# Normal Coordinate Analysis of Coupled Reactions. Application to Anionic σ Complexes of 1,3,5-Trinitrobenzene with Hydroxide and Alkoxide Ions in Water, Methanol-Water, and Ethanol-Water Mixtures[1]

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Abstract: The kinetics of 1 : 2 complex formation between 1,3,5-trinitrobenzene (TNB) and the three nucleophiles HO^-, MeO^-, and EtO^- have been measured by the stopped-flow technique. In the mixed solvents the competition between RO^- and HO^- results in the formation of three different 1:2 complexes (TNB·$2RO^-$, TNB·$2HO^-$, TNB·(RO^-)(HO^-)). This should give rise to three chemical relaxation processes, but only two such processes could be observed. By applying the principles of normal coordinates to chemical reactions, it can be shown that in the not unlikely event where two of the complexes (TNB·$2RO^-$ and TNB·(RO^-)(HO^-)) dissociate with similar rates, one of the relaxation processes must indeed escape detection. A similar normal coordinate analysis demonstrates further that the reason why no cis-trans isomerism is observed in the 1 : 2 complexes may be an equality or similarity of rates of dissociation for the cis and trans isomer. A physical interpretation of the conclusions reached on the basis of mathematical relationships is offered.

Diadducts formed by the attack of a second molecule of nucleophile on Meisenheimer complexes have been reported in several systems.[3] If the nucleophile is an anion, the diadduct or 1 : 2 complex bears at least two negative charges which makes water a particularly favorable medium for its formation.[4] Thus, we expected that reactions such as eq 1 would proceed


$$RO^- = MeO^- \text{ or } EtO^-$$
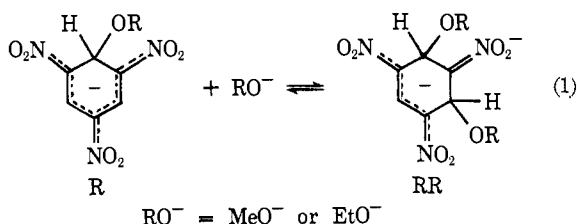
more easily to the right in alcohol-water mixtures of high-water content than in the respective pure alcohols.

In a previous paper we reported the kinetics of the 1 : 1 complex formation between 1,3,5-trinitrobenzene (TNB) and the bases HO^- and MeO^- or EtO^- in 22.5% MeOH–77.5% H_2O (v/v) or in 19% EtOH–81% H_2O (v/v), respectively.[5] It was mentioned that basic

solutions of TNB in these solvent mixtures are characterized by a total of four relaxation processes.

The two shortest relaxation times, τ_1 and τ_2, in a given solvent mixture arise from the reactions of Scheme I, where it is understood that the two com-

Scheme I
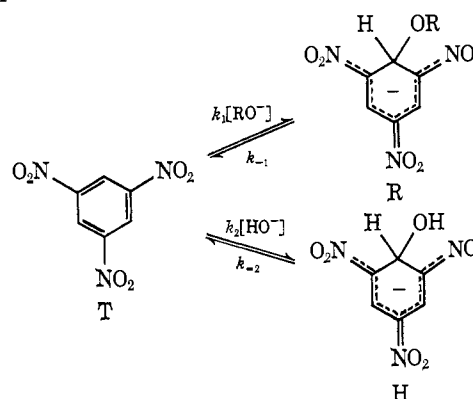
peting nucleophiles are in a mobile equilibrium according to eq 2. In both solvents the reaction with

$$ROH + HO^- \underset{}{\overset{K'}{\rightleftharpoons}} RO^- + H_2O \qquad (2)$$
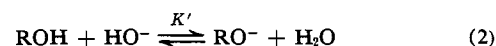
RO^- is responsible for the shortest relaxation time (τ_1).

In this paper we show that the third and fourth relaxation times, τ_3 and τ_4, are associated with the attack of a second molecule of base on R and H, respectively, to form the 1:2 complexes RR (eq 1), HH, and RH. This is shown in Scheme II.

(1) This is part XIII in the series "Intermediates in Nucleophilic Aromatic Substitution." Part XII: C. F. Bernasconi and H. S. Cross, *J. Org. Chem.*, **39**, 1054 (1974).
(2) Alfred P. Sloan Fellow, 1971–1973.
(3) For recent reviews, see (a) M. R. Crampton, *Advan. Phys. Org. Chem.*, **7**, 211 (1969); (b) M. J. Strauss, *Chem. Rev.*, **70**, 667 (1970).
(4) M. R. Crampton and M. El. Ghariani, *J. Chem. Soc. B*, 1043 (1971).
(5) C. F. Bernasconi and R. G. Bergstrom, *J. Org. Chem.*, **36**, 1325 (1971).
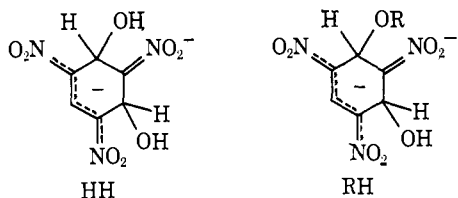
Scheme II

It is well known that the number of relaxation times in a reaction system is equal to $n - 1$, where n is the number of independent states in that system.[6] Thus, five relaxation times are expected; only four could be detected.

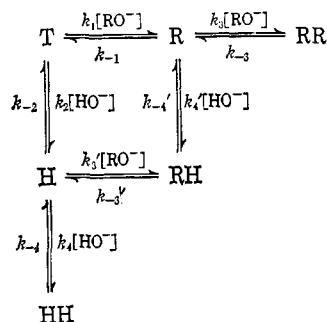An important part of this paper addresses itself to the reasons why only four relaxation processes are visible. These reasons can be understood by treating the coupled reactions of Scheme II in a similar way as one treats a multioscillator system, *i.e.*, by dealing with the "normal coordinates" of the reaction system.

Another aspect of the 1:2 complexes which recently has attracted some attention is the phenomenon of cis–trans isomerism. Cis–trans isomerism so far has only been demonstrated in the TNB–sulfite ion system.[7] There it manifests itself by an additional relaxation time[7a] as well as in the pmr spectrum.[7b,7c]

There is no *a priori* reason why RR, RH, and HH should not be present as cis and trans isomers as well. We earnestly sought an additional relaxation time in the (simpler) system TNB + HO⁻ in pure water but could not detect any. Again applying the concept of normal coordinates or "normal modes of reaction," the non-detectability of the additional relaxation time can be rationalized.

The theoretical aspects of normal coordinate analysis referring to chemical reactions have been treated by several authors,[6,8] and there has been a number of applications to experimental situations.[9]

Results

Reaction of TNB with HO⁻ in Water. The kinetic determinations were carried out in a stopped-flow

(6) M. Eigen and L. DeMaeyer, *Tech. Org. Chem.*, 8, 893 (1963).

(7) (a) C. F. Bernasconi and R. G. Bergstrom, *J. Amer. Chem. Soc.*, 95, 3603 (1973); (b) M. J. Strauss and S. P. B. Taylor, *ibid.*, 95, 3813 (1973); (c) M. R. Crampton and M. J. Willison, *J. Chem. Soc., Chem. Commun.*, 215 (1973).

(8) See, *e.g.* (a) K. Kustin, D. Shear, and D. Kleitman, *J. Theor. Biol.*, 9, 186 (1965); (b) H. J. G. Hayman, *Trans. Faraday Soc.*, 66, 1402 (1970); (c) G. G. Hammes and P. R. Schimmel, *Enzymes*, 2, 67 (1970); (d) G. Schwartz, *Rev. Mod. Phys.*, 40, 206 (1968); (f) C. F. Bernasconi, "Relaxation Kinetics," Academic Press, New York, N. Y., in preparation.

(9) See, *e.g.* (a) G. G. Hammes and J. I. Steinfeld, *J. Amer. Chem. Soc.*, 84, 4639 (1962); (b) M. Eigen in "Fifth Nobel Symposium," S. Claesson, Ed., Interscience, New York, N. Y., 1967, p 333; (c) K. Kirschner, E. Gallego, I. Schuster, and D. Goodall, *J. Mol. Biol.*, 58, 29 (1971); (d) K. Kustin and S.-T. Liu, *J. Chem. Soc., Dalton Trans.*, 278 (1973).

spectrophotometer by mixing TNB with NaOH solutions and monitoring changes in light absorption between 400 and 500 nm. The base concentration in these and in all other experiments reported in this paper was in a large excess over that of TNB, thus assuring pseudo-first-order conditions throughout.

Two well separated relaxation effects were observed. The faster process (τ_2) is associated with the previously studied[10] formation of H (eq 3), whereas the slower

$$T + HO^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} H \qquad (3)$$
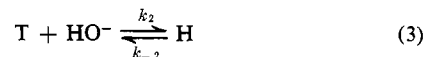
process (τ_4) can be attributed to the formation of HH (eq 4).

$$H + HO^- \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} HH \qquad (4)$$
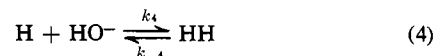
Our data are summarized in Table I. A plot of $1/\tau_2$

Table I. Reactions of HO⁻ with TNB in Water at 25°[a] (Formation of H (τ_2) and of HH (τ_4))

[NaOH]₀, M	μ,[b] M	τ_2^{-1},[c] sec⁻¹	$10^2 \times \tau_4^{-1}$,[d] sec⁻¹
0.10	2.0		8.1 ± 0.4
0.20	2.0		8.9 ± 0.5
0.30	2.0		8.9 ± 0.5
0.50	2.0		8.5 ± 0.5
0.75	2.0		9.2 ± 0.5
1.00	2.0		10.5 ± 0.6
1.50	2.0		10.5 ± 0.8
2.00	2.0		12.0 ± 1.0
0.03	3.0		6.9 ± 0.4
0.05	3.0	9.5 ± 0.2	6.7 ± 0.4
0.10	3.0	11.8 ± 0.3	7.0 ± 0.4
0.20	3.0	14.6 ± 0.4	
0.30	3.0	18.1 ± 0.4	
0.50	3.0	25.0 ± 0.5	
1.00	3.0		9.6 ± 0.4
1.50	3.0		12.8 ± 0.4
2.00	3.0		15.3 ± 0.5
2.50	3.0		18.2 ± 1.0

[a] [TNB]₀ = 10⁻⁵ M. [b] NaCl added as needed. [c] Monitored at 450 nm. [d] Monitored at 495 nm.

vs. [NaOH]₀ (not shown) is linear as called for by eq 5.

$$1/\tau_2 = k_2[\text{NaOH}]_0 + k_{-2} \qquad (5)$$

At an ionic strength of 3.0 M, we obtain $k_2 = 33.9$ M^{-1} sec⁻¹, $k_{-2} = 8.0$ sec⁻¹, and $K_2 = k_2/k_{-2} = 4.21$ M^{-1}. This compares with $k_2 = 37.5$ M^{-1} sec⁻¹, $k_{-2} = 9.8$ sec⁻¹, and $K_2 = 3.78$ M^{-1} at an ionic strength of 0.5 M;[10a] it is evident that the effect of the ionic strength is minimal as expected for the charge type of reaction 3.

Two plots of $1/\tau_4$ *vs.* [NaOH]₀ at two different ionic strengths are shown in Figure 1. The concentration dependence of $1/\tau_4$ is consistent with eq 6, valid when

$$1/\tau_4 = \frac{k_4 K_2[\text{NaOH}]_0^2}{1 + K_2[\text{NaOH}]_0} + k_{-4} \qquad (6)$$

$1/\tau_2 \gg 1/\tau_4$ which holds true throughout. At low base concentration, the dependence of $1/\tau_4$ is quadratic ($K_2[\text{NaOH}]_0 \ll 1$, $1/\tau_4 = k_4 K_2[\text{NaOH}]_0^2 + k_{-4}$) but becomes linear at high concentration ($K_2[\text{NaOH}]_0 \gg 1$, $1/\tau_4 = k_4[\text{NaOH}]_0 + k_{-4}$); k_4 was determined from the

(10) (a) C. F. Bernasconi, *J. Amer. Chem. Soc.*, 92, 4682 (1970); (b) L. H. Gan and A. R. Norris, *Can. J. Chem.*, 49, 2490 (1971).
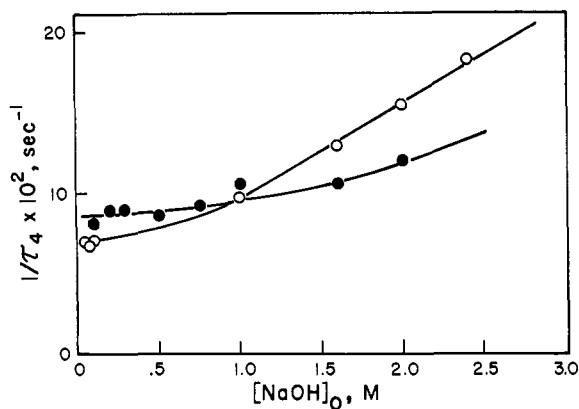
Figure 1. 1:2 complex formation between TNB and HO^- in water ($\bullet$) at $\mu = 2.0\,M$ and ($\bigcirc$) at $\mu = 3.0\,M$.

slope of the linear portion ($[NaOH]_0 \geq 1\ M$) of the plot and k_{-4} from the intercept. The various rate coefficients are summarized in Table III. There is a marked dependence on the ionic strength particularly for k_4, as expected for such a reaction.

1:2 Complexes between TNB and Base in 22.5% MeOH–77.5% H_2O and in 19% EtOH–81% H_2O. Two additional relaxation processes beyond those discussed in our earlier report[5] can be observed in the SF apparatus. The respective reciprocal relaxation times, $1/\tau_3$ and $1/\tau_4$, are summarized in Table II; $1/\tau_3$ is

Table II. Reactions in Mixed Solvents at 25° (Formation of RR, RH (τ_3), and HH (τ_4))[a]

[NaOH]$_0$, M	$10^2 \times \tau_3^{-1}$, sec^{-1}[b] 22.5% MeOH–77.5% H_2O	19% EtOH–81% H_2O	$10^2 \times \tau_4^{-1}$, sec^{-1}[c] 22.5% MeOH–77.5% H_2O	19% EtOH–81% H_2O
0.02	26 ± 5^d			
0.04	36 ± 5^d	25 ± 5^d		6.7 ± 1.3^d
0.05			10.9 ± 2.0^d	
0.10	43 ± 8^d	23 ± 5^d	12.3 ± 2.0^d	
0.20	43 ± 8^d	20 ± 5^d	11.0 ± 2.0^d	7.0 ± 1.4^d
0.30	66 ± 7	27 ± 5^d		$7.4 + 1.3^d$
0.35	82 ± 6	32 ± 5		
0.40	99 ± 6	45 ± 5		
0.45	143 ± 10	54 ± 4		
0.50		63 ± 5		8.8 ± 1.8
0.55		77 ± 5		
0.60		100 ± 6	12.2 ± 1.5	8.9 ± 1.8
0.65		125 ± 8		
0.75				9.4 ± 1.8
1.00			13.4 ± 1.5	9.3 ± 1.8
1.50			12.7 ± 1.5	8.9 ± 1.8

[a] Ionic strength maintained at 3 M by addition of NaCl as needed; $[TNB]_0 = 4 \times 10^{-5}\ M$ at the lowest base concentrations, otherwise 2×10^{-5} or $10^{-5}\ M$. [b] Monitored at 495 nm. [c] Monitored at 425 nm. [d] Calculated by computer analysis; see text.

strongly dependent on base concentration as shown by the representative plot in Figure 2, whereas $1/\tau_4$ depends very little on concentration.

It should be pointed out that at low-base concentration the separation between τ_3 and τ_4 was not very large; here the relaxation times were evaluated by a computer curve fitting procedure.[11] At the very highest base concentrations used there was some interference between τ_3 and τ_2 which necessitated a similar
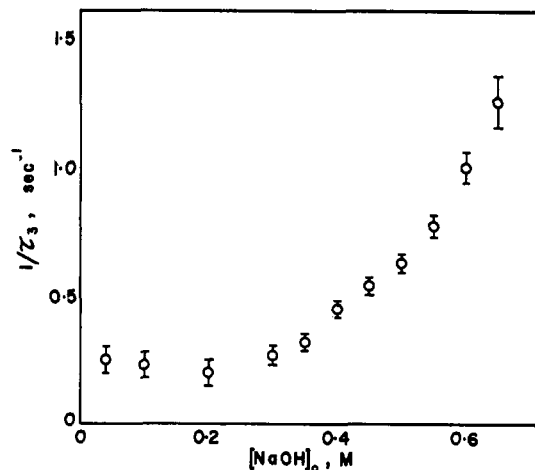
(11) See footnote 8 in ref 5.

Figure 2. $1/\tau_3$ in 19% EtOH–81% H_2O.

analysis.[11] This is why the error limits have been estimated quite generously (Table II).

Turning our attention to the data, we note at the outset that in both solvent mixtures the values for $1/\tau_4$ are very close to k_{-4} determined in pure water for the dissociation of HH. On the other hand, $1/\tau_3$ is considerably larger and increases much more steeply with base concentration than $1/\tau_4$ in pure water. We tentatively conclude that τ_4 is essentially associated with reaction 4 whereas the reactions involving alkoxide ion attack on R (eq 7) and/or H (eq 8) are responsible for τ_3.

$$R + RO^- \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} RR \tag{7}$$

$$H + RO^- \underset{k_{-3}'}{\overset{k_3'}{\rightleftharpoons}} RH \tag{8}$$

Analysis of the data based on these identifications indeed affords rate coefficients which establish that HO^- is not only a worse nucleophile than MeO^- or EtO^- but a worse leaving group as well, in agreement with earlier work.[5] On the other hand a reversed identification would lead to an opposite conclusion and would be rather difficult to rationalize.

Identification of Relaxation Times and Determination of Rate Coefficients. Of the five theoretically expected relaxation times two are accounted for by the relatively rapid formation of the two 1:1 complexes, whereas the reactions involving the 1:2 complexes should give rise to the other three. We can only observe two of these, τ_3 and τ_4. We now show which one is escaping detection; in the Discussion we will suggest possible reasons.

The analysis is greatly facilitated by the fact that the two processes of Scheme I can be treated as rapid equilibria and furthermore because under a good many conditions $1/\tau_3 \gg 1/\tau_4$ ($\tau_4/\tau_3 \geq 10$ at $[NaOH]_0 \geq 0.65\ M$ in ethanol–water, $\tau_4/\tau_3 \geq 10$ at $[NaOH]_0 \geq 0.5\ M$ in methanol–water), indicating that the equilibrations $R \rightleftharpoons RR$ and $H \rightleftharpoons RH$ are much faster than the equilibrations $H \rightleftharpoons HH$ and $R \rightleftharpoons RH$. Though τ_3 and τ_4 get closer at low-base concentrations, this is not critical for the analysis, as will become apparent.

For purposes of economy in the equations to follow, we introduce the following abbreviations referring to Scheme II.

$$K_{1R} = K_1[RO^-] = k_1[RO^-]/k_{-1}$$

$$K_{2H} = K_2[HO^-] = k_2[HO^-]/k_{-2}$$

$$k_{3R} = k_3[RO^-]; \quad k_{3R}' = k_3'[RO^-]$$

$$k_{4H} = k_4[HO^-]; \quad k_{4H}' = k_4'[HO^-]$$

We now write the rate equations which describe the approach to the final equilibrium state

$$d\Delta RR/dt = k_{3R}\Delta R - k_{-3}\Delta RR \tag{9}$$

$$d\Delta RH/dt = k_{3R}'\Delta H - k_{-3}'\Delta RH + k_{4H}'\Delta R - k_{-4}'\Delta RH \tag{10}$$

$$d\Delta HH/dt = k_{4H}\Delta H - k_{-4}\Delta HH \tag{11}$$

with $\Delta R = [R] - [R]_e$, $\Delta RR = [RR] - [RR]_e$, $\Delta RH = [RH] - [RH]_e$, $\Delta H = [H] - [H]_e$, and $\Delta HH = [HH] - [HH]_e$, where the subscript "e" refers to the final equilibrium concentrations.

Since the reactions involving HO^- as a nucleophile and as a leaving group (k_{4H}, k_{4H}', k_{-4}, k_{-4}') are much slower than the ones involving RO^- (k_{3R}, k_{3R}', k_{-3}, k_{-3}'), the process of eq 11 does not make significant progress on the time scale relevant to eq 9 and 10 and thus can be dealt with separately. Furthermore, for the same reasons the terms $k_{4H}'\Delta R$ and $k_{-4}'\Delta RH$ in eq 10 can be neglected.

On the other hand, eq 9 and 10 are strongly coupled. This is because k_{3R}' must be very similar to k_{3R} since both refer to the attack of RO^- on the 3 position of very similar monoadducts, and for the same reason k_{-3}' must be similar to k_{-3}.

The solutions to these two simultaneous differential equations are found as follows.[6] By combining the mass balance, eq 12, with the equilibrium relationships in eq 13 and 14

$$\Delta T + \Delta R + \Delta H + \Delta RR + \Delta RH = 0 \tag{12}$$

$$\Delta R = K_{1R}\Delta T \tag{13}$$

$$\Delta H = K_{2H}\Delta T \tag{14}$$

one obtains

$$\Delta T = -D(\Delta RR + \Delta RH) \tag{15}$$

with

$$D = (1 + K_{1R} + K_{2H})^{-1} \tag{16}$$

Substituting ΔR and ΔH by the expressions 13 and 14, respectively (with ΔT according to eq 15 and 16), and using the symbol x_I for ΔRR and x_{II} for ΔRH, one can write eq 9 and 10 as follows

$$dx_I/dt = a_{11}x_I + a_{12}x_{II} \tag{17}$$

$$dx_{II}/dt = a_{21}x_I + a_{22}x_{II} \tag{18}$$

with

$$a_{11} = -k_{3R}K_{1R}D - k_{-3} \tag{19}$$

$$a_{12} = -k_{3R}K_{1R}D \tag{20}$$

$$a_{21} = -k_{3R}'K_{2H}D \tag{21}$$

$$a_{22} = -k_{3R}'K_{2H}D - k_{-3}' \tag{22}$$

The solutions to the general eq 17 and 18 are the sums of two exponentials of the general form

$$x_I = A_{11}e^{-t/\tau_I} + A_{12}e^{-t/\tau_{II}} \tag{23}$$

$$x_{II} = A_{21}e^{-t/\tau_I} + A_{22}e^{-t/\tau_{II}} \tag{24}$$

The relaxation times, τ_I and τ_{II}, are found by solving the secular determinant of the coefficients a_{ij}[6] which leads to a quadratic equation with the two roots given by eq 25.

$$1/\tau_I, 1/\tau_{II} = -\frac{a_{11} + a_{22}}{2} \mp \sqrt{\left(\frac{a_{11} + a_{22}}{2}\right)^2 + a_{12}a_{21} - a_{11}a_{22}} \tag{25}$$

If we now assume k_{-3}' and k_{-3} not only to be similar but equal in magnitude, the analytical expressions for $1/\tau_I$ and $1/\tau_{II}$ become very simple and are given by eq 26 and 27. With the additional assumption $k_3 =$

$$1/\tau_I = (k_{3R}K_{1R} + k_{3R}'K_{2H})D + k_{-3} \tag{26}$$

$$1/\tau_{II} = k_{-3} \tag{27}$$

k_3', eq 26 can be further simplified; after replacing the various short symbols and expressing $[RO^-]$ in terms of $[NaOH]_0$[12] we obtain eq 28.

$$1/\tau_I = \frac{K(KK_1 + K_2)k_3[NaOH]_0^2}{(1 + K)(1 + K + (KK_1 + K_2)[NaOH]_0)} + k_{-3} \tag{28}$$

Among the experimental relaxation times, only the concentration dependence of $1/\tau_3$ is consistent with eq 28, and thus we identify τ_3 with τ_I.

The constants k_3 and k_{-3} were determined as follows. In ethanol-water we have $(KK_1 + K_2)[NaOH]_0 \geq 10(1 + K)$ at $[NaOH]_0 \geq 0.45$ so that eq 28 can be reduced to eq 29. Thus, k_3 is found from the slope of

$$1/\tau_I = 1/\tau_3 = \frac{K}{1 + K}k_3[NaOH]_0 + k_{-3} \tag{29}$$

the plot of $1/\tau_3$ vs. $[NaOH]_0$ at $[NaOH]_0 \geq 0.45$ M; k_{-3} is simply the ordinate intercept of the same plot.

In methanol-water eq 29 becomes only valid at $[NaOH]_0 \geq 1.3$ M, whereas a strong interference with τ_2 precluded measurements of τ_3 at $[NaOH]_0 > 0.45$ M. Hence, k_3 was chosen as to give the best fit between the experimental data and eq 28. No value of k_3 was found which would give a perfect fit with all data points; inasmuch as the data between 0.3 and 0.45 M are considered the most reliable (least interference with either τ_4 or τ_2), we chose a k_3 value which gave the best fit with these points.

Let us now turn our attention to τ_{II}. Equation 27 predicts $1/\tau_{II}$ to be independent of base concentration and to have a constant value equal to k_{-3}. We note that the experimental $1/\tau_4$ is, within the limits of error, almost concentration independent. However, the magnitude of $1/\tau_4$ is considerably below that required for $1/\tau_{II}$, and thus we cannot identify τ_{II} with τ_4. We conclude that τ_{II} (to which we later will refer to as τ_3') is in-

(12) $[RO^-] = [NaOH]_0K/(1 + K)$ and $[HO^-] = [NaOH]_0/(1 + K)$ where $K = [RO^-]/[HO^-] = K'\chi_{ROH}/\chi_{H_2O}$; χ_{ROH} and χ_{H_2O} are mole fractions. For K', defined by eq 2, we used Murto's[13] values: $K' = 4.5$ in methanol-water and $K' = 0.65$ in ethanol-water. Thus, $K = 0.58$ in 22.5% MeOH-77.5% H_2O (v/v), $K = 0.047$ in 19% EtOH-81% H_2O.

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

Table III. Summary of Results

	H₂O		22.5% MeOH-77.5% H₂O	19% EtOH-81% H₂O
	$\mu = 2\ M$	$\mu = 3\ M$	$\mu = 3\ M$	$\mu = 3\ M$
k_1, M^{-1} sec^{-1}			2460[a]	7700[a,b]
k_{-1}, sec^{-1}			134[a]	32[a,b]
$K_1 = k_1/k_{-1}$, M^{-1}			18.3[a]	241[a,b]
k_2, M^{-1} sec^{-1}		33.9 ± 1.0	8.8[a]	70.2[a,b]
k_{-2}, sec^{-1}		8.0 ± 0.3	8.5[a]	6.8[a,b]
$K_2 = k_2/k_{-2}$, M^{-1}		4.21 ± 0.25	1.03[a]	10.3[a,b]
k_3, M^{-1} sec^{-1}			7.5 ± 2	45 ± 6
k_{-3}, sec^{-1}			0.20 ± 0.05	0.20 ± 0.05
$K_3 = k_3/k_{-3}$, M^{-1}			37 ± 16	225 ± 100
k_4, M^{-1} sec^{-1}	2.2 ± 0.4 × 10⁻²	5.7 ± 0.5 × 10⁻²		
k_{-4}, sec^{-1}	8.2 ± 1.0 × 10⁻²	6.8 ± 0.8 × 10⁻²	11 ± 3 × 10⁻²	7.0 ± 1.5 × 10⁻²
$K_4 = k_4/k_{-4}$, M^{-1}	0.27 ± 0.008	0.84 ± 0.17		

[a] Reference 5. [b] $\mu = 0.5\ M$.

visible under our experimental conditions and that τ_4 is associated with reaction 4 (rate eq 11).

An analytical expression for $1/\tau_4$ can easily be found by treating all other reactions in Scheme II as rapid pre-equilibria ($K_3 = k_3/k_{-3}$, $K_3' = k_3'/k_{-3}'$), which allows eq 11 to be written as

$$d\Delta\text{HH}/dt = -(1/\tau_4)\Delta\text{HH} \tag{30}$$

with

$$1/\tau_4 = \frac{K_2 k_4 [\text{NaOH}]_0{}^2}{(1+K)^2 + (1+K)(KK_1 + K_2)[\text{NaOH}]_0 + K(KK_1K_3 + K_2K_3')[\text{NaOH}]_0{}^2} + k_{-4} \tag{31}$$

Since one would expect k_4 to be no higher than in the more polar purely aqueous solvent, it becomes apparent that the first term in eq 31 is quite small compared to k_{-4} at all base concentrations, and thus eq 31 simplifies to eq 32. This explains the virtually negligible con-

$$1/\tau_4 \approx k_{-4} \tag{32}$$

centration dependence of $1/\tau_4$ in both solvent mixtures (Table II).[14]

Discussion

Rate and Equilibrium Constants of the Various Complexes. All kinetic parameters determined in this study along with those relating to the 1:1 complexes are summarized in Table III. Because of several problems indicated earlier, the error limits in our parameters are relatively high. An additional uncertainty in the k_3 values arises from the fact that they depend on the value of K' which is only available at a lower ionic strength[13] than used in this study.

Nevertheless, several features clearly emerge from our results. (1) Just as for the 1:1 complexes, the order of stability and of the rate of formation of the 1:2 complexes is EtO⁻ > MeO⁻ ≫ HO⁻. On the other hand, the rates of dissociation do not differ greatly among the three diadducts of TNB with EtO⁻, MeO⁻, and HO⁻.

(14) It should be recalled at this point that the separation between τ_3 and τ_4 amounts to a factor of 10 or greater only at relatively high base concentrations. Thus, eq 28 and 31 are strictly valid only at these higher concentrations. However, this is of no consequence to evaluation of the respective rate coefficients; k_3 is evaluated at high-base concentrations where the equations are in fact valid, whereas k_{-3} and k_{-4} correspond to $1/\tau_3$ and $1/\tau_4$, respectively, at [NaOH]₀ = 0, where the relations $1/\tau_3 = k_{-3}$ and $1/\tau_4 = k_{-4}$ hold regardless of the separation between the two relaxation times.

(2) Formation of the diadducts is very much slower than that of the monoadducts with all three nucleophiles. This confirms similar findings in the TNB–sulfite ion system[7a] and appears to be a general phenomenon. That this is mainly due to a transition state effect can be particularly well illustrated with the ethoxide complexes, since at the ionic strength chosen the stability constants K_1 and K_3 are about the same, but $k_1/k_3 \approx 171$ and $k_{-1}/k_{-3} \approx 214$.

Normal Coordinate Analysis. I. No Cis–Trans Isomerism for HH in Aqueous Solution? In the TNB·SO₃²⁻ system three relaxation effects, attributed to the formation of a 1:1 complex and of two isomeric (cis and trans) 1:2 complexes, were observed.[7a] The isomeric diadducts have very similar stability constants, but one of the isomers (presumably the cis) forms and dissociates about 100 times more slowly than the other. This was rationalized by an electrostatic repulsion between the two sulfite moieties, visualized to be mainly effective in the transition state of the cis isomer.

No evidence for a third relaxation effect was found in the TNB·HO⁻ system. We were also unsuccessful in obtaining pmr evidence for cis–trans isomerism.[7b,c] One possible interpretation is that one of the isomers does not form at all or to such a small extent as to remain undetected. This is not an attractive explanation. Quite to the contrary, since the special effects of the sulfite system cannot operate here, one would expect the cis and trans isomers not only to be of about equal stability but also to form and dissociate at about the same rates.

We show now that if in Scheme III (the superscripts

Scheme III
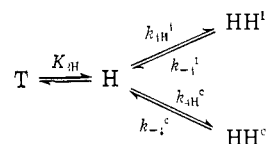
"c" and "t" refer to cis and trans) the cis and trans isomers dissociate at the same rate, $k_{-4}^c = k_{-4}^t = k_{-4}$, one of the two slow relaxation times would in fact not be observable in a SF experiment.

Let us first derive the expressions for the two slow relaxation times, $1/\tau_4$ and $1/\tau_4'$, based on Scheme III where equilibration between T and H is rapid. For our pair of coupled reactions we obtain again two

equations of the general form of eq 17 and 18 with

$$x_I = \Delta HH^t \tag{33}$$

$$x_{II} = \Delta HH^c \tag{34}$$

$$a_{11} = -k_{4H}{}^t K_{2H}/(1 + K_{2H}) - k_{-4} \tag{35}$$

$$a_{12} = -k_{4H}{}^t K_{2H}/(1 + K_{2H}) \tag{36}$$

$$a_{21} = -k_{4H}{}^c K_{2H}/(1 + K_{2H}) \tag{37}$$

$$a_{22} = -k_{4H}{}^c K_{2H}/(1 + K_{2H}) - k_{-4} \tag{38}$$

Equation 25 combined with eq 35–38 affords

$$1/\tau_I = 1/\tau_4 = \frac{K_2(k_4{}^t + k_4{}^c)[\text{NaOH}]_0{}^2}{1 + K_2[\text{NaOH}]_0} + k_{-4} \tag{39}$$

$$1/\tau_{II} = 1/\tau_4' = k_{-4} \tag{40}$$

Note that eq 39 is identical with eq 6 if we substitute $k_4 = k_4{}^t + k_4{}^c$. Evidently, τ_4' is the missing relaxation time. The reason why it is missing is that the "normal coordinate,"[6,8] or "normal concentration variable," y_4', associated with τ_4' is equal to zero in a SF experiment, as is shown now.

The normal coordinates, defined by eq 41, can be

$$dy_i/dt = -(1/\tau_i)y_i; \quad y_i = y_{i0}e^{-t/\tau_i} \tag{41}$$

considered as the principal axes of the system and are found by the an affine coordinate transformation.[6,8] They are a linear combination of the true concentration variables, x_i, eq 42. The mathematical operations

$$y_i = \sum m_{ij}x_i \tag{42}$$

for transforming a set of x_i's into a set of y_i's, i.e., to find the m_{ij}'s, involve some matrix algebra and have been described elsewhere.[6,8]

For a system of two coupled reactions (eq 17 and 18) the two normal concentration variables are given by eq 43 and 44. Substituting y_4 for y_I, y_4' for y_{II}, τ_4 for τ_I,

$$y_I = x_I - \frac{a_{11} + 1/\tau_I}{a_{21}} x_{II} \tag{43}$$

$$y_{II} = -\frac{a_{22} + 1/\tau_{II}}{a_{12}} x_I + x_{II} \tag{44}$$

τ_4' for τ_{II}, and taking into account eq 33–40, we obtain

$$y_4 = \Delta HH^t + \Delta HH^c \tag{45}$$

$$y_4' = -(k_4{}^c/k_4{}^t)\Delta HH^t + \Delta HH^c \tag{46}$$

According to eq 41 a relaxation effect will escape detection when $y_{i0} = 0$ ("zero amplitude").

In our SF experiment we have at $t = 0$, $[\text{HH}^t] = [\text{HH}^c] = 0$, and thus $\Delta HH_0{}^t = -[\text{HH}^t]_e$ and $\Delta HH_0{}^c = -[\text{HH}^c]_e$. From the equilibrium relationship in eq 47 it follows that indeed $y_{40}' = 0$ (eq 48).

$$\frac{\Delta HH_0{}^c}{\Delta HH_0{}^t} = \frac{[\text{HH}^c]_e}{[\text{HH}^t]_e} = \frac{K_4{}^c}{K_4{}^t} = \frac{k_4{}^c}{k_4{}^t} \tag{47}$$

$$y_{40}' = -\frac{k_4{}^c}{k_4{}^t} \Delta HH_0{}^t + \Delta HH_0{}^c = 0 \tag{48}$$

The physical meaning of this result is the following. The normal mode of the system associated with y_4 is simply the equilibration between H and the sum of HH^t and HH^c, and y_4 is a measure of the progress of this equilibration. This process is independent of whether

HH^c and HH^t are or are not in equilibrium with each other. Hence the equilibration between HH^c and HH^t is in turn independent of the equilibration between H and the sum of HH^t and HH^c. It must therefore correspond to the second normal mode, associated with y_4'; thus, y_4' is a measure of the progress of the equilibration between HH^c and HH^t. Hence, the physical meaning of the $y_4' = 0$ is that when $k_{-4}{}^c = k_{-4}{}^t$ nucleophilic attack on H yields HH^c and HH^t in a ratio which *is equal to their final equilibrium ratio from the very beginning; i.e., equilibration along the second normal mode is not necessary.*

Our conclusion is that despite the failure of kinetic or pmr investigations to provide any positive evidence of cis–trans isomerism in the diadduct between TNB and HO⁻, such isomerism cannot be ruled out.

II. Why is τ_3' Missing in the Mixed Solvents? There are two possible interpretations. The first is based on reasoning very similar to the one used in the cis–trans isomer problem discussed above. From eq 43 and 44 we obtain, after appropriate substitutions (y_3 for y_I, y_3' for y_{II}, τ_3 for τ_I, τ_3' for τ_{II}, ΔRR for x_I, ΔRH for x_{II}, and eq 19–22, 26, 27), the following expressions for the normal concentration variables

$$y_3 = \Delta RR + \Delta RH \tag{49}$$

$$y_3' = -(K_{2H}k_3'/K_{1R}k_3)\Delta RR + \Delta RH \tag{50}$$

Again we can show that in a SF experiment the effect associated with τ_3' is invisible because $y_{30}' = 0$, a consequence of the fact that RR and RH form directly in the right ratio and a further equilibration between the two is redundant.

This interpretation hinges on the assumption that $k_{-3}' = k_{-3}$; if this assumption is not valid, e.g., because of a statistical factor of 2 favoring k_{-3}, one could still rationalize the absence of τ_3' as follows.

At very low-base concentrations ($k_{3R}K_{1R}D \ll k_{-3}$, $k_{3R}'K_{2H}D \ll k_{-3}'$) the relaxation times are given by

$$1/\tau_I = 1/\tau_3 = k_{3R}K_{1R}D + k_{-3} \approx k_{-3} \tag{51}$$

$$1/\tau_{II} = 1/\tau_3' = k_{3R}'K_{2H}D + k_{-3}' \approx k_{-3}' \tag{52}$$

with the normal concentration variables

$$y_3 = \Delta RR \tag{53}$$

$$y_3' = \Delta RH \tag{54}$$

Even if k_{-3}' and k_{-3} are not identical, they are expected to be close. Since τ_3 and τ_3' are dominated by k_{-3} and k_{-3}', respectively, the two relaxation times will not be well separated. But this is precisely the concentration range where τ_3 and τ_4 are also rather close and where τ_3 and τ_4 had to be evaluated by computer fitting of the relaxation curves. Though the fit was excellent assuming the relaxation curves were the result of superposition of two exponentials only (τ_3 and τ_4), we cannot exclude that the curves are perhaps a superposition of three (or more) exponentials (τ_3, τ_3', τ_4) and that τ_3' might be there after all.

At high-base concentration, on the other hand, there can be no question that τ_3' is indeed missing since τ_3 and τ_4 are well separated and the relaxation curves are clean exponentials. One can show, however, that τ_3' would become invisible if the extinction coefficients of the two diadducts were equal, i.e., $\epsilon_{RR} = \epsilon_{RH}$; in view

of the great similarity between RR and RH, this could well be the case although in the TNB·SO$_3{}^{2-}$ system the spectra of the cis and the trans isomer differ somewhat from each other.[7a]

At a base concentration where $k_{3R}K_{1R}D \gg k_{-3}$ and $k_{3R}'K_{2H}D \gg k_{-3}'$, eq 25 simplifies to eq 55 and 56,

$$1/\tau_I = 1/\tau_3 = k_{3R}K_{1R}D + k_{3R}'K_{2H}D \qquad (55)$$

$$1/\tau_{II} = 1/\tau_3' = \frac{k_{3R}k_{-3}'K_{1R} + k_{3R}'k_{-3}K_{2H}}{k_{3R}K_{1R} + k_{3R}'K_{2H}} \qquad (56)$$

whereas the normal coordinates are given by eq 49 and 50.

The change in OD associated with τ_3' can be expressed by eq 57. Taking into consideration eq 13–15, we can write eq 58.

$$\Delta OD = \{\epsilon_T \Delta T + \epsilon_R \Delta R + \epsilon_H \Delta H + \\ \epsilon_{RR} \Delta RR + \epsilon_{RH} \Delta RH\}l \qquad (57)$$

$$\Delta OD = \{-D(\epsilon_T + \epsilon_R K_{1R} + \epsilon_H K_{2H})(\Delta RR + \\ \Delta RH) + \epsilon_{R2} \Delta RR + \epsilon_{RH} \Delta RH\}l \qquad (58)$$

Since at high-base concentration we have $1/\tau_3 \gg 1/\tau_3'$, equilibration along the first normal mode is essentially complete ($t \gg \tau_3$ and thus $\Delta RR + \Delta RH = y_3 = y_{30}e^{-t/\tau_3} \approx 0$) before equilibration along the second normal mode has made any progress. As a consequence eq 58 reduces to

$$\Delta OD = (\epsilon_{RR} - \epsilon_{RH})l\Delta RR \qquad (59)$$

If $\epsilon_{RR} = \epsilon_{RH}$, $\Delta OD = 0$.

The physical meaning of this result is that at high-base concentrations practically all TNB is rapidly converted to either RR or RH and the process associated with τ_3' is merely a redistribution between RR and RH which remains invisible if $\epsilon_{RR} = \epsilon_{RH}$. Note that this applies only at high but not at low-base concentrations; i.e., at low-base concentrations τ_3' would not vanish even if $\epsilon_{RR} = \epsilon_{RH}$.

We believe the truth lies somewhere between these two interpretations; i.e., k_{-3} and k_{-3}' are probably very similar but not identical. This would make y_{30}' very small but not quite zero. But since ϵ_{RR} and ϵ_{RH} are also similar though probably not identical, the

ΔOD associated with τ_3' must be quite small at high-base concentrations, regardless of the size of y_{30}'. Both factors combined lead to such a small relaxation amplitude that it escapes detection.

III. Cis–Trans Isomerism in the Mixed Solvents. If we were to assume that each 1:2 complex forms as a mixture of cis and trans isomers, the entire reaction scheme would include nine states (Scheme IV) and the

Scheme IV
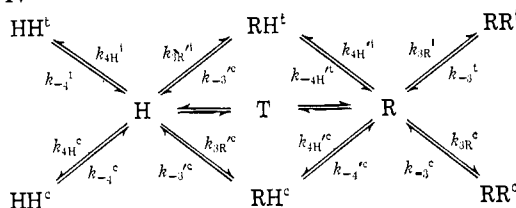
theoretical number of relaxation times should be eight. But since in aqueous solution it appears that $k_{-4}{}^c = k_{-4}{}^t$ it is not unreasonable to assume $k_{-3}{}^c = k_{-3}{}^t$, $k_{-3}'^c = k_{-3}'^t$, $k_{-4}{}^c = k_{-4}'^t$, and $k_{-4}'^c = k_{-4}'^t$ in the mixed solvents. It can easily be shown that under these conditions the three additional relaxation times arising from the cis–trans isomerism would be invisible in the SF experiment because for each diadduct the cis and trans isomers form directly in their equilibrium ratio and thus the three additional normal coordinates are all zero.

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. Sodium hydroxide solutions were prepared from Titrisol (Merck).

Kinetic Measurements. They were made on a Durrum stopped-flow spectrophotometer. Absorption changes were monitored between 400 and 500 nm. The wavelength for any given run was chosen empirically such as to assure a maximum amplitude of the particular relaxation process under study and a minimum amplitude of the other processes closest to it.

Calculations on Quinonoid Compounds. II. Ground-State Properties of Quinones

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Abstract: A series of 36 quinones has been investigated by SCF molecular orbital calculations. The theoretically derived results have been correlated with available data on heats of atomization, structure, dipole moments, carbonyl stretching frequencies, and electrochemical behavior. With the exception of the carbonyl stretching frequency data, the agreement was good.

A prior paper in this series has described the application of a π-electron SCF–LCAO molecular orbital technique to the calculation of energies, structures,

and related properties for quinonoid hydrocarbons.[2] It would be valuable if similar calculations were made

(1) NDEA Fellow, 1971–present.

(2) G. J. Gleicher, D. D. Newkirk, and J. C. Arnold, *J. Amer. Chem. Soc.*, 95, 2526 (1973).