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Photolysis of *meta*-Disubstituted Benzenes in Low Temperature Matrices

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Photolysis of *para*-disubstituted benzenes in low temperature matrices has been studied extensively in our laboratory.[2] It has been concluded that photo-ionization occurs predominantly for the compounds having amino-substituents, and the β-fission in the side-chain occurs predominatly for the compounds having hydroxyl or methoxyl groups. In the present note, studies on the photolysis of *m*-aminophenol, *m*-phenylenediamine, *m*-anisidine and *m*-methoxyphenol are reported.

Organic solvents used as transparent matrices are ethanol, EPA (ether-isopentane-ethanol, 5 : 5 : 2 by volume), EP (ether-isopentane, 1 : 1), EM (ether-methylcyclohexane, 1 : 1), and MP (methylcyclohexane-isopentane, 1 : 3). Approximately 8 m*l* of a 1×10^{-4}M solution was put into a quartz cell of 1 cm path length, degassed by the freeze-pump-thaw technique, and the cell was sealed. The transparent samples in liquid nitrogen contained in a quartz Dewar were illuminated for 20—60 sec using a 250 W high-pressure mercury lamp and appropriate filter combinations.

Assignment of the Species Formed by the Photolysis Electronic absorption spectra of free radicals formed by ultraviolet irradiation of *m*-aminophenol are shown in Fig. 1a (region B). It is concluded that the products are cation radicals by reasons similar to those discussed in Ref. 1, that is to say: (1) When biphenyl, as an electron acceptor, was added to the EPA solution of *m*-aminophenol irradiated at 77°K, the absorption spectrum of biphenyl anion appeared together with the cation spectrum. (2) The absorption spectrum was obtained by irradiation in polar solvents, but not in non-polar solvents. (3) By irradiation in the infrared region or by heating the photo-product, luminescence attributable to the recombination of cation radicals and ejected electrons was observed.

By the similar reasons to those for the case of *m*-aminophenol, it has been concluded that the products of photolysis of *m*-phenylenediamine and *m*-anisidine at 77°K are assigned to their cation radicals. For the case of *m*-phenylenediamine irradiated at 77°K a spectrum (from 420 to 490 mμ) appeared at first which is undoubtedly attributable to the cation radical. On prolonged irradiation, the spectrum in this region gradually weakened and after irradiation for 15 min, a new spectrum began to appear in the region from 330 to 350 mμ. At least a large part of this new spectrum remained after warming to room temperature, and hence seems to be due to a permanent dissociation product.

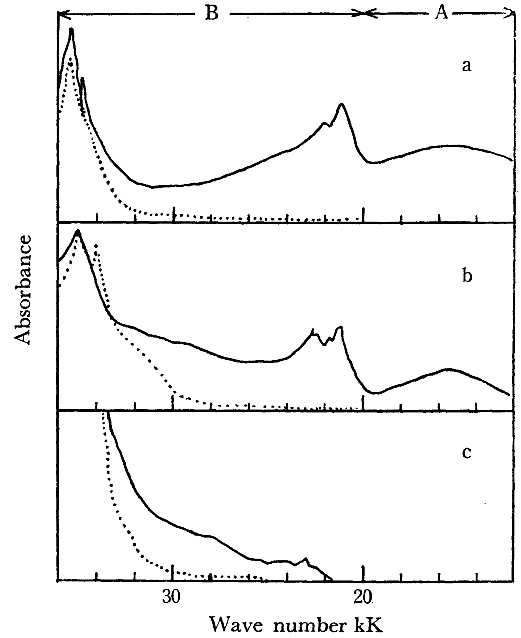

Fig. 1. Electronic absorption spectra of free radicals (region B) and solvated electrons (region A).
The dotted line shows the spectrum before UV irradiation. a, *m*-aminophenol. b, *m*-aminophenol in an alkaline EPA solution. c, *m*-methnoxyphenol.

The irradiation of *m*-aminophenolate anion in alkaline EPA solution caused a spectrum shown in Region B of Fig. 1b. The product has been assigned to the radical $H_2NC_6H_4O\cdot$ by the similar reasons as those described in a previous paper.[2] For *m*-methoxyphenol, it has been concluded by the following reasons that the irradiation yielded the neutral radical, $H_3COC_6H_4O\cdot$, whose spectrum is shown in Fig. 1c.: (1) The radical was produced even in a non-polar solvent, MP. (2) The broad absorption spectrum of the solvated electron did not appear in the near infrared region. (3) Even if biphenyl was added to the MP solution of *m*-

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methoxyphenol, the absorption bands of biphenyl anion did not appear. (4) The shape of the absorption spectrum is similar to that of *m*-benzosemiquinone radical, $HOC_6H_4O\cdot$, obtained by Land and Porter using flash photolysis.[3]

Solvated Electron Spectra. When *m*-aminophenol in various organic matrices is irradiated at 77°K in the ultraviolet region using a Toshiba UV-D25 glass filter which transmits light from 275 to 370 mμ and from 700 to 750 mμ, the matrix colored yellow owing to the formation of cation radicals. On the other hand, when a Toshiba UV-D25 filter was combined with an aqueous nickel sulfate (transmitting light from 275 to 370 mμ), the matrix colored bluish yellow. The absorption spectrum is shown in Fig. 1a, and the broad absorption band in the near infrared region (region A) can be attributable to the solvated electrons by the following reasons: (1) The sample showed a very feeble afterglow at 77°K to dark-adapted eye. It also showed emission stimulated by the infrared light or by warming. The luminescence spectra was found to correspond to the fluorescence and phosphorescence of *m*-aminophenol. (2) The intensity of the broad absorption band in the near infrared region decreased by the infrared irradiation of the sample. (3) The absorption maximum in the near infrared region shifts to the shorter wavelength as the solvent becomes more polar (Fig. 2). The similar shift was observed by Dorfman and his co-workers for the spectra of solvated electrons obtained by pulse-radiolysis.[4] For *m*-phenylenediamine and *m*-anisidine, similar absorption spectra of solvated electrons are also observed.

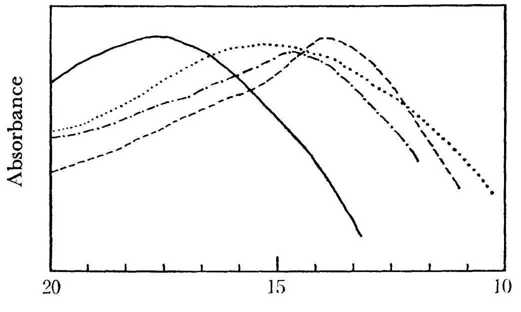

Fig. 2. Electronic absorption spectra of solvated electrons formed by UV irradiation of *m*-aminophenol in various solvents.
——— ethanol, ········ EPA, – – – – EP, ·——· EM

Albrecht states that the great majority of electrons photoejected from TMPD have a very limited range in rigid 3-methyl pentane, each electron finding a matrix trap within the coulomb field of its partner TMPD cation radical.[5] In our results, it may also be concluded that the solvated electrons are under the influence of the cation radicals since a small but definite shift of the absorption maxima is observed for different cation radicals (Fig. 3).

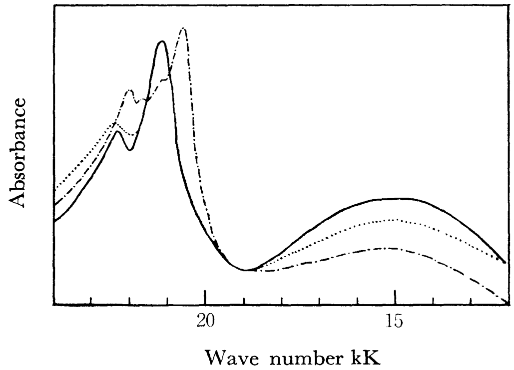

Fig. 3. Electronic absorption spectra of solvated electrons formed by UV irradiation of *m*-aminophenol (———), *m*-anisidine (·········), and *m*-phenylenediamine (·——·——·).

It has been reported by McClain and Albrecht that TMPD cation radicals cannot be bleached perfectly by infrared irradiation in 3-MP at 77°K, and some more energetic photons (385 mμ) did bleach some of the $TMPD^+$ remaining after the infrared effect was exhausted.[5] They concluded that the incompleteness of the IR bleaching was due to very deep trapping of some of the electrons. However, in our work the broad absorption band of solvated electrons (300—800 mμ) disappeared completely by irradiation with red light (wavelengths longer than 600 mμ). The intensity of the absorption spectrum of the cation radicals decreased only slightly. This decrease was still more slight in the solvents containing ethanol. From these facts, the following conclusion may be drawn: The traps of the solvated electrons are not very deep, but rather shallow. A small part of the electrons stimulated by irradiation recombine with cation radicals and the remaining part of them react with impurities or with the solvent itself, especially with ethanol.

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