A Kinetic Study of the Reaction of Ethoxide Ion with 2,4,6-Trinitrotoluene and 2,4,6-Trinitrotoluene-d_3[1]

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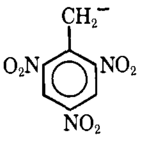
Abstract: The kinetics of reaction of ethoxide ion with 2,4,6-trinitrotoluene (TNT) and TNT fully deuterated at the methyl position (TNT-d_3) have been investigated by means of a stopped-flow technique. The rate-determining step in the reaction is shown to be the transfer of a proton from the methyl group of the TNT to the ethoxide ion. The forward rate constants for the reaction of TNT with ethoxide ion in ethanol and ethanol-*O-d* are 138 and 250 M^{-1} sec^{-1}, respectively, at 25°. The corresponding rate constants for TNT-d_3 are 19.8 and 39.1 M^{-1} sec^{-1}. Under the experimental conditions a second species is formed in sufficient amount to affect the kinetic analysis. This species may be a σ complex of TNT and ethoxide ion.

Aromatic nitro compounds react with alkoxides to give a variety of colored products.[2] In the case of 2,4,6-trinitrotoluene (TNT), the attack of ethoxide ion in ethanol solution leads to two main colored species.[3a] At high concentrations of TNT ($\sim 10^{-3}$ *M*) and ethoxide (~ 0.1 *M*) a brown species is formed, originally tentatively identified as a charge-transfer complex.[3b] At low concentrations of TNT ($\sim 10^{-5}$ *M*) and ethoxide ($\sim 10^{-3}$ *M*), the main product is a purple species with absorption maxima at approximately 370 and 520 nm;[3a] Caldin and Long considered this species to be the 2,4,6-trinitrobenzyl anion (TNT$^-$, I). They showed that the reverse reaction involving loss of the purple species to give TNT and ethoxide ion occurs at the rate expected for the reaction of TNT$^-$ with ethanol; in addition, they noted that the picrate ion also possesses an absorption maximum at a wavelength close to 370 nm. More recently TNT$^-$ has been postulated as an intermediate in hydrogen exchange reactions in pyridine–heavy water[4] and dimethylformamide–heavy water mixtures[5] and in the reaction of TNT in tetrahydrofuran–methanol solution with aqueous hypochlorite.[6] On the other hand, Bowden and Stewart[7] did not detect proton loss from TNT in a heavy water–dimethyl sulfoxide solution of NaOD.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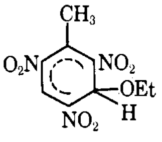
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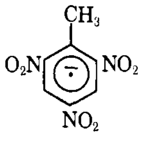
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Although proton nmr studies have proved very useful in establishing structures of products from many reactions of aromatic nitro compounds with bases,[2] there is no direct nmr evidence for the structures of the purple and brown products. Indeed, Servis[8] has concluded that formation of a benzyl-type anion is very unlikely; he also found no evidence for the presence of a σ complex (II). Servis suggested that a radical anion (III) may be formed even though Russell and Janzen[9] detected little or no radical formation when TNT interacts with potassium *tert*-butoxide in dimethyl sulfoxide solution. Recent electron spin resonance studies[10] of the reaction of methoxide ion with various aromatic nitro compounds show that high concentrations of radical anion can be produced in dimethyl sulfoxide at high base concentrations (~ 1 *M*) but that low radical concentrations result if ethanol is the solvent and the base concentration is less than 10^{-2} *M*. Extinction coefficients of these radical anions are probably relatively low,[1b] and it is unlikely that the radical anion of TNT would be readily observed by optical means under these conditions particularly if the initial TNT concentration were less than 10^{-4} *M*.

In order to evaluate the importance of proton transfer in the formation of the purple species and the possible formation of other species in this system, we have investigated the kinetics of reaction of ethoxide ion with TNT and TNT fully deuterated at the α carbon (TNT-d_3) in ethanol solution. Rates of reaction have also been determined for the solvent ethanol-*O-d* (EtOD) and the kinetic solvent isotope effect thus obtained.

Experimental Section

Materials. TNT was treated with activated charcoal and recrystallized twice from carbon tetrachloride, mp 80.5–81.0° (uncor). TNT-d_3 was prepared by addition of 1 ml of 0.97 *M* NaOD to 5 g of TNT dissolved in heavy water–dimethylformamide (10:90, 100 ml). Exchange was virtually complete after 4 hr at room temperature.[5] The solution was poured onto a mixture of 100 g of ice and 2 ml of sulfuric acid (1 *N*) and the product dried. The exchange procedure was repeated on this material and the TNT-d_3 (4.2 g) isolated. This product was treated with activated charcoal and recrystallized from carbon tetrachloride, mp 80.0–80.5°.

The extent of deuteration was determined by nmr analysis of the methyl hydrogens: found, 99%; calcd, 99.6%.

Absolute ethanol and EtOD (Merck Sharp and Dohme) were distilled from magnesium and iodine and stored under dry nitrogen.

Stock solutions of sodium ethoxide in ethanol and EtOD were

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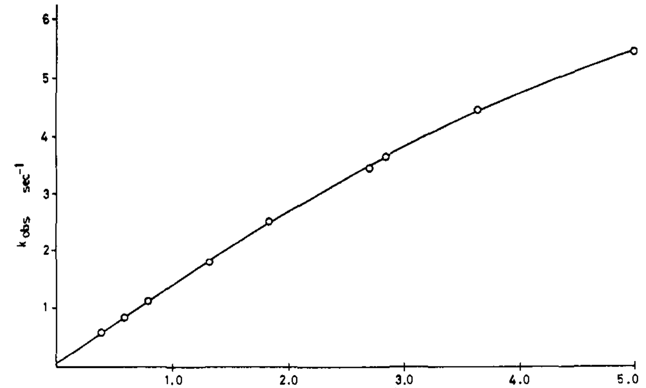

Figure 1. k_{obsd} for the formation of the purple species as a function of concentration of sodium ethoxide in ethanol at 25°: initial concentration of TNT, 2–10 × 10^{-5} *M*.

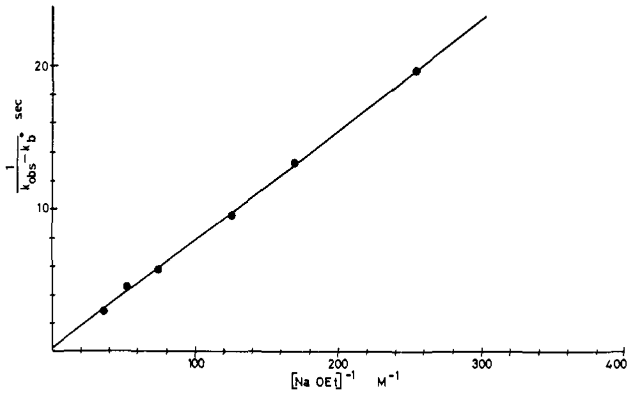

Figure 2. $1/(k_{obsd} - k_b^0)$ as a function of 1/[NaOEt]. Kinetic data obtained for the reaction of TNT with sodium ethoxide in ethanol at 25°.

prepared and stored in an atmosphere of dry nitrogen; they were standardized immediately before use.

Procedure. Kinetic measurements were carried out by means of a Durrum-Gibson stopped-flow apparatus whose cell compartment and drive syringe chamber were maintained at 25.0 ± 0.1°. Changes in concentration of the complex were normally followed by monitoring the absorbance at 520 nm, but in some cases the changes in absorbance at 630 and 370 nm were also recorded.

Concentrations of ethoxide ion were in the range 1–40 × 10^{-3} *M*, dependent upon the system being studied, and TNT and TNT-d_3 concentrations were in the range 2–10 × 10^{-5} *M*. Absorbances of some of the final solutions were slightly greater than unity and a calibration procedure was adopted in order to reduce the error in determining such absorbances from the oscilloscope trace. The position of the oscilloscope trace was determined for each of a series of potassium permanganate solutions at a wavelength of 524 nm and compared with the absorbance determined by means of a Cary 14 spectrophotometer. For absorbances below 0.5, the correction was negligible.

Results and Discussion

The reaction of TNT (2–10 × 10^{-5} *M*) with ethoxide ion (1–40 × 10^{-3} *M*) in ethanol at 25° was observed to give rise to a purple solution. At equilibrium, the solution has absorption maxima at 371 nm (ϵ 8300 l. mol^{-1} cm^{-1}) and 514 (13,500) and a broad shoulder centered at 621 nm (ϵ 7500 l. mol^{-1} cm^{-1}). The plots of log $(A_\infty - A_t)$ *vs.* time are linear up to 80–90% completion of reaction (A_∞ and A_t are the absorbances at 520 nm at times ∞ and *t*, respectively). The derived first-order rate constant at 25°, k_{obsd}, for a base concentration of 0.01 *M* is 1.35 ± 0.02 sec^{-1}. When TNT-d_3 is used as substrate, a purple solution with an identical absorption spectrum is produced, and the first-order rate constant for formation of the purple species at a base concentration of 0.01 *M* is 0.195 ± 0.004 sec^{-1}. The rate-determining step of the reaction producing the purple species is therefore subject to a large primary isotope effect in accord with abstraction of a proton from the methyl group of the TNT to give the TNT$^-$ ion.

The concentration of the TNT$^-$ ion is obtained directly from the absorbance at 520 nm because the extinction coefficient of the brown species which is simultaneously formed is much smaller than that of TNT$^-$ at this wavelength,[3b] and the equilibrium constant for its formation is relatively low. The rate constant for its formation is, however, higher than that for the formation of TNT$^-$[3b] with the result that it attains almost its equilibrium concentration before much of the TNT is converted to TNT$^-$. Formation of the brown species therefore reduces the concentration of free TNT at any stage of the reaction. Experimentally it is found that a slight curve is obtained when first-order constants, k_{obsd}, are plotted against ethoxide ion concentration (Figure 1). In the analysis of results outlined below, it is assumed that this curvature arises solely from the effect of the formation of the brown species on the TNT concentration.[11]

On the simplest reaction mechanism, the purple TNT$^-$ ion is produced directly by

$$\text{TNT} + \text{OEt}^- \rightleftharpoons \text{TNT}^- + \text{EtOH} \quad \text{(in EtOH)} \qquad (1)$$

the rate constant for the forward reaction is k_f, and the first-order rate constant for the reverse reaction is k_b^0, the solvent ethanol being in great excess. The brown species is produced by reaction 2, for which the equilibrium constant is K_2. Provided that reaction 2

$$\text{TNT} + \text{OEt}^- \rightleftharpoons \text{TNT}\cdot\text{OEt}^- \qquad (2)$$

is always at its equilibrium position, the first-order rate constants for individual experiments should vary with base concentration according to eq 3. An approximate estimate of k_b^0 is obtained from a plot of k_{obsd} *vs.* ethoxide ion concentration. Equation 3 is then rewritten in the form

$$k_{obsd} = \frac{k_f[\text{OEt}^-]}{1 + K_2[\text{OEt}^-]} + k_b^0 \qquad (3)$$

$$\frac{1}{k_{obsd} - k_b^0} = \frac{1}{k_f[\text{OEt}^-]} + \frac{K_2}{k_f} \qquad (4)$$

and k_f and K_2 are obtained from a plot of $1/(k_{obsd} - k_b^0)$ *vs.* 1/[OEt$^-$]. The experimental results fit this theoretical analysis as shown in Figure 2. The value of k_f obtained from this treatment is some 15% higher than that obtained from a plot of k_{obsd} *vs.* base concentration, *i.e.*, neglecting reaction 2.

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[11] A possible alternative explanation is that the curvature in the k_{obsd} *vs.* [base] plot arises from association of sodium and ethoxide ions. However, Bernasconi's recent work[12] confirms that a very rapid reaction occurs at 25° to give a significant equilibrium concentration of a complex, presumably Caldin's brown species,[3b] and we think that this is the more likely source of the curvature. Unpublished results on the reactions of higher alkoxides with TNT give further support to our interpretation.[13]

[12] C. F. Bernasconi, *J. Org. Chem.*, 36, 1671 (1971).

[13] E. Buncel, A. R. Norris, K. E. Russell, and P. Sheridan, unpublished results.

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Table I. First-Order Rate Constants for the Reaction of Ethoxide Ion with TNT at 25°[a]

10^5[TNT], M	10^3[OEt$^-$], M	k_{obsd}, sec^{-1}
5.30	3.9	0.61
5.30	5.9	0.86
2.43	7.6	1.10
5.40	12.8	1.68
10.1	13.3	1.83
10.1	19.0	2.45
8.03	27.0	3.48
10.1	28.5	3.64
5.4	36.4	4.40
10.1	38.0	4.76

[a] Analysis of these results leads to estimates of k_f and k_b^0 of 138 ± 3 M^{-1} sec^{-1} and 0.08 ± 0.02 sec^{-1}, respectively.

Some of the experimental values of k_{obsd} are given in Table I. The derived values of k_f and k_b^0 show no significant trend over a fourfold change in TNT concentration. Similar results are obtained if wavelengths of 370 or 630 nm are used for analysis. k_b^0 is derived from a small intercept and the uncertainty in its magnitude is therefore large.

Values of k_{obsd}, k_f, and k_b^0 have also been obtained for the reaction

$$\text{TNT-}d_3 + \text{OEt}^- \rightleftharpoons \text{TNT-}d_2^- + \text{EtOD} \quad \text{(in EtOD)} \quad (5)$$

employing the method of analysis outlined above; the results are summarized in Table II.

Table II. Rate Constants, k_f and k_b^0, for Reaction of TNT and TNT-d_3 with Ethoxide Ion in Ethanol and EtOD at 25°

Reaction	Substrate	k_f, M^{-1} sec^{-1}	k_b^0, sec^{-1}	k_f/k_b^0, M^{-1}
1	TNT	138 ± 3[a]	0.08 ± 0.02[a]	1700 ± 500
5	TNT-d_3	39.1 ± 0.8	0.02 ± 0.005	2000 ± 500
6	TNT	250 ± 10		
7	TNT-d_3	19.8 ± 0.8		

[a] Error estimates based on a least-squares analysis.

For the reactions

$$\text{TNT} + \text{OEt}^- \rightleftharpoons \text{TNT}^- + \text{EtOH} \quad \text{(in EtOD)} \quad (6)$$

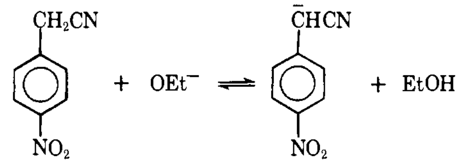
$$\text{TNT-}d_3 + \text{OEt}^- \rightleftharpoons \text{TNT-}d_2^- + \text{EtOD} \quad \text{(in EtOH)} \quad (7)$$

the above method of analysis may not be valid because the substrate may undergo isotopic change during the course of the kinetic experiment; in the absence of internal return,[14] TNT will eventually be converted to TNT-d_3 in reaction 6 and TNT-d_3 to TNT in reaction 7. The influence of such exchange should be most noticeable in the slow reactions of TNT-d_3 with ethoxide, and it is observed that for reaction 7 at low base concentrations, plots of log $(A_\infty - A_t)$ *vs.* time are curved. Such curvature is not observed with reactions 1, 5, and 6 under the same experimental conditions, but it is possible that A_∞ for reaction 6 is slightly affected by isotopic exchange. Values of k_{obsd} for reactions 6 and 7 have thus been obtained by the method of initial rates, *i.e.*, for conditions when no significant exchange could have occurred. At high base concentrations, the values of k_{obsd} agree within experimental error with those obtained from the integrated rate equation. The derived values of k_f for reactions 6 and 7 are given in Table II; values of k_b^0 for these reactions have not been included because of the uncertainties discussed above.

The ratio of the rate constants for the reaction of ethoxide ion with TNT and TNT-d_3 in ethanol is 7.0 ± 0.5 at 25°. The corresponding isotope effect for the reactions in the solvent EtOD is 6.4 ± 0.4. The kinetic solvent isotope effect for TNT is 1.81 ± 0.11 at 25°, and for TNT-d_3 it is 1.97 ± 0.15. The values of k_f and k_b^0 give a rough estimate of the equilibrium constant for reaction 1 of approximately 2000 M^{-1}; Caldin and Long[3a] obtained a value of 2040 M^{-1} at 25°, and in separate equilibrium studies we have arrived at a value of 1750 ± 100 M^{-1}. There is considerable uncertainty in the value of k_b^0, and the indirect estimate of the equilibrium constant is therefore very approximate. The equilibrium constant for reaction 2, K_2, is relatively low; kinetic analysis by means of eq 4 leads to the result that $K_2 = 6 \pm 3\ M^{-1}$ at 25°.

Bernasconi has recently published[12] a stopped-flow and temperature-jump study of the TNT–ethoxide reaction at 25°. He establishes the existence of a rapid preequilibrium at 25° with forward rate constant in the range 1500–3000 M^{-1} sec^{-1}. He estimates the equilibrium constant for this reaction, tentatively identified as Meisenheimer complex formation, to be in the range 7.5–37.5 M^{-1} at 25°; even the minimum value of 7.5 M^{-1} is sufficient to account for the curvature observed in the k_{obsd} *vs.* [base] plot (Figure 1). Bernasconi's value of k_f, the rate constant for formation of TNT$^-$, is 82 ± 4 M^{-1} sec^{-1} at 25° which is significantly lower than the value obtained in the present work, but the ratio k_f/k_b^0 is 1800 M^{-1}, in agreement with the above results.

The results for the reaction of ethoxide ion with TNT and TNT-d_3 in ethanol may be compared with those obtained by Caldin, Kasparian, and Tomalin[15] for the reaction of ethoxide ion with 4-nitrobenzyl cyanide in the same solvent. This latter process is also subject to a large primary isotope effect, particularly at low temperatures, and has accordingly been formulated as the proton transfer reaction (eq 8). The results for the 4-nitrobenzyl cyanide reaction differ from those for TNT in that the plots of the observed first-order rate constant *vs.* base concentration for individual runs are linear and the rate constant for the forward reaction (eq 8) is unexpectedly low at the highest temperatures at which experiments were performed. Caldin, *et al.*, concluded that the first stage involves the formation of an intermediate complex, possibly a σ complex, the proton transfer taking place in the second stage of the reaction (eq 9). In the present study of the ethoxide–TNT reaction in ethanol, and also in other alkoxide–TNT reactions in the corresponding alcohols,[13] the plots of observed first-order rate constant *vs.* base con-



$$\text{4-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{CN} + \text{OEt}^- \rightleftharpoons \text{4-NO}_2\text{C}_6\text{H}_4\overset{-}{\text{C}}\text{HCN} + \text{EtOH} \quad (8)$$

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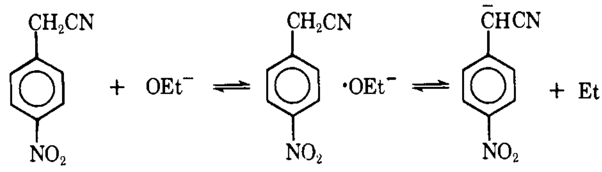

(9)

centration are curved. The results are interpreted in terms of the *simultaneous* formation of a complex, probably the σ complex II,[12] the reaction having a low equilibrium constant (6 M^{-1}) at 25°; the possibility that this complex is an intermediate in the formation of the TNT⁻ ion is not, however, excluded by the kinetic results.

The reactions of ethoxide ion with TNT and TNT-d_3 proceed at almost twice the rate in EtOD as the respective reactions in ethanol. The kinetic solvent isotope effects of 1.81 and 1.97 at 25° may be compared with the following values: 1.96 for σ-complex formation between methoxide ion and 2,4-dinitroanisole in methanol,[16] 1.67 for σ-complex formation between methoxide ion and 2-cyano-4,6-dinitroanisole in methanol,[17] 1.84 for σ-complex formation between ethoxide ion and 2,4-dinitrochlorobenzene in ethanol,[18] and 1.92 for the reaction between ethoxide ion and 1,3,5-trinitrobenzene in ethanol.[19] Bunton and Shiner[20] have suggested that such solvent isotope effects arise principally from differences in zero-point energy changes during formation of the activated complex in the two solvents (see also ref 21). Desolvation occurs during the formation of the activated complex of ethoxide ion and TNT, and this results in a change in the stretching frequencies of the OH bonds concerned. On a simple electrostatic model the expected value of k_f(EtOD)/k_f(EtOH) is 1.28 at 25°, and on a covalent model the expected value is 2.09. The estimates are very approximate because the stretching frequencies are not accurately known, and no attempt has been made to take into account possible changes in solvation of nitro groups of the TNT. The estimates do, however, bracket the experimental value of k_f(EtOD)/k_f(EtOH), and the desolvation model provides a reasonable explanation of the kinetic solvent isotope effect. A similar explanation has been put forward[18] for the kinetic solvent isotope effect observed in the reaction of ethoxide ion with 2,4-dinitrochlorobenzene.

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New Anionic Rearrangements. XIV.[1] Temperature-Dependent Proton Nuclear Magnetic Resonance of Organosilylhydrazine Anions[2,3]

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Abstract: The rearrangement of organosilylhydrazine anions has been studied by variable-temperature proton nmr spectroscopy, and approximate rates have been determined from coalescence temperatures for nonequivalent organosilyl groups. Spectra are included for lithium tris(trimethylsilyl)hydrazide (**1a**) and the N,N and N,N′ isomers of various lithium bis(organosilyl)methylhydrazides. Evidence is presented for a dimer–monomer equilibrium of **1a** in diethyl ether in which intramolecular organosilyl migration takes place in the dimer and monomer forms at different rates. Low-temperature proton nmr also provides evidence for formation of mixed aggregates of alkyllithium and lithium bis(trimethylsilyl)methylhydrazide.

The 1,2 anionic rearrangement of bis(organosilyl)-hydrazines in which organosilyl groups move from one nitrogen to another has been described in a recent series of papers.[4–8] The rearrangement is rapid, intramolecular, base catalyzed, and proceeds to equilibrium.[6] The kinetics of the catalyzed rearrangement and a tentative description of the mechanism of reaction have also been presented.[7] Protonation and deprotonation are the rate-determining steps in the catalytic rearrangement. Since the process is catalyzed

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