Registry No. 6, 98-95-3; **7**, 528-29-0; **8**, 100-25-4; **9**, 4110-35-4; **10**, 606-20-2; **11**, 350-46-9; **12**, 70-34-8; **13**, 97-00-7; **14**, 606-21-3; **15**, 20039-23-0; **16**, 1930-72-9; **17**, 118-97-8; **18**, 2497-91-8; **19**, 606-37-1; **20**, 2578-45-2; **21**, 16013-85-7; **22**, 3934-20-1; **23**, 1193-21-1; **24**, 4316-93-2; **25**, 4774-14-5; **26**, 253-82-7; **27**, 99-65-0; **28**, 99-35-4; **29**, 121-89-1; **30**, 2508-19-2; **31**, 618-71-3; **32**, 121-81-3; **33**, 88-88-0; **34**, 2401-85-6; **35**, 113748-36-0; **36**, 6549-03-7; **37**, 13772-69-5; **38**, 2401-86-7; **39**, 954-50-7; **40**, 5190-68-1; H_2, 1333-74-0; HO, 14280-30-9.

Single-Electron Transfer in Aromatic Nucleophilic Addition and Substitution in Aqueous Media

Radu Bacaloglu,* Clifford A. Bunton,* and Francisco Ortega

Contribution from the Department of Chemistry, University of California, Santa Barbara, California 93106. *Received June 5, 1987. Revised Manuscript Received December 22, 1987*

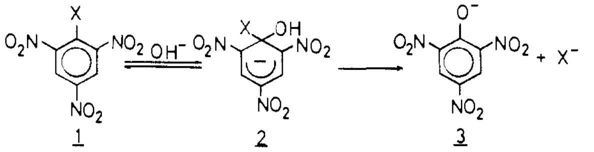
Abstract: Reactions of 1,3,5-trinitrobenzene, 2,4,6-trinitrochlorobenzene, and 2,4,6-trinitrobenzenesulfonate ion with OH^- in water and water–DMSO do not occur by a rate-limiting, single-step, addition of OH^- but involve very rapid formation of a π-complex of substrate and OH^-, which forms a charge-transfer complex of arene anion and hydroxyl radicals by single-electron transfer. In polar solvents the charge-transfer complexes rearrange to σ 1- or 3-complexes. The 1-complexes eliminate the leaving group to form the substitution product in a slow or fast step, and the 3-complexes can form long-lived dianionic σ-complexes or return to charge-transfer complexes. Rate and/or equilibrium constants of the individual steps can be calculated by computer simulation based on relaxation theory. Calculated overall equilibrium constants of addition or second-order rate constants of overall substitution in dilute OH^- agree with experimental values.

Aromatic nucleophilic substitutions and additions are strongly assisted by electron-withdrawing groups such as NO_2. The generally accepted aromatic nucleophilic substitution mechanism (S_NAr) involves rate-limiting formation of a σ or Meisenheimer complex, as in Scheme I.[1]

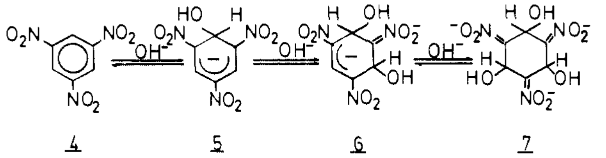
This mechanism is consistent with much experimental evidence. For example, Meisenheimer complexes (**2**) have been characterized,[2] and the frequently observed reactivity order for X of F $\gg$ Cl $\simeq$ Br $\simeq$ I has been ascribed to rate-limiting formation of **2**.[3] The reactivity sequence Br > Cl > F, which is occasionally observed, is explained in terms of a slow second step.[4] In some systems similar reactivities have been observed with X = SOPh, Br, Cl, I, SO_2Ph, and OPh as leaving groups, which is consistent with rate-limiting addition, but the very high reactivities observed with X = F, NO_2, and $ArSO_3$ are hard to explain solely in terms of an inductive effect of X.[3]

Substituent effects on overall substitution often follow the Hammett equation with σ^- parameters and high values of ρ,[1b] but there are exceptions.[5] Rates of nucleophilic aromatic substitution in aqueous or alcoholic solvents generally follow the N_+ scale, which is consistent with rate-limiting addition, and reactivity–selectivity relations do not apply.[6] General-base catalysis is often observed in aminolysis when X is a relatively poor leaving group, and its departure can be rate limiting.[1,7,8] However, in some reactions the order with respect to the nucleophile (or base) is larger than the predicted value of 2.[9,10]

Scheme I



Scheme II



Substrate–nucleophile π-complexes[9b,11,12] and anion radicals[13] appear to be intermediates in some aromatic substitutions, especially in aprotic solvents. Chain reaction involving radical anions has also been postulated.[13g] In some other cases anion radicals have been identified by ESR spectroscopy, but because of their slow formation, they were not considered to be reaction intermediates in polar hydroxylic solvents.[14] There is strong evidence

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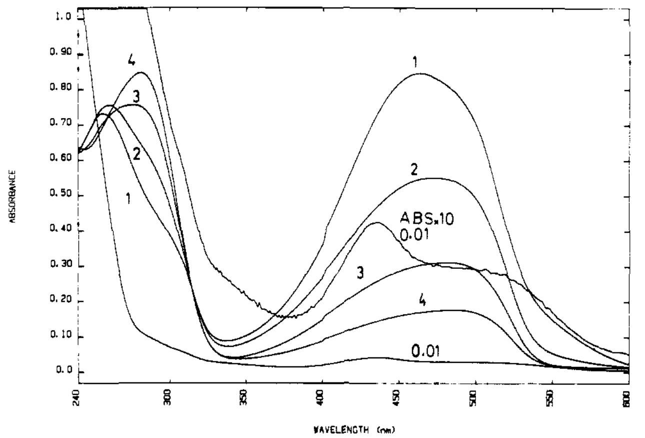

Figure 1. Absorbance of 1,3,5-trinitrobenzene (4×10^{-5} M) in aqueous NaOH at indicated concentrations (M).

in apolar solvents for the radical chain $S_{RN}1$ mechanism of aromatic substitution.[15] Nucleophilic aromatic photosubstitution involves electronically excited substrate–nucleophile complexes with radical anion character.[16] These observations are inconsistent with the mechanism shown in Scheme I, but the classical mechanism was assumed to be correct for reactions in polar hydroxylic solvents.

Our observation of two intermediates between substrate and addition or substitution products in water or aqueous DMSO is not explained in terms of Scheme I.[17-19] Our hypothesis is that the first intermediate is a π-complex of substrate and OH^- [11a,b] and that it rapidly gives a charge-transfer complex of an arene radical anion and $^{\bullet}OH$, which then forms a Meisenheimer complex. We have developed a multistep reaction treatment based on relaxation theory,[18] and we apply it to the addition of OH^- to 1,3,5-trinitrobenzene and substitution on 2,4,6-trinitrochlorobenzene and 2,4,6-trinitrobenzenesulfonate in H_2O and 1:1 (v/v) H_2O–DMSO, i.e., under the conditions in which the classical mechanism (Scheme I) has been applied.

Results

1,3,5-Trinitrobenzene (4). At low [OH^-] Meisenheimer complex, **5**, is formed[20-23] (Scheme II), and it absorbs at 260, 300, 445–450, and 475–485 nm. With increasing [OH^-] the absorbance at 400–500 nm decreases as dihydroxy complex, **6**, gradually appears, and at high [OH^-] the visible absorbance disappears because of formation of the trihydroxy complex, **7**.[20c,e] Our evidence agrees with these assignments. In water λ_{max} of the Meisenheimer complex is red-shifted (from 464 to 485 nm) as [OH^-] is increased from 1 to 4 M. The dihydroxy complex, **6**, which appears at [OH^-] > 1 M, has a lower absorbance at ca. 485 nm and a higher absorbance at 257 nm relative to those of **5**. The trihydroxy complex, **7**, that is formed at high [OH^-] has λ_{max} at 281 nm (Figure 1).

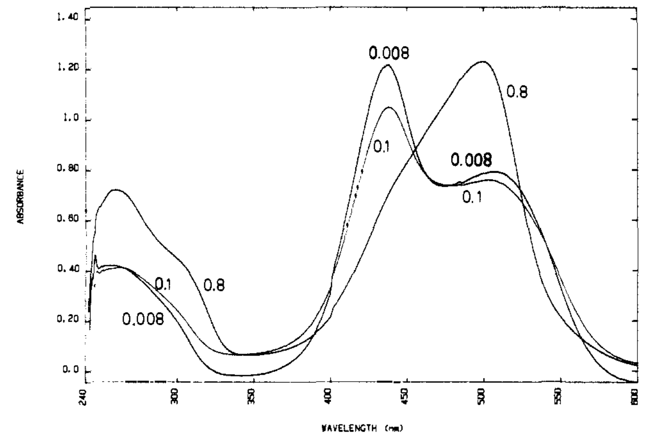

Figure 2. Absorbance of 1,3,5-trinitrobenzene (4×10^{-5} M) in 1:1 (v/v) H_2O–DMSO 1 s after mixing at indicated NaOH concentrations (M).

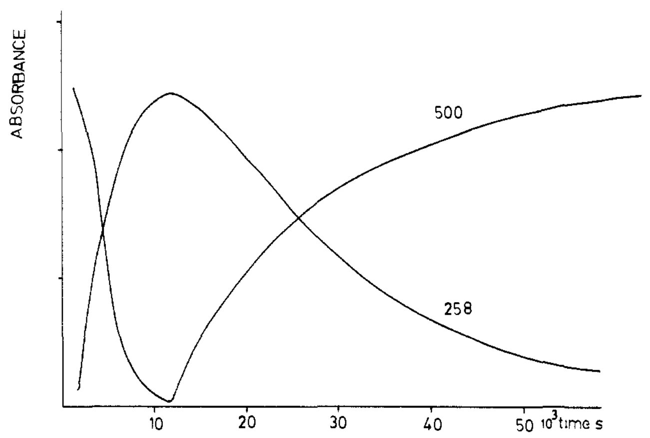

Figure 3. Stopped-flow spectral trace for reaction of 1,3,5-trinitrobenzene (5×10^{-5} M) with 0.05 M OH^- in 1:1 (v/v) H_2O–DMSO at indicated wavelengths (nm) (ordinate arbitrary).

In 1:1 (v/v) DMSO–H_2O the monohydroxy complex, **5**, has λ_{max} at 440 and 510 nm, and the dihydroxy complex, **6**, has λ_{max} at 500 and 259 nm and a shoulder at 303 nm (Figure 2). We could not dissolve enough NaOH in aqueous DMSO to obtain the trihydroxy complex, **7**.

The absorbance of the monohydroxy complex, **5**, in aqueous DMSO changes slightly with an increase of [OH^-] from 0.008 to 0.1 M and then sharply in 0.8 M OH^- (Figure 2) due to the deprotonation of **5** (cf. ref 20l) or to formation of the dihydroxy complex, **6**. The structures of the mono- and dihydroxy complexes, **5** and **6**, in D_2O–DMSO have been confirmed by proton NMR spectrometry (ref 24 and Experimental Section).

Rate and equilibrium constants for addition of OH^- to 1,3,5-trinitrobenzene had been examined in water and aqueous organic solvents, sometimes on the erroneous assumption that the forward reaction is first order in [OH^-] (k_f) and the reverse reaction is zero order in [OH^-] (k_d). The rate and equilibrium constants in water calculated in this way are respectively within the limits k_f = 27–38 $M^{-1}\ s^{-1}$, k_d = 8–13.4 s^{-1} and 1.8–4.2 M^{-1}.[20f,g,h,i,j] Our spectrophotometrically measured equilibrium constants for formation of the monohydroxy Meisenheimer complex are 2.7 and 1130 M^{-1} in H_2O and 1:1 (v/v) H_2O–DMSO, respectively, and for formation of trihydroxy complex from substrate, K = 1.1 M^{-3} in H_2O. The equilibrium constant for formation of the dihydroxy complex was not measured spectrally because of interference by other complexes.

We observed a species absorbing at 500 nm in a reaction that was too fast to be followed by stopped-flow spectrometry. This species disappeared to give a second intermediate absorbing at 258 nm, which was converted relatively slowly into the mono-

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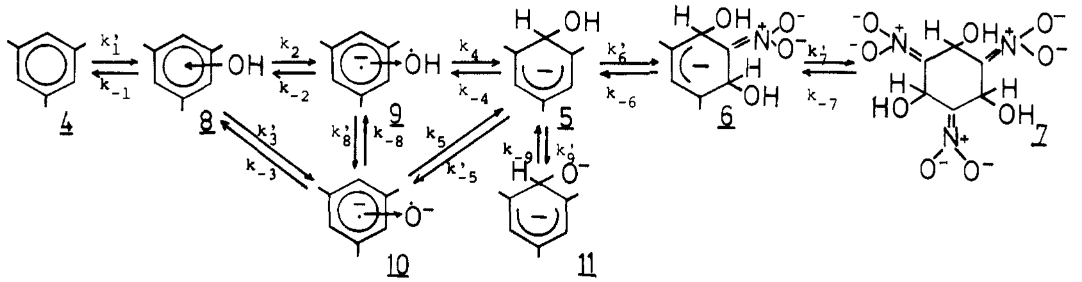
Scheme III



— denotes $-NO_2$; $k'_1=k_1[OH^-]$; $k'_3=k_3[OH^-]$; $k'_{-5}=k_{-5}[OH^-]$; $k'_6=k_6[OH^-]$; $k'_7=k_7[OH^-]$; $k'_8=k_8[OH^-]$; $k'_9=k_9[OH^-]$.

Table I, Reciprocal Relaxation Times for Addition of OH^- to 1,3,5-Trinitrobenzene in Water[a]

	τ_1^{-1}		τ_2^{-1}		$10^3\tau_3^{-1}$	
[NaOH], M	500 nm[b]	258 nm[c]	258 nm[b]	500 nm[c]	550 nm[b]	282 nm[c]
0,05				13.8		
0.125				15.5		
0,25				19.6		
0.5	832, 860	730,[d] 720[e]	27.3	27.1	96.5	
0.6		756,[d] 708[e]				
0.7		768,[d] 680[e]		43.5[f]		
0.8		776,[d] 746[e]				
0.9		764,[d] 708[e]				
1.0	818, 796	850,[d] 746[e]		58.6	104	86.1
1.5	926, 900		100	98.7	109	108
2.0	1020, 1030		151	162	130	130
2.5	1120, 1060		252	242	148	147
3.0					167	166
3.5					172	
4.0					187	

[a] At 25.0 °C; τ^{-1} in s^{-1}. [b] Disappearance. [c] Appearance. [d] Ionic strength 1 M (NaCl). [e] Ionic strength 2 M (NaCl). [f] At 0.75 M NaOH.

hydroxy Meisenheimer complex, **5** (Figure 3). This kinetic behavior was found in both H_2O and aqueous DMSO over a wide range of $[OH^-]$. An intermediate absorbing at 500 nm had already been seen, but not investigated, in the reaction of **4** with OH^- in aqueous cationic micelles.[25]

We followed three relaxations in water: (i) τ_1^{-1}, disappearance of the first intermediate at 500 nm and appearance of the second at 258 nm; (ii) τ_2^{-1}, disappearance of the second intermediate at 258 nm and appearance of complex, **5**, at 500 nm; (iii) τ_3^{-1}, disappearance of **5** at 550 nm and appearance of trihydroxy complex, **7**, at 282 nm (Table I). These results suggest that the species that we observe at 500 and 258 nm are on the overall reaction path, and we show later that at least the second intermediate must be on the reaction path. Because formation of the di- and trihydroxy complexes (**6** and **7**) has a common relaxation, the final step of the reaction should be faster than the penultimate one.

We suggest that the first intermediate is a substrate–OH^- π-complex[11a,b] and that the second is a charge-transfer complex formed by an electron transfer from nucleophile to substrate. This assignment is consistent with earlier observations on reactions of nitroarenes. 1,3,5-Trinitrobenzene is an excellent electron acceptor and forms π-complexes with various donors.[12,26] Formation of π-complexes with alkoxide ions or amines has been followed kinetically by Caldin and co-workers, who used low temperatures to slow the reactions.[11a,b] Their activation parameters show that formation of these complexes would have first-order rate constants much greater than 10^3 s^{-1} under our conditions. The equilibrium constants for formation of π-complexes of **4** and ethoxide ion in ethanol at low temperature (−70 to −100 °C) are ca. 2×10^3 M^{-1} but are much lower (0.4–5 M^{-1}) for reaction with other donors at 25–30 °C.[26c] The complexes have at least one absorbance band between 350 and 550 nm.[26c]

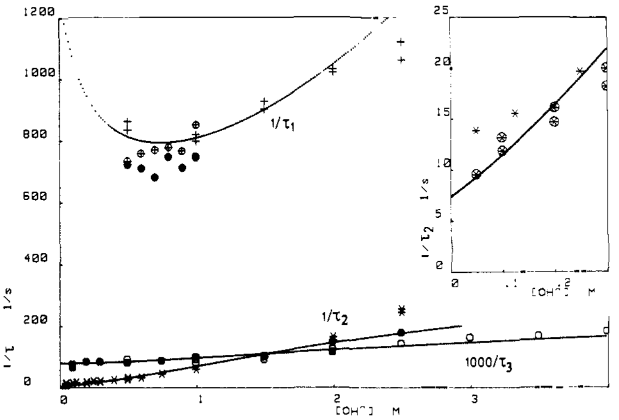


Figure 4. Simulation of values of τ^{-1} for reaction of 1,3,5-trinitrobenzene with aqueous NaOH (Table I). Values of τ_2^{-1} (■) and τ_3^{-1} (⊛) from ref 20g,k; (⊕, ●) at 1 and 2 M ionic strength.

We suggest that the second intermediate is a charge-transfer complex of an anion radical and ·OH. Other plausible intermediates are a free anion radical, an aryl anion, or an adduct of OH^- to nitro groups,[17-19] but they can be excluded. Radical anions absorb strongly between 250 and 350 nm and at 400–500 nm[26f,27] or 800–1000 nm,[13g] but the intermediate that we observe is almost certainly not a free anion radical, based on the absence of ESR signals in alkaline solutions of 1,3,5-trinitrobenzene in aqueous organic solvents and even in some organic solvents.[13a] However, in the accompanying paper we show that with 1,3,5-trinitrobenzene in excess over OD^- in $DMSO-D_2O$, there is broadening of the NMR signal of the substrate, which is probably due to its interaction with the charge-transfer complex.[19] If an aryl anion was formed reversibly from substrate and OH^- and was on the reaction path, exchange of arene hydrogens would be very rapid. Such exchange is observed, but at relatively high $[OH^-]$ it is much slower than the overall addition to trinitrobenzene.[19] Addition of OH^- to the nitro group is excluded because there is no exchange with $H_2{}^{18}O$ in alkaline solution.[19a]

The reciprocal relaxation time, τ_2^{-1}, is higher than first order in $[OH^-]$ (Table I), suggesting that there is a base catalysis. This catalysis is due to the deprotonation of an intermediate, which we write as the charge-transfer complex, **9** (Scheme III). The ·OH radical has $pK_a = 11.8$[28] so deprotonation of **9** to **10** could occur in the alkaline solution that we studied. In Scheme III we

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Table II. Equilibrium Constants for the Individual Steps in the Addition of OH^- to 1,3,5-Trinitrobenzene[a]

	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, M^{-1}	K_9, M^{-1}
H_2O[b]	0.16	0.578	2.61	26.7	5.94	0.729	0.47	4.52	*e*
H_2O–DMSO[d]	1.47	2.71	13.9	257	50.1	1060	*e*	4.40	0.015

[a] At 25.0 °C. [b] Calculated equilibrium constants for formation of monohydroxy and trihydroxycomplexes are 2.5 M^{-1} and 0.9 M^{-3}; observed values are 2.6[c] or 2.7 M^{-1} [20c,e] and 1.1 M^{-3}.[c] [c] This work. [d] Calculated and observed equilibrium constants for formation of the monohydroxy complex are 1020 and 1130 M^{-1}.[c] [e] Deprotonation of Meisenheimer complex in water or formation of trihydroxy complex in H_2O/DMSO was not observed.

Table III. Rate Constants for the Individual Steps in the Addition of OH^- to 1,3,5-Trinitrobenzene[a]

	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}	k_6, M^{-1} s^{-1}	k_{-6}, s^{-1}
H_2O	618	1069	939	359	245	9.16	164	27.6	0.062	0.085
H_2O–DMSO	1270	468	1780	128	139	0.54	173	3.45	0.339	3.2×10^{-4}

[a] At 25.0 °C. k_7 and k_{-7}, as well as k_8 and k_{-8}, represent fast relaxations following slower ones (Scheme IV) and cannot be calculated.

make the logical assumption that the π-complex, **9**, is also on the overall reaction path, but in our conditions it is formed very rapidly from substrate (cf. ref 11a,b) so it may be formed in a side equilibrium.

The trihydroxy complex, **7** (Scheme III), was observed only in H_2O, and the deprotonated complex, **11**, only in aqueous DMSO.

The various rate and equilibrium constants for the reactions in Scheme III were calculated by using relaxation theory. The system is much too complex for application of the simplified theory,[29] and we used a general numerical method based on diagonalization of a matrix of the linearized rate equations.[18] The overall simulation of values of τ^{-1} is shown in Figure 4. We calculated the equilibrium constants between **4** and **8**, **6** and **7**, and **9** and **10** (Table II) and the rate constants for the various steps (Table III). The equilibrium and rate constants from Tables II and III are slightly different from those published earlier[18] for the same reaction, but neglecting **7** and with fewer experimental data. We use these newly calculated rate and equilibrium constants to calculate the overall equilibrium constants for addition of OH^-, and these values agree well with experimental values (Table II). The values of τ_2^{-1} in dilute aqueous OH^- and those from other sources are shown in the insert (Figure 4).

Most of our experiments were in the absence of added salts, but our values of τ^{-1} for the final two relaxations are very similar to those of Bernasconi,[20g,k] who used 1–3 M ionic strength (shown in Figure 4) and of Crampton (2 M ionic strength).[20l] The first relaxation, τ_1^{-1}, had not been observed, so we made a few measurements at 1 and 2 M ionic strength (Table I and Figure 4). Although these values are slightly smaller than those with no added salt, we conclude that there is no significant salt effect on any of the relaxations, and our simulations were based on data for reactions in the absence of added salt.

We also observed three relaxations in the addition of OH^- to 1,3,5-trinitrobenzene in 1:1 (v/v) DMSO–H_2O, which we ascribe to (i) τ_1^{-1}, disappearance of π-complex, **8**, followed at 500 nm and appearance of charge-transfer complexes, **9** and **10**, at 258 nm, (ii) τ_2^{-1}, disappearance of **9** and **10** and appearance of monohydroxy Meisenheimer complex, **5**, and (iii) τ_3^{-1}, disappearance of **5** and appearance of dihydroxy complex, **6** (Table IV). The simulation of values of τ^{-1} is shown in Figure 5, and the calculated individual rate constants are in Tables II and III.

2,4,6-Trinitrochlorobenzene (1a). Reaction of **1a** with OH^- was originally postulated to follow Scheme I, but with a relatively slow conversion of the 1-Meisenheimer complex, **2**, into product, **3**,[20f] although this mechanism required slower loss of Cl^- than OH^-. However, the observed complex was later shown to be a 3-Meisenheimer complex by NMR spectroscopy[30] and also by its reaction with CF_3CO_2H, which regenerates the initial chloro derivative.[31] A revised mechanism was suggested[32] (Scheme IV).

Table IV. Reciprocal Relaxation Times for Addition of OH^- to 1,3,5-Trinitrobenzene[a]

[NaOH], M	τ_1^{-1} 500 nm[b]	τ_1^{-1} 258 nm[c]	τ_2^{-1} 258 nm[b]	τ_2^{-1} 500 nm[c]	τ_3^{-1} 440 nm[b]	τ_3^{-1} 500 nm[c]
0.01				5.11		
0.025			19.4	21.7		
0.05	443	464		20.1		
0.1		476	40.9	41.9		
0.15	495	506				
0.2	544	511		76.2		
0.25	570	563				
0.3				106		
0.4			111	113	0.122	0.130
0.5				130		
0.6				144	0.155	0.152
0.8					0.265	0.272
1.0					0.376	0.374

[a] At 25 °C in 1:1 (v/v) H_2O–DMSO; τ^{-1} in s^{-1}. [b] Disappearance. [c] Appearance.

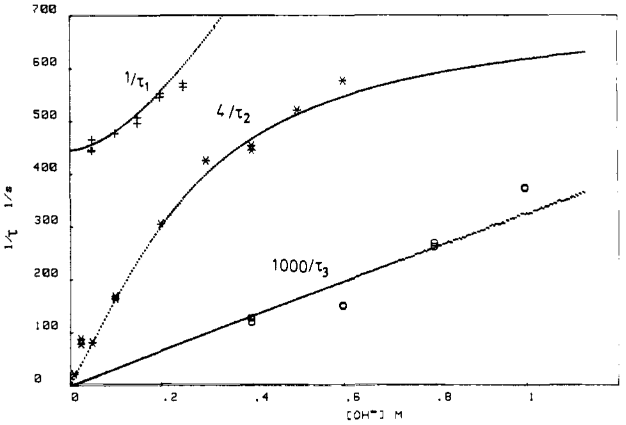
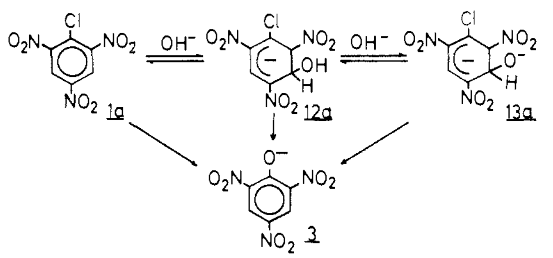


Figure 5. Simulation of values of τ^{-1} for reaction of 1,3,5-trinitrobenzene with OH^- in 1:1 (v/v) H_2O–DMSO (Table IV).

Scheme IV



A problem with this mechanism is that it is not obvious how **12a** and **13a** are converted into **3**, and evaluation of the individual rate constants required that they be subject to large salt effects. However, this conversion would be understandable if an intermediate was on the reaction path between **1a** and **12a**.

The overall reaction, like addition to 1,3,5-trinitrobenzene (**4**), involves very rapid formation of an intermediate, probably a

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(29) (a) Bernasconi, C. F. *Relaxation Kinetics*; Academic: New York, 1976. (b) Bernasconi, C. F. In *Tech. Chem.* (*N.Y.*) **1985**, *6*, 425.

(30) Crampton, M. R.; El Ghariani, M. A.; Khan, H. A. *Tetrahedron* **1972**, *28*, 3299.

(31) Syper, L.; Barycki, J. *Tetrahedron* **1972**, *28*, 2233.

(32) Gibson, B.; Crampton, R. M. *J. Chem. Soc., Perkin Trans. 2* **1979**, 648.

Table V. Reciprocal Relaxation Times for Reaction of OH^- with 2,4,6-Trinitrochlorobenzene[a]

[NaOH], M	τ_1^{-1}	τ_2^{-1}			$10^3\tau_3^{-1}$			$10^4\tau_4^{-1}$	
	260 nm[c]	260 nm[b]	360 nm[c]	490 nm[c]	240 nm[b]	360 nm[c]	490 nm[b]	274 nm[b]	360 nm[c]
0.001					0.54	0.56			
0.005					2.3	2.6			
0.01					6.9	6.8			
0.03					14.0	13.0			
0.05					21.5	22.3			
0.125		9.0	10.6	10.2		47	45		
0.25	1000	7.6	7.9	6.2		68	67		
0.5	968[d]	7.4	8.1	7.7		65	65		
0.75	992		10.8	10		53	53		
1.0	1080		14.3	13.6		33	37	62	72
1.5	1230[e]		24.0	23.9		22	30	41	37
2.0						23	25	27	29
2.5						22	26	27	28

[a] At 25.0 °C, in water; τ^{-1} in s^{-1}. [b] Disappearance. [c] Appearance. [d] τ_1^{-1} = 1000 followed at 500 nm.[b] [e] τ_1^{-1} = 1160 followed at 260 nm in 1.25 M NaOH.[c]

Table VI. Equilibrium Constants for Individual Steps in the Reaction of OH^- with 2,4,6-Trinitrochlorobenzene[a]

solvent	K_1, M^{-1}	K_2	K_3, M^{-1}	K_4	K_5, M	K_6, M^{-1}	K_8, M^{-1}	K_9, M^{-1}
H_2O	0.143	0.860	1.67	2.28	1.17	41.9	0.51	46.8
H_2O–DMSO	1.65	0.807	1.89	319	136	b	10.8	275

[a] At 25.0 °C. [b] Dihydroxy Meisenheimer complex was not observed in H_2O–DMSO.

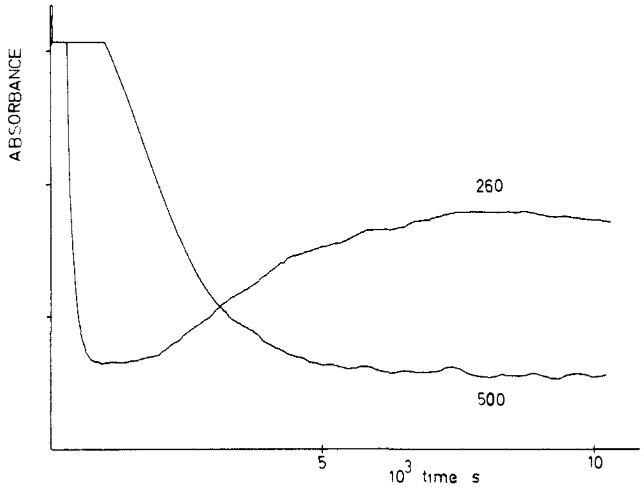

Figure 6. Stopped-flow spectral trace for reaction of 2,4,6-trinitrochlorobenzene (5 × 10^{-5} M) with 1 M OH^- in water at indicated wavelengths (nm) (ordinary arbitrary).

π-complex, absorbing at 500 nm, and its conversion into another intermediate, probably a charge-transfer complex, which can be followed by stopped-flow spectrometry at 500 or 260 nm (Figure 6). There is then parallel formation of trinitrophenoxide ion (**3**) and 3-Meisenheimer complex, **12a**, as shown in Figure 7 for reaction in aqueous 0.1 M OH^-. A peak at 360 nm and a shoulder at 400 nm are due to **3**, a peak at ca. 500 nm is due to **12a**, and a peak at 240 nm is due to unreacted substrate (spectrum at 2 s, Figure 7). Under these conditions substrate and 3-Meisenheimer complex should be in equilibrium via the π-complex and charge-transfer complex, and trinitrophenoxide ion (**3**) is generated slowly by return of 3-Meisenheimer complex, **12a**, to charge-transfer complex, **15a** (spectra at 10, 20, and 80 s (Figure 6)).

In aqueous 2.5 M OH^- 3-Meisenheimer complex, **12a**, is initially formed in parallel with some trinitrophenoxide ion (**3**) (spectrum at 5 s, Figure 8), and **12a** can then give either **3** or the 3,5-dihydroxy Meisenheimer complex, **17a**, which absorbs at 260 nm (spectra at 12.5 and 32.5 s, Figure 8). At high [OH^-] the absorbance of the 3-Meisenheimer complex is blue-shifted to 450 nm, due to formation of a dianion, and that of 2,4,6-trinitrophenoxide ion (**3**) is red-shifted to 390 nm, because of formation of its 3,5-dihydroxy Meisenheimer complex, **18a** (see ref 33).

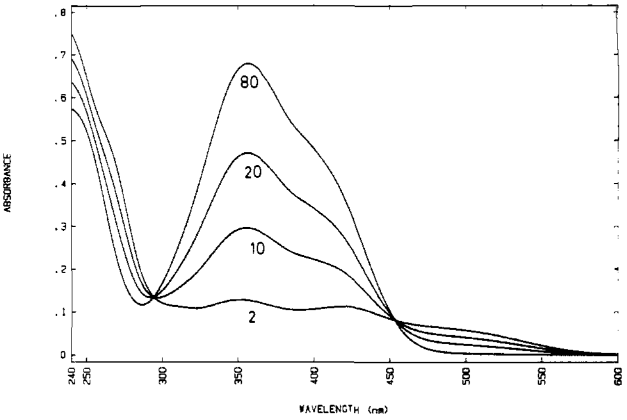

Figure 7. Absorbance spectra of 2,4,6-trinitrochlorobenzene after mixing with aqueous 0.1 M OH^- at the indicated times (s).

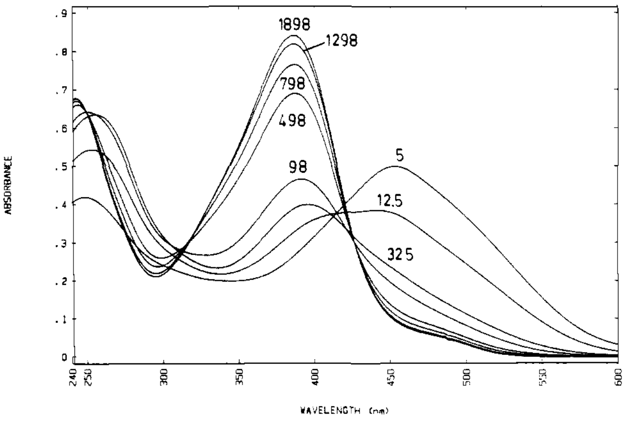

Figure 8. Absorbance spectra of 2,4,6-trinitrochlorobenzene after mixing with aqueous 2.5 M OH^- at the indicated times (s).

The blue shift of the absorbance of the dihydroxy Meisenheimer complex, **17a**, of 2,4,6-trinitrochlorobenzene (**1a**) is due to the three nitro groups being out of conjugation with the unsaturated system. The nitro groups in positions 2 and 6 are twisted out of plane, as in 2,4,6-trinitrochlorobenzene,[34] and that in position 4

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(33) (a) Abe, T. *Nature (London)* **1960**, *187*, 234. (b) Gold, V.; Rochester, C. H. *J. Chem. Soc.* **1964**, 1722.

(34) (a) Holden, J. R.; Dickson, C. *J. Phys. Chem.* **1967**, *71*, 1129. (b) Willis, J. S.; Stewart, J. M.; Ammon, H. L.; Preston, S.; Ghyas, R. E.; Harris, P. M. *Acta Crystallogr., Sect. B* **1971**, *B27*, 786.

Table VII. Rate Constants for Individual Steps in the Reaction of OH^- with 2,4,6-Trinitrochlorobenzene[a]

solvent	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}	k_6, M^{-1} s^{-1}	k_{-6}, s^{-1}	k_{10}, s^{-1}	k_{11}, s^{-1}
H_2O[b]	904	1040	1190	707	89.9	39.4	44.9	38.4	0.26	0.0061	4.31	
H_2O–DMSO	260	322	320	169	206	0.65	210	1.54			6.76	97.0

[a] At 25.0 °C. [b] Calculated second-order rate constant at $[OH^-] \rightarrow 0$ is 0.53 M^{-1} s^{-1}; observed value is 0.46 M^{-1} s^{-1}.

Table VIII. Reciprocal Relaxation Times for the Reaction of Dilute OH^- with 2,4,6-Trinitrochlorobenzene[a]

	$10^3\tau_3^{-1}$		
10^3[NaOH], M	290 nm[b]	360 nm[c]	490 nm[b]
0.8	3.52	3.73	3.39
1.0	10.5	10.0	9.27
2.0	10.7	11.0	10.1
3.0	9.23	9.57	8.91
4.0	7.23	7.7	6.95
8.0	6.06	6.95	5.7
10.0	6.85	6.62	6.59
20.0	6.10	6.12	6.03

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

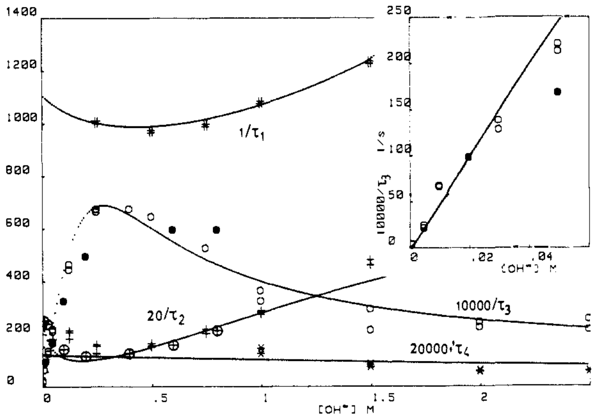

Figure 9. Simulation of values of τ^{-1} for reaction of aqueous OH^- with 2,4,6-trinitrochlorobenzene (Table V). Values of τ_2^{-1} (⊕) and τ_3^{-1} (■) are from ref 32.

is out of conjugation by addition to positions 3 and 5. This dihydroxy complex is very slowly converted into final product, **3** (spectra at 498–1898 s, Figure 8). The trinitrophenoxide ion (**3**) is therefore formed in three steps with very different rates: (i) from substrate, **1a**, via **14a** and charge-transfer complexes (**15a** and **16a**), (ii) from the 3-Meisenheimer complex, **12a**, and (iii) from the 3,5-dihydroxy Meisenheimer complexes, **17a** (Scheme V).

We identified two fast, τ_1^{-1} and τ_2^{-1}, and two much slower relaxations, τ_3^{-1} and τ_4^{-1}, which accord with our spectral evidence (Table V). These observations fit Scheme V. The calculated individual rate constants are in Table VI and VII, and the simulation is shown in Figure 9. Some of the τ^{-1} values are similar to rate constants of Crampton et al.,[32] who used solutions of 2 M ionic strength, and their results are in Figure 9, although we did not use them in the simulations. Therefore, as in addition to 1,3,5-trinitrobenzene, salt effects seem to be relatively unimportant. We calculate from our rate constants a second-order rate constant in dilute OH^- that is similar to the observed value as $[OH^-] \rightarrow 0$ (Table VII). Reaction of **1a** with OH^- in 1:1 (v/v) H_2O–DMSO is similar to that in H_2O. We could not use very high $[OH^-]$ in aqueous DMSO, so we saw no 3,5-dihydroxy Meisenheimer complex, but the blue-shifted absorbance of the 3-Meisenheimer complex suggests that it was deprotonated.[20l,32] These results are consistent with our observation of three, rather than four, relaxations (Tables VIII and IX). The simulation of τ^{-1} values is shown in Figure 10, and rate and equilibrium constants are in Tables VI and VII. Our simulation shows that 1-Meisenheimer complex always goes forward to product (cf. ref 30 and 32), and we cannot estimate the actual values of $k_{12} + k'_{12}[OH^-]$, k_{-10}, and k_{-11}.

Table IX. Reciprocal Relaxation Times for Reaction of OH^- with 2,4,6-Trinitrochlorobenzene[a]

	τ_1^{-1}		τ_2^{-1}			$10^3\tau_3^{-1}$	
[NaOH], M	260 nm[b]	490 nm[c]	260 nm[c]	360 nm[b]	490 nm[b]	360 nm[b]	490 nm[c]
0.03		540		5.14	5.81	6.2	6.1
0.05	544	527	7.84	7.96	11.5	6.2	6.1
0.10	575	558	14.2	18.2	14.5	5.55	5.45
0.15			31.8	30.2	32.1	5.30	5.20
0.20	612	611	35.0	34.2	39.2	4.95	5.05
0.25		600		41.2	48.7	4.80[d]	4.20[d]
0.40		670		85.1	72.8	4.00	4.10
0.50				111	111	4.10	4.10
0.60						3.50	3.40
0.90					137	3.20[e]	3.36[e]
1.00					151	3.27	3.44

[a] At 25.0 °C in 1:1 (v/v) H_2O–DMSO; τ^{-1} in s^{-1}. [b] Appearance. [c] Disappearance. [d] With 0.3 M NaOH. [e] With 0.8 M NaOH.

Table X. Reciprocal Relaxation Times for Reaction of Dilute OH^- with 2,4,6-Trinitrobenzenesulfonate Ion in Water[a]

[NaOH], M	0.01	0.02	0.03	0.04	0.05	0.06	0.08	0.1
$10^3\tau_3^{-1}$, s^{-1}	0.26	0.52	0.81	1.08	1.40	1.69	2.36	3.05

[a] At 25.0 °C; disappearance at 360 nm.

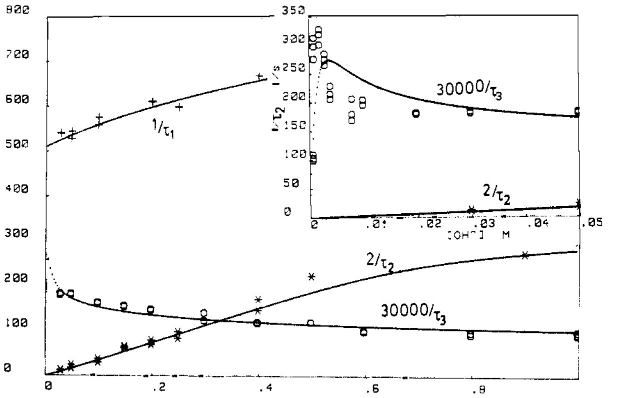

Figure 10. Simulation of values of τ^{-1} for reaction of OH^- with 2,4,6-trinitrochlorobenzene in 1:1 (v/v) H_2O–DMSO (Tables VIII and IX).

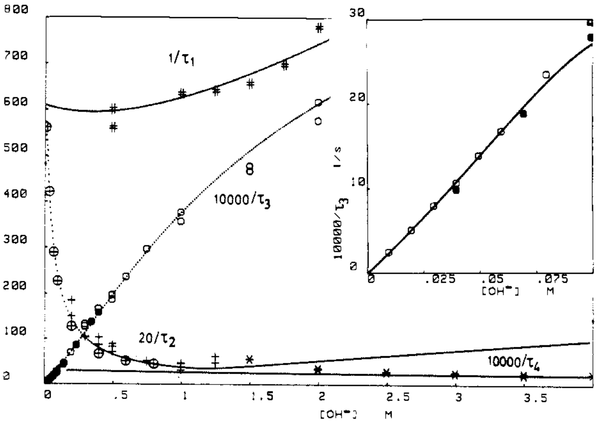

Figure 11. Simulation of values of τ^{-1} for reaction of aqueous OH^- with 2,4,6-trinitrobenzenesulfonate ion (Table X and XI). Values of τ_2^{-1} (⊕) are from ref 35b and values of τ_3^{-1} (■) are from ref 35a.

2,4,6-Trinitrobenzenesulfonate Ion (1b). The reciprocal relaxation time for formation of 2,4,6-trinitrophenoxide ion by the overall reaction of **1b** with dilute aqueous OH^- has a higher order

Scheme V

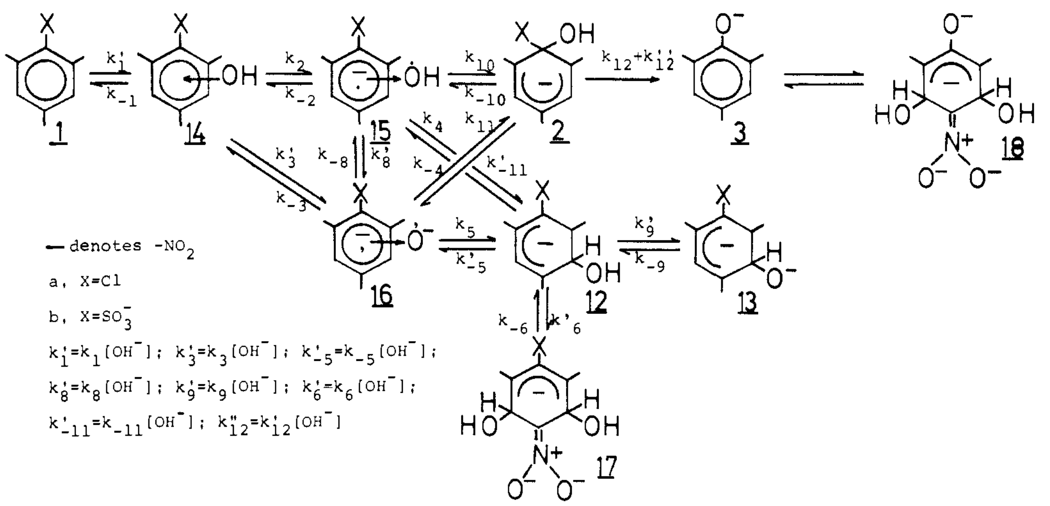

Table XI. Reciprocal Relaxation Times for Reaction of OH^- with 2,4,6-Trinitrobenzenesulfonate Ion in Water[a]

[NaOH], M	τ_1^{-1} 500 nm[b]	τ_2^{-1} 260 nm[b]	τ_2^{-1} 500 nm[c]	$10^3\tau_3^{-1}$ 360 nm[c]	$10^3\tau_3^{-1}$ 500 nm[b]	$10^4\tau_4^{-1}$ 260 nm[b]	$10^4\tau_4^{-1}$ 360 nm[c]
0.2		7.4	9.2	7.3			
0.3		5.2	5.1	13.5	13.0		
0.4		4.3	5.1	17	17		
0.5	600[d]	3.5	4.4	20	19		
0.6				24	24		
0.75		2.4	2.5	30	30		
1.0	634	1.5	2.2	36	38		
1.25	640	2.3	3.0				
1.5	656			48	47	54	55
1.75	696						
2.0	778			62	58	32	34
2.5						28	26
3.0						25	23
3.5						23	20
4.0						22	

[a] At 25.0 °C; τ^{-1} in s^{-1}. [b] Disappearance. [c] Appearance. [d] $\tau_1^{-1} = 560$ at 260 nm.

than first in $[OH^-]$. This result was earlier explained in terms of a base-catalyzed decomposition of 1-Meisenheimer complex, **2b**.[35a] However, the reciprocal relaxation times for formation of the 3-Meisenheimer complex, **12b**, could be rationalized only if it is formed in equilibrium with its deprotonated dianion, **13a**.[35b]

The suggested scheme for reaction of OH^- with **1b** is similar to that for the chloride. Short-lived intermediates are seen, and experimental values of τ^{-1} are in Tables X and XI and Figure 11. Figure 11 includes literature data for the second[35b] and third relaxations.[35a] The simulation of our rate data, based on Scheme V, is shown in Figure 11, and the individual equilibrium and rate constants are in Tables XII and XIII.

It is useful to compare these constants with those for reaction of the chloride, **1a**. While for reaction of **1a** the 1-Meisenheimer complex is in steady state, for reaction of the sulfonate, **1b**, the 1-Meisenheimer complex is not in a steady state, and $k_{12} + k'_{-12}[OH^-]$ is smaller than k_{-10} and k_{-11}. The slow elimination of SO_3^{2-} from the 1-Meisenheimer complex, **2b**, is base catalyzed and either concerted with or subsequent to proton transfer. These differences are due to the relatively poor leaving ability of SO_3^{2-}.

As for the other substrates, our rate data, with no added salt, agree with literature data for reaction in solutions of high ionic strength.[35b] Our simulation predicts the unexpected sharp decrease of τ_2^{-1} with increasing $[OH^-]$ ($[OH^-] < 0.15$ M) observed by Crampton,[35b] although we did not use his data in the simulation (Figure 11). Observed and calculated overall second-order rate constants in dilute OH^- agree reasonably well (Table XIII), even though the computed value is based on the assumption either of equilibrium between **2b** and substrate or of **2b** as in steady state, whereas neither of these approximations strictly applies.

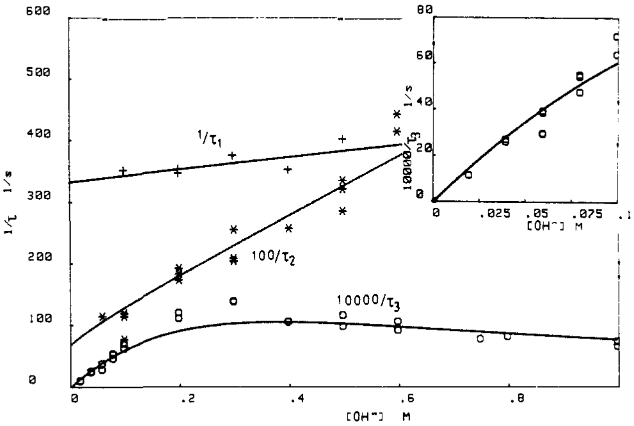

Figure 12. Simulation of values of τ^{-1} for reaction of OH^- with 2,4,6-trinitrobenzenesulfonate ion in 1:1 (v/v) H_2O–DMSO (Table XIV).

The data for reaction of **1b** with OH^- in 1:1 (v/v) DMSO–H_2O also fit our model. The overall scheme is similar to that for reaction in H_2O, except that we observed no 3,5-dihydroxy Meisenheimer complex, **17b** (Figure 12 and Tables XII, XIII, and XIV). In addition, in aqueous DMSO elimination of SO_3^{2-} from **2b** appears to be fast and it is a steady-state intermediate, and we cannot compute values of k_{-10} and $k_{12} + k'_{12}[OH^-]$. As with other reactions there is good agreement between observed and calculated second-order rate constants for the overall reaction in dilute OH^- (Table XIII).

Discussion

Relaxation theory, as applied to the mechanism of nucleophilic aromatic addition and substitution (Schemes III and V), allows fitting of kinetic data for three or four consecutive reactions whose rate constants differ by 7–8 orders of magnitude and correctly predicts values of equilibrium constants and second-order rate constants as $[OH^-] \rightarrow 0$. Our schemes also fit data for reactions of OH^- with 1,3-dinitronaphthalene,[18] its derivatives,[19b] and 3,5-dinitrobenzoic acid derivatives, and we see similar behavior with such heterocyclic compounds as nitropyridines and -pyrimidines and their derivatives.

The first step in our reaction (Scheme III or V) involves an interaction between nucleophile and substrate to form a π-complex (**8**, **14**). It is followed by a single-electron transfer from the nucleophile to substrate to form a charge-transfer complex (**9**, **10**, **15**, **16**). For activated substrates, such as nitroarenes, this transition does not necessary imply a very high energy,[36] because

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[35] (a) Bunton, C. A.; Ihara, Y.; Wright, L. J. *J. Org. Chem.* **1976**, *41*, 2520. (b) Crampton, R. M. *J. Chem. Soc., Perkin Trans. 2* **1978**, 343.

Table XII. Equilibrium Constants for Individual Steps in the Reaction of OH^- with 2,4,6-Trinitrobenzenesulfonate Ion[a]

solvent	K_1, M^{-1}	K_2	K_3, M^{-1}	K_4	K_5, M	K_6, M^{-1}	K_8, M^{-1}	K_9, M^{-1}	K_{10}	K_{11}, M
H_2O	0.16	1.76	1.12	0.024	0.306	493	0.63	20.7	1.55	2.43
H_2O–DMSO	1.02	0.71	0.76	0.89	*b*		1.08	6.9		*b*

[a] At 25.0 °C. [b] These steps do not contribute to the overall reaction.

Table XIII. Rate Constants of Individual Steps in the Reaction of OH^- with 2,4,6-Trinitrobenzenesulfonate Ion[a]

solvent	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}
H_2O[b]	1130	640	222	198	0.88	37.0	0.0036	0.012
H_2O–DMSO[c]	284	398	106	139	0.26	0.29		

solvent	k_6, $M^{-1}s^{-1}$	k_{-6}, s^{-1}	k_{10}, s^{-1}	k_{-10}, s^{-1}	k_{11}, s^{-1}	k_{-11}, M^{-1} s^{-1}	k_{12}, s^{-1}	k''_{12}, M^{-1} s^{-1}
H_2O[b]	1.75	0.0035	0.17	0.11	2.11	0.87	0.12	0.065
H_2O–DMSO[c]			0.11					

[a] At 25.0 °C. [b] The second-order rate constant as $[OH^-] \rightarrow 0$ calculated by an equilibrium approximation is 0.050 M^{-1} s^{-1}, and under the assumption that the 1-hydroxy Meisenheimer complex is in steady state, it is 0.025 M^{-1} s^{-1}; the observed value is 0.037 M^{-1} s^{-1}. [c] Calculated second-order rate constant as $[OH^-] \rightarrow 0$ is 0.079 M^{-1} s^{-1}; observed value is 0.067 M^{-1} s^{-1}.

Table XIV. Reciprocal Relaxation Times for Reaction of OH^- with 2,4,6-Trinitrobenzenesulfonate Ion[a]

		τ_2^{-1}			$10^3\tau_3^{-1}$		
[NaOH], M	τ_1^{-1} 260 nm[c]	260 nm[b]	360 nm[c]	500 nm[c]	260 nm[b]	360 nm[c]	500 nm[b]
0.02					1.21	1.21	
0.04					2.75	2.65	
0.06					3.99	3.91	3.00
0.08					5.56	5.48	4.80
0.1	350	0.76	1.13	1.13		7.25	6.45
0.2	345[d]	1.91	1.72	1.82		12.2	11.3
0.3	374	2.07	2.03	2.54		14.1	14.0
0.4	352	2.56				10.7	10.8
0.5	401	2.85	3.20	3.34		10.0	11.8
0.6			4.13	4.41		10.8	9.4
0.75			5.03	5.44		8.0	8.4[e]
1.0						6.8	7.6

[a] At 25.0 °C in 1:1 (v/v) H_2O–DMSO; τ^{-1} in s^{-1}. [b] Disappearance. [c] Appearance. [d] τ_1^{-1} = 352 s^{-1} at 500 nm. [e] In 0.8 M OH^-.

the calculated energies of the lowest unoccupied orbitals of selected nitroarenes are lower than those of n-occupied orbitals of many nucleophiles.[13g36a,b] Our own AM-1 calculations using the AMPAC program (M. J. Dewar et al., QCPE-506) indicate that approach of OH^- to the center of 1,3,5-trinitrobenzene corresponds to one-electron transfer to the aromatic system and a gain of ca. 34 kcal mol^{-1} at ca. 2.2 Å. This enthalpy gain is larger than the solvation enthalpy of OH^- (ca. 21.3 kcal mol^{-1} in H_2O[37]).

Interaction of the two partners in the charge-transfer complex (**9**, **10**, **15**, **16**) leads to formation of the new bond in a 1- or 3-Meisenheimer complex (**5**, **2**, or **12**), depending upon the charge density in the aromatic partner. The relative longevity of these charge-transfer complexes between radicals is due to a high delocalization of the unpaired electron and steric hindrance to the subsequent coupling reaction.[36c] Although individual reaction steps involve single-electron transfers, reactions in aqueous media apparently do not involve *free* radical anion intermediates, which probably play a role in media of low water content.[13] In the accompanying paper,[19] we show that, in some reactions in aqueous DMSO, anion radicals may "leak" away from the postulated charge-transfer complex and be detected by NMR spectrometry. In this way free radical anions can be generated in apolar media, which leads to chain and radical anion substitution[13g,15] or other radical reactions.[31,38] In appropriate conditions the transfer of a second electron to the radical anion gives a reduction.[36d] The postulated formation of a charge-transfer complex therefore makes a synthesis of what were regarded as completely different reaction mechanisms in polar and apolar solvents.

The 1- and 3-Meisenheimer complexes of 1-substituted 2,4,6-trinitrobenzenes have different stabilities, because the 3-complex is destabilized by secondary steric effects. Both the 2- and 6-nitro groups are twisted out of plane in 2,4,6-trinitrochlorobenzene (**1a**)[34] and 2,4,6-trinitrophenetole[39] and also presumably in their 3-Meisenheimer complexes, but much less so in the 1-complex.[40] The 3-Meisenheimer complexes of 1-substituted 2,4,6-trinitrobenzenes are formed faster than the 1-complexes, probably due to primary steric effects. The 3-Meisenheimer complex then slowly rearranges, with formation of the more stable 1-Meisenheimer complex and then of the substitution product.

The Meisenheimer complex of OH^- and 1,3,5-trinitrobenzene appears to act as a hydride donor toward some oxidants,[20e] but in their absence there is a slow loss of nitro groups to give 3,5-dinitrophenol,[20e] probably through a 1-Meisenheimer complex.[20e,41]

At high $[OH^-]$ the Meisenheimer complexes may be deprotonated.[20l] The equilibrium constants of these ionizations (K_9, Tables VI and XII and Scheme V) are between 20 and 47 M^{-1} in water. Despite salt effects they are similar to the constants estimated by Crampton (5–15 M^{-1}) for related equilibria.[20l] At high $[OH^-]$ di- or even trihydroxy Meisenheimer complexes are formed, and these reactions may also involve π-complexes and charge-transfer complexes (cf. Schemes III and V), but the relative rates of these steps are such that the individual relaxations are not separated.

Some conclusions can be drawn regarding the influence of structural changes and solvent effects on aromatic nucleophilic substitution in water or water–DMSO (Tables II, III, VI, VII, XII, and XIII). The postulated initial electron transfer is generally much faster than formation of the Meisenheimer complexes in 1-substituted derivatives (i.e., 2,4,6-trinitrochlorobenzene or 2,4,6-trinitrobenzenesulfonate), which is consistent with extensive hydrogen exchange between the arene group and water,[19] even before product is formed. With 1,3,5-trinitrobenzene (**4**) in 1:1 (v/v) DMSO–H_2O conversion of the charge-transfer complex (**9**, **10**) into Meisenheimer complex, **5**, is relatively fast, and then we see no exchange before **5** is formed (ref 19 and Tables II and III). In the accompanying paper we present evidence for exchange via an intermediate charge-transfer complex.[19]

Equilibria involving OH^- are favored by DMSO, which reduces hydration of OH^- and increases deprotonation of both the charge-transfer complexes (**9** and **15**) and the Meisenheimer complexes (**5** and **12**). However, electron transfer from nucleophile to substrate in the π-complex is faster in water than in aqueous

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DMSO, probably because solvation of nitro groups increases their electron-withdrawing effect. Collapse of the charge-transfer complex to Meisenheimer complex is favored by DMSO, probably because it reduces hydration of the nitro groups and increases the density of an unpaired electron in the aromatic nucleus. As noted earlier, addition of DMSO to H_2O destabilizes the 1-Meisenheimer complex of 2,4,6-trinitrobenzenesulfonate by the same effect, so that loss of SO_3^{2-} becomes fast.

Formation of Meisenheimer complexes via the charge-transfer complexes is base catalyzed, but this catalysis is relatively unimportant with the sulfonate, **1b**, because of the unfavorable effect of the negative charge.

Finally, we note that many classical organic reactions have been considered to follow polar pathways with two-electron transfers between nucleophile and electrophile, but there is now evidence for single-electron transfers in many of these reactions, including electrophilic aromatic substitution,[42] S_N2 reactions,[43,44] and addition of organometallic reagents.[45,46] In some, but not all, of these reactions free radical intermediates have been detected, especially in apolar media. Stepwise mechanisms involving single-electron transfers could also occur in nucleophilic addition to activated alkenes and to preformed carbocations and, by microscopic reversibility, in S_N1 reactions. This hypothesis is also consistent with Ritchie's evidence that nucleophilic additions to carbocations and nitrohaloarenes do not follow the reactivity–selectivity principle.[6]

In all these reactions it is reasonable to expect that there will be strong electrostatic interactions as reagents come together, so that charge-transfer complexes could form. The electron transfer should be much faster than rearrangement of atoms, based on the Franck–Condon principle, and it should be followed by steps that lead to the formation of new covalent bonds, which may be relatively slow and involve partitioning to various products.

Two-electron transfers, as designated by curved arrows, are descriptively convenient, but they are inconsistent with two tenets of quantum mechanics—that electrons are indistinguishable and that electronic motion is much faster than that of nuclei.[43]

Experimental Section

Materials. Purification of the substrates has been described.[19] Solvents were made up by volume with freshly vacuum-distilled DMSO and CO_2-free, redistilled, deionized water.

Spectral Data. Spectra were measured on Hewlett-Packard 8450 or 8451 diode array spectrometers. The single-beam Hewlett-Packard 8451 spectrometer was used for repetitive scanning of the faster reactions, and spectra could be taken every 0.1 s if necessary. Substrate in MeCN (5–10 μL) was added to a well-stirred reaction mixture in a 1-cm cuvette by use of a CR-700 Hamilton syringe. The stirring rate was chosen to avoid cavitation. We used phenolphthalein as an indicator to show that mixing was complete within 1 ± 0.2 s.

Kinetics. The faster reactions were followed on a Durrum stopped-flow spectrometer at 25.0 °C, and the slower reactions on a Hewlett-Packard 8451 spectrometer with the mixing method already described. The mixing time in the stopped-flow spectrometer was ca. 0.7 ms, based on tests consisting of mixing Malachite Green with water, phenolphthalein with OH^-, or phenolphthalein in alkaline solution with HCl. In all these mixing experiments, immediately after triggering, we saw an apparent increase of absorbance, followed by a decrease, and then, after ca. 0.7 ms, an approximately constant base line. The time constant of the amplifier was 0.1 ms. For some reactions with half-lives of ca. 0.5 s, data from the diode array and stopped-flow spectrometers agreed. With $[OH^-] < 0.01$ M, solutions were made up in a glovebox under N_2, and substrate was added through a septum cap. The wavelengths were chosen for the convenience of kinetic measurements and to avoid overlapping absorbances, and they are not necessarily at absorbance maxima. In particular, we were forced to follow the increase and subsequent decrease of **9**, **10**, **15**, and **16** at ca. 260 nm because other species interfered spectrally at higher wavelengths.

For some reactions, e.g., parallel formation of Meisenheimer complex and 2,4,6-trinitrophenoxide ion from 2,4,6-trinitrobenzenesulfonate, we used a scanning stopped-flow OLIS spectrometer to examine the spectral range 350–600 nm. 3-Meisenheimer complex is formed simultaneously with the phenoxide ion in a fast relaxation, and then, in a second much slower step, it is transformed into more phenoxide ion.

The quoted values of τ^{-1} are the mean of at least 3 values for the slower relaxations and 5–10 values for the faster relaxations. They were calculated by a simple integrated first-order equation and also by computer simulation of the variation of absorbance with time. There were no significant discrepancies between values from the two procedures. Relaxations do not depend, in the limit of experimental errors, on the substrate concentration, which was varied between 10^{-5} and 10^{-4} M. The uncertainty in values of $\tau_1^{-1} > 500$ s^{-1} is much larger than for the other data. These relaxations are at the extreme of rate that is measurable by a conventional stopped-flow spectrometer, but despite uncertainties in the absolute values of τ_1^{-1}, consistent data were obtained at two wavelengths. These relaxations are slower in aqueous DMSO than in water, and with other substrates, such as 1,3-dinitronaphthalene derivatives[19b] and derivatives of 3,5-dinitrobenzoic acid, values of τ_1^{-1} as low as 200 s^{-1} were observed. All relaxations were followed at two or more wavelengths.

Simulation of reciprocal relaxation times was carried out on a Hewlett-Packard 310 microcomputer.[18] The program is based on general relaxation theory, with diagonalization of the determinantal equation matrix and a Powell minimization subroutine. The objective computer simulation and the fitting minimize the sum of the absolute values of the errors in values of τ^{-1}. This procedure gives equal weight to all values of τ^{-1}, even though those for the first relaxation are much less accurate than the others, and seems to us to be better than use of subjective weighting of data. This method requires careful identification of the relaxations, and it is desirable to use more than one wavelength in following the reactions. The general procedure for analyzing the relaxations has been described.[18] The relaxations could be followed only over particular ranges of $[OH^-]$. For example, we could not follow τ_1 in dilute OH^- and we had to use relatively concentrated OH^- to follow some of the slower relaxations. However, the simulations of τ^{-1} are shown over the whole range of OH^-.

The values of derived rate constants for the individual reactions depend not only upon the experimental data but also upon the power of the computer and the time available for the simulation. Our values would be better had we used a more powerful computer, but we consider that they are accurate enough to justify our general conclusions.

Due to the complex mathematical treatment of experimental data and the use of a simple microcomputer, it is difficult to estimate the errors in the derived equilibrium and rate constants. We believe that these errors are at most within 20–30% but are in many cases much smaller, so that the quoted values have been truncated to three significant figures (see appendix, Supplementary Material). The agreement between observed and calculated rate and equilibrium constants shows that our calculated rate constants are not seriously in error. With these rate constants time–concentration profiles for all components of the system may be calculated by numerical integration (R. J. McKinney and F. J. Weigert, Quantum Chemistry Program Exchange, Program QCMP022) and subsequently used for recalculation of different relaxations that agree with the experimental ones (see appendix, Supplementary Material).

The absolute values of these rate constants do not affect our general conclusions. The simulation of the relaxations of such a wide order of magnitude and representing very complex rate profiles against $[OH^-]$ provides strong support for our schemes.

Equilibrium Constants. The equilibrium constant for the formation of the mono-Meisenheimer complex of 1,3,5-trinitrobenzene was measured spectrophotometrically in H_2O or 1:1 (v/v) H_2O–DMSO at 25 °C in dilute NaOH (0.005–0.1 M). Formation of the trihydroxy Meisenheimer complex is relatively slow, and it was examined in more concentrated aqueous NaOH. The spectra were obtained after 6–8 half-lives of conversion. The Benesi–Hildebrand[47] equation was used to calculate equilibrium constants from absorbances at 440 and 500 nm.

NMR Spectra. A Nicolet T-300 spectrometer was used. On addition of 0.025 M NaOD to 1,3,5-trinitrobenzene (0.024 M), dissolved in 3:7 (v/v) D_2O–DMSO-d_6 the singlet (9.12 ppm) was replaced by the signal

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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.

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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

Radu Bacaloglu,* Clifford A. Bunton,* and Francisco Ortega[1]

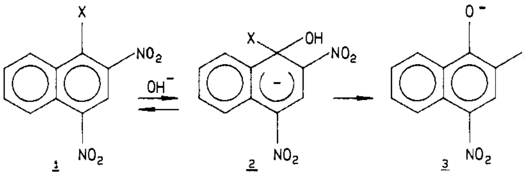
Contribution from the Department of Chemistry, University of California, Santa Barbara, California 93106. *Received October 8, 1987*

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.

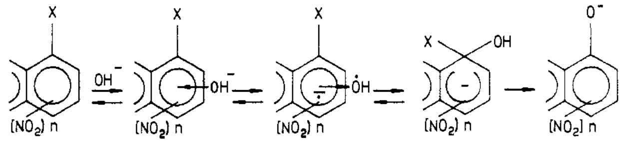
Nucleophilic aromatic substitution in aqueous solvents is generally written[2] as a rate-limiting formation of a short-lived Meisenheimer complex, as shown in Scheme I for reactions of dinitronaphthalene derivatives with OH^-.

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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