representing the valence deformation around the F atoms attached to the sulfur atom, the subtraction of the oriented reference density yields similar local results, but the bonds remain depleted of charge.

All attempts failed to make bond peaks visible midway between the S–F atoms by creating properly oriented reference densities for S. The trigonal-bipyramidal arrangement of the sulfur atom can be described by sp^2, d_{xz}, p_z, and d_{y^2} hybridization for the equatorial σ and π, and the axial σ orbitals, respectively. After subtracting the aspherical density calculated from these assumed hybrid orbitals, the charge-depleted region seemed to be unaffected. The reason for this failure must be the loss of net charge at the sulfur that cannot be compensated by a neutral reference density even if it should be properly oriented.

Conclusion

The accurate single-crystal X-ray diffraction measurement on $F_4S{=}C(CH_3)CF_3$ proves that both parts of the molecule, the $S{=}CC_2$ and the $F^{ax}{}_2S{=}C$ part, are flat. These so defined planes have a dihedral angle of only 3–4°. This molecule therefore does not undergo nonclassical distortions, as does its triple-bonded relative, $F_3S{\equiv}CCF_3$.[39]

The electron deformation density of $F_4S{=}C(CH_3)CF_3$ exhibits detailed features of the bonding, especially if the oriented atom model (OAM) is used for the promolecule. The difficulty of this method, if applied to atoms with a higher valence state, is that no trivial oriented reference density can be established, as is the case for atoms of low valence state. It must be realized that the preconception used in the interpretation of charge redistribution will influence the results.[33]

Acknowledgment. This work has been supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

Supplementary Material Available: Listings of atomic parameters and least-squares planes (7 pages); listings of observed and calculated structure factors (65 pages). Ordering information is given on any current masthead page.

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Mechanism of Reaction of Hydroxide Ion with Dinitrochlorobenzenes

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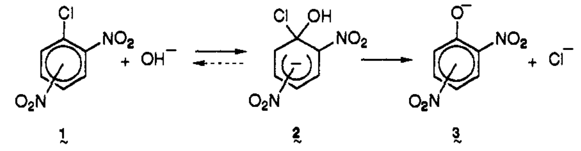
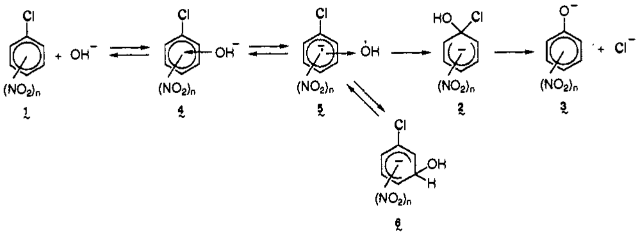
Abstract: Formation of dinitrophenoxide ion from 2,4- and 2,6-dinitrochlorobenzene (2,4- and 2,6-DNCB) and OH^- (OD^-) in 70:30 and 80:20 (v/v) DMSO–H_2O (D_2O) is accompanied by extensive ^1H NMR line broadening of unreacted substrate and exchange of arene hydrogen with D_2O, which is quantitative at the 3-position of 2,4-DNCB. Unproductive Meisenheimer complexes are detected spectrophotometrically in the course of reaction. For reaction of 2,4-DNCB, the Meisenheimer 3-complex is formed first and then the more stable 5-complex can be detected and characterized by NMR spectrometry. There is no hydrogen exchange of Meisenheimer complexes or dinitrophenoxide ions and their ^1H NMR signals are not broadened. These results do not fit the classical mechanism of single-step nucleophilic addition, but they, and the kinetic results, are fitted by a reaction scheme involving single-electron transfer from OH^- to give a charge-transfer complex of $OH^\bullet$ and a radical anion which collapses to give Meisenheimer complexes and aryl oxide ion. This scheme is consistent with MO calculations by the AM1 method.

The mechanism of aromatic nucleophilic substitution of dinitrochlorobenzenes (**1**), for example, in polar, hydroxylic, solvents has been assumed to involve rate-limiting formation of a σ or Meisenheimer complex (**2**), as in Scheme I for reaction of OH^- with 2,4- or 2,6-dinitrochlorobenzene (2,4- and 2,6-DNCB).[2] Loss of Cl^- from **2** should be fast in polar solvents. Unproductive Meisenheimer complexes form in the course of some reactions.

Scheme I



Scheme II



Anion radicals are intermediates in aromatic nucleophilic substitutions in apolar solvents[3] and radical chain reactions have also been identified,[4] in contrast to the behavior in polar, hydroxylic, solvents. However, recent kinetic and NMR spectroscopic evidence suggests that reaction occurs by electron transfer from the nucleophile into the antibonding orbital of the aromatic

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Table I. Reciprocal Relaxation Times for the Reaction of 2,4-Dinitrochlorobenzene

DMSO–H_2O, 70:30 (v/v)						DMSO–H_2O, 80:20 (v/v)							
											$10^3\tau_3^{-1}$,[e] s^{-1}		
$[OH^-]$, M	τ_1^{-1},[a] s^{-1} 800–1000 nm, inc	$[OH^-]$, M	τ_2^{-1},[b] s^{-1} 512 nm, inc	$[OH^-]$, M	$10^3\tau_3^{-1}$,[c] s^{-1} 412 nm, inc	$[OH^-]$, M	τ_1^{-1},[d] s^{-1} 630 nm, inc	$[OH^-]$, M	τ_2^{-1},[c] s^{-1} 510 nm, inc	$[OH^-]$, M	370 nm, inc	420 nm, inc	510 nm, dec
0.024	31.8	0.0125	4.53	0.048	2.24	0.05	27	0.0043	1.19	0.0045	3.68	3.54	2.80
0.0465	31.9	0.024	4.90	0.093	4.90	0.06	27.0[f]	0.009	1.33	0.031	10.2	10.2	13.2
0.070	35.4	0.0465	5.23	0.16	9.34	0.07	30.8	0.01	1.36	0.056	16.0	15.9	15.5
							27.5[f]	0.015	1.39	0.074	18.3	17.4	18.0
0.095	38.4	0.070	5.26	0.19	9.39	0.088	32.6	0.019	1.38	0.104	24.5	22.7	21.6
					10.6			0.028	1.57	0.120	28.6	29.3	27.7
0.135	37.9	0.095	5.18	0.27	15.1	0.09	32.0	0.03	1.63	0.186	33.5	31.8	33.2
0.160	42.3			0.37	20.3			0.037	1.70				
					20.4			0.05	1.90				
0.185	45.6			0.43	22.2				1.90[g]				
					25.2			0.06	1.91				
									1.79[g]				
								0.07	1.89				
									2.02[g]				
								0.087	2.19				
									2.1[g]				
								0.09	2.12				
								0.10	2.35				
								0.11	2.25[g]				

[a] 5×10^{-3} M DNCB. [b] 1.75×10^{-4} M DNCB. [c] 5×10^{-5} M DNCB. [d] 5×10^{-4} M DNCB. [e] 10^{-5} M DNCB. [f] 640 nm, inc. [g] 640 nm, dec.

substrate to give an intermediate, which we show as a charge-transfer complex (**5**), that in polar solvents collapses to productive or unproductive Meisenheimer complexes (Scheme II).[5] This scheme includes a very short lived π or encounter complex of substrate and OH^- (**4**). Complex **5** could dissociate in apolar solvents to radicals, so this model predicts that reactions in polar and apolar solvents have common initial steps.

Scheme II fits kinetic data for both addition and substitution reactions of OH^- with trinitrobenzene and dinitronaphthalene derivatives, provided that deprotonation of **5** is taken into account.[5b–d] These reactions sometimes involve exchange of arene hydrogens with D_2O and line broadening of the ^1H NMR signals of substrate, and charge-transfer complexes were assumed to be involved in these processes. In some overall substitutions, aryl oxide product was exchanged more than unreacted substrate, so that exchange involved an intermediate on the reaction path of substitution.[5d] Semiempirical MO calculations suggest that charge-transfer complexes could be on the reaction path and that they would readily collapse to Meisenheimer complexes.[5f]

Reactions of dinitrohalobenzenes with anionic nucleophiles (concentration <0.1 M) in hydroxylic solvents typically have simple second-order kinetics and have been assumed to follow Scheme I, with inclusion in some cases of unproductive Meisenheimer complexes, e.g., **6**, that do not go directly to aryl oxide product.[6,7] However, there is exchange of arene hydrogens in reactions of 2,4- and 2,6-DNCB with OD^- in D_2O–DMSO, and the ^1H signals of 2,6-DNCB are broadened during reaction.[5d] These observations are not accounted for by the reactions in Scheme I. We therefore examined these reactions in detail in aqueous DMSO and used NMR spectroscopy to examine exchange and signal broadening. In the earlier work with trinitrobenzene and dinitronaphthalenes the NMR experiments were made in less aqueous solvents than those used for the kinetics,[5] but in the present work we used solvents of similar composition for both the kinetic and NMR work.

Kinetic evidence for the reactions of trinitrobenzenes (and dinitronaphthalenes) shown in Scheme II came from observation of a very fast relaxation due to formation of a postulated charge-transfer complex **5** and slower relaxations due to its conversion into aryl oxide ion **3** and interconversion with Meisenheimer complex **6**.[5a–c] We attempted to observe similar relaxations in reactions of OH^- with 2,4- and 2,6-DNCB, which are much less reactive than derivatives of trinitrobenzene and dinitronaphthalene. Reactions were followed in aqueous DMSO.

Only one relaxation is seen in the reaction of dilute OH^- with 2,4-DNCB in solvents of high water content,[2] but an unproductive Meisenheimer complex had been detected in 80:20 (v/v) DMSO–H_2O.[6a] There was some evidence for rapid formation of a Meisenheimer 3-complex with subsequent formation of a postulated 5-complex, but this first step was not followed kinetically.[6a] Structural assignments were based only on UV spectrometry, so we planned to verify them by NMR spectroscopy and to analyze the multistep kinetics in detail.

Results

2,4-Dinitrochlorobenzene. We observed three relaxations for reactions of 2,4-DNCB with OH^- in 70:30 and 80:20 (v/v) DMSO–H_2O. The fastest relaxation, τ_1, was followed in 80:20 (v/v) DMSO–H_2O as an increase of absorbance at 630–640 nm with 5×10^{-4} M substrate, but it had a low amplitude in 70:30 (v/v) DMSO–H_2O, so here we used 5×10^{-3} M substrate and avoided interference by other intermediates and product by following increasing absorbance at 800–1000 nm. We observed two other relaxations in both solvents. The faster, τ_2, was followed as an absorbance increase at 510–512 nm or decrease at 640 nm, and the third, τ_3, was followed by an absorbance increase at 370–420 nm or decrease at 510 nm. These relaxations could be followed with dilute substrate (Table I and Figure 1).

The slowest relaxation is due to formation of 2,4-dinitrophenoxide ion. Hasegawa and Abe had observed rapid formation of a species absorbing at ca. 600 nm, which was rapidly converted into one absorbing at ca. 510 nm in 0.017 M OH^- (90:10 DMSO–H_2O).[7c] They assigned absorbances at ca. 600 and 510 nm to Meisenheimer 3- and 1-complexes, respectively, although the latter would be expected to go rapidly to the phenoxide ion.[2,5–7] Crampton et al. observed similar species in 80:20 (v/v) DMSO–H_2O and, based on the values of λ_{max}, assumed that the first formed species was the Meisenheimer 3-complex and the second the 5-complex.[6a]

It is difficult to use NMR spectrometry in DMSO-d_6–D_2O to determine the structure of the Meisenheimer complex because

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Table II. Reciprocal Relaxation Times for the Reaction of 2,6-Dinitrochlorobenzene

DMSO–H_2O, v/v										
50:50		70:30				80:20				
	$10^3\tau^{-1}$,[a] s^{-1}		τ_1^{-1},[b] s^{-1}		$10^3\tau_2^{-1}$,[a] s^{-1}		τ^{-1},[b] s^{-1}			$10^3\tau_2^{-1}$,[a] s^{-1}
$[OH^-]$, M	450 nm, inc	$[OH^-]$, M	530 nm, inc	$[OH^-]$, M	450 nm, inc	$[OH^-]$, M	540 nm, inc	560 nm, inc	$[OH^-]$, M	450 nm, inc
0.1	0.0939	0.024	15.4	0.0480	0.70	0.0125	6.87	6.78	0.0045	0.29
0.2	0.203	0.047	15.1	0.093	1.28	0.025	6.97	6.76	0.031	1.5
0.4	0.539	0.095	15.4	0.19	2.51	0.037	6.54	6.18	0.056	2.53
0.5	0.740	0.135	14.8	0.27	3.51	0.059	6.27	6.16	0.074	4.30
0.6	0.795	0.185	14.4	0.37	4.59	0.060	6.65	6.16	0.104	6.63
0.8	1.41	0.20	14.2	0.43	5.43	0.10	5.97	5.68	0.127	8.04
1.0	2.07								0.15	10.0
1.2	2.78								0.19	12.75
1.4	3.25									
1.6	4.50									

[a] 5×10^{-5} M DNCB. [b] 5×10^{-3} M DNCB.

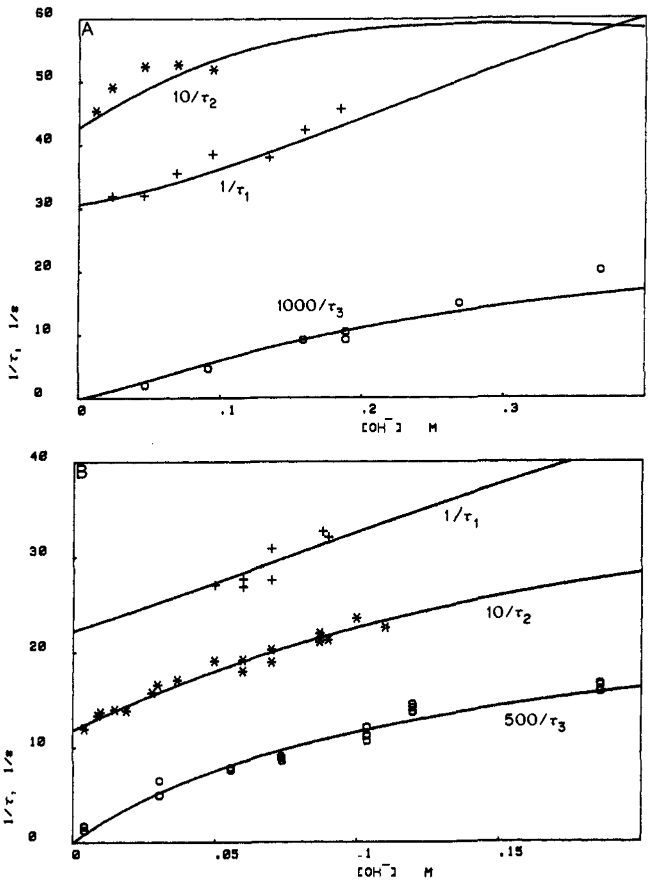

Figure 1. Values of τ^{-1} for reaction of 2,4-dinitrochlorobenzene with OH^-. (A) in 70:30 (v/v) DMSO–H_2O; (B) in 80:20 (v/v) DMSO–H_2O. The lines are calculated.

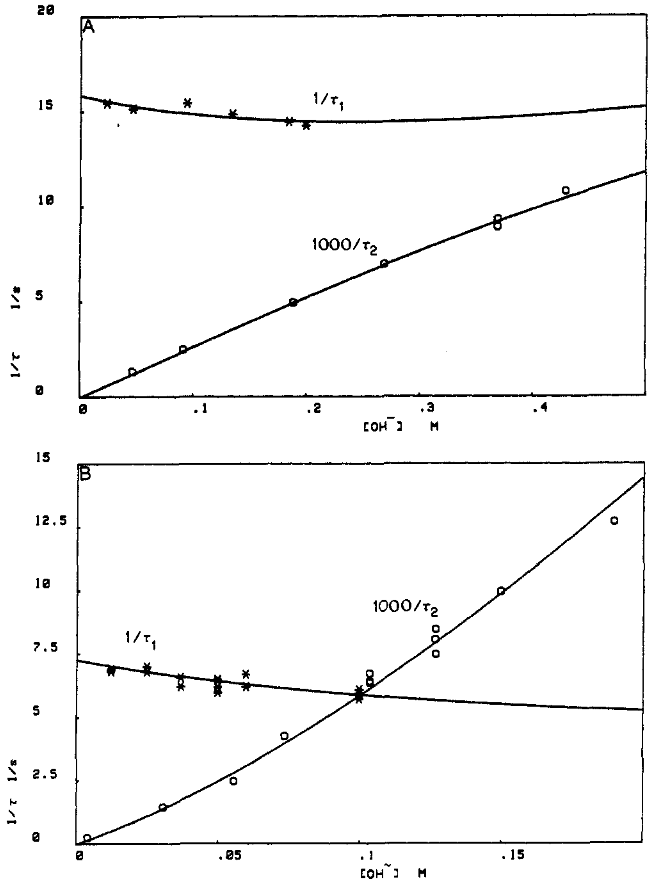

Figure 2. Values of τ^{-1} for reaction of 2,6-dinitrochlorobenzene with OH^-. (A) in 70:30 (v/v) DMSO–H_2O; (B) in 80:20 (v/v) DMSO–H_2O. The lines are calculated.

very rapid hydrogen exchange at position 3 eliminates this ^1H signal.[5] However, by examining the spectrum in DMSO-d_6–H_2O with solvent suppression of the ^1H signal we showed that the second relaxation is due to formation of Meisenheimer 5-complex; cf. ref 8. Equilibrium between Meisenheimer 3- and 5-complexes of 2,4-DNCB is expected to favor the latter,[6-9] and our MO calculations support this conclusion. Therefore the fastest relaxation involves formation of a Meisenheimer 3-complex, and the second a Meisenheimer 5-complex. Crampton et al. used Me_4NOH in 80:20 (v/v) DMSO–H_2O and followed only the two slower relaxations kinetically.[6a] Our values of τ_2^{-1} and τ_3^{-1} are similar to those reported earlier, although we used KOH instead of Me_4NOH.

2,6-Dinitrochlorobenzene. We saw only one relaxation followed at 450 nm for reaction of 2,6-DNCB with OH^- in 50:50 (v/v) DMSO–H_2O corresponding to formation of the phenoxide ion, and τ^{-1} followed eq 1 (Table II). This relaxation was also followed

$$10^4\tau^{-1} = 8.21[OH^-] + 11.8[OH^-]^2 \qquad (1)$$

at 450 nm in 70:30 and 80:20 (v/v) DMSO–H_2O. A faster relaxation, τ_1, was seen in 80:20 (v/v) DMSO–H_2O with relatively high [substrate] as an absorbance increase at 540–560 nm (Table II and Figure 2). There was indication of a third, very fast, relaxation for reaction in 80:20 (v/v) DMSO–H_2O with 0.05 M OH^- and 5×10^{-3} M DNCB with increasing absorbance at 450 nm and $\tau^{-1} \approx 10^3$ s^{-1}, but the amplitude was too low for the relaxation to be followed quantitatively.

Sulfite ion and 2,6-DNCB form a Meisenheimer 3-complex absorbing at 550 nm,[8] so the fast relaxation (Table II) is probably

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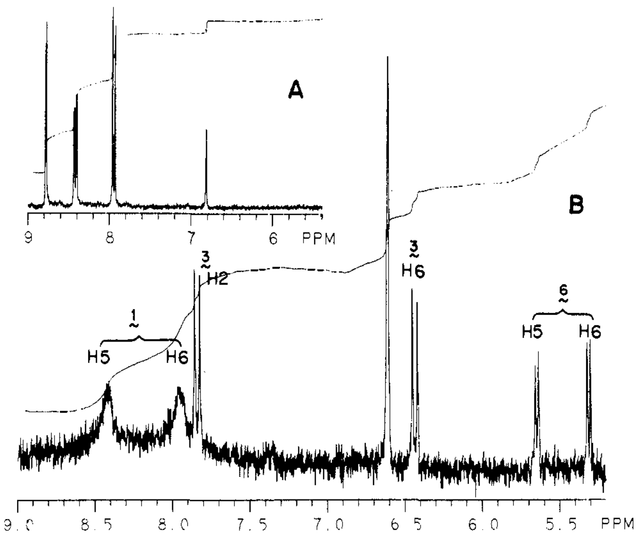


Figure 3. NMR spectrum of 2,4-dinitrochlorobenzene (0.05 M in 70:30 (v/v) DMSO-d_6–D_2O) with mesitoate ion as standard (6.6–6.8 ppm). (A) before addition of OD^-; (B) 1 min after addition of 0.13 M KOD at 25 °C.

due to formation of the Meisenheimer 3-complex of OH^- and 2,6-DNCB, but it is so short-lived that we could not obtain its NMR spectrum on a conventional instrument.

NMR Experiments. There is extensive hydrogen exchange at position 3 of 2,4-DNCB in DMSO–D_2O/OD^-.[5d] We have now used NMR spectroscopy to determine the structure of one of the nonproductive Meisenheimer complexes formed during reaction with OH^- in DMSO–H_2O.

The NMR spectrum of 2,4-DNCB in 70:30 (v/v) DMSO-d_6–D_2O (Figure 3A) has signals at 8.78 (d, $J = 2.7$ Hz), 8.42 (dd, $J = 8, 2.7$ Hz), and 7.95 ppm (d, $J = 8$ Hz) corresponding to hydrogens at positions 3, 5, and 6, respectively. The signal at position 3 disappears on addition of 0.13 M KOD and the other two signals broaden considerably (Figure 3B). Sharp signals of 2,4-dinitrophenoxide ion appear at 7.84 (d, $J = 9.6$ Hz, H5) and 6.44 ppm (d, $J = 9.6$ Hz, H6), and there are sharp signals of a Meisenheimer complex at 5.64 (d, $J = 6$ Hz, H5) and 5.32 ppm (d, $J = 6$ Hz, H6) by analogy with the sulfite complexes.[8] There are no signals of H3 of phenoxide ion, Meisenheimer complex, or unreacted substrate due to the rapid exchange. The signals of mesitoate ion, when added as standard, do not broaden in these, or any other, NMR experiments and are at 6.6–6.8 ppm.

We confirmed these results by examining the ^1H NMR spectrum in 80:20 (v/v) DMSO-d_6–H_2O and 0.13 M KOH at 2 °C with solvent suppression and short accumulation times. The spectrum (Figure 4) obtained within 2 min of mixing differs from that in D_2O–DMSO (Figure 3) in that we now see signals of H3 at 8.52 (Meisenheimer 5-complex) and 8.67 ppm (2,4-dinitrophenoxide ion) as well as the signals at positions 5 and 6 (cf. Figure 3). The spectrum obtained with solvent suppression is of poor quality in the region of the ^1H_2O signal (Experimental Section), but not so much as to invalidate our conclusions, and signals of the Meisenheimer complex (H5, H6) are in the expected region, cf. Figure 3. The chemical shifts of the signals of the Meisenheimer 5-complex are consistent with those of sulfite complexes of dinitrobenzene derivatives,[8] and with signals for reaction in DMSO-d_6–D_2O (Figure 3B). We saw no signal of 2,4-DNCB in the ^1H spectrum in DMSO-d_6–H_2O + OH^- (Figure 4), in part because some of the substrate had been converted into Meisenheimer complex and phenoxide ion, but also because signals of unreacted DNCB were so broad that they were lost in the noise (Figures 3 and 4). We did not see signals that could be ascribed to a Meisenheimer 3-complex because it has a short lifetime and is present only in low concentration.

We confirmed these results by reacting 2,4-DNCB partially with 0.13 M KOD in 80:20 (v/v) DMSO-d_6–D_2O and then adding excess DCl to stop the reaction. The spectrum then had sharp ^1H signals at positions 5 and 6 of 2,4-DNCB and 2,4-dinitrophenoxide ion, but no signals at position 3 (supplementary material, Figure S1). All these solutions contained mesitoate ion.

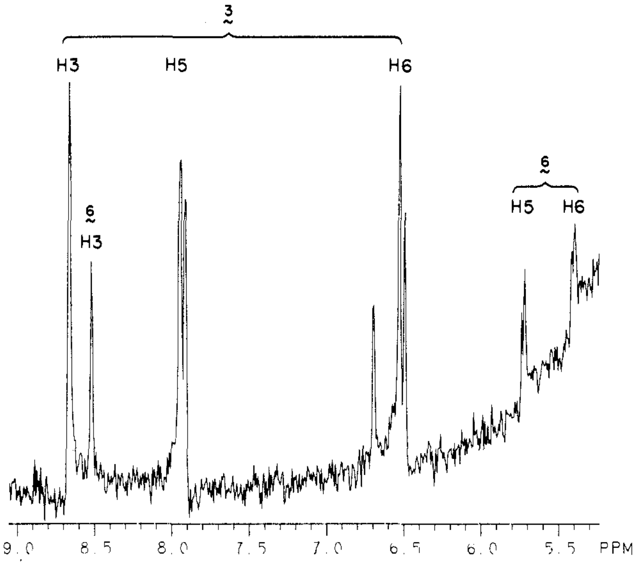


Figure 4. NMR spectrum of 2,4-dinitrochlorobenzene (0.05 M) with 0.13 M KOH in 80:20 (v/v) DMSO-d_6–H_2O at 2 °C, 2 min after mixing, with mesitoate ion as standard (ca. 6.7 ppm).

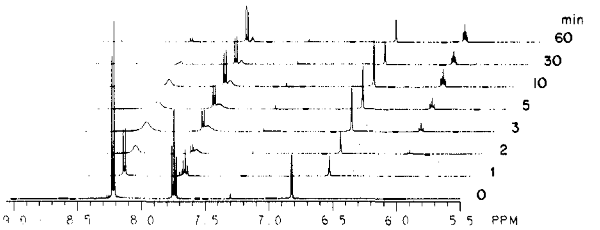
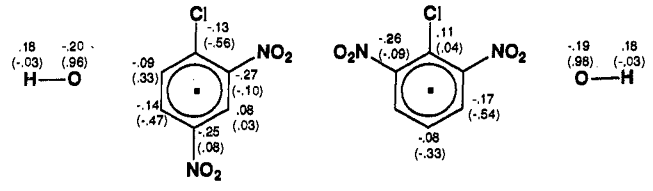


Figure 5. NMR spectrum of 2,6-dinitrochlorobenzene (0.037 M) in 72:28 (v/v) DMSO-d_6–D_2O, before ($t = 0$ min) and after addition of 0.05 M KOD, with mesitoate ion as standard, at 25 °C.

When we followed the reaction of 0.03 M 2,6-DNCB with 0.01 or 0.1 M KOD in 50:50 (v/v) DMSO-d_6–D_2O, we saw neither exchange nor ^1H line broadening in the NMR spectrum (not shown), but there is broadening (and exchange) in less aqueous media. Signals of 2,6-DNCB are sharp in 72:28 (v/v) DMSO-d_6–D_2O [8.22 (2 H at C3,5, d, $J = 8.1$ Hz) and 7.74 ppm (H at C4, t, $J = 8.1$ Hz)] (Figure 5). Within 2 min after addition of 0.05 M KOD, the ^1H signals broaden considerably, with $\Delta\nu_{1/2} \approx 27$ Hz, but no apparent change of chemical shift, and sharp signals of the phenoxide ion appear [7.80 (2 H at C3,5, d, $J = 8.1$ Hz) and 6.08 ppm (H at C4, t, $J = 7.5$ Hz)] (Figure 3B). After almost complete reaction (60 min) there are sharp signals of the phenoxide ion, with the triplet at 6.08 ppm now appearing as an apparent quintet at 6.09 ppm due to overlapping of the original triplet ($J = 8.1$ Hz) with a doublet ($J = 8.1$ Hz) but the same chemical shift. This partial exchange at C3,5 perturbs the coupling and integration gives ca. 24% exchange. These results are consistent with those observed earlier with substrate in excess over OD^-.[5d] Signals of the phenoxide and mesitoate ion were sharp. Line widths, $\Delta\nu_{1/2}$, of the broadened signals were ca. 30 Hz, but the "sharp" signals had $\Delta\nu_{1/2} \approx 2$ Hz, so the broadening is not due to instrumental artifacts or to changes in the medium due to addition of OD^-. Signals of the residual substrate begin to resharpen after 30 min because the concentration of the charge-transfer complex becomes so low that it does not interact, and exchange electrons, with substrate. The small signal at 7.3 ppm is an inert impurity, which was not removed by recrystallization of this sample of 2,6-DNCB, it was not present in other samples. Reaction of 0.04 M 2,6-DNCB with excess KOD (0.2 M) was also followed in 72:28 (v/v) DMSO-d_6–D_2O. There was extensive broadening of the signals of the substrate after 2 min,



2,4-DNCB **2,6-DNCB**

Figure 6. Charge distributions and spin densities (in parentheses) of charge-transfer complexes.

Table III. Formation Enthalpies of Charge-Transfer and Meisenheimer Complexes[a]

	2,4-DNCB	2,6-DNCB
CTC (**5**)	−24.9	−16.4
3-MC (**8**)	−84.0	−83.4
5-MC (**6**)	−87.7	
ipso-MC	−86.1	−86.9

[a] In kcal mol^{-1} relative to substrate + OH$^-$ with $\Delta H_f = -33.7$ kcal mol^{-1} for OH$^-$ (*Handbook of Chemistry and Physics*; Weast, R. C., Astle, M. J., Eds.; CRC Press; Boca Raton, FL, 1984) and calculated ΔH_f of 34.3 and 36.7 kcal mol^{-1} for 2,4- and 2,6-DNCB, respectively.

but not of the phenoxide ion (supplementary material, Figure S2).

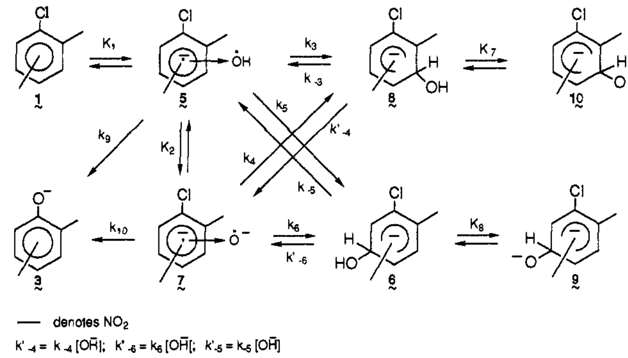
MO Calculations. The AM1 semiempirical method[10] was used to predict the geometries and formation enthalpies of various nitrobenzenes, dinitronaphthalenes, and their derivatives and the related charge-transfer and Meisenheimer complexes.[5f] The geometries of the substrates and relative stabilities of the Meisenheimer complexes agreed reasonably well with experimental results, even though the MO calculations involve approximations and relate to the gas phase at 0 K. The calculations predict that the charge-transfer complexes should form readily from substrates and OH$^-$. The charge-transfer complex of 1,3,5-trinitrobenzene and OH$^-$ had minimum enthalpy with $\dot{O}$H located ca. 2.2 Å above the center of the ring, and we based our calculations for the charge-transfer complexes of 2,4- and 2,6-DNCB on this geometry.[11] Charges and spin densities of the complexes are shown in Figure 6 and enthalpies for the substrates and intermediates are in Table III. The predicted geometry of 2,6-DNCB agrees well with that determined by electron diffraction.[12] As with other nitroarenes, Meisenheimer complexes are predicted to be more stable than charge-transfer complexes, and enthalpy decreases in conversion of substrates and OH$^-$ into charge-transfer complexes will be markedly offset by initial-state hydration. The calculations predict that there will be extensive transfer of charge from OH$^-$ into an antibonding orbital of the nitroarene with corresponding high spin density on OH.[5f,13]

The calculated enthalpies of Meisenheimer complexes of 2,4-DNCB decrease in the sequence 3 > 1 > 5 (Table III) and the first formed 3-complex readily equilibrates with the more stable 5-complex. Conversion into the 1-ipso complex is effectively irreversible because it rapidly loses Cl$^-$ to form 2,4-dinitrophenoxide ion.

The Meisenheimer 3-complex of 2,6-DNCB has a higher enthalpy than the 1-ipso complex, which should go rapidly to 2,6-dinitrophenoxide ion; so it is understandable that we saw little Meisenheimer complex in this overall reaction.

Comparison of the formation enthalpies of the charge-transfer and Meisenheimer complexes with those of 1,3-dinitrobenzene and 1,3,5-trinitrobenzene[5f] are informative. Formation enthalpies of intermediates are consistently more favorable for 1,3,5 trinitrobenzene, but are slightly more favorable for 2,4-DNCB than for 1,3-dinitrobenzene. Formation enthalpies are slightly more favorable for 1,3-dinitrobenzene than for 2,6-DNCB, especially as regards the charge-transfer complex.

Scheme III



Discussion

Reactions of dinitrohalobenzenes with dilute OH$^-$ in solvents of high water content are first order in each reagent, consistent with the classical mechanism (Scheme I), and it can be modified to include formation of unproductive Meisenheimer complexes for reaction in less aqueous solvents and with trinitrohalobenzenes.[2,6,7] However, it is not useful to assign mechanisms merely on the basis of arbitrarily chosen limiting conditions. We are attempting to develop mechanisms that not only fit rate data over the whole range of experimental conditions but also fit NMR and exchange results and are consistent with predictions based on MO calculations (Figures 1–6, Table III, and ref 14).

We observed only one relaxation in the reaction of 2,6-DNCB with OH$^-$ in 50:50 (v/v) DMSO–H_2O, and τ^{-1} fitted eq 1 up to 1.8 M OH$^-$ (Table II). The deviations from linearity could be ascribed to kinetic salt effects but a detailed analysis of reactions of OH$^-$ with di- and trinitroarene derivatives showed that kinetic salt effects are not very important in water and in 50:50 (v/v) DMSO–H_2O.[5b] We also saw deviations from linearity in plots of τ^{-1} against OH$^-$ for the slowest relaxation of 2,4-DNCB (Figure 1), but the curvature is opposite to that for reaction of 2,6-DNCB so it is unlikely to be due only to salt effects.

We saw more than one relaxation for reactions in 70:30 and 80:20 (v/v) DMSO–H_2O. Variations of τ^{-1} with [OH$^-$] for reactions of di- and trinitroarenes and the derived rate and equilibrium constants were fitted by a computer simulation based on relaxation theory,[5b,c,e,15] and we applied this treatment to reactions of 2,4- and 2,6-DNCB with Scheme III, which is similar to those used earlier (structures **6**, **8** and **9**, **10** are identical for reactions involving 2,6-DNCB). Assignments of the relaxations were based on electronic and NMR spectrometry. We could not follow quantitatively the very fast relaxation ($\tau^{-1} \approx 300$–800 s^{-1}) that had been seen with trinitrobenzenes and dinitronaphthalenes,[5b,c] although we have qualitative evidence for its existence, but with a very low amplitude. We therefore wrote Scheme III with substrate in equilibrium with charge-transfer complexes and did not explicitly consider formation of π complexes, as postulated for reactions of trinitrobenzenes and dinitronaphthalenes[5] where, based on the results of Caldin and co-workers, substrates and π complexes should be in equilibrium at 25 °C.[16]

The computer simulations are shown in Figures 1 and 2, where the lines are calculated and the equilibrium and individual rate constants are in Tables IV and V. Some of the intermediates are in rapid equilibria and then only equilibrium constants are

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(10) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

(11) As noted earlier,[5f] formation enthalpies for these nitro compounds have been corrected by subtracting 10.1 kcal mol^{-1} for each nitro group. Heats of formation of the nitroarenes calculated by the AM1 method are systematically 10.1 kcal mol^{-1} more positive than the experimental values.[5f]

(12) Batyukhnova, O. G.; Vilkov, L. V.; Sadova, N. I.; Pankrushev, Yu. A. *Zh. Strukt. Khim.* **1984**, *25*, 166.

(13) (a) Nagakura, S.; Tanaka, J. *Bull. Chem. Soc. Jpn.* **1959**, *32*, 734. (b) Nagakura, S. *Tetrahedron* **1963**, *19* (Suppl. 2), 361.

(14) Dotterer, S. K.; Harris, R. L. *J. Org. Chem.* **1988**, *53*, 777.

(15) Bernasconi, C. F. *Relaxation Kinetics*; Academic Press: New York, 1976.

(16) Allen, C. R.; Brook, A. J.; Caldin, E. F. *J. Chem. Soc.* **1961**, 2171, and references cited.

Table IV. Equilibrium Constants of Individual Steps in Reaction of Nitrochloroarenes

compound DMSO–H_2O, v/v	K_1, M^{-1}	K_2, M^{-1}	K_3	K_4, M	K_5	K_6, M	K_7, M^{-1}	K_8, M^{-1}
2,4-DNCB								
70:30	1.00	3.91	1.46	0.37	4.74	1.21	5.17	2.66
80:20	1.98	3.89	2.16	0.55	5.17	1.42	2.95	3.09
2,6-DNCB								
70:30	0.092	2.88	4.30	1.49			2.18	
80:20	0.088	4.40	4.93	1.12			3.77	
TNCB[a]								
0:100	0.12	1.94	2.28	1.17			46.8	
50:50	1.34	2.34	319	136			275	

[a] Reference 5b.

Table V. Individual Rate Constants in Reactions of Nitrochloroarenes

	2,4-DNCB[a]		2,6-DNCB[a]		TNCB[b]	
constant	70:30[c]	80:20[c]	70:30[c]	80:20[c]	0:100[c]	50:50[c]
k_3, s^{-1}	45.7	50.1	70.9	36.7	89.9	206
k_{-3}, s^{-1}	31.3	23.2	16.5	7.43	39.4	0.65
k_4, s^{-1}	62.6	40.5	24.0	4.54	44.9	210
k_{-4}, $M^{-1}\ s^{-1}$	168	73.0	16.0	4.05	38.4	1.54
k_5, s^{-1}	20.5	6.20				
k_{-5}, s^{-1}	4.32	1.20				
k_6, s^{-1}	5.93	6.55				
k_{-6}, $M^{-1}\ s^{-1}$	4.89	4.92				
k_9, s^{-1}	0.049	0.23	0.14	0.46	4.31	6.76
k_{10}, s^{-1}	0.18	0.37	0.04	0.59		97.0

[a] From Scheme III. [b] Reference 5b. [c] DMSO–H_2O, v/v.

Table VI. Limiting Second-Order Rate Constants in Dilute OH^-

compound	DMSO–H_2O, v/v	10^3k, $M^{-1}\ s^{-1}$ [a]		
		I	II	III
2,4-DNCB	70:30	2.4	2.8	2.3
	80:20	14	11	11
2,6-DNCB	50:50			0.82
	70:30	0.62	0.63	0.70
	80:20	1.3	1.5	1.5

[a] I, $k = K_1k_9$; II, calculated by simulation; III, experimental values from initial slope of τ^{-1} against $[OH^-]$.

calculated. All the equilibria are written as involving a forward reaction with OH^-; i.e., for proton transfers they are the inverse of basicity constants.

The computer simulation of reactions of 2,4-DNCB predicts that monoanionic Meisenheimer complexes are very rapidly converted into dianionic species by OH^-. We show this rapid reaction as a deprotonation because it was not represented by a relaxation. Formation of dihydroxy Meisenheimer complex is not expected to be rapid with a dinitrobenzene derivative, and in addition, values of K_7 and K_8 are not very sensitive to water content of the solvent (Table IV). We note that for reaction of 2,6-DNCB (Scheme III), **6** and **8** are equivalent, as are the dianions **9** and **10**.

The rate and equilibrium constants can be used to predict limiting values of τ^{-1} for formation of dinitrophenoxide ions in dilute OH^-. This calculation can also be made with eq 2, which

$$\tau^{-1} = K_1k_9[OH^-] \qquad (2)$$

neglects the existence of the deprotonated charge-transfer and unproductive Meisenheimer complexes under these conditions, or by complete simulation, and either set of values agrees reasonably well with experimental values (Table VI).

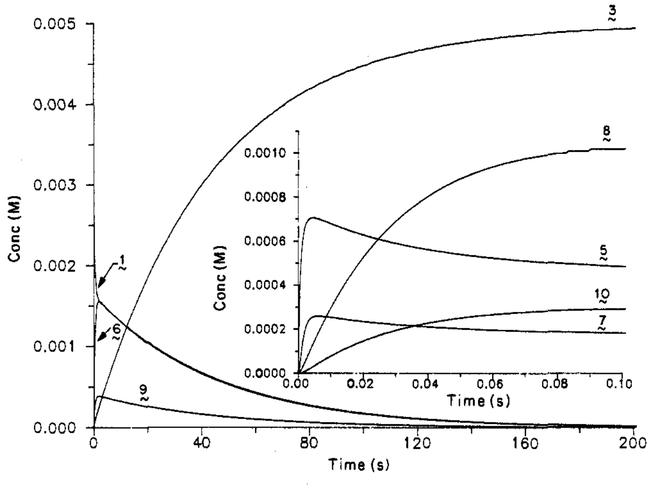

Figure 7. Predicted variation of concentrations of products and intermediates with time for reaction of 2,4-DNCB with 0.1 M OH^- in 80:20 (v/v) DMSO–H_2O.

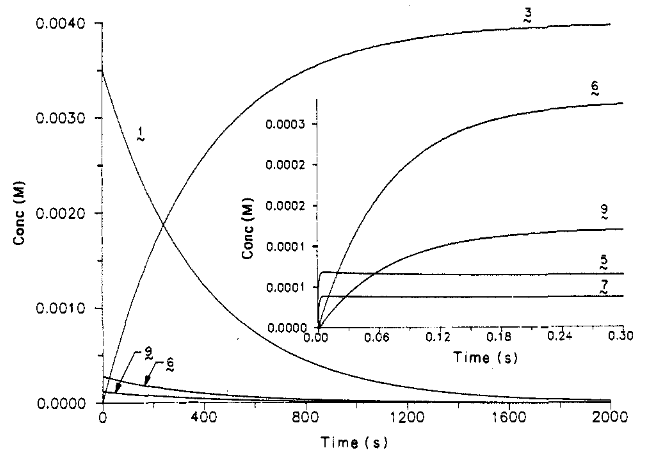

Figure 8. Predicted variation of concentrations of product and intermediates with time for reaction of 2,6-DNCB with 0.2 M OH^- in 70:30 (v/v) DMSO–H_2O.

Variations of concentrations of substrate, intermediates, and products with time can be calculated from the equilibrium and rate constants (Tables IV and V) by numerical integration,[17] and examples are shown in Figures 7 and 8. The kinetic data predict that in reaction of 2,4-DNCB with 0.1 M OH^- in 80:20 (v/v) DMSO–H_2O there will be a maximum of ca. 38% Meisenheimer 5-complex in the course of reaction, and this estimate is consistent with observed absorbances (Experimental Section). The prediction is that there will be only a small amount of Meisenheimer complex formed during reaction of 2,6-DNCB, and consistently we had to use relatively high [2,6-DNCB] to see the appropriate relaxation (Table II). The value of k_{10} in 70:30 (v/v) DMSO–H_2O is very low (Table V), and therefore the related reaction path is not very important and this value is uncertain.

Predicted variations of concentration with time (Figures 7 and 8) can be used to recalculate values of τ^{-1} under the appropriate conditions, and these values agree well with experimental values (Table VII). This calculation provides a test of the validity of the simulation and assignments of the relaxations.[5b] It is important

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[17] McKinney, R. J.; Weigert, F. J. Quantum Chemistry Program Exchange, Program QCMP022.

Table VII. Experimental and Calculated Values of τ^{-1}

compound	DMSO–H_2O, v/v	[OH^-], M	relaxtn	species	τ^{-1}, s^{-1} calcd	τ^{-1}, s^{-1} exptl
2,3-DNCB	80:20	0.1	1	**8**[a]	27	32
				10[a]	28	
			2	**6**[a]	2.4	2.4
				9[a]	2.4	
				8[b]	2.2	
				10[b]	2.5	
			3	**3**[a]	23×10^{-3}	23×10^{-3}
				1[b]	22×10^{-3}	
2,6-DNCB	70:30	0.2	1	**8**[a]	14.6	14.2
				10[a]	14.7	
			2	**3**[a]	2.5×10^{-3}	2.5×10^{-3}
				1[b]	2.68×10^{-3}	

[a] Formation. [b] Disappearance.

to recognize that relaxation theory has a great advantage over traditional methods in that values of τ^{-1} can be calculated by following any property of the system that varies linearly with concentration. Therefore, relaxations in the present system can be followed at any convenient wavelength, provided that Beer's law is obeyed and relaxations have a first-order kinetic form.[15]

Structural and Medium Effects. Individual equilibrium and rate constants for reactions of the dinitrochlorobenzenes are compared with those for 2,4,6-trinitrochlorobenzene (TNCB) in Tables IV and V, although reaction of TNCB was followed only in water and in 50:50 (v/v) DMSO–H_2O.[5b] Equilibrium constants for formation of unproductive Meisenheimer complexes decrease in the sequence TNCB > 2,4-DNCB > 2,6-DNCB, consistent with stabilizing effects of nitro groups and steric hindrance to resonance in 2,6-DNCB.[8,18] The AM1 calculations predict a dihedral angle of 54.6° between the nitro groups and the plane of the ring, in excellent agreement with the value of 54.1° from electron diffraction.[12]

Comparisons of equilibrium and rate constants in Tables IV and V are complicated by differences in solvent, but acid–base equilibrium constants for deprotonation of charge-transfer complexes (K_2) are not very sensitive to substituents on the arene ring because the OH residue in the complexes does not carry much negative charge. The equilibrium constants are not very different from that for deprotonation of $\dot{O}H$.[19]

Equilibrium constants for deprotonation of the Meisenheimer complexes of 2,4- and 2,6-DNCB (Table IV and Scheme III) are not very different, but that for the monohydroxy Meisenheimer complex of TNCB is larger despite unfavorable solvent effects. This difference is to be expected because of electron withdrawal by the additional nitro group.

Both rate and equilibrium constants for conversion of substrates into Meisenheimer 3-complexes (**8**) increase markedly in the sequence 2,6-DNCB < 2,4-DNCB < TNCB (Tables IV and V) despite differences in solvent composition. Values of ln K (where K is the overall equilibrium constant) correlate reasonably well with enthalpies of formation from reactants calculated by the AM1 method (Tables III and IV) despite differences in solvent composition.[20]

Line Broadening and Exchange. The kinetic simulations predict the existence of intermediates between reactants and the productive, ipso, and nonproductive Meisenheimer complexes. Even though we cannot follow quantitatively the relaxations involved in formation of charge-transfer complex intermediates, their existence is predicted by dependences of τ^{-1} on [OH^-], even in the reaction of 2,6-DNCB in 50:50 (v/v) H_2O–DMSO, where only one relaxation is observed (Table II and eq 1).

Broadening of ^1H NMR signals in reactions of nitroarenes with electron donors is well-known in apolar media,[21] and radical anions should rapidly exchange an electron with the parent nitroarene.[5a,d] The electronic structures of our postulated charge-transfer complexes are similar to those of radical anions so the observed line broadening in the course of overall substitution of 2,4- and 2,6-DNCB is readily explained by electron exchange between parent nitroarene and charge-transfer complex, which broadens the NMR signals of the parent.

The hypothesis that the line broadening is due to a side reaction that generates a radical anion does not fit the evidence. First, there is quantitative formation of aryl oxide ion in all these reactions in aqueous media. Second, there is extensive line broadening at the beginning of reaction and it decreases as reaction progresses.[5d] For reactions with 2,4- and 2,6-DNCB in excess over OH^- (OD^-), signals of substrate sharpen when OH^- (OD^-) is completely used up and signals of aryl oxide and mesitoate ion are always sharp, because these ions do not interact with the charge-transfer complex (Figures 3–5).

In many of the reactions of OH^- with nitroarenes and their derivatives, substrate and charge-transfer complex equilibrate in early stages of the overall reaction and the probability of exchange is related to the product of their concentrations. There is little charge-transfer complex present in reaction of 2,6-DNCB in 50:50 (v/v) DMSO–H_2O and therefore signals are not expected to broaden. We saw little line broadening in reactions of trinitrobenzenes and dinitronaphthalenes, probably because substrates go readily to charge-transfer complexes, which rapidly give Meisenheimer complexes and/or products. Therefore charge-transfer complexes do not build up enough to interact with substrate.

Exchange of arene hydrogens in the course of reaction is not explained by the classical mechanism (Scheme I). Substrate deprotonation by OH^- to form an arene anion[22] does not explain the exchange because it is larger in product than in unreacted substrate for some dinitroarene derivatives.[5d] Therefore exchange must occur in an intermediate between substrate and Meisenheimer complexes, and a charge-transfer complex is a reasonable candidate.

Exchange is regioselective and occurs wholly at position 3 in 2,4-DNCB (Figures 3 and 4), although qualitative models of electronic effects suggest that deprotonation by an external base should also occur at the 5-position[18] (ortho and para to NO_2). The charge-transfer complex of OH^- and 1,3,5-trinitrobenzene has the OH residue located symmetrically ca. 2.2 Å above the plane of

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(18) (a) Ingold, C. K. *Structure and Mechanism in Organic Chemistry*, 2nd ed.; Cornell University Press: Ithaca, NY, 1969; Chapter 2. (b) Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 3rd ed.; Harper and Row: New York, 1987; Chapter 1.

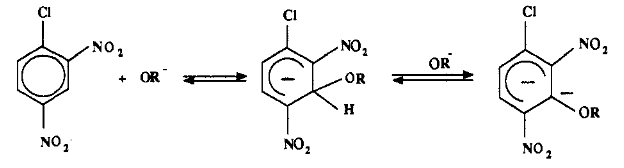
(19) Bard, A. J.; Parsons, P.; Jordan, J. *Standard Potentials in Aqueous Solution*; Marcel Dekker: New York, 1985; p 59.

(20) The enthalpy of formation of the Meisenheimer 3-complex of TNCB from reactants, calculated by the AM1 method, is -72.5 kcal mol^{-1}.

(21) (a) Layloff, T.; Miller, T.; Adams, R. N.; Fah, H.; Horsfield, A. P. *Nature* (*London*) **1965**, *205*, 382. (b) Katkova, N. M.; Bilkis, I. I.; Shein, S. M. *Kinet. Katal.* **1974**, *15*, 1138. (c) Katkova, N. M.; Bilkis, I. I.; Shein, S. M. *Izvest. Akad. Nauk Ser. Khim.* **1974**, 771. (d) Meot-Ner, M.; Neta, P. *J. Phys. Chem.* **1986**, *90*, 4648.

(22) (a) Shatenshtein, A. I. *Adv. Phys. Org. Chem.* **1963**, *1*, 156. (b) Streitweiser, A.; Hammons, J. H. *Prog. Phys. Org. Chem.* **1965**, *3*, 41. (c) Buncel, E.; Zabel, W. A. *J. Am. Chem. Soc.* **1967**, *89*, 3082. (d) Crampton, M. R.; Gold, V. *J. Chem. Soc. B* **1966**, 498.

Scheme IV



1 **11** **12**

the ring,[5f] and we used this geometry in estimating the reaction enthalpies given in Table III. However, this geometry may not be optimum for 2,4-DNCB because the OH residue in the charge-transfer complex has an overall, but small, negative charge and its interactions with the dipolar nitro groups should cause it to locate preferentially toward the 3-position. Exchange is probably intramolecular, with exchange involving arene CH and OD on the charge-transfer complex, and in that event, location of the OD (OH) residue close to position 3 will strongly favor exchange at this position.[23] If this explanation of the regiospecific exchange is correct regarding the geometry of the charge-transfer complex of 2,4-DNCB, the AM1 calculations (Table III) are underestimating the favorable reaction enthalpy. Location of OH near position 3 also explains kinetically controlled formation of Meisenheimer 3- rather than 5-complex (Figures 7 and 8, Table V), although formation of the latter is thermodynamically controlled.

A reviewer suggested an alternative mechanism of exchange and line broadening to that based on the reaction in Schemes II and III. Deprotonation of a Meisenheimer 3-complex (**11**) of 2,4-DNCB would generate the dianion (**12**) that could readily exchange an electron with substrate with consequent line broadening and exchange (Scheme IV). This reaction scheme is similar to that postulated by Guthrie and Nutter to explain formation of *tert*-butoxynitrobenzene from nitrobenzene and potassium *tert*-butoxide in tetrahydrofuran.[24] This solution is, however, much more basic than those used in our work.

This mechanism has some weaknesses. (i) Meisenheimer complex (**11**) should be a very weak acid, and much weaker than 2,4-DNCB itself. (ii) The Meisenheimer 3-complex (**11**) is a very transient species and is rapidly converted into the Meisenheimer 5-complex (ref 6a, Figures 3 and 4), and its deprotonation would give exchange at position 5, whereas there is little exchange at this position.

There is only limited hydrogen exchange in reaction of 2,6-DNCB with OD^-, consistent with a low equilibrium constant for formation of the charge-transfer complex and the less favorable reaction enthalpy (Table III). However, exchange is at position 3, and if the OH residue in the charge-transfer complex is displaced from the center of the ring toward this position, our AM1 calculations underestimate the favorable enthalpy of formation (Table III). We note that kinetic data and AM1 calculations predict that TNCB readily forms a charge-transfer complex and there is extensive exchange in the reaction with OD^-.[5d]

Conclusions. The classical mechanism of single-step nucleophilic addition to di- and trinitroarenes does not explain the kinetic results, provided that a wide range of conditions is analyzed. Observation of hydrogen exchange and NMR line broadening requires inclusion of intermediates that can be formed by a single-electron transfer from the nucleophile, and we postulate as the simplest explanation that these species are on the overall reaction path.

There is considerable evidence for single-electron transfers as general mechanisms in nucleophilic and electrophilic additions and substitutions.[25] This mechanistic model nicely fits correlations of nucleophilicity in polar media with vertical ionization or oxidation potentials.[26,27] Reactions of nucleophiles with activated arenes give addition or substitution products in polar hydroxylic solvents and radical-derived products in nonaqueous media,[3] but these differences do not require fundamental differences in mechanism if we accept that first formed charge-transfer complexes may collapse intramolecularly in polar and dissociate to free radicals in apolar media.

There is extensive evidence for the presence of free radical anions in reactions of arenes with nucleophiles in nonaqueous media,[3,4] although in some systems they may be formed via side reactions not on the path of the main products. However, we conclude that *free* radical species are not involved in our reactions in aqueous media, but that radicaloid species, e.g., **5** and **7** (Schemes II and III), are on the reaction path. These intermediates can exchange in D_2O and also form transient complexes with substrate to give NMR line broadening without impairing their collapse to give unproductive or productive Meisenheimer complexes and finally substitution products.

Experimental Section

Materials. Materials and procedures were as described.[5b]

Kinetics. Reactions were followed in a Durrum stopped-flow spectrometer or in Model 8450 or 8451 HP diode array or Beckman spectrophotometers at 25.0 °C as described.[5b,c] Relaxations followed first-order kinetics and [substrate] was selected to give reasonable absorbance changes. We followed formation of the Meisenheimer 3-complex of 2,4-DNCB at high wavelengths, well above λ_{max} to avoid interference with other species, and therefore had to use concentrations higher than those used in kinetic studies of trinitrobenzenes and dinitronaphthalenes.[5b,c,e]

NMR Spectra. Nicolet NT-300 or GN-500 spectrometers were used at 25 °C unless specified. Samples usually contained mesitoate ion as a standard. Spectra were generally taken in DMSO-d_6–D_2O at 25 °C, except for some reactions of 2,4-DNCB, which were examined in DMSO-d_6–H_2O–OH^- with solvent suppression at 2 °C. These spectra were run on the NT-300 because of its faster sample loading, but they suffered in quality, especially by comparison with those in D_2O, because of the solvent suppression and the requirement that we took the spectra in a short time forced us to use only a few accumulations without shimming after addition of KOH. The rising base line at lower than 5.5 ppm (Figure 4) is due to the partial suppression of the signal of ^1H_2O, which was due to a compromise between sensitivity and complete solvent suppression, especially in the region 5.5–5.7 ppm where there are signals (^{1}H5, ^{1}H6) of the Meisenheimer complex. In addition base-catalyzed hydrogen exchange between $(CD_3)_2SO$ and H_2O generated some HOD, which exchanged (to a limited extent) with 2,4-DNCB at the 3-position. Concentrations and lifetimes of the Meisenheimer 3-complex were such that we could not hope to see its NMR spectrum, although that of the 5-complex is easily seen. We could not use NMR spectrometry to examine the Meisenheimer complex of 2,6-DNCB because it is formed in very low concentration.

Kinetic Simulations. The multistep kinetics were analyzed by using relaxation theory with computer simulation on an HP 310 computer as described.[5c] Values of some of the derived kinetic parameters are uncertain, because particular reaction paths did not contribute significantly to the overall reaction.

The quality of the simulations was tested by using numerical integration with the Gear algorithm[17] to predict variations of concentrations of substrate, intermediates, and product with time.[5b] These variations were then used to recalculate τ^{-1} values and they agreed well with experimental values. Predictions of the amount of Meisenheimer 5-complex of 2,4-DNCB were in qualitative agreement with absorbances in the

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(23) We previously discussed this exchange as an intermolecular process, directly involving OD^- (OH^-) or D_2O (H_2O), but these explanations were not easily reconciled with the principle of microscopic reversibility or with charge distributions.[5d,f] Intramolecular exchange, within the charge-transfer complex, avoids these problems.

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range 370-420-510 nm measured on an HP 8450 spectrometer as soon as possible after mixing and assuming an extinction coefficient of ca. 10^4 at 510 nm.

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Supplementary Material Available: Figure S1, ^{1}H NMR spectrum of 0.05 M 2,4-DNCB after addition of 0.13 M KOD in 80:20 (v/v) DMSO-d_6-D_2O and further addition of 0.15 M DCl after 2 min, and Figure S2, ^{1}H NMR spectrum of 0.04 M 2,6-DNCB on addition of 0.2 M KOD in 72:28 (v/v) DMSO-d_6-D_2O at 25 °C as a function of time, and with mesitoate ion as standard (2 pages). Ordering information is given on any current masthead page.

Remote Electronic Perturbation of π-Facial Stereoselectivity in [4+2] Cycloadditions to Isodicyclopentafulvenes. The Consequences of *p*-Phenyl Substitution[1]

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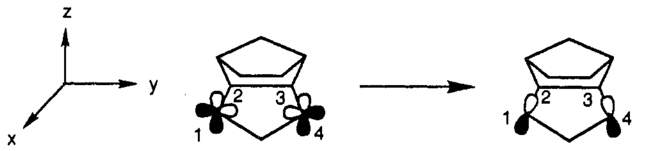
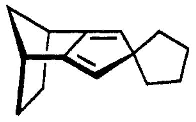
Abstract: Isodicyclopentafulvenes that carry an exocyclic para-substituted phenyl group as in **11** enter into Diels-Alder cycloaddition with highly reactive dienophiles exclusively from below the plane. The situation with the more sterically hindered and less reactive (*Z*)-1,2-bis(phenylsulfonyl)ethylene is one where addition occurs from both faces. The variation in the ratio **18**:**19** as a function of the group X adheres well to a linear free energy relationship involving $\sigma_R{}^+$ constants, especially when the NO_2 and CN examples are excluded. Photoelectron spectroscopic studies involving **11** provide insight into their orbital energies. A linear relationship was noted to exist between the **18**:**19** ratios and the fulvene HOMO-LUMO gaps. Competition experiments are also described, and theoretical studies are reported. The collective data provide the first evidence that long-range electronic effects can affect Diels-Alder stereoselection.

The extent of σ/π interaction within an isodicyclopentadiene is recognized to be dependent on the relative orbital energies of the interacting wave functions and on the size of the interaction matrix element $F_{\mu\nu}$. As $F_{\mu\nu}$ increases, interaction is enhanced and the terminal diene π lobes experience a remarkable, although modest, disrotation.[3] As seen in structures **1** and **2**, this phenomenon stems from superpositioning of the p_y component originating in the σ frame with the p_z component of the π network. The sense of disrotation is controlled by the sign of the p_y coefficient. If p_y and p_z are of the same sign, the lobes in question are rotated toward the methano bridge as in the illustration. The parent isodicyclopentadiene adopts this sense of twist.[4] When the signs of p_y and p_z are opposed, rotation occurs in the opposite sense.



1 **2**

Alteration in the extent and direction of disrotation has been held responsible for the π-facial stereoselectivity exhibited by dienes of this class in various cycloaddition reactions.[5,6] Indeed, we have earlier demonstrated that changes in the kinetically preferred direction of diene capture can be brought on by appropriate substitution of the cyclopentadiene methylene group or the apical methano bridge carbon.[7-9] In spirocyclopentane **3**, for example, the terminal π lobes are outwardly splayed and an above-plane approach is favored by a dienophile.[9] The lower analogue **4** experiences π-bond rotation in the opposite sense in response to the proximal cyclopropane ring, and [4+2] cycloaddition occurs from the below-plane direction in order to minimize the four-electron destabilization energy.[9]



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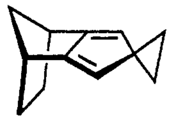

4

As concerns **5** and **6**, long-range through-bond interactions act to reduce the size of the p_y coefficient. This should translate into a diminished capacity to govern stereoselectivity. These hydrocarbons are in fact notable in that insignificant diastereoface discrimination is demonstrated in their Diels-Alder reactions.[7,8]

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