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THE INTERACTION OF p-DINITROBENZENE WITH SODIUM HYDROXIDE IN AQUEOUS DIMETHYL SULFOXIDE

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The interaction of p-dinitrobenzene with hydroxide ion in aqueous dimethyl sulfoxide was studied by visible spectroscopy. The formation of the p-dinitrobenzene anion-radical was initially found. From the time-dependence of the radical, the radical seems to be a precursor in the displacement of one nitro group.

It is well-known that in o- and p-dinitrobenzene one of the nitro groups is easily displaced by hydroxyl and methoxyl groups. No Meisenheimer complexes of o- and p-dinitrobenzene have been observed in the substitutions, although many Meisenheimer complexes formed from m-dinitrobenzene derivatives in alkaline dimethyl sulfoxide (DMSO) have been reported.1) From ESR spectroscopy Russell et al.2) found the anion-radicals formed from substituted nitrobenzenes and m-dinitrobenzene in t-butanol or in DMSO in the presence of t-butoxide ion.

In the present work, an attempt has been made to investigate the interaction of p-dinitrobenzene with hydroxide ion in aqueous DMSO by visible spectroscopy.

Electronic absorption spectra of the DMSO solutions all containing 2%(v/v) water were measured with a Hitachi rapid scan spectrophotometer RSP-2 (having the path length of 1.0 cm) and with a Hitachi recording spectrophotometer EPS-3 (having the path length of 1.00 cm) at room temperature. Water was always used as a reference.

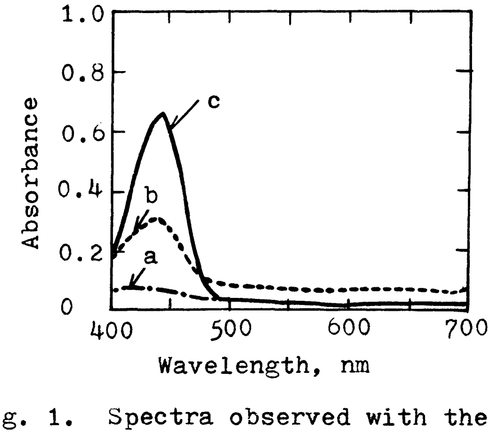


Fig. 1. Spectra observed with the DMSO solution containing p-dinitrobenzene (2.4×10^{-5} M) and sodium hydroxide (3.9×10^{-3} M) at 26°C. Times measured after the mixing: a, 31 msec; b, 1 sec; c, 30 sec and 1 min.

As shown in Fig. 1, the DMSO solution containing p-dinitrobenzene and hydroxide ion finally gives the 432-nm band, the peak position and shape of which are similar to those of the band of the same solution of p-nitrophenol. The final product is, therefore, p-nitrophenoxide ion (in 74-88% yield). Fig. 1 shows the slight absorptions in the region above 500 nm at 1 sec after the mixing. Fig. 2 shows that the decrease in the absorbance at 550 nm correlates to the

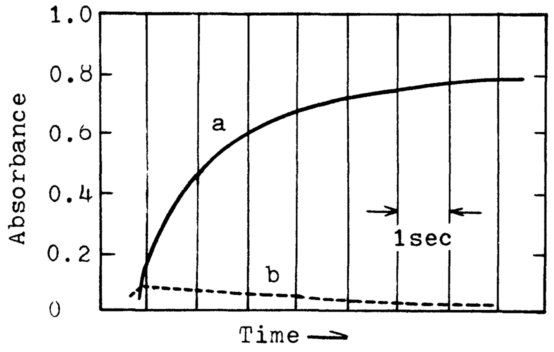


Fig. 2. Time-dependence of the absorbances of the DMSO solution containing p-dinitrobenzene (3.0×10^{-5} M) and sodium hydroxide (3.9×10^{-3} M) at 25°C: a, at 440 nm; b, at 550 nm.

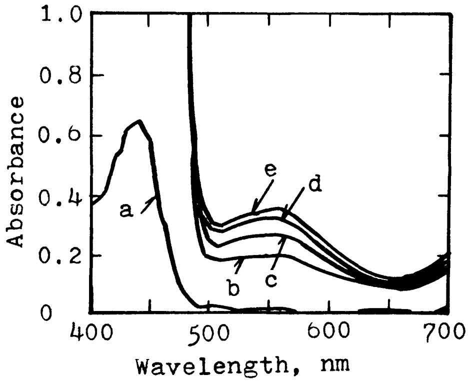


Fig. 3. Spectra observed with the DMSO solution containing p-dinitrobenzene (8.8×10^{-4} M) and sodium hydroxide (3.9×10^{-3} M) at 27°C. Times measured after the mixing: a, 32 msec; b, 5 sec; c, 10 sec; d, 20 sec; e, 30 sec and 1 min.

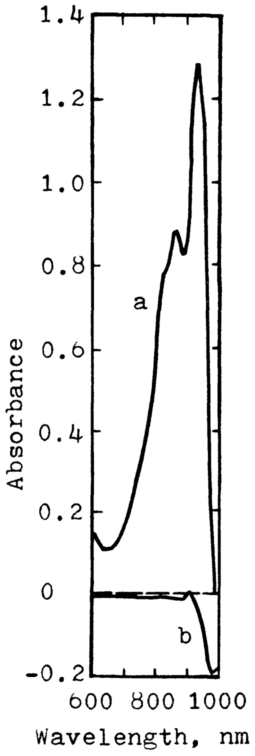


Fig. 4. The spectrum (curve a) observed (by the recording spectrophotometer) with the DMSO solution containing p-dinitrobenzene (8.8×10^{-4} M) and sodium hydroxide (3.9×10^{-3} M) at ca. 2 min after the mixing at 24°C. The curve b is the spectrum of DMSO.

increase of the 440-nm absorbance, due to the formation of p-nitrophenoxide ion.

Figs. 3 and 4 distinctly indicate that the DMSO solutions of p-dinitrobenzene and hydroxide ion initially show absorption bands in the visible and near-infrared regions. These bands gradually disappeared.

The peak position and shape of the band in Fig. 4 are similar to those of the band of the p-dinitrobenzene anion-radical observed by Shida and Iwata3) in a γ-irradiated rigid solution in 2-methyltetrahydrofuran at 77°K. The band in Fig. 4 is, therefore, ascribed to the p-dinitrobenzene anion-radical. The formation of the radical in DMSO is not due to electron transfer from methylsulfinyl carbanion to p-dinitrobenzene,4) because the solution of p-dinitrobenzene and sodium hydroxide in aqueous N,N-dimethylformamide initially showed the same band as shown in Fig. 4.

The weak band at ca. 560 nm in Fig. 3 probably corresponds to the weak 474-nm band of the p-dinitrobenzene anion-radical in the rigid solution.3) The 560-nm

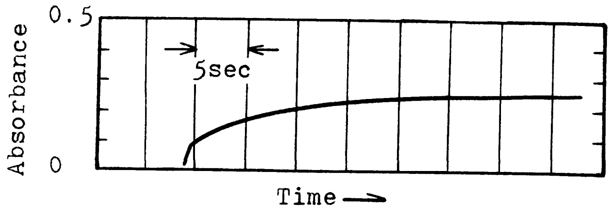
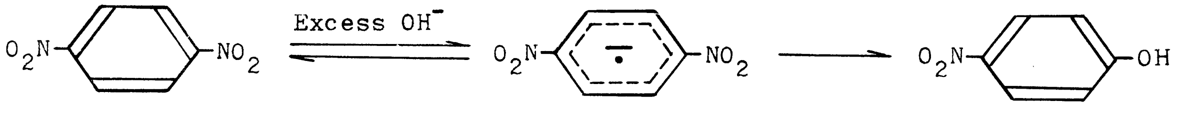


Fig. 5. Time-dependence of the absorbance (at 550 nm) of the DMSO solution containing p-dinitrobenzene (7.7×10^{-4} M) and sodium hydroxide (3.9×10^{-3} M) at 25°C.

band gradually disappeared. The initial band at ca. 440 nm in Fig. 3 differs from the 432-nm band of Fig. 1 in shape. The initial band in Fig. 3 seems to correspond to the 420-nm band of the p-dinitrobenzene anion-radical in the rigid solution.3)

Fig. 5 shows that the concentration of the p-dinitrobenzene anion-radical reaches a steady state soon after the mixing. In the case of the solution of p-dinitrobenzene at the concentration such as 7.7×10^{-4} M, the change in the absorbance at 550 nm could not be pursued until the absorbance decreased, since the rapid scan spectrophotometer could not record the change on a memoriscope for more than 50 sec. The appearance of the steady state is characteristic of the concentration change of B in the consecutive-reaction type of $A \xrightarrow{k_1} B \xrightarrow{k_2} C$ (where $k_1 \ll k_2$). The concentration in the steady state in Fig. 5 may be estimated to be roughly a tenth of the initial concentration of p-dinitrobenzene, since the molar extinction coefficient of the 474-nm band of the p-dinitrobenzene anion-radical in the rigid solution is 5×10^3.3) Accordingly, the appearance of the steady state in Fig. 5 together with the correlation for the time-dependence of the absorbances at 440 and 550 nm in Fig. 2 suggests that the p-dinitrobenzene anion-radical is a reactive precursor in the following consecutive reaction:



The appearance of the p-dinitrobenzene anion-radical in the substitution will support the electron transfer theory proposed by Nagakura and Tanaka5) for the aromatic substitution. From ESR experiments, Fendler et al.6) have reported that the Meisenheimer complex of potassium 1-methoxy-2-cyano-4,6-dinitrocyclohexadienate is, at least partially, involved in the formation of the 3,5-dinitrobenzonitrile anion-radical.

The DMSO solution containing o-dinitrobenzene and sodium hydroxide ion also showed the bands assigned to the o-dinitrobenzene anion-radical before the appearance of the band due to o-nitrophenoxide ion.

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