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Studies on the Interactions of 1-Substituted 2,4-Dinitrobenzenes with Hydroxide Ion in Aqueous Dimethyl Sulfoxide by Means of the Rapid Scan Spectrophototometer

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The initial interactions of *m*-dinitrobenzene, 2,4-dinitroanisole, 2,4-dinitrofluorobenzene, and 2,4-dinitrochlorobenzene with hydroxide ion in aqueous dimethyl sulfoxide were studied with a rapid scan spectrophotometer. In all the cases, the first transient colored-species assigned to 1-hydroxy-3-substituted-2,6-dinitrocyclohexadienates were observed at initial stages before the formations of the second colored-species having the π-electronic structures of 1,3-dinitropentadienyl anion were complete.

In the interactions of aromatic polynitro compounds with nucleophiles, many transient colored-species have been detected by NMR and visible spectroscopies before the appearances of the thermodynamically stable colored-species.[1] No example has been reported of the initial transient colored-species formed from 1-X-2,4-dinitrobenzenes (X=H, CH_3O, halogeno) and bases.

An attempt has, therefore, been made to pursue the changes of the visible absorption spectra of the dimethyl sulfoxide (DMSO) solutions of *m*-dinitrobenzene, 2,4-dinitroanisole, 2,4-dinitrofluorobenzene, and 2,4-dinitrochlorobenzene in the presence of hydroxide ion.[2]

Experimental

All the dinitrobenzenes used were available commercially and were purified by recrystallization or by distillation. DMSO was dried with calcium hydride and fractionated under reduced pressure.

Electronic absorption spectra at various stages of a reaction path in solution were measured with a Hitachi rapid scan spectrophotometer RSP-2. The apparatus was equipped with an automatically controlled mixing cell, and could operate for the use of the continuous flow method. The mixing cell having the path length of 1.0 cm was roughly controlled at 25 °C by means of a thermocirculator. In the wavelength range from 220 to 700 nm it took 150 msec to record a spectrum on a memoriscope. The possible error in determining absorption positions with the spectrophotometer was estimated to be within 5 nm from the comparison between the spectra of the same solution, the one being recorded by the rapid scan spectrophotometer and the other being measured by a Hitachi recording spectrophotometer EPS-3.

The DMSO solutions subjected to the spectral measurements contained 2 or 10% (by volume) water. The DMSO solutions containing the corresponding amounts of water in the absence of both the dinitrobenzenes and sodium hydroxide were used as references.

Results

The spectral changes observed are shown in Figs. 1—4. In all the cases, the first colored-species having

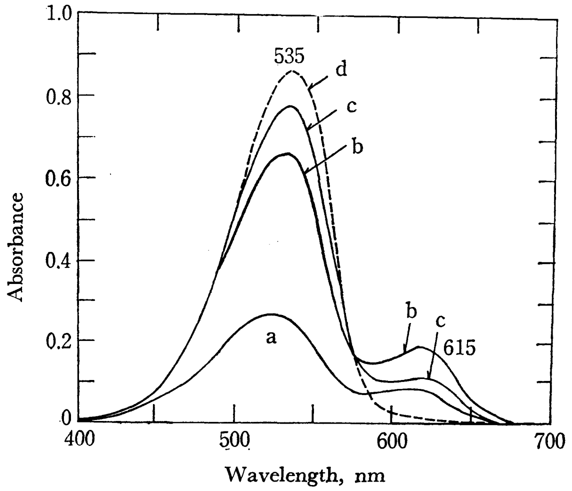

Fig. 1. Spectra observed with the DMSO solution containing *m*-dinitrobenzene (3.2×10^{-5} mol/l), sodium hydroxide (2.3×10^{-3} mol/l) and water (2% by volume). Times measured after the mixing: a, 19 msec; b, *ca.* 1/3 sec; c, 2 sec; d, 10 sec.

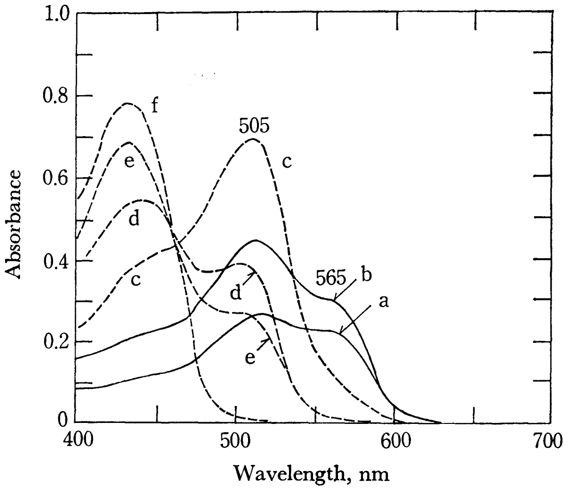

Fig. 2. Spectra observed with the DMSO solution containing 2,4-dinitroanisole (4.8×10^{-5} mol/l), sodium hydroxide (2.3×10^{-3} mol/l) and water (2% by volume). Times measured after the mixing; a, *ca.* 1/3 sec; b, 1 sec; c, 5 sec; d, 2 min; e, 4 min; f, 25 min.

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[1] For the recent reviews and references see: (a) M. J. Strauss, *Chem. Rev.*, **70**, 667 (1970); b) J. G. Tillett, *Ann. Rept. Progr. Chem. B* (Chem. Soc. London), **67**, 63 (1970); c) F. Millot, J. Morel, and F. Terrier, *C. A. Acad. Sci. Paris, Ser. C*, **274**, 23 (1972); d) M. R. Crampton and H. A. Khan, *J. Chem. Soc. Perkin Trans.* II, **1972**, 733. e) F. Terrier, F. Millot, and R. Schaal, *ibid.*, **1972**, 1192. f) F. Terrier, A. P. Chatrousse and R. Schaal, *J. Org. Chem.*, **37**, 3010 (1972); g) M. R. Crampton, M. A. El Ghariani, and H. A. Khan, *Tetrahedron*, **28**, 3299 (1972); h) M. P. Simonnin, M. J. Lecourt, F. Terrier, and C. A. Dearing, *Can. J. Chem.*, **50**, 3558 (1972).

[2] This paper was reported in a preliminary form: Y. Hasegawa and T. Abe, *Chem. Lett.*, **1972**, 985.

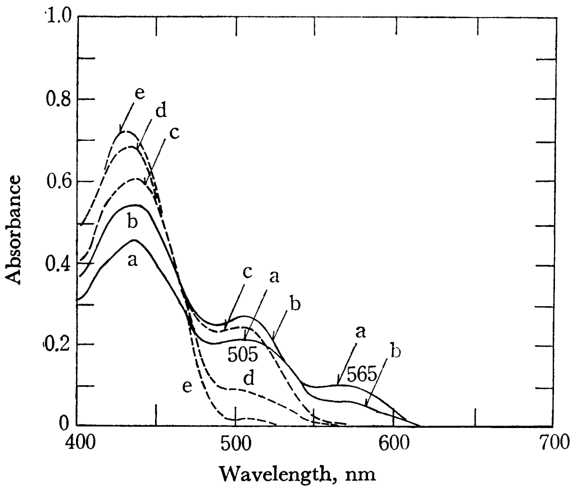


Fig. 3. Spectra observed with the DMSO solution containing 2,4-dinitrofluorobenzene (4.8×10^{-5}mol/l), sodium hydroxide (2.3×10^{-3}mol/l), and water (2% by volume). Times measured after the mixing: a, *ca.* 1/3 sec; b, 5 sec; c, 30 sec; d, 5 min; e, 12 min.

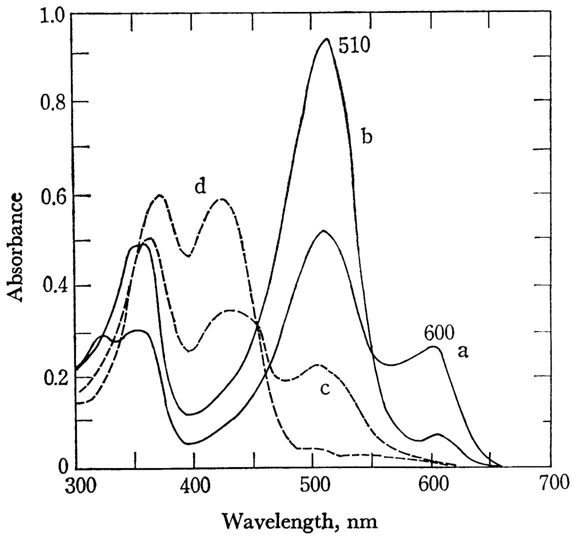
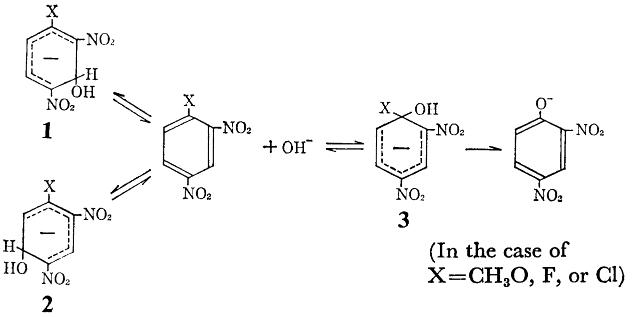


Fig. 4. Spectra observed with the DMSO solution containing 2,4-dinitrochlorobenzene (4.9×10^{-5}mol/l), sodium hydroxide (1.7×10^{-2}mol/l), and water (10% by volume). Times measured after the mixing: a, *ca.* 1/3 sec; b, 10 sec; c, 2 min; d, 8 min.

absorption bands in the range of 550—650 nm appeared at the initial stages and disappeared within several seconds after mixings. After the complete disappearances of the first colored-species, the second colored-species having bands at around 500 nm remained and gradually disappeared. As the peaks of the second colored-species decreased in intensity, the intensities of bands at 375 and 430 nm increased except the case of *m*-dinitrobenzene. The bands at 375 and 430 nm are due to 2,4-dinitrophenoxide ion, because the same alkaline solution of 2,4-dinitrophenol in DMSO containing 2% (by volume) water showed bands at 375 and 430 nm. The reaction product of 2,4-dinitrophenoxide ion agreed with the results of Bowden and Cook.[3] The peak intensity at 535 nm in Fig. 1 decreased very slowly after thermal equilibrium had been reached.

Discussion

From the analogy with the interactions of 2,4-dinitro-6-Y-anisoles (Y=F, Cl, CF_3, CN) with methoxide ion,[1e,4—6] the possible structures of the colored species are restricted to the following types **1**—**3**. This is supported by the theoretical calculations leading to the prediction that the stablization energies of 1,3- and 1,5-dinitropentadienyl anions (1.736 and 1.111 eV, respectively) are considerably great compared with that (0.004 eV) of 2,4-dinitropentadienyl anion.[7] The colored-species of the types **2** and **3** are expected to show absorption bands at the same range, because they have the similar π-electronic systems of 1,3-dinitropentadienyl anion.



(In the case of X=CH_3O, F, or Cl)

It has been known from visible and NMR spectroscopies that the methoxide complexes having the π-electronic structures of 1,3- and 1,5-dinitropentadienyl anions in media rich in DMSO show longer-wavelength bands at the ranges of *ca.* 505 nm and of 585—640 nm, respectively.[1,4—6] Accordingly, the first and second colored-species may be assigned, respectively, to the structure of the type **1** and to what has the same π-electronic structure with 1,3-dinitropentadienyl anion. According to Crampton,[8] the first colored-species should be the kinetically controlled products and the second colored-species should be thermodynamically more stable.

It is known from Figs. 1—4 that the substituents such as CH_3O, F, and Cl shift the band of the first colored-species of 1-hydroxy-2,6-dinitrocyclohexadienate (X=H in **1**) to the blue.

From the comparison with the band (λ_{max}=505 nm) of the methoxide complex of 2,4-dinitroanisole, having the established structure of 1,1-dimethoxy-2,4-dinitrocyclohexadienate,[1a] the band of the second colored-species formed from 2,4-dinitroanisole may be due to the similar structure **3** (X=CH_3O).

According to Crampton *et al.*,[1g] the second colored-species formed from 2,4-dinitro-fluorobenzene and

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[3] K. Bowden and R. S. Cook, *J. Chem. Soc. B*, **1971**, 1771.

[4] F. Millot and F. Terrier, *Bull. Soc. Chim. France*, **1969**, 2692.

[5] F. Terrier and M. P. Simonnin, *ibid.*, **1971**, 677.

[6] F. Terrier, J. C. Hallé and M. P. Simonnin, *Org. Magn. Resonance*, **3**, 361 (1971).

[7] H. Hosoya, S. Hosoya and S. Nagakura, *Theoret. chim. Acta*, **12**, 117 (1968).

[8] M. R. Crampton, *Advan. Phys. Org. Chem.*, **7**, 211 (1969).

-chlorobenzene should be ascribed to the structures of the type **2** (X=F, Cl), since they have reported that the additions of bases occur not at the carbons carrying chlorines but at the 3-positions in picryl chloride and in 2,6-dinitrochlorobenzene derivatives.

Recently, from ESR studies Bellobono *et al.*[9] reported that the stable colored-species formed from *m*-dinitrobenzene and methoxide ion in DMSO containing 2% (by volume) methanol was the anion-radical of *m*-dinitrobenzene. However, the second colored-species formed from *m*-dinitrobenzene may be assigned to the structure **3** (X=H), because the band shape of the second colored-species in Fig. 1 does not resemble that of the 530-nm band of the *m*-dinitrobenzene anion-radical with a distinct vibrational structure.[10] Moreover, the anion-radical shows bands at 385 and 415 nm.[10] As mentioned by Crampton,[8] the anion-radical is probably a minor product.

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[9] I. R. Bellobono, A. Gamba, G. Sala, and M. Tampieri, *J. Amer. Chem. Soc.*, **94**, 5781 (1972).

[10] T. Shida and S. Iwata, *J. Phys. Chem.*, **75**, 2591 (1971).