of monohydroxy Meisenheimer complex, **5** (singlets at 8.23 (2 H) and 6.07 ppm (1 H)). In 0.05 M NaOD the signals of the dihydroxy complex, **6**, appeared (singlets at 8.36 (1 H) and 5.28 ppm (2 H)). With higher [NaOD] we saw no evidence for formation of trihydroxy complex, although there is electronic spectral evidence for its formation in aqueous NaOH. The solubility of 1,3,5-trinitrobenzene in D_2O is low, and because of hydrogen exchange[19] we could not use a long accumulation time, so we have no NMR evidence for complex formation in D_2O.

Acknowledgment. Support of this work by the National Science Foundation (Organic Chemical Dynamics Program) and the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged. Award of a NATO grant to F.O. is gratefully acknowledged. We thank Dr. T. C. Bruice for use of a scanning stopped-flow spectrometer, Dr. R. M. Crampton for sending us unpublished results, and Dr. F. J. Weigert for providing us with his GEAR program for chemical kinetics.

Registry No. 1a, 88-88-0; **1b**, 16655-63-3; **3**, 14798-26-6; **4**, 99-35-4; **5**, 113976-48-0; **6**, 63657-42-1; **7**, 113976-51-5; **12a**, 113976-49-1; **17a**, 113976-50-4.

Supplementary Material Available: Appendix illustrating the way in which the significance and error of rate constants have been evaluated and the calculation of time-concentration profiles by using an integration program for the reactions of 1,3,5-trinitrobenzene, 2,4,6-trinitrochlorobenzene, and 2,4,6-trinitrobenzenesulfonate with OH^- (8 pages). Ordering information is given on any current masthead page.

Single-Electron Transfer in Aromatic Nucleophilic Substitution in Reaction of 1-Substituted 2,4-Dinitronaphthalenes with Hydroxide Ion

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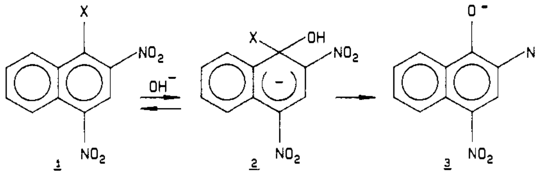
Received October 8, 1987

Abstract: Reactions of 1-substituted 2,4-dinitronaphthalenes with OH^- in water-DMSO involve very rapid formation of a π-complex of the substrate and OH^-, and then promotion of an electron from the unpaired n-orbital of OH^- to the antibonding π^*-orbital of the substrate gives a charge-transfer complex. For chloro and bromo derivatives these complexes rearrange to 3-Meisenheimer complexes and to 1-complexes that immediately give naphtholate product. But with the fluoro and dialkylamino derivatives only 1-Meisenheimer complexes are detected and they decompose relatively slowly to the naphtholate. With the 1-methoxy derivative no 3-Meisenheimer complex is detected, and the 1-Meisenheimer complex goes rapidly to naphtholate. The slow decomposition of the fluoro and dialkylamino 1-Meisenheimer complexes is base catalyzed. Rate and equilibrium constants for the individual reactions can be estimated by the application of relaxation theory. The differences in reactivity of 1-substituted 2,4-dinitronaphthalenes are due not only to the electronic and steric effects of the leaving groups, as predicted by the simple slow addition-fast elimination mechanism but also to changes in the rates of the individual reaction steps and partitioning of the intermediates.

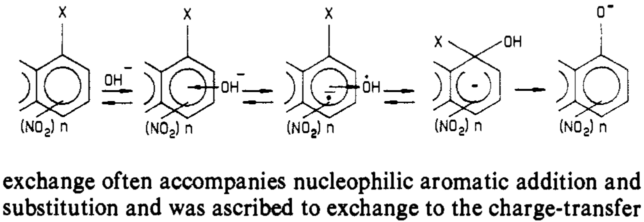
Nucleophilic aromatic substitution in aqueous solvents is generally written[2] as a rate-limiting formation of a short-lived Meisenheimer complex, as shown in Scheme I for reactions of dinitronaphthalene derivatives with OH^-.

This reaction scheme cannot explain reactions of OH^- with nitroarenes that appear to involve rapid formation of a π-complex that is rapidly transformed into a charge-transfer complex of an arene radical anion and a hydroxyl radical, and this complex collapses to reactive, or unreactive, Meisenheimer complexes.[3,4] This mechanism is consistent with the identification of π-complexes[5] and anion radicals[6] as intermediates in nucleophilic aromatic substitutions, especiallly in aprotic solvents. Hydrogen exchange often accompanies nucleophilic aromatic addition and substitution and was ascribed to exchange to the charge-transfer complex with water.[4a]

Scheme I



Scheme II



An oversimplified reaction seequence (Scheme II) does not include possible formation of a 3-Meisenheimer complex (cf. ref 3 and 4b) that does not go directly to products or of deprotonated charge-transfer or Meisenheimer complexes.

In this paper we discuss reactions of OH^- with a series of 1-substituted 2,4-dinitronaphthalenes (**1a-e**, X = Cl, Br, F, CH_3O, and morpholino) and analyze the effect of X upon the various reaction steps.

Results

1-Chloro- and 1-Bromo-2,4-dinitronaphthalene (1a,b). These compounds have similar reactivities toward OH^- and are inter-

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[1] The award of a NATO grant for F.O. is gratefully acknowledged.

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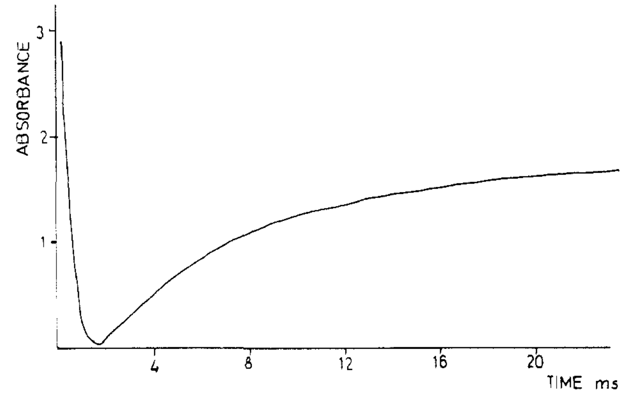

Figure 1. Time dependence of absorbance at 255 nm for the reaction of 1-chloro-2,4-dinitronaphthalene (**1a**) (5×10^{-5} M) with 1 M KOH in 1:1 (v/v) DMSO:H_2O at 25.0 °C (arbitrary ordinate).

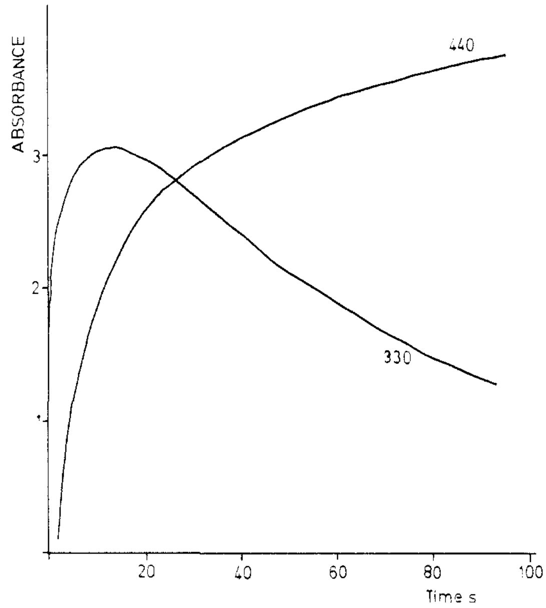

Figure 2. Time dependence of absorbance at 330 and 440 nm for the reaction of 1-chloro-2,4-dinitronaphthalene (**1a**) (5×10^{-5} M) with 0.6 M KOH in 1:1 (v/v) DMSO:H_2O at 25.0 °C (arbitrary ordinate).

mediate in reactivity between the 1-chloro(bromo)-2,4-dinitro- and 1-chloro-2,4,6-trinitrobenzenes. The reported relative rates for the overall reaction depend upon the nucleophile.[7-10]

Attack of OH^- upon 1-chloro-2,4,6-trinitrobenzene gives both the phenoxide ion and a 3-Meisenheimer complex that slowly disappears,[4b,11] but no such complex has been reported for substitutions upon the corresponding 1-chloro(bromo)-2,4-dinitronaphthalenes, and we therefore examined the possible formation of this and other intermediates.

When **1a** is mixed with OH^- in 1:1 (v/v) H_2O:DMSO, a species absorbing at 520 nm is formed too rapidly to be followed in a stopped-flow spectrometer. It rapidly disappears and a species absorbing at 255 nm appears with a similar reciprocal relaxation time. The disappearance at 520 nm is difficult to follow accurately because of interference due to mixing that also gives an absorbance decrease. It is therefore convenient to follow the increase of absorbance at 255 nm (Figure 1). This second intermediate gradually disappears and a new absorbance, followed at 330 nm, appears with the same relaxation time. This absorbance at 330 nm goes through a maximum and eventually 2,4-dinitronaphtholate is formed and it absorbs at 440 nm (Figure 2 and Table I). These slower steps can also be followed by repetitive scanning of the reaction mixture (Figure 3). The first scan was made 2 s after mixing and an intermediate appears with maxima or shoulders at 260, 290, 360, and 450 nm. There is parallel formation of 2,4-dinitronaphtholate ion, which absorbs at 270, 390, and 440 nm, and the intermediate has disappeared within 300 s and the spectrum is that of the naphtholate ion. The reaction of 1-bromo-2,4-dinitronaphthalene is similar.

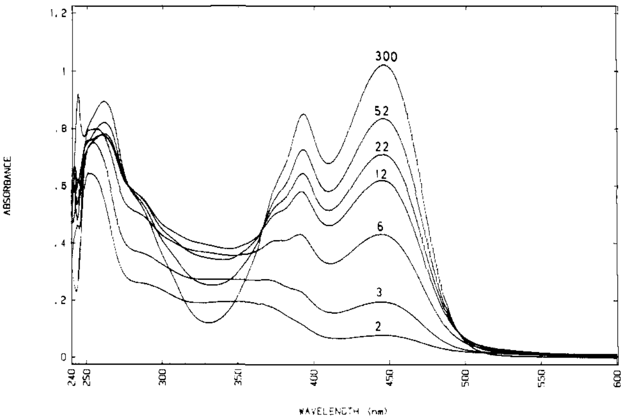

Figure 3. Repetitive scan of absorbance for the reaction of 1-chloro-2,4-dinitronaphthalene (**1a**) (5×10^{-5} M) with 1 M KOH in 1:1 (v/v) DMSO:H_2O at 25.0 °C. Time in seconds is indicated for each scan.

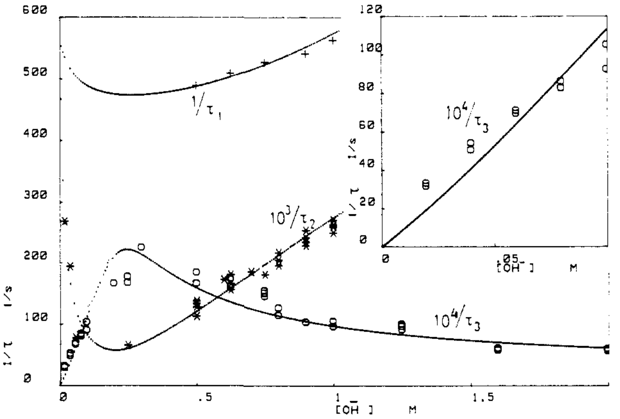

Figure 4. Simulation of the relaxation times for the reaction of 1-chloro-2,4-dinitronaphthalene (**1a**) with KOH in 1:1 (v/v) DMSO:H_2O at 25.0 °C.

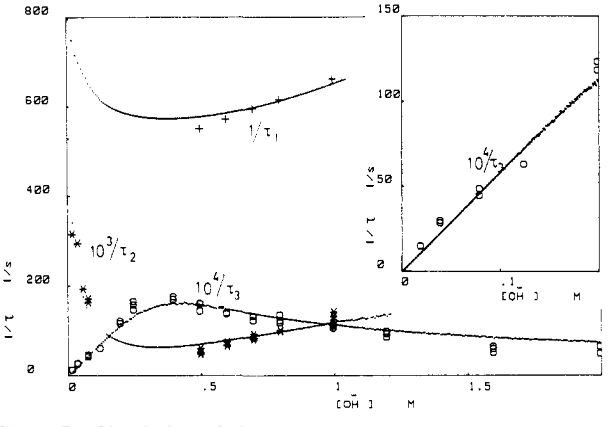

Figure 5. Simulation of the relaxation times for the reaction of 1-bromo-2,4-dinitronaphthalene (**1b**) with KOH in 1:1 (v/v) DMSO:H_2O at 25.0 °C.

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Table I. Reciprocal Relaxation Times for the Reaction of 1-Chloro-2,4-dinitronaphthalene (**1a**) with OH^{-a}

	$1/\tau_1$	$10^3/\tau_2$				$10^4/\tau_3$		
[KOH], M	255 nm^b	255 nm^c	330 nm^b	440 nm^b	520 nm^b	330 nm^c	520 nm^c	440 nm^b
0.02			267^d			32.4		34.1
0.04			193^d			51.4		55.0
0.06			77^d			70.4		72.0
0.08						83.6		87.9
0.1						93.3		106
0.2						169		
0.25		65.2				170		180
0.3						228		
0.5	488	127	137	112	133	169		187
0.625	508	155	172^e	165	180	164		177
0.75	526	180	185^f			148	153	157
0.8			204	195	216	117		129
0.9	540	227	233	240	252	106		106
1.0	562	248	261	258	269	99		107
1.25						103	94	99.5
1.6						63.9	61.1	60.9
2.0						62.7	60.0	63.0

[a] At 25.0 °C in 1:1 (v/v) DMSO:H_2O; $1/\tau$ in s^{-1}. [b] Appearance. [c] Disappearance. [d] At 360 nm. [e] 0.6 M OH^-. [f] 0.7 M OH^-.

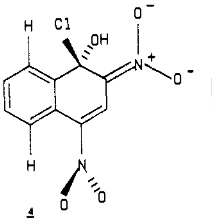
Table II. Reciprocal Relaxation Times for the Reaction of 1-Bromo-2,4-dinitronaphthalene (**1b**) with OH^{-a}

	$1/\tau_1$	$10^3/\tau_2$				$10^4/\tau_3$		
[KOH], M	255 nm^b	255 nm^c	355 nm^c	440 nm^b	520 nm^b	520 nm^c	330 nm^c	440 nm^b
0.02			313				15.4	15.5
0.04			293				29.1	30.4
0.06			192					
0.08		170	162				45.2	49.2
0.125								63.5
0.2							124	119
0.25						160	168	149
0.4							172	178
0.5	548	50.0		46.5	58.8	162	163	146
0.6	570	66.1		64.0	73.8	142		140
0.7	594	78.5		82.1	91.0	135		125
0.8	614	99.0		97.9		120	125	138
1.0	660	130		122	140	116	113	108
1.2						87.5	101	95.8
1.6						53.6	61.6	66.6
2.0						51.4	66.9	

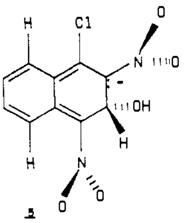
[a] At 25.0 °C in 1:1 (v/v) DMSO:H_2O; $1/\tau$ in s^{-1}. [b] Appearance. [c] Disappearance.

Three relaxations (τ_1, τ_2, and τ_3) can be followed for reaction of OH^- with 1-chloro and 1-bromo-2,4-dinitronaphthalene (**1a,b**) (Tables I and II and Figures 4 and 5). The first, followed by an increase at 255 nm, we postulate to involve conversion of a π-complex into a charge-transfer complex; cf. ref 4. The second relaxation we postulate to involve disappearance of a charge-transfer complex and was followed at 255nm, and parallel formation of a third intermediate was followed at 330 and 520 nm and the naphtholate ion was followed at 440 nm. This third intermediate, formed from the charge-transfer complex, is probably a 1- or 3-Meisenheimer complex. Only a 1-Meisenheimer complex is formed by attack of OH^- on dinitronaphthalene (**1**, X = H) and it absorbs at 360 and 490–540 nm,[12,13] but the situation may be more complex for an overall substitution, and this question is considered next.

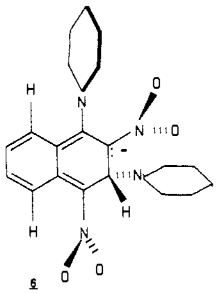
We know of no X-ray determination of the structure of 2,4-dinitronaphthalene or its Meisenheimer complex, but in 1,5-dinitronaphthalene both nitro groups are twisted out of the molecular plane by about 50° because of interaction with peri hydrogens.[14] Nitro groups adjacent to the halogen are twisted out of plane in 1-chloro- and 1-bromo-2,4-dinitrobenzene,[15] and this situation should hold for the corresponding naphthalene derivatives; thus in 1-chloro-2,4-dinitronaphthalene both nitro groups will be out of plane. However, in Meisenheimer complexes of trinitroanisole and phenetole the 2- and 6-nitro groups are not twisted out of plane.[16] Addition to C-1 in a 1-halo-2,4-dinitronaphthalene should therefore increase conjugation with the 2-nitro group, by allowing its coplanarity with the aromatic ring, but addition at C-3 decreases conjugation relative to that in the initial state, as shown in structures **4** and **5**.



4



5



6

These steric effects give a blue shift in the absorbance, and in the only reported formation to date of a long-lived 3-Meisenheimer complex the rapidly formed piperidino derivative (**6**) absorbs at 330 and 440 nm.[17] By analogy we assume that the

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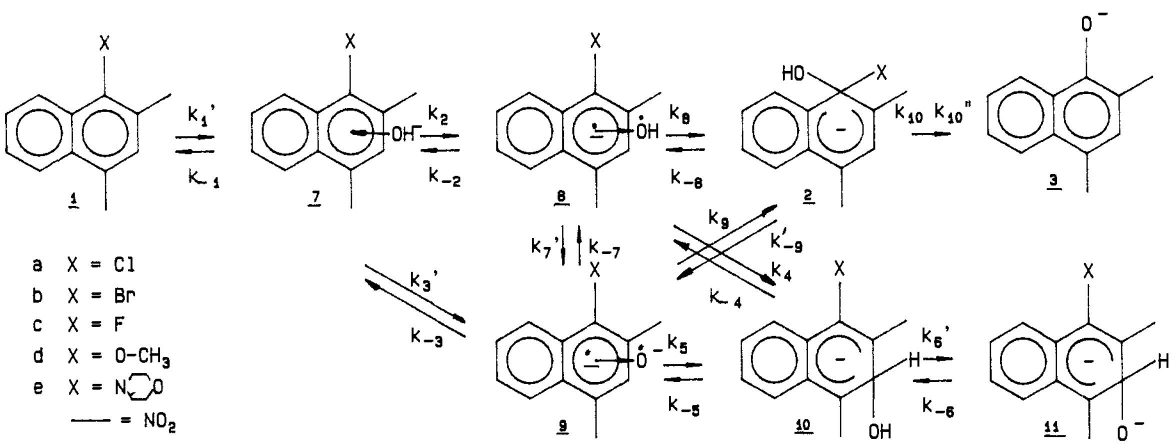
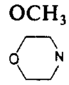
Scheme III



$k_1' = k_1[OH^-]$ $k_{-5}' = k_{-5}[OH^-]$ $k_6' = k_6[OH^-]$ $k_7' = k_7[OH^-]$ $k_{-9}' = k_{-9}[OH^-]$ $k_{10}'' = k_{10}'[OH^-]$

$k_3' = k_3[OH^-]$

Table III. Equilibrium Constants for the Reactions of 1-Substituted 2,4-Dinitronaphthalenes[a]

X	K_1, M^{-1}	K_2	K_3, M^{-1}	K_4	K_5, M	K_6, M^{-1}	K_7, M^{-1}	K_8	K_9, M
F	0.429	0.902	5.61				6.21	5.18	0.832
Cl	0.110	0.184	2.89	1.56	0.101	157	15.6		
Br	0.106	0.152	2.48	1.66	0.101	105	16.3		
OCH_3	0.176	1.14	5.29				4.63		
	0.194	0.789	7.17				9.07	2.12	1.30
Cl[b]	1.65	0.807	1.89	319	136	275	10.8		

[a] 25.0 °C, 1:1 (v/v) DMSO:H_2O. [b] For 2,4,6-trinitrochlorobenzene.[4b]

intermediates from reaction of OH^- with **1a** and **1b** absorbing at 260, 290, and 360 and very weakly at 450 nm (Figure 3) are the 3-complexes formed in parallel with the 1-complexes which rapidly lose halide ion to give the naphtholate ion. Eventually the 3-Meisenheimer complexes disappear and the final reaction products are formed in the third relaxation. The proposed overall reaction is shown in Scheme III, which also includes deprotonated charge transfer and Meisenheimer complexes **9** and **11**, respectively (cf. ref 4).

We used the kinetic analysis based on relaxation theory that has been described elsewhere.[18] The variations of the reciprocal relaxation times, τ^{-1}, with $[OH^-]$ (Tables I and III) are accounted for in terms of the rate and equilibrium constants for the various reactions shown in the overall Scheme III (Tables III and IV and Figures 4 and 5). These complex variations can be rationalized in terms of Scheme III. Values of τ_2^{-1} for formation of the 3-Meisenheimer complex (**10**) decrease sharply with increasing $[OH^-]$ and then increase. In dilute OH^- (0.02 M) base-catalyzed formation of the 3-Meisenheimer complex (**10**) can be neglected, but with increasing OH^- the equilibrium between **8** and **9** is favored (Scheme III) and **9** goes forward more slowly than **8**, as shown by the values of k_4 and k_5, or k_8 and k_9 (Table IV). At high OH^- an increase in the equilibrium formation of the complexes **7** and **8** leads to an increase in τ_2^{-1}.

In dilute OH^- τ_3^{-1}, which is governed largely by formation of naphtholate product, increases approximately linearly with $[OH^-]$ (Figures 4 and 5). There is no buildup of intermediate complexes, and the rate constants (k°_{c}) calculated from an equilibrium approximation agree well with the observed values (k°_{ex}) (Table IV). However, with an increase of $[OH^-]$, there is a buildup of the unreactive complexes **10** and **11** and a consequent slowing of the formation of the naphtholate ion.

It is more difficult to explain the decrease in τ_1^{-1} with OH^- in dilute OH^- predicted by relaxation theory (Figures 4 and 5), although because of the small absorbance changes under these conditions we could not test this prediction experimentally. We believe that in dilute OH^- τ_1^{-1} is governed mainly by values of k_2 and k_{-2}. With increasing $[OH^-]$ the charge-transfer complex **8** is deprotonated to give complex **9**, which returns more slowly to π-complex **7** than **8** (Table IV), and τ_1^{-1} decreases. These complex reactions cannot be rationalized, even qualitatively, except in terms of a scheme that allows all the rate constants to be included in predictions of values of the three reciprocal relaxation times.

Fluoro-, Methoxy-, and Morpholino-2,4-dinitronaphthalene (1c,d,e). Loss of halide ion from a 1-Meisenheimer complex should be fast for chloro and bromo derivatives in aqueous solvents, but the situation may be different with poor leaving groups.

Only 1-Meisenheimer complexes have been identified by NMR spectrometry in reactions of 1-methoxy-2,4-dinitronaphthalene with alkoxide ions,[12,13,19] and they absorb at 350 and 500 nm. However, in DMSO–MeOH with a higher DMSO content than 75% a transient species absorbing at 505 nm, with a shoulder at 550–600 nm, has been assumed to be a 3-Meisenheimer complex.[20] Reactions of aliphatic amines with 1-methoxy-2,4-dinitronaphthalene in similar conditions give only 1-complexes, based on NMR spectrometry,[21,22] and they absorb at 320–350 and 500–520 nm.[21] Similar observations have been made on reactions of MeO^- with 1-piperidino-2,4-dinitro- or -cycanonaphthalenes.[23] There is, however, evidence for short-lived 3-Meisenheimer complexes in reactions of 1-(dialkylamino)-2,4-dinitronaphthalene with MeO^- in 9:1 DMSO:MeOH.[24] These results suggest that 1- rather than 3-Meisenheimer complexes are formed preferentially in reactions of 1-methoxy- or 1-(dialkylamino)-2,4-dinitronaphthalene, except perhaps in dipolar aprotic solvents.

In 1:1 (v/v) DMSO:H_2O we saw three relaxations in reactions of OH^- with 1-morpholino- and 1-fluoro-2,4-dinitronaphthalene (**1e,c**) and two in the reaction with the 1-methoxy derivative (**1d**) (Tables V–VII). The wavelengths were chosen to give maximum absorbance changes and do not necessarily correspond to λ_{max} of the intermediates.

In these reactions a species absorbing at ca. 500 nm was formed too rapidly to be followed by stopped-flow spectrometry. It is

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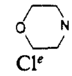
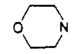
Table IV. Rate Constants for the Reactions of 1-Substituted 2,4-Dinitronaphthalenes[a]

X	k_2, s^{-1}	k_{-2}, s^{-1}	k_3, M^{-1} s^{-1}	k_{-3}, s^{-1}	k_4, s^{-1}	k_{-4}, s^{-1}	k_5, s^{-1}	k_{-5}, M^{-1} s^{-1}
F	285	316	701	125				
Cl	103	560	1270	440	2.00	1.28	0.039	0.387
Br	125	824	1270	512	2.58	1.55	0.039	0.384
OCH_3	632	553	2110	398				
	571	724	3140	437				
Cl[e]	260	322	320	169	206	0.65	210	1.54

X	k_8, s^{-1}	k_{-8}, s^{-1}	k_9, s^{-1}	k_{-9}, M^{-1} s^{-1}	k_{10}, s^{-1}	k'_{10}, M^{-1} s^{-1}	$k°_c$, M^{-1} s^{-1}	$k°_{ex}$, M^{-1} s^{-1}
F	21.2	4.09	119	143	0.798	0.235	1.59[b]	1.63
Cl	4.85	(4.77)	0.95	(14.5)	(119)		0.098[c]	0.099
Br	3.68	(11.2)	0.222	(11.0)	(184)		0.059[c]	0.057
OCH_3	8.10	(120)	0.005	(8.35)	(56.1)		0.51[b]	0.44
	0.942	0.446	0.369	0.284	0.294	1.49	0.095[d]	0.088
Cl[e]	6.76		97.0					

[a] At 25.0 °C in 1:1 (v/v) DMSO:H_2O. In parentheses are calculated values with no chemical significance; see text. [b] Calculated from the equilibrium approximation $k°_c = k_{10}K_1K_2K_8$. [c] Calculated from the equilibrium approximation $k°_c = k_{10}K_1K_2$. [d] Calculated from the steady-state approximation $k°_c = k_8K_1K_2k_{10}/(k_{-8} + k_{10})$. [e] For 2,4,6-trinitrochlorobenzene.[4b]

Table V. Reciprocal Relaxation Times for the Reaction of 1-Methoxy-2,4-dinitronaphthalene with OH^- [a]

[KOH], M	$1/\tau_1$ 330 nm[b]	$10^3/\tau_2$ 330 nm[c]	$10^3/\tau_2$ 440 nm[b]
0.02		9.3	9.4
0.04		18.5	18.2
0.06		27.1	27.4
0.08		36.8	36.2
0.1		48.1	46.1
0.15		69.8	68.1
0.2	528	83.0	81.0
0.3		144	158
0.4		170	156
0.5	584	199	
0.6	574[d]	224	
0.8	642	213	
1.0	722	202	
1.2		203	
1.4		190	
1.6		202	
2.0		186	

[a] At 25.0 °C in 1:1 (v/v) DMSO:H_2O; $1/\tau$ in s^{-1}. [b] Appearance. [c] Disappearance. [d] 0.7 M KOH.

Table VI. Reciprocal Relaxation Times for the Reaction of 1-Morpholino-2,4-dinitronaphthalene with OH^- [a]

[KOH], M	$1/\tau_1$ 330 nm[b]	$10^2/\tau_2$ 330 nm[b]	$10^3/\tau_3$ 330 nm[c]	$10^3/\tau_3$ 440 nm[b]
0.01			0.66	0.65
0.03			2.35	2.39
0.05			3.91	4.09
0.08			6.69	7.09
0.1			8.20	7.9
0.15			16.0	14.7
0.2			21.9	22.6
0.3	594			
0.4	516		46.3	48.4
0.5	556	140	64.0	70.5
0.6	578	162		
0.7		182	101[d]	115[d]
0.8	786	204		
0.9	856	232		
1.0	926	236	165	166
1.2			192	188
1.6			234	240

[a] At 25.0 °C in 1:1 (v/v) DMSO:H_2O; $1/\tau$ in s^{-1}. [b] Appearance. [c] Disappearance. [d] 0.75 M KOH.

probably a π-complex, 7 (Scheme III), and it disappears as species absorbing at 330 or 440 nm appear. We assume that this second species is a charge-transfer complex, as in similar reactions (Figures 4 and 5, Tables I and II, and ref 4b).

Table VII. Reciprocal Relaxation Times for the Reaction of 1-Fluoro-2,4-dinitronaphthalene with OH^- [a]

[KOH], M	$1/\tau_1$ 440 nm[b]	$1/\tau_2$ 440 nm[c]	$10^3/\tau_3$ 440 nm[c]
0.04			100
0.10	330	13.6	158
0.15			178
0.2	336	36.0	185
0.3	324	51.2	230
0.4	342	71.4	261
0.5	350	93.6	
0.6	375	103	295
0.7	408	124	
0.8	420	147	331
0.9	430	169	
1.0	480	201	333
1.2			320
1.4			331
1.6			325
1.8			300
2.0			325

[a] At 25.0 °C in 1:1 (v/v) DMSO:H_2O; $1/\tau$ in s^{-1}. [b] Disappearance. [c] Appearance.

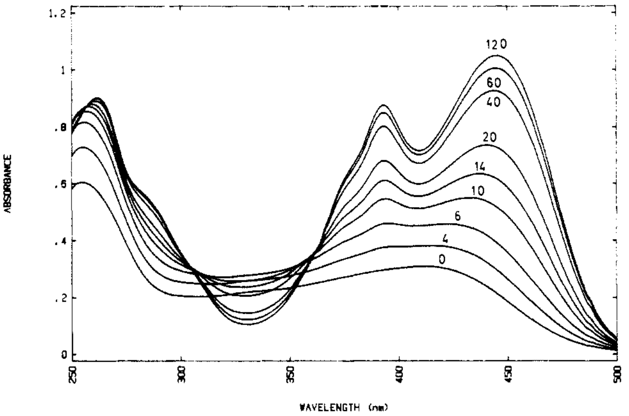


Figure 6. Repetitive scan of absorbance for the reaction of 1-morpholino-2,4-dinitronaphthalene (**1e**) (5×10^{-5} M) with 0.4 M KOH in 1:1 (v/v) DMSO:H_2O at 25.0 °C. Time in seconds is indicated for each scan.

With 1-methoxy-2,4-dinitronaphthalene (**1d**) the postulated charge-transfer complex goes readily to the naphtholate ion, but with the 1-fluoro and 1-morpholino derivatives we see a third intermediate, but the identification is difficult. This problem is illustrated for reaction of the 1-morpholino derivative (**1e**), which has λ_{max} at 260 and 420 nm (Figure 6). Within 6 s of addition of OH^- absorbances increase and are red shifted, and then the

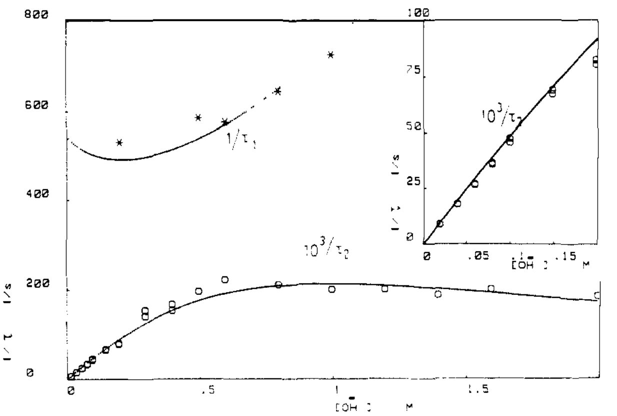


Figure 7. Simulation of the relaxation times for the reaction of 1-methoxy-2,4-dinitronaphthalene (**1d**) with KOH in 1:1 (v/v) DMSO:H_2O at 25.0 °C.

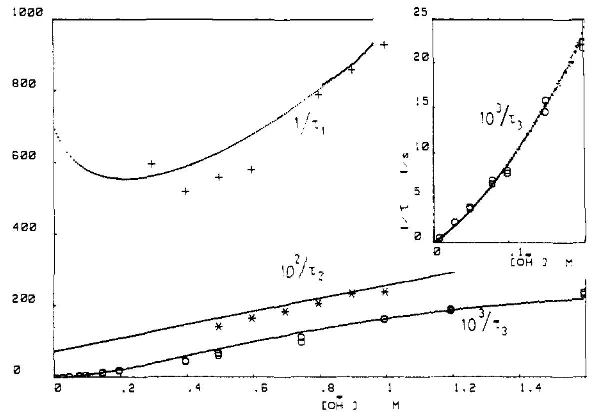


Figure 8. Simulation of the relaxation times for the reaction of 1-morpholino-2,4-dinitronaphthalene (**1e**) with KOH in 1:1 (v/v) DMSO:H_2O at 25.0 °C.

naphtholate ion appears, absorbing at 270, 390, and 440 nm. It is convenient to follow absorbance at 330 nm, because it goes through a maximum with time, and also absorbance of the naphtholate ion at 440 nm.

From evidence in the literature we assume that 1- rather than 3-Meisenheimer complexes are formed in additions to 1-methoxy- or 1-aminodinitronaphthalene. In systems in which 3-Meisenheimer complexes build up in concentration, e.g., with the trinitrobenzenes and **1a**,**b**, we see decreases in values of τ_3^{-1} with increasing [OH^-] (Figures 4 and 5, Tables I and II, and ref 4b), but we do not see this behavior with the fluoro, methoxy, or morpholino derivatives (**1c**,**d**,**e**) (Figures 7–9 and Tables V–VII). The rate data can be simulated in terms of Scheme III, on the assumption that 3-Meisenheimer complexes do not build up and that in the reactions of fluoro and morpholino derivatives the 1-Meisenheimer complex, **2**, is an observable intermediate, which goes relatively slowly to product, **3** (Figures 7–9). The rate and equilibrium constants are in Tables III and IV, and the calculated and observed second-order rate constants for overall reaction in dilute OH^- agree (Table IV).

Discussion

The reaction Scheme III for substitution reactions of OH^- with the dinitronaphthalenes is similar to those for addition to 1,3-dinitronaphthalene and addition and substitution reactions of trinitrobenzenes.[4b,18] The main differences are that we do not see dihydroxy Meisenheimer complexes with the naphthalene derivatives, and 3-Meisenheimer complexes (**10**) are seen only with 1-chloro- and 1-bromo-2,4-dinitronaphthalene (**1a**,**b**), although they may be present in low concentration in reactions of the other derivatives.

Formation of 3-Meisenheimer complexes from the chloro and bromo derivatives (**1a**,**b**) is due to the inductive effect that favors

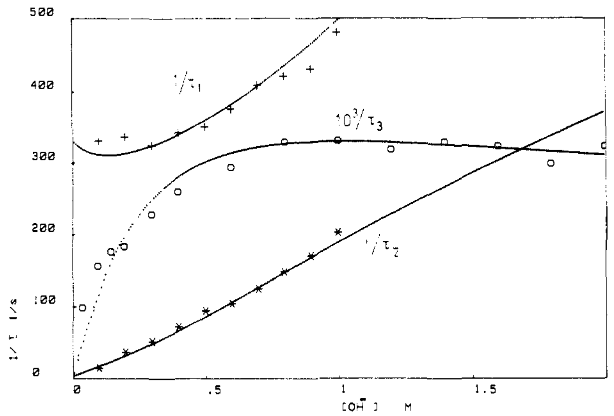


Figure 9. Simulation of the relaxation times for the reaction of 1-fluoro-2,4-dinitronaphthalene (**1c**) with KOH in 1:1 (v/v) DMSO:H_2O at 25.0 °C.

addition to the aromatic system and to a steric effect that decreases reactivity at position 1, and rapid loss of Cl^- or Br^- means that 1-Meisenheimer complexes should not build up. The small fluorine atom with its large inductive effect and the slow loss of F^- permit buildup of 1-Meisenheimer complex, **2**, and make possible observation of its base-catalyzed decomposition to the naphtholate ion. This conclusion is consistent with other evidence, especially for aminolysis of fluoronitro derivatives, which involve slow elimination of fluoride ion.[25] Acid decomposition of the Meisenheimer complex of 2,4,6-trinitrofluorobenzene with alkoxide ion gives only trinitrophenyl ether, but with the chloro derivative both 1- and 3-Meisenheimer complexes can form, and decomposition of the 3-complex regenerates substrate and only the 1-complex gives the ether.[26]

Some overall reactions of alkyl aryl ethers activated by nitro or cyano groups are general or specific base catalyzed, even in some protic solvents, which is consistent with buildup of slowly decomposing 1-Meisenheimer complexes.[21a,27] However, in our conditions the 1-Meisenheimer complex of OH^- and 1-methoxy-2,4-dinitronaphthalene does not build up and it is a steady-state intermediate (Table IV). But base catalysis becomes important in the morpholino derivative because of slow elimination of the leaving group (Table IV).

Separation of the individual rate and equilibrium constants for reactions of the trinitrobenzene and dinitronaphthalene derivatives allows comparison of the factors that control overall reaction rates. Values of the constants for reactions of 1-chloro-2,4,6-trinitrobenzene and 1-chloro-2,4-dinitronaphthalene in 1:1 (v/v) DMSO:H_2O are compared in Tables III and IV.

The estimated value of K_1 for formation of the π-complex is larger in the 1,3,5-trinitrobenzene derivative, but values of K_2 are similar and K_3 for the naphthalene is larger. These differences are consistent with the naphthalene derivative being a more hydrophobic substrate and a weaker Lewis acid but having a more stable anion radical. Equilibrium constants for formation of 3-Meisenheimer complexes (K_4 and K_5) are consistently low with the naphthalene derivatives, and these complexes are less acidic, as shown by values of K_6. The higher acidity of the charge-transfer complex of the naphthalene derivatives, as shown by values of K_7 (and K_3), suggests that here there is a favorable interaction of the orbitals of the formal $^{\bullet}O^-$ moiety with the very polarizable π-system of the formal anion radical.

The higher overall reactivity of the benzene derivative is apparently due to the larger value of K_1 for formation of the π-

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complex and to the faster conversion of the charge-transfer complex into Meisenheimer complexes; cf. values of k_4, k_{-4}, k_5, k_{-5}, and k_8, k_9 (Table IV). The extended conjugation of the naphthalene system should reduce the charge densities due to an unpaired electron in the 1- and 3-positions and the conversion rates to the corresponding Meisenheimer complexes.

The higher overall reactivities of 1-fluoro- and 1-methoxy-2,4-dinitronaphthalene (**1c**,**d**), as compared with those of the chloro and bromo derivatives (**1a**,**b**), are due in part to the absence of (unproductive) 3-Meisenheimer complexes. The low overall reactivity of the 1-morpholino derivative (**1e**) is due to the slow formation of the 1-Meisenheimer complex (see values of k_8, k_9, Table IV) and to its slow decomposition (see k_{10}, k'_{10}), both consequences of the relatively low electronegativity of a nitrogen atom.

The so-called "element effect" played a major role in the development of mechanistic ideas regarding nucleophilic aromatic substitution,[2] and despite some anomalies,[4b] it has been a remarkably successful concept. However, even if the reactivity sequence in the series F, OR, Cl, Br, NR_2 corresponds to the expectations for a slow nucleophilic attack and fast elimination, the predictions are valid only for the OR, Cl, and Br derivatives, which react following this mechanism.

Our reaction scheme (Scheme III) differs from the generally accepted one (Scheme I) by including a π-complex and a charge-transfer complex between two radicals that is formed by promotion of one electron from the unpaired n-orbital of the nucleophile to an antibonding π^*-orbital of the aromatic system. One-electron transfers in ionic reactions have been widely discussed,[28] and Pross postulates[29] that they occur in all ionic reactions. The difference between processes in which a single-electron transfer can or cannot be observed is due mainly to the localization of the first transferred electron and to steric interactions. If the transferred electron is localized in the vicinity of the original nucleophile and there is no important steric interference to formation of the new bond, the charge-transfer complex has a very short life and may not be observed. With polynitrobenzenes[4] and -naphthalenes delocalization of the unpaired electron increases the life of the charge-transfer complexes, so that their formation and disappearance can be followed. In addition, steric interactions involving ortho nitro groups hinder formation of Meisenheimer complexes. If the lifetime of the charge-transfer complexes is relatively long, they can dissociate to radical anions that can be observed by ESR[6] or NMR[4] spectroscopy and can generate a radical chain substitution[6d] or overall reduction.[30] This dissociation is unfavorable in polar protic solvents that encompass the charge-transfer complex in a solvent cage, but it becomes much easier in apolar solvents.

In our model the charge-transfer complexes (**8** and **9**) control formation of either reactive, 1-, or unreactive, 3-, Meisenheimer complexes (**2** and **10**, respectively). The overall rate of nucleophilic substitution depends upon the rate of formation of the charge-transfer complex and its partitioning between return to π-complex and conversion into 1- or 3-Meisenheimer complexes.

Exchange of arene or azine hydrogens in the course of addition or overall substitution has been observed with a large number of activated arenes or azines.[3,4a] In some systems substrate deprotonation cannot explain the exchange, which must involve exchange of an intermediate with D_2O. Charge-transfer complexes (**8** and **9**) are similar to anion radicals[31] in that they have high electron densities in the aromatic system and are relatively strong bases.

Experimental Section

Materials. The preparation and purification of the substrates have been described.[4a] Reactions were followed in 1:1 (v/v) H_2O:DMSO with redistilled DMSO and redistilled CO_2-free H_2O. The substrates are not sufficiently soluble for reactions to be followed in H_2O with no added organic solvent.

Kinetics. Reactions were followed spectrometrically as described elsewhere,[4b] with 5×10^{-5} M substrate. The rapid disappearance of the π-complexes was followed qualitatively at ca. 500 nm, but because of the low value of K_1, as compared with that for the trinitrobenzenes,[4] the decrease of absorbance was small and we therefore generally followed the first relaxation in the range 255–340 nm, except for reaction of **1c**, where all the relaxations could be followed at the same wavelength of 440 nm. Reactions were followed at wavelengths that were chosen so as to allow reasonable separation of the relaxations and adequate absorbance changes. Some of the relaxations could be followed only over a limited range of $[OH^-]$. This limitation was most serious for the first relaxation in dilute OH^- and for stopped-flow experiments, where solubility limited the usable concentration of OH^- to 1 M. The general procedure for analyzing the relaxations using relaxation theory and computer simulation on a Hewlett-Packard 300 microcomputer has been described,[4b,18] and Figures 4, 5, 7, and 9 were computer generated as were the equilibrium and rate constants in Tables III and IV. For some reactions intermediates were in steady state and then the computed values of some rate constants have no chemical significance. For example, **2** is in steady state in reactions of **1a**,**b**,**d** and the data can be fitted by a range of values of k_{-8}, k_{-9}, and k_{10} provided that their ratios do not change and that they are not less than those quoted. The computer simulations were made over the full range of $[OH^-]$, even through our present experimental methods do not allow us to examine all of this range.

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Registry No. 1a, 2401-85-6; **1b**, 2401-86-7; **1c**, 954-50-7; **1d**, 13772-69-5; **1e**, 113748-36-0.

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