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THE PHOTO BROMINATION OF P-NITRO TOLUENE

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Theoretical Considerations

The halogenation of benzene and its homologues in general results in addition, nuclear substitution and side chain substitution. With the exception of dichloro toluenehexachloride addition compounds are known only in the case of benzene. Side chain halogen reacts with alcoholic silver nitrate, while nuclear halogen does not. Benzenehexachloride, the only addition compound the behaviour of which has been studied, does not react with alcoholic silver nitrate, but upon treatment with alcoholic soda it decomposes to form a trisubstitution product, thereby liberating half of the added halogen. Estimation of the three types of compounds depends on these reactions.

In general, rise of temperature, light and the absence of moisture favour side chain substitution, while catalysts, among which may be mentioned iodine and the halides of iron, aluminium, etc., favour nuclear substitutions. Concerning addition reactions little appears to be known beyond the fact that they are catalysed by light.

Several theories of the mechanism of side chain and nuclear substitution reactions have been put forward. Most workers agree in attributing side chain substitution to molecular halogen. In support of this theory is the fact that side chain substitution is catalysed by light. Moreover in the case of the bromination of toluene it has been shown that the most effective wave lengths are those corresponding to the absorption bands of molecular bromine.

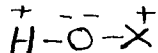
Bancroft, however, attributes side chain substitution to an excess of positive halogen ions.

Holleman (Rec. des Trav. chim. des Pays-Bas, 22, 435, 1908), supposes that nuclear substitution is brought about by perhalides such as HBr_3 ; Cohen (J. O. S., 92, 1623, 1910) also favors this explanation. This would account for the action of halogen carriers and for the negative effect of increase of temperature. Moreover when the reaction is carried out in nitrobenzene a distinct decrease in the amount of side chain substitution has frequently been noticed. According to the investigations of Cohen (loc. cit.) polyiodides are formed to a far greater extent in this solvent than in other so-called neutral solvents such as carbon tetrachloride. He therefore explains the decrease in the side chain substitution by supposing that nuclear substitution takes place to an appreciable extent due to the great increase in perhalides molecules present.

Bancroft (J. Physical Chem., 1908, 12, 420), on the other hand believes that nuclear substitution is brought about by an excess of negative ions which excess results from the addition of positions ions to halogen molecules thus:

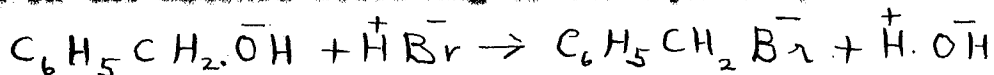
This view is directly opposed to that of Fry, (J.A.C.S., 36, 1035, 1914). Fry considers that in benzene the hydrogen atoms in the positions 1, 3, 5 are negative, while those in positions 2, 4, 6 are positive. He points out that the conditions promoting nuclear substitution, i.e., moisture, low temperature and absence of light, also promote the formation and stability of hypochlorous and of

hypobromous acid in each of which the halogen functions positively according to the valence formula

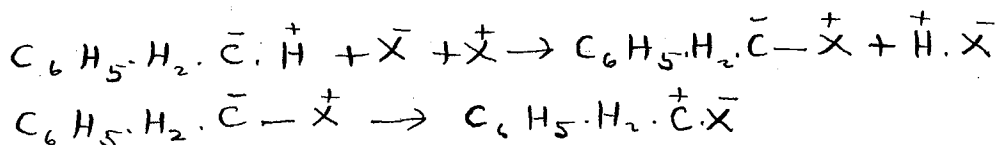


He considers that nuclear substituted halogen is always positive, since it fails to react with silver nitrate to form silver halide, in which it would of necessity be negative, and since it enters in the ortho and para positions to the negative methyl radicle. He therefore supposes that nuclear substitution is brought about by hypochlorous and hypobromous acids which effect the interchange of positive halogen atoms with positive hydrogen atoms of the nucleus. If water is regarded as a typical halogen carrier this explanation of its action throws light on the role played by carriers in general. These may be considered as catalysing the reaction through the formation of halogen addition compounds which dissociate to give a negative radicle and a positive halogen ion, which latter causes substitution in the nucleus.

According to Fry, side chain halogen is negative since, for example, benzyl bromide is formed by the direct action of hydrobromic acid on the alcohol according to the equation:



and since benzyl bromide is easily hydrolyzed. But the hydrogen which is replaced is ^{positive} ~~negative~~ and Fry therefore conceives the reaction to be one of oxidation and reduction according to the equations:



In this connection it is interesting to note that recently

Beines (J.C.S., 121, 2810, 1922), investigated the bromination of phenol and came to the conclusion that nuclear substitution is preceded by the formation of addition compounds of hypobromous acid. This assumption is supported by the fact that he was able to prepare tribromophenol by the direct action of hypobromous acid.

We come now to some of the more specific problems presented by the photo-bromination of toluene. In the absence of catalysts the main product is always benzyl bromide, though the presence of moisture may bring about considerable nuclear substitution also. In studying the rate of the reaction Bruner and Czarnecki (Bull. Ac. Cr., 1910, 516) found that traces of oxygen effected the rate so greatly that reproducible results could be not obtained. They attributed the action of oxygen to the formation of unstable oxides of bromine which act as catalysts. They were able to eliminate this disturbing influence by the addition of a small quantity of iodine to the reaction mixture. They suggested that the iodine unites to form a more stable oxide, in this way eliminating the effect of oxygen on the reaction. They found that in the presence of a trace of oxygen the reaction proceeds regularly, and is monomolecular when the concentration of the bromine is small. They also found that the temperature coefficient was unusually high for a photo-chemical reaction, namely, 1.8, a fact which is held by Andrich and Le Blanc (Zeitsch Wiss, Photo-Chem., 1916, 15, 217) to result from the increasing decomposition of perhalide molecules with increasing temperature.

Bruner and Lahocinski (Bull. Ac. Cr. 1910, 560) investigated a peculiar after effect which occurs when the reaction has been

carried out in the presence of oxygen. This after effect causes further quantities of bromine to react with the mixture in the dark. It lasts for six hours or more but is destroyed by heating to 100° C. for two hours, or by the addition of oxidisable substances, such as hydrobromic acid or iodine. Hydrochloric acid does not have this effect. It does not occur when the reaction is carried out in the presence of carbon dioxide, nitrogen or hydrogen. They attribute it to an oxide of bromine which catalyses substitution in the side chain. In agreement with this view they observed that oxygen is strongly absorbed during the reaction and the reaction mixture is colored yellow.

In this connection it is interesting to note that Cohen (Loc. cit.) refers to a similar yellow solution obtained in the chlorination of toluene. He states that it is discharged by the addition of iodine or hydrochloric acid or by washing with water.

Andrich and Le Blanc (Loc. cit.) studied the photo-bromination of toluene at 15° and 25° C. They measured the amount of hydrobromic acid evolved and also the amount of bromine removed by alcoholic silver nitrate. They found the relation between these quantities very variable and that the latter quantity often exceeded the former. On carrying out the reaction in the presence of excess of oxygen they found that the quantity of bromine removed by the alcoholic silver nitrate was greatly increased, being in some cases 40% greater than that evolved as hydrobromic acid. Bruner had previously noticed a similar discrepancy in the photo-bromination of propylbenzol, of which he said "die Reaktionsprodukte halten den Bromwasserstoff hartnäckig auf". Andrich and Le Blanc noticed that these reaction mixtures had a yellow colour which was

destroyed by washing with water. Working with dry solutions they found that the presence of oxygen greatly increased the yield of side chain bromine but also greatly decreased the rate of the reaction. In the presence of excess of oxygen they found that a moist solution and one covered by a layer of water react differently. In the first, the speed of the reaction is increased and the yield of side chain bromine decreased by the moisture. Similar results had been obtained by Cohen in the chlorination of toluene. When the reaction mixture is covered by a layer of water, on the other hand, the rate of the reaction is slightly decreased and the yield of side chain bromine greatly decreased. In air, however, the presence of moisture or of excess of water has little effect upon the ~~MIXTURE~~ reaction. These results they attribute to the formation of catalysts and they consider it not unlikely that in the presence of excess and of deficiency of oxygen the catalysts are different, in which case their results would seem to indicate that the first is decomposed by water while the latter is not.

They suspected that the deficiency in hydrobromic acid evolved was due to oxidation. They therefore passed a mixture of hydrobromic acid and oxygen through illuminated toluene. They were able to effect considerable bromination by this means. The resulting mixture was yellow and possessed oxidising and phenolic properties. Finally they carried out the reaction in a gas burette and measured the amount of oxygen absorbed and the amount of hydrobromic acid decomposed. On the assumption that the