_{\text{sol}}^- \rightarrow \text{H}_2 + 2\text{CH}_3\text{O}^-$

- [51] $e_{aq}^- + H_2O_2 \rightarrow OH^- + OH$
- [52] $H + (CH_3)_2CHOH \rightarrow H_2 + (CH_3)_2\dot{C}OH$
- [53] $H + (CH_3)_2CHOH \rightarrow H_2 + CH_3CHOH\dot{C}H_2$
- [54] $OH + (CH_3)_2CHOH \rightarrow H_2O + (CH_3)_2\dot{C}OH$
- [55] $OH + (CH_3)_2CHOH \rightarrow H_2O + CH_3CHOH\dot{C}H_2$
- [56] $(CH_3)_2\dot{C}OH + H_2O_2 \rightarrow (CH_3)_2CO + H_2O + OH$
- [57] $CH_3CHOH\dot{C}H_2 + (CH_3)_2CHOH \rightarrow (CH_3)_2CHOH + (CH_3)_2\dot{C}OH$
- [58] $2CH_3CHOH\dot{C}H_2 \rightarrow 2,5\text{-hexanediol or } (CH_3)_2CO + (CH_3)_2CHOH$
- [59] G(acetone): refer to p.15
- [60] G(-H₂O₂): refer to p.16
- [61] -d[H₂O₂]/dt: refer to p.17
- [62] $\dot{C}H_2OH + H_2O_2 \rightarrow HCHO + H_2O + OH$
- [63] $2\dot{C}H_2OH \rightarrow \text{ethylene glycol or } HCHO + CH_3OH$
- [64] $(CH_3)_2\dot{C}OH + OH^- \rightarrow (CH_3)_2\dot{C}O^- + H_2O$
- [65] $O^- + (CH_3)_2CHOH \rightarrow OH^- + CH_3CHOH\dot{C}H_2$
- [66] G(acetone): refer to p.38
- [67] $CH_3CHOH\dot{C}H_2 + (CH_3)_2\dot{C}O^- \rightarrow \text{termination}$
- [68] $2(CH_3)_2\dot{C}O^- \rightarrow \text{termination}$
- [69] G(acetone): refer to p.44
- [70] 1/G(acetone): refer to p.45
- [71] k₁₉: refer to p.47
- [72] $\dot{C}H_2OH + OH^- \rightarrow \dot{C}H_2O^- + H_2O$
- [73] $R + OH^- \rightarrow RHO + e_{sol}^-$
- [74] $R + OH^- \rightarrow RH + O^-$
- [75] G(HCHO): refer to p.56



[77] $\text{G}(\text{HCHO})$: refer to p.59



APPENDIX II: CALCULATION OF N₂O CONCENTRATIONS

Using data given in the International Critical Tables (52), nitrous oxide concentrations were converted from pressures measured at 26 °C on the mercury manometer. The solubilities of N₂O in aqueous NaOH and KOH solutions at 26 °C were calculated from the solubilities given at 0, 10, and 20 °C assuming that $\log S(\text{N}_2\text{O})$ varied as T^{-1} where $S(\text{N}_2\text{O})$ is the solubility of N₂O in M/cm Hg and T is the Absolute temperature. The solubility of N₂O at any concentration of aqueous NaOH or KOH was then obtained by interpolation of a plot of $\log S(\text{N}_2\text{O})$ vs. [NaOH] or [KOH] (M) assuming linearity of this relationship over the range of base concentrations used experimentally. Since the concentrations of 2-propanol used were always low, it was assumed that the presence of 2-propanol did not alter the solubility of N₂O. This was not the case with methanol where pure methanol was used in a majority of the experiments; it was assumed that at a given base concentration the solubility of N₂O in pure methanol was given by the product of its solubility in water with the ratio of its solubility in neutral methanol (15.4×10^4 M/cm Hg at 26 °C) to that in neutral water (2.88×10^4 M/cm Hg at 26 °C). Typical values are given in Table II.1. Solubilities in solutions containing both methanol and water were assumed proportional to the mole fraction of methanol.

TABLE II.1

Variation of $S(N_2O)$ (M/cm Hg) with concentration of KOH and concentration of NaOH.

[KOH] (M)	$10^4 \times S(N_2O)$ in H_2O (M/cm Hg)	$10^4 \times S(N_2O)$ in CH_3OH (M/cm Hg)
0 - 10^{-2}	2.88	15.4
0.0265	2.86	15.4
0.0673	2.84	15.3
0.100	2.83	15.2
0.120	2.81	15.1
0.173	2.75	14.8
0.263	2.73	14.6
0.510	2.59	13.9

[NaOH] (M)	$10^4 \times S(N_2O)$ in H_2O (M/cm Hg)
0 - 10^{-3}	2.88
0.00910	2.87
0.0870	2.79
0.100	2.77
0.320	2.56

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