2186 BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 47 (9), 2186—2188 (1974) [Vol. 47, No. 9

Interactions of 1-Substituted 2,4-Dinitrobenzenes with Methoxide and Hydroxide Ions in Dimethyl Sulfoxide with a Rapid Scan Spectrophotometer

Yoshinori Hasegawa

College of General Education, Tohoku University, Kawauchi, Sendai 980

(Received January 7, 1974)

The interactions of *m*-dinitrobenzene and 1-substituted 2,4-dinitrobenzenes with sodium methoxide in methanolic dimethyl sulfoxide were studied with a rapid scan spectrophotometer. A similar study of 1-substituted 2,4-dinitrobenzenes with sodium hydroxide in aqueous dimethyl sulfoxide was carried out. Except for a few cases, the first transient colored-complexes of 3-substituted 2,6-dinitrocyclohexadienates were observed at initial stages before the complete formation of second colored-complexes having the π-electronic structures of 1,3-dinitropentadienyl anion.

In the interactions of aromatic dinitro compounds with nucleophiles, the initial formation of the kinetically-favored colored-complexes has been detected before the appearance of the thermodynamically-stable colored-complexes.[1,2] In the methoxide additions to *m*-dinitrobenzene and 2,4-dinitroanisole, thermodynamically-stable 1-methoxy-2,4-dinitrocyclohexadienate and 1,1-dimethoxy-2,4-dinitrocyclohexadienate, respectively, were detected by NMR and visible spectroscopy, but no kinetically-favored colored-complexes were detected.[3]

Studies have been made on the interactions of *m*-dinitrobenzene and 1-substituted 2,4-dinitrobenzenes with sodium methoxide in methanolic dimethyl sulfoxide (DMSO) with a rapid scan spectrophotometer. In order to extend the preceding study on the interactions of 1-substituted 2,4-dinitrobenzenes with sodium hydroxide,[1] the spectral changes of the DMSO solutions of some 1-substituted 2,4-dinitrobenzenes in the presence of sodium hydroxide have also been given.

Experimental

The dinitrobenzenes used are presented in Table 1. 2,4-Dinitrophenyl phenyl ether and 2,4-dinitrophenyl *p*-nitrophenyl ether were prepared according to Bost and Nicholson[4] and were recrystallized from methanol. Commercial dinitrobenzenes were purified by recrystallization or distillation.

Methanol was used for spectrophotometry. Sodium methoxide solutions were prepared by the reaction of clean sodium with methanol. Concentrations were determined by titration with a standard acid. DMSO was dried with calcium hydride and fractionated under reduced pressure.

A Hitachi rapid scan spectrophotometer RSP-2 was used to measure visible absorption spectra at various stages of a reaction path in solution. The mixing cell having a path length of 1.0 cm was controlled at 25 °C with a thermo-circulater. Details of the apparatus and measurement were given in a previous paper.[1]

Results and Discussion

Interactions of m*-Dinitrobenzene and 2,4-Dinitroanisole with Sodium Methoxide.* When *m*-dinitrobenzene (6.4×10^{-5} M) was mixed with excess sodium methoxide (2.3×10^{-2} M) in DMSO–methanol (98/2, v/v), two colored-species having absorption maxima at 525 and 605 nm appeared 32 ms after mixing. 1/3 s after mixing, the first colored-species ($\lambda_{\max}=605$ nm) disappeared and formation of the second ($\lambda_{\max}=525$ nm) was complete. The second colored-species has been assigned to 1-methoxy-2,4-dinitrocyclohexadienate.[3a] It is known that the methoxide complexes having the π-electronic structures of 1,5-dinitropentadienyl anion in media rich in DMSO show longer wavelength bands in the range 585—640 nm.[1,5] The first colored-species is assigned to 1-methoxy-2,6-dinitrocyclohexadienate.

Spectra of 2,4-dinitroanisole in the presence of sodium methoxide showed the first ($\lambda_{\max}=560$ nm) and second ($\lambda_{\max}=505$ nm) colored-species, attributed to 1,3-dimethoxy-2,6-dinitrocyclohexadienate and 1,1-dimethoxy-2,4-dinitrocyclohexadienate, respectively.

Interactions of 2,4-Dinitrofluorobenzene, 2,4-Dinitrochlorobenzene, 2,4-Dinitrophenyl Phenyl Ether and 2,4-Dinitrophenyl p*-Nitrophenyl Ether with Sodium Methoxide.* All the solutions of these nitro compounds, containing sodium methoxide in a large excess, finally showed spectra similar to the spectrum of 1,1-dimethoxy-2,4-dinitrocyclohexadienate due to further reaction of methoxide ion with the resulting product of 2,4-dinitroanisole. In order to observe only the spectra of the colored-species formed from sodium methoxide and the nitro compounds, spectral measurements were carried

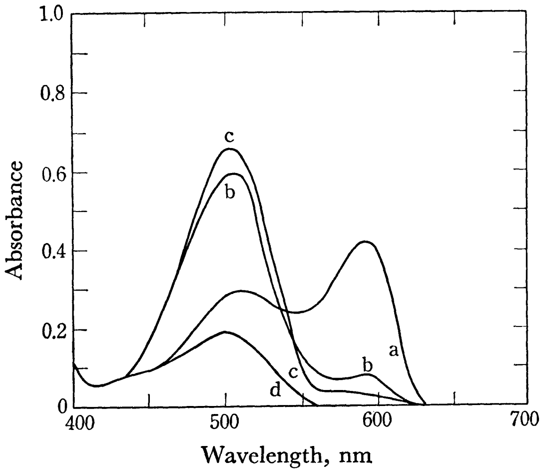
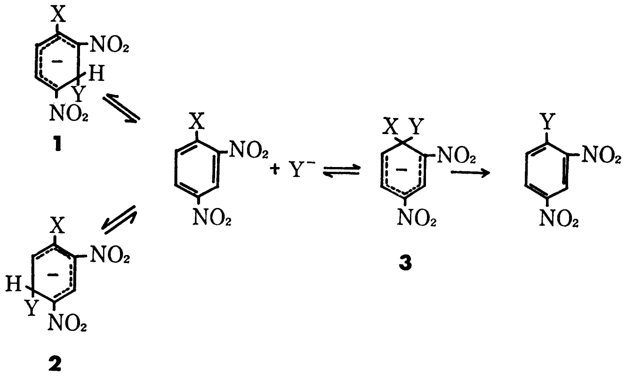


Fig. 1. Spectra observed with the DMSO solution containing 2,4-dinitrochlorobenzene (1.7×10^{-3}M), sodium methoxide (2.3×10^{-4} M) and methanol (2% by volume). Times measured after mixing: a, 30 ms; b, 1/3 s; c, 5 s; d, 30 s.

out under conditions where the concentration of the nitro compounds was several times larger than that of sodium methoxide.

The spectra observed with the DMSO solution containing 2,4-dinitrochlorobenzene (1.7×10^{-3} M), sodium methoxide (2.3×10^{-4} M) and methanol (2% by volume) are shown in Fig. 1. The first colored-species having an absorption peak at 590 nm appeared at initial stages and disappeared several seconds after mixing. Afterward the second colored-species having a peak at 505 nm gradually disappeared. The first colored-species is 1-methoxy-3-chloro-2,6-dinitrocyclohexadienate (**1**; X=Cl, Y=OMe). The second colored-species can be assigned to 2,4-dinitrocyclohexadienate which has the same π-electronic structures as 1,3-dinitropentadienyl anion of type **2** or **3** (X=Cl, Y=OMe).



According to Crampton *et al.*,[6] the second colored-species should be ascribed to 1-methoxy-2,4-dinitro-5-chlorocyclohexadienate (**2**; X=Cl, Y=OMe).[1]

Spectra of 2,4-dinitrofluorobenzene, 2,4-dinitrophenyl phenyl ether and 2,4-dinitrophenyl *p*-nitrophenyl ether in the presence of sodium methoxide showed similar changes in the range 450—650 nm. The absorption maxima are listed in Table 1.

Interaction of 2,4-Dinitrotoluene with Sodium Methoxide. Spectra of 2,4-dinitrotoluene in the presence of sodium methoxide are shown in Fig. 2. At 3 s after mixing, the absorption bands initially observed at 530 and 600 nm disappeared and the bands at 410 and 650 nm remained. The bands at 530 and 600 nm are assigned to 2,4-dinitrocyclohexadienate of type **2** or **3** (X=CH_3, Y=OMe) and to 1-methoxy-3-methyl-2,6-dinitrocyclohexadienate (**1**; X=CH_3, Y=OMe), respectively. According to Pollitt and Saunders,[7] the bands at 410 and 650 nm are assigned to 2,4-dinitrobenzyl anion produced from 2,4-dinitrotoluene by loss of a proton.

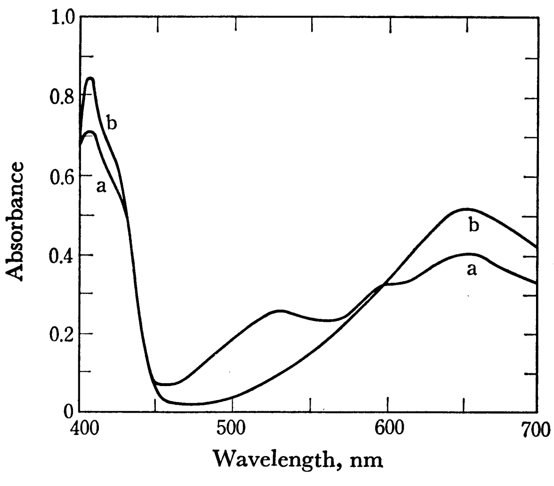


Fig. 2. Spectra observed with the DMSO solution containing 2,4-dinitrotoluene (4.0×10^{-5} M), sodium methoxide (5.9×10^{-3} M) and methanol (0.5% by volume) Times measured after mixing: a, 28 ms; b, 3 s.

Interactions of 2,4-Dinitrobenzoic Acid, 2,4-Dinitrobenzenesulfonic Acid, 2,4-Dinitrophenyl Thiocyanate and 2-(2,4-Dinitrophenylthio)benzothiazole with Sodium Methoxide. The absorption maxima of the colored-species obtained are listed and assigned in Table 1.

Interactions of 2,4-Dinitrophenyl Phenyl Ether, 2,4-Dinitrophenyl p*-Nitrophenyl Ether, 2,4-Dinitrophenyl Thiocyanate and 2-(2,4-Dinitrophenylthio)-benzothiazole with Sodium Hydroxide.* The spectra observed with the DMSO solution containing 2,4-dinitrophenyl phenyl ether (4.9×10^{-5} M), sodium hydroxide (2.3×10^{-3} M) and water (2% by volume) are shown in Fig. 3. The first colored-species having an absorption peak at 580 nm appeared at initial stages and disappeared within a minute. After the complete disappearance of the first colored-species, the second colored-species having a peak at 520 nm remained and then gradually disappeared. As the peak of the second colored-species decreased in intensity, the intensities of two peaks at 375 and 430 nm increased. The first and second colored-species are assigned to 1-hydroxy-3-phenoxy-2,6-dinitrocyclohexadienate (**1**; X=OPh, Y=OH) and to 2,4-dinitrocyclohexadienate of type **2** or **3** (X=OPh, Y=OH), respectively. The bands at 375 and 430 nm are due to 2,4-dinitrophenoxide ion.[1]

Spectra of 2,4-dinitrophenyl *p*-nitrophenyl ether, 2,4-dinitrophenyl thiocyanate and 2-(2,4-dinitrophenylthio)benzothiazole in the presence of sodium hydroxide

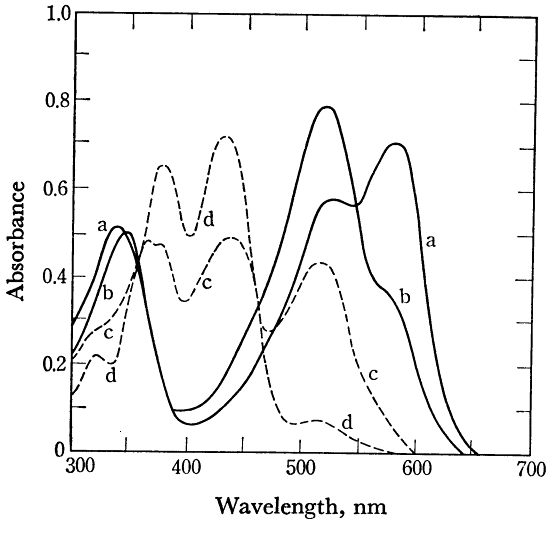
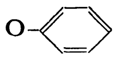
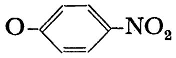
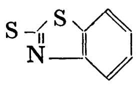


Fig. 3. Spectra observed with the DMSO solution containing 2,4-dinitrophenyl phenyl ether (4.9×10^{-5} M), sodium hydroxide (2.3×10^{-3} M) and water (2% by volume). Times measured after mixing: a, 1/3 s; b, 10 s; c, 4 min; d, 20 min.

TABLE 1. VISIBLE ABSORPTION MAXIMA (nm)

	Y			
X	OH[a)] complex		OMe[b)] complex	
	Type **1**	Type **2** or **3**	Type **1**	Type **2** or **3**
H	615[c)]	535[c)]	605	525
F	565[c)]	505[c)]	570	500
Cl	600[c,d)]	510[c,d)]	590	505
OMe	565[c)]	505[c)]	560	505
	580	520	570	515
	590	515	580	505
CH_3	Not observed	Not observed	600[e)]	530[e)]
COO^-	650[f)]	550[f)]	590	530
SO_3^-	Not observed	520	Not observed	520
SCN	600	480	590	485
	605	510	595	510

a) In DMSO–H_2O (98/2, v/v). b) In DMSO–MeOH (98/2, v/v). c) Ref. 1. d) In DMSO–H_2O (90/10, v/v). e) In DMSO–MeOH (99.5/0.5, v/v). f) In DMSO–H_2O (99/1, v/v).

showed similar changes. The absorption maxima of the colored-species are listed in Table 1.

Interactions of 2,4-Dinitrobenzoic Acid, 2,4-Dinitrobenzenesulfonic Acid and 2,4-Dinitrotoluene with Sodium Hydroxide. The absorption maxima of the colored-species obtained are listed in Table 1. In the presence of sodium hydroxide, 2,4-dinitrotoluene has bands at 410 and 650 nm attributed to 2,4-dinitrobenzyl anion, giving no hydroxide complex.

Substituent Effect on 2,6-Dinitrocyclohexadienate. We see from Table 1 that the substituents such as F and Cl except COO^- at 3-position shift the absorption bands of both 1-methoxy-2,6-dinitrocyclohexadienate and 1-hydroxy-2,6-dinitrocyclohexadienate towards blue. In contrast, the spectra of 4-substituted 2,6-dinitroanisole with methoxide ion show that the substituents such as F and Cl shift the band of 1,1-dimethoxy-2,6-dinitrocyclohexadienate towards red,[5b)] and that electron-withdrawing substituents such as CF_3 shift it towards blue.[5b)] The substituents at 3-position may produce a blue shift by twisting the nitro-groups from the planes of the rings, as described by Pollitt and Saunders in their studies on the Janovsky reaction.[7)]

The author thanks Professor T. Abe for valuable suggestions.

References

1) Recent reviews and references are cited in: Y. Hasegawa and T. Abe, This Bulletin, **46**, 2756 (1973).

2) M. R. Crampton and H. A. Khan, *J. Chem. Soc. Perkin Trans. II*, **1972**, 1173. M. R. Crampton, M. A. El Ghariani, and H. A. Khan, *ibid.*, **1972**, 1178. M. R. Crampton and H. A. Khan, *ibid.*, **1972**, 2286. M. R. Crampton and H. A. Khan, *ibid.*, **1973**, 710. H. Wennerström and O. Wennerström, *Acta Chem. Scand.*, **26**, 2883 (1972).

3) a) M. R. Crampton and V. Gold, *J. Chem. Soc., B*, **1966**, 498; b) M. R. Crampton and V. Gold, *ibid.*, **1966**, 893; c) R. Foster and C. A. Fyfe, *Tetrahedron*, **21**, 3363 (1965); d) R. Foster, C. A. Fyfe, P. H. Emslie, and M. I. Foreman, *ibid.*, **23**, 227 (1967); e) W. E. Byrne, E. J. Fendler, J. H. Fendler, and C. E. Griffin, *J. Org. Chem.*, **32**, 2506 (1967).

4) R. W. Bost and F. Nicholson, *J. Amer. Chem. Soc.*, **57**, 2368 (1935).

5) a) F. Millot and F. Terrier, *Bull. Soc. Chim. France*, **1969**, 2692; b) F. Terrier and F. Millot, *ibid.*, **1970**, 1743; c) F. Terrier and M. P. Simonnin, *ibid.*, **1971**, 677; d) F. Terrier, J. C. Hallé, and M. P. Simonnin, *Org. Magn. Resonance*, **3**, 361 (1971).

6) M. R. Crampton, M. A. Ghariani, and H. A. Khan, *Tetrahedron*, **28**, 3299 (1972).

7) R. J. Pollitt and B. C. Saunders, *J. Chem. Soc.*, **1965**, 4615.