THE UNIVERSITY OF MANITOBA

ANTHRAQUINONE AND ANTHRAQUINONE-2-SULFONATE

AS PHOTOCATALYSTS IN THE PRODUCTION OF

HYDROGEN PEROXIDE

by

RHONDA G. SMERCHANSKI

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ABSTRACT

Photochemical processes leading to the production of hydrogen peroxide are investigated.

Specifically, anthraquinone in isopropanol/benzene solutions and anthraquinone-2-sulfonate in aqueous solutions are examined for their hydrogen peroxide producing potential. The hydroxylation of anthra-quinone-2-sulfonate in aqueous solutions is explored. Hydroxylation by hydroxyl radical is refuted, and a mechanism proposed in which hydroxylation occurs by addition of a water molecule and/or hydroxyl ion to anthraquinone-2-sulfonate radical cation.

ACKNOWLEDGEMENTS

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INTRODUCTION

During the last century, fossil fuels have become increasingly important as energy sources and, unfortunately, their rate of use is accelerating. From the amount of fossil fuels yet to be mined and mankind's escalating rate of consumption, scientists have predicted a time when these fuels will be depleted. Unless alternate energy sources can be developed, that future time will be bleak.

For the present, other power sources do exist. Atomic, geothermal, water, solar thermal and wind energies are being used. However, these constitute a small portion of the world's energy consumption. If a way could be found to transform the sun's radiant photochemical energy into some storable form, then whole new avenues for power would present themselves. In particular, the form that one of the "storable forms" could take would be as a chemical compound produced by an "endothermic" photochemical reaction. This compound would then be available at any time as a source of energy (upon decomposition). If this is to be the case, then the overall process of storing light energy in a chemical compound and the subsequent decomposition to get back the energy would have to conform to the following:

$$X \xrightarrow{h\nu} Y \qquad \dots\dots 1 \qquad \text{"endothermic"}$$

$$Y \longrightarrow X \qquad \dots\dots 2 \qquad \text{exothermic}$$

1) ΔH for reaction 2 should return a reasonable percentage of the radiant energy available in reaction 1.

2) Compound X should be cheap and in large abundance.

3) Compound Y should be easy to isolate and store.

4) Reaction 2 should be efficient and cause no pollution.

5) Reaction 1 should be efficient and occur easily.

6) The light used should be visible light.

7) The cost of operating the process should be feasible.

Photosynthesis satisfies only four of the above conditions. The decomposition of its products is often polluting and does not liberate more than approximately 2% to 5% of the initially available light energy (5).

Hydrogen peroxide as a candidate for a chemical energy carrier would appear reasonable. It could theoretically be made from water and oxygen (both abundant, cheap materials) and could be decomposed catalytically into steam and oxygen (releasing 23.9 kcal/mole with no pollution). There remains the problem of finding an inexpensive, efficient way of photochemically converting water and oxygen into hydrogen peroxide. Since the direct irradiation of water and oxygen with visible light to produce peroxide is not feasible, the process must involve a photocatalyst. Such a catalyst can either be photochemically oxidized with concurrent reduction of oxygen to hydrogen peroxide or the catalyst may be photochemically reduced with water followed by a thermal reaction with oxygen to give peroxide. That is, either step 1 or 2 below could be photochemical.

$$2H^+ + O_2 + C^X \longrightarrow H_2O_2 + C^{X+2} \qquad \ldots\ldots 1$$

$$C^{X+2} + H_2O \longrightarrow C^X + \tfrac{1}{2}O_2 + 2H^+ \qquad \ldots\ldots 2$$

$$H_2O + O_2 \longrightarrow H_2O_2 + \tfrac{1}{2}O_2$$
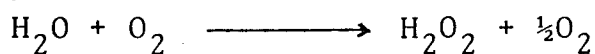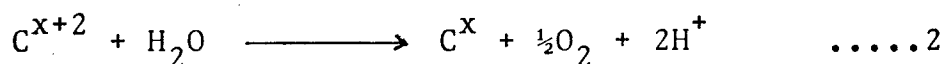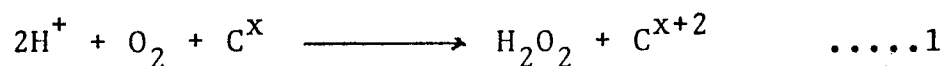
Two possibilities that might be considered for the catalyst are a metal ion or an organic compound. Unfortunately, the use of metal ions is impractical as they tend to decompose the hydrogen peroxide. That would leave the organic compound as the alternative.

Industrially (6), hydrogen peroxide is made using 2-ethyl-anthraquinone by the following process:
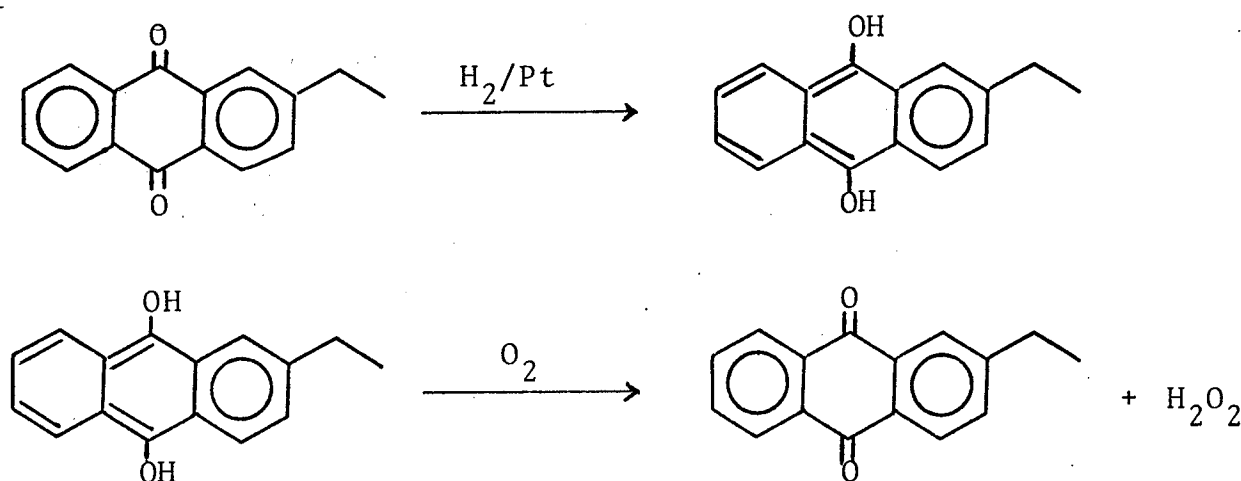
The latter reaction is a thermal process. Thus if a way could be found to produce anthraquinol (or a derivative) photochemically, anthraquinone (or a derivative) could be used for the organic compound catalyst.

In 1954, J.L. Bolland and H.R. Cooper (1) concluded that irradiation of anthraquinone in alcoholic solutions gave hydrogen peroxode in aerated solutions and the quinol in deaerated solutions. The reaction can be seen in Figure I.

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Figure I. Bolland and Cooper's (1)
reaction scheme for the irradiation
of anthraquinone in alcoholic solutions.

with oxygen,

$$\text{[anthraquinone-2-SO}_3^-\text{]} \xrightarrow{\ h\nu\ } \text{[anthraquinone-2-SO}_3^-\text{]}^*$$

$$\text{[anthraquinone-2-SO}_3^-\text{]}^* + CH_3-\underset{\underset{OH}{|}}{C}H-CH_3 \longrightarrow \text{(9-OH-10-O}\cdot\text{-anthracene-2-SO}_3^-) + CH_3-\underset{\underset{OH}{|}}{\overset{\cdot}{C}}-CH_3$$

$$\text{(9-OH-10-O}\cdot\text{-anthracene-2-SO}_3^-) + O_2 \longrightarrow \text{(anthraquinone-2-SO}_3^-) + HO_2^-$$

$$CH_3-\underset{\underset{OH}{|}}{\overset{\cdot}{C}}-CH_3 + O_2 \longrightarrow HO_2^- + CH_3-\underset{\underset{O}{\|}}{C}-CH_3$$

$$2\,HO_2^\cdot \longrightarrow H_2O_2 + O_2$$

without oxygen,

$$\text{(anthraquinone-2-SO}_3^-) + CH_3-\underset{\underset{OH}{|}}{\overset{\cdot}{C}}-CH_3 \longrightarrow \text{(9-OH-10-O}\cdot\text{-anthracene-2-SO}_3^-) + CH_3-\underset{\underset{O}{\|}}{C}-CH_3$$

$$2\,\text{(9-OH-10-O}\cdot\text{-anthracene-2-SO}_3^-) \rightleftharpoons \text{(anthraquinone-2-SO}_3^-) + \text{(9,10-diOH-anthracene-2-SO}_3^-)$$
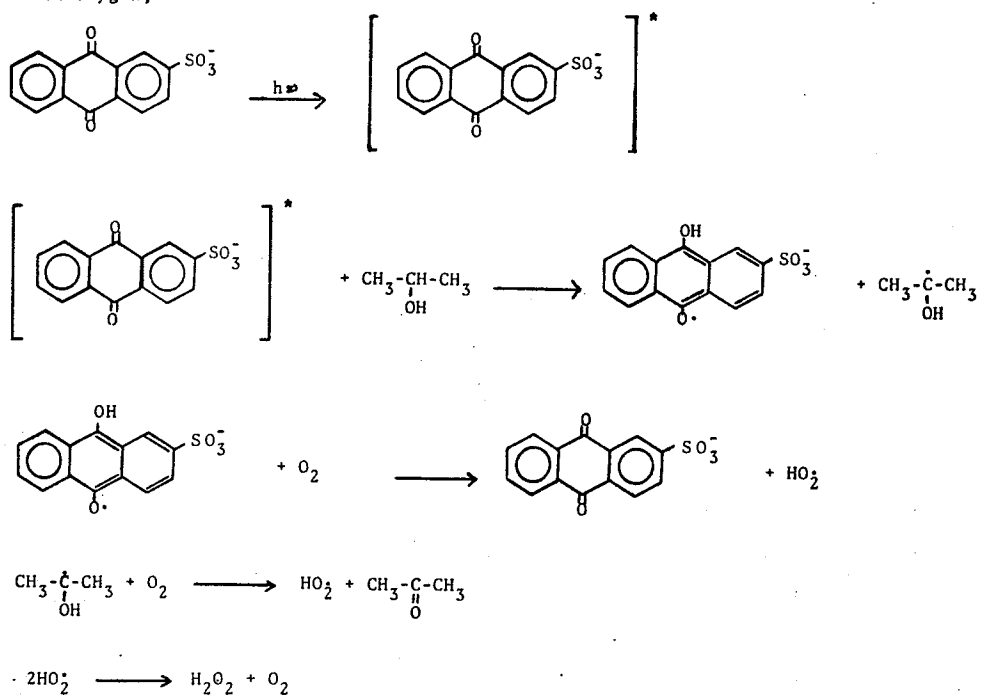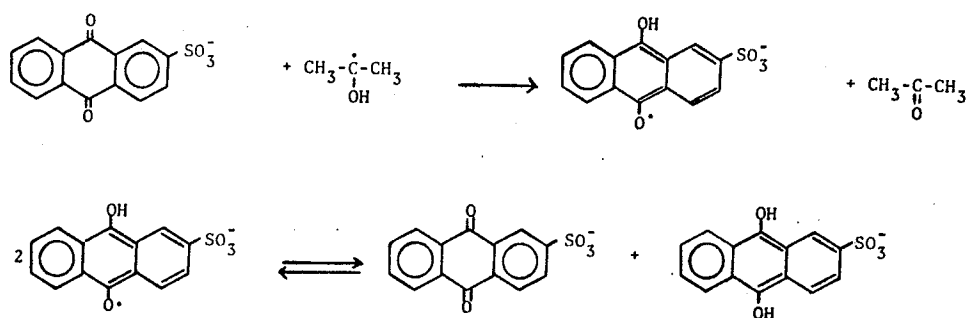
In 1958, Bridge and Porter (7) confirmed the primary steps in the sequence by flash photolysis and in 1960, Wells (8), from his work, substantiated that the mechanism involved an α-hydrogen abstraction from the alcohol by the photoexcited quinone with high quantum efficiency. From this information a photo-chemical pathway to the making of hydrogen peroxide was indicated. Experiments to determine the maximum yields of peroxide, the effect of oxygen concentration on the reaction and the effect of varying amounts of quinone or isopropyl alcohol immediately presented themselves. The next question to settle, however, was overall efficiency. The net summation of the above mechanism can be taken as:

$$CH_3\text{-}\underset{\underset{OH}{|}}{CH}\text{-}CH_3 + O_2 \xrightarrow{h\nu} CH_3\text{-}\underset{\underset{O}{\|}}{C}\text{-}CH_3 + H_2O_2$$
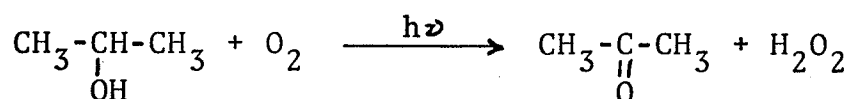
and upon working out the thermodynamics, the reaction can be found to be exothermic.

The first requirement for the ideal solar energy process still remained to be satisfied. Recalling the criteria for a solar energy process it seemed desirable to make hydrogen peroxide from water and oxygen with anthraquineone-2-sulfonate as catalyst. That is:

$+ H_2O + O_2 \longrightarrow$

$+ H_2O_2 + \tfrac{1}{2}O_2$
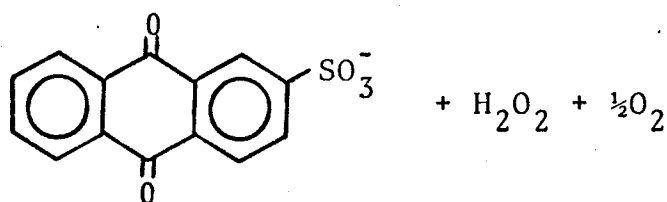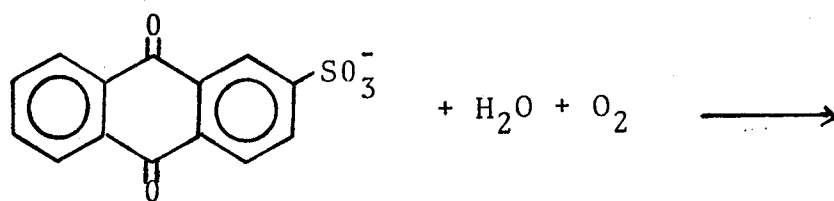
The initial step would be hydrogen (or electron)
abstraction from water.

+ H$_2$O $\longrightarrow$

+ $\cdot$OH
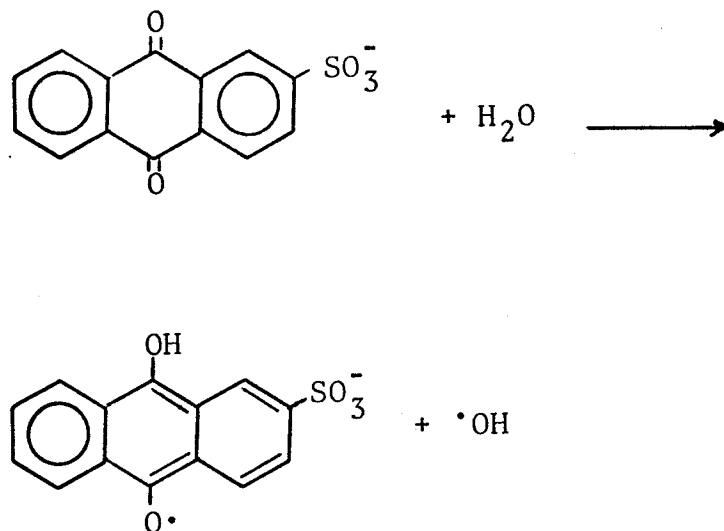
Hopefully the hydroxyl radicals would couple to give
hydrogen peroxide and the quinone radical release
its hydrogen atom to an oxygen molecule to give the
peroxy radical (HO$_2^{\cdot}$) which would disproportionate
with itself to hydrogen peroxide and oxygen. This then
would be an "endothermic" solar energy process.

In 1960, Wells (9) observed that, upon irradia-
tion, anthraquinone-2-sulfonate in water/alcohol
solutions did give some hydrogen peroxide as product.
However he noted a side reaction that occured which
resulted in colored products (from the anthraquinone-2-
sulfonate) that were not removable by air oxidation.
Mooney and Stonehill (2) found that irradiated anthra-
quinone-2-sulfonate in pure water and in aqueous alkali
resulted in "reddish yellow soluble products" as well
as hydrogen peroxide. Since similar products were
obtained by the action of Fenton's reagent on anthra-
quinone-2-sulfonate, they proposed that the coloured

products were hydroxylated derivatives of anthraquinone-
2-sulfonate. Their reaction scheme can be seen in
Figure II.

Figure II. Mooney and Stonehill's (2)
reaction scheme for the irradiation
of anthraquinone-2-sulfonate in water
and in aqueous alkali.

one of several possible hydroxy products
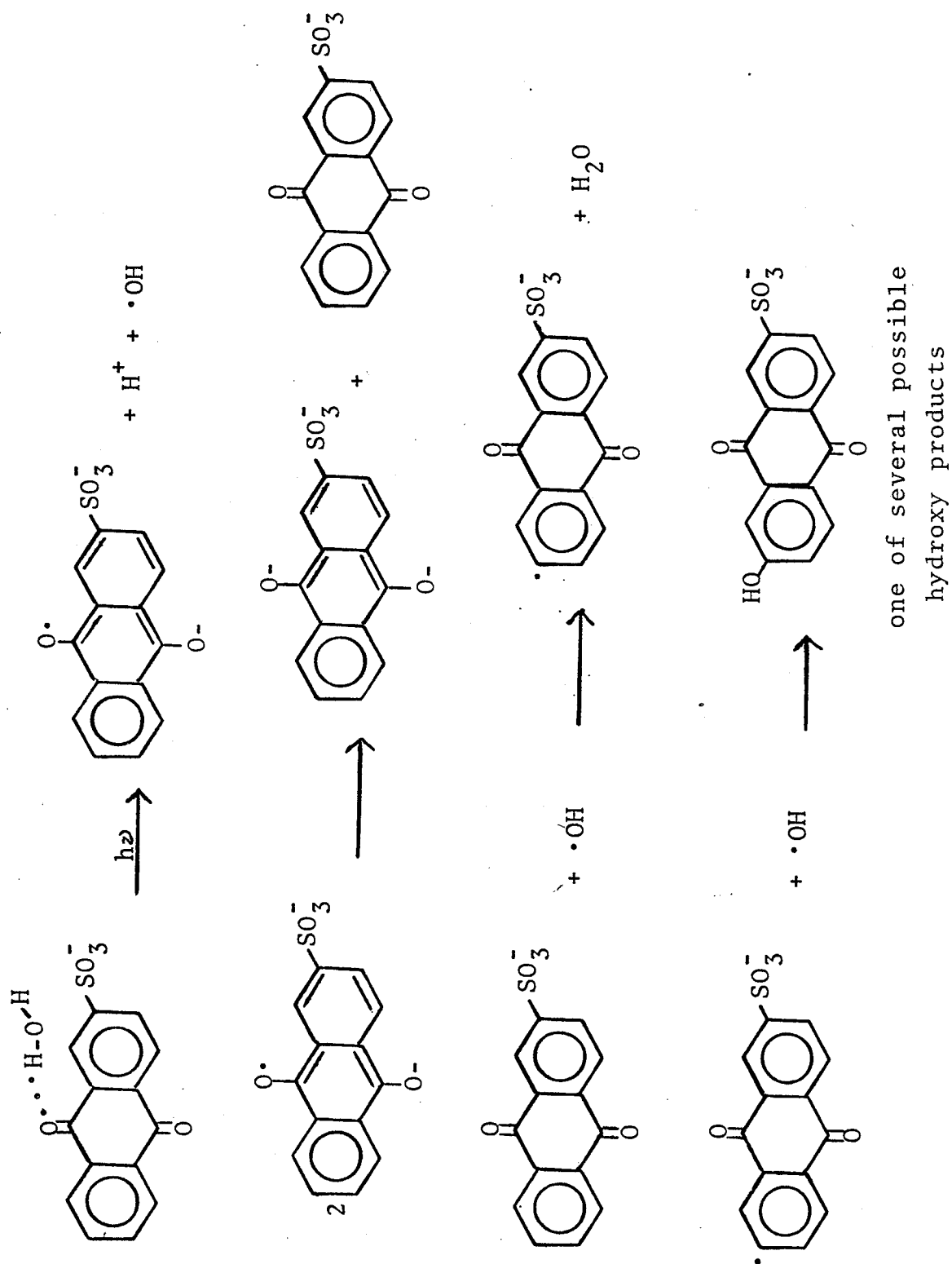
In other words, the hydroxyl radical produced attacks
the anthraquinone or anthraquinol ring in the β position.
(Since there are three β positions open for attack, the
β hydroxyanthraquinone-2-sulfonate obtained as product
includes the 3, 6 and 7 hydroxyanthraquinone-2-sulfonate
derivatives.) Broadbent (10) subsequently confirmed
the presence of β hydroxyanthraquinone-2-sulfonate and,
in addition, noted that irradiation of dilute acid
solutions gave a mixture of α and β hydroxy derivatives.
(There are four α positions open for hydroxyl radical
attack and the α hydroxyanthraquinone-2-sulfonate obtained
as product includes the 1, 4, 5 and 8 hydroxyanthraquinone-
2-sulfonate derivatives.)

It now appeared that, in the system under consider-
ation for a solar energy process, a hydrogen atom was
being abstracted from water but the hydroxyl radical
left ultimately led to the hydroxylated products. In
other words, the "catalyst" would be destroyed as fast
as any hydrogen peroxide would be produced. This then
is not the answer to an ideal solar energy process.

Nevertheless, in examining these mechanisms and
others put forth by different researchers, it became
apparent that there were peculiarities connected with
the system and there were discrepancies as to how the
hydroxylation actually occurred. Since the solar energy
aspect of the project was impeded it seemed appropriate
at the time to investigate the controversies with a view
to settling them.

Phillips, Worthington, McKellar and Sharpe (3),
from flash and continuous photolysis studies of anthra-
quinone-2-sulfonate in neutral aqueous solutions, put
forth for consideration a mechanism for the hydroxylation
reaction similar to that for xanthene dyes (11). Photo-
excited quinone abstracts an electron from ground state

quinone to form a radical cation that then reacts with hydroxyl ion or water to give ground state quinone and hydroxyl radical. This radical then reacts with ground state quinone to give colored hydroxylated derivatives. See Figure III.

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Figure III. Phillips' et al (3)
reaction scheme for the hydroxylation
of anthraquinone-2-sulfonate in water.
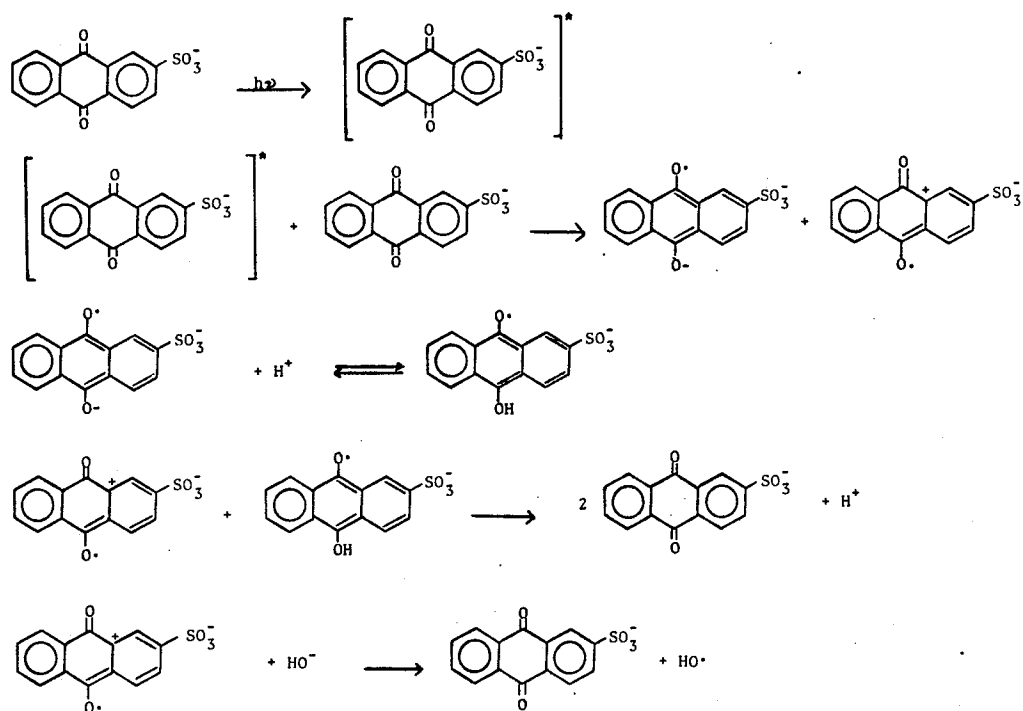
and in oxygenated solutions,

$$O_2^{\cdot -} + O_2^{\cdot -} \longrightarrow O_2^{=} + O_2$$

$$2HO_2^{\cdot} \longrightarrow H_2O_2 + O_2$$

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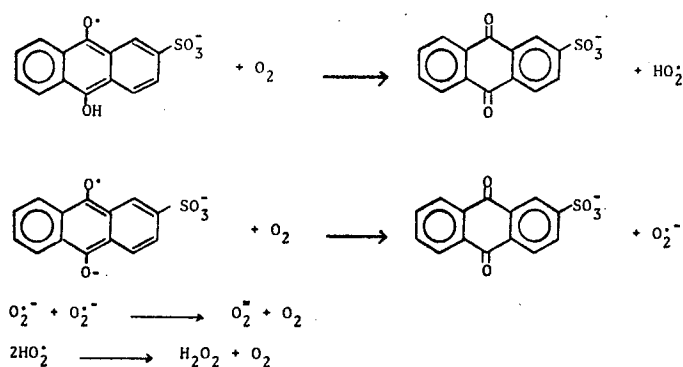
and in deoxygenated solutions only,
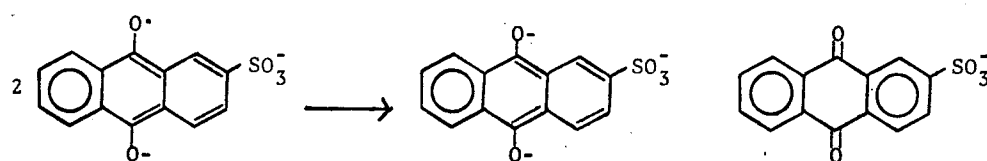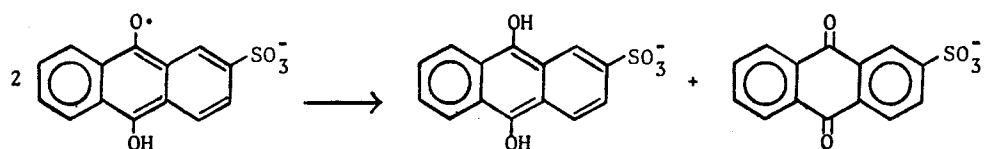
and hydroxylation,
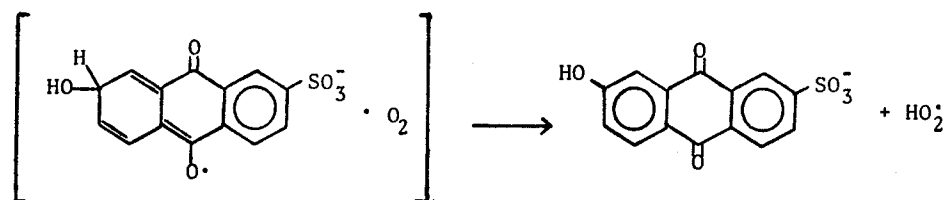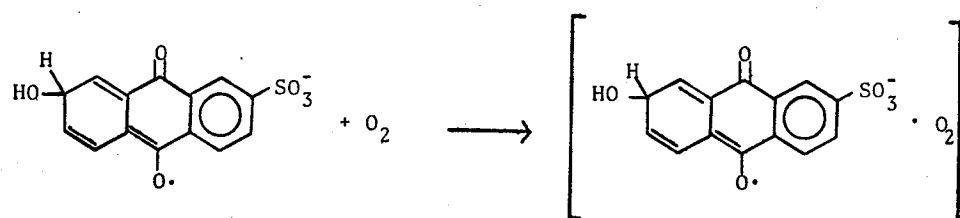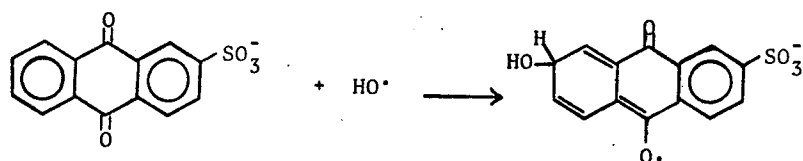
Broadbent and Newton (12) agreed with Phillips et al. that hydroxylated products arise from reactions of anthraquinone-2-sulfonate with hydroxyl radical (generated by photolysis). They disagreed with Phillips' et al. postulate that hydroxyanthraquinone-sulfonates come from coupling the quinone hydroxyl radical adduct with oxygen followed by elimination of peroxy radical. Broadbent and Newton had found that photolysis in the absence of oxygen yielded hydroxylation.

Until this point, the mechanisms in water were concerned with abstraction of a hydrogen atom and back attack of the hydroxyl radical. As more information was collected, these mechanisms were incapable of explaining all of the data.

Clark and Stonehill (13), in their paper, included a plot of rate of photohydroxylation vs anthraquinone concentration. This rate appeared dependent on quinone concentration and increased approximately three times upon going from a quinone concentration of 5.0×10^{-4} m/l to 1.0×10^{-2} m/l. If the photohydroxylation occurred by attack of hydroxyl radical (formed as a result of excited quinone abstracting a hydrogen atom from water, as all the previous workers suggest) then quinone concentration should not affect the rate (as there is nothing else that competes for the hydroxyl radical). But, from the indications of their data, it appeared that anthraquinone competes with some reactive species for hydroxyl radical. The aforementioned mechanisms do not properly account for this.

Also Clark and Stonehill indicated that the rate of photohydroxylation increased with increasing hydroxide ion concentration (at a constant quinone concentration). Again the hydroxyl radical mechanism does not account for this fact.

Clark and Stonehill hoped to account for these
facts by postulating suitable modifications to the
previous mechanisms. See Figure IV.

Figure IV.   Clark and Stonehill's (4)
reaction scheme for the hydroxylation
of anthraquinone-2-sulfonate in water
both anaerobically and aerobically.

for oxygenated solutions,

and the peroxide,
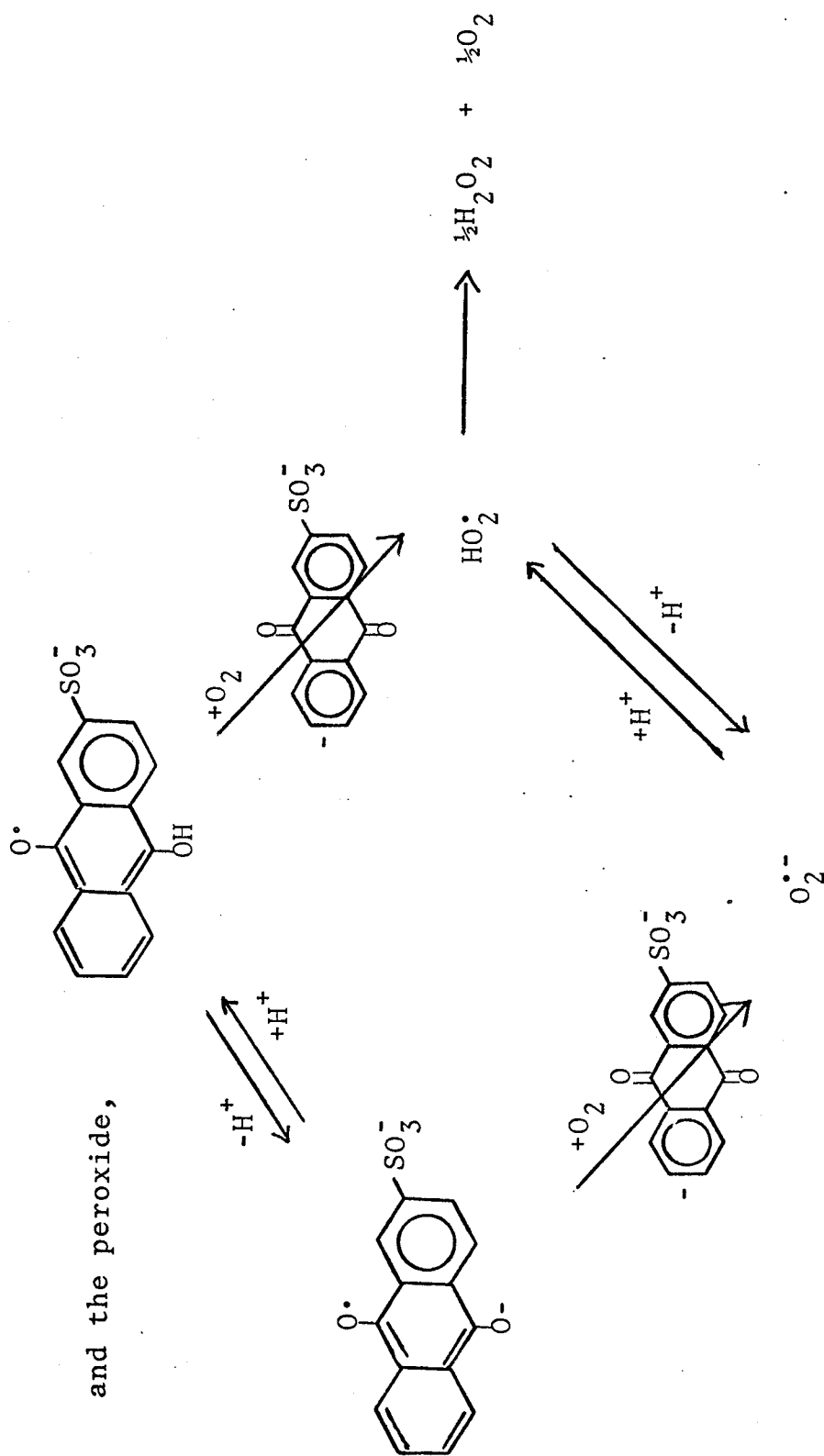
for deoxygenated solutions (depending on pH),
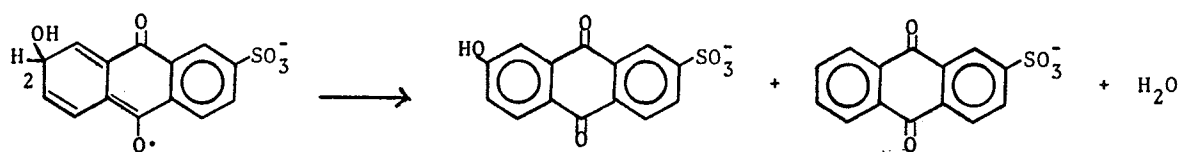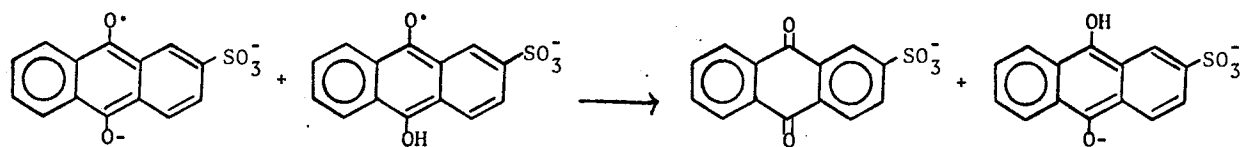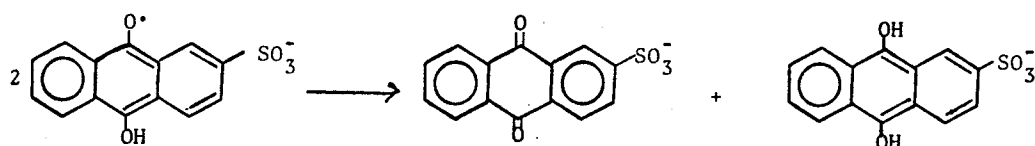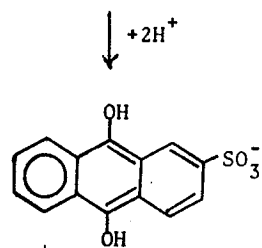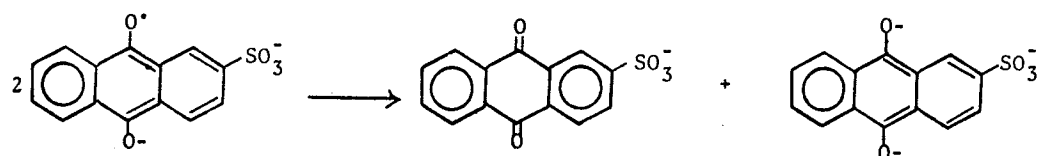
Above pH 10.5 only β hydroxyanthraquinone-2-sulfonate
is observed as a product.   Clark and Stonehill's account-
ing for this fact is not very satisfactory.   At lower
pH, α and β hydroxy products are both found and in a
constant ratio of 2:3.   They proposed a pH dependent
equilbrium between α hydroxyquinone radical, α hydroxy-
quinone radical anion, β hydroxyquinone radical and
β hydroxyquinone radical anion.
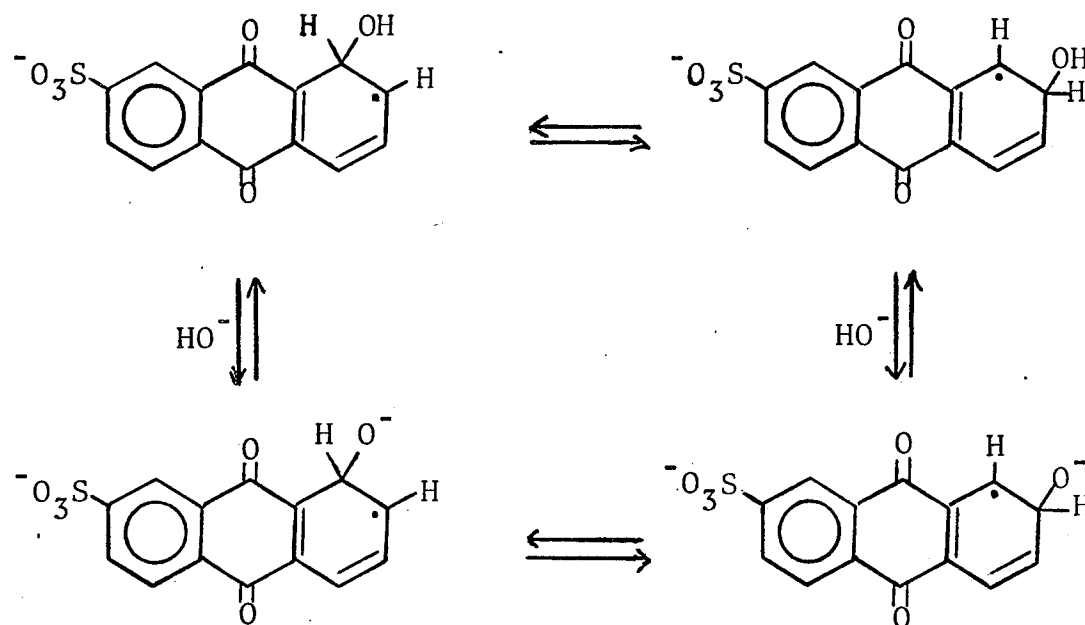
It seems unlikely that at pH 10.5 the α hydroxyquinone
radical will ionize at the hydroxylic position as there
seems to be no precedent for assuming such a high
acidity of the OH.

To verify Clark and Stonehill's second mechanism
(and Broadbent's) the effect of isopropyl alcohol on
the quantum yield of hydroxylated products would have
to be examined.   Burchill and Smith (14) found that in
γ radiolysis (where attack is by hydroxyl radical)

0.1% by volume isopropanol quenches all hydroxylation.
If this same amount of isopropanol quenches the photo-
chemical hydroxylation, then Clark and Stonehill (and
Broadbent) may be right about the participation of
hydroxyl radical in the photoreaction (competition by
isopropanol for photoexcited anthraquinone being possible).
But if at higher isopropanol concentrations hydroxylation
still occurs, then the second mechanism could be wrong.

In γ irradiating degassed solutions, Burchill and
Smith found that removing oxygen gave complete dis-
appearance of products. No hydroxylation or peroxide
was detected. Clark and Stonehill, and Broadbent found
with anaerobic photolysis (as compared to aerobic photo-
lysis) that similar hydroxylated products were obtained
together with quinol and semiquinone. These unusual
results indicated a need for studying degassed solutions
(with the hope of resolving what actually is occurring).
Also, since base in aerobic conditions gave a greater
rate of photohydroxylation than in neutral solutions,
it would seem desirable to examine its effect on
hydroxylation under anaerobic conditions.

Kuzmin, Chibisov and Karyakin (15) sought to reveal
the formation of semiquinone radicals by one electron
oxidation of carbonate anions. They observed that
addition of sodium carbonate to aqueous solutions of
anthraquinone-2-sulfonate gave electron transfer.

$$+ \quad CO_3^{=}$$

$$+ \quad CO_3^{\cdot -}$$
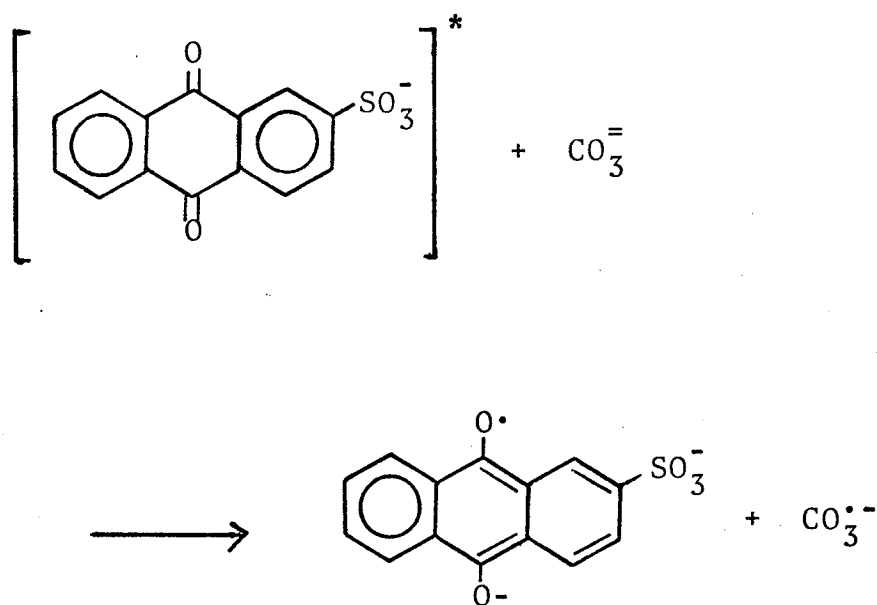
In the air saturated case, only carbonate radical anion was observed as the semiquinone was proportedly quenched

$$+ \quad O_2$$

$$+ \quad O_2^{\cdot -}$$
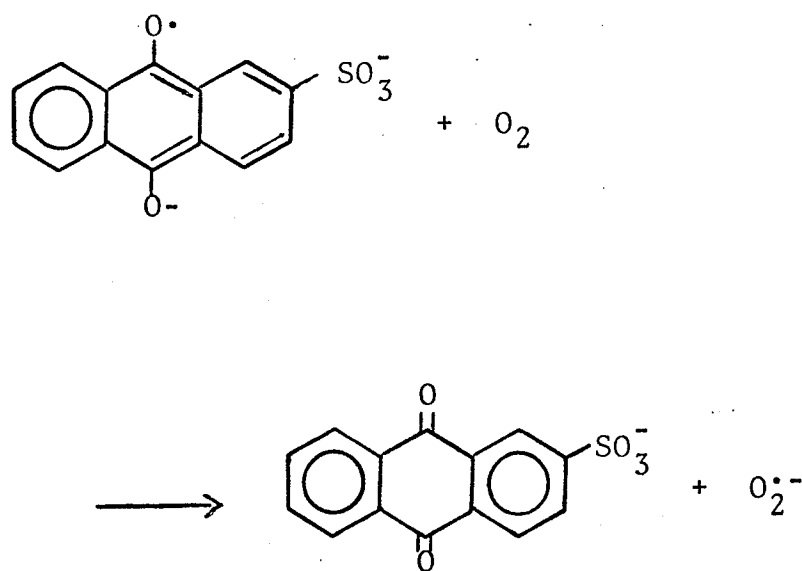
The carbonate radical anion then terminated with the oxygen radical anion.

$$CO_3^{\cdot -} + O_2^{\cdot -} \longrightarrow O_2 + CO_3^{=}$$
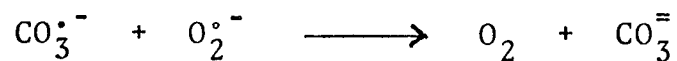
It would appear that no peroxide was formed and no hydroxylation occurred. However, there was no statement of types of product obtained or how much product was obtained, if any. The efficiency of the carbonate anion as a quencher was not mentioned.

Since Kuzmin et al. did not indicate the effect of carbonate anion on products formed, a study in this area appeared interesting. Perhaps the carbonate anion could interfere with the reaction so as to prevent hydroxylation yet yield hydrogen peroxide. (Indeed, if such is the case, the solar energy aspect of the system could be revived).

DISCUSSION

The works of Bolland and Cooper (1), Bridge and
Porter (7) and Wells (8) pointed out that the
irradiation of aerated alcoholic anthraquinone solutions
gave hydrogen peroxide. Since we were interested in
hydrogen peroxide as a chemical energy carrier (for a
solar energy process), our attention was attracted by
this photochemical reaction. Accordingly, a study of
the practical aspects of this system was conducted.

In their papers, Bolland and Cooper, Bridge
and Porter, and Wells indicated that 9,10-anthracene-
diol (hereinafter designated as quinol) was an inter-
mediate in the reactions that produced peroxide. The
irradiation of anthraquinone and the alcohol produced
quinol which then reduced oxygen to give peroxide.
In order to detect quinol, we carried out a mass
spectrometric study of the products of anaerobic
irradiation. An isopropanol and benzene solution
containing anthraquinone was anaerobically irradiated.
A low voltage mass spectrograph was carried out on an
evaporated sample taken from the irradiated solution.
Mass peaks appeared at 210, 208 and 194 which were
assigned to the following compounds.
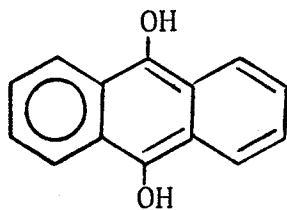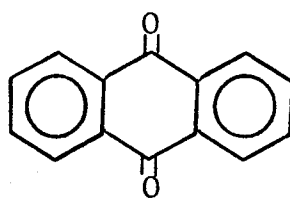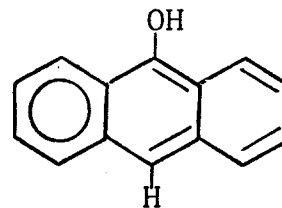
210   208   194

As a cross check, catalytic hydrogen reductions of
anthraquinone first in benzene and then in chloroform
were done.   Low voltage mass spectrographs were taken.
Mass peaks which appeared at 212, 210, 208 and 194
indicated the presence of similar compounds.
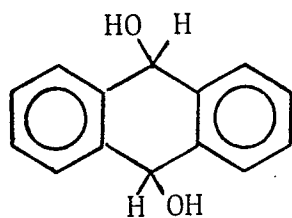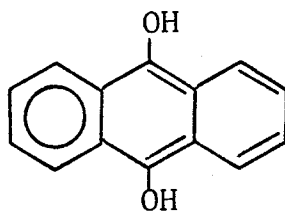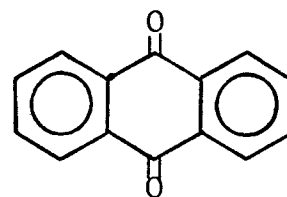
212   210   208
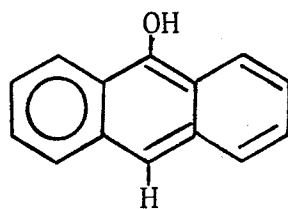
194

Thus it appeared that quinol was present in the system
and was an intermediate in the photochemical production
of hydrogen peroxide.   However, the presence of anthrone
(mass 194) in the mass spectrometer indicated that
perhaps the reaction might be more involved than just
the reduction of quinone to quinol and the reduction
of oxygen by quinol.   The formation of anthrone
could be brought about by loss of water from the
doubly reduce anthraquinone (mass 212) in the irradiated
solution.   If this is so, then it must be determined
whether or not anthrone formation constitutes a loss

of anthraquinone (and hence peroxide producting power)
or if the anthrone enters into production of hydrogen
peroxide. Accordingly, anthrone was synthesized from
anthraquinone (16). It was oxygenated and irradiated
simultaneously. No peroxide was formed. This would
indicate that anthrone does not photochemically produce
peroxide and if formed in the irradiation of anthra-
quinone would constitute an unproductive side reaction.
However, since anthrone appears in the mass spectro-
graph of both catalytically and photochemically
reduced anthraquinone, one might suspect that perhaps
all or most of the anthrone is actually formed in the
mass spectrometer (by dehydration of the doubly
reduced anthraquinone (mass 212)). Confirmation of
this suspicion was obtained when a mass spectrograph
was taken of an anaerobically irradiated and sub-
sequently oxygenated anthraquinone in benzene and
isopropanol solution. No anthrone was present in the
mass spectrograph. Since anthrone does not oxidize
to anthraquinone and if anthrone was a product of a side
reaction during irradiation, it should be present in
the mass spectrograph. Its absence here implies that
the anthrone present in the mass spectrograph of the
photochemically and catalytically reduced quinone is
formed in the mass spectrometer. One could then
conclude that anthrone does not form from a side
reaction in the irradiated solution and does not
constitute a loss of anthraquinone and hence does not
result in a loss of peroxide producing power.

   As we were intrigued with this system for a solar
energy process and had undertaken to study the practical

aspects of it, the next step was to find out how
effective the system would be in its production of
peroxide. Firstly, the efficiency of the oxidation
of quinol by oxygen was determined. This was done by
anaerobically irradiating a solution of anthraquinone
in isopropanol and benzene and then oxygenating and
testing periodically during oxygenation for peroxide.
The amount of peroxide present was a measure of the
extent of oxidation of quinol. Secondly the maximum
chemical yield of hydrogen peroxide was determined.
This was approached in two ways. While a solution
was being anaerobically irradiated, samples were
periodically removed, oxygenated and titrated for peroxide.
The amount of peroxide present was a measure of the degree
of reduction of quinone. Correspondingly aerobic
irradiations were carried out and peroxide concentrations
measured as a function of time. These were an indica-
tion of the progress of reduction of quinone with con-
comittant oxidation of quinol. The maximum limits of
peroxide production were found by titrating these
solutions for peroxide after long lengths of irradia-
tion times. Presumably in the anaerobic solutions
this would indicate the limit of reduction of quinone
and in the aerobic solutions this would indicate the
point at which peroxide is photochemically decomposed
as fast as it is made.

To determine the efficiency of the oxidation of
quinol by oxygen, a solution of anthraquinone in
benzene and isopropanol was irradiated anaerobically.
Oxygenation was commenced after irradiating and the
sample tested for peroxide at various time intervals.

Figure V. Plot showing length
of oxygenation time required
to oxidize reduced anthraquinone.

concentration of H_2O_2 x 10^{-3} (m/l)

duration of oxygenation (min)

plot I

plot II

exclusion of sample from laboratory lights
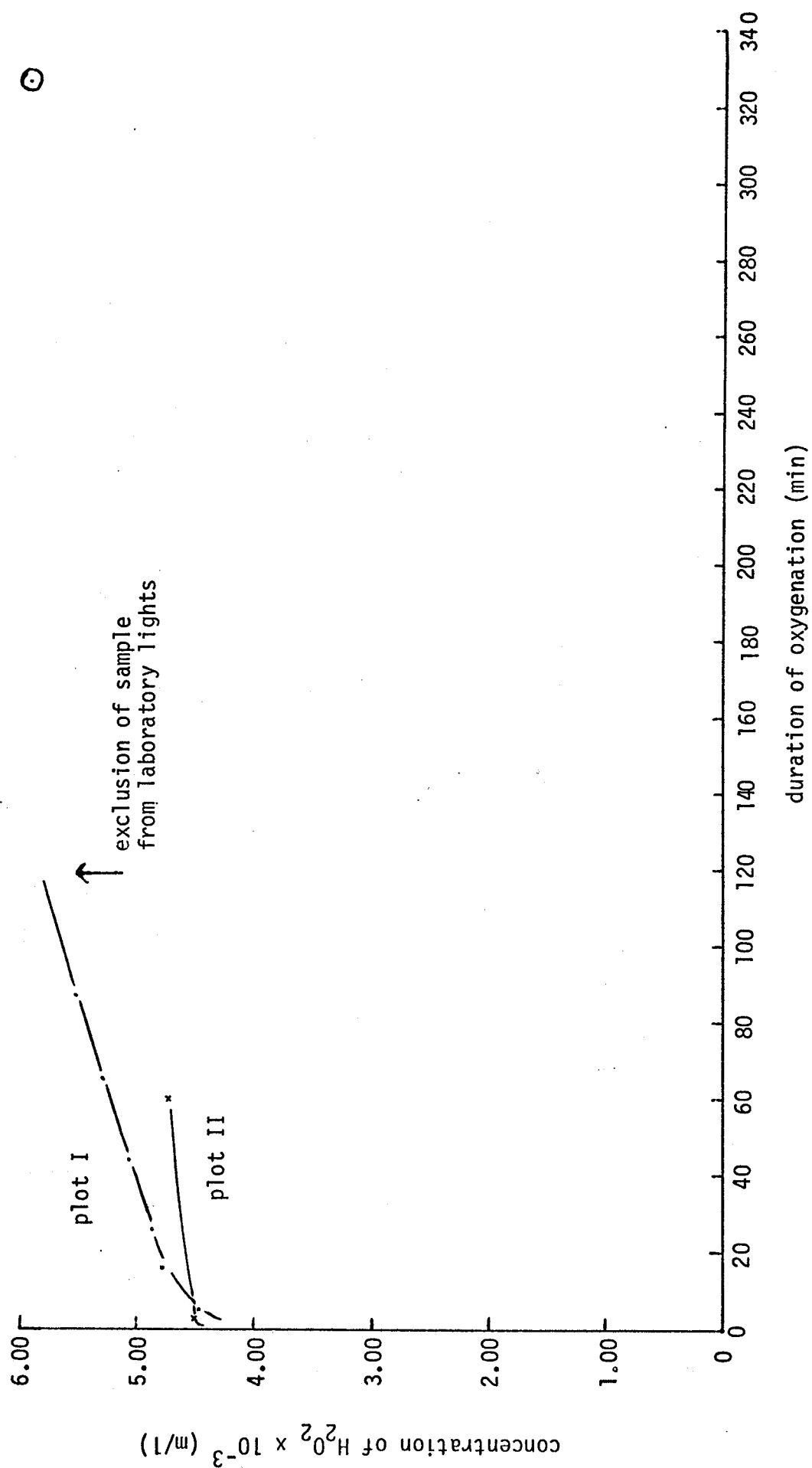
After about two hours, the sample was excluded from the
laboratory lights and oxygenation carried out for an
additional three and one-half hours. At that time,
the sample was again tested for peroxide. This experi-
ment is represented as "plot I" on Figure V. The
experiment was repeated but the sample was blanketed
with aluminum foil prior to any oxygenation and then
oxygenated in the dark. This experiment is represented
as "plot II" on Figure V. If Figure V is examined,
it can be noted that the majority of peroxide is formed
rather rapidly within the first few minutes of oxy-
genation. This initial rapid peroxide production
appeared to be oxygen diffusion controlled, (another
factor that somewhat substantiated this, was that often
when titrating a blank, the characteristic green color
of reduced quinone disappeared between the removal of
the sample from the irradiated solution and its
addition to the titrating erlenmeyer). Returning to
Figure V and examining plot I, it can be seen that the
initial rapid peroxide production appears to be followed
by a slower production of hydrogen peroxide. This
slower production of excess peroxide appeared to be
caused by the laboratory lights activating the following
process,

$$CH_3\text{-}CH\text{-}CH_3 \;+\; O_2 \quad \xrightarrow{h\nu} \quad$$
$$\overset{OH}{}$$

$$CH_3\text{-}C\text{-}CH_3 \;+\; H_2O_2$$
$$\overset{\;}{O}$$
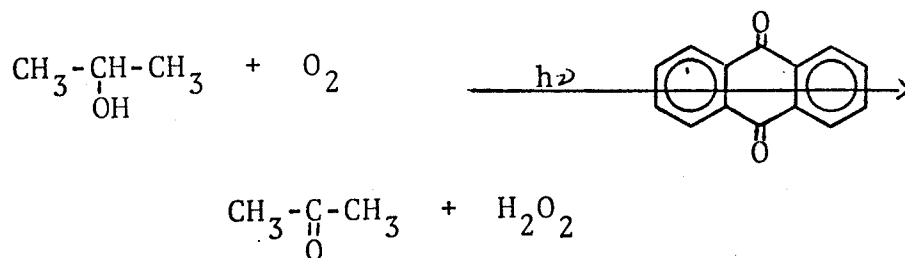
In other words, the excess peroxide production was a light catalysed reaction involving anthraquinone. This appeared more evident when light was excluded from the sample. The experimental system then experienced a marked decrease in peroxide production (this is represented by plot I). Further, the anthraquinone was involved in the appearance of extra peroxide. On oxygenating an isopropanol, benzene and hydrogen peroxide solution (in the absence of anthraquinone) exposed to laboratory light, no additional peroxide was produced. In plot II, when the sample was blanketed with foil before oxygenation, the rate of production of excess peroxide was considerably less than the rate of production in the non-blanketed sample.

One could then conclude from the data that the conversion of reduced quinone and oxygen to peroxide and quinone is not light catalysed and occurs very fast, possibly diffusion controlled with respect to oxygen. Excess peroxide arises from stray light reducing anthraquinone to subsequently yield more peroxide.

To obtain the maximum anaerobic chemical yield of peroxide and to follow the extent of reduction of quinone with irradiation time, a solution of anthra-quinone in benzene and isopropanol was irradiated anaerobically. Part of the solution was withdrawn at various time intervals, oxygenated and tested for peroxide. This experiment is represented as "plot I" on Figure VI. A second identical run was conducted. This experiment is represented as "plot II" on Figure VI. To follow the progress of reduction of quinone with concomittant oxidation of quinol, a solution of anthraquinone in benzene and isopropanol was irradiated aerobically. Part of the solution

was withdrawn at various time intervals and tested for peroxide. This experiment is represented as "plot III" on Figure VI.

These plots on Figure VI take expected shapes. In the case of plot III where oxygen was present during irradiation, peroxide concentration shows a rapid almost linear increase with irradiation time. As soon as a quinone molecule is reduced, an oxygen molecule oxidizes it, returning a quinone and a peroxide molecule. The quinone molecule is then ready to start the cycle again. Plots I and II appear somewhat asymptotic. This would make sense as the reduction of quinone eventually reaches a limit. This limit accordingly appears as amount of peroxide present.

However, an interesting detail of both plots I and II is that neither graph reaches the concentration of peroxide that would signify a hundred percent reduction of quinone. Under anaerobic conditions, one would expect the majority of quinone to be reduced and if all the quinone were reduced, then the number of moles of peroxide should be the same as the number of moles of quinone initially present. The concentrations of peroxide determined however, ranged from zero to half of this amount. Two possible explanations could be that quinol is acting as an internal filter (17) which upon reaching half the concentration of initially present quinone prevents any further reduction of quinone or, quinol is acting as a triplet quencher of excited state quinone and competes with isopropanol for photoexcited quinone.

Lastly, examination of plot I (as compared to plots II and III) shows that it appears to start at a

Figure VI. Plot showing the extent of
reduction of anthraquinone with irradi-
ation time under anaerobic conditions,
the maximum chemical yield of hydrogen
peroxide under anaerobic conditions and
the extent of reduction of anthraquinone
with concomittant oxidation of anthra-
quinone-9,10-diol with irradiation time
under aerobic conditions.

concentration of H_2O_2 x 10^{-3} (m/l)

duration of irradiation (min)

plot I

plot II

plot III
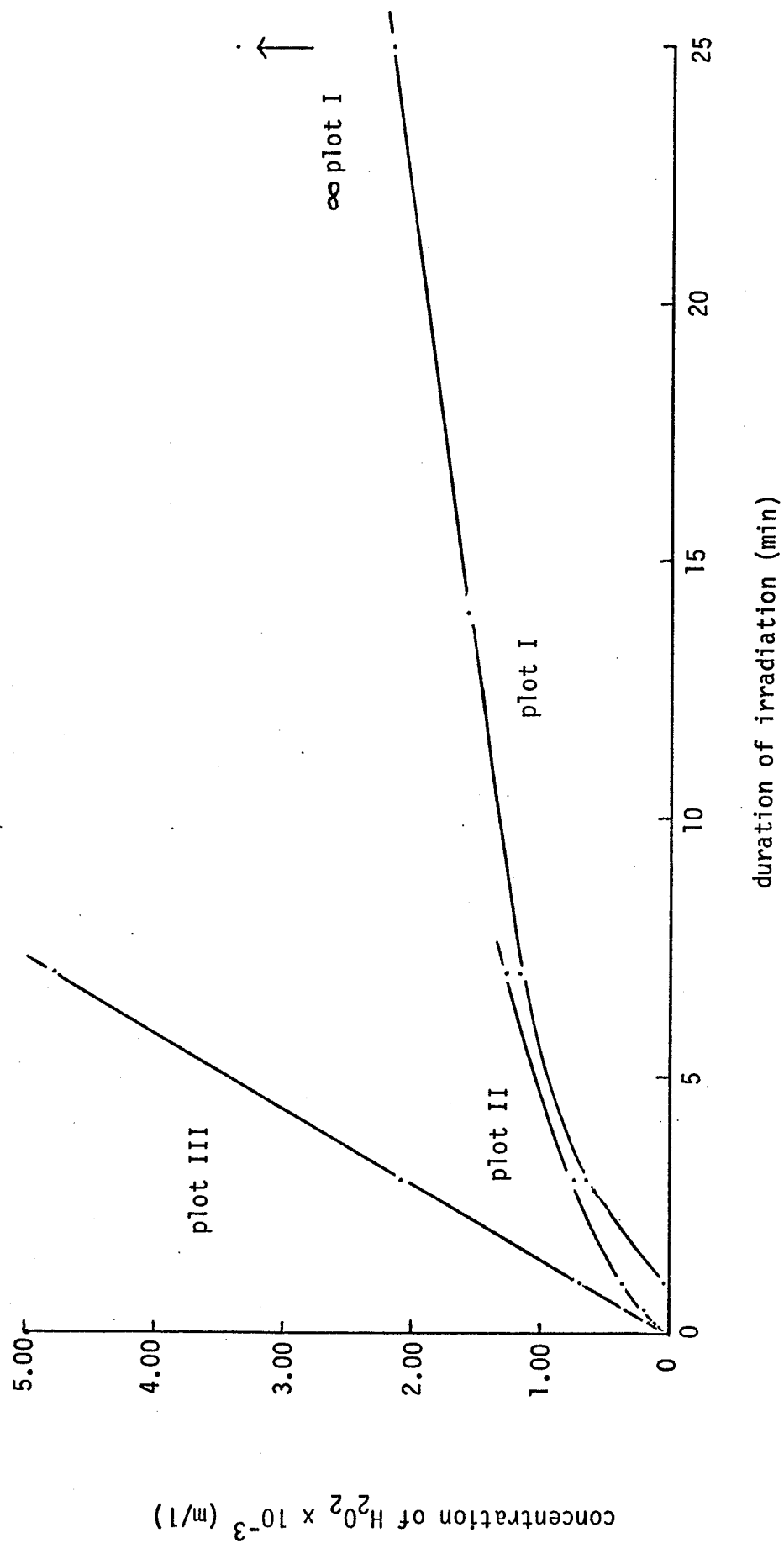
peroxide value other than zero. Since the values
plotted on the graph were corrected with a blank and
sample oxygenations were carried out for a sufficient
length of time for all the quinol to reconvert to
quinone, the non-zero value could be due to the lamp
not being up to full intensity during the irradiation
of the initial few samples.

Since plot III on Figure VI did not show signs
of leveling off (i.e. the attaining of the maximum
possible yield of peroxide for the aerobic system),
a further experiment was conducted to determine where
this maximum lay. A solution of anthraquinone in
benzene and isopropanol was oxygenated while being
irradiated. The solution was tested for peroxide after
an extended length of time. A peroxide concentration
strength of 1% was indicated.

It would seem that so far, this anthraquinone/
isopropanol system is a good candidate for the con-
version of solar energy to chemical energy. Recalling
the seven criteria set out in the introduction for the
ideal solar energy process:
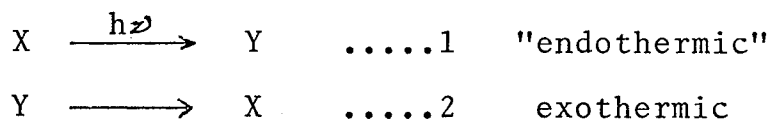
$$X \xrightarrow{h\nu} Y \quad \ldots\ldots 1 \quad \text{"endothermic"}$$

$$Y \longrightarrow X \quad \ldots\ldots 2 \quad \text{exothermic}$$

1) ΔH for reaction 2 should return a reasonable
   percentage of the radiant energy available
   in reaction 1.
2) Compound X should be cheap and in large
   abundance.
3) Compound Y should be easy to isolate and
   store.
4) Reaction 2 should be efficient and cause no
   pollution.
5) Reaction 1 should be efficient and occur
   easily.

6) The light used should be visible light.

7) The cost of operating the process should be
    feasible.

conditions 2, 4, 5 and 6 are satisfied. For condition 2,
"compound X" which is anthraquinone, does not need to
be present in great quantities to produce a large amount
of peroxide. Under oxygen saturated conditions, a 0.1%
solution of quinone can produce a 1% solution of per-
oxide and the quinone can be recycled. For condition
4, the conversion of quinol to quinone occurs very
quickly and efficiently (Figure V). For condition 5,
the conversion of anthraquinone to its quinol is very
sensitive to light and occurs easily, the quinone being
easily reduced. For condition 6, visible light can be
used, (as solutions of anthraquinone and isopropanol
left on the bench for a while indicated peroxide). As
far as conditions 3 and 7 are concerned, research
into these areas was not conducted at any time. It is
condition 1 that is not satisfied here. The reaction
ideally should return a reasonable amount of light
energy initially available but as indicated in the
introduction, the overall reaction is not "endothermic"
but exothermic. In other words, the reaction

$$CH_3\text{-}CH\text{-}CH_3 \ + \ O_2 \quad \xrightarrow{h\nu} \quad$$
$$\underset{OH}{|}$$

$$CH_3\text{-}\underset{O}{\overset{\|}{C}}\text{-}CH_3 \ + \ H_2O_2$$
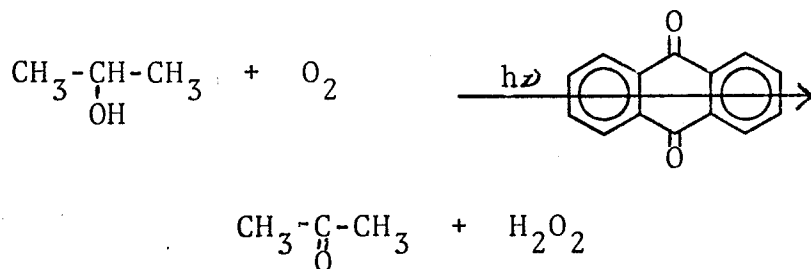
does not store light energy. Thus we turned to the
idea of making hydrogen peroxide from water and oxygen
using anthraquinone-2-sulfonate as catalyst.

$$H_2O \;+\; O_2 \;\xrightarrow{h\nu}\; \text{(anthraquinone-2-sulfonate, } SO_3^-\text{)} \; H_2O_2 \;+\; \tfrac{1}{2}O_2$$
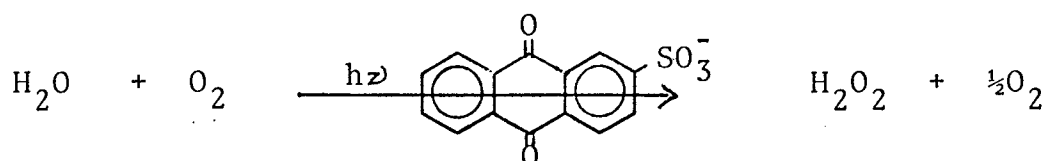
Condition 1 would now be satisfied as this reaction
does store light energy (the decomposition of hydrogen
peroxide to water and oxygen yields 23.9 kcal/mole).
Hopefully, conditions 2, 4, 5 and 6 would still be
fulfilled. A solution of anthraquinone-2-sulfonate
and water was consequently prepared and irradiated
anaerobically and subsequently oxygenated. The
solution was tested for peroxide. Some was present
but in vastly smaller quantities than experienced
with anthraquinone and isopropanol. The experiment
was then repeated but the sample was irradiated aerob-
ically. There was more peroxide than in the anaerobic
irradiation of the aqueous anthraquinone-2-sulfonate
solution but less peroxide than in the analogous irra-
diation of anthraquinone and isopropanol. The decreases
found in the peroxide production inferred that the
conversion of quinone to quinol was inefficient and
occurred with some difficulty. Furthermore, the prod-
uction of peroxide was accompanied by hydroxylation of
the anthraquinone-2-sulfonate (as evidenced by the for-
mation of a deep red colour). This resulted in the des-
truction of our "catalyst" and put the solar energy
idea in jeopardy. Our attention then turned to the

hydroxylation process. In what manner was it occurring and could the system be altered to reduce or eliminate hydroxylation? If this hydroxylation could be eradicated, there would still be hope for the solar energy project.

The hydroxylation of anthraquinone-2-sulfonate in aqueous solutions had been noticed by other workers. Mooney and Stonehill (2), Broadbent and Newton (12), Phillips et al. (3) and Clark and Stonehill (4) all had put forth mechanisms by which hydroxylation occurred. The common feature of these mechanisms was the generation of hydroxyl radicals which then attacked anthraquinone-2-sulfonate to give the hydroxy product. Only Clark and Stonehill included a different mechanism for hydroxylation other than attack by hydroxyl radical. They postulated that excited state quinone added a hydroxide ion (addition of water with elimination of hydrogen ion or addition of hydroxide ion directly) and that this adduct was then reduced by another anthraquinone to give the radical quinone adduct.

If as the majority of the researchers suggested, the hydroxylation occurred by hydroxyl radical then the possibility existed that some other species could either intercept the hydroxyl radical before it reached an anthraquinone-2-sulfonate molecule, or act as a reducing agent for excited state quinone. In this way, a halt or at least a reduction of hydroxylation of quinone could be brought about. Hopefully, the species interfering with hydroxylation would not hamper peroxide production.

The first choice for an interfering species was carbonate anion. It might act as a reducing agent for excited state quinone.

41
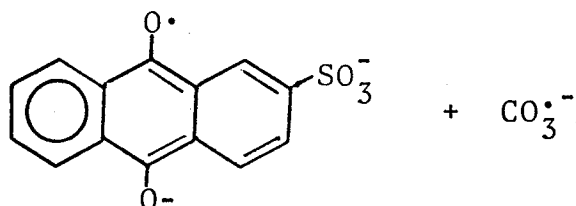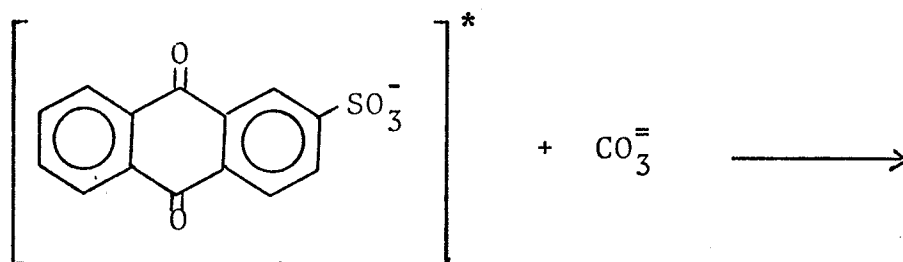
Indeed, Kuzmin et al (15) on the basis of their flash
photolysis data on anthraquinone-2-sulfonate surmised
that the addition of sodium bicarbonate to aqueous
anthraquinone-2-sulfonate solutions did not give this
electron transfer. To be an effective hydroxylation
arrester however, the carbonate radical anion species
should approximate a path as outlined below. If the
carbonate radical anion were to undergo coupling,

it might then hydrolyse to yield hydrogen peroxide
and the carbonate anion. Furthermore, if the anthra-
quinone-2-sulfonate radical anion were to yield its
electron to oxygen to give oxygen radical anion, then
the protonated forms of this could couple and lead
to more hydrogen peroxide.

$$\text{(anthraquinone semiquinone radical dianion)} + O_2 \longrightarrow \text{(anthraquinone-2-sulfonate)} + O_2^{\cdot -}$$

$$O_2^{\cdot -} \xrightarrow[\;+H^+\;]{+H_2O \;\; -HO^-} HO_2^{\cdot}$$

$$2HO_2^{\cdot} \longrightarrow H_2O_2 + O_2$$
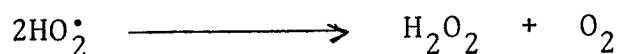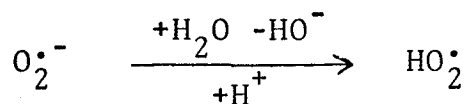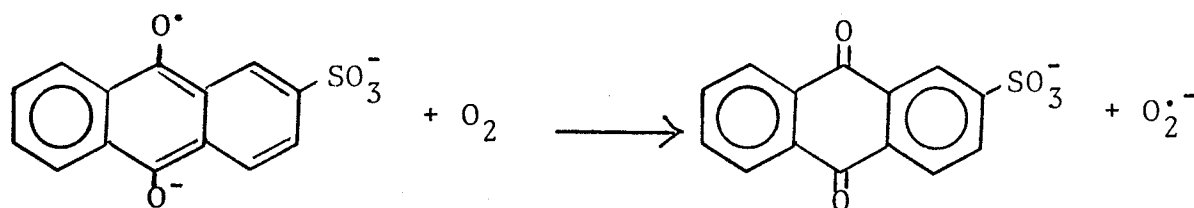
Kuzmin et al (15), however, indicated in their paper
that such was not the case. They indicated that semi-
quinone was quenched with oxygen and that the oxygen
radical anion disproportionated with the carbonate
radical anion to give oxygen and carbonate anion.

$$\text{(anthraquinone semiquinone radical)} + O_2 \longrightarrow \text{(anthraquinone radical-2-sulfonate)} + O_2^{\cdot -}$$

$$O_2^{\cdot -} + CO_3^{\cdot -} \longrightarrow O_2 + CO_3^{=}$$
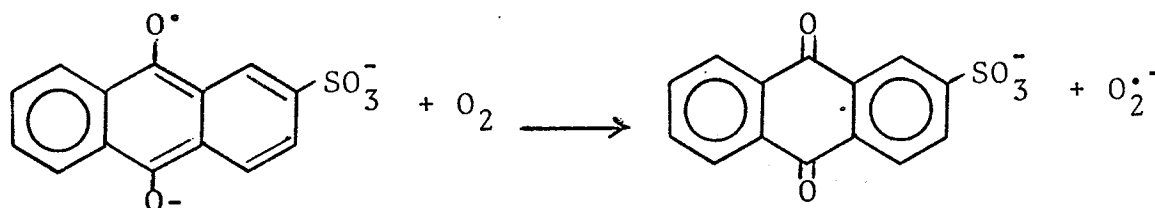
This implied that no peroxide was formed and no hyd-
roxylation took place. Since there was no report

concerning the products and we were in doubt as to the efficiency of carbon dioxide and carbonate anion as quenchers, we investigated their effect on peroxide production and hydroxylation.

Preliminary experiments were effected using, in one case, sodium bicarbonate and in another, carbon dioxide and the production of peroxide examined. Solutions of anthraquinone-2-sulfonate in water were prepared. To one solution sodium bicarbonate was added and this was aerobically irradiated and then checked for peroxide. Less peroxide was found than in the analogous irradiation of anthraquinone-2-sulfonate in water. Another solution was irradiated with a 1:1 mixture of carbon dioxide and oxygen aerating it and then checked for peroxide. Again less peroxide was found than in the aerobic irradiation of anthraquinone-2-sulfonate in water. A further set of more detailed experiments were carried out in which the quantum yields for both hydroxylation and peroxide were determined. Five solutions of anthra-quinone-2-sulfonate in water were prepared. The first one was irradiated with oxygen aeration, the second was irradiated with a 2:1 mixture of carbon dioxide and oxygen, the third was irradiated with a 5:1 mixture of carbon dioxide and oxygen, the fourth was irradiated with pure carbon dioxide and the fifth was irradiated with sodium bicarbonate added to it and with oxygen aeration.

Sample	$\Phi_{H_2O_2}$*	$\Phi_{hydroxylation}$**
1	0.100	0.065
2	0.031	0.044
3	0.026	0.049
4	0.000	0.038
5	0.047	0.069

Table I. Effect of carbon dioxide and carbonate anion on the quantum yields of peroxide and hydroxylation of anthraquinone-2-sulfonate.

* $\Phi_{H_2O_2}$ = quantum yield of hydrogen peroxide

** $\Phi_{hydroxylation}$ = quantum yield of hydroxyanthraquinone-2-sulfonate

As can be seen from these results (Table I) neither carbon dioxide nor the carbonate anion prevented hydroxylation. Compared to the aerobic oxygenated irradiation of anthraquinone-2-sulfonate in water, carbonate anion resulted in just as much hydroxylation, and half the amount of peroxide, pure carbon dioxide resulted in half the amount of hydroxylation and gave no peroxide, and the mixtures of carbon dioxide and oxygen still showed hydroxylation and gave reduced amounts of peroxide. The presence and quantities of hydroxylation and peroxide indicated that our proposed reaction scheme (where no hydroxylation was to occur) was not entirely correct. Kuzmin's et al path was not entirely correct either (again no hydroxylation was to occur). Perhaps some combination of the two existed. Since peroxide amounts were lowered with carbon dioxide and carbonate anion, the coupling of the carbonate radical anions probably did not occur. Peroxide was more than likely produced from the reaction of semiquinone with oxygen and the

oxygen radical anion then either disproportionated with carbonate radical anion or went on to produce peroxide. This availability of an alternate path for oxygen radical anion would give lower peroxide yields. Hydroxylation (if it arises from a hydroxyl radical) could have come about in the manners proposed by Mooney and Stonehill (2), Broadbent and Newton (12), Phillips et al (3) and Clark and Stonehill (4). Hydroxylation was also lowered, as an alternate reaction path would have been available involving anthraquinone-2-sulfonate that did not include hydroxylation (transfer of an electron from carbonate anion to photoexcited quinone and thence from semiquinone to oxygen). None the less, hydroxylation still occurred and peroxide production was affected adversely and we abandoned the idea of having carbon dioxide and carbonate anion as compounds to rehabilitate the practicability of the solar energy process.

A second reagent that would hopefully interfere with the hydroxylation process was nitrate ion. We thought that it would have acted in a similar manner as had been proposed for carbonate anion. A solution of anthraquinone-2-sulfonate in water was prepared and some potassium nitrate added. This was aerobically irradiated and then tested for peroxide. Less peroxide was found than in the analogous irradiation of anthraquinone-2-sulfonate in water and hydroxylation still took place. The nitrate anion could not have been reacting as proposed (it could have undergone reactions similar to the system to which carbonate anion had been added). Without examining the effect of the nitrate anion further, we discarded it.

A last attempt to eliminate hydroxylation was

made with ferrous ion. It was hoped that if hydroxyl
radicals were present (and were the cause of hydroxyla-
tion) that they would react with the ferrous ion and
be unavailable for hydroxylation of anthraquinone-2-
sulfonate. A solution of anthraquinone-2-sulfonate in
water was prepared and some ferrous sulfate added.
This was aerobically irradiated and then checked for
peroxide. The results of this experiment indicated
that ferrous ion was a poor selection. Not only was
hydroxylation not curtailed but no peroxide was to be
found in the system either (this should have been
anticipated as metal ions catalyse destruction of
hydrogen peroxide).

It seemed that despite our attempts to eliminate
hydroxylation, it accompanied the production of peroxide.
At this point, the solar energy aspect of the project
was abandoned and our attention turned in more detail
to the business of hydroxylation. As the introduction
describes, discrepancies arose between the mechanisms
proposed by various researchers for the hydroxylation
of anthraquinone-2-sulfonate. It was our intention
to attempt to resolve these discrepancies or propose
alternatives and in that way eliminate them.

As discussed previously, researchers proposed
mechanisms for hydroxylation which all involved a
hydroxyl radical (with the exception of one of
Clark and Stonehill's that involved a water molecule
or hydroxide ion reacting with excited state quinone -
vida infra). The hydroxyl radical proportedly arose
from the abstraction (by excited state quinone or
semiquinone cation) of a hydrogen atom from water
or an electron from hydroxide ion. This hydroxyl

radical then attacked the quinone to give hydroxylated
products. In aerated γ radiolysis of anthraquinone-2-
sulfonate in water, hydroxylation takes place by
hydroxyl radical (18).

$$H_2O \xrightarrow{\quad\wedge\wedge\wedge\wedge\quad} HO\cdot \ + \ e^-_{aq} \ + \ H^+$$
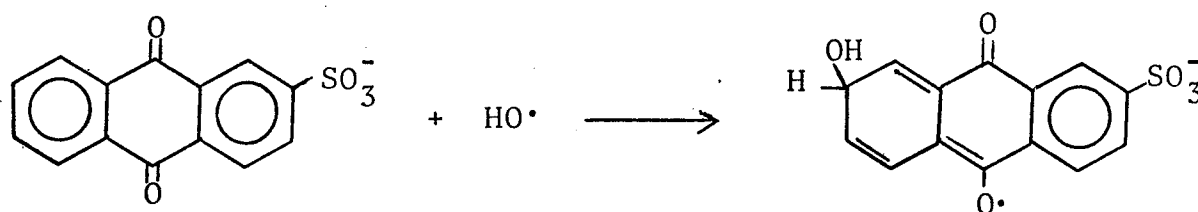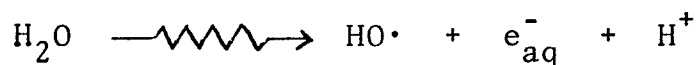
Burchill and Smith (14) discovered that when isopropanol
was present in concentrations greater than 0.1% by
volume, all hydroxylation ceased. This meant that
hydroxyl radical, instead of reacting with quinone
was probably reacting with isopropanol.

$$HO\cdot \ + \ CH_3\text{-}\underset{OH}{CH}\text{-}CH_3 \longrightarrow HOH \ + \ CH_3\text{-}\underset{OH}{\overset{\bullet}{C}}\text{-}CH_3$$
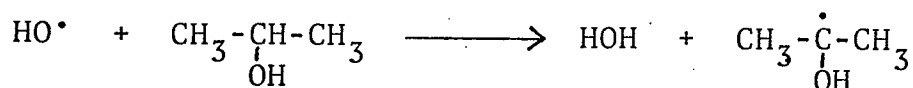
If such a low concentration of isopropanol quenches
hydroxylation in γ radiolysis, then the same amount
of isopropyl alcohol should quench hydroxylation in
photolysis - if hydroxylation occurs by hydroxyl
radical. We therefore conducted a study of the
effect of isopropanol on photohydroxylation of
anthraquinone-2-sulfonate with the object in mind
of determining the concentration of isopropanol at

which hydroxylation ceased. Eight solutions of anthra-
quinone-2-sulfonate in water and isopropanol were
prepared. They were made by volume with isopropanol
to the following percentages; 0.0%, 0.1%, 1.0%, 2.0%
3.0%, 4.0%, 5.0% and 10.0% respectively. They were
oxygenated during irradiation and the quantum yields
of hydroxylation determined.

Sample	% by volume isopropanol	$\Phi_{total\ hydroxylation}$
1	0.0%	0.038
2	0.1%	0.040
3	1.0%	0.027
4	2.0%	0.020
5	3.0%	0.016
6	4.0%	0.016
7	5.0%	0.013
8	10.0%	0.006

Table II. Effect of isopropanol on the quantum yield of hydroxyl-
ation of anthraquinone-2-sulfonate.

These results (Table II) can be seen on Figure VII.
It was quite obvious that the amount of isopropanol
required for quenching hydroxylation in the case of
Ɣ radiolysis was not the same as required in the case
of photolysis. (If the same amounts had been required,
then it could be inferred that hydroxylation occurred
by hydroxyl radical). Photolysis, however, required
roughly one hundred fold more to bring hydroxylation
levels down towards a zero value. This means that a
different route of hydroxylation that did not involve
hydroxyl radicals was most likely involved.

The other mechanism proposed for hydroxylation
was that of Clark and Stonehill (4). It involved a

Figure VII. Plot showing the effect of
isopropanol concentration on hydroxylation
of anthraquinone-2-sulfonate.

% by volume isopropyl alcohol

Φ total hydroxylation
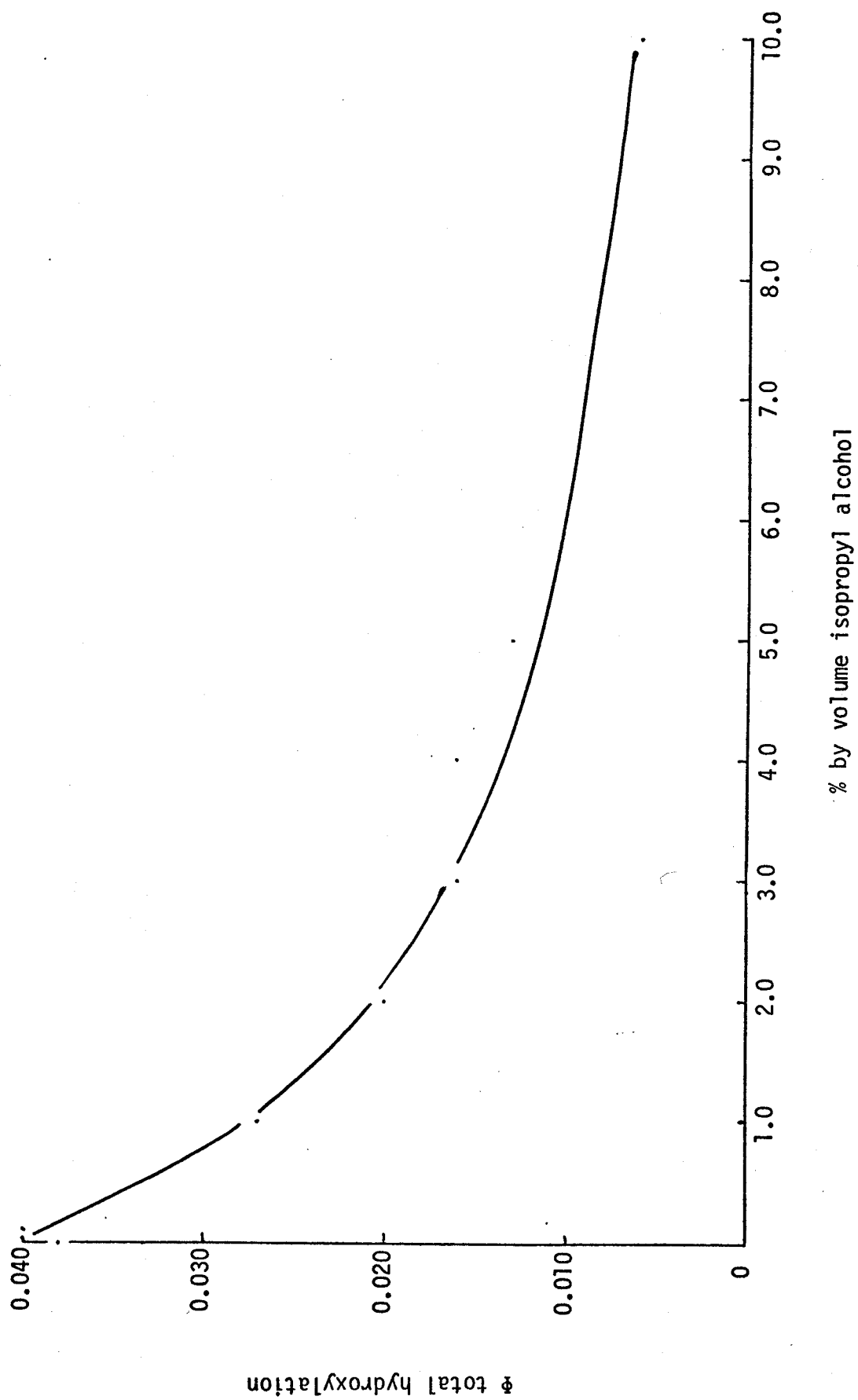
water molecule (or hydroxide ion) reacting with excited
state quinone to give hydroxyl ion adduct. This went on
to react with anthraquinone-2-sulfonate to give quinone
hydroxy radical adduct and quinone radical anion. The
radical adduct then resulted in hydroxylated product. In
deoxygenated solutions they proposed that the hydroxyl
radical adduct disproportionated with itself to give yields
of hydroxyquinone that were half the size of the aerated
yields.

hydroxide ion adduct

hydroxy radical adduct
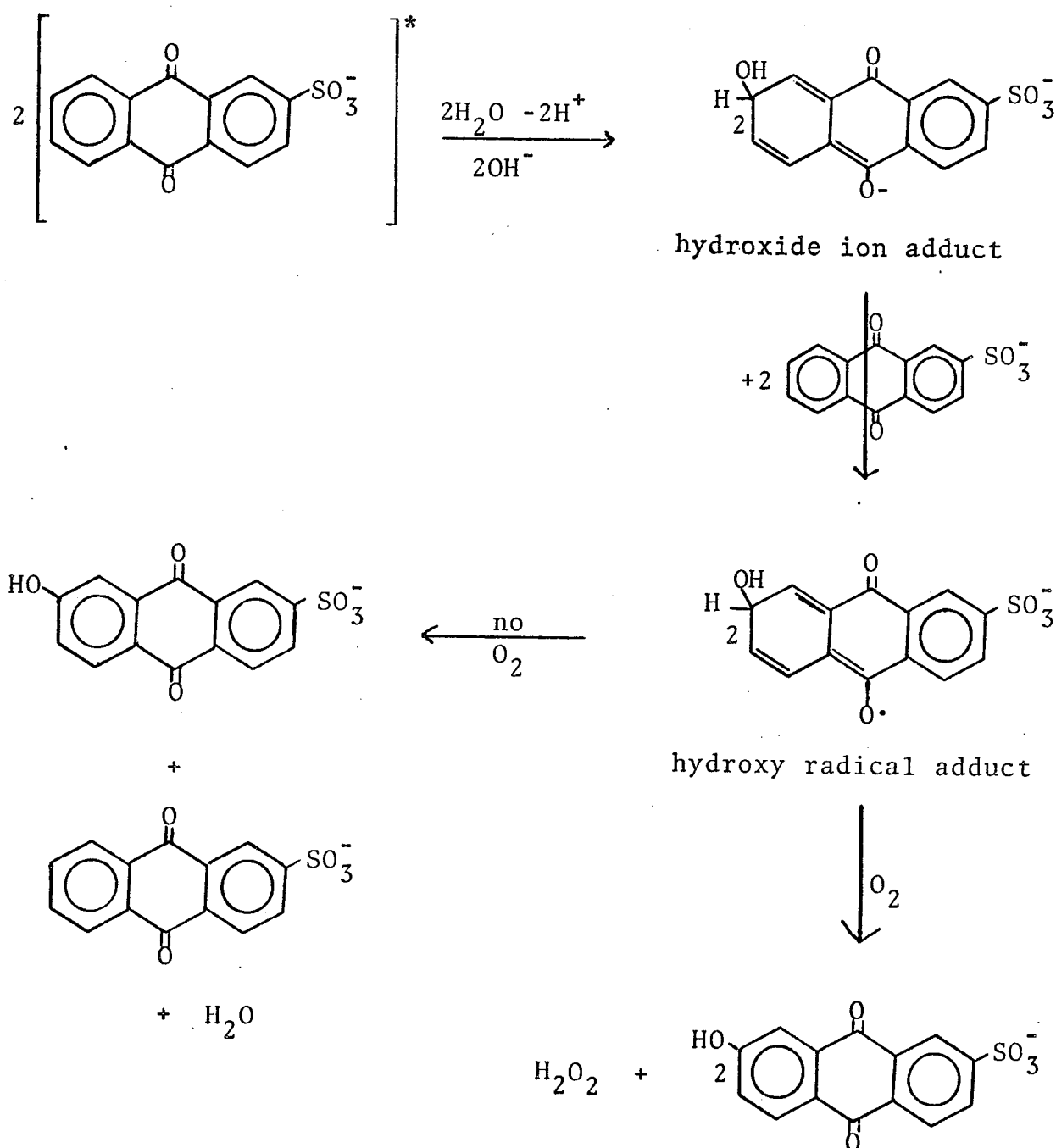
In the γ radiolysis of deaerated aqueous anthra-
quinone-2-sulfonate solutions, Burchill and Smith (14)
found a total absence of any products. No peroxide or
hydroxylation was present. This implied that the quinone
hydroxyl radical adduct (formed by reacting hydroxyl
radical and quinone) and the quinone radical anion
(formed by reacting aqueous electrons and quinone) were
disproportionating to give back quinone. This reaction
is the reverse of Clark and Stonehill's (4) suggested
mechanism.

$$H_2O \; \longrightarrow\!\!\bigwedge\!\!\bigwedge\!\!\bigwedge\!\!\longrightarrow \; {}^{\bullet}OH \; + \; H^+ \; + \; e^-_{aq}$$

$$+ \; {}^{\bullet}OH \; \longrightarrow$$

$$+ \; e^-_{aq} \; \longrightarrow$$
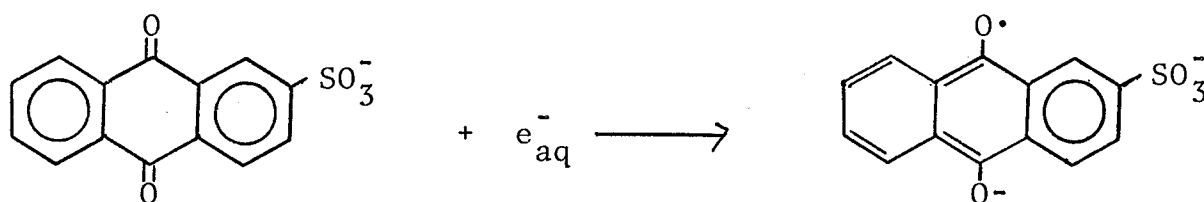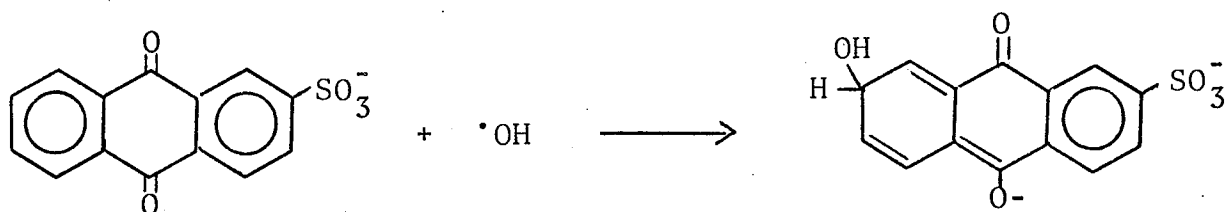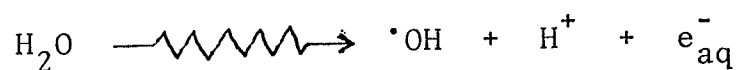
and
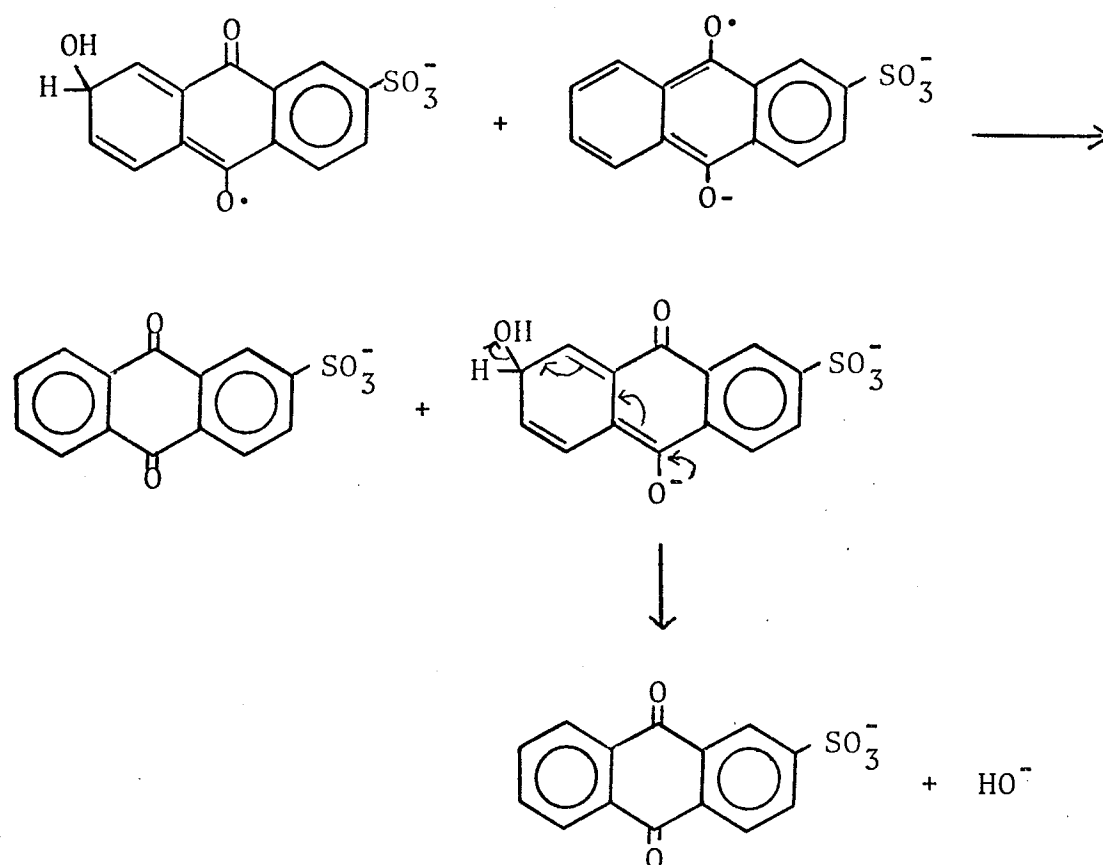
Burchill and Smith (14) also carried out δ radiolyses of the system in the presence of nitrous oxide. The amount of hydroxylated product (without oxygen present) was half the amount expected based on total radical yield. Scavenging of aqueous electrons by nitrous oxide prevents the formation of quinone radical anion and the quinone hydroxy radical adduct could only disproportionate with itself.

$$H_2O + \text{—}\wedge\wedge\wedge\rightarrow HO^{\circ} + H^{+} + e_{aq}^{-}$$

$$H^+ + e^-_{aq} + N_2O \longrightarrow HO^{\bullet} + N_2$$
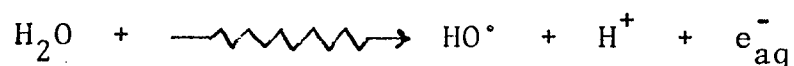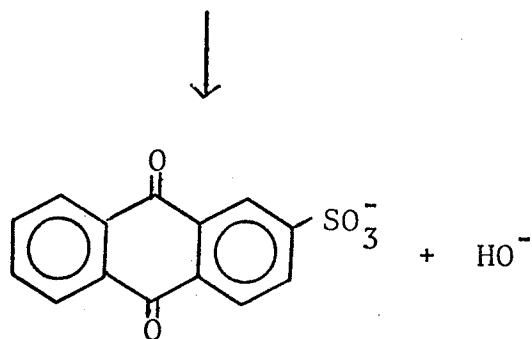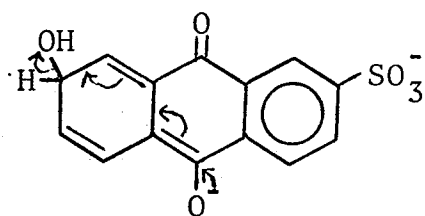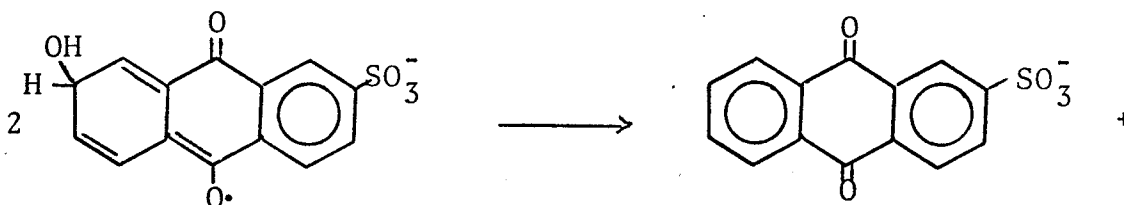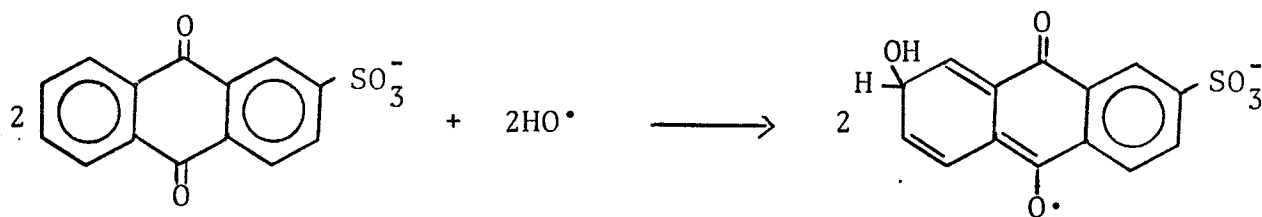
Upon degassing solutions of anthraquinone-2-sulfonate in water and irradiating them we found that, for hydroxylation, the results were similar to those of Burchill and Smith's (14) and contrary to those of Clark and Stonehill's (4,13). As can be seen (Table III)

negligible hydroxylation occurred in absence of oxygen (no titratable peroxide was found either).

$\Phi_{hydroxylation}$ aerated	$\Phi_{hydroxylation}$ degassed
0.038	0.009

Table III.   Comparison of the quantum yields of hydroxylation in aerated and degassed solutions.

A change in the water quality and a repeat of the experiment gave different results. The quantum yield for hydroxylation was reduced even further, to 0.004. (The quantum yield of peroxide determined spectrophotometrically was 0.002). The fact that a change in water quality changed hydroxylation lead us to believe that there was an oxidative impurity present in the types of water used and that this impurity was responsible for the trace of hydroxylation of the anthraquinone-2-sulfonate found.

Since our experimental results for the photolysis of quinone were the same as for the radiolysis of quinone, it is possible to conclude that quinone hydroxy radical adduct and quinone radical anion were present in photolysis. Since Burchill and Smith (14) have demonstrated that the back reaction of these two species occurred rapidly compared to the self-disproportionation of the quinone hydroxy radical adduct (in the γ radiolysis of degassed solutions) one could further conclude that this applies to photolytic solutions. In other words, photolytically
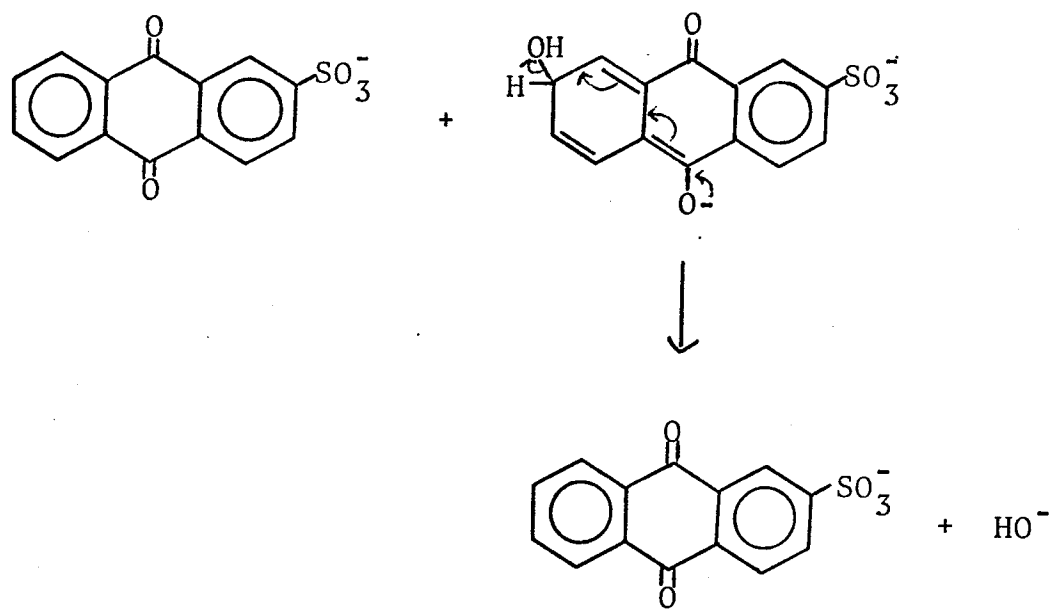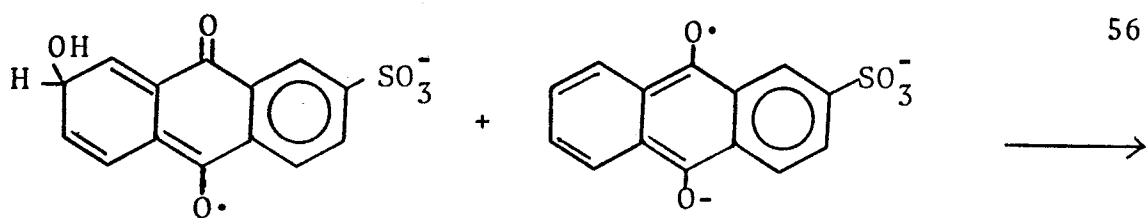
is occurring much faster than
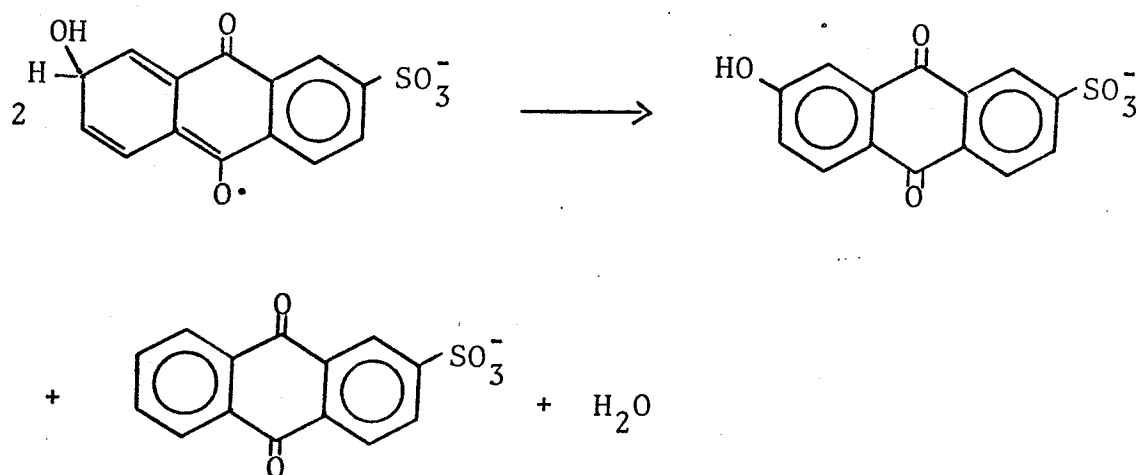
and no hydroxylation is occurring.

Moreover, when 1.0% isopropanol was added, no hydroxylation was found (in aerated 1.0% isopropanol solutions, the quantum yield for hydroxylation was 0.027). Isopropanol gave rise to higher concentrations of radical anion. This might have acted to cause an increase in the rate of disproportionation of radical anion and hydroxy radical adduct to quinone and the oxidative impurity (which probably was the cause of hydroxylation in the absence of isopropanol) would not have a chance to affect hydroxylation of the quinone. These experimental findings of ours, and of Burchill and Smith (14) indicate that Clark and Stonehill's (4) suggested mechanism was acting in reverse. That is, oxidation of the hydrated quinone by quinone cannot be important as we find the reverse reaction is exceedingly fast. If this is true then some other pathway different than attack of water (or hydroxide ion) on excited state quinone must be occurring to bring about hydroxylation.

From the discussion above, the mechanisms postu-lated by previous researchers were not in keeping with our experimental results. It was our aim to change the mechanism so that it could better account for the data collected by us concerning aqueous anthraquinone-2-sulfonate solutions. Our mechanism does not involve a hydroxyl radical nor reaction of water or hydroxide ion with excited state quinone. See Figure VIII.

Figure VIII. Our reaction scheme for
the hydroxylation of anthraquinone-2-
sulfonate and the production of peroxide
in aqueous and aqueous/alcoholic solutions.

k_3

k_d

k_1 $CH_3-CH-CH_3$ $\overset{|}{OH}$

k_2

k_4 $+H_2O$ $-H^+$ $+HO^-$

$CH_3-\overset{OH}{\underset{OH}{C}}-CH_3$ +

H^+ +

k_7 O_2

k_8 O_2

$CH_3-\overset{O}{C}-CH_3$ + $HO_2^{\cdot}$

+ $HO_2^{\cdot}$

k_9

H_2O_2 + O_2

one of several possible
hydroxy adducts

k_5 $2O_2$

$2HO_2^{\cdot}$ +

one of several possible
hydroxy products

k_6

H_2O_2 + O_2
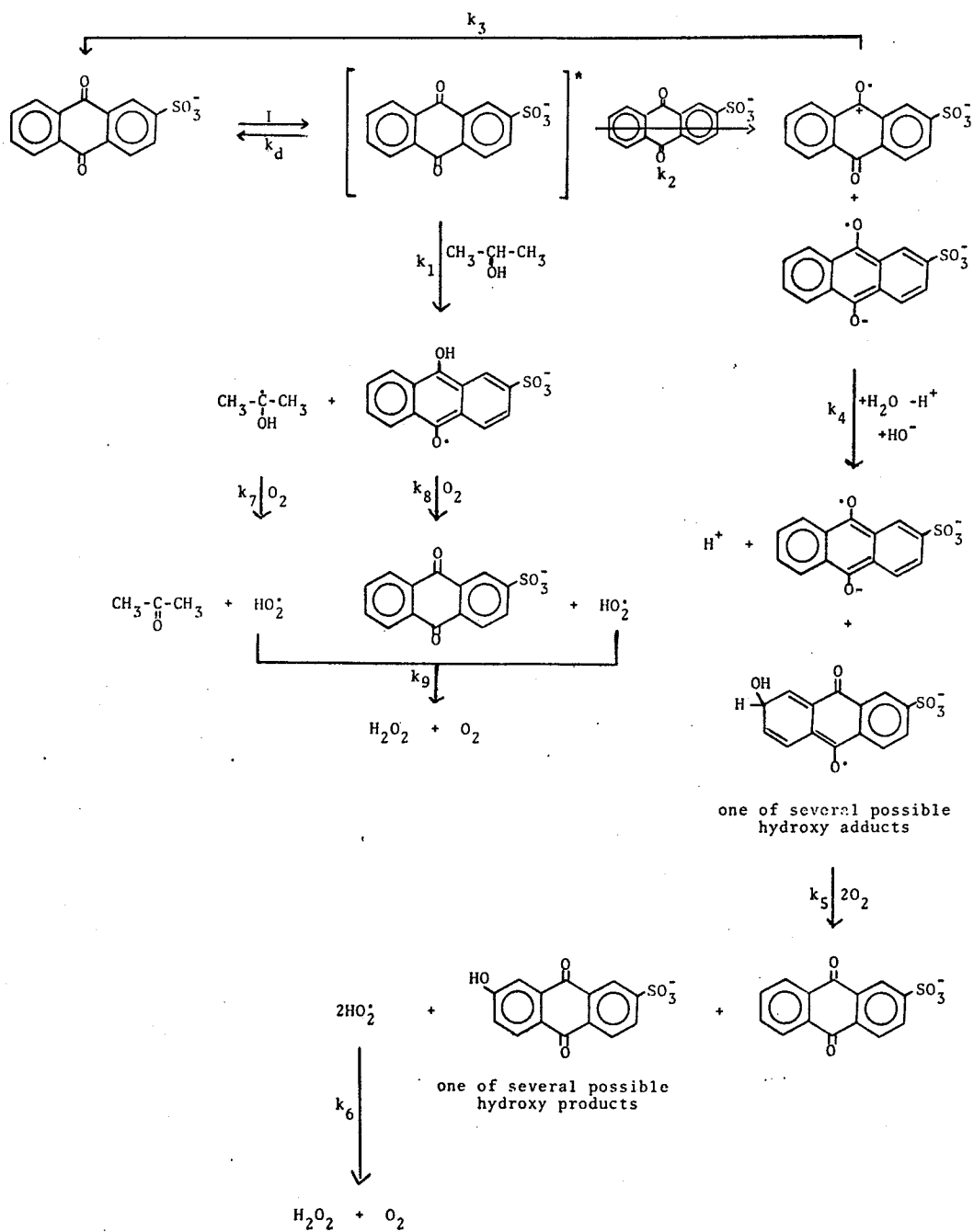
If this is a reasonable mechanism, then its validity can be verified kinetically. If one assumes k_5, k_6, k_7, k_8 and k_9 to be fast, then

$$d(H_2O_2)/dt = k_4(AQ^{\cdot -})(AQ^{\cdot +})(H_2O) + k_1(ipa)(AQ^*) \quad \ldots\ldots 1$$

where

$AQ^{\cdot -} =$

$AQ =$

$AQ^{\cdot +} =$

$AQOH =$

one of several possible hydroxy products

$AQ^* =$

$ipa = CH_3-\underset{\underset{OH}{|}}{CH}-CH_3$
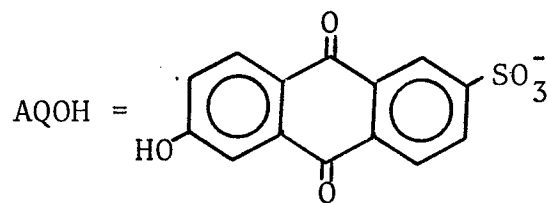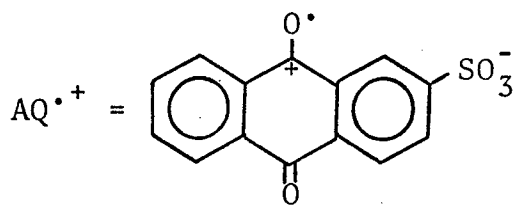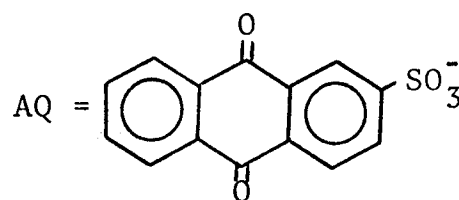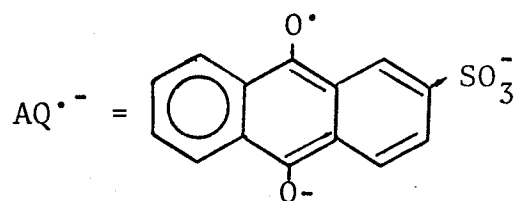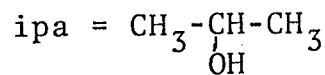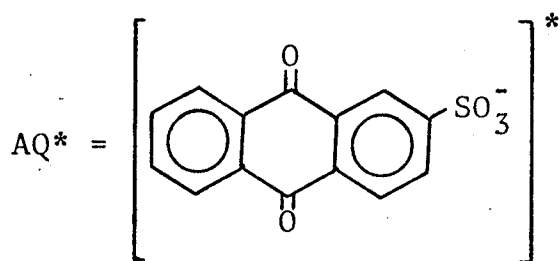
$$d(AQOH)/dt = k_4(AQ^{\cdot -})(AQ^{\cdot +})(H_2O) \quad \ldots\ldots 2$$

$$d(AQ^{\cdot -})(AQ^{\cdot +})/dt = k_2(AQ)(AQ*) - k_3(AQ^{\cdot -})(AQ^{\cdot +})$$

$$- k_4(H_2O)(AQ^{\cdot -})(AQ^{\cdot +}) \qquad .....3$$

and, $d(AQ*)/dt = I - k_d(AQ*) - k_1(ipa)(AQ*)$

$$- k_2(AQ*)(AQ) \qquad .....4$$

At steady state, $d(AQ^{\cdot -})(AQ^{\cdot +})/dt = 0$ (equation 3)

$\therefore$ $k_2(AQ)(AQ*) - k_3(AQ^{\cdot -})(AQ^{\cdot +}) - k_4(H_2O)(AQ^{\cdot +})(AQ^{\cdot -}) = 0$

and, $(AQ^{\cdot -})(AQ^{\cdot +}) = k_2(AQ)(AQ*)/(k_3 + k_4(H_2O))$ $.....5$

Also at steady state, $d(AQ*)/dt = 0$ (equation 4)

$\therefore$ $I - k_d(AQ*) - k_1(ipa)(AQ*) - k_2(AQ*)(AQ) = 0$

and, $(AQ*) = I/(k_d + k_1(ipa) + k_2(AQ))$ $.....6$

Substitute 5 and 6 in 1,

$$d(H_2O_2)/dt = k_4 \left[\frac{k_2(AQ)}{k_3 + k_4(H_2O)} \cdot \frac{I}{k_d + k_1(ipa) + k_2(AQ)} \right] (H_2O)$$

$$+ k_1(ipa) \left[\frac{I}{k_d + k_1(ipa) + k_2(AQ)} \right]$$

$$= I \left[\frac{k_4 k_2(AQ)(H_2O)}{(k_3 + k_4(H_2O))(k_d + k_1(ipa) + k_2(AQ))} \right. $$

$$\left. + \frac{k_1(ipa)}{k_d + k_1(ipa) + k_2(AQ)} \right]$$

and, $(d(H_2O_2)/dt) \cdot (1/I)$ and the quantum yield of peroxide being synonomous, then

$$\Phi_{H_2O_2} = \frac{1}{k_d + k_1(ipa) + k_2(AQ)} \left[\frac{k_4 k_2 (AQ)(H_2O)}{k_3 + k_4(H_2O)} + k_1(ipa) \right]$$

.....7

Substitute 5 and 6 in 2,

$$d(AQOH)/dt = k_4 \left[\frac{k_2(AQ)}{k_3 + k_4(H_2O)} \cdot \frac{I}{k_d + k_1(ipa) + k_2(AQ)} \right] (H_2O)$$

$$= I \left[\frac{k_4 k_2 (AQ)(H_2O)}{k_3 + k_4(H_2O)} \cdot \frac{1}{k_d + k_1(ipa) + k_2(AQ)} \right]$$

and, $(d(AQOH)/dt) \cdot (1/I)$ and the quantum yield for hydroxylated quinone being synonomous, then

$$\Phi_{AQOH} = \frac{1}{k_d + k_1(ipa) + k_2(AQ)} \frac{k_4 k_2 (AQ)(H_2O)}{k_3 + k_4(H_2O)}$$

.....8

Divide 7 by 8,

$$\frac{\Phi_{H_2O_2}}{\Phi_{AQOH}} = 1 + \frac{\left[k_3 + k_4(H_2O)\right] k_1(ipa)}{k_4 k_2 (AQ)(H_2O)}$$

$$= 1 + \left[\frac{k_3}{k_2 k_4 (AQ)(H_2O)} + \frac{1}{k_2(AQ)} \right] k_1(ipa)$$

.....9

and plot $\Phi_{H_2O_2}/\Phi_{AQOH}$ vs (ipa) (Figure IX) at some constant quinone concentration. One could expect that a straight line with an intercept of 1 should result, if our proposed mechanism is correct. If one examines Figure IX, it can be seen that the resultant plot was not quite straight but slightly curved. This is due

Figure IX. Plot showing the correlation between $\Phi_{H_2O_2}/\Phi_{hydroxylation}$ and the concentration of isopropanol.

$(AQ) = 3.891 \times 10^{-3}$ M
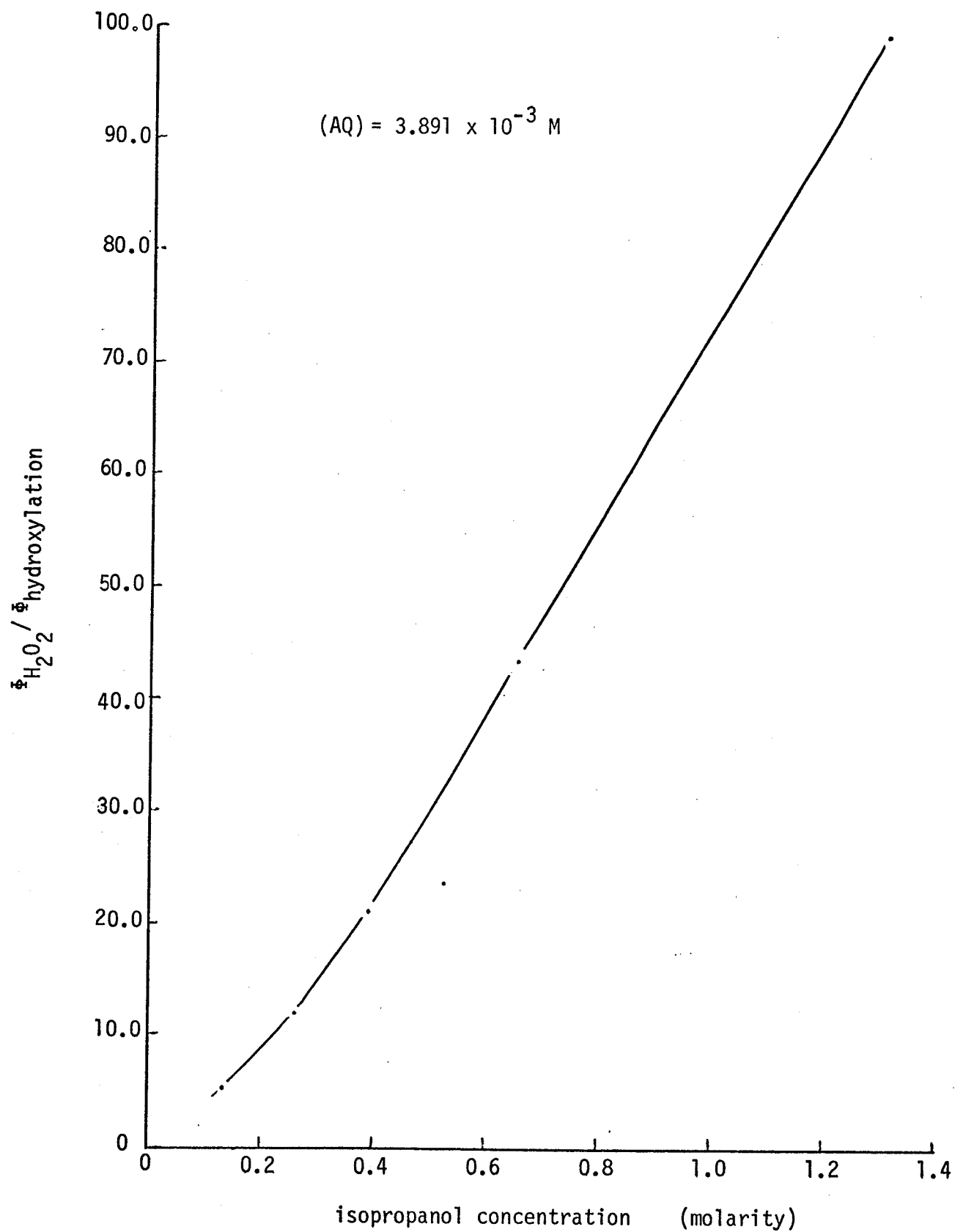
to the fact that the slope, $\left[\dfrac{k_3}{k_2 k_4 (AQ)(H_2O)} + \dfrac{1}{k_2(AQ)}\right]$

is not constant, for the concentration of water changes
upon going from a solution of anthraquinone-2-sulfonate
in water with no isopropanol to one that is 10.0% in
isopropanol. If there was a way of allowing for the
differences that the change in water concentration
makes, the line in all probability would be straight.
The values for 0.0% and 0.1% isopropanol were not
plotted as the quantum yields for peroxide were less
than the quantum yields for hydroxylation. This was
more than likely due to large errors in titrating small
amounts of peroxide. The titre was often quite small and
several titrations of the anthraquinone-2-sulfonate
solutions with low or no amounts of isopropanol in
them gave varying amounts of peroxide. In other words,
the quantum yields for peroxide could easily have been
the same as or more than the quantum yields for hydrox-
ylation. (Clark and Stonehill (4) reported equal
amounts of hydroxyquinone and peroxide.)

Another plot can be performed to check the mechanism.
Subtract 8 from 7 and invert,

$$\Phi_{H_2O_2} - \Phi_{AQOH} = \frac{k_1(ipa)}{k_d + k_1(ipa) + k_2(AQ)}$$

$$\frac{1}{\Phi_{H_2O_2} - \Phi_{AQOH}} = 1 + \left[\frac{k_d}{k_1} + \frac{k_2(AQ)}{k_1}\right]\frac{1}{(ipa)} \qquad \ldots\ldots 10$$

and plot $1/(\Phi_{H_2O_2} - \Phi_{AQOH})$ vs $1/(ipa)$ (Figure X) at

some constant quinone concentration. One could again
expect that a straight line with an intercept of one

66

Figure X. Plot showing the correlation
between $1/(\Phi_{H_2O_2} - \Phi_{hydroxylation})$ and
the inverse of the concentration of
isopropanol.

67

$(AQ) = 3.891 \times 10^{-3}$ M
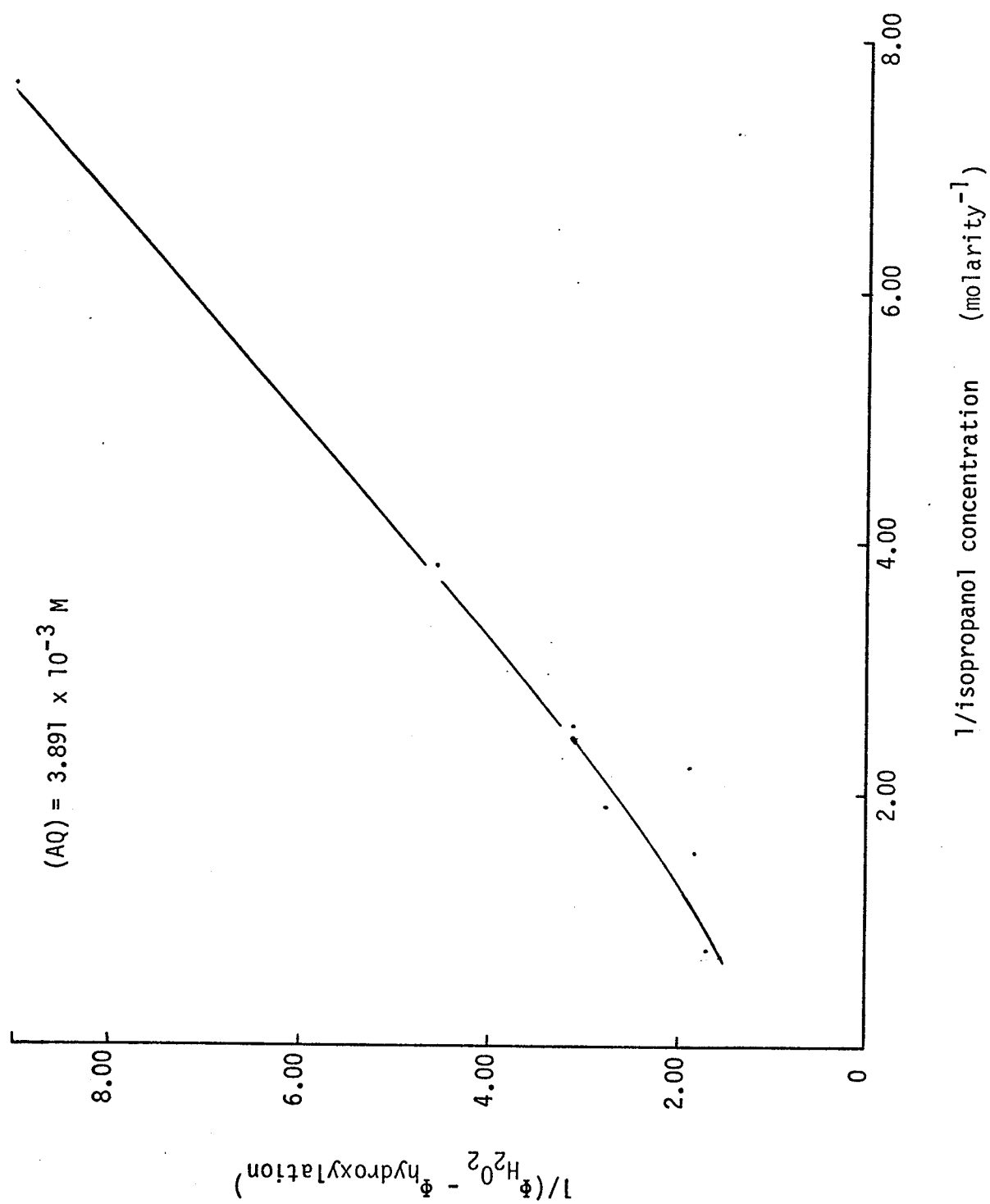
should result (i.e. the proposed mechanism would be consistent with the data). An examination of Figure X shows that the points fell on a reasonably straight line and that the intercept was one. The values for 0.0% and 0.1% isopropanol were again not plotted for the same reasons as before. The Figures IX and X however, do show that there was a correlation between our proposed mechanism and the data.

Further evidence to support our mechanism was that Clark and Stonehill (13) found the rate of photo-hydroxylation to be dependent on the concentration of anthraquinone-2-sulfonate. Although we did not conduct any thorough quinone dependence studies, our mechanism allowed for Clark and Stonehill's fact (see equation 8). Also Clark and Stonehill found the rate of photohydroxylation to increase as hydroxide ion concentration increased. We found the same results in our laboratory - hydroxylation increased upon going from a neutral anthraquinone-2-sulfonate solution to a basic one and from a neutral anthraquinone-2-sulfonate isopropanol solution to a basic one with the same concentration of isopropanol. Our mechanism is consistent with this because it seems reasonable that the negatively charged hydroxide ion would attack the semiquinone cation more readily than a neutral water molecule. This would act to speed up the conversion of semiquinone cation to hydroxylated semiquinone, which ultimately would give increased hydroxylation. In addition, in benzene/isopropanol solution where hydroxylation did not occur, we found that an increase in anthraquinone concentration caused the quantum yield for peroxide to decrease. Our mechanism could account for this,
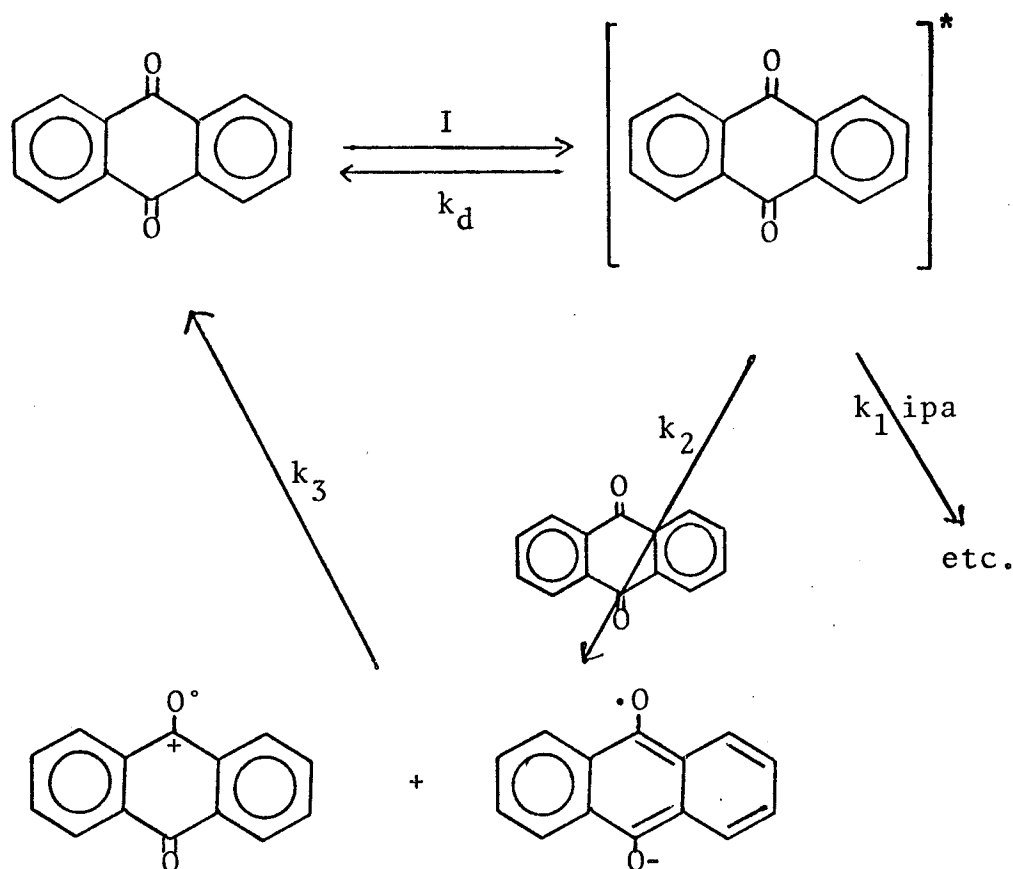
An increase in anthraquinone concentration would cause
more excited state quinone to convert to the radical
cation and radical anion rather than react with isop-
ropanol to produce peroxide. This would act to (and
indeed did) lower the quantum yield for peroxide.
(This quenching of excited state quinone does not
necessarily have to be by radical cation and radical
anion, it could be a triplet exiplex or a similar
self-quenching process.) Lastly, the anthraquinone-
2-sulfonate system did not show any dependence on
light intensity or on dose (changing the lamp from
a mercury/xenon one to a mercury one did not affect
the quantum yields either in the presence or absence

of isopropanol nor did time of irradiation affect the quantum yields either in the presence or absence of isopropanol). This would imply that the reaction was monophotonic. In conclusion, the mechanism proposed by us is in harmony with the information collected on the system.

One last matter remained to be examined - the existence of only β hydroxyanthraquinone-2-sulfonate above pH 10.5. Since α and β had been formed below this pH one would anticipate that both α and β would be formed above it. A possible reason for its absence could be that hydroxide ion exclusively and more efficiently attacks the β position of the quinone radical cation. If this is true, a linear drop off in the amount of α would be expected with increasing pH. If one examines the plot by Clark and Stonehill (4,p1682) it can be seen that the drop off was sharp at pH 10.5 and was not linear with pH. Perhaps then, exclusive attack by hydroxyl ion at the β position is not the reason for selective production of β above pH 10.5. Another possible reason for the occurrence of only β above pH 10.5 could be that the quinone hydroxyl radical adduct (formed by reacting quinone radical cation with hydroxyl ion) is ionizing at the hydroxylic position and interconverting (4).
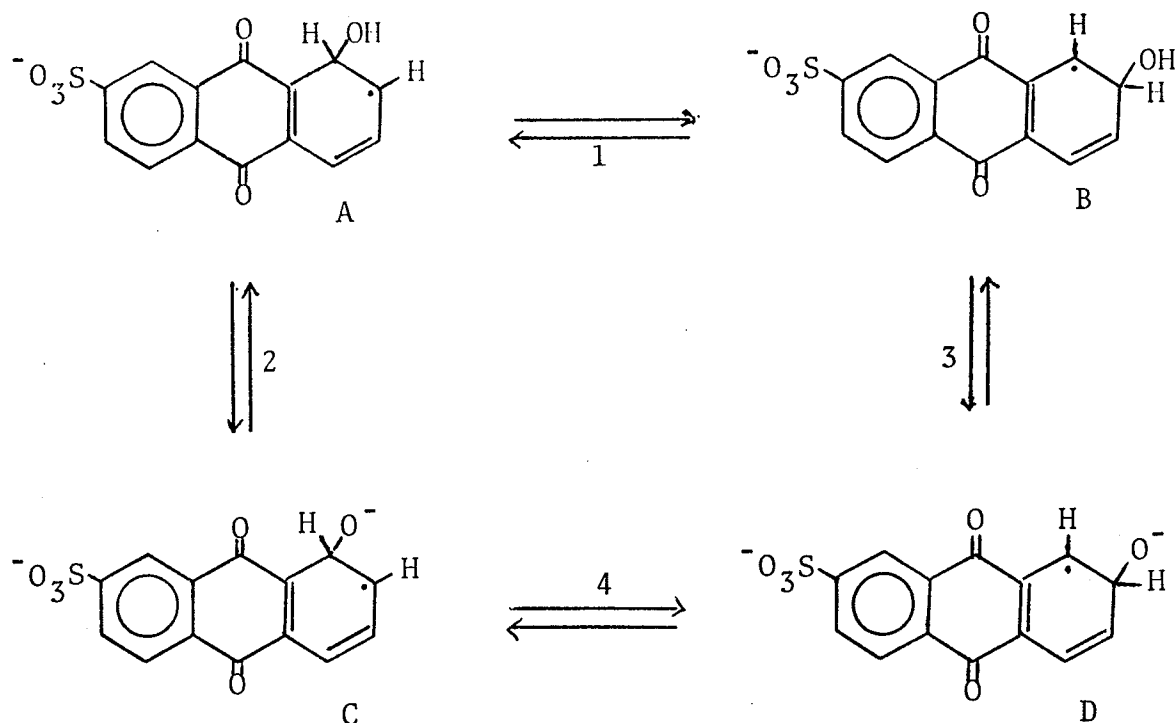
The base might be abstracting the alcoholic hydrogen (steps 2 and 3) although this seems unreasonable as the pK$_a$ values for alcohols are somewhat higher than pH 10.5. Also the hydrogen attached to the hydroxyl bearing carbon would probably be preferentially abstracted as this would lead to the radical anion of hydroxylated quinone.
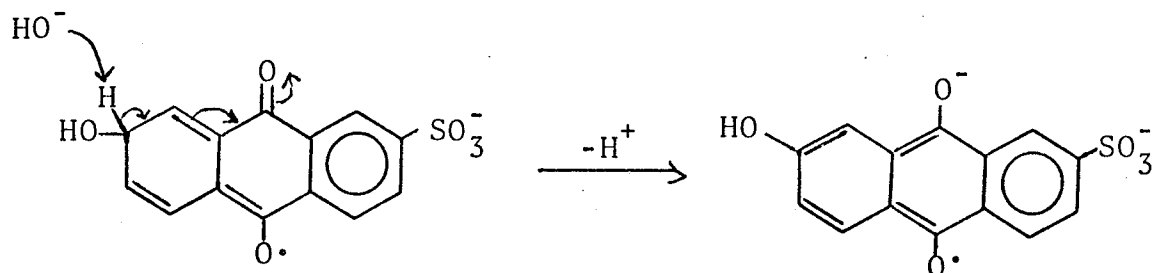
In degassed solutions the presence of base gave hydroxy-
lation. The fact that hydroxylated products were
absent in degassed solutions with no base, implies
that base somehow interfers with the disproportiona-
tion of B and quinone radical anion (vida supra).
As indicated above, it could be possible that the base
abstracts the alcoholic hydrogen. The resultant
species D, (instead of disproportionating with the
quinone radical anion) could then disproportionate   .
with itself.
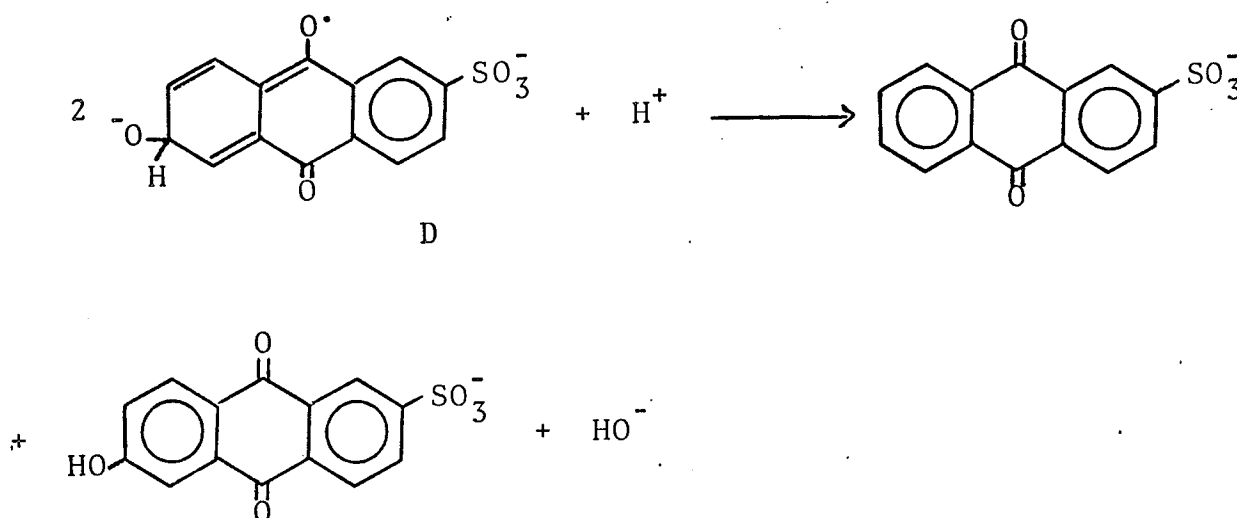
This would give half the amount of hydroxylation as
might be obtained in the corresponding aerated solutions
where we expect all of D to be converted to hydroxylated
product by reaction with oxygen. Indeed this was found
to be the case,with the quantum yield for hydroxylation
in aerated solutions being 0.095 and in degassed
solutions 0.045 (hydroxide ion was at a concentration
of 0.02N).

If the base interferes with the disproportiona-
tion of β and quinone radical anion by abstracting
the hydrogen attached to the hydroxyl bearing carbon,
the resultant radical anion would be converted to
hydroxyanthraquinone upon exposure to air.
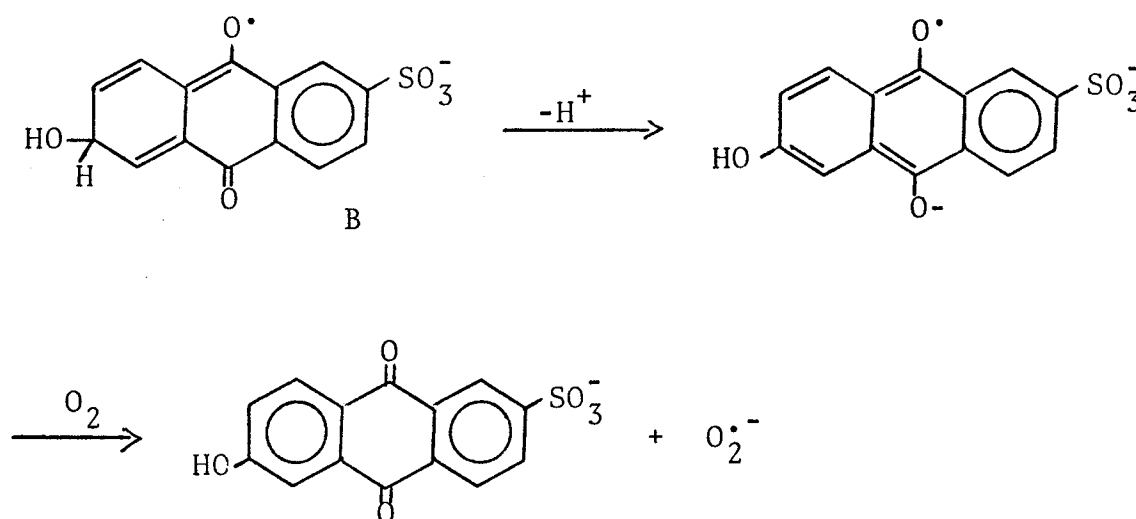
In other words, the same amount of hydroxylation should
occur in the degassed solutions and the corresponding
aerated solutions. Since it did not, but was halved
in degassed solutions, the mechanism involving the
abstraction of the alcoholic hydrogen seems more
reasonable. It may be possible then, that a mechanism
like Clark and Stonehill's for the formation of β
hydroxyanthraquinone-2-sulfonates is operating as this
is more consistant with the data. (At one point we
also considered that the anthraquinone-2-sulfonate
might be undergoing photosubstitution of the sulfonate
group to give β hydroxyanthraquinone. This is not
so, as experiments to detect β hydroxyanthraquinone
and bisulfite were unsuccessful.)

A final question arises in the arguments as to the exclusive formation of β product above pH 10.5 (other than the unlikely ionization of the hydroxylic hydrogen). Clark and Stonehill thought that ionization of the hydroxylic group in the hydroxyl radical adducts could lead to equilibrium of α and β hydroxyl radical adducts (as illustrated above). However, it seems improbable that in an irradiation of a basic oxygen saturated anthraquinone-2-sulfonate solution, that oxygen does not intercept any of A to create α hydroxyanthraquinone-2-sulfonate, and also that A lives long enough to just equilibrate to the β species but again is not intercepted by oxygen. An experiment that makes this appear even more improbable is that the addition of isopropanol to oxygenated and degassed solutions of anthraquinone-2-sulfonate gave hydroxylation that was cut by five-sixths (in going to the degassed solution). This decrease of hydroxylation could arise from the fact that when isopropanol is present more quinone radical anion is formed. By virtue of its increased concentration it might disproportionate with either A or B thereby lowering the quantum yield of hydroxylation. If quinone radical anion could intercept the hydroxy radical adduct then could not oxygen do the same? No alternate mechanism could be conceived that would satisfactorily explain the experimental data and, the true events behind the selective formation of β hydroxyanthraquinone-2-sulfonates above pH 10.5 still remain to be determined.

EXPERIMENTAL

Mass spectra were recorded on a Finnigan 1015 mass spectrometer. Ultraviolet/visible spectra were recorded on a Cary 14 spectrophotometer. Optical densities were measured by a Bausch and Lomb spectronic 20.

QUANTUM YIELDS

Equipment

A 200 watt HBO Osram mercury lamp and a 200 watt Hanovia mercury/xenon lamp were used as light sources in quantum yield determinations. Before reaching the sample, the light was passed through a Jarrell Ash monochromator Model No.82410 set to isolate light of λ = 366 nm. The power source used for the lamp was an Oriel Universal Arc Lamp, Model C-30.

Actinometry

Light intensities were measured by a slightly altered method of Parker's (19) potassium ferrioxalate actinometry. The following solutions were prepared:

1) 0.1 N sulfuric acid solution: 2.78 ml of concentrated sulfuric acid were diluted to 1,000 ml.

2) 0.2% 1,10-phenanthroline monohydrate solution: 0.200 g of 1,10-phenanthroline monohydrate were dissolved in water and diluted to 100 ml with water.

3) buffer solution: 49.224 g of sodium acetate and 10.00 ml of concentrated sulfuric acid were dissolved in water and diluted to 1,000 ml with water.

4) 0.2000 M ferric ammonium sulfate solution: 9.6442 g of $Fe(NH_4)(SO_4)_2 \cdot 12H_2O$ were dissolved in 0.1 N sulfuric acid and diluted to 100 ml with 0.1 N sulfuric acid.

5) 0.6000 M potassium oxalate solution: 9.9720 g of potassium oxalate were dissolved in 0.1 N sulfuric acid and diluted to 100 ml with 0.1 N sulfuric acid.

6) potassium ferrioxalate solution: 3.0 ml of the 0.2000 M ferric ammonium sulfate solution and 3.0 ml of the 0.6000 M potassium oxalate solution were diluted in the dark to 100 ml with 0.1 N sulfuric acid.

3.0 ml of the potassium ferrioxalate solution were irradiated for three minutes with the mercury/xenon lamp and for one and a half minutes with the mercury lamp. After the irradiated solution was thoroughly mixed, a 1.0 ml aliquot was taken and mixed with 1 to 2 ml of the buffer solution and of the phenanthroline solution and diluted to 10.0 ml with distilled water. 3.0 ml of the potassium ferrioxalate solution were left in the dark. A 1.0 ml aliquot from this solution was treated in the same manner as the irradiated solution. This was used as a blank. These solutions were allowed to stand a few minutes and the optical densities measured at 510 mu. The lamp intensity was calculated as follows:

$$I = \frac{(O.D. \; F \; (V))}{\Phi \; A \; t}$$

$$O.D. = \text{optical density at 510 mu.}$$

$$F = \frac{\text{volume of dilution}}{\text{volume of aliquot of irradiated solution}} \times \frac{10^{-3}}{\varepsilon \, l} \cdot$$

$$= \frac{10.0 \text{ ml}}{1.0 \text{ ml}} \times \frac{10^{-3}}{1.21 \times 10^{-4}} \frac{1}{\text{l/mole cm.}}$$

V = volume of potassium ferrioxalate solution irradiated.

= 3.0 ml.

Φ = quantum yield of ferrioxalate.

= 1.21 at 3660 $\overset{o}{A}$.

A = amount of light absorbed (>0.999 at 3660 $\overset{o}{A}$).

t = time of irradiation.

$$= \frac{(O.D.)}{t} \times \frac{\frac{10.0}{1.0} \times \frac{10^{-3}}{1.21 \times 10^{-4}}}{0.999 \times 1.21} \times 3.0 \text{ ml Einsteins/min.}$$

$$= \frac{(O.D.)}{t} \times 2.068 \times 10^{-6} \text{ Einsteins/min.}$$

Product Analysis

Hydrogen peroxide was determined in the following manner. Irradiated samples (of 5.0 ml volumes unless otherwise indicated) were rinsed into 250 ml erlenmeyer flasks containing 20 ml water; 1.0 to 1.5 g potassium biphthallate; 0.1 g ammonium molybdate; 1.0 to 2.0 g of potassium iodide and 20 drops of starch solution (0.200 g in 100 ml of water). The I_3^- ion was allowed to develop and then titrated with 0.01 N sodium thiosulfate solution. Similarily, unirradiated samples were titrated and used as blanks.

$$3I^- + 2H^+ + H_2O_2 \xrightarrow{(NH_4)_2MoO_4} 2H_2O + I_3^-$$

$$I_3^- + 2S_2O_3^= \longrightarrow 3I^- + S_4O_6^=$$
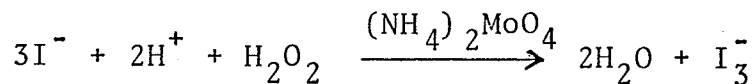
The 0.01 N thiosulfate solution was diluted from a 0.1 N solution. This solution was standardized according to a slightly altered method of Fisher and Peters (20). Instead of the aliquot method, amounts of potassium iodate were exactly weighed out (between 0.1000 and 0.2000 g); 75 ml of water added; 3.0 g of potassium iodide added and 2 ml of 6F HCl added. This was then titrated with the thiosulfate solution.

$$IO_3^- + 8I^- + 6H^+ \longrightarrow 3I_3^- + 3H_2O$$

$$I_3^- + 2S_2O_3^= \longrightarrow 3I^- + S_4O_6^=$$
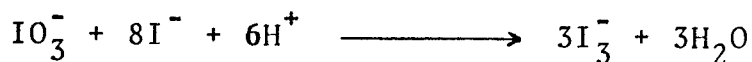
Hydroxylation was measured as follows: to irradiated samples of 5.0 ml volumes; 0.17 ml of a 3.02 N potassium hydroxide solution was added. The optical density of these solutions was then measured at $\lambda = 476$ mu and $\lambda = 491$ mu. Unirradiated samples of the same size were treated in a like manner and used as blanks.

The determination of the quantum yields of hydroxylation was carried out as follows:

$$\Phi_\alpha = \frac{C_\alpha V}{It} \qquad\qquad \Phi_\beta = \frac{C_\beta V}{It}$$

$C_\alpha =$ concentration of α hydroxyanthraquinone-2-sulfonate.

$C_\beta =$ concentration of β hydroxyanthraquinone-2-sulfonate.

$V =$ volume of anthraquinone-2-sulfonate solution irradiated.

$I =$ lamp intensity.

$t =$ time of irradiation of the anthraquinone-2-sulfonate solution.

The concentrations of α and β were determined by solving the simultaneous equations,

$$A_{491} = \mathcal{E}_{\alpha_{491}} C_\alpha l + \mathcal{E}_{\beta_{491}} C_\beta l \qquad \ldots\ldots 1$$

$$A_{476} = \mathcal{E}_{\alpha_{476}} C_\alpha l + \mathcal{E}_{\beta_{476}} C_\beta l \qquad \ldots\ldots 2$$

In their paper, Clark and Stonehill (13) included extinction coefficients for α at $\lambda = 491$ mu and for β at $\lambda = 491$ mu and $\lambda = 476$ mu,

$$\mathcal{E}_{\alpha_{491}} = 5.65 \times 10^3 \text{ 1/mole cm.}$$

$$\varepsilon_{\beta_{491}} = 3.40 \times 10^3 \text{ 1/mole cm.}$$

$$\varepsilon_{\beta_{476}} = 3.60 \times 10^3 \text{ 1/mole cm.}$$

No value for α at λ = 491 mu was included. However, for neutral solutions, they reported that the molar ratio of α to β was three to two. This information was enough to calculate a value for the extinction coefficient for α at λ = 491 mu.

$$C_\beta = 2/3 C_\alpha$$

$$A_\alpha = \varepsilon_\alpha C_\alpha l \qquad\qquad \ldots\ldots 3$$

$$A_\beta = \varepsilon_\beta 2/3 C_\alpha l \qquad\qquad \ldots\ldots 4$$

The total extinction coefficient at a particular wavelength was then calculated.

$$A_\alpha + A_\beta = \varepsilon_\alpha C_\alpha l + \varepsilon_\beta 2/3 C_\alpha l$$

$$= C_\alpha l \ (\varepsilon_\alpha + 2/3 \varepsilon_\beta) \qquad\qquad \ldots\ldots 5$$

Therefore at λ = 491 mu,

$$A_{491} = C_\alpha l \ (\varepsilon_{\alpha_{491}} + 2/3 \varepsilon_{\beta_{491}}). \qquad \ldots\ldots 6$$

and at λ = 476 mu,

$$A_{476} = C_\alpha l \ (\varepsilon_{\alpha_{476}} + 2/3 \varepsilon_{\beta_{476}}) \qquad \ldots\ldots 7$$

Division of 7 by 6 gave

$$\frac{A_{476}}{A_{491}} = \frac{\varepsilon_{\alpha_{476}} + 2/3\varepsilon_{\beta_{476}}}{\varepsilon_{\alpha_{491}} + 2/3\varepsilon_{\beta_{491}}} \qquad \ldots\ldots 8$$

Numerous readings were taken for A_{476} and A_{491} and the ratio A_{476}/A_{491} was found to be 0.945 (this was averaged from ten individual ratios). Using Clark and Stonehill's given values for the extinction coefficients (of α at λ = 491 mu and of β) equation 8 gave $\varepsilon_{\alpha_{476}}$ a value of 5.09 x 10^3.

Returning to equations 1 and 2, C_{α} and C_{β} were calculated. (The only unknown parameter was the cell length. This was determined from the ferrioxalate actinometry where εl = 1.21 x 10^{-4} 1/mole cm. and ε = 1.111 x 10^{-4} 1/mole which gave $l = \varepsilon l/\varepsilon$ = 1.09 cm.) Therefore, from equations 1 and 2

$$C_{\alpha} = \frac{3.92A_{491} - 3.71A_{476}}{3.63 \times 10^3}$$

$$C_{\beta} = \frac{6.16A_{476} - 5.54A_{491}}{3.63 \times 10^3}$$

Degassing

5.0 ml samples were placed in drawn-out test tubes, degassed by the freeze-thaw technique to below 10^{-3} torr and sealed off.

Materials Used

The materials used in the determination of the quantum yields were:

sodium thiosulfate   (reagent grade)

sodium bicarbonate   (reagent grade)

potassium bipthallate   (reagent grade)

ammonium molybdate   (reagent grade)

potassium iodide   (reagent grade)

starch   (reagent grade)

nitrogen gas   (Linde Union Carbide Canada Ltd.)

oxygen gas (Linde Union Carbide Canada Ltd.)

carbon dioxide gas (Canada Liquid Air Co. Ltd.)

potassium hydroxide   (reagent grade)

isopropyl alcohol   (technical grade and distilled
                           twice)

benzene   (technical grade and distilled twice)

anthraquinone   (technical grade and recrystallized
                     three times)

anthraquinone-2-sulfonate   (technical grade and
                               recrystallized three times)

Both the isopropyl alcohol and benzene were distilled before using. The anthraquinone was recrystallized three times from chloroform. The anthraquinone-2-sulfonate was recrystallized two times from water (the initial recrystallization was treated with decolorizing charcoal), once from a 50/50 mixture of ethanol and water and lastly from distilled water.

All aqueous solutions unless otherwise stated were made using water that had been doubly distilled and put through Illinois Water Treatment Co. deionizing columns (Research Model and Puritan Model).

Quantum Yield Data

a) effect of anthraquinone concentration on hydrogen
peroxide production in benzene/isopropyl alcohol
solutions.

1) 6.0 ml samples from a 3.602×10^{-3} M
anthraquinone in 50/50 benzene/isopropyl
alcohol solution were irradiated.
They were oxygenated before and during
irradiation. 0.001 N sodium thio-
sulfate solution was used to titrate.

Sample	I*(Einsteins/min)	Einsteins	$\Phi_{H_2O_2}^{**}$
1	1.241×10^{-7}	7.446×10^{-7}	1.075
2	1.324×10^{-7}	7.944×10^{-7}	0.990

* I = lamp intensity
** $\Phi_{H_2O_2}$ = quantum yield of hydrogen peroxide

2) 6.0 ml samples from a 6.003×10^{-2} M
anthraquinone in 50/50 benzene/isopropyl
alcohol solution were irradiated.
They were oxygenated before and during
irradiation. 0.001 N sodium thio-
sulfate solution was used to titrate.

Sample	I (Einsteins/min)	Einsteins	$\Phi_{H_2O_2}$
1	2.578×10^{-7}	1.547×10^{-6}	0.863
2	2.295×10^{-7}	1.377×10^{-6}	0.944
3	2.316×10^{-7}	1.390×10^{-6}	0.838

b) effect of carbon dioxide gas on hydroxylation and hydrogen peroxide production in water solutions of anthraquinone-2-sulfonate.

1) 5.0 ml samples from a 6.019×10^{-3} M anthraquinone-2-sulfonate in water solution were irradiated. They were aerated with a 2:1 carbon dioxide/oxygen mixture before and during irradiation. 0.01 N sodium thiosulfate was used to titrate.

Sample	I (Einsteins/min)	Einsteins	$\Phi_{H_2O_2}$	Φ_α*	Φ_β**	C_α*** m/l	C_β**** m/l
1	6.397×10^{-7}	1.919×10^{-5}	0.031	—	—		
2	6.452×10^{-7}	7.097×10^{-6}		0.019	0.025	2.72×10^{-5}	3.55×10^{-5}

*Φ_α = quantum yield of α hydroxy quinone
**Φ_β = quantum yield of β hydroxy quinone
***C_α = concentration of α hydroxy quinone
****C_β = concentration of β hydroxy quinone

2) The immediately previous run was repeated but the samples were aerated with a 5:1 carbon dioxide/oxygen mixture before and during irradiation.

Sample	I (Einsteins/ min)	Einsteins	$\Phi_{H_2O_2}$	Φ_α	Φ_β	C_α m/l	C_β m/l
1	6.383×10^{-7}	1.915×10^{-5}	0.026				
2	6.445×10^{-7}	7.090×10^{-6}		0.019	0.031	2.67×10^{-5}	4.33×10^{-5}

3) Again a repeat was carried out but the samples
were aerated with carbon dioxide only,
before and during irradiation.

Sample	I (Einsteins/ min)	Einsteins	$\Phi_{H_2O_2}$	Φ_α	Φ_β	C_α m/l	C_β m/l
1	5.329×10^{-7}	1.599×10^{-5}	0				
2	5.439×10^{-7}	5.983×10^{-6}		0.017	0.021	2.02×10^{-5}	2.50×10^{-5}

c) effect of sodium bicarbonate on hydroxylation and
hydrogen peroxide production in water solutions of anthra-
quinone-2-sulfonate.

1) 5.0 ml samples from a 6.019×10^{-3} M anthra-
quinone-2-sulfonate and 0.1 M sodium bi-
carbonate in water solution were irradiated.
They were oxygenated before and during
irradiation. 0.01 N sodium thiosulfate
was used to titrate.

Sample	I (Einsteins/ min)	Einsteins	$\Phi_{H_2O_2}$	Φ_α	Φ_β	C_α m/l	C_β m/l
1	5.460×10^{-7}	1.638×10^{-5}	0.047				
2	5.535×10^{-7}	5.535×10^{-6}		0.030	0.039	3.31×10^{-5}	4.30×10^{-5}

d) effect of isopropyl alcohol on hydroxylation and hydrogen peroxide production in water solutions of anthraquinone-2-sulfonate.

1) 5.0 ml samples from a 3.891×10^{-3} M anthraquinone-2-sulfonate in water solution were irradiated. They were oxygenated before and during irradiation. 0.01 N sodium thiosulfate was used to titrate.

Sample	I (Einsteins/min)	Einsteins	$\Phi_{H_2O_2}$	Φ_α	Φ_β	C_α m/l	C_β m/l
1	5.473×10^{-7}	6.568×10^{-5}	0.012	—	—		
2	5.515×10^{-7}	5.515×10^{-6}		0.022	0.016	2.40×10^{-5}	1.75×10^{-5}

2) 5.0 ml samples from a 3.891×10^{-3} M anthraquinone-2-sulfonate and 0.1% isopropyl alcohol (by volume) in water solution were irradiated. They were oxygenated before and during irradiation. 0.01 N sodium thiosulfate was used to titrate.

Sample	I (Einsteins/min)	Einsteins	$\Phi_{H_2O_2}$	Φ_α	Φ_β	C_α m/l	C_β m/l
1	5.846×10^{-7}	3.508×10^{-5}	0.029	—	—		
2	5.866×10^{-7}	5.866×10^{-6}		0.021	0.019	2.42×10^{-5}	2.24×10^{-5}

3) 5.0 ml samples from a 3.891×10^{-3} M anthraquinone-2-sulfonate and 1.0% isopropyl alcohol (by volume) in water solution were irradiated. They were oxygenated before and during irradiation. 0.01 N sodium thiosulfate was used to titrate.

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Sample	I (Einsteins/min)	Einsteins	$\Phi_{H_2O_2}$	Φ_α	Φ_β	C_α m/l	C_β m/l
1	6.976×10^{-7}	2.093×10^{-5}	0.167				
2	6.893×10^{-7}	6.893×10^{-6}		0.014	0.013	1.93×10^{-5}	1.78×10^{-5}
3	6.783×10^{-7}	2.035×10^{-5}	0.172				
4	6.631×10^{-7}	3.979×10^{-5}	0.107				
5	6.604×10^{-7}	3.962×10^{-5}	0.107				

4) 5.0 ml samples from a 3.891×10^{-3} M anthra-
quinone-2-sulfonate and 2.0% isopropyl
alcohol (by volume) in water solution were
irradiated. They were oxygenated before
and during irradiation. 0.01 N sodium thio-
sulfate was used to titrate.

Sample	I (Einsteins/min)	Einsteins	$\Phi_{H_2O_2}$	Φ_α	Φ_β	C_α m/l	C_β m/l
1	6.631×10^{-7}	1.989×10^{-5}	0.239				
2	6.032×10^{-7}	6.032×10^{-6}		0.010	0.010	1.23×10^{-5}	1.19×10^{-5}

5) 5.0 ml samples from a 3.891×10^{-3} M anthra-
quinone-2-sulfonate and 3.0% isopropyl
alcohol (by volume) in water solution were
irradiated. They were oxygenated before and
during irradiation. 0.01 N sodium thio-
sulfate was used to titrate.

Sample	I (Einsteins/ min)	Einsteins	$\Phi_{H_2O_2}$	Φ_α	Φ_β	C_α m/l	C_β m/l
1	6.121 x 10⁻⁷	1.836 x 10⁻⁵	0.335	—	—		
2	6.280 x 10⁻⁷	6.280 x 10⁻⁶		0.012	0.004	1.48 x 10⁻⁵	5.27 x 10⁻⁶

6) 5.0 ml samples from a 3.891×10^{-3} M anthra-quinone-2-sulfonate and 4.0% isopropyl alcohol (by volume) in water solution were irradiated. They were oxygenated before and during irradiation. 0.01 N sodium thio-sulfate was used to titrate.

Sample	I (Einsteins/ min)	Einsteins	$\Phi_{H_2O_2}$	Φ_α	Φ_β	C_α m/l	C_β m/l
1	5.046 x 10⁻⁷	1.514 x 10⁻⁵	0.378	—	—		
2	5.101 x 10⁻⁷	5.101 x 10⁻⁶		0.009	0.007	9.02 x 10⁻⁶	7.14 x 10⁻⁶

7) 5.0 ml samples from a 3.891×10^{-3} M anthra-quinone-2-sulfonate and 5.0% isopropyl alcohol (by volume) in water solution were irradiated. They were oxygenated before and during irradiation. 0.01 N sodium thio-sulfate was used to titrate.

Sample	I (Einsteins/ min)	Einsteins	$\Phi_{H_2O_2}$	Φ_α	Φ_β	C_α m/l	C_β m/l
1	7.748 $\times 10^{-7}$	2.324 $\times 10^{-5}$	0.510				
2	7.803 $\times 10^{-7}$	7.803 $\times 10^{-6}$		0.007	0.005	1.11 $\times 10^{-5}$	8.50 $\times 10^{-6}$
3	5.570 $\times 10^{-7}$	1.671 $\times 10^{-5}$	0.619				

8) 5.0 ml samples from a 3.891×10^{-3} M anthra-
quinone-2-sulfonate and 10.0% isopropyl
alcohol (by volume) in water solution were
irradiated. They were oxygenated before and
during irradiation. 0.01 N sodium thio-
sulfate was used to titrate.

Sample	I (Einsteins/ min)	Einsteins	$\Phi_{H_2O_2}$	Φ_α	Φ_β	C_α m/l	C_β m/l
1	5.935 $\times 10^{-7}$	1.781 $\times 10^{-5}$	0.595				
2	5.935 $\times 10^{-7}$	6.529 $\times 10^{-6}$		0.003	0.004	3.37 $\times 10^{-6}$	4.93 $\times 10^{-6}$

e) effect of degassing on hydroxylation and hydrogen
peroxide production in neutral water solutions of
anthraquinone-2-sulfonate.
   i) effect on hydroxylation and hydrogen peroxide
      production with and without isopropyl alcohol.
      1) 5.0 ml samples from a 3.891×10^{-3} M anthra-
         quinone-2-sulfonate in water solution were
         degassed and then irradiated. They were
         opened, oxygenated and titrated with 0.01 N
         sodium thiosulfate.

Sample	I (Einsteins/min)	Einsteins	$\Phi_{H_2O_2}$	Φ_α	Φ_β	C_α m/l	C_β m/l
1	5.377×10^{-7}	5.377×10^{-6}		0.003	0.006	2.86×10^{-6}	6.46×10^{-6}
2	5.542×10^{-7}	5.542×10^{-6}		0.003	0.007	2.83×10^{-6}	7.98×10^{-6}
3	4.722×10^{-7}	2.833×10^{-5}	0				
4	4.715×10^{-7}	2.829×10^{-5}	0				
5	4.687×10^{-7}	1.406×10^{-5}		0.003	0.005	6.91×10^{-6}	1.50×10^{-5}

2) 5.0 ml samples from a 3.891×10^{-3} M anthra-quinone-2-sulfonate and 1.0% isopropyl alcohol (by volume) in water solution were degassed and then irradiated. They were opened, oxygenated and titrated with 0.01 N sodium thiosulfate.

Sample	I (Einsteins/min)	Einsteins	$\Phi_{H_2O_2}$	Φ_α	Φ_β	C_α m/l	C_β m/l
1	2.447×10^{-7}	2.569×10^{-5}	0.062				
2	2.564×10^{-7}	1.923×10^{-5}	0.046				
3	2.607×10^{-7}	1.564×10^{-5}		0.0005	-	1.56×10^{-6}	-
4	2.516×10^{-7}	2.642×10^{-5}	0.059				
5	2.506×10^{-7}	1.504×10^{-5}		-	0.0010	-	3.06×10^{-6}

ii) effect of changing the lamp on hydroxylation
   without isopropyl alcohol.
   1) 5.0 ml samples from a 3.891×10^{-3} M anthra-
      quinone-2-sulfonate in water solution were
      degassed and then irradiated. They were
      opened, oxygenated and their optical
      density taken.

Sample	I (Einsteins/ min)	Einsteins	Φ_α	Φ_β	C_α m/l	C_β m/l
1	2.802×10^{-7}	3.362×10^{-5}	0.002	0.003	1.05×10^{-5}	2.04×10^{-5}
2	4.687×10^{-7}	1.406×10^{-5}	0.003	0.005	6.91×10^{-6}	1.50×10^{-5}

iii) effect of changing water quality on hydroxylation,
   without isopropyl alcohol.
   1) 5.0 ml samples from a 3.891×10^{-3} M anthra-
      quinone-2-sulfonate in water solution were
      degassed and then irradiated. They were
      opened, oxygenated and their optical
      density taken.

Sample	I (Einsteins/ min)	Einsteins	Φ_α	Φ_β	C_α m/l	C_β m/l
1	2.802×10^{-7}	3.362×10^{-5}	0.002	0.003	1.05×10^{-5}	2.04×10^{-5}
2	5.378×10^{-7}	5.378×10^{-6}	0.003	0.006	2.86×10^{-6}	6.46×10^{-6}
3	5.542×10^{-7}	5.542×10^{-6}	0.003	0.007	2.83×10^{-6}	7.98×10^{-6}

2) 5.0 ml samples from a 3.891 x 10^{-3} M anthra-
quinone-2-sulfonate in water solution were
degassed and then irradiated. The water
used was distilled first from an alkaline
solution of potassium permanganate and
then from an acid solution of potassium
dichromate. The samples were opened,
oxygenated and their optical density taken.

Sample	I (Einsteins/ min)	Einsteins	Φ_α	I_β	C_α m/l	C_β m/l
1	2.358 x 10^{-7}	2.830 x 10^{-5}	0.0006	0.003	3.67 x 10^{-6}	1.95 x 10^{-5}

iv) effect of changing water quality on hydrogen
peroxide production, without isopropyl alcohol.
1) 5.0 ml samples from a 3.891 x 10^{-3} M anthra-
quinone-2-sulfonate in water solution were
degassed and then irradiated. They were
opened, oxygenated and titrated with 0.01 N
sodium thiosulfate.

Sample	I (Einsteins/min)	Einsteins	$\Phi_{H_2O_2}$
1	4.708 x 10^{-7}	2.825 x 10^{-5}	0
2	4.715 x 10^{-7}	2.829 x 10^{-5}	0

2)   5.0 ml samples from a 3.891×10^{-3} M anthra-
quinone-2-sulfonate in water solution were
degassed and then irradiated. The water
used was the same as used in e) iii) 2).
The samples were opened, oxygenated and
titrated with 0.01 N sodium thiosulfate.

Sample	I(Einsteins/min)	Einsteins	$\Phi_{H_2O_2}$
1	3.133×10^{-7}	5.639×10^{-5}	0

3)   5.0 ml samples from a 3.891×10^{-3} M anthra-
quinone-2-sulfonate in water solution were
degassed and then irradiated. The water
used was the same as used in e) iii) 2).
The samples were washed into 10.0 ml volume-
trics and 2.5 ml of potassium iodide/ammonium
molybdate solution added and made up to the
mark with potassium bipthallate buffer
solution. Blanks were made from degassed,
irradiated samples made up to 10.0 ml with
the buffer solution only. The ultraviolet
spectra of these were then taken to obtain
the absorption of the triiodide ion at
350 mu.

Sample	I (Einsteins/min)	Einsteins	$\Phi_{H_2O_2}$
1	5.852×10^{-7}	3.511×10^{-5}	0.002

f) effect of hydroxide ion on hydroxylation in degassed
water solutions of anthraquinone-2-sulfonate, with and
without isopropyl alcohol.

      1) 5.0 ml samples from a 3.891 x 10^{-3} M anthra-
          quinone-2-sulfonate and 0.02 N potassium
          hydroxide in water solution were degassed
          and then irradiated. The water used was the
          same as used in e) iii) 2). The samples
          were opened, oxygenated and their optical
          density taken.

Sample	I (Einsteins/min)	Einsteins	Φ_β	C_β m/l
1 (sealed)	3.205×10^{-7}	5.128×10^{-6}	0.078	7.965×10^{-5}
1 (opened)	3.205×10^{-7}	5.128×10^{-6}	0.048	4.900×10^{-5}

      2) 5.0 ml samples from a 3.891 x 10^{-3} M anthra-
          quinone-2-sulfonate, 0.02 N potassium
          hydroxide and 1.0% isopropyl alcohol (by
          volume) in water solution were degassed
          and then irradiated. They were opened,
          oxygenated and their optical density taken.

Sample	I (Einsteins/min)	Einsteins	Φ_β	C_β m/l
1	6.680×10^{-7}	6.680×10^{-6}	0.012	1.60×10^{-5}
2	6.652×10^{-7}	2.993×10^{-5}	0.010	6.00×10^{-5}

g) effect of hydroxide ion on hydroxylation in aerated
water solutions of anthraquinone-2-sulfonate, with and
without isopropyl alcohol.

1) 5.0 ml samples from a 3.891×10^{-3} M anthra-
quinone-2-sulfonate and 0.02 N potassium
hydroxide in water solution were irradiated.
The water used was the same as used in
e) iii) 2). They were oxygenated before and
during irradiation. Their optical density
was taken.

Sample	I (Einsteins/min)	Einsteins	Φ_β	C_β m/l
1	7.100×10^{-7}	7.100×10^{-6}	0.093	1.315×10^{-4}
2	6.893×10^{-7}	4.825×10^{-6}	0.098	9.475×10^{-5}

2) 5.0 ml samples from a 3.891×10^{-3} M anthra-
quinone-2-sulfonate, 0.02 N potassium hydr-
oxide and 1.0% isopropyl alcohol (by volume)
in water solution were irradiated. They were
oxygenated before and during irradiation.
Their optical density was taken.

Sample	I (Einsteins/min)	Einsteins	Φ_β	C_β m/l
1	6.631×10^{-7}	5.305×10^{-6}	0.062	6.605×10^{-5}

h) effect of lamp intensity on the system.
   i) effect of lamp intensity on hydroxylation in
      neutral water solutions of anthraquinone-2-
      sulfonate, no isopropyl alcohol.
      1) 5.0 ml samples from a 3.891 x 10^{-3} M anthra-
          quinone-2-sulfonate in water solution were
          irradiated. The water used was the same
          as used in e) iii) 2). They were oxygenated
          before and during irradiation. Their
          optical density was taken.

Sample	I (Einsteins/min)	Einsteins	ϕ_α	ϕ_β	C_α m/l	C_β m/l
1	7.010 x 10^{-7}	7.010 x 10^{-6}	0.028	0.017	3.92 x 10^{-5}	2.36 x 10^{-5}
2	3.364 x 10^{-7}	3.364 x 10^{-6}	0.029	0.015	1.98 x 10^{-5}	1.00 x 10^{-5}

   ii) effect of lamp intensity on hydrogen peroxide
       production in neutral water solutions of anthra-
       quinone-2-sulfonate, with isopropyl alcohol.
       1) 5.0 ml samples from a 3.891 x 10^{-3} M anthra-
           quinone-2-sulfonate and 5.0% isopropyl
           alcohol (by volume) in water solution were
           irradiated. They were oxygenated before and
           during irradiation. 0.01 N sodium thio-
           sulfate was used to titrate.

Sample	I (Einsteins/min)	Einsteins	$\phi_{H_2O_2}$
1	7.079 x 10^{-7}	2.124 x 10^{-5}	0.567
2	7.004 x 10^{-7}	2.101 x 10^{-5}	0.614
3	3.302 x 10^{-7}	9.906 x 10^{-6}	0.616

i) effect of dose of irradiation on the system.
    i) effect of time of irradiation on hydroxylation
      in neutral water solutions of anthraquinone-2-
      sulfonate, no isopropyl alcohol.
        1) 5.0 ml samples from a 3.891×10^{-3} M anthra-
           quinone-2-sulfonate in water solution were
           irradiated. The water used was the same as
           used in e) iii) 2). They were oxygenated
           before and during irradiation. Their
           optical density was taken.

Sample	I (Einsteins/min)	Einsteins	Φ_α	Φ_β	C_α m/l	C_β m/l
1	5.797×10^{-7}	2.899×10^{-6}	0.020	0.024	1.14×10^{-5}	1.39×10^{-5}
2	5.797×10^{-7}	5.797×10^{-6}	0.025	0.016	2.93×10^{-5}	1.87×10^{-5}

   ii) effect of time of irradiation on hydrogen peroxide
      production in neutral water solutions of anthra-
      quinone-2-sulfonate, with isopropyl alcohol.
        1) 5.0 ml samples from a 3.891×10^{-3} M anthra-
           quinone-2-sulfonate and 5.0% isopropyl
           alcohol (by volume) in water solution were
           irradiated. They were oxygenated before and
           during irradiation. 0.01 N sodium thio-
           sulfate was used to titrate.

Sample	I (Einsteins/min)	Einsteins	$\Phi_{H_2O_2}$
1	5.590×10^{-7}	1.677×10^{-6}	0.590
2	5.763×10^{-7}	3.458×10^{-6}	0.703

j) test for the presence of the sulfurous ($SO_3^=$) ion.

    1)   5.0 ml samples from a 3.891×10^{-3} M anthra-
quinone-2-sulfonate in water solution were
irradiated. They were oxygenated before
and during irradiation. The samples were
then rinsed into a flask containing 20 ml
water and 20 drops starch solution. This
was then titrated with a 0.0095 M triiodide
solution (prepared from mixing iodine and
potassium iodide in water). The end point
was then indicated by the starch iodide
blue colored complex. The triiodide solution
was standardized against the thiosulfate
solution.

Sample	I (Einsteins/min)	Einsteins	$\Phi_{SO_3^=}$
1	3.688×10^{-7}	2.213×10^{-5}	0

QUALITATIVE EXPERIMENTS

Equipment

A 450 watt Hanovia medium pressure mercury lamp
(679A) in a water cooled jacket was used as a light
source in the qualitative experiments. Light of all
wavelengths was allowed to reach the sample. No mono-
chromater was used. The samples were placed adjacent
to the water cooled jacket. The water used in these
experiments (unless designated "tap water") was doubly
distilled and put through Illinois Water Treatment Co.
deionizing columns (Research Model and Puritan Model).

Materials Used

The materials used in the qualitative experiments
were the same ones as used in the quantum yield experi-
ments with the addition of chloroform (technical grade)
and 10% palladium on charcoal (reagent grade).

Qualitative Experiments Data

a) experiment to produce anthraquinone-diol.

    1) catalytic hydrogenation

A solution of 3.85×10^{-3} moles of anthra-
quinone, 80.0 ml benzene and 100.0 mg of
10% palladium on charcoal was prepared.
This was hydrogenated for three hours.
Mass spectrum: m/e 214, 210, 208, 194.

A solution of 2.40×10^{-3} moles of anthra-
quinone, 180.0 ml chloroform and 100.0 mg
of 10% palladium on charcoal was prepared.
Hydrogen gas was bubbled through the solution
for twenty-four hours. The mixture was heated
during this time. The temperature was kept
at about 50°C.
Mass spectrum: m/e 212, 210, 208, 194.

2)   photolytic reduction

A solution of 1.0 x 10^{-3} moles of anthra-
quinone, 20.0 ml isopropyl alcohol and
60.0 ml benzene was prepared. The solution
was irradiated for nine and three-quarters
hours. After three and one-quarter and nine
and three-quarters hours, mass spectra were
run.

Mass spectrum: m/e 210, 208 (three and one-
                 quarter hours).

Mass spectrum: m/e 210, 208, 196, 194 (nine
                 and three-quarters hours).

No nitrogen gas was passed through the solution.
Thin layer chromatography separations of the
product mixture were unsuccessful.

b) determination of the length of time required to
oxidize reduced anthraquinone.

1)   A solution of 9.01 x 10^{-4} moles of anthra-
quinone, 75.0 ml isopropyl alcohol and 75.0 ml
benzene was prepared. The solution was
nitrogenated before and during irradiation.
Irradiation was carried out for one hour.
A 15.0 ml sample was taken before oxygenation
and titrated with 0.01 N sodium thiosulfate.
Oxygenation was then commenced and 15.0 ml
samples were taken at various time intervals
and titrated.

Sample	Duration of Oxygenation	Titre Sodium Thiosulfate Used	Concentration H_2O_2 (m/1)
1	0 min	0.06 ml	
2	5 min	13.51 ml	4.48×10^{-3}
3	16 min	14.39 ml	4.78×10^{-3}
4	26 min	14.67 ml	4.87×10^{-3}
5	44 min	15.28 ml	5.07×10^{-3}
6	65 min	15.93 ml	5.29×10^{-3}
7	87 min	16.65 ml	5.53×10^{-3}

The remaining liquid was then excluded from all light (duration of oxygenation time = 117 min). After a total of 327 min of oxygenation a 15.0 ml sample was titrated.

Sample	Duration of Oxygenation	Titre Sodium Thiosulfate Used	Concentration H_2O_2 (m/1)
1	327 min	17.86 ml	5.95×10^{-3}

The above experiment was then repeated but the liquid was excluded from all light before any oxygenation was done and then oxygenated in the dark.

Sample	Duration of Oxygenation	Titre Sodium Thiosulfate Used	Concentration H_2O_2 (m/1)
1	0 min	0.00 ml	
2	3 min	13.50 ml	4.50×10^{-3}
3	60 min	14.22 ml	4.74×10^{-3}

2) Blank: A solution of 4.80 x 10^{-4} moles of
    anthraquinone, 40.0 ml isopropyl alcohol and
    40.0 ml benzene was prepared. This solution
    was not irradiated, but oxygenated for
    nineteen and one-half hours. A 15.0 ml
    sample was titrated with 0.005 N sodium
    thiosulfate.

Sample	Duration of Oxygenation	Titre Sodium Thiosulfate Used	Concentration H_2O_2 (m/l)
1	19.5 hrs	6.43 ml	1.07×10^{-3}

Mass spectrum: m/e 208.

c) experiment to determine whether or not more hydrogen
peroxide is formed in an oxygenating system containing
hydrogen peroxide.

1) A solution of 1.6 x 10^{-4} moles of hydrogen
    peroxide, 80.0 ml isopropyl alcohol and 80.0
    ml benzene was prepared. The solution was
    not irradiated, but oxygenated for eighteen
    hours. 15.0 ml samples of this solution
    were taken and titrated with 0.01 N sodium
    thiosulfate at time intervals.

Sample	Duration of Oxygenation	Titre Sodium Thiosulfate Used	Concentration H_2O_2 (m/l)
1	0 min	3.20 ml	1.07×10^{-3}
2	7 min	3.22 ml	1.07×10^{-3}
3	10 min	3.15 ml	1.05×10^{-3}
4	30 min	3.17 ml	1.06×10^{-3}
5	18 hrs	3.16 ml	1.05×10^{-3}

d) experiment to sythesize anthrone from anthraquinone (16).

 1) 10.4 g anthraquinone, 10.0 g granulated tin
 and 75.0 ml glacial acetic acid were mixed.
 This was boiled for two hours and then 25.0
 ml concentrated hydrochloric acid added. The
 liquid was then filtered and 10.0 ml water
 added. Anthrone crystallized and was then
 collected. It was washed with water and
 recrystallized from a 3:1 mixture of benzene
 and petroleum ether. 6.0 g of anthrone
 were collected.
 Mass spectrum: m/e 194.

e) mass spectra.

 1) Mass spectra were taken of 1) an irradiated,
 oxygenated anthraquinone solution and
 2) a catalytically hydrogenated anthra-
 quinone solution that had been allowed to
 sit for three weeks.
 1) Mass spectrum: m/e 210, 208, 194.
 2) Mass spectrum: m/e 208, 194.

f) experiment to determine whether or not hydrogen
peroxide is formed from irradiating anthrone.

 1) A solution of 1.03×10^{-3} moles of anthrone,
 40.0 ml isopropyl alcohol and 40.0 ml benzene
 was prepared. The solution was oxygenated
 before and during irradiation. Irradiation
 was carried out for nineteen and one-half
 hours. The organic layer was extracted with
 tap water and both layers subsequently titrated
 with 0.005 N sodium thiosulfate.

Sample	Titre Sodium Thiosulfate Used	Concentration H_2O_2 (m/l)	Total Volume of Layer
1	0.15 ml	3.75×10^{-6}	150 ml (organic)
2	3.00 ml	7.50×10^{-5}	100 ml (water)

Mass spectrum: m/e 194.

g) experiment to see whether or not anthrone is present after an anaerobically irradiated solution of quinone is oxygenated.

1) A solution of 9.01×10^{-4} moles of anthraquinone, 75.0 ml isopropyl alcohol and 75.0 ml benzene was prepared. The solution was nitrogenated before and during irradiation. Irradiation was carried out for one hour. A mass spectrograph was done on an evaporated sample taken from the oxygenating solution. Mass spectrum: m/e 208.

h) determination of the extent of reduction of anthraquinone with irradiation time under anaerobic conditions, and the extent of reduction of anthraquinone with concomittant oxidation of anthraquinone-9,10-diol with irradiation time under aerobic conditions.

1) A solution of 9.01×10^{-4} moles of anthraquinone, 75.0 ml isopropyl alcohol and 75.0 ml benzene was prepared. The solution was nitrogenated before and during irradiation. Irradiation was carried out for over an hour. 15.0 ml samples of this solution were oxygenated for five minutes and then titrated with 0.01 N sodium thiosulfate at time intervals.

Sample	Duration of Irradiation	Titre Sodium Thiosulfate Used	Concentration H_2O_2 (m/1)
1	0 min	0.29 ml	
2	1 min	1.20 ml	3.03×10^{-5}
3	3 min	2.20 ml	6.33×10^{-4}
4	7 min	3.76 ml	1.16×10^{-3}
5	14 min	5.04 ml	1.58×10^{-3}
6	25 min	6.86 ml	2.19×10^{-3}
7	∞ (1 hr)	10.47 ml	3.39×10^{-3}

2) A solution the same as above was prepared. 15.0 ml samples were measured out and stored in the dark. Two samples were irradiated at the same time for the same length of time. One was oxygenated and the other nitrogenated. After irradiation, the latter was oxygenated for five minutes and then renitrogenated for five minutes. The former was nitrogenated for five minutes. The samples were then titrated with 0.01 N sodium thiosulfate.

Sample	Duration of Irradiation	Titre Sodium Thiosulfate Used	Concentration H_2O_2 (m/l)
1*	0 sec	0.00 ml	
2*	15 sec	0.45 ml	1.50×10^{-4}
3*	30 sec	0.98 ml	3.27×10^{-4}
4*	60 sec	2.09 ml	6.97×10^{-4}
5*	3 min	6.25 ml	2.08×10^{-3}
6*	7 min	14.31 ml	4.77×10^{-3}
1**	0 sec	0.00 ml	
2**	15 sec	0.30 ml	1.00×10^{-4}
3**	30 sec	0.54 ml	1.80×10^{-4}
4**	60 sec	1.07 ml	3.57×10^{-4}
5**	3 min	2.20 ml	7.33×10^{-4}
6**	7 min	3.80 ml	1.27×10^{-3}

* initially oxygenated samples
** initially nigrogenated samples

i) experiment to determine the system's maximum production of hydrogen peroxide.

    1) A solution of 9.01×10^{-4} moles of anthraquinone, 75.0 ml isopropyl alcohol and 75.0 ml benzene was prepared. The solution was oxygenated before and during irradiation. 15.0 ml samples of this solution were titrated with 0.101 N sodium thiosulfate at time intervals.

Sample	Duration of Irradiation	Titre Sodium Thiosulfate Used	Concentration H_2O_2 (m/1)
1	99 min	11.10 ml	3.74×10^{-2}
2	168 min	13.20 ml	4.44×10^{-2}

j) experiment to determine whether or not hydrogen peroxide is formed from irradiating anthraquinone-2-sulfonate in water.

1) A solution of 1.61×10^{-3} moles of anthraquinone-2-sulfonate and 150.0 ml tap water was prepared. The sample was nitrogenated before and during irradiation. A 15.0 ml sample was taken after irradiation and oxygenated for two hours. It was titrated with 0.005 N sodium thiosulfate.

Sample	Duration of Irradiation	Titre Sodium Thiosulfate Used	Concentration H_2O_2 (m/1)
1	35 min	1.6 ml	2.67×10^{-4}

2) The foregoing was repeated except that the sample was oxygenated before and during irradiation and 40.0 ml sample was taken and titrated with 0.01 N sodium thiosulfate.

Sample	Duration of Irradiation	Titre Sodium Thiosulfate Used	Concentration H_2O_2 (m/1)
1	213 min	8.1 ml	1.01×10^{-3}

k) experiment to determine whether or not ferrous ion effects hydrogen peroxide production in aqueous solutions of anthraquinone-2-sulfonate.

> 1) A solution of 100.0 ml of a 0.01 N ferrous sulfate aqueous (tap water) solution and 50.0 ml of a 0.003 N anthraquinone-2-sulfonate aqueous (tap water) solution was prepared. It was irradiated for forty-five minutes. No peroxide was indicated but a reddish precipitate was observed on the bottom of the reaction vessel.

l) experiment to determine whether or not sodium bicarbonate effects hydrogen peroxide production in aqueous solutions of anthraquinone-2-sulfonate.

> 1) A solution of 75.0 ml of 4.07×10^{-3} M anthraquinone-2-sulfonate aqueous (tap water) solution and 75.0 ml of a 0.1 M sodium bicarbonate aqueous (tap water) solution was prepared. It was oxygenated before and during irradiation. A 40.0 ml sample was titrated with 0.01 N sodium thiosulfate.

Sample	Duration of Irradiation	Titre Sodium Thiosulfate Used	Concentration H_2O_2 (m/1)
1	213 min	0.09 ml	1.13×10^{-5}

m) experiment to determine whether or not potassium nitrate effects hydrogen peroxide production in aqueous solutions of anthraquinone-2-sulfonate.

> 1) A solution of 75.0 ml of a $4.07 \ 10^{-3}$ M anthraquinone-2-sulfonate aqueous (tap water) solution and 75.0 ml of a 1.0×10^{-3} M potassium nitrate aqueous (tap water)

solution was prepared. It was oxygenated
before and during irradiation. A 40.0 ml
sample was titrated with 0.01 N sodium
thiosulfate.

Sample	Duration of Irradiation	Titre Sodium Thiosulfate Used	Concentration H_2O_2 (m/l)
1	213 min	4.0 ml	5.00×10^{-4}

n) experiment to determine whether or not carbon dioxide
gas affects hydrogen peroxde production in aqueous
solutions of anthraquinone-2-sulfonate.

    1)   A solution of 4.07×10^{-3} M anthraquinone-
2-sulfonate in water was prepared. It was
aerated with equal amounts of carbon dioxide
and oxygen during irradiation. A 40.0 ml
sample was titrated with 0.01 N sodium
thiosulfate.

Sample	Duration of Irradiation	Titre Sodium Thiosulfate Used	Concentration H_2O_2 (m/l)
1	6 min	1.66 ml	2.08×10^{-4}

o) experiment to determine whether or not hydroxy
anthraquinone is formed from the irradiation of an
aqueous solution of anthraquinone-2-sulfonate.

    1)   A solution of 3.891×10^{-3} M anthraquinone-
2-sulfonate and 0.02 N potassium hydroxide
in water was prepared. It was oxygenated
before and during irradiation. The solution
was then made acidic and extracted with
ether. The aqueous and organic layers were
then separated and the ether layer washed

with basic water. The absorbance of this
basic water layer was then checked.

Sample	Duration of Irradiation	Absorbance of Sample	Concentration of hydroxyanthraquinone (m/1)
1	30 min	0.0	0.0

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