Kinetic and Spectral Study of Some Reactions of 2,4,6-Trinitrotoluene in Basic Solution. I. Deprotonation and Janovsky Complex Formation[1]

CLAUDE F. BERNASCONI

University of California, Santa Cruz, California 95060

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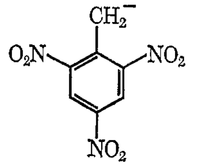
Three relatively fast kinetic processes can be detected in reactions of 2,4,6-trinitrotoluene (TNT) with lyate ions in methanol, ethanol, and in 50% dioxane–50% water. With the base in excess over TNT, formation of the 2,4,6-trinitrobenzyl anion (TNT^-) is the principal process. At high base concentration a second much faster process emerges, which is difficult to identify but could be due to a Meisenheimer complex (MC) coupled to a radical-anion formation. When TNT is in excess over the base, formation of a Janovsky complex (JC) between TNT^- and a second molecule of TNT is observed, which is identified through its visible spectrum. Rate constants of TNT^- and JC formation and reversion were measured. Preliminary spectral evidence indicates that in 10% dioxane–90% water TNT behaves differently from the other solvent systems.

The reaction of 2,4,6-trinitrotoluene (TNT) with strong bases has been interpreted as to produce the 2,4,6-trinitrobenzyl anion (TNT^-),[2,3] as shown in eq 1.

$TNT + B \rightleftharpoons$



$+ BH$ (1)

TNT^-

Extensive kinetic investigations of this reaction in ethanolic solutions have been reported[2] and some evidence supporting formation of TNT^-, including the observation of a large primary deuterium isotope effect,[2b] was advanced.[2]

Later, hydrogen exchange experiments in dimethylformamide–D_2O[3b] and in pyridine–D_2O[3c] provided more direct evidence in support of proton abstraction from the methyl group, though Bowden and Stewart[4] could not detect any appreciable hydrogen exchange in alkaline aqueous dimethyl sulfoxide. Furthermore Servis[5] argued against the possibility of TNT^- formation on the grounds of a comparison with the acidity of 2,4,6-trinitroaniline and "the generally known fact that amines are on the order of 10^{10} more acidic than corresponding hydrocarbons." Nevertheless, Crampton[6] states in a recent review that "present evidence suggests, on balance, that the violet color produced in alcoholic media is due to TNT^-, though adducts formed by the addition of alkoxide ion, or the TNT^- itself, to TNT may be produced in some circumstances."

Ainscough and Caldin[7] have indeed observed another interaction between TNT and the ethoxide ion in ethanol at high base concentrations. This interaction was attributed to a charge transfer (CT) complex, though the possibility of a Meisenheimer complex (MC)[8] was not excluded.

We expected that a thorough kinetic investigation of the interaction of TNT with OH^- in aqueous solution, with CH_3O^- in methanolic solution, and some further study with EtO^- in ethanolic solution would yield a better understanding of the chemistry of TNT. We wish now to report the first part of such a study.

Results

TNT and CH_3O^- in Methanol.—A temperature-jump[9] study of this system at wavelengths between 415 and 585 mμ revealed the presence of three well-separated relaxational processes, which we shall designate by τ_1, τ_2, and τ_3. Under the conditions used in this study, τ_1 is found to be in the time range of about 1 or 2 msec and τ_2 between 0.3 and 1 sec, whereas for τ_3 the time range is between 10 and 30 msec.

The two slower relaxation times (τ_2 and τ_3) were easily measurable; representative oscilloscope traces are displayed in Figure 1b and c. τ_1 on the other hand, was barely detectable with the technique available; Figure 1a shows an oscilloscope trace, where this latter process can be recognized as a little hump on top of the other curve (τ_3). No study of the concentration dependence of τ_1 could be carried out and only a very crude estimate of the relaxation time could be made from this or similar pictures; τ_1 is believed to be somewhere between 0.4 and 2.0 msec.

τ_2 and τ_3 as determined at various concentrations of TNT and $NaOCH_3$ in CH_3OH are reported in Table I; the electrolyte concentration was kept constant at 0.5 *M* in all runs by addition of appropriate amounts of $NaClO_4$. The slowest process, τ_2, can be observed over a wide concentration range of $NaOCH_3$ and TNT; most measurements of τ_2 were made with $NaOCH_3$ in large excess over TNT, though two experiments were performed with TNT in large excess over $NaOCH_3$ and three experiments where the concentrations of both reactants were low and the same or of the same order of magnitude.

Two observations are noteworthy. (1) The relative amplitudes (fractional change of optical density immediately following a temperature jump, ΔOD/OD) are appreciably greater when the base concentration exceeds the TNT concentration compared to the converse situation. (2) When τ_2^{-1} is plotted *vs.* the sum of [TNT] + [NaOMe], one recognizes two sets of points: τ_2^{-1} values determined from experiments where

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[1] Supported in part by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is made to the donors of this fund.

[2] (a) E. F. Caldin and G. Long, *Proc. Roy. Soc. Ser. A*, **226**, 263 (1955); (b) J. A. Blake, M. J. B. Evans, and K. E. Russell, *Can. J. Chem.*, **44**, 119 (1966).

[3] (a) K. G. Shipp and L. A. Kaplan, *J. Org. Chem.*, **31**, 857 (1966); (b) E. Buncel, K. E. Russell, and J. Wood, *Chem. Commun.*, 252 (1968); (c) R. E. Miller and W. F. K. Wynne-Jones, *J. Chem. Soc.*, 2375 (1959).

[4] K. Bowden and R. Stewart, *Tetrahedron*, **21**, 261 (1965).

[5] K. L. Servis, *J. Amer. Chem. Soc.*, **89**, 1508 (1967).

[6] M. R. Crampton, *Advan. Phys. Org. Chem.*, **7**, 211 (1969).

[7] J. B. Ainscough and E. F. Caldin, *J. Chem. Soc.*, 2546 (1956).

[8] J. Meisenheimer, *Justus Liebigs Ann. Chem.*, **323**, 205 (1902).

[9] M. Eigen and L. DeMaeyer in "Technique of Organic Chemistry," Vol. VIII, part 2, Interscience, New York, N. Y., 1963, p 895.

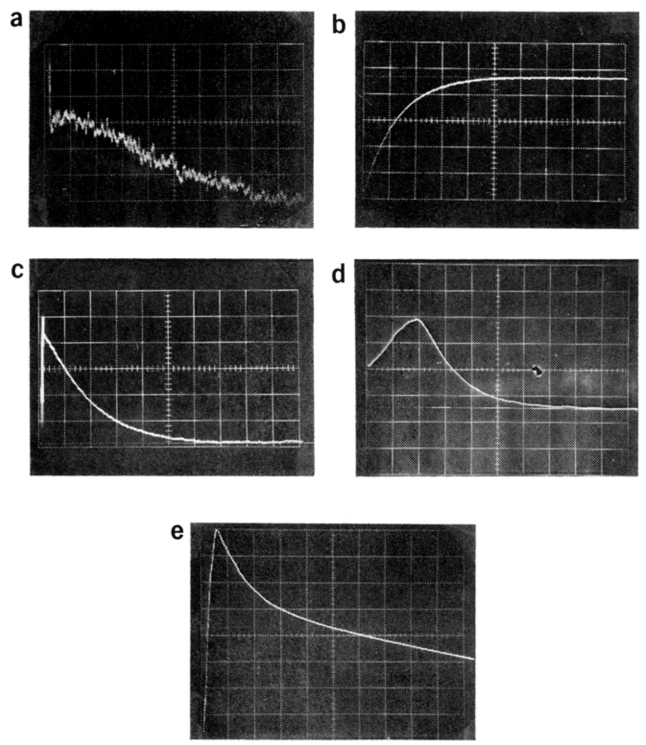


Figure 1.—Representative oscilloscope traces (ordinate in arbitrary units): (a) τ_1 in methanol, $[\mathrm{NaOMe}]_0 = [\mathrm{TNT}]_0 = 0.005$ *M*, 450 mμ, 2 msec/horizontal division, temperature-jump method; (b) τ_2 in methanol, $[\mathrm{NaOMe}]_0 = 0.05$ *M*, $[\mathrm{TNT}]_0 = 4 \times 10^{-4}$ *M*, 500 mμ, 0.5 sec/horizontal division, temperature-jump method; (c) τ_3 in methanol, $[\mathrm{NaOMe}]_0 = 0.001$ *M*, $[\mathrm{TNT}]_0 = 0.06$ *M*, 425 mμ, 10 msec/horizontal division, temperature-jump method; (d) τ_1 in ethanol, $[\mathrm{NaOEt}]_0 = 0.15$ *M*, $[\mathrm{TNT}]_0 = 5 \times 10^{-5}$ *M*, 438 mμ, 5 msec/horizontal division, stopped-flow method; (e) τ_1 in 50% dioxane–50% water, $[\mathrm{NaOH}]_0 = 0.2$ *M*, $[\mathrm{TNT}]_0 = 10^{-4}$ *M*, 460 mμ, 100 msec/horizontal division, stopped-flow method.

TABLE I

INTERACTION OF TNT WITH MeO^- IN METHANOL

$[\mathrm{NaOCH_3}]_0$, *M*	$[\mathrm{TNT}]_0$, *M*	$[\mathrm{NaClO_4}]$, *M*	τ_2^{-1}, sec^{-1}	τ_3^{-1}, sec^{-1}
≈0.0005	0.0005	0.5	0.94 ± 0.15	
0.002	0.002	0.5	1.08 ± 0.05	
0.008	0.002	0.49	1.24 ± 0.06	
0.05	0.0004	0.45	1.74 ± 0.10	
0.10	10^{-4}	0.40	2.34 ± 0.13	
0.15	10^{-4}	0.35	2.93 ± 0.20	
0.20	10^{-4}	0.30	3.92 ± 0.30	
≈0.0002	0.01	0.50		29.3 ± 1.5
≈0.001	0.01	0.50		30.5 ± 1.5
≈0.001	0.02	0.50		32.2 ± 1.5
≈0.001	0.04	0.50		39.3 ± 1.8
≈0.001	0.06	0.50	1.26 ± 0.07 (1.30)	51.4 ± 2.6
≈0.0005	0.08	0.50		59.8 ± 3.0
≈0.0005	0.10	0.50	1.66 ± 0.12 (1.71)	65.4 ± 3.2
≈0.0005	0.12	0.05		75.1 ± 3.5

either [NaOMe] ≫ [TNT] or where both reagents were at very low concentrations lie on a straight line, whereas τ_2^{-1} values from experiments where [TNT] ≫ [NaOMe] are definitely below that line (Figure 2).

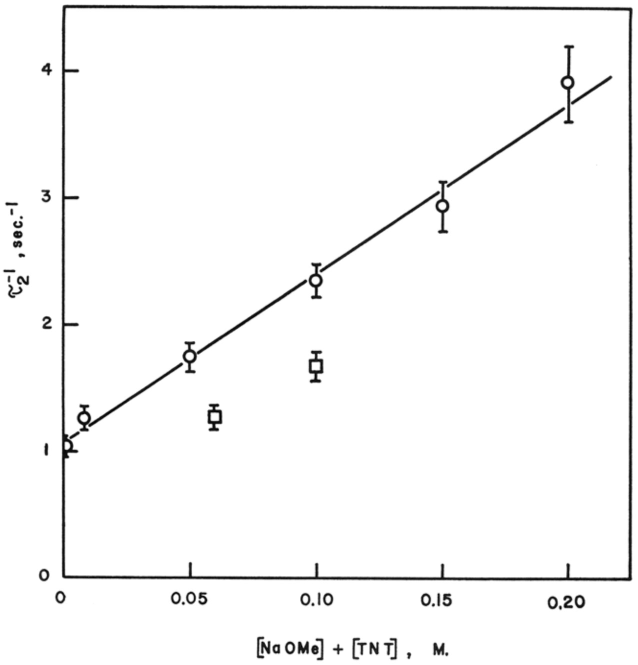


Figure 2.—Reaction of TNT with NaOMe in methanol; τ_2^{-1} as function of [NaOMe] + [TNT], □ for [TNT] ≫ [NaOMe], ○ for all the others.

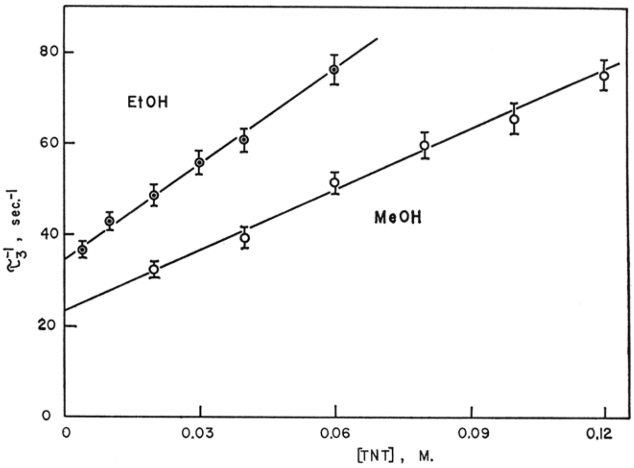


Figure 3.—Reaction of TNT with TNT^-; τ_3^{-1} as function of [TNT], ○ in methanol, ⊙ in ethanol.

These apparent anomalies are resolved when τ_3 is considered. τ_3^{-1} values could easily be measured only when TNT was chosen as the excess component; in fact, τ_3 was then the predominant process. On the other hand, when the base is in excess, τ_3 is hardly detectable at all and only observed when the TNT concentration is fairly high. Moreover, in a series of temperature-jump experiments, the relative amplitudes (ΔOD/OD) of τ_3 remain about the same when the TNT concentration is increased, or even increased slightly, instead of decreasing steadily as is normally the case for a straightforward bimolecular reaction in which the relaxational behavior is monitored at some wavelength of product absorption.

When τ_3^{-1} is plotted *vs.* TNT concentration, a straight line results (Figure 3).

The foregoing experimental observations, as well as some spectral data discussed below, are consistent with Scheme I, R being $\mathrm{CH_3}$. According to this scheme, τ_2 would arise from deprotonation of TNT to form the 2,4,6-trinitrobenzyl anion TNT^- and τ_3 from the reaction of TNT^- with a second molecule

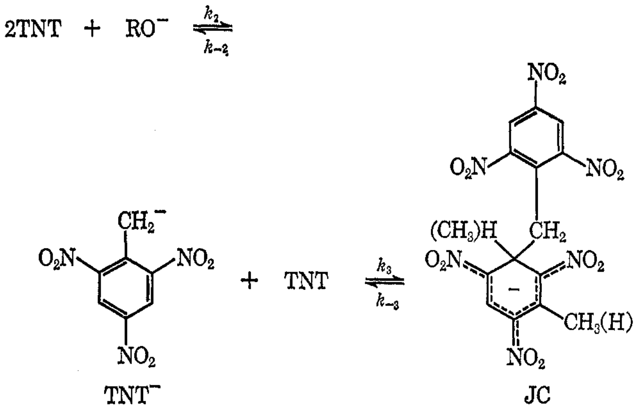
TABLE II

RATE AND EQUILIBRIUM CONSTANTS FOR DEPROTONATION AND JANOVSKY COMPLEX FORMATION OF TNT IN BASIC METHANOL, ETHANOL, AND 50% DIOXANE–50% WATER AT 25°

		Methanol	Ethanol	50% dioxane–50% water
TNT + RO^-	k_2 (M^{-1} sec^{-1})	13.3 ± 0.6	82 ± 4 (62.5[a])	2.42 ± 0.12
$k_2 \downarrow\uparrow k_{-2}$	k_{-2} (sec^{-1})	1.07 ± 0.1	$4.5 \pm 0.5 \times 10^{-2}$	$7.5 \pm 1.0 \times 10^{-3}$
TNT^-	$K_2 = \frac{k_2}{k_{-2}}$ (M^{-1})	12.4 ± 1.7 (7.1)[b]	1820 ± 270 (2040)[c]	323 ± 50
TNT + TNT^-	k_3 (M^{-1} sec^{-1})	442 ± 20	700 ± 35	3400 ± 120
$k_3 \downarrow\uparrow k_{-3}$	k_{-3} (sec^{-1})	3.5 ± 1.5	34.5 ± 2.5	30 ± 3
JC	$K_3 = \frac{k_3}{k_{-3}}$ (M^{-1})	18.9 ± 2.0	20.3 ± 2.2	113 ± 15

[a] Reference 2a, at 19.1°. [b] Reference 22. [c] Reference 2a, at 25°.

SCHEME I



R = C_2H_5, CH_3, or H

of TNT to form the Janovsky[10,11] complex (JC). It is to be noted that the position of nucleophilic attack on TNT is unspecified. The origin of the barely detectable fast relaxation time, τ_1, can not be inferred from our experiments however.

Let us examine how the kinetic data do indeed fit with the proposed reaction scheme. The analytical expressions for τ_2 and τ_3 are relatively simple because $\tau_2 \gg \tau_3$ throughout. They are set forth in eq 2

$$\frac{1}{\tau_2} = k_2\left([\mathrm{TNT}] + [\mathrm{RO}^-]\,\frac{1 + 2K_3[\mathrm{TNT}]}{1 + K_3([\mathrm{TNT}] + [\mathrm{TNT}^-])}\right) + k_{-2}\,\frac{1 + 2K_3[\mathrm{TNT}^-]}{1 + K_3([\mathrm{TNT}] + [\mathrm{TNT}^-])} \quad (2)$$

and 3,[13] where all concentrations refer to their equilibrium values; K_3 is defined as k_3/k_{-3}.

$$\frac{1}{\tau_3} = k_3([\mathrm{TNT}] + [\mathrm{TNT}^-]) + k_{-3} \quad (3)$$

In principle, at least one of the terms in eq 2 or 3 should contain a correction factor taking into account the fast equilibrium process giving rise to τ_1. The very small amplitude of τ_1 suggests, that, whatever this process is, the equilibrium must strongly favor the reactants under the present reaction conditions so that this correction factor is equal to 1 for all practical purposes; as seen below, this is borne out by the strict adherence of the experimental data to eq 2 and 3.

In the experiments conducted for the determination of τ_3, $[\mathrm{TNT}]_0 \gg [\mathrm{NaOMe}]_0$ throughout, so that eq 3 is reduced to eq 4, where [TNT] is now equivalent

$$\frac{1}{\tau_3} = k_3[\mathrm{TNT}] + k_{-3} \quad (4)$$

to the stoichiometric concentration. Thus from the slope and intercept of the straight line in Figure 3, k_3 and k_{-3} were calculated; they are reported in Table II.

The experiments pertaining to τ_2 fall into two categories.

(1) The concentration of TNT is low with either $[\mathrm{NaOMe}]_0 \gg [\mathrm{TNT}]_0$ or $[\mathrm{NaOMe}]_0 \approx [\mathrm{TNT}]_0$. In either situation $K_3[\mathrm{TNT}] \ll 1$ and $K_3([\mathrm{TNT}] + [\mathrm{TNT}^-]) \ll 1$ and eq 2 becomes eq 5, where the

$$\frac{1}{\tau_2} = k_2([\mathrm{RO}^-] + [\mathrm{TNT}]) + k_{-2} \quad (5)$$

equilibrium concentrations can be replaced by the stoichiometric concentrations. A plot of τ_2^{-1} *vs.* ([NaOMe] + [TNT]) is indeed linear as shown in Figure 2; k_2 and k_{-2} were determined from the slope and intercept and are set forth in Table II.

(2) The second category of experiments are those where $[\mathrm{TNT}]_0 \gg [\mathrm{NaOMe}]_0$, so that eq 2 becomes eq 6. For two experiments with the same concentra-

$$\frac{1}{\tau_2} = k_2[\mathrm{TNT}] + k_{-2}\,\frac{1}{1 + K_3[\mathrm{TNT}]} \quad (6)$$

tion of the excess component, the excess component being NaOMe in the first, TNT in the second case, eq 6 predicts τ_2^{-1} to be lower by an amount equivalent to $k_{-2}K_3[\mathrm{TNT}]/(1 + K_3[\mathrm{TNT}])$ in the second case. The numbers in parentheses in Table I for the experiments at 0.06 and 0.1 M TNT refer to such relaxation times calculated from k_2, k_{-2}, and K_3 with reference to eq 6. As can be seen, the agreement between these and the experimental values is well within the experimental error.

The observation of large relative amplitudes with τ_2 when [NaOMe] ≫ [TNT] but small ones when [TNT] ≫ [NaOMe], as well as the fact that the amplitudes of τ_3 increase slightly and then approximately level off when the TNT concentration is in-

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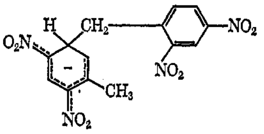
(10) (a) J. V. Janovsky and L. Erb, *Ber.*, **19**, 2155 (1886); (b) R. J. Pollitt and B. C. Saunders, *J. Chem. Soc.*, 4615 (1965).

(11) Foster and Mackie[12] have previously suggested that a Janovsky complex is formed from 2,4-dinitrotoluene and ethoxide ion in ethanol.



(12) R. Foster and R. K. Mackie, *Tetrahedron*, **19**, 691 (1963).

(13) For general methods of derivation of equations like 2, 3, and others to follow below, see ref 9.

Table III

Interaction of TNT with EtO^- in Ethanol

$[NaOEt]_0$, M	$[TNT]_0$, M	$[NaClO_4]$, M	τ_1^{-1}, sec^{-1}	τ_2^{-1}, sec^{-1}	τ_3^{-1}, sec^{-1}
$\approx 2.5 \times 10^{-4}$	5×10^{-5}	0.40		0.057 ± 0.002	
$\approx 5 \times 10^{-4}$	5×10^{-5}	0.40		0.089 ± 0.003	
0.001	5×10^{-5}	0.40		0.121 ± 0.005	
0.002	5×10^{-5}	0.40		0.218 ± 0.01	
0.005	5×10^{-5}	0.395		0.45 ± 0.02	
0.01	5×10^{-5}	0.39		0.97 ± 0.03	
0.02	5×10^{-5}	0.38		1.90 ± 0.07	
0.03	5×10^{-5}	0.37		2.54 ± 0.10	
0.05	5×10^{-5}	0.35		3.99 ± 0.20	
0.075	5×10^{-5}	0.325		5.94 ± 0.24	
0.10	5×10^{-5}	0.30	179 ± 50	7.53 ± 0.30	
0.15	5×10^{-5}	0.25	209 ± 30	10.0 ± 0.40	
0.20	5×10^{-5}	0.20	235 ± 20	12.6 ± 0.60	
0.20	5×10^{-6}	0.20	165 ± 15		
0.20	2.5×10^{-5}	0.20	204 ± 20		
0.20	10^{-4}	0.20	283 ± 30		
0.20	2×10^{-4}	0.20	355 ± 35[a]		
$\approx 4 \times 10^{-4}$	0.004	0.20			36.6 ± 1.5
$\approx 10^{-4}$	0.01	0.20			42.0 ± 2.0
$\approx 2 \times 10^{-4}$	0.01	0.20			42.9 ± 2.0
$\approx 6 \times 10^{-4}$	0.01	0.20			40.6 ± 2.0
$\approx 2 \times 10^{-4}$	0.02	0.20			48.5 ± 2.2
$\approx 2 \times 10^{-4}$	0.03	0.20			55.7 ± 2.5
$\approx 2 \times 10^{-4}$	0.04	0.20			60.7 ± 2.5
$\approx 2 \times 10^{-4}$	0.06	0.20			76.2 ± 3.0

[a] The value of τ_1 does not change when 10^{-2} M or 5×10^{-2} M of 2-methyl-2-nitrosopropane is added.

creased, are equally consistent with the proposed scheme as will be shown now.[14]

The amplitude for τ_2, under the condition [NaOMe] $\gg$ [TNT], is given by eq 7, whereas for [TNT] $\gg$ [NaOMe] it is given by eq 8; ΔOD is the change in optical density; ΔK_2 and ΔK_3 are the changes in equilibrium constants K_2 and K_3 brought about by the temperature jump. These equations are derived in the Appendix; they are valid at those wavelengths chosen for monitoring the reaction, where only TNT^- and JC contribute significantly to the light absorption.

$$\frac{\Delta OD}{OD} = \frac{\Delta K_2}{K_2(1 + K_2[RO^-])} \tag{7}$$

$$\frac{\Delta OD}{OD} = \frac{\Delta K_2}{K_2(1 + K_2[TNT] + K_2K_3[TNT]^2)} + \frac{\Delta K_3[TNT]}{(1 + K_3[TNT])(1 + K_2[TNT] + K_2K_3[TNT]^2)} \tag{8}$$

Let us compare two experiments, where the excess component in the first is NaOMe, in the second TNT, and its concentration is 0.1 M in either case. With K_2 and K_3 from Table II, one calculates $\Delta OD/OD = 0.036\ \Delta K_2$ from eq 7 and $\Delta OD/OD = 0.0176\ \Delta K_2 + 0.0076\ \Delta K_3$ from eq 8. $\Delta OD/OD$ in the latter experiment must indeed be much smaller[14] than in the former for two reasons. (1) The ΔK_2 factor is smaller. (2) ΔK_3 has a different sign from ΔK_2 as is apparent from Figure 1b and c. Thus the experimental observation of larger amplitudes where [NaOMe] $\gg$ [TNT] but small amplitudes when [TNT] $\gg$ [NaOMe] is consistent with Scheme I.

The amplitude of τ_3, for which all experiments were conducted with [TNT] $\gg$ [NaOMe], is given by eq 9, which is also derived in the Appendix. Equation 9

$$\frac{\Delta OD}{OD} = \frac{\Delta K_3[TNT](\epsilon_{JC} - \epsilon_{TNT^-})}{(1 + K_3[TNT])(\epsilon_{TNT^-} + \epsilon_{JC}K_3[TNT])} \tag{9}$$

shows that the amplitude and its concentration dependence should be a function of the wavelength. At a wavelength where the relation of the extinction coefficients is $\epsilon_{TNT^-} \gg \epsilon_{JC}$, $|\Delta OD/OD|$ increases with increasing TNT concentration until it reaches a plateau of $|\Delta OD/OD| = \Delta K_3/K_3$ when $K_3[TNT] \gg 1$. On the other hand, when $\epsilon_{JC} \gg \epsilon_{TNT^-}$, $|\Delta OD/OD|$ will decrease indefinitely with increasing TNT concentration. Our experiments that were performed at 425 mμ, where $\epsilon_{TNT^-} = 4400$ and $\epsilon_{JC} = 5600$, lie somewhere between these extremes. (Determination of the extinction coefficients is discussed below.) Thus eq 9 becomes eq 10. By inserting K_3 from Table II, one

$$\frac{\Delta OD}{OD} = \frac{\Delta K_3[TNT]}{(1 + K_3[TNT](3.67 + 4.67\ K_3[TNT])} \tag{10}$$

can calculate the amplitude; it increased slightly from $\Delta OD/OD = 2.68 \times 10^{-3}\ \Delta K_3$ at 0.02 M TNT to $3.16 \times 10^{-3}\ \Delta K_3$ at 0.04 M TNT; at 0.06 M TNT it is $3.14 \times 10^{-3}\ \Delta K_3$, at 0.08 M TNT it is $2.99 \times 10^{-3}\ \Delta K_3$, and at 0.12 M TNT it is $2.58 \times 10^{-3}\ \Delta K_3$. This is entirely consistent with experimental observation.

TNT and EtO^- in Ethanol.—This system has been studied before under conditions where [NaOEt] $\gg$ [TNT].[2a,7] The rate coefficient (k_2) for TNT deprotonation and the equilibrium constant (K_2) for this process,[2a] as well as an approximate rate coefficient (k_1) for a fast reaction attributed to a CT-complex formation,[7] were reported. The aims of the present study was to find evidence for the Janovsky complex, to measure directly the rate of reprotonation of TNT^-

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[14] In these comparisons only the absolute values of $\Delta OD/OD$ are considered.

TABLE IV

INTERACTION OF TNT WITH OH^- IN 50% DIOXANE–50% WATER

$[NaOH]_0$, M	$[TNT]_0$, M	[NaCl], M	τ_1^{-1}, sec^{-1}	$10^3 \times \tau_2^{-1}$, sec^{-1}	τ_3^{-1}, sec^{-1}
0.001	5×10^{-5}	0.2		8.2 ± 2.0	
0.001	2×10^{-4}	0.2		8.5 ± 2.0	
0.002	2×10^{-4}	0.2		10.7 ± 2.0	
0.005	5×10^{-5}	0.195		18.1 ± 2.0	
0.025	2×10^{-5}	0.175		71.5 ± 4.0	
0.05	2×10^{-5}	0.15		132 ± 6.5	
0.075	2×10^{-5}	0.125		196 ± 10	
0.10	2×10^{-5}	0.10		238 ± 15	
0.10	10^{-4}	0.10	8.2 ± 3.0		
0.20	10^{-4}		9.2 ± 2.0		
0.20	2×10^{-5}		9.4 ± 2.0		
$\approx 4 \times 10^{-4}$	0.002	0.20			33.8 ± 4.0
$\approx 4 \times 10^{-4}$	0.005	0.20			48.2 ± 1.5
$\approx 2 \times 10^{-4}$	0.01	0.20			64.5 ± 2.5
$\approx 2 \times 10^{-4}$	0.015	0.20			77.7 ± 2.8
$\approx 2 \times 10^{-4}$	0.02	0.20			97.2 ± 3.0

(k_{-2}), and to get some preliminary idea on the nature of the fast process reported by Ainscough and Caldin.

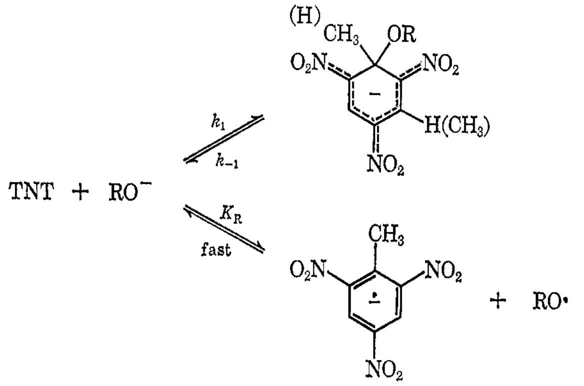
Experiments in the stopped-flow and temperature-jump apparatus showed indeed the presence of three relaxation times, with a similar pattern as in methanol; *i.e.*, τ_1 is the fastest, τ_2 the slowest, and τ_3 intermediate and only present at relatively high TNT concentrations. τ_2 and τ_3 are attributed to the processes of Scheme I, just as for methanol. The results are summarized in Table III.

Though there is appreciable interference by τ_2 except at the highest three base concentrations used, τ_1 is much more easily measured in this system than it is in methanol; Figure 1d shows an oscilloscope trace at high base concentration. This is primarily due to the relative slowness of the reaction, which allows use of the stopped-flow technique instead of the temperature-jump technique and to the higher stability of the species giving rise to τ_1 in ethanol than in methanol.

As can be seen from the results in Table III, τ_1 not only depends on the concentration of the excess component (ethoxide) but on the TNT concentration as well. There are several possible interpretations for these observations. A Meisenheimer complex formation by attack of EtO^- on TNT coupled to a fast radical producing equilibrium, as shown in Scheme II, is the one we currently favor, though other possibilities can not be excluded by the data at hand.

If we assume that the equilibrium constant K_R for radical formation is small,[15] the τ_1 values allow crude estimates for k_1, k_{-1}, and K_1. These estimates are reported in the Discussion where it is shown that they are consistent with the hypothesis of Meisenheimer complex formation.

SCHEME II



τ_2 was evaluated over a rather large range of ethoxide concentrations with the base in large excess. A plot of τ_2^{-1} *vs.* concentration is shown in Figure 4. Unlike the MeO^-/methanol system, the plot shows a definite downward curvature at high base concentration. Such curvature can be rationalized in terms of the fast preequilibrium giving rise to τ_1, the consequence of which is an expression of the form of eq 11, where

$$\frac{1}{\tau_2} = k_2[RO^-]\frac{1}{1 + f([RO^-])} + k_{-2} \qquad (11)$$

$f([RO^-])$ is a function of base concentration. The exact form of this function depends on the nature of the process responsible for τ_1. At low RO^- concentrations, $f([RO^-])$ becomes small compared to 1, so that eq 11 simplifies to eq 12, which is equivalent

$$\frac{1}{\tau_2} = k_2[RO^-] + k_{-2} \qquad (12)$$

to eq 5 under the conditions $[RO^-] \gg [TNT]$; k_2 and k_{-2} can be determined in the usual way from slope and intercept. They are reported in Table II.

τ_3 was determined in the temperature-jump apparatus with TNT as the excess component. The amplitudes displayed a similar behavior as in methanol. A plot of τ_3^{-1} *vs.* the TNT concentration is shown in Figure 3; it obeys eq 4. k_3 and k_{-3} were determined in the usual manner.

TNT and OH^- in 50% Dioxane–50% Water.—As in methanol and ethanol, temperature-jump and stopped-flow experiments showed the presence of three relaxation times. The data are summarized in Table IV. τ_2 and τ_3 are again attributed to the two processes

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[15] This assumption seems justified because attempts to find independent evidence for radical formation have so far been inconclusive. No radicals can be detected by electron spin resonance in equilibrated reaction solutions, nor does the addition of 2-methyl-2-nitrosopropane, a well-known radical trapping agent,[16,17] have any effect on τ_1. However, there is a weak, slowly developing (several minutes after mixing) electron spin resonance signal characteristic of a nitroxide radical[17] when 2-methyl-2-nitrosopropane is added to the reaction solution.

[16] A. Mackor, Th. A. J. W. Wajer, and Th. J. De Boer, *Tetrahedron*, 1623 (1968).

[17] E. G. Janzen and R. J. Blackbum, *J. Amer. Chem. Soc.*, **90**, 5909 (1968).

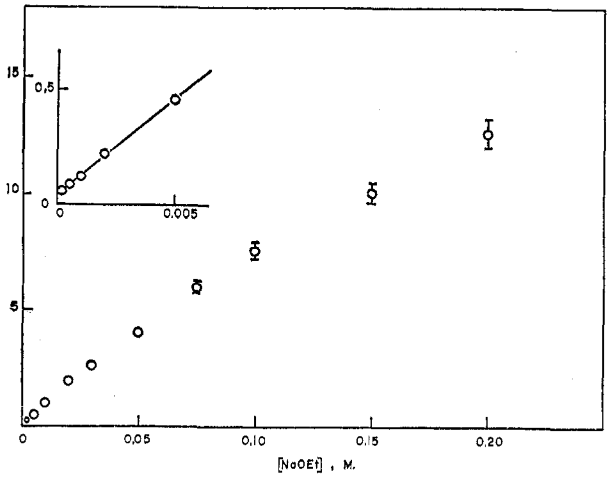


Figure 4.—Reaction of TNT with NaOEt in ethanol; τ_2^{-1} as function of [NaOEt].

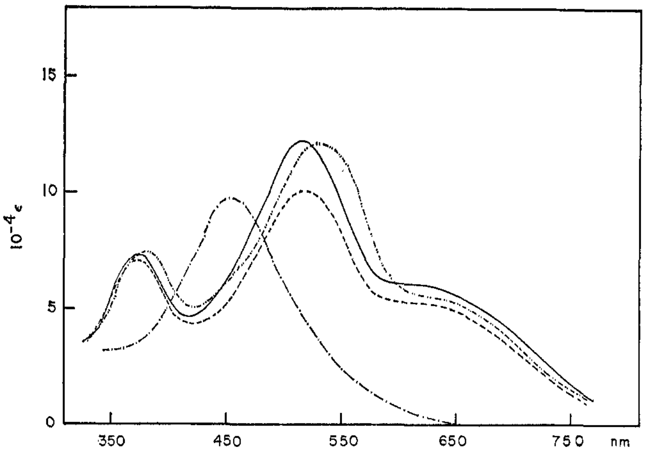


Figure 5.—Spectra of TNT^- in methanol (— — —), ethanol (———), and in 50% dioxane–50% water (—··—); spectrum of a solution of 10^{-3} *M* NaOH and 10^{-4} *M* TNT in 10% dioxane–90% (—·—). The units on the ordinate are arbitrary for the latter spectrum.

in Scheme I. τ_1, though more easily detectable than in methanol, could not be studied over an extended range of concentrations as in ethanol, due to strong interference with τ_2 under all practical conditions. A representative oscilloscope trace of τ_1 is shown in Figure 1e. τ_1 was evaluated by extrapolating the approximately straight second portion of the curve back to the zero and using this line as the infinity value for the superimposed exponential. There is considerable uncertainty in these τ_1 values, mainly because of some arbitrariness in the slope of the extrapolated lines.

In analogy to the ethanol system, τ_1 is tentatively attributed to Meisenheimer complex formation. The data do not allow a decision as to whether there is a radical-forming preequilibrium according to Scheme II.

τ_2 and τ_3 on the other hand are easy to measure. The values of τ_2 at the lowest base concentrations were determined by classical photometric methods. The percentage error for τ_2 is larger at low base concentrations due to interference with a slow unidentified side reaction. A plot of τ_2^{-1} *vs.* hydroxide concentration (not shown) is linear in accordance with eq 12, yielding k_2 and k_{-2}. Similarly, when τ_3^{-1} is plotted *vs.* TNT concentration, a straight line results (not shown) as predicted by eq 4. The rate coefficients are summarized in Table II.

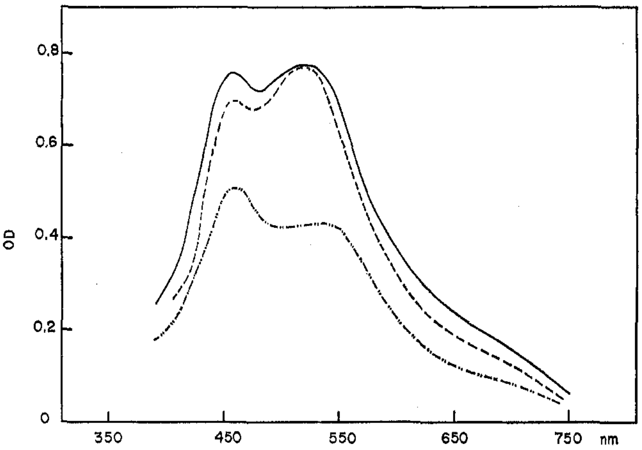


Figure 6.—Spectra of basic TNT solutions in various solvents: — — — in methanol (0.07 *M* TNT, 1.23 × 10^{-4} *M* NaOMe), ——— in ethanol (0.05 *M* TNT, 8.05 × 10^{-5} *M* NaOEt), —··— in 50% dioxane–50% water (0.02 *M* TNT, 6.60 × 10^{-5} *M* NaOH).

Spectra.—In Figure 5 spectra of TNT^- are shown in methanol, ethanol, and in 50% dioxane–50% water; they were calculated on the basis of spectra of TNT solutions with large excesses of base combined with our kinetically determined equilibrium data. The reliability of the extinction coefficients, which is affected by the limits of error in the kinetic determinations, by the absolute magnitude of K_2, and by the stability of the solutions toward slow decomposition, is estimated to be ±5% in ethanol and ±10% in methanol and in 50% dioxane.

In comparison, a spectrum of TNT in the presence of excess base in 10% dioxane–90% water is remarkably different and shows that a relatively minor change in medium has a significant effect on the chemistry of TNT. Though the species giving rise to this spectrum has not yet been identified, preliminary experiments in this laboratory indicate that radicals are formed, and that TNT^-, if formed at all, must be a very transient species.

Spectra where TNT is the excess component are shown in Figure 6. They are distinctly different from the spectra of TNT^-, owing to the contribution from JC. By means of eq 13, spectra of pure JC can be

$$\epsilon_{JC} = \frac{OD - \epsilon_{TNT^-}[TNT^-]}{[JC]} \tag{13}$$

calculated from the spectra in Figure 6; $[TNT^-]$ and [JC] are easily found from eq 14 and 15, where

$$[TNT^-] = \frac{K_2[TNT][RO^-]_0}{1 + K_2[TNT] + K_2K_3[TNT]^2} \tag{14}$$

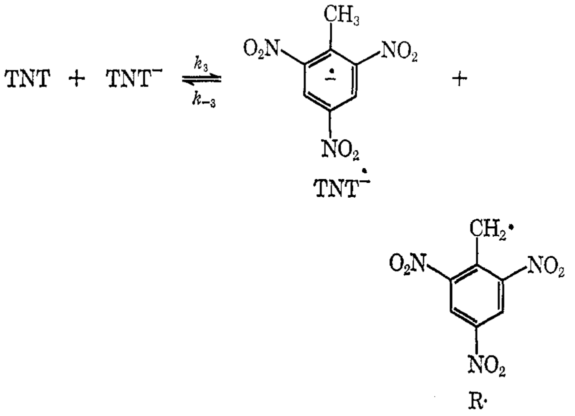
$$[JC] = \frac{K_2K_3[TNT]^2[RO^-]_0}{1 + K_2[TNT] + K_2K_3[TNT]^2} \tag{15}$$

$[RO^-]_0$ is the "stoichiometric" concentration. $[RO^-]_0$, which was only in the order of 5 × 10^{-5} *M* to 10^{-4} *M*, had to be determined indirectly, due to possible error introduced by some absorbed CO_2. This was done by assuming that JC does not absorb above 680 mμ and that consequently all absorption above 680 mμ in Figure 6 is due to TNT^-. Thus by the ability to calculate the concentration of TNT^- from ϵ_{TNT^-}, $[RO^-]_0$ could be inferred indirectly; incidentally it turned out that about 25% of the base had been neutralized by CO_2.

Calculated spectra of JC are shown in Figure 7; their uncertainty is estimated at ±20% due to the indirect multistep procedure of obtaining them. These spectra are characteristic of Janovsky complexes.[12,18]

Discussion

Evidence for TNT^- and JC Formation.—Direct structural proof through nmr spectroscopy is not feasible,[5,6] probably owing to the production of radicals which wipe out the spectrum.[5,6] In view of these reports,[5,6] of some of our own observations, and of findings by Russell and Janzen[19,20] that other nitrotoluenes easily undergo free-radical reactions in basic solution, the possibility that τ_3 might arise from reaction 16 instead of JC formation must be considered briefly. Reaction 16 requires τ_3 to be described by



(16)

eq 17 (instead of eq 3) which, under the condition

$$\frac{1}{\tau_3} = k_3([\mathrm{TNT}] + [\mathrm{TNT}^-]) + k_{-3}([\mathrm{TNT}^{\cdot -}] + [\mathrm{R}\cdot]) \qquad (17)$$

$[\mathrm{TNT}] \gg [\mathrm{NaOR}]$, reduces to eq 18 (*cf.* eq 4). Taking

$$\frac{1}{\tau_3} = k_3[\mathrm{TNT}] + k_{-3}([\mathrm{TNT}^{\cdot -}] + [\mathrm{R}\cdot]) \qquad (18)$$

into consideration that $[\mathrm{TNT}^{\cdot -}] = [\mathrm{R}\cdot]$ and expressing the radical concentrations in terms of reactant concentrations, eq 18 becomes eq 19. Equation 19

$$\frac{1}{\tau_3} = k_3[\mathrm{TNT}] + 2k_{-3}[\mathrm{TNT}]\sqrt{K_2K_3[\mathrm{RO}^-]} \qquad (19)$$

predicts τ_3^{-1} to depend on the alkoxide ion concentration even when it is the minor component; it also requires a plot of τ_3^{-1} to go through the origin. This is contrary to experimental evidence (Tables I, III, and IV, Figure 3).

Our conclusion that τ_3 does not arise from radical formation does not exclude that reaction 16 is nevertheless a minor process undetected by our methods; the impossibility to take nmr spectra[5,6] and our esr experiments in ethanol does indeed suggest the interference by free radicals, either arising from reaction 16 or some other process.

As far as the evidence for TNT^- formation is concerned, our observation of a JC arising from the interaction of a second molecule of TNT with the primary

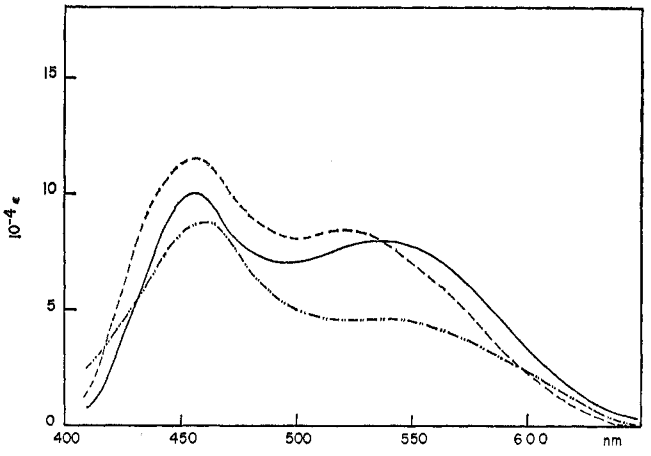


Figure 7.—Spectra of JC in methanol (— — —), ethanol (——), and in 50% dioxane–50% water (—· ·—).

product of the reaction between TNT and the lyate ion constitutes strong evidence that TNT^- is in fact this primary product in methanol, in ethanol, and in 50% dioxane–50% water. Such evidence is not available in 10% dioxane–90% water, and, in fact, the spectra in Figure 5 suggest that if TNT^- is present at all it is completely overshadowed by another species.

The results of our study in aqueous dioxane offer a possible interpretation for the apparently conflicting literature reports concerning hydrogen exchange. The Experiments of Bowden and Stewart[4] were performed in aqueous solutions containing 5–15 mol % of dimethyl sulfoxide.[21] Their solutions then were very aqueous and comparable to our 10% dioxane–90% water solution, which is confirmed by practically identical spectra of basic TNT solutions in the two media. As TNT^- plays only a very minor role if at all in these media, the insignificant hydrogen exchange reported by Bowden and Stewart finds a natural explanation.

On the other hand, when the water content of the mixed solvents is decreased, TNT^- apparently becomes the major species, as it does in methanol or ethanol, and the nearly complete rapid hydrogen exchange reported by Buncel,[3b] *et al.*, in 90% dimethylformamide–10% D_2O is easily rationalized.

Finally, findings of Miller and Wynne-Jones[3c] of a very slow exchange (23 atom % deuterium incorporated after 2–3 weeks in pyridine–D_2O with a very high pyridine content) can be understood by a consideration of the rate of TNT deprotonation. By extrapolating from k_2 in 50% dioxane–50% water, one can conclude that in such a weakly basic system the reaction must be very slow indeed, quite apart from the possible side reactions during this long period of time.

Kinetic and Equilibrium Data of TNT^- Formation.—A rate coefficient for TNT^- formation in ethanol[2a] as well as equilibrium constants in ethanol,[2a] in methanol,[22] and in ethylenediamine–water mixtures[23] has been reported previously. The agreement between the value of Caldin and Long[2a] for k_2 in ethanol and ours is very close, considering that their determination was made at 19.1°, and so is the agreement between the K_2 values in the same solvent. In methanol,

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[18] C. A. Fyfe, *Can. J. Chem.*, **46**, 3047 (1968).

[19] G. A. Russell and E. G. Janzen, *J. Amer. Chem. Soc.*, **84**, 4154 (1962).

[20] G. A. Russell and E. G. Janzen, *ibid.*, **89**, 300 (1967).

[21] K. Bowden, personal communication.

[22] R. Schaal and G. Lambert, *J. Chim. Phys. Physicochim. Biol.*, **59**, 1151 (1962).

[23] R. Schaal, *ibid.*, **52**, 796 (1955).

the correspondence between K_2 of Schaal and Lambert[22] and ours is judged satisfactory.

It is interesting to note that the rate coefficients for deprotonation of nitroethane by MeO^- in methanol is 16.4 M^{-1} sec^{-1} and by EtO^- in ethanol is 88.2 M^{-1} sec^{-1} [24] which are practically the same for deprotonation of TNT. These very slow rates confirm the expectation that the proton transfer is accompanied by a significant electronic rearrangement and that the charge in TNT^- is strongly delocalized.

Janovsky Complex.—Though the spectra in Figure 7 are typical for a Janovsky complex,[12,18] it is not possible to decide whether the TNT^- has attached itself to the 1 or 3 position of TNT.

Rate and equilibrium constants (k_3, k_{-3}, and K_3) in methanol and ethanol are very nearly the same, which is reasonable for an isoelectronic reaction in two protic solvents differing only in their dielectric constant. k_2 in 50% dioxane is significantly higher than in the alcohols, which is most likely due to a lesser ground state solvation. The reverse rate is practically unaffected so that the equilibrium constant K_3 is larger by about the same amount as k_3.

Meisenheimer Complex.—A comparison of the crude estimates for k_1, k_{-1}, and K_1 with analogous data for MC formation[25] between 1,3,5-trinitrobenzene (TNB) and alkoxide ions is interesting. For TNB in ethanol $k_1 = 33400\ M^{-1}\ \text{sec}^{-1}$, $k_{-1} = 27.5\ \text{sec}^{-1}$, and $K_1 = 1210\ M^{-1}$ whereas for TNT $1500 < k_1 < 3000\ M^{-1}\ \text{sec}^{-1}$, $80 < k_{-1} < 200\ \text{sec}^{-1}$, and $7.5 < K_1 < 37.5\ M^{-1}$. In methanol $k_{-1} = 305\ \text{sec}^{-1}$ for TNB, whereas $600 < k_{-1} < 3000\ \text{sec}^{-1}$ for TNT if τ_1 is assumed to be mainly determined by k_{-1}.

The fact that $k_1^{TNT} < k_1^{TNB}$, $k_{-1}^{TNT} > k_{-1}^{TNB}$, and $K_1^{TNT} \ll K_1^{TNB}$ is consistent with the hypothesis of a Meisenheimer complex, because of the electron-releasing and steric[26] effects of the methyl group in TNT; it gives some support to our hypothesis.

Experimental Section

Materials.—2,4,6-Trinitrotoluene (Eastman White Label) was recrystallized twice from ethanol, mp 81–82°. Reagent grade methanol and ethanol were used without further purification. Stock solutions of NaOMe and NaOEt were prepared by dissolving sodium metal in the respective solvents under a stream of dry nitrogen. *p*-Dioxane was purified by the method of Fieser[27] and was stored over lithium aluminum hydride, from which it was distilled as needed. The 50% dioxane–50% water mixture was prepared by diluting 5 vol of dioxane to a total of 10 vol with distilled water. 2-Methyl-2-nitrosopropane was kindly provided to us by Dr. J. K. Kim. Where low base concentrations ($\leq 10^{-3}$ M) were employed for kinetic or spectral determinations, carefully degassed solvents were used in order to minimize CO_2 interference.

Rate Measurements and Spectra.—The slow rates were measured on an automatized Kintrac VII[28] spectrophotometer at 450 mμ. Stopped-flow determinations were carried out on a Durrum[29] stopped-flow spectrometer between 425 and 500 mμ. The relaxation times listed in Tables III and IV represent average values of three to four single determinations. The temperature-jump experiments were done on a temperature-jump transient spectrometer from Messanlagen Gmbh.[30] Temperature jumps of 2° were applied. Relaxation times were determined at wavelengths between 415 and 585 mμ, depending on the optical density of the solutions. Each reported relaxation time represents the average of at least four relaxation curves. The electrolyte concentration was kept constant in the various series of runs by adding appropriate amounts of $NaClO_4$ or NaCl, respectively.

Spectra were taken on a Cary 14[31] uv spectrophotometer.

Registry No.—TNT, 118-96-7; MeO^-, 3315-60-4; EtO^-, 16331-64-9; HO^-, 14280-30-9.

Acknowledgment.—I am very thankful to Professor J. F. Bunnett for criticism and discussion, as well as to Dr. P. B. Chock for reading the manuscript.

Appendix

Amplitudes of Relaxational Processes.—The relative amplitude is defined as ΔOD/OD immediately following the temperature jump, *i.e.*, before reequilibration sets in. Under the assumption that only TNT^- and JC absorb,[32] the amplitude is given by eq 20

$$\frac{\Delta OD}{OD} = \frac{\epsilon_{TNT^-}\Delta[TNT^-] + \epsilon_{JC}\Delta[JC]}{\epsilon_{TNT^-}[TNT^-] + \epsilon_{JC}[JC]} \tag{20}$$

where $\Delta[TNT^-]$ and $\Delta[JC]$ are the displacement of the respective concentrations from their equilibrium value and $[TNT^-]$ and $[JC]$ are the equilibrium concentrations.

A. Amplitude of τ_2 when $[RO^-] \gg [TNT]$.—Here [JC] and ΔJC are negligible compared to $[TNT^-]$ and ΔTNT^-. After a temperature jump the displacement of $[TNT^-]$ from its new equilibrium value is given by eq 21 for $\Delta K_2 \ll K_2$, where ΔK_2 is the change of K_2 as a consequence of the temperature jump. Substituting ΔTNT from the mass balance, eq 22, one obtains after some rearrangements eq 23.

$$\Delta TNT^- = K_2[RO^-]\Delta TNT + \Delta K_2[RO^-][TNT] \tag{21}$$

$$\Delta TNT = -\Delta TNT^- \tag{22}$$

$$\Delta TNT^- = \frac{\Delta K_2[RO^-][TNT]}{1 + K_2[RO^-]} \tag{23}$$

$$[TNT^-] = K_2[RO^-][TNT] \tag{24}$$

Inserting eq 23 and eq 24 into eq 20 affords eq 7.

$$\frac{\Delta OD}{OD} = \frac{\Delta K_2}{K_2(1 + K_2[RO^-])} \tag{7}$$

B. Amplitude of τ_3 when $[TNT] \gg [RO^-]$.—In analogy to eq 21, ΔJC after a temperature jump is given by eq 25. The meaning of the subscript 3

$$\Delta JC_3 = K_3[TNT]\Delta TNT_3^- + \Delta K_3[TNT][TNT^-] \tag{25}$$

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[24] P. Jones, J. L. Longridge, and W. F. K. Wynne-Jones, *J. Chem. Soc.*, 3606 (1965).

[25] C. F. Bernasconi, *J. Amer. Chem. Soc.*, **92**, 4682 (1970).

[26] The steric effect can be visualized as hindrance to the attack by the nucleophile, if this attack is on the 1 position, though release of some steric strain between the methyl group and the two *o*-nitro groups by pushing the methyl group out of the plane of the benzene ring may partially compensate for that. If the attack is on the 3 position, steric strain may result from the interaction of the methyl group with the flanking nitro groups which have to be coplanar with the ring for an optimal delocalization of the negative charge.

[27] L. F. Fieser, "Experiments in Organic Chemistry," 3rd ed, D. C. Heath, Boston, Mass., 1957, p 284.

[28] Beckman Instruments, Inc., Richmond, Calif.

[29] Durrum Instrument Corp., Palo Alto, Calif.

[30] Messanlagen Gmbh, Göttingen, Germany.

[31] Cary Instruments, Monrovia, Calif.

[32] MC, $TNT^{-\cdot}$, or whatever species accounts for τ_1 is present at too low concentration levels to significantly contribute to the overall optical density, whereas the absorption of TNT is negligible at the wavelength chosen.

in ΔJC_3 and ΔTNT_3^- is to refer to the displacement from the fast equilibrium, reaction 3, only. With the mass balance, eq 26, one arrives at eq 27. When

$$\Delta JC_3 = -\Delta TNT_3^- \tag{26}$$

$$\Delta TNT_3^- = -\frac{\Delta K_3[TNT][TNT^-]}{1 + K_3[TNT]} \tag{27}$$

eq 24, 26, 27, and 28 are inserted into eq 20, one ob-

$$[JC] = K_3[TNT][TNT^-] \tag{28}$$

tains eq 9.

$$\frac{\Delta OD}{OD} = \frac{\Delta K_3[TNT](\epsilon_{JC} - \epsilon_{TNT^-})}{(1 + K_3[TNT])(\epsilon_{TNT^-} + \epsilon_{JC}K_3[TNT])} \tag{9}$$

C. Amplitude of τ_2 when [TNT] $\gg$ [RO$^-$].—In this situation ΔTNT_2^- and ΔJC_2 which refer to the equilibration of the slow reaction 2 are given by eq 29 and 30 where ΔTNT_{2+3}^- and ΔJC_{2+3} are the

$$\Delta TNT_2^- = \Delta TNT_{2+3}^- + \Delta TNT_3^- \tag{29}$$

$$\Delta JC_2 = \Delta JC_{2+3} - \Delta JC_3 \tag{30}$$

total displacement of the concentrations from the final equilibrium state. Note that

$$\Delta JC_2 = K_3[TNT]\Delta TNT_2^- \tag{31}$$

because with respect to reaction 2 equilibrium 3 is always established. This simplifies eq 20 to eq 32.

$$\frac{\Delta OD}{OD} = \frac{\Delta TNT_2^-}{[TNT^-]} \tag{32}$$

ΔTNT_{2+3}^- and ΔJC_{2+3} are given by eq 33 and 34,

$$\Delta TNT_{2+3}^- = K_2[TNT]\Delta RO_{2+3}^- + \Delta K_2[TNT][RO^-] \tag{33}$$

$$\Delta JC_{2+3} = K_3[TNT]\Delta TNT_{2+3}^- + \Delta K_3[TNT][TNT^-] \tag{34}$$

whereas eq 35 holds for the mass balance. Combining

$$\Delta TNT_{2+3}^- + \Delta RO_{2+3}^- + \Delta JC_{2+3} = 0 \tag{35}$$

eq 33, 34, and 35, one gets eq 36. Thus by inserting

$$\Delta TNT_{2+3}^- = \frac{\Delta K_2[TNT][RO^-] - K_2\Delta K_3[TNT]^2[TNT^-]}{1 + K_2[TNT] + K_2K_3[TNT]^2} \tag{36}$$

eq 27 and 36 into eq 29 and dividing by [TNT$^-$], eq 32 becomes eq 8.

$$\frac{\Delta OD}{OD} = \frac{\Delta K_2}{K_2(1 + K_2[TNT] + K_2K_3[TNT]^2)} + \frac{\Delta K_3[TNT]}{(1 + K_3[TNT])(1 + K_2[TNT] + K_2K_3[TNT]^2)} \tag{8}$$

The Intermediacy of Phenylpropargylene and Phenylethynylnitrene[1]

R. SELVARAJAN AND J. H. BOYER*

Chemistry Department, University of Illinois, Chicago Circle Campus, Chicago, Illinois 60680

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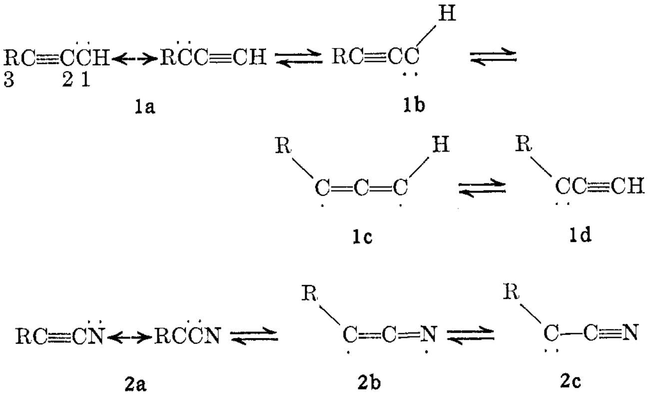
Diazomethane combines with phenylpropiolyl chloride to give 4-phenyl-1-diazo-3-butyn-2-one (**3**) and 3-chloroacetyl-4-phenylpyrazole (**4**). Phenylpropargylene (**1a**, R = C_6H_5), generated by irradiating the ketone **3**, abstracted hydrogen to produce benzylacetylene (**8**), phenylallene (**9**), and 1-methyl-2-phenylacetylene (**10**). Irradiation isomerized the allene **9** into the acetylene **8** but did not isomerize either of the acetylenes **8** and **10**. Phenylpropiolylcarbene (**5**) gave 4-phenyl-3-butyn-2-one (**7**) by hydrogen abstraction. A thermal Curtius reaction in different solvents transformed phenylpropiolyl azide (**11**) into phenylacetonitrile (**13**), but when the intermediate phenylethynyl isocyanate **12** was formed in aqueous ethanol it gave ethyl *N*-phenylacetylcarbamate (**15**) and *N,N'*-bisphenylethynylurea (**16**). A formal adduct between phenylpropiolylnitrene (**18**) and the isocyanate **12**, combined with ethanol, and subsequent isomerization gave 2-phenylethynyl-4- (or 5-) phenyl-5- (or 4-) carbethoxyaminooxazole (**17**) (tentative assignment). Irradiation of the azide **11** in methanol generated phenylethynylnitrene (**2a**, R = C_6H_5), which then reacted as phenylcyanocarbene (**2a**) to give α-methoxyphenylacetonitrile (**19**) by insertion and **13** by abstraction.

Centers of reactivity for propargylene (**1**, R = H) and ethynylnitrene (**2**, R = H) are displayed in formulas for respective resonance hybrids **1a** and **2a** and tautomers **1b–d** and **2b,c**; however, certain centers have such a low order of reactivity that they have not been detected. Propargylene and its methyl and phenyl derivatives, obtained by the photolysis of the appropriate diazopropyne, each showed electron paramagnetic resonance.[2] Triplet propargylene gave equal reactivity with olefins at C_1 and C_3. On the other hand, singlet propargylene reacted with olefins only at C_1, the position vacated by nitrogen.[2] Although phenylethynylnitrene (**2a**, R = C_6H_5) was presumed to have been initially formed from the irradiation of either phenylethynyl azide or phenylethynyl isocyanate, it reacted exclusively as phenylcyanocarbene (**2a**, R = C_6H_5).[3]

This report describes additional chemical properties pertaining to phenylpropargylene (**1a**, R = C_6H_5) and phenylethynylnitrene (**2a**, R = C_6H_5).



Diazomethane reacted with phenylpropiolyl chloride to give 4-phenyl-1-diazo-3-butyn-2-one (**3**) along with

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[1] Financial support was received from NASA Grant No. NGR-14-012-004.

[2] R. A. Bernheim, R. J. Kempf, J. V. Gramas, and P. S. Skell, *J. Chem. Phys.*, **43**, 196 (1965).

[3] J. H. Boyer and R. Selvarajan, *J. Amer. Chem. Soc.*, **91**, 6122 (1969).