The Stabilities of Meisenheimer Complexes. Part 24.[1] Some Reactions of 2,4,6-Trinitrotoluene and 2,4,6-Trinitrobenzyl Chloride with Bases

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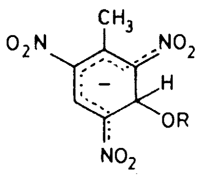
Kinetic and spectroscopic studies of the reaction of 2,4,6-trinitrobenzyl chloride (TNBCl) with alkoxides allow the identification of three processes resulting from 1 : 1 interaction. These are σ-complex formation by base addition at the 3- or 1-positions and transfer of a side-chain proton. In contrast with the behaviour of 2,4,6-trinitrotoluene the more stable σ-adduct derived from TNBCl results from addition at the 1-position and has a stability comparable with that of the conjugate base. Kinetic and equilibrium data are compared with those for reaction with bases of 2,4,6-trinitrotoluene (TNT) and 1,3,5-trinitrobenzene. It is shown that the hypochlorite ion is not sufficiently basic to give a σ-adduct with 1,3,5-trinitrobenzene in aqueous methanol, and it is suggested that the coloured species produced during the reaction of TNT with sodium hypochlorite in aqueous methanol result from reaction of TNBCl, the initial product, with alkoxide ions. In the presence of micelles of hexadecyltrimethylammonium chloride TNT reacts with bases to give a σ-adduct, which is thought to be a Janovsky complex.

THE reaction of 2,4,6-trinitrotoluene (TNT) with sodium hypochlorite yields the commercially important product 2,2′,4,4′,6,6′-hexanitrostilbene. 2,4,6-Trinitrobenzyl chloride (TNBCl) is likely to be an intermediate in this reaction and can be isolated in high yield during the initial stages.[2,3] The conversion is accompanied by the presence of intensely coloured species and it is with these that this paper is mainly concerned.

Likely modes of interaction of TNT, or TNBCl, with alkali are the formation of the conjugate base by transfer of a side-chain proton or formation of σ-adducts by base addition.[4] In the case of TNT there is now good evidence[5-7] that in the presence of alkoxide ions rapid formation of the adduct (1) is followed by production of the thermodynamically more stable anion (2). Kinetic and equilibrium data relating to these processes in methanol have been reported.[1] When TNT is in excess over the base, formation of a Janovsky complex by addition of a trinitrobenzyl anion to a second molecule of TNT has been observed.[5]



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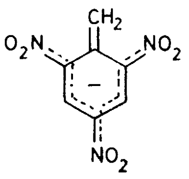

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TABLE 1

Reaction of 1,3,5-trinitrobenzene with sodium hypochlorite in 1 : 1 v/v methanol–water at 25°

[1,3,5-Trinitrobenzene]/M	[NaOCl] [a]/M	OD [b] (490 nm)	OD [c] (490 nm)	$k_{obs.}$[d]/s^{-1}
5 × 10^{-4}	0.025	0.005 24	0.007 45	8.1 ± 0.5
5 × 10^{-4}	0.063	0.008 77	0.0132	7.3 ± 1
5 × 10^{-4}	0.125	0.0182	0.0292	7.5 ± 1

[a] Buffered at pH 10. [b] After completion of the more rapid process —for 2 mm cell. [c] After completion of fast and slow colour-forming reactions—for 2 mm cell. [d] Refers to the slower of the two colour-forming processes.

In the presence of aqueous sodium sulphite both TNT and TNBCl give 1 : 1 and 1 : 2 adducts by sulphite attack at one or two unsubstituted ring-positions.[8] In liquid ammonia TNT forms a 1 : 1 adduct by amide ion addition at an unsubstituted ring-position and a 1 : 2 adduct by addition at the 1- and 3-positions.[9] A further possible mode of interaction between TNT or TNBCl and bases is electron transfer.[10]

RESULTS AND DISCUSSION

Commercially the reaction of TNT with sodium hypochlorite is carried out in tetrahydrofuran–methanol–water (2 : 1 : 2). The solution is maintained at pH 10.2. To provide some background information regarding the reactivity of the OCl$^-$ ion, measurements were initially made on the reaction of 1,3,5-trinitrobenzene with sodium hypochlorite in methanol–water (1 : 1 v/v).

Reaction of 1,3,5-*Trinitrobenzene and Sodium Hypochlorite.*—The visible spectrum measured on a conventional spectrophotometer, of a solution containing 1,3,5-trinitrobenzene (2 × 10^{-4}M) and sodium hypochlorite (0.05M) showed two peaks at λ 430 and 480 nm similar to those of alkoxide complexes.[4] Examination by stopped-flow spectrophotometry at 490 nm showed that two distinct colour-forming processes were present.

The faster was too rapid for measurement on the stopped-flow time-scale, while the slower had a half-life of *ca.* 0.1 s. These were followed by a much slower irreversible fading process. Data are in Table 1.

Possible nucleophiles are OH$^-$, OMe$^-$, or OCl$^-$ and our data are in accord with additions by hydroxide and methoxide only. Published data[11] indicate that under our experimental conditions the rate constant associated with methoxide addition to 1,3,5-trinitrobenzene has a value of *ca.* 300 s^{-1} while the corresponding value for hydroxide addition is *ca.* 10 s^{-1}. Thus the slower colour-forming reaction is attributed to hydroxide addition and the faster process, too fast to measure by the stopped-flow method, to methoxide addition. The constant ratio of optical densities at completion of the fast and slow colour-forming reactions is also in accord with addition of nucleophiles present in solution in a common ratio. If one of the processes were due to OCl^- addition the relative magnitude of the optical density change associated with this process would be expected to increase with increasing hypochlorite concentration. We conclude that the hypochlorite ion, the anion of hypochlorous acid, pK_a 7.53, is too weak a base to form σ-adducts with 1,3,5-trinitrobenzene in the solvent used.

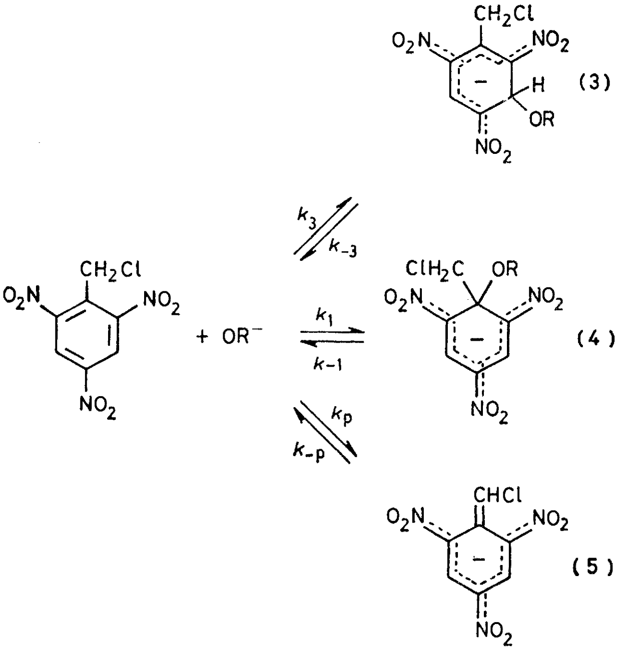
Reaction of 2,4,6-*Trinitrotoluene with Sodium Hypochlorite in Methanol–Water.*—Solutions of TNT (10^{-4}–10^{-3}M) and sodium hypochlorite (0.1M) in 1 : 1 v/v methanol–water are orange-red, the visible spectrum showing maxima at 430 and 510—520 nm.

In contrast to this, but in agreement with previous work,[1,5-7] solutions containing TNT and sodium methoxide in methanol–water gave the purple colour ($\lambda_{max.}$ 365, 510, and 650 nm) expected for the conjugate base (2).

These visible spectra indicate that the major coloured species produced from TNT in the presence of hypochlorite is not the conjugate base (2); although this latter species will presumably be an intermediate in the conversion of TNT to TNBCl. Also TNT is less susceptible to base addition than is 1,3,5-trinitrobenzene,[1,8] so that it is unlikely that direct addition of hypochlorite ions occurs to the TNT ring. It is also unlikely that the species we are observing is the Janovsky complex formed by attack of the trinitrobenzyl anion on TNT since this complex is reported to absorb at 450 and 550 nm in alcohol. (The positions of absorption maxima vary with the nature of the attacking base and are at longer wavelengths for carbon bases than for oxygen bases.[4])

It seemed probable that the colour observed in the reaction with hypochlorite might derive not from TNT itself but rather from the reaction of the intermediate TNBCl with hydroxide and/or methoxide ions. We have therefore examined the interaction of TNBCl with several alkoxides. For ease of interpretation we have worked with pure alcohols as solvents.

Reactions of 2,4,6-*Trinitrobenzyl Chloride with Alkoxides. General Consideration.*—Our results detailed below provide evidence for three modes of reversible 1 : 1 interaction of TNBCl with alkoxide ions. In order of decreasing rate these are addition at the 3-position to give (3), addition at the 1-position to give (4), and transfer of a side-chain proton to give (5). The data are interpreted in terms of the Scheme. Kinetic measurements were made by stopped-flow spectrophotometry in the visible region at 25°. Alkoxide was always in large excess over TNBCl so that first-order kinetics were obtained. The rates of the three processes are well separated. Hence the variations with base concentration of the rate coefficients are given by equations (1)—(3) where the subscripts, fast, med., and slow, denote the relative rates of the reactions. The derivation of (3) assumes that, as found, the value of K_1 is much larger than that of K_3. When $K_1[OR^-] \gg 1$ equation (3) reduces to (4).



SCHEME

$$k_{fast} = k_3[OR^-] + k_{-3} \qquad (1)$$

$$k_{med.} = \frac{k_1[OR^-]}{1 + K_3[OR^-]} + k_{-1} \qquad (2)$$

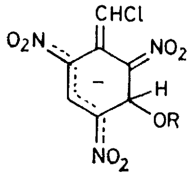
$$k_{slow} = \frac{k_p[OR^-]}{1 + K_1[OR^-]} + k_{-p} \qquad (3)$$

$$k_{slow} = \frac{k_p}{K_1} + k_{-p} \qquad (4)$$

Reaction of TNBCl with Sodium Methoxide in Methanol.—On mixing TNBCl (10^{-5}M) and sodium methoxide (10^{-2}M) in the stopped-flow spectrophotometer a species is produced with $\lambda_{max.}$ 430 and 510 nm, typical of a σ-adduct. The spectrum changes with time, eventually having maxima at 370, 430, 500, and 650 nm. The final spectrum is seen (Figure 1) to represent a mixture in roughly equal proportions of the initially produced σ-adduct and the conjugate base (5), whose spectrum was obtained by adding DABCO to TNBCl in DMSO.

^1H N.m.r. measurements show that the major species present at equilibrium are (4; R = Me) and (5). Spectra were recorded in 75 : 25 v/v methanol–DMSO using fully deuteriated solvents. Chemical shifts are in Table 2. The ring-protons of (5) are non-equivalent and give spin-coupled bands, *J* 2.3 Hz. No bands are observed attributable to (3). However in the presence of more than one equivalent of base new doublets, *J* 3 Hz, at 6.22 and 8.68 and a singlet at δ 7.55 are observed; these indicate the formation of the dianion (6; R = CD_3), analogous to the di-anion from TNT.[7]

The use of sodium methoxide rather than its deuteriated analogue allowed the observation of a band at δ 3.00 attributed to the added methoxy-group of (4; R = CH_3).



(6)

The n.m.r. spectra show that in the solvent system used *ca.* 60% of the 1 : 1 interaction results in base addition and *ca.* 40% in proton loss. Some preliminary measurements on the solvent dependence of the 1 : 1 interactions suggested that the fraction of base addition increases with the proportion of DMSO in the solvent.

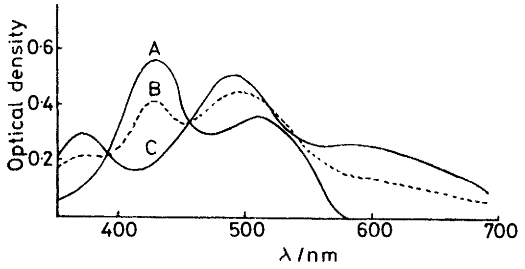


FIGURE 1 Visible spectra of TNBCl (4 × 10^{-5}M) in the presence of base. A, Spectrum measured by stopped-flow, of the σ-adduct (4) initially produced in the presence of 10^{-2}M-sodium methoxide in methanol; B, same solution at equilibrium; C, spectrum of the conjugate base (5) produced by the addition of 10^{-2}M-DABCO in DMSO solution

Kinetic and equilibrium data relating to dilute solutions of sodium methoxide in methanol were obtained by stopped-flow spectrophotometry and are in Table 3. Only two of the three possible processes associated with 1 : 1 reaction were observed, the missing process being formation of (3; R = Me). The data in Table 3 show that the values of the rate coefficients of the faster process, k_{med}, are independent of TNBCl concentration but increase with base concentration. A plot, not shown, of $k_{\text{med.}}$ *versus* sodium methoxide concentration is linear indicating that equation (2) approximates to $k_{\text{med.}} = k_1[\text{OMe}^-] + k_{-1}$, showing that $K_3[\text{OMe}^-] \ll 1$. The intercept and slope of this plot give values for k_1 770 ± 30 l mol^{-1} s^{-1} and k_{-1} 2.2 ± 0.2 s^{-1}. Combination of these values gives a value for K_1 ($=k_1/k_{-1}$) of 350 ± 50 l mol^{-1} which is in good agreement with values obtained from optical density measurements at 430 or 500 nm.

TABLE 3

Kinetic and equilibrium data for reaction of 2,4,6-trinitrobenzyl chloride with sodium methoxide in methanol at 25°

[NaOMe]/M	10^5 [TNBCl]/M	$k_{\text{med.}}/\text{s}^{-1}$	OD (430 nm) [a]	K_1/l mol^{-1}	OD (500 nm) [a]	K_1/l mol^{-1}	OD (500 nm) [b]	K_T/l mol^{-1}
0.001	1.0	3.0 ± 0.2	0.0077	360	0.0047	380	0.0079	590
0.002	1.0	3.9	0.0113	320	0.0075	390	0.012	640
0.002	5.0	3.9	0.051	270	0.033	320	0.055	540
0.002	10.0	4.0	0.0112	320	0.072	370	0.115	590
0.004	1.0	5.4	0.0164	330	0.0107	420	0.015	600
0.007	1.0	7.3	0.0205	340	0.0120	340	0.0168	540
0.010	1.0	10.1	0.0231	380	0.0132	350	0.0185	660

[a] After completion of σ-complex formation. OD for complete conversion (Benesi–Hildebrand plots) are 0.029 (430 nm) and 0.017 (500 nm); 2 mm cells. [b] After equilibration between σ-complex formation and proton transfer. OD for complete conversion is 0.213; 2 mm cells.

Values of the optical density at 500 nm after equilibration between (4; R = Me) and (5) give a value for K_T, the total equilibrium constant, of 600 ± 50 l mol^{-1}.

TABLE 2

Chemical shifts (δ) for products of reaction of TNBCl with methoxide

	Ring	Side-chain	Methoxy
TNBCl	9.09	5.00	
(4; R = CD_3)	8.75	4.70	
(4; R = CH_3)	8.70	4.68	3.00
(5)	8.20 (d) 8.50 (d)	6.90	
(6; R = CD_3)	6.22 (d) 8.68 (d)	7.55	

Hence from equation (5) we obtain a value for K_p of 250 l mol^{-1}. Rate measurements on the slow equilibration process were made at 500 nm and showed that in

$$K_T = K_1 + K_p \qquad (5)$$

the range 0.01—0.10M-sodium methoxide the value of k_{slow} (0.11 ± 0.01 s^{-1}) was independent of base concentration. This indicates that equation (4) is applicable, and using the known values of K_1 and K_p values were obtained for k_p 16 l mol^{-1} s^{-1} and k_{-p} 0.065 s^{-1}.

We attribute the failure to observe the formation of (3; R = Me) to the low stability expected for this adduct. For comparison the values of the equilibrium constants for methoxide attack at unsubstituted ring positions of related compounds are 1,3,5-trinitrobenzene[12] 20 l mol^{-1}; 2,4,6-trinitroanisole[13] 2.7 l mol^{-1}, and 2,4,6-trinitrotoluene[1] 0.07 l mol^{-1}. Hence at the base concentration used in the present work the concentrations of (3; R = Me) present in equilibrium with TNBCl and base are likely to be small. Further the value of 2.2 s^{-1} we observe for the rate constant for methoxide expulsion is considerably smaller than values usually found[12,13] (*ca.* 300 s^{-1}) when methoxide departs from a ring-carbon carrying hydrogen, providing independent kinetic evidence that the σ-adduct we are observing here is (4) rather than (3).

Reaction of TNBCl with Sodium Ethoxide in Ethanol.—The basicity of the ethoxide ion is greater than that of methoxide and here all the three processes of the Scheme were observed. Data are in Table 4. At base concentrations above 0.02M a fast colour-forming reaction is observed giving (3; R = Et) which has absorption maxima at 430 and 510 nm. The rate and amplitude of this process increase with increasing base concentration. Because of the subsequent equilibration to give (4) the measured rate coefficients, k_{fast}, are subject to quite large errors. Consequently a plot according to equation (1) gives a value for k_3 of 10^4 l mol^{-1} s^{-1} but has an uncertain intercept (k_{-3}).

TABLE 4

Kinetic data for the reaction of 2,4,6-trinitrobenzyl chloride with sodium ethoxide in ethanol at 25°

[NaOEt]/M	k_{fast}/s^{-1}	$k_{\text{med.}}$/s^{-1}	$k_{\text{med.}}$[a](calc)/s^{-1}	OD [b] (430 nm)	k_{slow}/s^{-1}
0.001		3.8 ± 0.2	4.1	0.029	
0.0015		5.0	5.1	0.029	0.0071
0.002		5.7	5.8	0.030	
0.003	35 ± 10	6.8	6.8	0.029	0.0067
0.005	60	7.4	7.7	0.029	0.0074
0.0075	85	8.7	8.8	0.030	0.0079
0.010	115				

[a] Calculated from equation (2) with K_3 700 l mol^{-1}, k_1 7 000 l mol^{-1} s^{-1}, and k_{-1} 0. [b] After completion of the second rate process, designated $k_{\text{med.}}$.

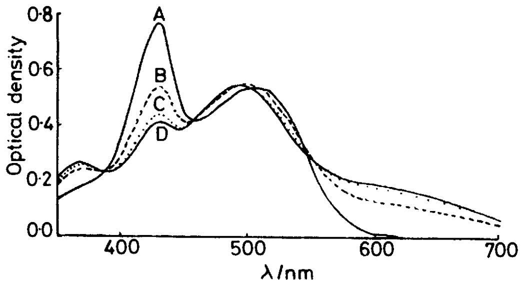


FIGURE 2 Visible spectra of TNBCl (5×10^{-5}M) and sodium ethoxide (1×10^{-3}M) in ethanol, taken at 2-min intervals, A—D. The spectra show the equilibration between (4; R = Et) and (5)

The second process is also colour-forming and gives (4; R = Et) which has a visible spectrum very similar to that of its isomer (3; R = Et). The similarity of these spectra is not unexpected in isomeric adducts from a trinitrobenzene derivative.[13] The variation with base concentration of $k_{\text{med.}}$ is fitted well by equation (2) with K_3 700 l mol^{-1} s^{-1} and k_{-1} negligibly small. The value of the optical density at completion of this process is independent of the base concentration down to 10^{-3}M indicating a very high value for K_1. We estimate that $K_1 > 10^4$ l mol^{-1}. Using the above value for K_3 and the known value for k_3 we calculate a value for k_{-3} ($= k_3/K_3$) of 14 s^{-1}.

In agreement with the above analysis, the ^{1}H n.m.r. spectrum of the more stable σ-adduct shows bands at δ 8.68 (ring protons), 4.68 (CH_2Cl), and 3.09 (OCH_2) as expected for (4; R = Et).

These reactions are followed by a much slower process whose progress can be followed by conventional spectrophotometry. The spectra in Figure 2 show this equilibration between (4; R = Et) and (5), the latter having maxima at 370, 500, and 650 nm. The rate constant for this process is independent of base concentration as expected for the case when $K_1[OR^-] \gg 1$.

Reaction of TNBCl with Isopropoxide Ions in Propan-2-ol.—The carbon basicity of the isopropoxide ion is very high,[14] so that values of K_3, K_1, and K_p will be large, with high values of the forward rate constants and low values of the reverse rate constants. It follows that the kinetically favoured species will equilibrate only very slowly to the thermodynamically preferred species.

On mixing TNBCl with sodium isopropoxide solutions a σ-adduct with $\lambda_{\text{max.}}$ 430 and 505 nm is rapidly produced. With time the lower wavelength band gradually decreases in intensity and a small peak develops at 380 nm. These changes are consistent with equilibration with the conjugate base (5). However the changes were so slow and were accompanied by irreversible decomposition reactions that they were not quantitatively studied. Rate coefficients for the rapid colour-forming reaction are in Table 5. In considering these data we must take account of the high degree of ion-association of sodium isopropoxide ($K_{\text{Na}^+,\text{PrO}^-}$ 1.9×10^4 l mol^{-1}).[15] A plot of rate coefficient against sodium isopropoxide

TABLE 5

Rate coefficients for the addition of isopropoxide to TNBCl [a] in propan-2-ol at 25°

10^4[NaOPr]/M	[$NaBPh_4$]/M	k_{fast}/s^{-1}
4.0		11 ± 1
7.0		20
10		32
20		46
40		73
70		118
100		162
5	0.01	5
20	0.01	20
35	0.01	33
50	0.01	54
10^4[NMe_4OPr]/M		
3		20
3.8		35
4.5		40
6.0		54
7.5		76
10		93

[a] [TNBCl] is 1×10^{-5}M. Optical density measurements indicate that conversion into adduct is virtually complete in every case.

concentration shows marked curvature. Using tetramethylammonium isopropoxide, where in dilute solutions association will be small, a straight line of slope 10^5 l mol^{-1} s^{-1} is obtained. In solutions containing added sodium ions, where ion-association will be nearly complete, a linear plot with slope 10^4 l mol^{-1} s^{-1} results. These data are reminiscent of those for isopropoxide addition to 1,3,5-trinitrobenzene [14] and indicate a much higher reactivity for the free isopropoxide ion than for its ion pair. We are unable to tell unequivocally whether these data refer to addition at the 3- or 1-position of TNBCl (n.m.r. mesurements were inconclusive) but consider the former possibility more likely since rate coefficients are similar to those for addition at an unsubstituted position in 1,3,5-trinitrobenzene. The failure to detect the isomerisation of (3) to (4) may reflect the similarities in the spectra of these species.

TABLE 6

Comparison of the reactions of 2,4,6-trinitrobenzyl chloride, 2,4,6-trinitrotoluene, and 1,3,5-trinitrobenzene with sodium methoxide in methanol and sodium ethoxide in ethanol at 25°

	k_3/l mol^{-1} s^{-1}	k_{-3}/s^{-1}	K_3/l mol^{-1}	k_1/l mol^{-1} s^{-1}	k_{-1}/s^{-1}	K_1/l mol^{-1}	k_p/l mol^{-1} s^{-1}	k_{-p}/s^{-1}	K_p/l mol^{-1}
TNBCl–Methoxide			<20	770	2.2	350	16	0.065	250
TNT–Methoxide [a]	280	3 000	0.07				13.3	1.1	12.4
TNB–Methoxide [b]	7 300	330	20						
TNBCl–Ethoxide	10 000	14	700	7 000	<1	>10 000			
TNT–Ethoxide [c]							82	0.045	1 800
TNB–Ethoxide [b]	40 000	20	2 000						

[a] Refs. 1 and 5. [b] Ref. 12 (refers to addition at an unsubstituted position). [c] Ref. 5.

Comparison with Other Substrates of the Reaction of TNBCl with Alkoxides.—Data are summarised in Table 6 where they are compared with corresponding data for 2,4,6-trinitrotoluene and 1,3,5-trinitrobenzene. One of the most noteworthy features is that the σ-adducts formed by alkoxide addition to the 1-position of TNBCl have considerably greater thermodynamic stability than those formed in addition to the 3-position. This contrasts with the behaviour of TNT where σ-adducts are observed only from attack at the 3-position.[1,7] One important factor favouring alkoxide addition at the 1-position in the case of TNBCl is likely to be the greater inductive withdrawal of the CH_2Cl group compared with the CH_3 group. However steric factors may be the main consideration. Thus formation of (4) will result in considerable relief of steric strain as the CH_2Cl group is bent from the ring-plane. This factor will be less important for the less strained TNT molecule.

The rate data indicate that addition at the 1-position is slower than at the 3-position, although the main difference is in the rates of alkoxide departure, expulsion from the 1-position being considerably slower than from the 3-position.

Previous results [8] have shown that sulphite attack on TNBCl and TNT occurs exclusively at unsubstituted ring-positions. The failure to observe sulphite attack at the 1-position of TNBCl may reflect the unfavourable steric effects of two very bulky groups attached to the same carbon atom.

The value of K_p, the equilibrium constant for transfer of a side-chain proton, is *ca*. 20 times larger for TNBCl than for TNT. As expected the electronegative chlorine atom enhances the acidity of the adjacent proton. However the acidity of 4-nitrobenzyl chloride is reported [16] to be higher by a factor of *ca*. 700 than that of 4-nitrotoluene. The reduction in the trinitro-series of the acid-enhancing effect of the chlorine atom may be due to unfavourable steric interaction in (5) between the chlorine and adjacent nitro-group to which the trinitrobenzyl anion (2) is not subject.

The overall effect is that in contrast to TNT, where the thermodynamically stable product of reaction with alkoxides is the trinitrobenzyl anion, the reaction of TNBCl with alkoxides results in the formation at equilibrium of both the σ-adduct (4) and the conjugate base (5). It is very probable that the visible spectrum referred to previously, obtained in the reaction of TNT with sodium hypochlorite in aqueous methanol, derives from σ-adducts formed by methoxide–hydroxide addition to TNBCl perhaps together with the conjugate base (5).

Micellar Effects on the Reaction of TNT with Bases.—In previous work [17] it has been shown that the presence of surfactants may enhance the rate of colour formation between TNT and bases in aqueous solution. It was assumed [17] that the coloured species produced was the trinitrobenzyl anion (2).

We have examined the effect of hexadecyltrimethylammonium chloride on the reaction in water between TNT and two bases, potassium hydroxide or 3,3′-diaminodipropylamine. Visible spectra obtained in the presence of potassium hydroxide and surfactant are in Figure 3 and show the formation of a species with $\lambda_{max.}$ 445 and 530 nm. With time an irreversible decomposition to a species with $\lambda_{max.}$ 350 nm occurs. That this is a micellar phenomenon is shown by the variation in the relative rate of colour formation with surfactant concentration (Figure 4). The visible spectrum of the species obtained when the base used is 3,3′-diaminodipropylamine rather than potassium hydroxide also shows maxima at 445 and 530 nm.

Clearly these spectra indicate formation of a σ-adduct rather than the trinitrobenzyl anion. It is possible that these σ-adducts result from direct attack of the hydroxide ion or the amine on the TNT ring. However the similarity of the spectra obtained in the presence of two different bases is difficult to rationalise on this basis.

In fact the positions of the absorption maxima are quite similar to those (450 and 550 nm) reported[5] for the Janovsky complex formed by attack of the trinitrobenzyl anion on TNT. Also close examination of Figure 3 and other spectra shows that in the very early stages a band at 370 nm is present and that the ratio of optical densities at 530 and 445 nm decreases with time. This suggests that the trinitrobenzyl anion, $\lambda_{max.}$ 365, 510, and 650 nm, is initially present in low concentration. Thus we suggest that in the environment of the cationic micelles initial formation of the trinitrobenzyl anion is followed by Janovsky complex formation.

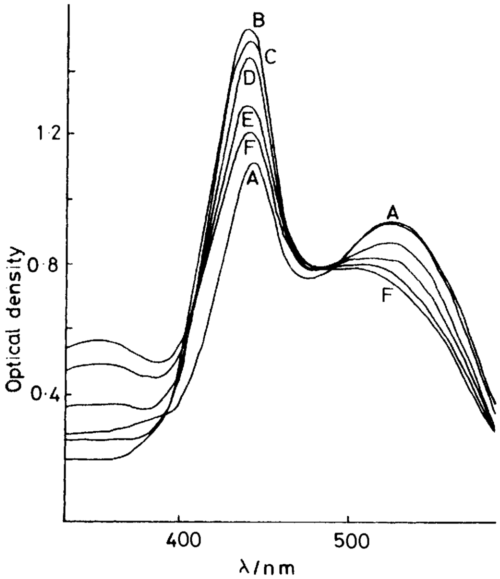


FIGURE 3 Visible spectra of 2,4,6-trinitrotoluene (10^{-4}M), potassium hydroxide (10^{-3}M) ,and hexadecyltrimethylammonium chloride (3×10^{-3}M) in water at 2-min intervals, A—F

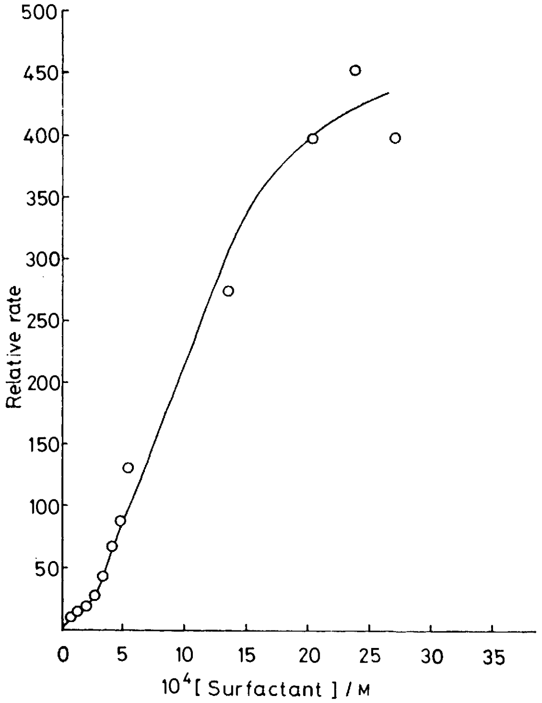


FIGURE 4 Dependence on concentration of hexadecyltrimethylammonium hydroxide of the initial rate of colour formation between TNT (10^{-4}M) and potassium hydroxide (10^{-3}M)

EXPERIMENTAL

2,4,6-Trinitrotoluene, m.p. 82° (lit.,[18] 82°), and 2,4,6-trinitrobenzyl chloride, m.p. 85° (lit.,[2] 85°), were prepared by standard methods. Solutions of sodium alkoxides were prepared by solution of clean pieces of sodium in AnalaR alcohol and were titrated against standard acid. Solutions of tetramethylammonium isopropoxide were prepared by dilution of a concentrated aqueous solution of tetramethylammonium hydroxide with AnalaR propan-2-ol (the solution so prepared contained <0.1% water). Commercial sodium hypochlorite solutions were diluted with water and standardised by titration with sodium thiosulphate after the addition of excess of potassium iodide. Solutions of hypochlorite of pH 10 were prepared by dilution, just before use, of a concentrated solution with an aqueous solution of borax buffer.

^{1}H N.m.r. measurements were made with a Bruker HX90E instrument modified for Fourier-transform operation and using a deuterium lock. Chemical shifts were measured relative to internal tetramethylsilane. Visible spectra were measured using Unicam SP 500 or 8000 instruments, or a Canterbury stopped-flow spectrophotometer. All kinetic measurements were made at 25° with base in large excess over substrate so that first-order kinetics were obtained. The slow reaction, designated k_{slow}, of TNBCl with sodium ethoxide, and the colour formation of TNT with base in the presence of hexadecyltrimethylammonium chloride, were sufficiently slow to measure using a conventional spectrophotometer. Rate coefficients for other reactions were determined by mixing freshly prepared solutions of reagents in the stopped-flow spectrophotometer. In most cases the rates of the various processes occurring were well separated in time, so that steady 'infinity values' could be obtained. However there was some interference between the most rapid reactions, designated k_{fast} and $k_{med.}$, observed between TNBCl and sodium ethoxide. The procedure adopted to evaluate the rate coefficients was that of Bernasconi.[5] Thus $k_{med.}$ was determined from measurements of the exponential obtained after completion of the more rapid reaction. The change in optical density with time due to this process, $k_{med.}$, is in the early stages approximately linear. Hence the fast process, k_{fast}, appeared as an exponential superimposed on a straight line and could thus be evaluated.

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