Intermediates in Nucleophilic Aromatic Substitution. Part XIV.† Interaction of Lyate Ions with Polynitronaphthalenes

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Interaction of hydroxide ion with 1.3-dinitronaphthalene. 1,3.8- and 1.4.5-trinitronaphthalenes. and 1.3.6.8- 1.4.5.8-, and 1.3.5.8-tetranitronaphthalenes in aqueous dimethyl sulphoxide. aqueous dioxan. and water results in the equilibrium formation of the hydroxy Meisenheimer complexes of the appropriate polynitronaphthalenes. Similarly addition of methoxide ions to 1.5-dinitronaphthalene (in DMSO–MeOH 90 : 10 v/v), 1.3-dinitronaphthalene. 1.4.5- and 1.3.8-trinitronaphthalene. and 1.3.6.8-. 1,4,5.8-, and 1,3,5.8-tetranitronaphthalene (in methanol) results in the equilibrium formation of their methoxy Meisenheimer complexes. Rate constants for the formation and decomposition of these complexes and hence the equilibrium constants have been determined at 25°. Equilibrium constants have also been obtained from spectral data. Many Meisenheimer complexes liberate nitrite ions in a somewhat slower process. Rate constants for this process have also been determined by following either the rate of the decomposition of the complex. product formation. or nitrite ion liberation. Structures of the Meisenheimer complexes are substantiated by ^{1}H n.m.r. investigations and their stabilities are discussed comparatively.

KINETIC, thermodynamic, and structural investigations of intermediates in nucleophilic aromatic substitution, known as Meisenheimer or σ-complexes, have received considerable attention.[1-4] Particularly, effects of the number and kind of electron-withdrawing groups and of solvents on the stabilities of complexes (1)—(3) have been examined in detail.[5-30] Results of these studies established the order of stabilities to be $NO_2 > CN >$

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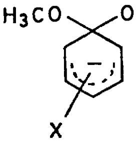
$SO_2CH_3 > CF_3 \approx CO_2CH_3 > I > SCH_3 \gg H$ for a given substituent X, and (1) > (2) > (3) for complexes having the same substituents quantitatively in terms of free energies of activation. These values were, generally, in substantial agreement with those estimated from the relative energies of reactants, transition states, and σ-complexes[31-35] as well as those predicted from additivities.[4] The latter method involved the utilization of estimated free energies of stabilization due to appropriate individual electron-withdrawing groups as well as that attributed to benzo-fusion.[4] For example, the free energy difference between the stabilities of (4a) and (5a) was estimated from process (1) to be 4.6 kcal mol^{-1}.[36] This value is in excellent agreement with that of 4.7

$$(4a) \longrightarrow \frac{-2\text{-NO}_2}{9.0} + \frac{\text{benzo-fusion}}{-7.0} + \frac{5\text{-NO}_2}{-2.8} + \frac{7\text{-NO}_2}{-3.8} \longrightarrow (5a) \qquad (1)$$

kcal mol^{-1}, obtained on treating the experimental data ($K_{(4a)}$ 3.7, $K_{(5a)}$ 1.1 × 10^4 l mol^{-1})[13] by equation (2).

$$\delta\Delta G = 2.3RT \log K_{(4a)}/K_{(5a)} \qquad (2)$$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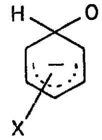
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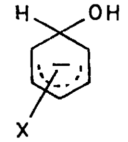
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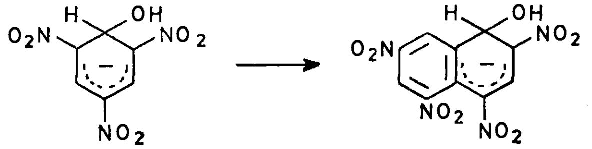
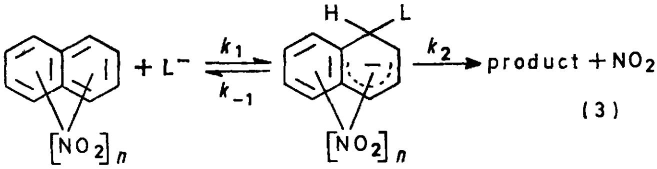

(4a) (5a)

Information on Meisenheimer complex stabilities allows, therefore, valuable predictions of relative reactivities and hence, contributes significantly toward establishing a logical framework for the mechanism of nucleophilic aromatic substitutions.

The validity of free energy correlations rests upon, of course, the extent of data utilized in their derivations. A fair amount of work is being directed toward the consolidation and verification of the proposed correlations by determining stabilities of additional Meisenheimer complexes either in terms of equilibrium constants or of free energies of activation. Recent calorimetric determinations of the enthalpies of activation for a series of Meisenheimer complexes, formed in the interaction of polynitroaromatic compounds with carbanions, for example, substantiated the validity of predictions made by treating constituting free energies of activation analogously to that of process (1).[36] Although of both synthetic and mechanistic interest, quantitative data on the stabilities of Meisenheimer complexes of polynitro-substituted naphthalenes are meagre. As a continuation of our work in this area[7,11,13,17] we have investigated the interactions of hydroxide and methoxide ions with di-, tri-, and tetra-nitronaphthalenes. These reactions are characterized by the attainment of equilibrium (3) of an intermediate complex, which subsequently decomposes.

The present paper reports kinetic, thermodynamic, and n.m.r. data on the interaction of lyate ions with these polynitronaphthalenes. The accompanying paper is devoted to exhaustive treatment of all the available data on the intermediates formed in nucleophilic aromatic substitutions.[37] Calculated and determined stabilities will be assessed critically.[37]



(3)

EXPERIMENTAL

Reagent grade (Aldrich) 1,3- (6) and 1,5-dinitronaphthalene (7) were used as received. The purity of these compounds was established by their m.p.s. and absorption and ^{1}H n.m.r. spectra.

1,3,8-Trinitronaphthalene (8) was prepared following a modified procedure of Hodgson,[38] 1,8-Dinitronaphthalene (Aldrich; 20 g, 91.7 mmol) was dissolved in concentrated sulphuric acid (100 ml; *d* 1.84) and then fuming nitric acid (14.2 ml; *d* 1.5) was added. The temperature was kept below 75°. After several hours, the mixture was cooled to 0°, filtered, and washed with a small amount of water. The resulting solid was recrystallized from acetone–water and dried *in vacuo*, m.p. 218° (lit.,[39,40] 218°).

1,4,5-Trinitronaphthalene (9) was prepared according to a modified procedure of Dimroth and Ruck.[41] 1,5-Dinitronaphthalene (Aldrich; 10 g, 45.8 mmol) was dissolved in concentrated sulphuric acid (50 ml) and fuming nitric acid (3.0 ml) was added. The temperature was kept below 30° and the reaction was allowed to proceed for 3 h. The mixture was then poured onto ice and the resulting solid material was collected, washed with water, and dried *in vacuo*. The product was then recrystallized from benzene and dried *in vacuo*, m.p. 148—149° (lit.,[39,40] 148—149°).

The preparation of 1,3,6,8-tetranitronaphthalene (5)

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has been described,[13] m.p. 205° (lit.,[39,40] 203—205°). 1,3,5,8- (10) and 1,4,5,8-tetranitronaphthalene (11) were prepared by modifying the reported procedures somewhat.[42,43] 1,5-Dinitronaphthalene (Aldrich; 19.5 g, 89.5 mmol) was added with stirring to a solution of fuming nitric acid (56 ml; *d* 1.52) and concentrated sulphuric acid (50 ml), which was cooled to 20°. This mixture was heated slowly to 80° and kept there for *ca.* 1 h. After cooling the reaction mixture to 5°, it was filtered to give a crystalline fraction A, and the filtrate was poured onto ice and filtered to give crystalline fraction B. Both fractions were dried *in vacuo* over phosphorus pentoxide. It was found that fraction A was (11) while fraction B was (10). Both (10) and (11) were recrystallized from acetone and ethanol, then dried *in vacuo*. After recrystallization, (11) had m.p. 343° (decomp.) (lit.,[39,40] 340—345°) and (10) 193—194° (lit.,[39,40] 194—195°).

The methoxy-complex of (6), (6b), was prepared by adding 4.5M methanolic potassium methoxide (0.27 ml, 1.21 mmol) to (6) (0.273 g, 1.25 mmol) in dry dioxan (3.0 ml). The red-purple crystals which formed were washed three times with both dry benzene and anhydrous ether under a dry nitrogen atmosphere, then dried *in vacuo* over phosphorus pentoxide. Upon heating, the crystals of (6b) decomposed between 112 and 120°.

The crystalline Meisenheimer complex (7b), formed by the interaction of sodium methoxide with (7), was isolated from the reaction mixture in dioxan. The brownish yellow crystals were filtered, washed with benzene and ether three times, then dried *in vacuo* over P_2O_5. Its decomposition temperature was 130 ± 10°.

The methoxy-complex of (8), (8b), was prepared by the addition of 4.6M-potassium methoxide (10.35 ml, 1.6 mmol) in methanol to a solution of (8) (0.4359 g 1.65 mmol) in dry dioxan (5 ml) under dry nitrogen. After evaporation of some of the solvent and cooling to 5°, some red-orange crystals formed. After filtration, the crystals were washed three times with dry benzene and anhydrous ether and dried over phosphorus pentoxide *in vacuo*. Upon heating, (8b) decomposed between 102 and 104°.

The methoxy-complex of (9), (9b), was prepared by the addition of 4.6M-potassium methoxide (0.70 ml, 3.2 mmol) in methanol to a solution of (9) (0.8708 g, 3.3 mmol) in dry dioxan (4 ml), under dry nitrogen. A dark, reddish brown solution resulted, which upon evaporation of some of the solvent with dry nitrogen, turned into a paste. After drying *in vacuo* over phosphorus pentoxide, brownish crystals formed which were subsequently washed five times with dry benzene and anhydrous ether. After subsequent redrying, the crystals of (9b) melted with decomposition between 126 and 129°.

The methoxy complex of (10), (10b), was prepared by the addition of 4.6M-potassium methoxide (0.08 ml, 0.37 mmol) in methanol to a solution of 1,3,5,8-tetranitronaphthalene (0.1262 g, 0.41 mmol) in dry dioxan (3 ml) under a stream of dry nitrogen. The reddish orange crystals which formed were then washed with dry benzene and anhydrous ether three times and dried *in vacuo* over phosphorus pentoxide. Upon heating, the 1,3,5,8-Meisenheimer complex crystals had m.p. 80—82°.

The preparation of the methoxy-complex of the (5), (5b), has been reported previously.[13]

Spectral grade anhydrous methanol and dimethyl sulphoxide (Fisher) were dried over Linde type 4A or 5A molecular sieves. Stock solutions of sodium hydroxide were prepared from 1.00M-NaOH ampoules (British Drug House) by dilution with doubly distilled water. Stock solutions of sodium methoxide in dry methanol were prepared by dissolving freshly cut sodium in dry methanol in a three-neck flask fitted with a condenser and a calcium chloride drying tube. The more concentrated sodium methoxide solutions were stored in polyethylene bottles under dry nitrogen. Dilute solutions were obtained by dilution of the concentrated stock solutions with dry methanol and were standardized, just prior to use by titration with standard 0.10N-hydrochloric acid (British Drug House) using lacmoid as the indicator. Stock solutions of the polynitronaphthalenes used in this study were prepared by accurately weighing solid samples and dissolving them in the appropriate solvent in volumetric flasks. Generally these solutions were prepared immediately prior to their use. Water content of nonaqueous solutions were determined to be 10—22 p.p.m. by gas–liquid partition chromatography, using a Porapac Q column.[44]

Absorption spectra were recorded on a Cary 14 or a Cary 118-C spectrophotometer using 1.00 cm matched quartz cells in the thermostatted cell compartment. In some cases, spectral data were obtained at each wavelength point by point on the Durrum model stop-flow system using established procedures.[45] The temperature was maintained at 25.0 ± 0.1° in spectral and kinetic studies by water circulation from a precision thermostat.

Since the equilibrium attainment of (5b) and (10b) is fairly rapid (half-times of reaction approach dead time of stop-flow cell), a special effort was made to avoid local concentration gradients in the stop-flow cell by using lower concentrations of methoxide ion.

Attainment of the equilibria for the formation of the lyate ion adducts, and their subsequent decomposition were followed spectrophotometrically under pseudo-first-order conditions $\{i.e.\ [(5)\text{—}(11)] \ll [L^-]\}$ to at least 90% conversion. Rate constants were calculated from linear plots of log $(A_\infty - A_t)$ against time in the usual manner. The wavelengths used to monitor absorbance changes due to formation of methoxy-complexes (6b)—(10b), (5b), and (11b) were 510, 380, 495, 485, 480, and 490 nm respectively; while those for formation of hydroxy-complexes (6a), and (8a)—(11a) were 515, 500, 500, 480, and 555 nm respectively.

Rate of nitrite ion release was determined by a slightly modified method of Rider and Mellon.[46] Aliquot portions of the reaction mixture were withdrawn at suitable intervals, quenched by water, and analysed for nitrite ion content. Absolute nitrite ion concentrations were determined by use of a calibration plot which related absorbances in the appropriate solutions at 520 nm to nitrite ion concentrations. Good first-order plots were obtained for the rate of nitrite ion release.

60 MHz ^{1}H N.m.r. spectra were obtained using either a Varian A-60 or T-60 spectrometer at probe temperatures of 41 ± 0.5 and 36 ± 0.5°, respectively. 100 MHz ^{1}H N.m.r. spectra were obtained using a Varian HA-100 spectrometer at 31.0 ± 0.5°. The spectra of the parent polynitronaphthalenes, isolated methoxy-complexes, or the

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in situ generated complexes were determined in deuteriated dimethylsulphoxide, (Mallinckrodt or Aldrich, 99.5% isotopically pure) using tetramethylsilane as the internal reference. The *in situ* generated complex spectra were obtained by reacting, *via* dropwise addition, 2.8—5.5M-$KOCH_3$ with 10% solutions of the appropriate polynitronaphthalenes in [$^2H_6$]DMSO and observing the spectral changes with time as the concentrated potassium methoxide was successively added. The chemical shifts are usually the average of at least three determinations using either a 25 or 50 Hz sweep widths and are accurate to ± 0.3 Hz. For 100 MHz work, the frequencies were directly read from an HP model 200-ABR audio oscillator and frequency counter.

RESULTS AND DISCUSSION

General Treatment of Data.—The addition of lyate ions, such as hydroxide or methoxide, to polynitronaphthalenes (5)—(11) results in the development of new absorption bands (Table 1) due to complex formation according to equation (3). The rate of equilibrium formation of these σ complexes could usually be conveniently followed by use of conventional kinetic techniques [17] or standard stop-flow procedures.[45] Measurement of the absorbance changes due to complex formation under pseudo-first-order conditions {*i.e.* $[L^-] \gg [(5)—(11)]$} yielded pseudo-first-order rate constants, k_ψ. Unless otherwise noted, under any set of solvent conditions, k_ψ values increased linearly with increasing lyate ion concentrations. This allowed for the calculation of the second-order rate constants for the formation, k_1, and the first-order rate constants for decomposition, k_{-1}, of the σ complexes from equation (4). The equilibrium constant, K, for complex formation can be determined from kinetic data from equation (5).

TABLE 1

Spectral data of δ complexes

Complex	Conditions	$\lambda_{max.}$/nm [a]	10^{-4} ε/cm^{-1} [a]
(5b)	MeOH–NaOMe	480	2.2 ± 0.2 [b]
(6a)	H_2O–NaOH, varied % DMSO	515	~2.0 [b]
(6b)	MeOH–NaOMe, varied % DMSO	510	~2.0 [b] (see Table 4)
(7b)	90 : 10 (v/v) DMSO–MeOH, NaOMe	380	1.8 ± 0.2 [c]
(8a)	H_2O–NaOH, varied % dioxan	500	1.9 ± 0.3 [c]
(8b)	MeOH–NaOMe	495	2.5 ± 0.5 [c]
(9a)	H_2O–NaOH, varied % dioxan	500	*d*
(9b)	MeOH–NaOMe	485	*d*
(10a)	H_2O–NaOH	480	2.0 ± 0.5 [b]
(10b)	MeOH–NaOMe	480	2.8 ± 0.2 [c]
(11a)	H_2O–H_2O, varied % dioxan	550	*d*
(11b)	NaOH–NaOMe, 1% dioxan	490	*d*
(12b)	90 : 10 (v/v) DMSO–MeOH, NaOMe	460	*d*

[a] Values correspond to those determined (or estimated) for neat solvent systems; *i.e.* pure methanol or water. [b] Values determined *via* estimation from spectral data obtained from either the dissolving of known amounts of isolated solid complexes in solvent with lyate ion or from addition of large excess of lyate ion concentration (amount required to complete equilibrium) to solutions of known parent polynitronaphthalene concentration. [c] Molar absorptivity values determined by use of equations (6)—(8). [d] Not possible to accurately estimate molar absorptivity values.

$$k_\psi = k_1[L^-] + k_{-1} \qquad (4)$$

$$K = k_1/k_{-1} \qquad (5)$$

In some instances, it was possible to determine the thermodynamic equilibrium constants for σ complex formation directly from spectral data by use of either the Benesi–Hildebrand treatment [equation (6)],[47] the Scott modification of it [equation (7)],[48] or by use of the graphical treatment of Drago [equation (8)] [49] where A and ε are the absorbance and the molar absorptivity of the σ complex, [PNN] is the polynitronaphthalene concentration, and $[L^-]$ refers to lyate ion concentration.

$$\frac{[\mathrm{PNN}]}{\mathrm{A}} = \frac{1}{\varepsilon} + \frac{1}{K\varepsilon}\left(\frac{1}{[\mathrm{L}^-]}\right) \qquad (6)$$

$$\frac{[\mathrm{PNN}][\mathrm{L}^-]}{\mathrm{A}} = \frac{[\mathrm{L}^-]}{\varepsilon} + \frac{1}{K\varepsilon} \qquad (7)$$

$$K^{-1} = \frac{A}{\varepsilon} - [\mathrm{L}^-] - [\mathrm{PNN}] + \frac{[\mathrm{PNN}][\mathrm{L}^-]}{A} \qquad (8)$$

In the Benesi–Hildebrand treatment, the intercept of the plot is equal to 1/ε; therefore, a small change in the slope can have a significant effect on ε and hence on K. Use of equation (7) or graphical use of equation (8) circumvents this problem and was used to calculate ε.

Subsequent to the rapid equilibrium attainment of the δ complexes, they slowly decompose to form final products, P, with the liberation of nitrite ion, NO_2^-, as shown in equation (3). This decomposition could be conveniently followed by either measuring the absorbance decrease of the σ complex, the absorbance increase due to product formation, or by measuring amount of nitrite ion liberation spectrophotometrically as a function of time. Pseudo-first-order rate constants for the decomposition, k_d, were calculated from linear plots of log (ΔA) against time.

There are two kinetically indistinguishable pathways by which the intermediate σ complex could decompose to form final products.[15,50,51] These two possible pathways, A and B, are shown in equation (9). Pathway A involves replacement of the nitrite ion by lyate ion in the complex *via* an intraunimolecular rate-determining step. Pathway B shows the bimolecular reaction involving direct nucleophilic attack of the lyate ion on the polynitronaphthalene parent compound which is in equilibrium with its σ complex. It is more probable that the final products are formed *via* path B through either a very short-lived, undetectable intermediate or more

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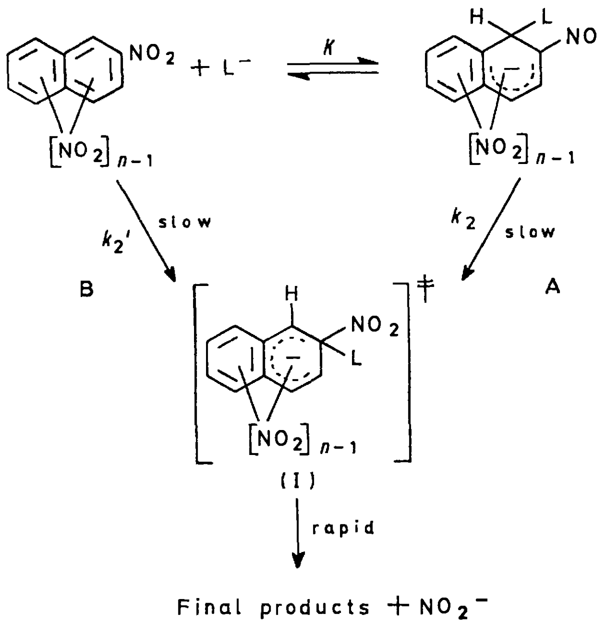
likely, a transition state, such as structure (I) in equation (9).[15,50]



(9)

For pathway A in equation (9), the observed pseudo-first-order decay rate, k_d, can be related to the equilibrium constant, K, and the unimolecular rate constant for decomposition to products, k_2, by use of equation (10).[15,50] The analogous equation for pathway B is

$$\frac{1}{k_d} = \frac{1}{k_2} + \frac{1}{Kk_2}\left(\frac{1}{[L^-]}\right) \qquad (10)$$

(11) where k'_2 is the bimolecular rate constant for final

$$\frac{1}{k_d} = \frac{1}{k'_2[L^-]} + \frac{K}{k'_2} \qquad (11)$$

product formation. The kinetic data will be treated by use of both equations (10) and (11).

Kinetics and Equilibria.—1,3-*Dinitronaphthalene* (6). The obtained pseudo-first-order rate constants, k_ψ, for the equilibrium attainment of (6a) in 2.80, 4.21, 5.61, and 7.01M-DMSO are listed in Table 2 as functions of sodium hydroxide concentrations. Values of k, k_{-1}, and $K(k_1/k_{-1})$ are also included in Table 2. Not unexpectedly, rate constants for the formation of (6a) increase while those for its decomposition decrease with increasing DMSO concentrations. This is in complete agreement with previous reports that DMSO stabilizes σ complexes.[4,10,16,24,28] A linear relationship is obtained on plotting log k_1 and log k_{-1} against DMSO concentration (Figure 1). Values of k_1 and k_{-1} in ' neat ' water were obtained by extrapolation to zero DMSO concentration.

The equilibrium attainment for the methoxy-complex of (6), (6b), could be spectrophotometrically followed under pseudo-first-order kinetics and the k_ψ rate constants obtained as a function of methoxide ion concentration are presented in Table 3. It is seen that the values of k_ψ decrease linearly with increasing methoxide ion. This implies, of course, that the equilibrium lies in favour of the reactants {*i.e.* for equation (4), k_1 $[L^-] \lesssim k_{-1}$} and is being approached from the opposite direction to that utilized for interaction of (6) with sodium hydroxide in aqueous DMSO.

TABLE 2

Interaction of sodium hydroxide with 1,3-dinitronaphthalene (6) in aqueous dimethyl sulphoxide at 25.0° [a]

[DMSO]/M	[NaOH]/M	k_ψ/s^{-1} [c]	k_1/l mol^{-1} s^{-1}	k_{-1}/s^{-1}	K/l mol^{-1}
0 [b]			0.29	1.12	0.26
			±0.05	±0.2	±0.05
2.80	0.10	0.51	1.20	0.39	3.0
	0.20	0.63	±0.08	±0.04	±0.5
	0.30	0.73			
	0.40	0.88			
	0.50	1.00			
4.21	0.10	0.57	2.88	0.25	12.0
	0.20	0.81	±0.10	±0.04	±0.5
	0.30	1.20			
	0.40	1.40			
	0.50	1.70			
5.61	0.10	0.8	7.70	0	77
	0.20	1.6	±0.10	±0.1	±10 [d]
	0.30	2.5			
	0.40	3.2			
	0.50	3.9			
7.01	0.010	0.20	11.4	0.08	140
	0.020	0.30	±0.1	±0.01	±10
	0.030	0.45			
	0.040	0.54			
	0.050	0.65			

[a] Attainment of equilibrium followed spectrophotometrically at 515 nm; [1,3-dinitronaphthalene] = 5.9×10^{-5}M. [b] Extrapolated values from Figure 1. [c] Error associated with these values is *ca.* ±5%. [d] This is the minimum value possible based on maximum value of k_{-1}.

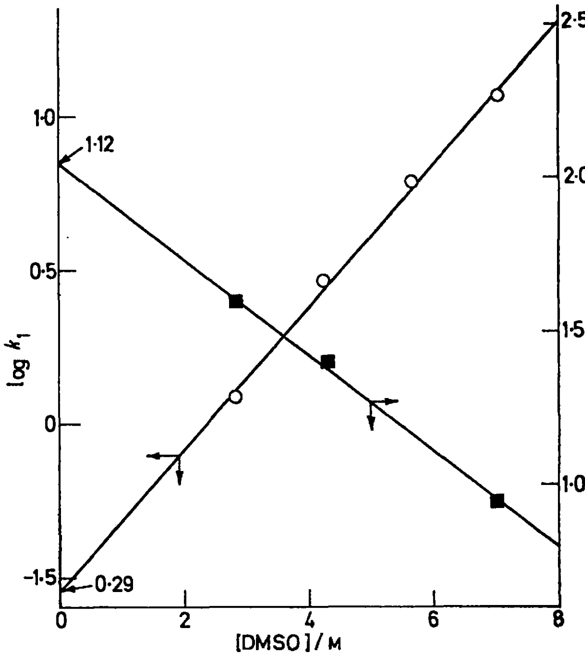


FIGURE 1 Plots of the rate constant for the formation, k_1, and decomposition, k_{-1}, of (6a) in water at 25.0° as functions of added DMSO

Values of k_1 and k_{-1} for formation of (6b) in methanol could not be directly obtained from this data without knowledge of the magnitude of the equilibrium constant for (6b). Since appreciable conversion of (6) to (6b) occurs only in highly basic media, an acidity function was used to determine the equilibrium constants for formation of (6b).[3,52,53]

TABLE 3

Interaction of sodium methoxide with 1,3-dinitronaphthalene (6) in methanol at 25.3°

[NaOMe]/M	J_M [a]	10^4[(6)]/M	k_ψ/s^{-1} [b]	$A_{510 \text{ nm}}$	$\log\left(\frac{[(6b)]}{[(6)]}\right)$ [c]	K_{eq}/l mol^{-1} [d]	k_1/l mol^{-1} s^{-1} [e]	k_{-1}/s^{-1} [f]
0.00 [g]						0.09 ± 0.0.01	11.2 ± 0.5	124 ± 4
0.025	15.10	7.3	121.5	0.042	−2.54	0.09	10.9	121.2
0.058	15.50	7.3	123.1	0.108	−2.18	0.09	11.0	122.4
0.080	15.75	4.4		0.105	−1.93	0.09		
0.101	15.94	7.3	118.8	0.200	−1.86	0.09	10.6	117.7
0.116	16.05	4.4		0.147	−1.77	0.09		
0.200	16.35	7.3	115.2	0.466	−1.48	0.09	10.2	113.2
0.202	16.35	4.4		0.275	−1.50	0.09		
0.300	16.55	7.3	107.5	0.836	−1.22	0.09	9.4	104.7
0.300	16.55	4.4		0.409	−1.31	0.09		
0.400	16.75	4.4		0.608	−1.14	0.09		
0.413	16.80	7.3	97.5	1.410	−0.93	0.09	8.4	94.0

[a] J_M Acidity function, values taken from ref. 54. [b] Determined by use of Durrum stop-flow spectrophotometer. [c] Calculated using measured absorbances and a molar absorptivity value of *ca.* 20 000 for σ complex (6b). [d] Calculated by use of equation (12). [e] Determined by use of relationship $k_1 = K_{eq}k_{-1}$. [f] Determined by use of relationship $k_{-1} = k_\psi/[K(\text{OMe}) + 1]$. [g] Extrapolated values from Figure 2, plot of k_1 (or k_{-1}) against [NaOMe].

The J_M acidity function derived for concentrated methanolic solutions of sodium methoxide by Terrier [52,54] was used [equation (12) where K_{eq} is the thermodynamic

$$J_M = \text{p}(K_{eq}K_{MeOH}) + \log\{[(6b)]/[(6)]\} \quad (12)$$

equilibrium constant for formation of (6b) in 'neat' methanol and K_{MeOH} is the autoprotolysis constant for methanol (pK_{MeOH} 16.92)].[52] The experimental determination of the ratio log{[(6b)]/[(6)]} in this method requires a knowledge of the molar absorptivity, ε, for complex (6b). The ε value for (6b) in pure DMSO has been reported to be *ca.* 30 000.[30] Since it is known that the amount of DMSO affects both wavelength and molar absorptivity values for σ complexes,[53,55] an ε value for (6b) in neat methanol was determined. This was done *via* measurement of absorbances of (6b) at several DMSO concentrations and extrapolation to zero DMSO concentration. Table 4 shows the spectral data from which an ε value of *ca.* 20 000 for (6b) in methanol was determined.

TABLE 4

Spectral data of (6b) in different methanol–DMSO solvent mixtures

DMSO (% v/v)	λ_{max}/nm	A_{max} [a]	ε
0 [b]	510	0.64 ± 0.06	(2.0 ± 0.5) × 10^4
30	510	0.805	2.5 × 10^4
40	510	0.860	2.7 × 10^4
50	511	0.925	2.9 × 10^4
60	512	0.950	2.9 × 10^4
70	513	0.965	3.0 × 10^4
80	514	0.990	3.1 × 10^4
90	515	1.010	3.1 × 10^4

[a] Absorbance due to complete complex formation of (6b) at a particular DMSO concentration; [(6)] = 3.2 × 10^{-5}M; [NaOMe] = 1.0M measured against appropriate blank solution. [b] Extrapolated to zero DMSO concentration.

Using this value, ratios of [(6b)]/[(6)] could be determined at different methoxide ion concentrations and the equilibrium constants were caculated by use of equation (12). Table 3 lists the different log {[(6b)]/[(6)]} terms as well as K_{eq} determined at different J_M values due to the methanolic sodium methoxide solvent system. A combination of these determined K_{eq} values with equation (5) and the k_ψ values with equation (4) allows for the calculation of k_1 and k_{-1} for formation of (6b). These values are also presented in Table 3 as function of NaOMe concentration. As can be seen from Figure 2, both k_1 and k_{-1} decrease curvilinearly with increasing concentration of sodium methoxide. Extrapolation to zero methoxide ion concentration in Figure 2 gives values of 11.2± 0.5 l mol^{-1} s^{-1} for k_1, and 124 ± 4 s^{-1} for k_{-1} in neat methanol. These results in pure methanol can be compared *via* extrapolation to those obtained previously for the same reaction in methanol–DMSO co-solvent system.[28] The two sets of values thus obtained agree quite well.

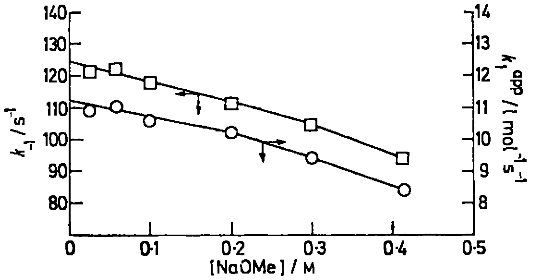


FIGURE 2 Plots of k_{-1} (□), and k_1 (○), for the interaction of methanolic sodium methoxide with (6) at 25.3°

1,5-Dinitronaphthalene (7). Compound (7) is con-

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[52] C. H. Rochester, 'Acidity Functions,' Academic Press, New York, 1970, pp. 740—752.

[53] M. R. Crampton, M. A. El Ghariani, and H. D. Khan, *J.C.S. Perkin II*, 1972, 1178.

[54] F. Terrier, *Ann. Chim. (France)*, 1969, **4**, 153.

[55] C. F. Bernasconi and H. S. Cross, *J. Org. Chem.*, 1974, **39**, 1054.

siderably less reactive towards nucleophiles than (6). Detailed investigations could only be carried out for the interaction of methoxide ion with (7) in 90 : 10 (v/v) DMSO–MeOH solutions. Interaction of methoxide ion to (7) results in formation of complex (7b) which has absorption band centred at 380 nm (Figure 3). The observed pseudo-first-order rate constants, k_ψ^{f}, 380 nm, were determined by stop-flow and are summarized in Table 5 as a function of methoxide ion concentration.

TABLE 5

Interaction of sodium methoxide with 1,5-dinitronaphthalene in DMSO–CH_3OH 90 : 10 (v/v) at 24.9°

$10^2[NaOCH_3]/M$	$A_{380\ nm}$	$k_\psi^{f,380\ nm}/s^{-1}$	$10^4k_\psi^{d,380\ nm}/s^{-1}$	$10^4k_\psi^{NO_2^-}/s^{-1}$	$10^5k_\psi^{f,460\ nm}/s^{-1}$
1.90		0.750		1.2	
2.20	0.240				
2.50			1.67		
2.77				2.0	
3.30			2.43		
3.60	0.310		2.64		
3.82		0.874			
4.50			4.21		
4.66					2.10
4.80				5.1	
5.00			6.10		
5.70		1.06			
5.90	0.430				
6.60					2.27
6.75		1.14			
7.90	0.490				
10.0			7.36		
11.8		1.43			
13.0		1.58			2.87
14.2					
15.5	0.605				

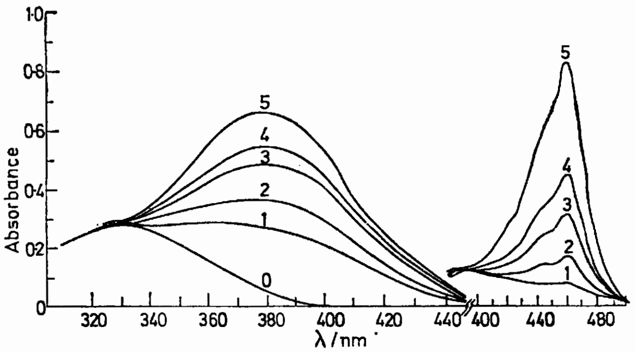
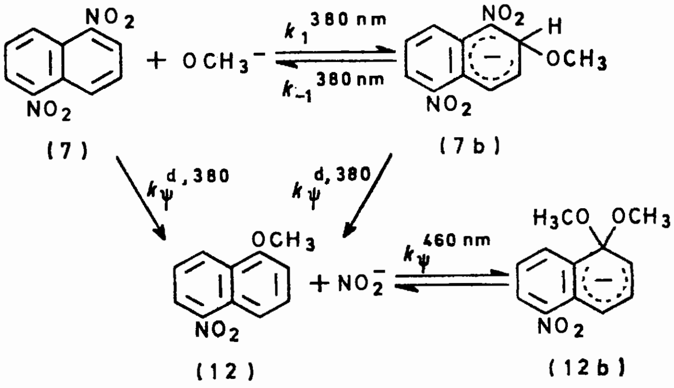


FIGURE 3 Absorption spectra of 5.0×10^{-5}M-(7) in DMSO–MeOH (90 : 10) (v/v). Left, immediately after mixing; right, one day subsequent to mixing. Concentration of sodium methoxide: 0 (0); 2.2×10^{-2}M (1); 3.6×10^{-2}M (2); 5.9×10^{-2}M (3); 7.9×10^{-2}M (4); 15.5×10^{-2}M (5)

By use of equation (4), values of 7.4 l mol^{-1} s^{-1} and 0.60 s^{-1} were calculated for $k_1^{380\ nm}$ and k_{-1}^{380nm} respectively. The kinetic equilibrium constant, K, was determined to be 12.3 l mol^{-1} by use of equation (5). This compares very well with the thermodynamic equation constant of 16.5 l mol^{-1} which was determined by use of equations (6) and (7).

Species (7b) decomposes slowly, by a first-order process, to product (12). The rate constant for this decomposition, k^{d}_{ψ}, ^{380} nm, increases with increasing methoxide ion concentrations. More significantly, nitrite ion is liberated at a rate which parallels the decomposition of (7b) (Table 5). At the completion of this process (95% reaction) one equivalent of nitrite ion has been liberated. In basic media, (12) is also unstable. It undergoes a first-order decomposition to (12b). In the alkaline media, (12b) is stable over days; however in acid it decomposes to (12). Upon addition of base, (12b) is re-formed from (12). Rate constants for the equilibrium formation of (12b) are also given in Table 5. These data are compatible with the Scheme which has been partially verified by a ^1H n.m.r. spectroscopic investigation.

1,3,8-Trinitronaphthalene (8). Interaction of (8) with hydroxide ion in aqueous dioxan results in formation of the hydroxy-complex (8a). The observed pseudo-first-order rate constants, k_ψ, increased as the lyate ion concentration increased and values of k_1, k_{-1}, and K at 0.133, 5.0, and 12.5% dioxan were determined by use of equations (4) and (5). The data in 25% dioxan shows some deviance from linearity in the plot of k_ψ against [^-OH] at high base concentrations. This could be the result of the true basicity of 25% aqueous dioxan media not paralleling the base concentrations in highly basic



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solutions [56,57] and due to changes in ionic strength of this medium. It was possible, however, to determine values of k_1, k_{-1}, and K by use of linear plot of k_ψ against [$^-$OH] in the 0—0.05M-base region. Values of k_ψ, k_1, k_{-1}, and K for the interaction of hydroxide ion with (8) in aqueous dioxan are given in Table **6**. At 5% dioxan, the equilibrium formation of (8a) was followed at three temperatures (Table 6) which allowed for the calculation of the Arrhenius parameters. From a fairly linear Arrhenius plot, values of 14.2 ± 1.9 kcal mol^{-1} and -9.4 ± 1.8 cal mol l^{-1} were calculated for $E_1^\ddagger$ and $\Delta S_1^\ddagger$, respectively. These values correspond closely to those obtained for similar Meisenheimer complexes.[3,4] Treatment of spectral data due to (8a) in 0.133% dioxan at different hydroxide ion concentrations by use of equations (6) and (7) resulted in a good linear relationship from which values of ($1.9 \pm 3 \times 10^{-4}$ l mol^{-1} cm^{-1}) and 42.8 ± 5 l mol^{-1} were calculated for ε and K. This equilibrium constant is in fair agreement with that determined kinetically by use of equation (5) (50 ± 20 l mol^{-1}). The kinetic equilibrium constants at 5% dioxan are also in fair agreement with those analogously determined from spectral data (see Table 6).

TABLE 6

Interaction of 1,3,8-trinitronaphthalene(8) with sodium hydroxide [a]

1,4-Dioxan (% v/v)	10^3[NaOH]/M	k_ψ/s^{-1} [b]	k_1/l mol^{-1} s^{-1}	k_{-1}/s^{-1}	K/l mol^{-1}
0 [c]			3.8 ± 1.1	0.12 ± 0.05	43 ± 15
0.133	2.0	0.133	5.0 ± 1.0	0.12 ± 0.04	50 ± 20 (42.8 ± 5) [d]
	4.0	0.142			
	5.0	0.147			
	6.0	0.154			
	8.0	0.158			
	10.0	0.170			
	20.0	0.230			
5.00 [e]	9.0	0.23	5.7 ± 0.1	0.17 ± 0.01	35 ± 5 (42.8) [d]
	18.0	0.26			
	26.0	0.34			
	40.0	0.42			
	45.0	0.44			
	90.0	0.70			
	140	0.98			
5.00 [e] (at 14.5°)	7.5	0.07	2.5 ± 0.2	0.05 ± 0.01	50 ± 12 (40.0) [d]
	14.5	0.10			
	28.7	0.12			
	60.0	0.19			
	92.5	0.26			
	137	0.40			
	180	0.45			
	300	0.80			
	343	0.90			
5.00 [e] (at 34.5°)	7.5	0.30	13.0 ± 0.1	0.25 ± 0.04	50 ± 10 (38.7) [d]
	14.7	0.50			
	28.7	0.56			
	60.0	0.96			
	138	2.00			
	200	2.80			
	343	4.71			
12.5 [e]	24.0	0.49	10.2 ± 0.1	0.25 ± 0.04	42 ± 7
	46.6	0.76			
	97.5	1.25			
	138	1.62			
	202	2.28			
25.0 [e]	11.0	0.40	18.7 ± 2 [f]	0.20 ± 0.05 [h]	100 ± 25
	22.0	0.66			
	32.5	0.87			
	51.8	1.30			
	94.0	2.00			
	133	2.42			
	268	3.58			

[a] [1,3,8-Trinitronaphthalene] = 7.3×10^{-5}M. Followed in a Beckmann Kintrac VII spectrophotometer at 500 nm at 25.0° unless stated otherwise. [b] Duplicate runs, each within ±4.0%. [c] Estimated values from plots of k_1 and k_{-1} against [dioxan]. [d] Obtained from absorbances by the use of equations (6) or (7). [e] Followed by stop-flow. [f] Values determined from fairly linear plot of k_ψ against [$^-$OH] in the 0—0.05M-NaOH region.

The limited solubility of (8a) in water necessitated the use of dioxan as co-solvent. Stabilities of (8a) were slightly enhanced with increasing concentrations of dioxan. Enhancement of the equilibrium constants for Meisenheimer complex formation by dipolar aprotic solvents is well recognized [58] and is generally the consequence of an increase in k_1 and a decrease in k_{-1}.[10,14,16] Interestingly, dioxan behaves somewhat differently. Enhanced stability of (8a), and of some other complexes

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[56] B. J. Yager and L. F. Kuntschik, *Texas J. Sci.*, 1971, **23**, 211.

[57] J. Janata and R. D. Holtby-Brown, *J.C.S. Perkin II*, 1973, 991.

[58] A. J. Parker, *Adv. Phys. Org. Chem.*, 1965, **5**, 173; A. J. Parker, *Chem. Rev.*, 1969, **69**, 1.

(see later) with increasing concentrations of dioxan as co-solvent is the result of either increases in *both* k_1 and k_{-1} or increases in k_1 while k_{-1} remains essentially constant. Values of k_1 and k_{-1} for the formation of (8a) are linear functions of dioxan concentrations. While the meaning of these linear relationships is not entirely clear [10,14,16] they are, once again, utilized for the extrapolation of rate constants to zero co-solvent concentrations. Table 6 contains these values.

Thermodynamic parameters for the reactions governed by k_1 and k_{-1} in the equilibrium formation of (8b) were calculated from linear Arrhenius plots and subsequent utilization of the absolute rate equation. Energies and entropies of activation both for the forward and reverse reaction (Table 7) resemble closely the corresponding values for the methoxy-adduct of 1,3,5-trinitrobenzene (E_1 10.8, E_{-1} 9.8 kcal mol^{-1}, $\Delta S^{\ddagger}_1$ −6.7, and $\Delta S^{\ddagger}_{-1}$ −16.3 cal mol^{-1} K^{-1}).[59,60]

TABLE 7

Interaction of 1,3,8-trinitronaphthalene with methanolic sodium methoxide[a]

Temp. (°C)	10^2[NaOCH$_3$]/M	$10^{-1}k\psi$/s^{-1}	k_1/l mol^{-1} s^{-1}	k_{-1}/s^{-1}	K/l mol^{-1} [b]
15.30	0.00		204.3	10.6	19.2 (13.7) [c]
	1.18	1.37			
	2.35	1.49			
	3.55	1.74			
	5.00	2.10			
	6.75	2.53			
	10.60	3.22			
25.30	0.00		304.6	22.0	13.8 (13.5) [c]
	0.40	2.37			(14.4) [d]
	0.90	2.48			
	2.00	2.86			(16.4) [c]
	2.60	3.06			
	3.85	3.11			
	5.60	3.78			
	7.90	4.50			
35.50	0.00		910.2	31.4	29.3 (16.7) [c]
	1.25	4.10			
	2.35	5.33			
	4.00	6.65			
	5.25	8.22			
	6.50	9.03			

E_1 12.2 ± 1.3 kcal mol^{-1} E_{-1} 11.5 ± 1.0 kcal mol^{-1} $\Delta S^{\ddagger}_1$ −7.9 ± 0.5 cal mol^{-1} K^{-1} $\Delta S^{\ddagger}_{-1}$ −15.0 ± 1.0 cal mol^{-1} K^{-1}

[a] [1,3,8-Trinitronaphthalene] = 7.5×10^{-5}M. Followed at 495 nm by stop flow. [b] Kinetic equilibrium constants, $K = k_1/k_{-1}$, unless stated otherwise. [c] Thermodynamic equilibrium constant, obtained from equations (6) and (7). [d] Thermodynamic equilibrium constant, obtained from equation (8).

Table 7 summarizes rate constants for the attainment of equilibrium for the methoxy-adduct of (8) in methanol, (8b), as well as values for k_1, k_{-1}, and K. In addition to determining these values kinetically, the equilibrium constants were also determined by use of equations (6)—(8). Figure 4 illustrates treatment of the data according to equations (6) and (8). Equilibrium constants calculated from these plots are in good agreement with those determined kinetically (Table 7).

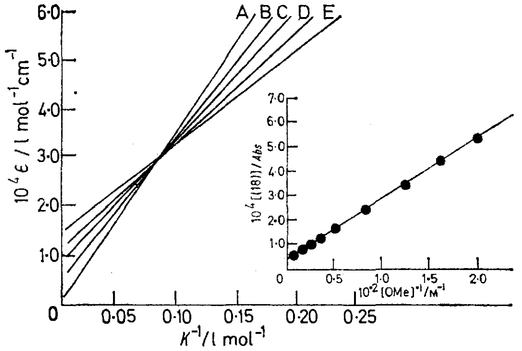


FIGURE 4 Drago plot of ε against K^{-1} for the formation of (8b) from 7.5×10^{-5}M-(8) in methanol at 25.30° at: 5.0×10^{-3}M-(A); 2.0×10^{-2}M-(B); 6.0×10^{-2}M-(C); 8.0×10^{-2}M-(D); and 1.0×10^{-1}M-(E)–sodium methoxide. The insert shows the same data treated by equation (6)

Subsequent to the attainment of the equilibrium, (8b) slowly decomposes to form the final products as shown by the general equation (9). This decay could be conveniently followed by measuring the decrease of absorbance due to (8b) spectrophotometrically as a function of time. Pseudo-first-order rate constants for the decomposition of (8b), k_d, were calculated from linear plots of log $(A_t - A_\infty)$ against time. Values of k_d, determined from both the *in situ* generated and isolated (8b) complex in appropriate methanolic sodium methoxide, agreed well (Table 8). A plot of $1/k_d$ against 1/[OCH$_3$] according to equations (10) or (11) should, therefore, give a straight line whose intercept and slope allows the calculation of K and k_2 or k_2' for the two possible kinetic pathways as shown in equation (9). Table 8 contains the obtained values for k_2, k_2', and K. Considering the uncertainties in taking intercepts, agreement among the equilibrium constants obtained kinetically from k_1/k_{-1} [equation (5)] from k_d [equations (10) or (11)] or from the absorbance [equations (6)—(8)] is satisfactory (Tables 7 and 8).

1,4,5-*Trinitronaphthalene* (9). Addition complexes of 1,4,5-trinitronaphthalene are considerably less stable than (8a or b). Attainment of the equilibrium could only be followed for the hydroxy-complex of (9), (9a), in

[59] V. Gold and C. H. Rochester, *J. Chem. Soc.*, 1964, 1692.

[60] C. F. Bernasconi, *J. Amer. Chem. Soc.*, 1970, **92**, 4687.

the presence of dioxan co-solvent. Rate constants for the equilibrium formation of (9a), k_ψ, increased linearly with increasing hydroxide ion concentration. Equations (4) and (5) were used, therefore, to calculate values of k_1, k_{-1}, and K. These values, at different dioxan concentrations, are given in Table 9. The satisfactory linear plot of k_1 against dioxan concentration (not shown) allows the determination of k_1 in neat water.

TABLE 8

Decomposition of the methoxy Meisenheimer complex of 1,3,8-trinitronaphthalene in methanol at 24.4° [a]

10^2[NaOCH$_3$]/M	$10^5k_d/s^{-1}$ [b]	$10^5k_2/s^{-1}$ [c]	$10^4k_{2'}$/l mol^{-1} s^{-1} [d]	K/l mol^{-1}
0.00		4.4 ± 1.4	3.4 ± 0.6	8.5 ± 1.5 [c] 7.0 ± 1 [d]
4.90	1.26 (1.23)			
6.67	1.58			
9.33	1.65 (1.68)			
18.3	3.00 (2.97)			
36.2	3.92			
73.3	5.04 (4.96)			

[a] [1,3,8-Trinitronaphthalene] = 6.6 × 10^{-5}M, followed spectrophotometrically at 495 nm. [b] Values in parentheses are obtained by following the decomposition of the isolated crystalline complex (8b). [c] Calculated from equation (10). [d] Calculated from equation (11).

TABLE 9

Interaction of 1,4,5-trinitronaphthalene with sodium hydroxide at 25.0° [a]

1,4-Dioxan (% v/v)	10[NaOH]/M	$10^2k_\psi/s^{-1}$	k_1/l mol^{-1} s^{-1}	$10^2k_{-1}/s^{-1}$	K/l mol^{-1}
0			0.08 ± 0.02 [b]	1.8 ± 1.0 [c]	7 ± 5 [d]
5.00	3.7	6.9	0.13 ± 0.01	1.6 ± 0.3	8 ± 2
	5.0	7.9			
	12.5	18.0			
	15.3	22.0			
10.00	5.0	8.6	0.14 ± 0.01	1.5 ± 0.5	11 ± 4
	7.6	11.9			
	9.9	14.1			
	12.5	18.2			
	15.0	22.3			
15.0	5.0	12.6	0.18 ± 0.02	2.5 ± 0.5	7.0 ± 2
	7.6	17.5			
	9.9	21.6			
	12.5	25.3			
	15.0	31.9			
20.0	5.0	12.7	0.22 ± 0.06	1.4 ± 0.8	25 ± 12
	7.6	18.7			
	10.0	22.4			
	12.4	30.6			
	15.0	35.2			
25.0	2.1	7.2	0.25 ± 0.02	2.4 ± 0.6	11.5 ± 3
	3.1	10.5			
	4.1	12.5			
	6.3	17.8			
	10.2	27.4			

[a] [1,4,5-Trinitronaphthalene] = (1—7) × 10^{-5}M, followed by the stop-flow spectrophotometer. [b] Extrapolated values from plots of k_1 against [dioxan]. [c] Estimated from plot of k_{-1} against [dioxan]. [d] $K = k_1/k_{-1}$; based on k_1 and k_{-1} as determined in footnotes *b* and *c*.

The reverse rate step, k_{-1}, did not vary appreciably (within experimental error) with dioxan concentration and a value was estimated for neat water. This allows the estimation of the rate and equilibrium constants for the formation of (9a) in water (Table 9). It is seen that (8a) is approximately six-fold more stable than (9a).

The lesser stability of Meisenheimer complexes formed from (9) as compared with those from (8), is even more evident from our investigations of the interaction of (9) with methanolic sodium methoxide. Addition of methanolic solutions of (9) results in the formation of a new absorption band, centred at 340—345 nm [ε (1.9 ± 0.4)10^4 l mol^{-1} cm^{-1}]. No detectable peak was apparently observed which could be ascribed to the formation of the methoxy Meisenheimer complex of (9), (9b). Taking point by point the spectrum 10—20 ms subsequent to mixing (9) with concentrated sodium methoxide, there appears to be a small peak, centred between 440—500 nm which could be due to (9b). Attempts to follow the equilibrium attainment of (9b) directly at this wavelength resulted in erratic and irreproducible results. Fast formation and decay as well as small absorbances are likely to be responsible for this failure. The absorption band at 340—347 nm is due to the formation of products, governed by rate constant k_2 or k_2' [equation (9)] rather than that due to a Meisenheimer complex. Rate constants for product formation, k_f, were calculated from good linear plots of log ($A_\infty - A_t$) against time. Table 10 presents k_f values as functions of sodium methoxide concentrations at different temperatures. These data can be treated by use of either equation (10) or (11) which allows for the calculation of k_2, k_2', and K values. Figure 5 illustrates plots of $1/k_f$ against $1/[OCH_3^-]$ and the obtained values for k_2, k_2', and K are given in Table 10. Activation energies and entropies of activation for product formation, governed by k_2' (or k_2) depending on the two possible paths, were calculated to be 15.8 ± 3.4 (18.0 ± 1 kcal mol^{-1}) and —5.1 ± 1.5 (—0.8 ± 0.3 cal mol^{-1} K^{-1}) respectively, from linear Arrhenius plots.

TABLE 10

Interaction of 1,4,5-trinitronaphthalene with sodium methoxide in methanol [a]

Temp. (°C)	$10^2[NaOCH_3]/M$	$10^3k_f/s^{-1}$ [b]	$10^3k_{NO_2^-}/s^{-1}$ [c]	$10^2k_2/s^{-1}$ [d]	$k_{2'}$/l mol^{-1} s^{-1} [f]	K/l mol^{-1}
14.3	3.94	2.34		*e*	0.05 ± 0.01	*e*
	6.87	3.86				
	9.18	6.35				
	15.0	14.4				
	47.0	205				
24.6	0.70		0.76	5 ± 2	0.10 ± 0.02	2.8 ± 0.3 [d]
	1.11		1.22	(5 ± 3)	(0.13 ± 0.02)	(2.3 ± 0.3) [d]
	2.25	2.74				2.0 ± 0.5 [f]
	2.60		2.12			(1.9 ± 0.05) [f]
	3.31	4.08				
	4.50	5.35				
	5.10		4.71			
	6.00	8.55				
	6.75	9.70				
	8.00	10.3	10.3			
	11.25	16.75				
	12.04		12.42			
	17.50	33.2				
	19.50	35.3	35.2			
35.0	1.08	5.10		20 ± 15	0.26 ± 0.04	1.6 ± 0.5 [f]
	3.16	8.80				1.5 ± 0.5 [d]
	6.17	15.9				
	7.33	23.7				
	11.7	45.7				
	13.7	57.6				
45.0	1.83	11.4		40 ± 5	0.6 ± 0.1	1.5 ± 0.2 [d]
	3.12	18.2				1.6 ± 0.3 [f]
	4.00	22.4				
	6.86	46.2				
	9.25	50.5				

[a] [1,4,5-Trinitronaphthalene] = 6.9 × 10^{-7}M. [b] Product build-up followed spectrophotometrically at 340 nm. [c] Pseudo-first-order rate constants for nitrite ion liberation. [d] Calculated from equation (10) using k_f values. Values in parentheses were analogously obtained using rate constants for nitrite ion liberation. [e] Intercept was too small to be meaningfully determined. [f] Calculated from equation (11) using k_f values. Values in parentheses were analogously obtained using rate constants for nitrite ion liberation.

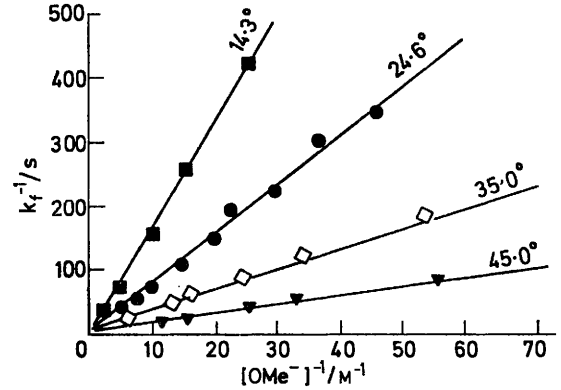


FIGURE 5 Plot of $1/k_f$ against $1/[OMe^-]$ for the formation of final product at 345 nm from the decomposition of (9b), at 14.3, 24.6, 35.0, and 45.0°

If k_f represents product formation [equation (9)] then this reaction should be paralleled by the liberation of one equivalent of nitrite ion. This is found to be the case; in most instances 70—100% of the nitrite ion is released. The rate of nitrite ion release follows first-order kinetics. The observed rate constants for nitrite ion release, $k_{NO_2^-}$, are also given in Table 10. Good agreement between rate constants for products formation, k_f, and those for nitrite ion release, $k_{NO_2^-}$, substantiate the proposed scheme. Furthermore, treating $k_{NO_2^-}$ values according to equation (10) or (11) ($k_f = k_{NO_2^-}$) results in a good linear relationship giving values for k_2, k_2', and K which are in good agreement with those obtained from k_f (Table 10). The equilibrium constant for the formation of the methoxy Meisenheimer complex of (9), (9b), is some seven times smaller than that for (8b). This and the analogous result for $K_{(9a)}/K_{(8a)}$ is explicable in terms of the proximity of the 4- and 5-nitro-groups with the resultant decrease in the resonance stabilization of the developing Meisenheimer complex.

1,3,6,8-*Tetranitronaphthalene* (5). Interaction of methanolic sodium methoxide with (5) results in the rapid development of a new absorption maxima at 480 nm, which is attributable to the formation of the methoxy Meisenheimer complex of (5), (5b). The observed pseudo-first-order rate constants for equilibrium attainment, k_ψ, increase linearly with increasing sodium methoxide concentration (Table 11). A plot of k_ψ against $[NaOCH_3]$ allows, therefore, the calculation of k_1. It is seen, however, that the intercept is very small and k_{-1} cannot be meaningfully obtained from this

TABLE 11

Interaction of 1,3,6,8-tetranitronaphthalene(5) with methanolic sodium methoxide [a]

Temp. (°C)	10^3[NaOCH$_3$]/M	k_ψ/s^{-1}	$10^{-4}k_1$/l mol^{-1} s^{-1}	k_{-1}/s^{-1} [b]	$10^{-3}K$/l mol^{-1} [c]
14.3	1.10	6.50	1.33		
	2.12	30.0			
	5.50	69.0			
	10.0	131			
	14.8	197			
	21.2	256			
25.3	1.10	23.0	2.32	$\lesssim 3$	$\gtrsim 7.7$
	2.50	61.5			
	5.70	137			
	6.80	182			
	10.0	222			
35.3	1.00	39.0	3.82	$\lesssim 8$	$\gtrsim 4.8$
	20.0	74.9			
	3.25	129			
	4.00	150			
	5.00	191			

E_1 8.2 ± 0.5 kcal mol^{-1} $\Delta S^\ddagger$ −11.8 ± 1.0 cal mol^{-1} K^{-1}

[a] [1,3,6,8-Tetranitronaphthalene] = 5×10^{-5}M. [b] Maximum value of k_{-1} as estimated from plot of k_ψ against [$^-$OMe] according to equation (4). [c] Minimum value of K calculated from equation (5) using maximum value of k_{-1}.

TABLE 12

Interaction of 1,3,5,8-tetranitronaphthalene(10) with aqueous sodium hydroxide at 24.6° [a]

10^4[NaOH]/M	10^3k_ψ/s^{-1}	$10^3k_{\mathrm{NO_2^-}}$/s^{-1}	k_1/l mol^{-1} s^{-1}	10^2k_{-1}/s^{-1}	(k_2) [c] or ($k_{2'}$) [d]	K/l mol^{-1}
2.50	22.3		12.8 ± 1	2.00 ± 0.08		(640 ± 20) [b]
5.00	25.9					
7.50	29.6					
10.0	32.5					
15.0	39.3					
25.0		1.33			(2.2 ± 0.1 × 10^{-3} s^{-1}) [c]	(590 ± 20) [c]
30.0		1.40			(1.2 ± 0.1 l mol^{-1} s^{-1}) [d]	(560 ± 20) [d]
50.0		1.67				
70.0		1.81				
100.0		1.92				

[a] [1,3,5,8-Tetranitronaphthalene] = 6.6×10^{-5}M, 0.17% dioxan, v/v. [b] Calculated from k_1/k_{-1}. [c] Calculated by using equation (10). [d] Calculated by using equation (11).

TABLE 13

Interaction of 1,3,5,8-tetranitronaphthalene (10) with methanolic sodium methodide [a]

Temp. (°C)	10^2[NaOCH$_3$]/M	$10^{-1}k_\psi$ [b] /s^{-1}	$10^{-3}k_1$/l mol^{-1} s^{-1}	k_{-1}/s^{-1}	K/l mol^{-1}
7.5	0.28	1.89	3.92	8.2	477.4
	0.50	2.50			
	0.80	3.91			
	1.10	5.37			
	1.88	8.20			
13.7	0.21	1.25	4.24	5.1	831.4
	0.50	2.23			
	0.75	3.45			
	1.00	4.84			
	1.25	5.85			
18.5	0.28	3.52	6.63	18.5	360.0
	0.50	5.06			
	0.75	6.38			
	1.10	8.51			
	2.00	15.9			
24.5	0.13	0.25	7.90	18.0	438
	0.25	0.36			
	0.50	0.55			
	0.75	0.78			
	1.20	1.10			
	1.70	1.54			
34.5	0.15	0.69	17.5	44.0	396
	0.29	0.82			
	0.49	1.28			
	0.61	1.50			
	0.78	2.00			
	1.00	2.20			

E_1 9.6 ± 2.0 kcal mol^{-1} E_{-1} 13.0 ± 0.4 kcal mol^{-1} $\Delta S^\ddagger_1$ −10.4 ± 1.5 cal mol^{-1} K^{-1} $\Delta S^\ddagger_{-1}$ −11.1 ± 5 cal mol^{-1} K^{-1}

[a] [1,3,5,8-Tetranitronaphthalene] = (5—8) × 10^{-5}M. [b] Results are reproducible to ±5%.

plot. A maximum value of k_{-1} is estimated from these plots from which a minimum value of K can be calculated. These values are also in Table 11. The activation parameters for formation of (5b) as determined from a linear Arrhenius plot is also given in Table 11.

Attempts to determine the equilibrium for the formation of (5b) from absorbance data by the Benesi–Hildebrand, Scott, or Drago methods met with failure, due to the completeness of the equilibrium even at very low *ca.* (10^{-6}M) reactant concentrations.

Decomposition of (5b) is extremely slow. Rate constants for product formation or nitrite ion liberation, therefore, were not obtained.

TABLE 14

Decomposition of the methoxy Meisenheimer complex of 1,3,5,8-tetranitronaphthalene (10) in methanol at 24.5° [a]

$10^2[NaOCH_3]$/M	$10^2k_d/s^{-1}$ [b]	(k_2) [c] or (k'_2) [d]	K/l mol^{-1}
0.49	1.13 (1.10)	0.018 ±0.002 s^{-1} [c]	300 ±20 [c]
0.76	1.37	5.5 ±0.1 l mol^{-1} s^{-1} [d]	280 ±20 [d]
1.15	1.43 (1.44)		
1.40	(1.58)		
1.56	1.64		
3.33	1.76 (1.79)		

[a] [1,3,5,8-Tetranitronaphthalene] = 8.0 × 10^{-5}M.

[b] Pseudo-first-order rate constants obtained by following the decay of (10b) at 490 nm. Values in parentheses are those determined from following the appearance of the final products at 345 nm, k_f. [c] Calculated by use of equation (10). [d] Calculated by use of equation (11).

TABLE 15

Liberation of nitrite ion from (10) in methanol at 24.5° [a]

$10^2[NaOCH_3]$/M	$10^2k_{NO^-_2}/s^{-1}$	% NO^-_2 released [b]	(k_2) [c] or (k_2') [d]	K/l mol^{-1}
0.60	1.27	78	0.025 ± 0.008 s^{-1} [c] 5.0 ± 0.5 l mol^{-1} s^{-1} [d]	130 ± 10 [c] 200 ± 25 [d]
0.83	1.50	90		
1.64	1.69	100		
2.20	1.85	87		
2.65	2.20	102		

[a] [(10)] = (5—9) × 10^{-5}M. [b] Percent of NO_2 released per mole of starting material (10). [c] Calculated by use of equation (10). [d] Calculated by use of equation (11).

1,3,5,8-*Tetranitronaphthalene* (10).—Addition of sodium hydroxide to 1,3,5,8-tetranitronaphthalene (10) results in the equilibrium of Meisenheimer complex (10a). Rate constants for the formation and decomposition of (10a) are in Table 12. Rate constants for nitrite ion liberation $k_{NO^-_2}$ were also determined at different sodium hydroxide ion concentrations. Values of k_2, k_2', and K were calculated from the slope and intercept of plot of data according to equations (10) or (11). All these results are summarized in Table 12.

Interaction of methanolic sodium methoxide with (10) results in the equilibrium formation of Meisenheimer complex (10b) which subsequently decomposes with the elimination of one equivalent of nitrite ion. The pseudo-first-order rate constant for the equilibrium attainment of (10b), and values for k_1, k_{-1}, and K in methanol at different temperatures are given in Table 13. Energies and entropies of activation were calculated from linear Arrhenius plots, and are included in Table 13.

Table 14 lists the pseudo-first-order rate constants for the decomposition of (10b), k_d, followed spectrophotometrically at 480 nm, as well as those for the product formation, k_f, at 345 nm. Rate constants for nitrite ion liberation have also been determined (Table 15). Reciprocals of these pseudo-first-order rate constants, $1/k_d$, $1/k_f$, and $1/k_{NO^-_2}$ plotted linearly, against the reciprocal of sodium methoxide concentration (Figure 6)

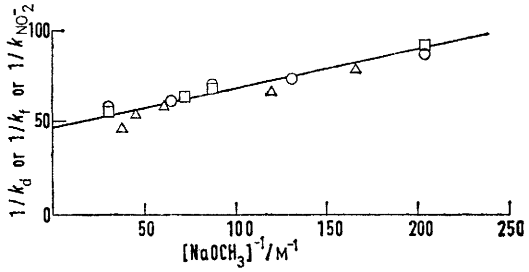


FIGURE 6 Plots of $1/k_d$ (○), $1/k_f$ (□), and $1/k_{NO^-_2}$ (△) against $1/[NaOCH_3]$ for the interaction of sodium methoxide with (10) at 24.5°

yield values of k_2 and K [using equations (10) or (11)]. Considering the uncertainties involved in obtaining equilibrium constants from these equations, agreement among the K values, determined by different methods (Tables 13—15) is fair. The equilibrium constant could not be determined from spectral data by use of the Benesi–Hildebrand, Scott, or Drago treatments because the equilibrium is complete even at very small sodium methoxide concentations.

1,4,5,8-*Tetranitronaphthalene* (11).—In contrast to (5), the stabilities of the Meisenheimer complexes (11a and b) formed by the interaction of hydroxide of methoxide ions with (11), are relatively small. Additionally the low solubility of (11) in water precluded kinetic determination in this media. Table 16 presents the k_ψ, k_1, k_{-1}, and K values for the interaction of hydroxide ion with (11) in water containing different amounts of dioxan as co-solvent. Relationships between k_1 or k_{-1} and the concentration of dioxan is not straight forward. The k_1 values in the 10—20% dioxan region remain essentially constant with increasing dioxan concentration, whereas at higher dioxan concentration the rate constant for the formation of (11a) increase with increasing concentrations of the dipolar aprotic solvent.

TABLE 16

Interaction of 1,4,5,8-tetranitronaphthalene(11) with sodium hydroxide at 25.0° [a]

1,4-Dioxan (% v/v)	10^2[NaOH]/M	k_ψ/s^{-1}	k_1/l mol^{-1} s^{-1}	k_{-1}/s^{-1}	K/l mol^{-1}
0 [b]			40 ± 10	0.10 ± 0.02	300 ± 100 (340 ± 30) [c]
10.0	1.0	0.66	39.5 ± 0.5	0.24 ± 0.04	170 ± 30
	2.5	1.16			
	5.0	2.38			
	7.5	3.18			
	10.0	4.47			
	15.0	5.85			
	20.0	7.98			
15.0	2.0	1.07	34.6 ± 0.5	0.35 ± 0.1	115 ± 25
	4.0	1.79			
	6.0	2.63			
	8.0	3.02			
	10.0	3.87			
20.0	2.0	1.30	35.0 ± 0.2	0.45 ± 0.05	80 ± 10
	4.0	1.85			
	6.0	2.56			
	8.0	3.27			
	10.0	3.83			
25.0	2.0	2.04	55.0 ± 0.1	1.00 ± 0.02	52 ± 4
	4.0	3.18			
	6.0	4.42			
	8.0	5.25			
	10.0	6.47			
30.0	2.0	3.20	94.5 ± 0.1	1.25 ± 0.05	75 ± 4
	6.0	6.58			
	8.0	8.75			
	10.0	10.7			
40.0	2.0	4.14	92 ± 5	2.4 ± 0.5	40 ± 10
	4.0	5.72			
	6.0	7.01			
	8.0	10.4			
	10.0	12.2			

[a] [1,4,5,8-Tetranitronaphthalene] = (4—8) × 10^{-5}M. [b] Estimated values from plots of k_1, k_{-1} against % dioxan in the 10—40% dioxan region. [c] Extrapolated from linear plot of log K against % dioxan in the 10—25% dioxan region.

TABLE 17

Interaction of 1,4,5,8-tetranitronaphthalene(11) with methanolic sodium methoxide [a]

Temp. (°C)	10^2[NaOCH$_3$]/M	k_ψ/s^{-1}	$10^{-3}k_1$/l mol^{-1} s^{-1}	k_{-1}/s^{-1}	K/l mol^{-1}
9.0	1.42	15.3	1.00	2.5 ± 1.0	420 ± 80
	2.08	19.3			
	3.42	26.9			
	7.50	73.6			
	8.65	95.3			
	23.8	245			
13.5	0.90	13.2	1.59	6.5	243
	1.65	26.6			
	2.88	45.0			
	4.50	84.0			
	7.00	130			
	11.7	195			
25.3	0.75 [b]	22.0	1.82 [b]	10.0 [b]	182 [b]
	0.90	23.0	1.96	10.0	196
	1.65	50.6			
	2.00 [b]	47.0			
	2.87	62.1			
	4.37 [b]	94.1			
	4.50	98.2			
	6.25 [b]	115			
	7.00	141			
	8.50 [b]	165			
34.0	1.00	38.0	2.89	19.0	152
	2.00	85.0			
	3.40	118			
	4.50	158			
	7.30	232			

E_1 7.25 ± 1.5 kcal mol^{-1} E_{-1} 12.0 ± 1.5 kcal mol^{-1} $\Delta S^\ddagger_1$ −21.1 ± 2.0 cal mol^{-1} K^{-1} $\Delta S^\ddagger_{-1}$ −15.7 ± 2.0 cal mol^{-1} K^{-1}

[a] [1,4,5,8-Tetranitronaphthalene] = 5.0 × 10^{-5}M, followed at 480 nm, unless stated otherwise. All of the solutions contained 1.0% dioxan (v/v). [b] Followed at 380 nm.

Conversely k_{-1} increases curvilinearly with increasing dioxan concentration. The overall effect of dioxan on the equilibrium constant ($K = k_1/k_{-1}$) manifest in an initial logarithmic decrease of K values, up to 25% dioxan, while in the 25—40% dioxan region, K remains independent of changes in the solvent composition. Although fully expected, such a complicated solvent effect on Meisenheimer complex equilibria has not been encountered previously. Clearly dioxan affects the activity coefficients of initial and transition states of the species involved in a unique manner. The equilibrium constant for the formation of (11a) obtained from extrapolation of the linear portion of log K against dioxan concentration (not shown), should be viewed with reservation and considered to be accurate only within an order of magnitude.

TABLE 18

Kinetic parameters for Meisenheimer complexes of polynitrosubstituted naphthalenes at 25°

Structure	σ Complex	k_1/l mol^{-1} s^{-1}	k_{-1}/s^{-1}	K/l mol^{-1}
(II; L = OH, $R^1 = R^2 = H$)	(6a)	0.29 ± 0.05	1.12 ± 0.2	0.26 ± 0.05
(II; L = OMe, $R^1 = R^2 = H$)	(6b)	11.2 ± 0.5	124 ± 4	0.09 ± 0.01
(II; L = OH, $R^1 = NO_2$, $R^2 = H$)	(8a)	3.8 ± 1.1	0.12 ± 0.05	43 ± 15
(II; L = OMe, $R^1 = NO_2$, $R^2 = H$)	(8b)	304 ± 6	22 ± 3	13.8 ± 2
(II; L = OH, $R^1 = R^2 = NO_2$)	(5a)	250 [a]	0.225 [a]	1.1×10^4 [a]
(II; L = OMe, $R^1 = R^2 = NO_2$)	(5b)	2.3×10^4	($\lesssim$3)	($\gtrsim$7 700)
(III; L = OH, $R^1 = R^2 = H$)	(9a)	0.08 ± 0.02	0.018 ± 0.01	7.0 ± 5
(III; L = OMe, $R^1 = R^2 = H$)	(9b)			1.5
(III; L = OH, $R^1 = NO_2$, $R^2 = H$)	(11a)	40 ± 10	0.10 ± 0.02	320 ± 100
(III; L = OMe, $R^1 = NO_2$, $R^2 = H$)	(11b)	1 820	10	182
(III; L = OH, $R^1 = H$, $R^2 = NO_2$)	(10a)	12.8 ± 1	0.02 ± 0.08	640 ± 20
(III; L = OMe, $R^1 = H$, $R^2 = NO_2$)	(10b)	7 900	18	428

[a] Ref. 13.

Addition of sodium methoxide to dilute methanolic solutions of (11) results in the formation of a brownish yellow colour which has absorption maxima at 380 and 480 nm (Figure 7). The attainment of equilibrium for the methoxy-complex of (11), (11b), was followed at different temperatures (Table 17). Values of k_1 and k_{-1} were obtained from linear plots of k_ψ against [Na-OCH$_3$]. At 25°, rate constants for the formation and decomposition of (11b) were determined by following the equilibrium attainment at both 380 and 480 nm. There is good agreement between the rate and equilibrium constants determined at these two wavelengths (Table 17).

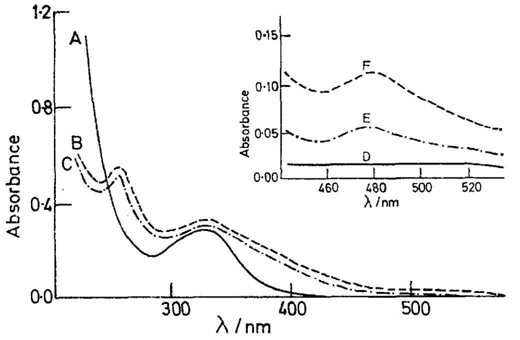


FIGURE 7 Absorption spectra of 4.1×10^{-5}M-(11) using a pair of 1.0 cm matched cells at 25.0°: A, in methanol; B, in 4.1×10^{-2}M methanolic NaOMe; C, in 8.7×10^{-2}M methanolic NaOMe. The insert shows the stop-flow point by point spectra of 8.0×10^{-5}M-(11) at 25.3° obtained after 60 ms reaction at the following methoxide ion concentrations: D, 0.00M; E, 5.0×10^{-2}M; F, 9.0×10^{-1}M

Following the rapid equilibrium attainment of (11b), there was a rather slow decrease of the 480 nm absorbance paralleled by a slow increase in the absorbance of the 330 nm peak, presumably due to product formation. Consistent with this idea was the observation of the slow liberation of nitrite ion at a rate which paralleled the absorbance changes. Rates of decomposition were not, however, determined quantitatively.

σ Complex Stability.—Table 18 summarizes the rate and equilibrium data obtained for formation of σ complexes from polynitronaphthalenes. The relative order of stability of either the hydroxy (a) or methoxy (b) Meisenheimer complexes is (7) < (6) < (9) < (8) < (11) < (10) < (5). This order of stability can be rationalized in terms of differences in the extent of electron delocalization due to both the number and location of the nitro-substituents in the parent compounds.

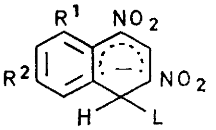
Specifically, there are two families of complexes whose stabilities can be compared and contrasted; namely, those of general structures (II) and (III). σ Complexes of (6), (8), and (5) fit general structure (II) and are conventional σ complexes in that the incoming lyate ion orients itself so that it is both *ortho* and *para* with respect to the two nitro-groups in the ring undergoing substitution.

The stability order of (6) < (8) < (5) parallels the increase in number of the nitro-groups in the second aromatic ring system. This is primarily the consequence of significant electron delocalization over the added nitro-group and π system of the second aromatic ring and a smaller inductive effect of the additional nitro-groups in the parent naphthalenes. In general, the order of stability is the composite effect of a substantial increase in forward equilibrium step, k_1, and a gradual decrease of reverse step, k_{-1}, on going from σ complexes (6) to (8) to (5). These results substantiate the belief that electronic effects can indeed be transmitted from one aromatic ring system to other rings undergoing substitution in substituted naphthalenes.[17]

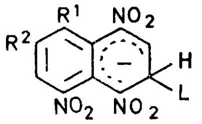
The sigma complexes of (9)—(11) appear to be of general type (III) in that the incoming nucleophile orients itself *ortho* and *meta* with respect to the two nitro-groups in the ring undergoing attack. These apparently appear to be the first reported naphthalene σ complexes of this type. The order of stability of these complexes is (7) < (9) < (11) < (10) and this order again reflects the effect of both the number and position of nitro-group present in the second aromatic ring on reactions occurring in the first ring system. σ Complexes of (10) or (11) are more stable than those of (9) because they have an additional nitro-group present which can delocalize developing charge density. The effect of location of the nitro-group is seen when comparing the relative stability of (10) to (11). Even though both have two nitro-groups in the second ring, (10) is of greater stability than (11). This is presumably due to the close proximity of the *peri*-nitro-groups in (11) which results in a decrease in the extent of electron delocalization in complexes of (11) owing to non-coplanarity of the nitro-groups with the π-system.[17]

It is also interesting to note that for naphthalenes with the same number of nitro-groups, complexes of type (II) are of greater stability than the corresponding ones of type (III). This is again presumably due to unfavourable steric interactions between the two *peri*-nitro-groups in complexes of type (III) which cause a loss of coplanarity of the nitro-groups which results in a decrease of electron delocalization, thus reduced stability.

Solvent Effects on Stability of σ Complexes.—The effects of added dipolar aprotic solvents such as DMSO [45] and to a lesser extent DMF [26] on the rate and equilibrium constants of formation of σ complexes has been well documented.[4,10,16,24,26,28] In general the enhanced stability is due to an increase in k_1 and a decrease in k_{-1} as the amount of dipolar aprotic co-solvent is increased. The increase in k_1 is attributed to the enhanced nucleophilicity of the lyate ion which results from desolvation of the small, highly charged lyate ion as the percentage of dipolar aprotic component is increased. The decrease in k_{-1} is presumably due to the enhanced solvation of the large, polarizable anionic σ complexes in DMSO or DMF co-solvent.[4] Indeed, comparison of all available data suggests that there is a linear free energy type correlation between either the specific rate [24] or equilibrium [37] constants of σ complexes and the amount of dipolar aprotic cosolvent present.



(II)



(III)

Data obtained in DMSO on the rate and equilibrium constants for formation of hydroxy-complex of (6), (6a) (Table 2) or methoxy-complex (6b), conforms well with these expectations.

Conversely, the effects of added dioxan are markedly different (Tables 6, 9, and 16). It is seen that increasing amounts of dioxan (0—25%) only slightly increase the magnitude of rate of formation, k_1, of hydroxy-complexes (8a), (9a), and (11a). These results are similar to those observed for DMSO except that the rates increase to a lesser extent in dioxan.

The decomposition rates, k_{-1}, of the hydroxy-complexes appear to remain essentially constant [for (8a) and (9a)] or increase [for complex (11a)] as the amount of dioxan co-solvent is increased. Apparently, dioxan does not stabilize the large σ complexes as effectively as DMSO. These results are in agreement with observations of Bowden [61,62] who reported that ' unlike DMSO, dioxan cannot effectively solvate and stabilize extended-charge structures such as Meisenheimer complexes.' [61] As often stated,[58] complete understanding of the role solvents play on reaction rates requires elucidation of their effects on the relative activity coefficients of the initial and transition states. Evidently, the relative changes of the activity coefficients of σ complexes (8a), (9a), and (11a) and of the transition states leading to their decomposition in dioxan are significantly different than that in DMSO.

The changes in equilibrium constant as a factor of dioxan concentration are the result of specific changes in k_1 and k_{-1}. As can be seen, depending on exact effects on k_1 and k_{-1}, the equilibrium constant can increase [for (8a)], decrease [for (11a)] or essentially remain constant [(9a)] as dioxan concentration is varied. This is again quite different behaviour from that exhibited by DMSO or DMF.

Thus, incremental changes in dioxan concentration does not lead to regular or predictable changes in k_1, k_{-1}, or K as was found using DMSO or DMF co-solvent.[24,37]

^{1}H *N.m.r. Studies.*—The ^{1}H n.m.r. data for the isolated or *in situ* formed Meisenheimer complexes and their parent polynitronaphthalenes are in Tables 19—21.

TABLE 19

^{1}H N.m.r. spectra of 1,3,8-trinitronaphthalene (8) and its methoxy Meisenheimer complex (8b) [a]

	(8)	(8b)
	τ	
	0.40 (d, 2-H)	1.24 (d, 2-H) (1.22)
	0.98 (d, 4-H)	4.16 (d, 4-H) (4.22)
	1.17 (m, 5-, 7-H)	2.22 (m, 5-, 7-H) (2.23)
	1.90 (t, 6-H)	2.65 (dd, 6-H) (2.70)
	J/Hz	
$J_{2,4}$	2.3	2.0
$J_{5,6}$	7.9	7.0
$J_{6,7}$	7.9	7.8

[a] Chemical shifts at 100 MHz, in [$^2H_6$]DMSO with Me_4Si as standard. Values in parentheses are chemical shifts for the *in situ* generated complexes, by the dropwise addition of 2.8M-$KOCH_3$ to 10% solutions of the trinitronaphthalene in [$^2H_6$]DMSO.

These data are consistent with the structural assignments given for complexes (7b)—(10b) and (12b). The arguments supporting these assignments are entirely ana-

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[61] K. Bowden, R. F. Cook, and M. J. Price, *J. Chem. Soc.* (*B*), 1971, 1778.

[62] K. Bowden and M. J. Price, *J. Chem. Soc.* (*B*), 1971, 1784.

TABLE 20

^{1}H N.m.r. spectra of 1,4,5-(9), 1,3,5,8-(10), and 1,4,5,8- tetranitronaphthalene (11) and their Meisenheimer complexes [a]

(9)	(10)	(11)	(9b)	(10b) [c]
		τ		
	0.18 (d, 2H)		0.56 (q, 6-H) (0.58) [b]	0.825 (d, 2-H)
1.35 (m, 2-, 3-, 6-, 8-H)				
1.82 (q, 7-H)			3.11 (t, 7-H) (3.14)	
	0.51 (d, 4H)		2.87 (q, 8-H) (2.90)	1.38 (d, 4-H)
			4.73 (d, 2-H) (4.76)	1.73 (d, 6-H)
	0.85 (d, 6-, 7-H)			
			4.93 (d, 3-H) (4.98)	3.76 (d, 7-H)
		1.17 (d, 2-, 3-, 6-, 7-H)		
		J/Hz		
$J_{6,7}$ 8.7			$J_{6,7}$ 7.9 (7.9)	
$J_{7,8}$ 7.2			$J_{7,8}$ 7.9 (7.8)	
	$J_{2,4}$ 2.2		$J_{6,8}$ (1.5)	$J_{2,4}$ 2.4
	$J_{6,7}$ 2.0		$J_{2,3}$ (3.6)	$J_{6,7}$ 9.8

[a] Chemical shifts at 100 MHz, in $[^2H_6]$DMSO unless stated otherwise with Me$_4$Si as standard. [b] Values were obtained for the complex generated *in situ* by the addition of 4.00M aqueous KOH to *ca.* 2M solutions of (9) in $[^2H_6]$DMSO. [c] Values were obtained for the complex generated *in situ* by the addition of 2.90M-KOCH$_3$ in MeOH to *ca.* 2M solutions of (10) in $[^2H_6]$DMSO.

logous to those advanced previously [13,63,64] and will, therefore, not be reiterated here.

TABLE 21

Spectra of 1,5-dinitronaphthalene (7) and its methoxy Meisenheimer complex (7b)

(7)		(7b)
	τ	
2.035 [a] (q, 3-, 7-H)		4.75 (m, 2-H)
1.545 [a] (dd, 2-, 6-H)		4.30 (d, 3-H)
1.37 [a] (dd, 4-, 8-H)		2.90 (m, 6-, 7-, 8-H)
	J/Hz	0.82 (m, 4-H)
$J_{4,3}$ 8.1 (~8.0) [c]		
$J_{2,3}$ 8.6 (~8.0) [c]		
$J_{2,4}$ 1.0 (~1.0) [c]		

[a] Average value determined from lines of maximum intensity. [c] Coupling constant in DMAC, reported by P. R. Wells, *J. Chem. Soc.*, 1963, 1967.

Literature reports show that in many activated aromatic systems, initial attack of the nucleophile has been observed by ^{1}H n.m.r. calorimetric, u.v.–visible spectral, and stop-flow techniques to occur at different positions on the ring resulting in the formation of relatively short-lived transients which quickly revert to the thermodynamically more stable σ complexes.[3,4,9,24,28] However, the ^{1}H n.m.r. data of the *in situ* generated complexes studied in this work show no evidence to suggest the presence of such short-lived transients. Hence, in these experiments, no additional resonances could be observed and therefore, on the ^{1}H n.m.r. time scale, these transients are either not formed or are not detectable under the experimental conditions employed.

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[4/2688 *Received, 23rd December,* 1974]

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[63] R. Foster, C. A. Fyfe, P. H. Emslie, and M. I. Foreman, *Tetrahedron Letters*, 1967, 227.

[64] S. Sekiguchi and T. Shiojima, *Bull. Chem. Soc. Japan*, 1973, **46**, 693.