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PHOTOLYSIS OF p-DISUBSTITUTED BENZENES IN LOW-TEMPERATURE RIGID SOLVENTS

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The photolysis of p-disubstituted benzenes, X_1--X_2, is one of the subject of photochemistry which is fairely well investigated[1-3]. In the case where X_1, X_2 = NH_2 or $N(CH_3)_2$, an electron is ejected forming Wurster's cations, which remain stable at 77°K matrices. In the cases of phenol and toluene, or their derivatives[3], side-chain photolysis occurs predominantly, forming phenoxy or benzyl radicals, also stable in the 77°K matrix.

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[1] G. N. Lewis and D. Lipkin, *J. Am. Chem. Soc.*, **64**, 2801 (1942).

[2] G. N. Lewis and J. Bigeleisen, *J. Am. Chem. Soc.*, **65**, 520, 2419, 2424 (1943).

[3] G. Porter and E. Strachan, *Trans. Faraday Soc.*, **54**, 1595 (1958).

It might be generally concluded, from these earlier observations, that the higher the ionization potential of the substituent group, side-chain photolysis is the more predominant, and the lower the ionization potential, photo-ejection of electrons occurs the more easily.

We have obtained some interesting results on the photolysis of substituted benzenes at 77°K as shown below.

Hydroquinone is known to form the radical •O--OH by the low temperature photolysis[2-4]. We have photolysed p-methoxyphenol, HO--OCH$_3$ (I), and its anion $^-$O--OCH$_3$ (II) formed by the addition of sodium hydroxide in ethanol solutions, and p-dimethoxybenzene, H$_3$CO--OCH$_3$ (III). The photolysis was done in deoxygenerated, transparent ethanol solutions at 77°K, by use of a 250W high pressure mercury lamp. As shown in Figure 1, the characteristic features of the absorption spectra of the photolysed products of these three compounds are the same and very similar to the spectrum of the radical, •O--OH. The only reasonable conclusion drawn from this result is that the product formed is the radical •O--OCH$_3$. Hence what happened in the photolysis is thought to be as follows: in the case of I, the dissociation of the OH bond; in the case of II, electron-

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[4] H. Linschitz, J. Rennert, and T. M. Korn, *J. Am. Chem. Soc.*, **76**, 5839 (1954).

ejection; in the case of III, the dissociation of the O-CH_3 bond. These results also agree with the general rule mentioned above.

FIG. 1

Absorption spectra observed by the photolysis of
(a) , (b) , and (c) ,
at 77°K.

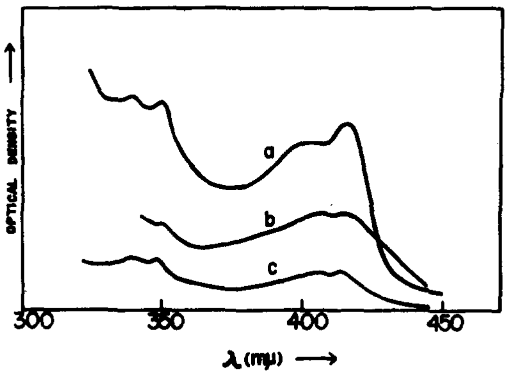
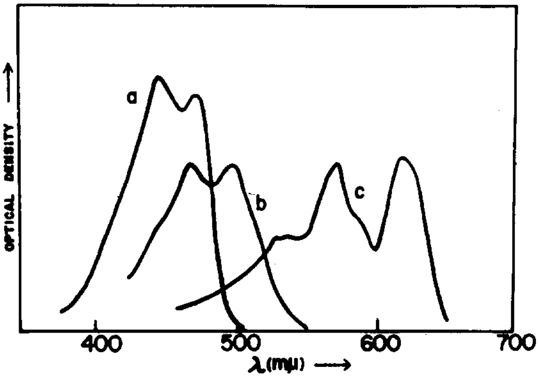
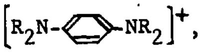
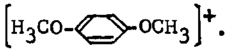


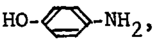
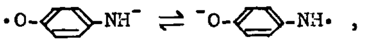
FIG. 2

(a) Absorption spectrum observed by the photolysis of H_3CO-⬡-OCH_3 in the 1:1 mixture of concentrated sulfuric acid and acetic acid at 77°K. (b) The absorption spectrum of the p-phenylene diamine cation, $[NH_2$-⬡-$NH_2]^+$, in ethanol at 77°K. (c) The absorption spectrum of the Wurster's blue cation, $[(CH_3)_2N$-⬡-$N(CH_3)_2]^+$, in ethanol at 77°K.



We found that the 1:1 mixture of concentrated sulfuric acid and acetic acid forms a transparent rigid glass at 77°K. In this matrix, the photolysis of compound III produced a substance with an absorption spectrum shown in Figure 2, which is quite different from the spectra in Figure 1. The spectrum is rather similar to those of Wurster's cations , which are also shown in figure 2 for comparison. Therefore, it might be tentatively concluded that the substance produced here is the cation radical, .

In the present work, it was also found that the photolysis of hydroquinone, , in alkaline solution at 77°K, that is the ethanol solution containing either NaOH, KOH, NH_3, etc., produces the semiquinone-ion radical, . This was confirmed from the fact that the spectrum is identical to that of the semiquinone-ion radical produced by auto-oxidation by air, whose structure has been determined from the ESR study by Venkataraman and Fraenkel[5].

Finally, in the case of the photolysis of p-aminophenol, , at 77°K, we obtained different spectra in neutral ethanol and in alkaline ethanol used as rigid solvents. We assign the species in the former case to be  and that in the latter case to be a radical expressed by the resonance form , since the two kinds of spectra are analogous to the spectra of  and , respectively.

Further studies including the ESR study are going on at our laboratory and the complete result will be published later.

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[5] B. Venkataraman and G. K. Fraenkel, J. Am. Chem. Soc., 77, 2707 (1955).