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INTERACTIONS OF 1-SUBSTITUTED 2,4-DINITROBENZENES WITH HYDROXIDE ION IN AQUEOUS DIMETHYL SULFOXIDE

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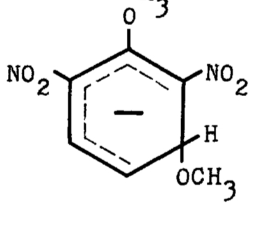
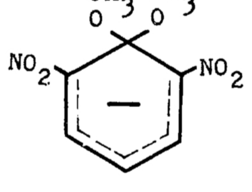
The interactions of 2,4-dinitroanisole, 2,4-dinitrochlorobenzene and m-dinitrobenzene with hydroxide ion in aqueous dimethyl sulfoxide were studied by a rapid scan spectrophotometer. The transient colored species of 2,6-dinitrocyclohexadienate were initially observed before the formations of the colored species of 2,4-dinitrocyclohexadienate were complete.

We have made the present study from the following view-points: (1) In the methoxide solution of 2,6-dinitroanisole in dimethyl sulfoxide (DMSO), the transient colored species of I (λmax = 488 nm) is initially observed before the colored species of II (λmax = 595 nm) is formed.[1,2] In the case of 2,4-dinitro-6-X-anisoles (X = F, Cl, CF$_3$, CN), various transient species formed by the covalent additions of methoxide ion at the 3- and 5-carbons carrying hydrogens are initially observed.[1,3,4] Initial transient colored-species have never been observed for the interactions of 1-X-2,4-dinitrobenzenes with hydroxide or alkoxide ion. (2) Although many kinetic studies on the reactions of 1-halogeno-2,4-dinitrobenzenes with bases have been made and several reviews written,[5-12] no intermediates like IV have been found.

We, therefore, measured the visible absorption spectra of 2,4-dinitroanisole, 2,4-dinitrochlorobenzene and m-dinitrobenzene in aqueous DMSO in the presence of hydroxide ion, using a Hitachi rapid scan spectrophotometer RSP-2. The apparatus was equipped with an automatically controlled mixing cell. Path length was 1.0 cm. The results are shown in Figs. 1-3.

Figs. 1-3 show that each transient colored-species having a band at 565, 595 or 615 nm is initially produced from 2,4-dinitroanisole, 2,4-dinitrochlorobenzene or


I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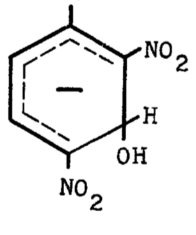
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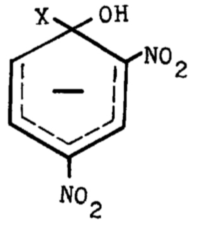
IV

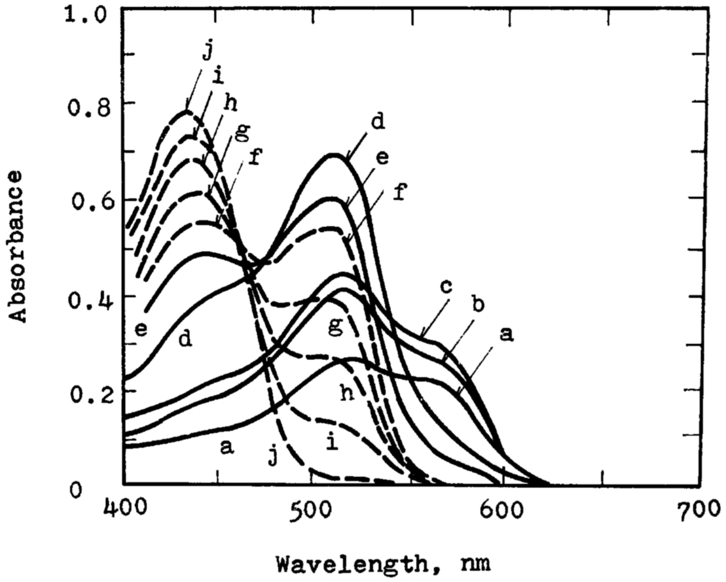

Fig. 1. Rapid scan spectra observed with the DMSO solution containing 2,4-dinitroanisole(4.8×10^{-5} mol/l), sodium hydroxide(2.3×10^{-3} mol/l) and water(2% by volume) at 25°C. Times measured after the mixing: a, 1/3 sec; b, 2/3 sec; c, 1 sec; d, 5 sec; e, 10 sec; f, 30 sec; g, 2 min; h, 4 min; i, 9 min; j, 25 min.

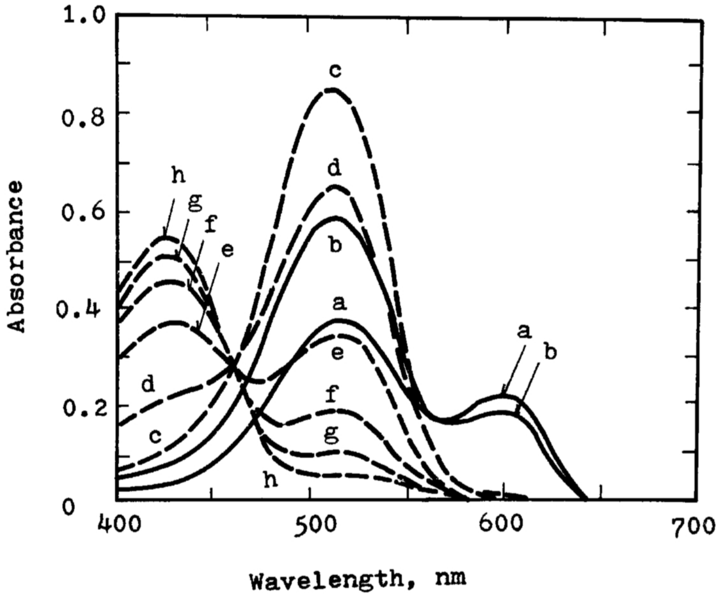

Fig. 2. Rapid scan spectra observed with the DMSO solution containing 2,4-dinitrochlorobenzene(4.9×10^{-5} mol/l), sodium hydroxide(1.7×10^{-2} mol/l) and water(10% by volume) at 25°C. Times measured after the mixing: a, 1/3 sec; b, 1 sec; c, 10 sec; d, 1 min; e, 3 min; f, 5 min; g, 7 min; h, 10 min.

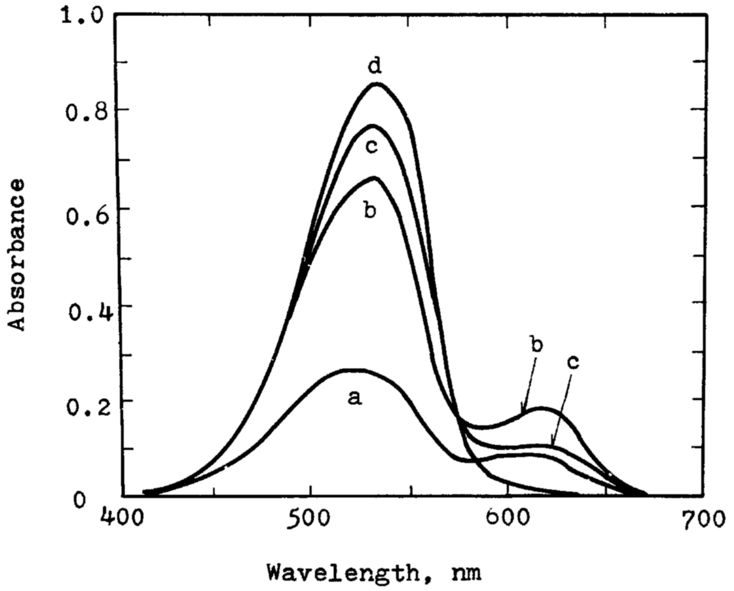

Fig. 3. Rapid scan spectra observed with the DMSO solution containing m-dinitrobenzene(3.2×10^{-5} mol/l), sodium hydroxide(2.3×10^{-3} mol/l) and water(2% by volume) at 25°C. Times measured after the mixing: a, 19 msec; b, 1/3 sec; c, 2 sec; d, 10 sec.

m-dinitrobenzene, respectively. The transient colored species may be ascribed to the structure III (X = OCH_3, Cl, H), since their bands appear in the same range as 2,6-dinitrocyclohexadienates do.[1,2,13,14)]

Both the reactions of 2,4-dinitroanisole and 2,4-dinitrochlorobenzene with hydroxide ion give 2,4-dinitrophenol as the only detectable product.[15)] The absorption bands at 430 nm in Figs. 1 and 2 are the same as 2,4-dinitrophenol has in the same solvent. The structure of the methoxide complex of 2,4-dinitroanisole is established to be 1,1-dimethoxy-2,4-dinitrocyclohexadienate.[16-18)] The colored species of 2,4-dinitroanisole with the 505-nm band can be ascribed to the structure IV (X = OCH_3), since the band is similar to that for the methoxide complex of 2,4-dinitroanisole.[13,16,19)] Moreover, the structure IV is strongly supported by the appearance of the isosbestic point at 465 nm in Fig. 1, since the isosbestic point means that 2,4-dinitrophenol is produced directly from the colored species with 505-nm band. The similarity in spectral behaviors of Figs. 1 and 2 suggests that the colored species of 2,4-dinitrochlorobenzene with a band at 510 nm should be associated with the structure IV (X = Cl). The structure replaced by CH_3O instead of OH in IV (X = H) is suggested by Crampton and Gold[16)] for the colored species with a band at 520 nm, produced from m-dinitrobenzene and methoxide ion. Similarly, the band at 535 nm in Fig. 3 may be due to the structure IV (X = H), since the band is similar to the corresponding bands for 2,4-dinitroanisole and 2,4-dinitrochlorobenzene.

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