

Intermediates in Nucleophilic Aromatic Substitution. V.¹ Kinetic Study of Meisenheimer Complexes of 1,3,5-Trinitrobenzene with Hydroxide and Alkoxide Ions in Ethanol-Water and Methanol-Water Mixtures²

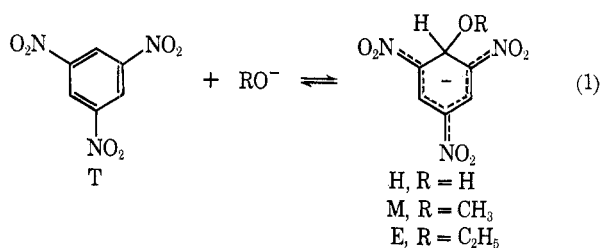
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The kinetics of reversible Meisenheimer complex formation between 1,3,5-trinitrobenzene and the respective lyate ions in 19% ethanol-81% water (v/v) and in 22.5% methanol-77.5% water (v/v), respectively, has been studied by the temperature-jump and stopped-flow methods. These very aqueous mixed solvents approximate a "common" solvent for the three equilibrium reactions concerned. The rate coefficients for nucleophilic attack and for leaving group departure respectively are 7700 $M^{-1} \text{ sec}^{-1}$ and 32.0 sec^{-1} for EtO^- in ethanol-water, 2425 $M^{-1} \text{ sec}^{-1}$ and 254 sec^{-1} for MeO^- in methanol-water, 70.2 $M^{-1} \text{ sec}^{-1}$ and 6.8 sec^{-1} for HO^- in ethanol-water, and 17.1 $M^{-1} \text{ sec}^{-1}$ and 10.5 sec^{-1} for HO^- in methanol-water. A change from pure methanol and ethanol to the mainly aqueous solvents has an expected small retarding effect (three- or fourfold) on the rate of nucleophilic attack by MeO^- and by EtO^- , whereas leaving group departure is practically unaffected.

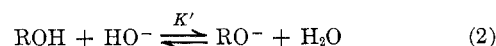
Recently we reported a kinetic study on the Meisenheimer complex forming equilibria between 1,3,5-trinitrobenzene (T) and the lyate ions in water, methanol, and ethanol¹ (eq 1). One of our general objectives is to



study leaving group reactivities in nucleophilic aromatic substitutions.³ The work reported¹ provided information about leaving group reactivities of HO^- , MeO^- , and EtO^- with respect to the model reaction 1 in the solvents mentioned. Though interesting, this comparison of the three bases in three different solvents suffers from the fact that a solvent effect may account for at least part of the reported differences.

The aim of this and subsequent studies to be reported shortly is to provide data on reaction 1 in a "common" solvent. Because of the inherent nature of protic solvents such a "common" solvent can only be approximated. We have chosen predominantly aqueous alcohol-water mixtures with alcohol contents around

20%. The choice of the alcohol content was dictated by the need of a sufficient equilibrium concentration of RO^- arising from equilibrium 2 on the one hand and



the wish to keep the solvent as aqueous as possible on the other. For the lack of a better criterion, the content for the various alcohols was chosen so as to give mixtures of equal dielectric constants at 25°, $D = 67.5$,⁴ for all the solvents whenever possible. In this first account we report on our findings in 19% ethanol-81% water (v/v) and 22.5% methanol-77.5% water (v/v).

Experimental Section

Materials.—1,3,5-Trinitrobenzene (Eastman White Label) was recrystallized twice from ethanol, mp 123°. Reagent grade methanol and ethanol were used without further purification.

Rate and Equilibrium Measurements.—Stopped-flow determinations were performed on a Durrum stopped-flow spectrometer. The relaxation times listed in Tables I and II represent average values of three or four oscilloscope pictures taken from two and frequently more independently prepared reactant solutions. The reproducibility of the τ_2 values in methanol-water was less satisfactory than the others; these τ_2 values represent the average of up to six independent determinations.

The temperature-jump experiments were carried out on a temperature-jump transient spectrometer from Messanlagen GmbH. Temperature jumps of 1° were found to be adequate for the systems under study. Reported relaxation times represent the average of three or four oscilloscope pictures taken from two independently prepared reactant solutions.

(1) Part IV: C. F. Bernasconi, *J. Amer. Chem. Soc.*, **92**, 4682 (1970).

(2) 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.

(3) C. F. Bernasconi, *J. Amer. Chem. Soc.*, **92**, 129 (1970).

(4) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold, New York, N. Y., 1950, p 118.

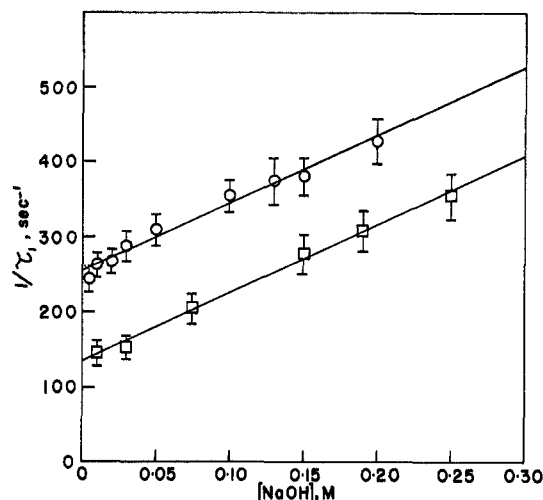


Figure 1.— τ_1 in 22.5% methanol-77.5% water (v/v); O with 0.5 M NaCl, \square with 3 M NaCl.

TABLE I
REACTIONS OF MeO^- AND HO^- WITH
1,3,5-TRINITROBENZENE IN 22.5% METHANOL-77.5%
WATER (v/v) AT 25°

[NaOH] ₀ , M	[TNB] ₀ × 10 ⁶ M	Electrolyte concn, ^a M	1/τ ₁ , ^b sec ⁻¹	1/τ ₂ , ^c sec ⁻¹
0.005	40	0.5	244 ± 17	
0.01	30	0.5	263 ± 18	
	30	3.0	145 ± 15	
	2	0.5		10.7 ± 0.9
	2	3.0		9.2 ± 0.5
0.02	30	0.5	267 ± 18	
	2	3.0		8.8 ± 0.5
0.03	30	0.5	287 ± 20	
	2	0.5		10.6 ± 0.5
	30	3.0	152 ± 12	
	2	3.0		9.0 ± 0.5
0.05	20	0.5	310 ± 20	
	2	0.5		11.0 ± 0.5
	2	3.0		9.0 ± 0.5
0.075	20	3.0	205 ± 20	
	2	0.5		10.8 ± 0.5
	2	3.0		8.8 ± 0.6
0.10	20	0.5	355 ± 20	
0.13	20	0.5	376 ± 30	
0.15	14	0.5	380 ± 25	
	14	3.0	277 ± 25	
	2	0.5		11.4 ± 0.7
	2	3.0		9.1 ± 1.0
0.19	14	3.0	308 ± 26	
0.20	12	0.5	427 ± 30	
	2	0.5		12.1 ± 0.8
	2	3.0		9.0 ± 1.0
0.25	12	3.0	354 ± 30	
0.30	1	0.5		12.5 ± 1.2
0.35	1	0.5		12.7 ± 1.5
0.40	1	0.5		12.7 ± 1.2

^a NaCl added as needed. ^b Observed at 535 nm by temperature-jump method. ^c Observed at 425 nm by stopped-flow method.

Absorbance measurements for equilibrium determinations were made on a Gilford spectrophotometer with thermostatted cuvettes.

Results

Solutions of T in basic 19% aqueous ethanol and 22.5% aqueous methanol are characterized by several

TABLE II
REACTIONS OF EtO^- AND HO^- WITH
1,3,5-TRINITROBENZENE IN 19% ETHANOL-81%
WATER (v/v) AT 25°^a

[NaOH] ₀ , M	[TNB] ₀ × 10 ⁶ M	1/τ ₁ , sec ⁻¹ ^b	1/τ ₂ , sec ⁻¹ ^c
0.005	2		7.13 ± 0.35
0.010	2	36.3 ± 4.0 ^d	
	1.5		7.40 ± 0.37
0.020	1.5		8.05 ± 0.40
0.030	2	39.2 ± 4.0 ^d	
	1.5		8.32 ± 0.41
0.040	1.5		8.76 ± 0.44
0.050	2	55.7 ± 7.0 ^d	
	0.4		9.11 ± 0.45
0.075	0.4		9.64 ± 0.48
0.10	10	63 ± 5.0	
	0.4		10.2 ± 0.5
0.13	10	74 ± 3.5	
	0.4		10.5 ± 0.5
0.15	10	85 ± 4.0	
	0.3		11.0 ± 0.5
0.17	10	89 ± 4.3	
	0.3		11.3 ± 0.6
0.19	10	99 ± 4.5	
	0.3		11.5 ± 0.6
0.22	10	112 ± 5	
	0.3		11.7 ± 0.6
0.25	10	117 ± 6	
	0.3		11.9 ± 0.6

^a Total electrolyte concentration maintained at 0.5 M by addition of NaCl as needed. ^b Determined at 535 nm by the temperature-jump method. ^c Determined at 500 nm by the stopped-flow method. ^d Calculated by computer.

relaxational processes in the time range from a few milliseconds to about 20 sec. Depending on reaction conditions such as base concentration and electrolyte concentration, one observes at least four but possibly five or more relaxation processes, mostly well separated, which can be attributed to equilibrium reactions. Furthermore, there is at least one slow process with a half-life >15 min which is believed to be an irreversible decomposition of TNB.

In this report we are concerned with only the two fastest processes (with relaxation times τ_1 and τ_2) which arise from the reactions of eq 1 leading to complexes H and E in ethanol-water and to H and M in methanol-water. In a subsequent paper we will deal with 1:2 complexes formed by the attack of two lyate ions on T which give rise to the longer relaxation times and necessitate an involved kinetic analysis.

In methanol-water the two relaxation times are well separated under all conditions, *i.e.*, $\tau_2 \gg \tau_1$.⁵ τ_1 was measured by the temperature-jump method.⁶ The data which are summarized in Table I show a strong dependence on base concentration. When τ_1^{-1} is plotted *vs.* the stoichiometric base concentration $[\text{NaOH}]_0$, a straight line results. Figure 1 shows such plots at two different electrolyte concentrations.

τ_2 was measured by the stopped-flow method. It is only very slightly concentration dependent; plots of τ_2^{-1} *vs.* $[\text{NaOH}]_0$ are shown in Figure 2.

In ethanol-water τ_1 is appreciably longer than in methanol-water, whereas τ_2 is about the same in both

(5) $\tau_2 \gg \tau_1$ means $\tau_2/\tau_1 \geq 10$.

(6) M. Eigen and L. DeMaeyer in "Technique of Organic Chemistry," Vol. VIII, Part 2, Interscience, New York, N. Y., 1963, p 895.

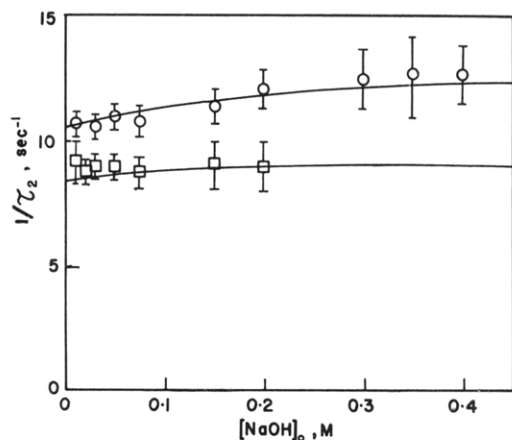


Figure 2.— τ_2 in 22.5% methanol–77.5% water (v/v); O with 0.5 M NaCl, \square with 3 M NaCl.

solvents. As a consequence, the relation $\tau_2 \gg \tau_1$ is just barely fulfilled, $\tau_2/\tau_1 \approx 7$ –10 for $[\text{NaOH}]_0 \leq 0.25 \text{ M}$, $\tau_2/\tau_1 \geq 10$ for $[\text{NaOH}]_0 \geq 0.25 \text{ M}$. Representative oscilloscope traces at low and at high base concentration are shown in Figure 3. It is noteworthy that τ_2 interferes rather strongly with τ_1 at low base concentrations (Figure 3A) but only insignificantly at high base concentrations (Figure 3B). This lesser interference is only to a small extent due to a larger separation of τ_1 and τ_2 at higher base concentration. The principal reason is a decrease in the amplitude (change in absorbance as a consequence of the temperature jump) of τ_2 relative to the amplitude of τ_1 when the base concentration is increased, which arises from a favorable interplay of the enthalpies of the various equilibria involved.⁷

Where the interference of τ_2 with τ_1 was appreciable, the relaxation times were evaluated with the help of a computer.⁸ Otherwise it was possible to use standard graphical procedures.

The data for the ethanol–water reactions are reported in Table II; plots of τ_1^{-1} and τ_2^{-1} in Figure 4 and 5 show a strong concentration dependence for τ_1 and weak dependence for τ_2 just as in methanol–water.

As will be shown below, the concentration dependence of τ_1^{-1} and τ_2^{-1} in both solvent systems is consistent with two distinct 1:1 T–base interactions which, in the light of all known evidence,^{1,10} can reasonably only be the Meisenheimer complexes M and H in aqueous methanol and E and H in aqueous ethanol, respectively. With reference to our previous study¹ on reaction 1 in pure methanol (M), pure ethanol (E), and pure water (H), where the relaxation times in both alcohols were found to be significantly shorter than in water, we fur-

(7) In the stopped-flow experiments, τ_2 interferes more strongly with τ_1 over the entire concentration range. It is for this reason that the temperature-jump rather than the stopped-flow technique was used for measuring τ_1 .

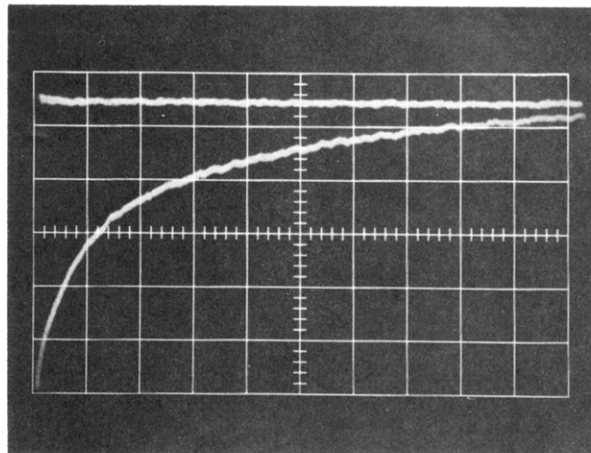
(8) A computer program proposed by Wiberg⁹ for first-order rate calculations was modified to calculate the parameters $\Delta A_1/\Delta A_0$, τ_1 and τ_2 which give the best fit between experimental absorbance data (A), and the function

$$\frac{\Delta A}{\Delta A_0} = \frac{\Delta A_1}{\Delta A_0} e^{-t/\tau_1} + \left(1 - \frac{\Delta A_1}{\Delta A_0}\right) e^{-t/\tau_2}$$

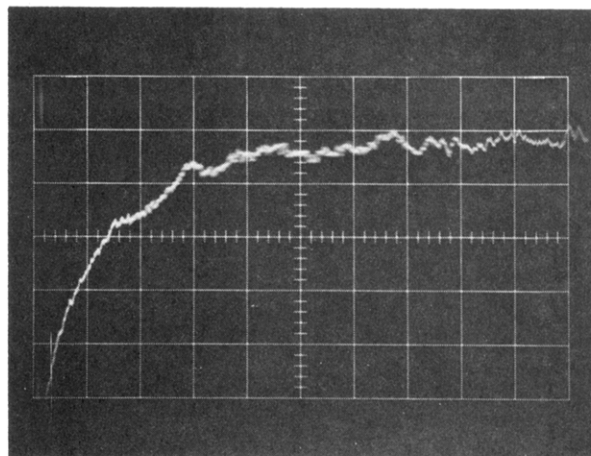
(9) K. B. Wiberg, "Physical Organic Chemistry," Wiley, New York, N. Y., 1966, p 570.

(10) For recent reviews of this evidence, see (a) R. Foster and C. A. Fyfe, *Rev. Pure Appl. Chem.*, **16**, 61 (1966); (b) E. Buncl, A. R. Norris, and K. E. Russell, *Quart. Rev., Chem. Soc.*, **22**, 123 (1968); (c) M. R. Cramp-ton, *Advan. Phys. Org. Chem.*, **7**, 211 (1969).

A



B



C

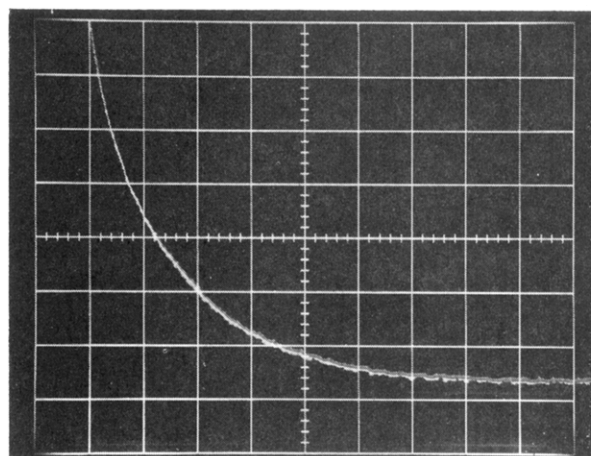
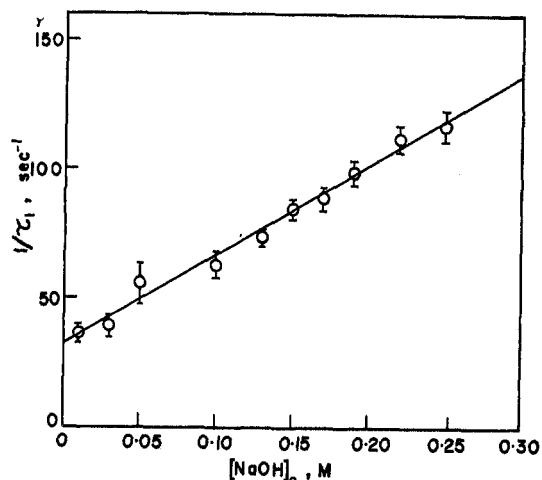
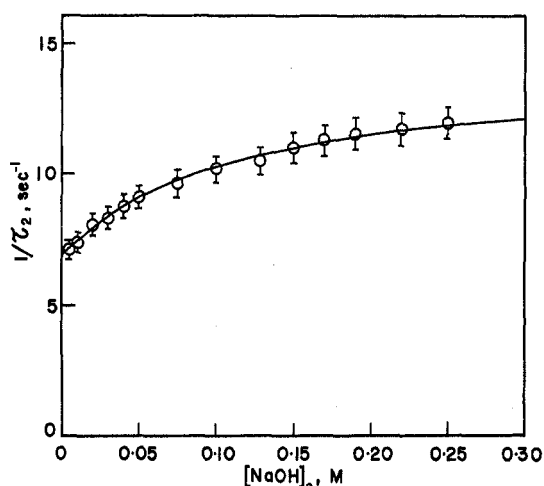
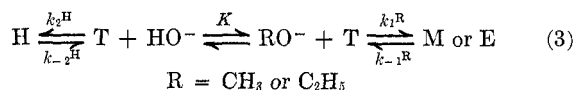


Figure 3.—Representative oscilloscope traces in 19% ethanol–81% water (v/v); A, τ_1 and τ_2 at $[\text{NaOH}]_0 = 0.03 \text{ M}$, $\lambda = 535 \text{ m}\mu$, 20 msec/division, temperature-jump method; B, τ_1 at $[\text{NaOH}]_0 = 0.19 \text{ M}$, $\lambda = 535 \text{ m}\mu$, 5 msec/division, temperature-jump method; C, τ_2 at $[\text{NaOH}]_0 = 0.19 \text{ M}$, $\lambda = 425 \text{ m}\mu$, 50 msec/division, stopped-flow method.

ther conclude that in our present study τ_1 is associated with MeO^- and EtO^- attack, respectively, whereas τ_2 is associated with HO^- attack in both solvents. A full justification for this interpretation is given in the Discussion.

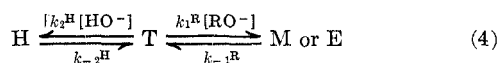
Figure 4.— τ_1 in 19% ethanol-81% water (v/v).Figure 5.— τ_2 in 19% ethanol-81% water (v/v).

We can describe our reaction systems by eq 3 which



includes the RO^-/HO^- equilibrium 2, though the solvent species have been omitted for simplicity. Equilibrium 2 is established very fast; the relaxation time associated with it could not possibly be determined by our methods.

In the general case, eq 3 calls for complex expressions relating τ_1 and τ_2 to reactant concentrations. However, all our experiments were performed with $[\text{NaOH}]_0 \gg [\text{T}]_0$, so that we can write the simplified eq 4.

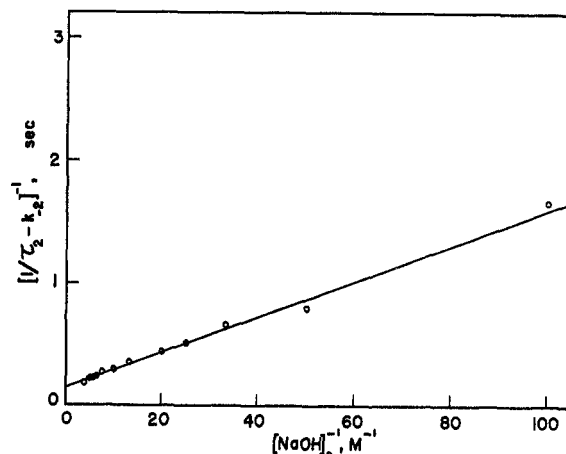


The RO^-/HO^- equilibrium has to be considered only for the calculation of the equilibrium concentrations of RO^- and HO^- by means of eq 5 and 6, where K is de-

$$[\text{RO}^-] = \frac{K}{1+K} [\text{NaOH}]_0 \quad (5)$$

$$[\text{HO}^-] = \frac{1}{1+K} [\text{NaOH}]_0 \quad (6)$$

$$K = \frac{[\text{RO}^-]}{[\text{HO}^-]} = K' \frac{\chi_{\text{ROH}}}{\chi_{\text{H}_2\text{O}}} \quad (7)$$

Figure 6.—Inversion plot of τ_2 in 19% ethanol-81% water (v/v).

finied by eq 7, χ_{ROH} and $\chi_{\text{H}_2\text{O}}$ being mole fractions. For K' we use Murto's¹¹ values, $K' = 4.5$ in methanol-water, $K' = 0.065$ in ethanol-water.

For $\tau_2 \gg \tau_1$ the relaxation times are straightforwardly derived according to well-established procedures⁶ and can be written as eq 8 and 9, where $K_1^{\text{R}} =$

$$\frac{1}{\tau_1} = k_1^{\text{R}} [\text{RO}^-] + k_{-1}^{\text{R}} \quad (8)$$

$$\frac{1}{\tau_2} = \frac{k_2^{\text{H}}[\text{HO}^-]}{1 + K_1^{\text{R}} [\text{RO}^-]} + k_{-2}^{\text{H}} \quad (9)$$

$k_1^{\text{R}}/k_{-1}^{\text{R}}$. Taking into consideration eq 5 and 6, they become eq 10 and 11.

$$\frac{1}{\tau_1} = \frac{k_1^{\text{R}} K}{1+K} [\text{NaOH}]_0 + k_{-1}^{\text{R}} \quad (10)$$

$$\frac{1}{\tau_2} = \frac{k_2^{\text{H}} [\text{NaOH}]_0}{1 + K + K K_1^{\text{R}} [\text{NaOH}]_0} + k_{-2}^{\text{H}} \quad (11)$$

In methanol-water eq 10 and 11 hold well under all conditions. In ethanol-water the separation of τ_1 and τ_2 , though not very large, is nevertheless sufficient to warrant the use of eq 10 and 11; the small deviation introduced compared to a more rigorous treatment⁶ is less than 5% and thus comparable with or less than the experimental error.

Equation 10 allows one to determine the various k_1^{R} and k_{-1}^{R} values from slopes and intercepts in Figures 1 and 4. They are reported in Table III as calculated from a least-squares analysis.¹² For the determination of k_2^{H} and k_{-2}^{H} , eq 11 is rearranged to eq 12, where k_{-2}^{H}

$$\frac{1}{\tau_2^{-1} - k_{-2}^{\text{H}}} = \frac{1+K}{k_2^{\text{H}} [\text{NaOH}]_0} + \frac{K K_1^{\text{R}}}{k_2^{\text{H}}} \quad (12)$$

is the intercept of a plot of τ_2^{-1} vs. $[\text{NaOH}]_0$. By plotting the left-hand side of eq 12 vs. $[\text{NaOH}]_0^{-1}$ ("inversion plot"), one should obtain a straight line. In principle this should allow k_2^{H} to be calculated (from slope) as well as K_1^{R} to be checked (from intercept) against its value derived from τ_1 .

In aqueous ethanol one indeed obtains a satisfactory linear inversion plot, Figure 6; k_2^{H} and K_1^{R} calculated by least-squares analysis¹² are reported in Table III. It is to be noted that the K_1^{R} values derived by the two methods agree very well. The curve as drawn in

(11) J. Murto, *Ann. Acad. Sci. Fenn., Ser. A2*, 117 (1962).

(12) These calculations were performed by an electronic desk computer, the Olivetti Programma 101.

TABLE III
RATE AND EQUILIBRIUM CONSTANTS FOR MEISENHEIMER COMPLEXES BETWEEN 1,3,5-TRINITROBENZENE AND
EtO⁻, MeO⁻, AND OH⁻ IN VARIOUS SOLVENTS AT 25°^a

	—19% EtOH-81% H ₂ O—		—22.5% MeOH-77.5% H ₂ O—		EtOH ^b	MeOH ^b	H ₂ O ^b
	τ_1 :E τ_2 :H	τ_1 :H τ_2 :E	τ_1 :M τ_2 :H	τ_1 :H τ_2 :M			
k_1^E (M ⁻¹ sec ⁻¹)	7700 ± 300	1550			33400 ^d		
k_{-1}^E (sec ⁻¹)	32.0 ± 3.0	68			27.5 ^d		
$K_1^E = k_1^E/k_{-1}^E$ (M ⁻¹)	241 ± 24 (248 ± 20) ^c	228			1210 ^d		
k_1^M (M ⁻¹ sec ⁻¹)			2425 ± 125 (2460 ± 130) ^e	29.5		7050 ^d	
k_{-1}^M (sec ⁻¹)			254 ± 9 (134 ± 6) ^e	10.5		305 ^d	
$K_1^M = k_1^M/k_{-1}^M$ (M ⁻¹)			9.55 ± 0.60 (18.3 ± 1.0) ^e	2.81		23.1 ^d	
k_2^H (M ⁻¹ sec ⁻¹)	70.2 ± 3.5	362	17.1 ± 1.7 ^f (8.8 ± 0.9) ^{e,f}	1410			37.5 ^g
k_{-2}^H (sec ⁻¹)	6.8 ± 0.4	32.0	10.5 ± 0.5 (8.5 ± 0.5) ^e	254			9.8 ^g
$K_2^H = k_2^H/k_{-2}^H$ (M ⁻¹)	10.3 ± 0.8	11.3	1.63 ± 0.08 ^f (1.03 ± 0.05) ^{e,f}	5.67			3.73 ^g

^a Unless otherwise stated total electrolyte concentration maintained at 0.5 M by addition of NaCl as required. ^b Reference 1. ^c From τ_2 by means of an inversion plot. ^d Electrolyte concn, 0.2 M NaClO₄. ^e Electrolyte concn, 3 M NaCl. ^f From equilibrium measurements. ^g Electrolyte concn, 1 M NaCl.

Figure 5 has been calculated from eq 11 with the values of k_2^H and K_1^E as determined from the inversion plot.

In methanol-water an inversion plot is not practical because the differences $\tau_2^{-1} - k_{-2}^H$ are of the same order of magnitude as the experimental error. One can determine k_2^H however from equilibrium measurements in the following way. The visible absorption of basic T solution is given by eq 13, where ϵ_M and ϵ_H are the ex-

$$A = \epsilon_M[M] + \epsilon_H[H] \quad (13)$$

inction coefficients of the respective Meisenheimer complex.^{13,14} The spectra of M and H in their respective pure solvents are known¹⁵ to be similar and are likely to be even more so in a common solvent. Thus we do not introduce a large error by assuming $\epsilon_M = \epsilon_H = \epsilon$ at wavelengths between 450 and 490 m μ . With this assumption and by expressing [M] and [H] in terms of known or measurable quantities, one obtains eq 14; a derivation is given in the Appendix. In com-

$$K_2^H = \frac{A + \frac{KK_1^M}{1+K} (A - \epsilon[T]_0) [\text{NaOH}]_0}{(\epsilon[T]_0 - A) \frac{[\text{NaOH}]_0}{1+K}} \quad (14)$$

ination with k_{-2}^H , k_2^H is then calculated. The values of K_2^H and k_2^H reported in Table III represent averages of two independent determinations each at 0.004 M and 0.01 M NaOH concentration, which gave virtually identical results.

The curves in Figure 2 have been calculated with reference to eq 11 by using k_2^H as determined from these equilibrium measurements. The fit with the experimental points is within the experimental error.

Discussion

Identification of τ_1 and τ_2 .—In Table III we have summarized the various rate coefficients which were

(13) $\epsilon_T = 0$ at the wavelengths chosen.

(14) The base concentration has to be low to avoid appreciable 1:2 complex formation.

(15) (a) V. Gold and C. H. Rochester, *J. Chem. Soc.*, 1692 (1964); (b) F. Čuta and J. Pišeký, *Chem. Listy*, **51**, 433 (1957); (c) T. Abe, *Bull. Chem. Soc. Jap.*, **33**, 41 (1960).

determined under the assumption that τ_1 is due to the formation of M or E, respectively, and that τ_2 is due to H formation in both systems.

A different set of rate coefficients can be calculated by assuming that it is the formation of H which gives rise to τ_1 , and alkoxide ion attack which leads to τ_2 . Instead of eq 8 and 9 we use eq 15 and 16, which by virtue

$$\frac{1}{\tau_1} = k_2^H[\text{HO}^-] + k_{-2}^H \quad (15)$$

$$\frac{1}{\tau_2} = \frac{k_1^R[\text{RO}^-]}{1 + K_2^H[\text{HO}^-]} + k_{-1}^R \quad (16)$$

of eq 5 and 6 are converted to eq 17 and 18. This

$$\frac{1}{\tau_1} = \frac{k_2^H}{1 + K} [\text{NaOH}]_0 + k_{-2}^H \quad (17)$$

$$\frac{1}{\tau_2} = \frac{k_1^R K [\text{NaOH}]_0}{1 + K + K_2^H [\text{NaOH}]_0} + k_{-1}^R \quad (18)$$

alternate set of rate coefficients derived by applying eq 17 and 18 to our experimental data is also included in Table III.

Finally the rate coefficients referring to equilibrium 1 in pure ethanol, methanol, and water are included for the purpose of comparison.

Let us compare the various rate coefficients in the mixed solvents with those in the pure solvents. In the "aqueous" solvent, k_1^M is decreased by a factor of about 2.9, k_1^E by a factor of about 4.3; k_{-1}^M and k_{-1}^E are almost unchanged except for k_{-1}^M at 3 M salt concentration, where it is about half as big as in methanol. Compared to pure water, k_2^H increases by a factor of about 2 in ethanol-water but decreases by approximately the same factor in methanol-water; k_{-2}^H only changes slightly in the mixed solvents. These small solvent effects are consistent with classical theory,¹⁶ the only slight discrepancy being the low value of k_2^H in methanol-water which will be discussed below.

(16) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p 345.

In contrast, the alternate set of coefficients based on the assumption that τ_1 is due to H, τ_2 to M or E formation leads to solvent effects which are difficult to rationalize. According to this interpretation a change from methanol to 22.5% aqueous methanol would reduce k_1^M by a factor of 240, k_{-1}^M by a factor of 29; the similar change from ethanol to 19% aqueous ethanol would decrease k_1^E by a factor of 22 and k_{-1}^E by a factor of 4. Finally the addition of 22.5% methanol to water would raise k_2^H by a factor of 38 and k_{-2}^H by a factor of 26, whereas the addition of 19% ethanol to water would augment k_2^H by nearly a factor of 10 and k_{-2}^H by a factor of over 3. Hence there can be no doubt that our identification of τ_1 with M and E and τ_2 with H is the only acceptable one.

Solvent Effects.—As pointed out above, the reduction of k_1^M and k_1^E in the "aqueous" solvents compared to pure methanol and ethanol, respectively, and the increase of k_2^H in ethanol-water are consistent with Ingold's¹⁶ theory. It should be emphasized at this point that the k_1^R , k_2^H , K_1^R , and K_2^H but not k_{-1}^R and k_{-2}^H depend on the values of K estimated by Murto;¹¹ if Murto's values should be in error, the rate coefficients dependent on them will contain a systematic error in addition to the standard deviations indicated in Table III.¹⁷ The magnitudes of K are such that in methanol-water the concentrations of MeO^- and HO^- are comparable to each other so that k_1^M , k_2^H , K_1^M , and K_2^H would be about equally affected by such a systematic error. In ethanol-water the equilibrium favors HO^- greatly over EtO^- so that only k_1^E and K_1^E but not k_2^H and K_2^H are very sensitive to errors in K .

Hence one should not attach too much importance to the *quantitative* aspect of the reported solvent effects on k_1^M , k_1^E , and k_2^H in methanol-water. The small reduction of k_2^H in this latter solvent compared to pure water might be partly due to such a systematic error in K , though interestingly Murto's¹⁸ rate coefficients for the comparable HO^- attack on 2,4-dinitrofluorobenzene in various methanol-water and ethanol-water mixtures which are based on the same K values show an increase in both mixtures as the alcohol content increases.

(17) There is also a probability of error at high electrolyte concentrations where K may be slightly different. For lack of more suitable data the same K has been used in our calculations, independent of electrolyte concentration.

(18) J. Murto, *Acta Chem. Scand.*, **18**, 1029 (1964).

Thus another rationalization may be in terms of a special solvation effect due to enhanced water structure in water of low alcohol content¹⁹ which is known to give rise to irregularities.^{19,20}

It is noteworthy that all the rate coefficients for leaving group departure are barely affected by the solvent changes. Thus the interesting reactivity pattern of the three bases found in the pure solvents is essentially unchanged. The abnormally low value for k_{-2}^H in relation to the equilibrium constant K_2^H when compared to k_{-1}^M and k_{-1}^E has been attributed to intramolecular hydrogen bonding to an ortho nitro group in H.¹

Salt Effect.—That the k_1^M values in the presence of 0.5 *M* and of 3 *M* NaCl come out to be virtually identical is somewhat surprising. Our working hypothesis that K is equal in both situations may be responsible for this result. k_{-1}^M (which does not depend on K for its evaluation) shows a significant salt effect which is similar to the one found for leaving group departure from the Meisenheimer complex between 2,4-dinitroanisole and MeO^- in methanol.²¹

Registry No.—1,3,5-Trinitrobenzene, 99-35-4; MeO^- , 3315-60-4; HO^- , 14280-30-9; EtO^- , 16331-64-9.

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Appendix

Derivation of Equation 14.—If we express $[M]$ and $[H]$ in eq 13 as functions of $[T]_0$ and assume $\epsilon_M \approx \epsilon_H \approx \epsilon$, we obtain eq 19. We can solve for K_2 which

$$A = \epsilon \frac{(K_1^M[\text{MeO}^-] + K_2^H[\text{HO}^-]) [T]_0}{1 + K_1^M[\text{MeO}^-] + K_2^H[\text{HO}^-]} \quad (19)$$

leads to eq 20. In combination with 5 and 6 eq 14 is

$$K_2 = \frac{A + K_1^M[\text{MeO}^-] (A - \epsilon[T]_0)}{(\epsilon[T]_0 - A) [\text{HO}^-]} \quad (20)$$

obtained.

(19) F. Franks and D. J. G. Ives, *Quart. Rev., Chem. Soc.*, **20**, 1 (1966).

(20) R. G. Bates in "Hydrogen Bonded Solvent Systems," A. K. Covington and P. Jones, Ed., Taylor and Francis Ltd., London 1968, p 49.

(21) C. F. Bernasconi, *J. Amer. Chem. Soc.*, **90**, 4982 (1968).