TABLE VI

NITRATION OF $PhCH_2CH_2Se(CH_3)_2ClO_4$ IN 68.7% SULFURIC ACID AT 25.0° [a]

Time, sec	0	900	1800	2700	3600	4800	6120	7200
OD (270 mμ)	0.042	0.073	0.100	0.123	0.147	0.170	0.197	0.208
$10^{-2} \times$ eq 1	0.053	0.094	0.132	0.164	0.196	0.228	0.264	0.279
k_2 l. mol^{-1} sec^{-1}		0.0138	0.0142	0.0142	0.0147	0.0145	0.0150	0.0142

[a] Initial concentration of selenonium salt and potassium nitrate = 5.96×10^{-3} *M*. Rate of nitration of **1** and **2** was also determined by analyzing the reaction mixture, at known time intervals, for nitric acid [W. D. Treadwell and H. Vontabel, *Helv. Chim. Acta*, **20**, 573 (1937)]. Reaction rates determined are given in Table II.

dimethylsulfonium perchlorate (**7**) was complete, the extinction coefficient was 8657 at 260 mμ. At 260 mμ *o*-, *m*-, and *p*-benzyldimethylsulfonium perchlorate (**11**, **12**, and **13**) had extinction coefficients of 5510, 7685, and 10,699, respectively. Assuming the ratio of isomers is the same as given in Table I, the calculated extinction coefficient for the reaction mixture is 8693 which is in good agreement with the actual value. Extinction coefficients for the other nitro isomers formed from the other aromatics were not determined, but it was assumed that the other isomers behaved similarly. There is no reason to believe that the side reactions are important since all of the extinction coefficients of the completely nitrated products were similar. The concentration of nitro compounds in the reaction mixture was determined by the method of Modro and Ridd[2] using the equation

$$x = Y\text{D} - \epsilon_1 a/\epsilon_2 - \epsilon_1$$

where x is the combined concentration of nitrated compounds, Y is the dilution factor during quenching, D is the experimental optical density, ϵ_1 and a are the extinction coefficient of the starting material and concentration of starting material, and ϵ_2 is the extinction coefficient corresponding to a complete reaction. The value of ϵ_1, ϵ_2, and the wavelengths used for following the nitration of the sulfonium and selenonium salts were as follows: **1**, $\epsilon_1 = 783$, $\epsilon_2 = 5696$ at 256 mμ; **7**, $\epsilon_1 = 272$, $\epsilon_2 = 8657$ at 260 mμ; **8**, $\epsilon_1 = 329$, $\epsilon_2 = 9880$ at 268 mμ; **9**, $\epsilon_1 = 63$, $\epsilon_2 = 7028$ at 266 mμ; **10**, $\epsilon_1 = 47$, $\epsilon_2 = 7383$ at 270 mμ. All of the aromatics gave good agreement with the second-order kinetic equation. A typical run is shown in Table VI.

Registry No.—**1**, 6203-16-3; **2**, 13118-29-1; **3**, 29005-91-2; **4**, 29032-26-6; **5**, 29005-92-3; **6**, 29032-27-7; **7**, 18624-67-4; **8**, 29032-28-8; **9**, 29005-94-5; **10**, 29032-29-9; **11**, 29005-95-6; **12**, 29005-96-7; **13**, 29005-97-8.

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Intermediates in Nucleophilic Aromatic Substitution. X.[1,2] Kinetic and Proton Magnetic Resonance Investigations of the Interaction of Nucleophiles with 1,3,6,8-Tetranitronaphthalene

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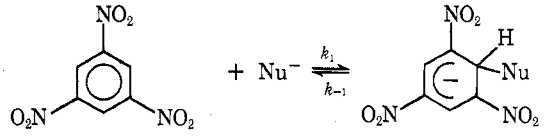
Equilibrium constants for the formation of complexes between 1,3,6,8-tetranitronaphthalene (**4**) and hydroxide and sulfite ions in water and between **4** and methoxide ions in methanol have been determined to be $(1.1 \pm 0.05)10^4$, $(1.8 \pm 0.1)10^4$, and *ca.* 10^4 l. mol^{-1}, respectively. The attainment of the equilibrium for the formation of the hydroxyl adduct of **4** (**5a**) has been followed kinetically in aqueous $Na_2B_4O_7$ buffers. The obtained data afforded rate constants for the formation (k_1) and for the decomposition (k_{-1}) of **5a**. Both k_1 and k_{-1} increase linearly with increasing buffer concentration. Solvent isotope effects of $k_1^{OH^-}/k_1^{OD^-} = 0.505$ and $k_{-1}^{OH^-}/k_{-1}^{OH^-} = 1.7$ have been determined for **5a**. Pmr investigations of the methoxyl and hydroxyl adducts of **4** have established that nucleophilic attack and rehybridization occur at C-4.

The interaction of 1,3,5-trinitrobenzene (**1**) with hydroxide,[4-6] sulfite,[6-8] and sulfide[7,8] ions in aqueous solutions as well as with alkoxide ions in alcohols[9-11] have been shown to involve the formation of Meisenheimer, or σ, complexes. Quantitative data for the equilibria



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and rate constants for these processes have become available recently.[4-11] The equilibrium constants for the formation of the corresponding complexes formed by the interaction of hydroxide ions with 1,2,3,5- (**2**) and 1,2,4,5-tetranitrobenzene (**3**)[12] afforded a comparison of the stabilities of the tri- and tetranitro-substituted cyclohexadienylide ions. Although kinetic

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[1] Part IX: E. J. Fendler, D. M. Camaioni, and J. H. Fendler, *J. Org. Chem.*, **36**, 1544 (1971).

[2] For recent reviews on Meisenheimer complexes and their relevance in nucleophilic aromatic substitution, see (a) R. Foster and C. A. Fyfe, *Rev. Pure Appl. Chem.*, **16**, 61 (1966); (b) E. Buncel, A. R. Norris, and K. E. Russell, *Quart. Rev., Chem. Soc.*, **22**, 123 (1968); (c) P. Buck, *Angew. Chem., Int. Ed. Engl.*, **8**, 120 (1969); (d) J. Miller, "Aromatic Nucleophilic Substitutions," Elsevier, Amsterdam, 1968; (e) M. R. Crampton, *Advan. Phys. Org. Chem.*, **7**, 211 (1969); (f) F. Pietra, *Quart. Rev., Chem. Soc.*, **23**, 54 (1969); M. J. Strauss, *Chem. Rev.*, **70**, 667 (1970).

[3] Address to whom inquiries should be sent.

[4] C. F. Bernasconi, *J. Amer. Chem. Soc.*, **92**, 4682 (1970).

[5] V. Gold and C. H. Rochester, *J. Chem. Soc.*, 1710 (1964).

[6] T. Abe, *Bull. Chem. Soc., Jap.*, **33**, 41 (1960).

[7] M. R. Crampton, *J. Chem. Soc. B*, 1341 (1967).

[8] F. Cuta and E. Beranek, *Collect. Czech. Chem. Commun.*, **23**, 1501 (1958).

[9] V. Gold and Rochester, *J. Chem. Soc.*, 1692 (1964).

[10] E. F. Caldin and G. Long, *Proc. Roy. Soc., Ser. A*, **226**, 263 (1955).

[11] G. Lambert and R. Schaal, *J. Chim. Phys.*, **59**, 1170 (1962).

[12] M. R. Crampton and M. El Ghariani, *J. Chem. Soc. B*, 391 (1970).

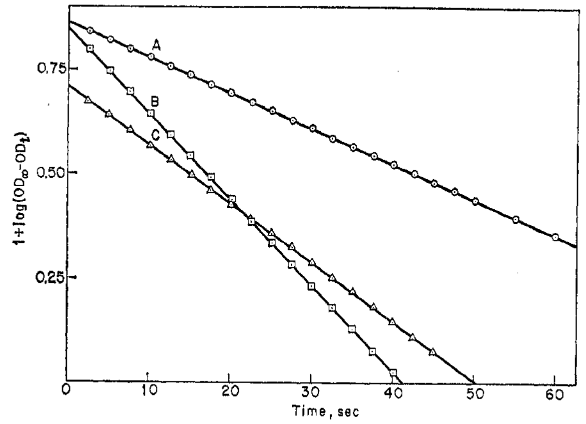

Figure 1.—Plot of log ($OD_\infty - OD_t$) against time for the attainment of equilibrium of **5a** in 2.00% dioxane at 25.00°, [**4**] = 1.25×10^{-4} *M*: A, D_2O, 1.00×10^{-2} *M* $Na_2B_4O_7$, [OD^-] = 6.9×10^{-6} *M*; B, H_2O, 2.00×10^{-2} *M* $Na_2B_4O_7$, [OH^-] = 6.34×10^{-6} *M*; C, H_2O, 3.00×10^{-2} *M* $Na_2B_4O_7$, [OH^-] = 3.03×10^{-5} *M*.

and structural information on Meisenheimer complexes of tri- and tetranitronaphthalenes is potentially very interesting, no investigations on such systems have been carried out. We have demonstrated previously that the stabilities of the alkoxy complexes of 1-alkoxy-2,4-dinitronaphthalene were some seven orders of magnitude greater than those for the corresponding 1,1-dialkoxy-2,4-dinitrocyclohexadienylides.[13] These results were not unexpected since the resonance energy required to stabilize 1,1-dialkoxynaphthalene complexes is considerably smaller than that for the corresponding benzene complexes.[14] As part of our systematic investigations of the structures and stabilities of naphthalene Meisenheimer complexes, we report the formation of σ complexes of hydroxide, sulfite, and methoxide ions with 1,3,6,8-tetranitronaphthalene (**4**) in water and methanol. The kinetic parameters for the formation and decomposition of the hydroxide ion adduct of **4** in water and deuterium oxide as well as proton magnetic resonance parameters for both the *in situ* generated hydroxyl and methoxyl complexes of **4** are also reported.

Experimental Section

The solvents and reagents were prepared, purified, and standardized as previously described.[15] *N,N*-dimethylacetamide, DMA (Baker analyzed reagent grade), was stored over Linde Type 5A Molecular Sieve and its purity was verified by its pmr spectrum.

1,3,6,8-Tetranitronaphthalene (**4**) was prepared by a modified procedure of Dhar.[16] 1,8-Dinitronaphthalene (10 g, 45.8 mmol) (Aldrich Chemical Co.) was added with stirring to a solution of 50 ml of fuming nitric acid (density 1.52) and 50 ml of concentrated sulfuric acid cooled to *ca.* 20°. The mixture was heated slowly (1 hr) to 80° and at 80–90° for 3 hr. After cooling the reaction mixture to room temperature, it was filtered giving crystalline fraction A, and the filtrate was poured into ice water and filtered giving crystalline fraction B. After drying *in vacuo,* both A and B were found to be crude **4** from their pmr spectra and melting points, the former being more pure. After recrystallization of A from 95% ethanol and drying *in vacuo*, the white needles of **4** melted at 203.5–204.5° (lit.[17] mp 203°).

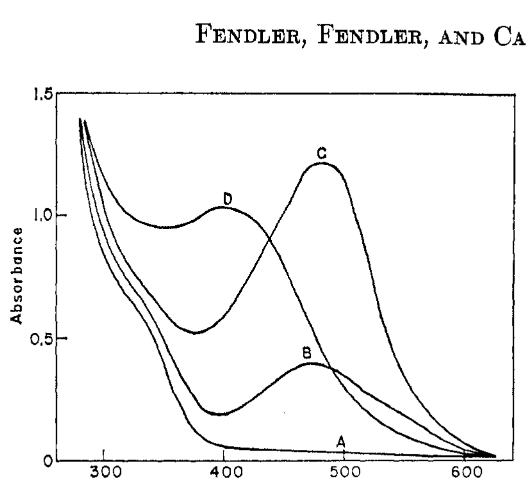

Figure 2.—Absorption spectra of **4** (1.35×10^{-4} *M*) at 25.00° using a pair of 1.00-cm matched cells: A, pH 8.02, 1.00×10^{-2} *M* $Na_2B_4O_7$; B, pH 9.06, 1.00×10^{-2} *M* $Na_2B_4O_7$; C, pH 10.00, 1.00×10^{-2} *M* Na_2HPO_4; D, 0.50 *M* NaOH.

The pH of the buffer solutions was measured with an Orion-801 digital pH meter at 25.0°. The pD value was obtained from the relationship, pD = pH + 0.4,[18] and the concentration of OD^- ions was calculated from the ionization constant of D_2O at 25.0°,[19] *i.e.*, pOD = 14.869 − pD.

Buffered sodium sulfite solutions were prepared immediately prior to use. The absorption spectra of **4** in the different solvent systems were recorded on a Cary 14 spectrophotometer. The attainment of the equilibrium for the formation of the hydroxyl adduct of 1,3,6,8-tetranitronaphthalene (**5a**) was followed at 480 nm in the thermostated cell compartment of a Beckman DU-2 spectrophotometer. The temperature inside the cells was measured and was maintained within ±0.02°. The mixing techniques for fast reactions have been described previously.[20] Good pseudo-first-order plots were obtained for the equilibrium attainment of **5a** in all cases. Typical plots are illustrated in Figure 1. All kinetic runs were carried out in solutions containing 2.00% dioxane. Nitrite ion determinations were carried out as previously described.[1,21]

Pmr spectra (60 MHz) were obtained with a Varian Associates A-60 spectrometer at ambient probe temperature (31°). All spectra were determined on solutions in DMSO-d_6 or in DMA using tetramethylsilane (TMS) as an internal standard; chemical shifts are given on the τ scale in parts per million relative to TMS (τ 10.00 ppm) and are accurate to ±0.03 ppm. Chemical shift data were taken from spectra determined at a sweep width of 500 Hz; the reported coupling constants are the average of at least three determinations at 50-Hz sweep widths and are accurate to ±0.2 Hz.

Results

The absorption spectra of 1,3,6,8-tetranitronaphthalene (**4**) at different pH values in buffered solutions are given in Figure 2. Below pH 8 there is no appreciable absorption at wavelengths longer than 400 nm. As the hydroxide ion concentration is increased, a new absorption band with a maximum at 480 nm develops. The maximum absorbance at this wavelength remains essentially constant over a decade of hydroxide ion concentrations indicating the establishment of the equilibrium. In the concentration range of $(2\text{–}100)10^{-6}$ *M*

$$\mathbf{4} + OH^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathbf{5a}$$

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[13] J. H. Fendler, E. J. Fendler, W. E. Byrne, and C. E. Griffin, *J. Org. Chem.*, **33**, 977 (1968).

[14] M. J. S. Dewar, "The Electronic Theory of Organic Chemistry," Oxford University Press, London, 1949, p 117.

[15] W. E. Byrne, E. J. Fendler, J. H. Fendler, and C. E. Griffin, *J. Org. Chem.*, **32**, 2506 (1967).

[16] S. N. Dhar, *J. Chem. Soc.*, **117**, 993 (1920).

[17] E. Lautemann and A. A. d'Aguiar, *Bull. Soc. Chim.*, **3**, 256 (1865).

[18] P. K. Glasoe and F. A. Long, *J. Phys. Chem.*, **64**, 188 (1960).

[19] A. K. Covington, R. A. Robinson, and R. G. Bates, *ibid.*, **70**, 3820 (1966).

[20] J. H. Fendler, E. J. Fendler, and C. E. Griffin, *J. Org. Chem.*, **34**, 689 (1969).

[21] We are indebted to Mr. D. M. Camaioni for these determinations.

hydroxide ion and 1.35 × 10^{-4} M **4**, it was possible to follow the equilibrium attainment of **5a** by measuring the rate of absorbance increase at 480 mm [$\epsilon_{480\ \text{nm}}$ for **5a** = (1.8 ± 0.2)10^4 cm^{-1} l. mol^{-1}]. Under the experimental conditions the observed pseudo-first-order rate constant for the attainment of equilibrium, k_{obsd}, is given by

$$k_{\text{obsd}} = k_1[\text{OH}^-] + k_{-1}$$

where k_1 is the second-order rate constant for the formation of **5a** and k_{-1} is the first-order rate constant for its decomposition.[1,13,20] The pseudo-first-order rate constants at a given pH, and hence the values for k_1 and k_{-1} were found to be dependent on the concentration of the buffer. The determined rate constants, k_ψ, k_1, and k_{-1}, at 1.0, 2.0, 3.0, and 4.0 × 10^{-2} M buffer are given in Table I. It can be seen that both k_1 and k_{-1} increase linearly with increasing buffer concentration (Figure 3). The equilibrium constant for the formation of **5a** at zero ionic strength has been calculated to be 1.11 × 10^4 l. mol^{-1}. The rate constant for the sodium tetraborate catalyzed complex formation, k', is 7.46 × 10^3 l.^2 mol^{-2} sec^{-1} and that for the decomposition, k_{-1}' = 0.23 l. mol^{-1} sec^{-1}.

TABLE I

INTERACTION OF 1,3,6,8-TETRANITRONAPHTHALENE (1.35 × 10^{-4} M) WITH HYDROXIDE IONS IN AQUEOUS BUFFERS AT 25.00° [a]

10^2 [$Na_2B_4O_7$], M	10^6[OH^-], M	k_{obsd}, sec^{-1}	$10^{-2}k_1$, l. mol^{-1} sec^{-1} [b]	10^2k_{-1}, sec^{-1} [c]	$10^{-4}K$, l. mol^{-1} [d]
1.00	2.69	2.44	3.33	2.38	1.40
	6.33	2.58			
	8.93	2.72			
	17.8	2.94			
	43.7	3.84			
	72.6	4.56			
	85.3	5.37			
	100.0	5.70			
2.00	6.34	3.12	4.06	2.80	1.45
	10.5	3.35			
	14.2	3.45			
	21.0	3.72			
	30.0	4.15			
3.00	2.86	3.42	4.60	3.27	1.41
	6.05	3.53			
	10.2	3.71			
	15.3	3.96			
	20.5	4.20			
	27.3	4.50			
	30.3	4.68			
	34.0	4.85			
4.00	5.64	3.68	5.55	3.38	1.65
	7.69	3.83			
	10.1	3.92			
	11.3	3.99			
	14.3	4.19			
	18.3	4.42			
	24.1	4.74			
	32.3	5.20			

[a] All solutions contain 2.00% dioxane by volume. [b] Obtained from the slope of k_{obsd} vs. [OH^-], M. [c] Obtained from the intercept of k_{obsd} vs. [OH^-], M. [d] $K = k_1/k_{-1}$.

At hydroxide ion concentrations greater than 10^{-3} M the absorbance gradually decreases with a concomitant hypsochromic shift until it reaches 395 nm at 1.0 M NaOH. Further increases in the hydroxide ion concentration, up to 5.0 M, do not alter the absorbance or the wavelength of the absorption maximum.

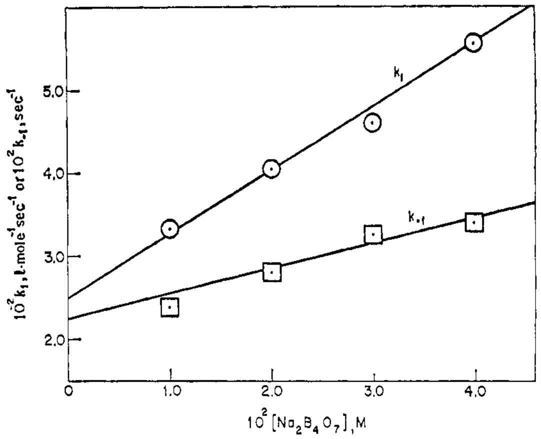

Figure 3.—Plot of k_1 (⊙) k_{-1} (⊡) vs. sodium tetraborate concentration.

TABLE II

INTERACTION OF 1,3,6,8-TETRANITRONAPHTHALENE (1.25 × 10^{-4} M) with DEUTERIOXIDE IONS AT 25.00° [a]

10^6[OD^-]	10^2k_{obsd}, sec^{-1}	$10^{-2}k$, l. mol^{-1}	10^2k_{-1}, sec^{-1}
1.99	1.58	6.60	1.40
6.90	1.94		
14.8	2.25		
21.4	3.01		
31.6	3.24		
32.4	3.52		
56.2	4.98		
100.0	8.12		

$$\frac{k_1{}^{\text{OH}^-}}{k_1{}^{\text{OD}^-}} = 0.505;^a \quad \frac{k_{-1}{}^{\text{OH}^-}}{k_{-1}{}^{\text{OD}^-}} = 1.7;^a \quad \frac{K^{\text{OH}^-}}{K^{\text{OD}^-}} = 0.298_a$$

[a] In 1.00 × 10^{-2} M $Na_2B_4O_7$ containing 1.00% dioxane by volume.

Using the obtained absolute absorbance at 480 nm for 1.0 × 10^{-4} M **4** in the pH 8.0–9.5 range (1.0^3 × 10^{-1} M sodium tetraborate), the equilibrium constant for the formation of **5a** has also been found to be 1.2 × 10^4 l. mol^{-1} from the linear Benesi–Hildebrand plot.[22]

The attainment of the equilibrium for the formation of **5a** has been measured in 1.00 × 10^{-2} M $Na_2B_4O_7$ in deuterium oxide at 25.00° (Table II). These data allowed the calculation of $k_1{}^{\text{OH}^-}/k_1{}^{\text{OD}^-}$ = 0.505, $k_{-1}{}^{\text{OH}^-}/k_{-1}{}^{\text{OD}^-}$ = 1.70, and $k^{\text{OH}^-}/k^{\text{OD}^-}$ = 0.298.

Sulfite ions, even at concentrations of 10^{-4} M, produce a new absorption band centered at 480 nm in dilute solutions of **4** (Figure 4). The absorbance of the adduct showed no decomposition within 2 hr.

At higher sulfite ion concentrations the absorbance decreases and shifts to shorter wavelengths in a manner similar to that observed for **5a**. Addition of acids to these solutions resulted in absorption spectra similar to that of **4** in the aqueous buffer solution in the absence of sulfite ions. The absence of absorbance above 400 nm in acidified solutions of **4** in the presence of Na_2SO_3 is taken as evidence that $SO_3{}^{2-}$ rather than $HSO_3{}^-$ is the

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[22] The Benesi–Hildebrand equation[23] is

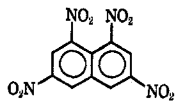
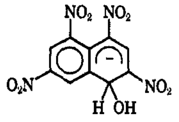
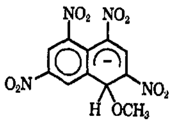
$$\frac{[4]}{A} = \frac{1}{\epsilon} + \frac{1}{K\epsilon[\text{OH}^-]}$$

where A is the absorbance in a 1.0-cm cell, ϵ is the molar extinction coefficient, and K is the equilibrium constant.

[23] H. A. Benesi and J. H. Hildebrand, *J. Amer. Chem. Soc.*, **71**, 2703 (1949).

TABLE III

PMR PARAMETES FOR 1,3,6,8-TETRANITRONAPHTHALENE AND ITS MEISENHEIMER COMPLEXES

	 **4**		 **5a**[a]		 **5b**[c]	
Solvent	DMSO-d_6	DMA	DMSO-d_6	DMA	DMSO-d_6	DMA
τ_2	0.08	−0.20	1.53	1.28	1.32	1.13
			1.39[b]	1.28[b]		
τ_4	0.80	0.71	4.13	3.87	4.03	3.92
			4.00[b]	3.96[b]		
τ_5	0.80	0.71	1.67	1.44	1.42	1.33
			1.50[b]	1.45[b]		
τ_7	0.08	−0.20	1.73	1.60	1.53	1.48
			1.60[b]	1.60[b]		
τ_{OCH_3}					6.92	6.82
τ_{OH}			6.19			
J_{24}	2.2	2.2	~0.6	~1.2	1.8	1.8
			~1.2[b]	~0.7[b]		
J_{45}					~0.5	~0.4
J_{57}	2.2	2.2	2.5	2.5	2.5	2.5
			2.5[b]	2.5[b]		

[a] Values were obtained for the complex generated *in situ* by the addition of 2.00 *M* aqueous KOH to *ca.* 2 *M* solutions of **4** in the indicated solvent unless specified otherwise. [b] Values were obtained using 5.00 *M* NaOH. [c] Values were obtained for the complex generated *in situ* by the addition of 5.05 *M* potassium methoxide in methanol to *ca.* 2 *M* solutions of **4** in the indicated solvent.

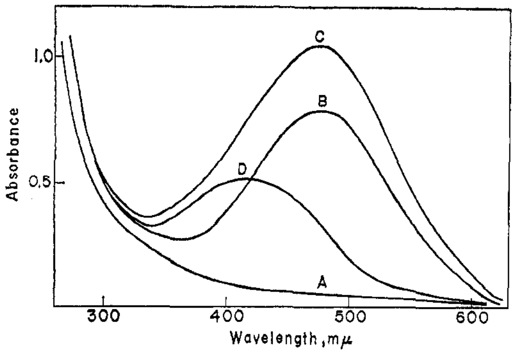


Figure 4.—Absorption spectra of **4** (6.23 × 10^{-5} *M*) at 25.00° using a pair of 1.00-cm matched cells: A, 1.00 × 10^{-2} *M* $Na_2B_4O_7$, pH 8.0; B, 1.00 × 10^{-4} *M* Na_2HSO_3, pH 8.0; C, 8.00 × 10^{-4} *M* Na_2SO_3, pH 8.00; D, 1.00 *M* Na_2SO_3, pH 8.00.

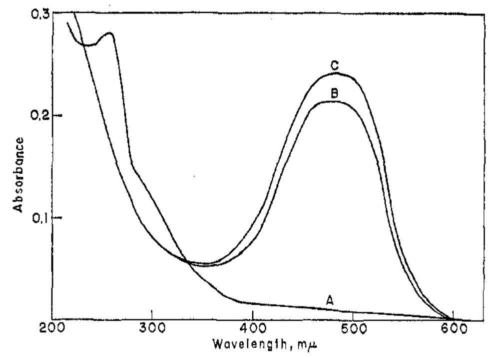


Figure 5.—Absorption spectra of **4** (1.0 × 10^{-5} *M*) at 25.00° using a pair of 1.00-cm matched cells: A, in methanol; B, in 5.23 × 10^{-4} *M* methanolic $NaOCH_3$; C, in 5.23 × 10^{-2} *M* methanolic $NaOCH_3$.

attacking nucleophile. The formation of the sulfite adduct of **4** is immeasurably fast by our techniques. From the absolute absorbances and the Benesi–Hildebrand equation we estimate ϵ_{480} = (1.8 ± 0.8)10^4 cm^{-1} l. mol^{-1} and K = (2.5 ± 1.0)10^4 l. mol^{-1} for the formation of the sulfite adduct of **4**. The rather large errors represent the uncertainties in obtaining values for ϵ from a very small intercept in the Benesi–Hildebrand plot and errors due to the low concentrations of **4** and SO_3^{2-} required to obtain suitable absorbances.

The spectra of **4** in methanol and methanolic sodium methoxide are given in Figure 5. The formation of the methoxyl complex of **4** even at concentrations of 5 × 10^{-5} *M* $NaOCH_3$ and 1 × 10^{-5} *M* **4** is almost complete. The equilibrium constant for the formation of this complex is estimated to be $\geq 10^4$ l. mol^{-1}. At these low concentrations of reactants no quantitative determination of the equilibrium constant is feasible with the present technique.

The formation of nitrite ions is extremely slow. At 45.0° and pH 10.60, 1 equiv of nitrite ion is formed after 100 hr. Furthermore, the nitrite ion production continues, indicating the subsequent loss of additional nitro groups. Attempts to analyze the data kinetically were unsuccessful.

The pmr parameters for 1,3,6,8-tetranitronaphthalene (**4**) and its hydroxyl and methoxyl complexes **5a** and **5b** in DMSO-d_6 and DMA are given in Table III.

Discussion

1,3,6,8-Tetranitronaphthalene (**4**) behaves analogously to 1,3,5-trinitrobenzene in that it reacts with nucleophiles such as hydroxide, sulfite, and alkoxide ions to form Meisenheimer-type complexes.[2] Quantitative data has only been obtained for the formation of the hydroxyl adduct of **4** (**5a**) and the ensuing discussion will be focused, therefore, on this complex.

The order of stability of Meisenheimer complexes parallels the extent of electron delocalization by the substituents. 1,1-Dialkoxynaphthalene Meisenheimer complexes have been found to be more stable than the corresponding cyclohexadienylides.[13,24] The equilib-

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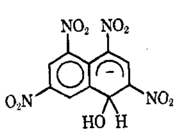
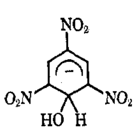
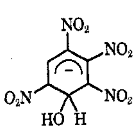
[24] J. H. Fendler and E. J. Fendler, *J. Org. Chem.*, **35**, 3378 (1970).

rium constant for the formation of the methoxyl complex of 1-methoxy-2,4-dinitronaphthalene, for example, is greater than that for the formation of 1,1-dimethoxy-2,4-dinitrocyclohexadienylide ion by a factor of 10^8.[13,25] The stability of the methoxyl complex of 1-methoxy-2,4,5-trinitronaphthalene is, on the other hand, only marginally greater than that of the 1,1-dimethoxy-2,4,6-trinitrocyclohexadienylide ion.[20,24] These results have been rationalized in terms of the proximity of the 4- and 5-nitro groups in 1-methoxy-2,4,5-trinitronaphthalene which is likely to decrease the extent of conjugation by steric hindrance.[24] The equilibrium constant for the formation of **5a** is, in fact, somewhat smaller than that for its 1,2,3,5-tetranitrobenzene analog (Table IV).

TABLE IV

KINETIC PARAMETERS FOR MEISENHEIMER COMPLEXES AT 25.00°

	 **5a**[a]	 **6a**[b]	 **7**[c]
k_1, l. mol^{-1} sec^{-1}	250	37.5	
k_{-1}, sec^{-1}	2.25×10^{-1}	9.8	
K, l. mol^{-1}	1.10×10^4	3.7	2.4×10^4

[a] At zero ionic strnegth. [b] Reference 4. [c] Reference 12.

Evidence from the pmr spectra of **5a** establishes that hydroxide ion adds at the 4 position of the naphthalene. Inspection of molecular models indicates that the incoming nucleophile is sterically hindered by the peri hydrogen in the 5 position of **4** and that rehybridization of C-4 to sp^3 should result in the relief of steric strain. A comparison of the rate constants for the formation and decomposition of **5a** and the hydroxyl adduct of **1** (**6a**)[4] ($k_1^{5a}/k_1^{6a} = 6.7$ and $k_{-1}^{6a}/k_{-1}^{5a} = 436$) reveals that the greater stability of **5a** with respect to **6a** is largely due to its slower rate of decomposition. Lack of kinetic data for the formation and decomposition of the hydroxyl adduct of **2** (**7**) does not allow similar comparisons for the tetranitro-substituted benzene and naphthalene complexes. Steric effects are, of course, not the only factors which determine the stability of complexes.

Increasing concentrations of the sodium tetraborate buffer linearly enhance both k_1 and k_{-1} although the effect is considerably more pronounced for the former (Table I and Figure 3). No such effects have been noted previously for the interaction of hydroxide ions with nitro-substituted aromatics in aqueous solutions.[4,12] The kinetic parameters for the formation and decomposition of **6a** were investigated at considerably higher hydroxide ion concentrations (0.02–0.60 M) and at a constant electrolyte concentration of 1.0 M maintained by the addition of appropriate amounts of sodium chloride.[4] Unlike the case of **5a** and **6a**, the equilibrium constant for the formation of the hydroxyl adduct of **2** (**7**) was not determined kinetically by following the rate of attainment of the equilibrium but was obtained from absolute absorbance measurements of **2** in the pH 9.2–10.6 region. Unfortunately these results for the stabilities of **5a**, **6a**, and **7** are, therefore, not comparable. Pronounced ionic strength affects, however, were observed in the interaction of sulfite ions with **1**, 2,4,6-trinitroanisole, and picramide.[7] Whether the rate enhancements of k_1 and k_{-1} for **5a** represent general base catalysis, electrolyte effects, or a combination of these, their origin must be sought in terms of their differential effects on the initial and transition states for both the forward (k_1) and the reverse (k_{-1}) reactions. Indeed, Bunton and Robinson have dissected the specific salt effects on the reaction of hydroxide ion with 2,4-dinitrochlorobenzene into their component effects on the initial and transition states.[26] Both states were found to be affected by electrolytes. The rate-determining step for this reaction is the formation of the Meisenheimer-type complex, *i.e.*, k_1 in the present notation. Choosing the decomposition of a solid Meisenheimer complex, 1,1-dimethoxy-2,4,6-trinitrocyclohexadienylide ion, in water and in electrolyte solutions as a model for investigating the reverse reaction, k_{-1} in the present notation, we have observed that electrolytes, once again, influence both the initial and transition states.[27] Furthermore, their effects essentially showed a reverse trend to that observed for k_1. It is not surprising, therefore, that the overall salt effects on the equilibrium constants may, in some cases, remain unnoticed.

The magnitude of the observed deuterium solvent isotope effects, enhancement of k_1 and retardation on k_{-1} (Table II), correspond closely to those obtained for the formation and decomposition of the 1,1-dimethoxy-2-cyano-4,6-dinitrocyclohexadienylide ion ($k_1^{CH_3OH}/k_1^{CH_3OD} = 0.6$ and $k_{-1}^{CH_3OH}/k_{-1}^{CH_3OD} = 1.36$)[20] and its decomposition in water ($k_{-1}^{H_2O}/k_{-1}^{D_2O} = 1.45$).[20] Solvent isotope effects of similar magnitude have been obtained for the equilibrium formation of the 1,1-dimethoxy-2,4-dinitrocyclohexadienylide ion ($K^{CH_3OH}/K^{CH_3OD} = 0.38$)[25] and for the ethoxy dechlorination of 2,4-dinitrochlorobenzene ($k_1^{EtOH}/k_1^{EtOD} = 0.5$).[28] Using the simple model of Bunton and Shiner,[29] Bernasconi has calculated the theoretical solvent isotope effect for the equilibrium formation of the dinitro-substituted Meisenheimer complexes to be $K^{CH_3OH}/K^{CH_3OD} = 0.47$ and interpreted the observed results as a secondary solvent isotope effect.[25] The observed solvent isotope effects on K_{5a} seem to be typical, therefore, for nucleophilic aromatic substitutions.

The structures of complexes **5a** and **5b** have been established from the pmr spectra obtained for the complexes generated *in situ* by the dropwise addition of the appropriate base (5.05 M methanolic potassium methoxide, 2.00 M aqueous potassium hydroxide, or 5.00 M aqueous sodium hydroxide) to *ca.* 2 M solutions of **4** in DMSO-d_6 or DMA. The spectrum of **4** in DMSO-d_6 consists of two doublets which, on the addition of methanolic potassium methoxide, decrease in intensity with the concurrent appearance and increase in intensity of an upfield one-proton doublet of doublets (τ 4.03), two one-proton doublets (τ 1.32 and 1.53), and a one-proton doublet of doublets at τ 1.42 (see Table III

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[25] C. F. Bernasconi, *J. Amer. Chem. Soc.*, **90**, 4982 (1968).

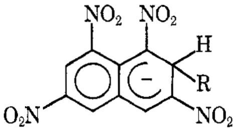
[26] C. A. Bunton and L. Robinson, *ibid.*, **90**, 5965 (1960).

[27] E. J. Fendler and J. H. Fendler, *Chem. Commun.*, 816 (1970).

[28] I. R. Bellobono, P. Beltrame, M. G. Cattania, and M. Simonetta, *Tetrahedron Lett.*, 2673 (1968).

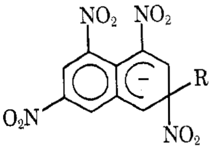
[29] C. A. Bunton and V. J. Shiner, *J. Amer. Chem. Soc.*, **83**, 3207 (1961).

and ref 30). The chemical shifts of the methoxyl resonances in DMSO-d_6 and DMA (τ 6.92 and 6.82, respectively) are similar to those found under comparable conditions for other methoxyl Meisenheimer complexes such as that of **1** (τ 6.88), 3,5-dinitrobenzonitrile (τ 6.93), and 1,3-dicyano-5-nitrobenzene (τ 7.20),[31] in which the sp^3 carbon at the site of attack bears a proton. In addition, the chemical shifts of the upfield resonances (τ 4.03 in DMSO-d_6) attributable to a methine proton clearly indicate the formation of a σ complex, in which C-2 or C-4 has been rehybridized from sp^2 to sp^3, as opposed to a π or charge-transfer complex. The Meisenheimer, or σ, complexes of **4** could result from attack of the nucleophile at C-4 forming **5a** or **5b** or at C-2 forming **8**. However, in the case of the methoxyl complex, the coupling of the methine proton resonance to the resonances at τ 1.32 and 1.53 in DMSO-d_6 ($J \sim$ 0.5 and 1.8 Hz) is only consistent with structure **5b** (see Table III and ref 30). It has been observed previously that the aromatic proton resonances of Meisenheimer complexes are relatively strongly shielded as compared to those of the parent aromatic compound[2,13,15,20,24] and that the magnitude of the upfield shift ($\Delta\delta$) for methoxyl Meisenheimer complexes of 1-alkoxy-2,4-dinitronaphthalenes[13] and 1-methoxy-2,4,5-trinitronaphthalene[24] reflects the relative charge densities at the various ring positions. Rehybridization of C-4 from sp^2 in **4** to sp^3 in **5a** and **5b** results in upfield shifts ($\Delta\delta$ 3.16–3.33 ppm) of the magnitude of those observed for **6a** and 1-methoxy-2,4,6-trinitrocyclohexadienylides (**6b**)^2 ($\Delta\delta$ 3.06–3.25 ppm). The H-2, H-5, and H-7 resonances also show the expected upfield shifts [H-2 ($\Delta\delta$ 1.08–1.45), H-5 ($\Delta\delta$ 0.62–0.87), and H-7 ($\Delta\delta$ 1.45–1.80 ppm)], but the magnitude of the upfield shifts of the H-7 resonance is considerably greater than that found for the sp^2 ring protons of **6a** and **6b** ($\Delta\delta$ 0.61–1.01 ppm).^{2} HMO calculations of π-electron densities of 1-methoxy-2,4-dinitronaphthalene and its methoxyl complex indicate that there is a slight increase in electron density in the second ring and that the negative charge is primarily localized in the nitro groups.[32] In the case of **5a** and **5b**, the appreciable upfield shifts of the H-5 and H-7 resonances as compared to that of H-2 indicate that the negative charge is considerably delocalized in the second ring and to a greater extent than in the case of the methoxyl complex of 1-methoxy-2,4,5-trinitronaphthalene.[24] The smaller $\Delta\delta$ for H-5 is explicable in terms of anisotropic deshielding of H-5 in the complex relative to the parent naphthalene, in which peri shielding by H-4 should be greater. This effect, however, obviously is small, resulting in a decrease in the relative chemical shifts, and is insufficient to overcompensate for the increase in electron density at H-5. The observed $\Delta\delta$ values indicate a large increase in negative charge density in the second ring and localization of the charge in the nitro groups on C-6 and C-8 as well as on C-1 and C-3 and are, therefore, in qualitative agreement with the results of the HMO calculations.



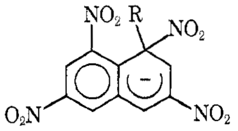
8, R = OCH_3 or OH

In the *in situ* generation of **5a** and **5b** no pmr evidence could be obtained either for the initial or subsequent formation of a species such as **8** or for a complex in which the nucleophile is bonded to a carbon atom bearing a nitro group (**9**). At least at high concentration in DMSO-d_6 and DMA, these pmr observations substantiate that a species such as **9** is a transition state rather than an intermediate in the production of nitrite ions and that the rate-determining step is its slow formation.



9, R = OCH_3 or OH

or



Registry No.—**4**, 28995-89-3; **5a**, 28984-28-3; **5b**, 28984-29-4.

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(30) The 60-MHz spectra of **4** and **5b** at sweep widths of 500 Hz and of **5b** at sweep widths of 50 Hz in DMSO-d_6 will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Reprint Department, ACS Publications, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit $3.00 for photocopy or $2.00 for microfiche.

(31) E. J. Fendler, J. H. Fendler, C. E. Griffin, and N. L. Arthur, unpublished results.

(32) P. Caveng, P. B. Fischer, E. Heilbronner, A. L. Miller, and H. Zollinger, *Helv. Chim. Acta*, **50**, 848 (1967).