mixture was refluxed for 2 h and hydrolyzed with water. The solvent was evaporated and the residue was distilled under reduced pressure (1 mm) to give 1.29 g (99% yield) of **24**. VPC analysis of the distillate showed a single peak: mp 225~226 °C after recrystalization from ethanol-benzene (25:8); mass spectrum, *m/e* 610 (M^+); ^1H NMR δ 0.24 (54 H, s, Me_3Si), 0.37 (12 H, s, Me_2Si). Anal. Calcd for $C_{22}H_{66}Si_{10}$: C, 43.20; H, 10.88. Found: C, 42.98; H, 11.27.

Isomerization of Tetracosamethyldodecasilane (25). A mixture of 1.06 g (1.46 mmol) of **25** and 0.09 g (0.68 mmol) of anhydrous aluminum chloride in 10 mL of benzene was refluxed for 5 h. After addition of 10 mL of 1.5 M methyllithium-ether solution to the mixture, the reaction mixture was refluxed for 2 h. The mixture was hydrolyzed with water as usual way. The solvent was evaporated and the residue was distilled under reduced pressure to give 1.00 g (95% yield) of crystals of **26**: mp 236 °C after recrystalization from ethanol-benzene (25:8); mass spectrum, *m/e* 726 (M^+); ^1H NMR δ 0.37 (54 H, s, Me_3Si), 0.48 (12 H, s, Me_2Si), 0.54 (12 H, s, Me_2Si). Anal. Calcd for $C_{26}H_{78}Si_{12}$: C, 42.90; H, 10.80. Found: 42.62; H, 10.92.

Acknowledgments. The cost of this research was defrayed by a Grant-in-Aid for Scientific Research by the Ministry of Education and Toray Science and Technology Grant to which our thanks are due. We also express our appreciation to Toshiba Silicone Co., Ltd. and Shin-etsu Chemical Co., Ltd. for a gift of organochlorosilanes.

Nucleophilic Addition to Olefins. 5.[1] Reaction of 1,1-Dinitro-2,2-diphenylethylene with Water and Hydroxide Ion in 50% Me_2SO–50% Water. Complete Kinetic Analysis of Hydrolytic Cleavage of the C=C Double Bond in Acidic and Basic Solution

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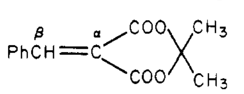
Received December 3, 1980

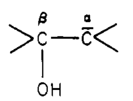
Abstract: Hydrolysis of 1,1-dinitro-2,2-diphenylethylene (**2**) to form benzophenone and dinitromethane (or its anion) was studied in 50% Me_2SO–50% H_2O and also in 50% Me_2SO–50% D_2O. Experiments were conducted over a pH range from ~1 to ~16. The data can be interpreted by Scheme I. Solvent isotope effects, observation of general acid and general base catalysis, and structure–reactivity relationships were used to assign rate-limiting steps under various conditions and to probe into the mechanistic details of the various steps. The major conclusions are the following. (1) The equilibrium constants for OH^- and water addition to **2** to form T_{OH}^- (Scheme I) are of comparable magnitude to those for the corresponding reactions of benzylidene Meldrum's acid (**1**), but the *rate* constants are much lower for **2** than for **1**. This indicates a higher intrinsic kinetic barrier for the nitro-activated olefin and fits into a previously reported pattern, according to which activating substituents that are most effective in delocalizing negative charge lead to the highest kinetic barrier. (2) Carbon protonation of T_{OH}^- follows an Eigen curve similar to that for 1,1-dinitroethane anion (Figure 7) but which is displaced upward by nearly 1 log unit. This indicates a higher intrinsic protonation rate because of a smaller charge delocalization in T_{OH}^- owing to an enhanced steric hindrance to coplanarity of the nitro groups in T_{OH}^-. (3) Intramolecular proton transfer from the OH group to the carbanionic site in T_{OH}^- (k_i in Scheme I) is insignificant, which is in contrast to the behavior of the addition complex between **2** and morpholine. (4) The base-catalyzed breakdown of T_{OH}^0 into benzophenone and dinitromethane anion occurs by rate-limiting oxygen deprotonation (k_3^B, k_3^{OH} in Scheme I), which implies that k_4 for $CH(NO_2)_2^-$ departure from T_{OH}^{0-} is $\gg 2 \times 10^9\ s^{-1}$, a remarkably high rate for a carbanionic leaving group. The water-catalyzed breakdown of T_{OH}^0 proceeds by a different mechanism, which is most likely concerted, with a transition state as **8** or possibly **9**. (5) The acid-catalyzed breakdown of T_{OH}^{2-} occurs by rate-limiting carbon protonation (k_6^{BH} in Scheme I), but the water-catalyzed breakdown follows a different mechanism. Various possibilities are discussed, and a slight preference is given to a preassociation mechanism (Scheme III).

Recently we reported a study of the hydrolysis of benzylidene Meldrum's acid (**1**) which leads to a cleavage of the C=C double

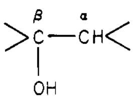


1

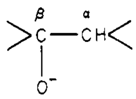
bond and the formation of benzaldehyde and Meldrum's acid.[2] The reaction involves four consecutive steps: (1) OH^- or water attack on the β carbon to form an addition complex T_{OH}^-, (2) protonation of the α carbon of T_{OH}^- to form T_{OH}^0, (3) deprotonation of the OH group of T_{OH}^0 to form the tetrahedral intermediate T_{OH}^{0-}, (4) breakdown of T_{OH}^{0-} into benzaldehyde and the anion of Meldrum's acid. Rate constants for the first three



T_{OH}^-



T_{OH}^0



T_{OH}^{0-}

steps could be determined, while that for the last step was estimated to be $\geq 10^{10}\ s^{-1}$. This latter value is remarkably high for the departure of a carbanionic leaving group from a tetrahedral intermediate but was accounted for by the low basicity of the carbanion[2] (pK_a value of Meldrum's acid is 4.83).

It seemed of interest to investigate other cases in order to ascertain whether this high rate of carbanion departure is particular to **1** or whether it is a general phenomenon.[3] A system

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[1] Part 4: Bernasconi, C. F.; Fornarini, S. *J. Am. Chem. Soc.* **1980**, *102*, 5329.

[2] Bernasconi, C. F.; Leonarduzzi, G. D. *J. Am. Chem. Soc.* **1980**, *102*, 1361.

[3] Jencks has also mentioned that the expulsion of weakly carbanionic leaving groups from similar intermediates is very fast; Jencks, W. P. *Acc. Chem. Res.* **1976**, *9*, 425.

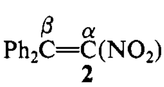
0002-7863/81/1503-4850$01.25/0

Table I. Hydrolysis of 1,1-Dinitro-2,2-diphenylethylene at High Base Concentrations in 50% Me_2SO–50% H_2O and in 50% Me_2SO–50% D_2O

[KOH] or [KOD], M	10^2k_{obsd} (H_2O), s^{-1}	10^2k_{obsd} (D_2O), s^{-1}	$k_{obsd}(H_2O)/k_{obsd}(D_2O)$
0.15	2.01	3.64	0.55
0.25	3.80	6.44	0.59
0.50	8.24	10.7	0.77
0.70[a]	14.9	17.5	0.85

[a] Ionic strength, 0.7 M.

with a carbanionic leaving group of comparably low basicity is 1,1-dinitro-2,2-diphenylethylene (**2**); the pK_a value of dinitro-



$$\overset{\beta}{Ph_2C}=\overset{\alpha}{C}(NO_2)_2$$

2

methane is 3.57.[4] This paper reports a study of the hydrolysis of **2**. Dinitromethane anion departure from T_{OH}^{0-} is shown to be indeed very fast. The hydrolysis of **2** shows additional features, not observed with **1**, which are also quite remarkable.

Results

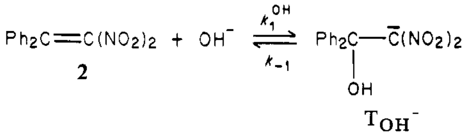
All experiments reported were conducted in 50% Me_2SO–50% water (v/v) or 50% Me_2SO–50% D_2O (v/v) at 20 °C, at a constant ionic strength of 0.5 M maintained by KCl, except for a few experiments noted in Table I. All kinetic runs were performed under pseudo-first-order conditions.

Hydrolysis in Basic Solution. The rate of hydrolysis of 1,1-dinitro-2,2-diphenylethylene (**2**) was measured in a pH range from 7.46 to ~16 (0.7 M KOH). The reaction was monitored at 363 nm (λ_{max} of $CH(NO_2)_2^-$) in a conventional spectrophotometer up to pH 14.36 and in a stopped-flow spectrophotometer at higher pH. The experiments were carried out in dilute phosphate buffers at pH 7.46–8.75, in dilute phenol buffers at pH 10.38–12.65, and in KOH solutions at pH ≥13.3. No buffer catalysis was observed in the phosphate and phenol buffers, but data reported below show catalysis by 2,4,6-trimethylphenol at pH 12.95–14.36.

The bulk of our results is summarized in Table S1,[5] and Figure 1 shows the pH dependence of the pseudo-first-order rate constant k_{obsd} (open circles). k_{obsd} was also measured in 50% Me_2SO–50% D_2O in phenol buffers and in KOD solutions. The data are included in Table S1 and Figure 1 (filled circles). In calculating pD values we have used the relationship pD = pH + 0.40,[6] where pH is the value obtained from the pH meter; the approximate validity of this relationship in the mixed solvent could be confirmed in HCl solution and is assumed to hold over the entire pH range. In plotting the data in Figure 1 the pD scale has been displaced from the pH scale in such a way that a given OH^- concentration on the pH profile corresponds to the same OD^- concentration on the pD profile.[7]

A few additional data at high KOH (KOD) concentrations are reported in Table I. The data in Figure 1 and Table I show that there is a kinetic solvent isotope effect of about 5.5 in the pH independent region which changes into an inverse isotope effect of about 0.6 to 0.8 at high base concentration.

Formation of T_{OH}^-. At pH ≥12.5 a second kinetic process is observed that is faster than the hydrolysis reaction. It refers to the formation of T_{OH}^- according to eq 1. T_{OH}^- was identified



$$\underset{\mathbf{2}}{Ph_2C{=}C(NO_2)_2} + OH^- \underset{k_{-1}}{\overset{k_1^{OH}}{\rightleftharpoons}} \underset{T_{OH}^-}{Ph_2\underset{OH}{C}{-}\bar{C}(NO_2)_2} \qquad (1)$$

T_{OH}^-

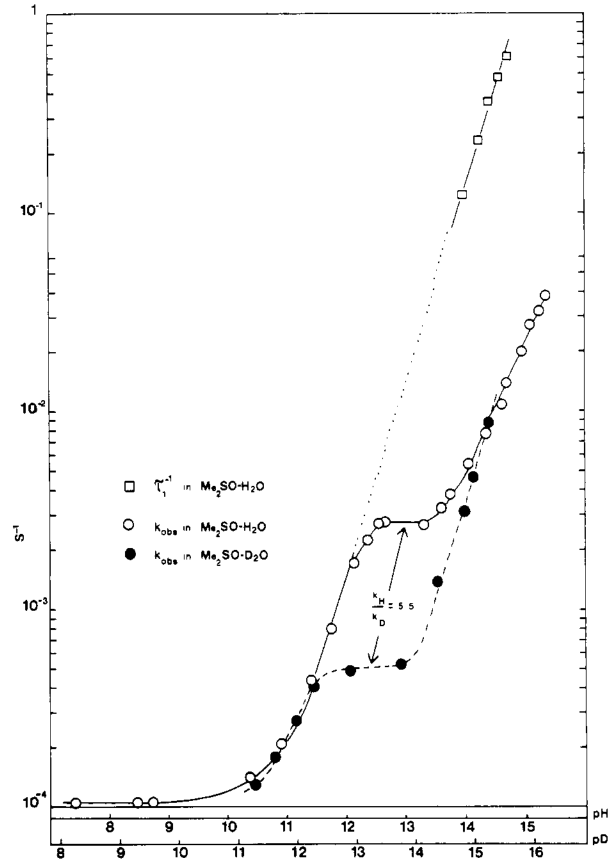


Figure 1. Rate–pH profiles. k_{obs} refers to overall hydrolysis reaction; τ_1^{-1} refers to OH^- addition to **2** (eq 1 and 2).

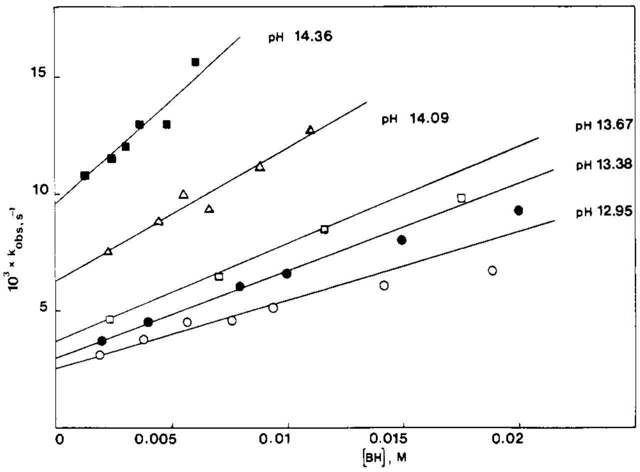


Figure 2. Catalysis of hydrolysis by 2,4,6-trimethylphenol buffers; BH = 2,4,6-trimethylphenol.

by its absorption spectrum (λ_{max} 380 nm, ϵ 6100), which is similar to that of addition complexes of **2** with other nucleophiles.[8]

The reciprocal relaxation time τ_1^{-1} (pseudo-first-order rate constant for equilibrium approach), which is given by eq 2, was

$$\tau_1^{-1} = k_1^{OH}[OH^-] + k_{-1} \qquad (2)$$

measured in the stopped-flow apparatus at 380 nm as a function of KOH concentration. The results are summarized in Table S2[5] and are also included in Figure 1 (squares). One obtains k_1 = 12.2 ± 0.6 M^{-1} s^{-1} by equating τ_1^{-1} with $k_1^{OH}[OH^-]$; k_{-1} is too small to be measured by this method but was obtained indirectly as described below.

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[4] Pearson, R. G.; Dillon, R. L. *J. Am. Chem. Soc.* **1953**, *75*, 2439.

[5] See paragraph concerning supplementary material at the end of this paper.

[6] Glascoe, P. K.; Long, F. A. *J. Phys. Chem.* **1960**, *64*, 188.

[7] pK_w = 15.93 in 50% Me_2SO–50% H_2O, pK_w = 16.78 in 50% Me_2SO–50% D_2O, determined as pH (pD) + 2.00 for a 0.01 M KOH (KOD) solution.

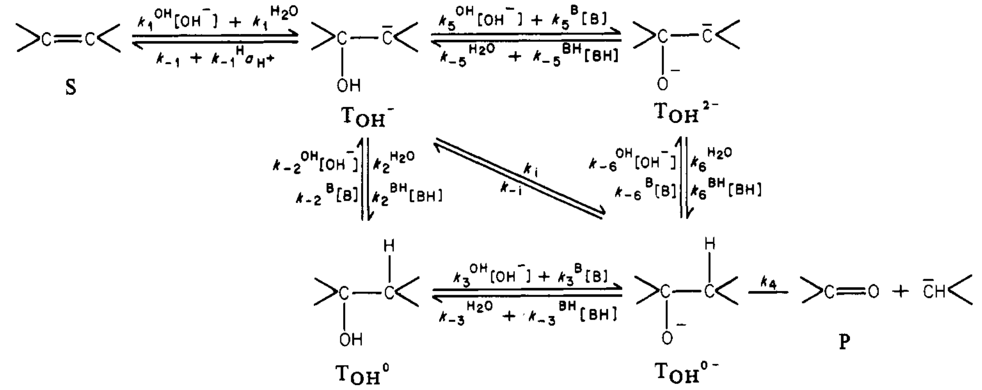
[8] (a) Bernasconi, C. F.; Carré, D. J. *J. Am. Chem. Soc.* **1979**, *101*, 2698; (b) Albeck, M., Hoz, S.; Rappoport, Z. *J. Chem. Soc., Perkin Trans. 2* **1975**, 628.

Table II. Kinetic Parameters Determined from the Hydrolysis Reaction at pH ⩾12.5 (pD ⩾12.0)

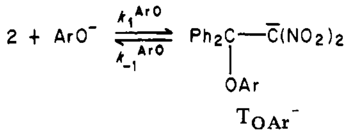
operational rate constant (eq 4)	mechanistic interpretation (Scheme I)	H_2O^a	D_2O^b	$k(H_2O)/k(D_2O)$
k_0, s^{-1}	$k_2^{H_2O}$	$2.80 \pm 0.14 \times 10^{-3}$ [c]	$5.10 \pm 0.25 \times 10^{-4}$ [d]	5.5 ± 0.6
		$2.25 \pm 0.12 \times 10^{-3}$ [e]	$5.0 \pm 1.0 \times 10^{-4}$ [e]	4.5 ± 1.0
k_{OH}, $M^{-1}\ s^{-1}$	see discussion	0.21 ± 0.02 [f]	0.29 ± 0.03 [f]	0.72 ± 0.15
		0.26 ± 0.03 [g]	0.30 ± 0.03 [g]	0.87 ± 0.15
k_{BH}, $M^{-1}\ s^{-1}$	k_2^{BH}	0.32 ± 0.02	0.08 ± 0.01	4.0 ± 0.7
k_B, $M^{-2}\ s^{-1}$	$K_5^{OH}k_6^{BH}$	14.1 ± 1.0	5.7 ± 0.6	2.5 ± 0.4

[a] In 50% Me_2SO–50% H_2O. [b] In 50% Me_2SO–50% D_2O. [c] From plateau of pH profile at pH ~13. [d] From plateau of pD profile at pD ~12.5. [e] From 2,4,6-trimethylphenol buffer data, eq 4. [f] From pH (pD) profile and data in Table I. [g] From 2,4,6-trimethylphenol buffer data.

Scheme I



Catalysis by 2,4,6-Trimethylphenol Buffer. General acid–base catalysis of the hydrolysis reaction was investigated in 2,4,6-trimethylphenol buffers. k_{obsd} was measured as a function of 2,4,6-trimethylphenol concentration at pH 12.95, 13.38, 13.67, 14.09, and 14.36. The data are summarized in Table S3[5] and displayed in Figure 2. The plots at pH 12.95, 13.38, and 13.67 appear to be slightly curved at high buffer concentrations, which is attributed to the rapid equilibrium reaction shown in eq 3



$$2 + ArO^- \underset{k_{-1}^{ArO}}{\overset{k_1^{ArO}}{\rightleftharpoons}} \underset{\substack{|\\ OAr \\ T_{OAr}^-}}{Ph_2C}\!-\!\bar{C}(NO_2)_2 \qquad (3)$$

(discussed in more detail below). Another, possible additional source of curvature is a buffer association of the type ArOH--$\bar{O}$Ar.[9]

The initial slopes of the buffer plots (Figure 2) are seen to increase with increasing pH, indicating catalysis not only by the acidic but also by the basic component of the buffer. The data can be fitted to an equation of the form[10]

$$k_{obsd} = k_0 + k_{OH}[OH^-] + (k_{BH} + k_B[OH^-])[BH] \qquad (4)$$

where BH stands for 2,4,6-trimethylphenol. The first two terms in eq 4 correspond to the intercepts in Figure 2; they are equivalent to k_{obsd} determined in the absence of catalyzing buffers (Figure 1), with k_0 corresponding to the plateau at pH ~12.5 and $k_{OH}[OH^-]$ corresponding to the pH-dependent leg at pH >13. The four rate constants (eq 4) that give the best fit with the data are summarized in Table II.

Similar data were obtained in 50% Me_2SO–50% D_2O at pD 13.40, 14.33, 14.71, and 15.10. They are reported in Table S4[5] and can be fitted to an equation that is analogous to eq 4, with the rate constants also reported in Table II.

Reaction 3 was detected independently as an additional relaxation process at 450 nm, which is faster than the hydrolysis or the attack of hydroxide ion on **2**. Its rate of equilibration was studied at pH 12.68; the reciprocal relaxation time which is reported in Table S5[5] as a function of 2,4,6-trimethylphenoxide ion concentration obeys the equation

$$\tau_{ArO}^{-1} = k_1^{ArO}[ArO^-] + k_{-1}^{ArO} \qquad (5)$$

with $k_1^{ArO} = 2.4 \pm 0.1 \times 10^{-1}\ M^{-1}\ s^{-1}$ and $k_{-1}^{ArO} = 1.4 \pm 0.1 \times 10^{-2}\ s^{-1}$.

Hence, the slight curvature in the buffer plots (Figure 2) is, at least in part, a consequence of tying up increasing amounts of **2** in the form of T_{ArO}^-. The curvature becomes insignificant at high pH because the equilibrium of eq 1 is increasingly shifted toward the side of T_{OH}^- (see next section), thereby compensating for any effect the equilibrium of eq 3 might have.

Mechanism of Hydrolysis in Basic Solution. The commonly accepted mechanism for hydrolytic cleavage of activated olefins in basic solution[11] is shown as pathway S → T_{OH}^- → T_{OH}^0 → T_{OH}^{0-} → P in Scheme I. The scheme includes another pathway that needs to be considered in strongly alkaline solution (S → T_{OH}^- → T_{OH}^{2-} → T^{0-} → P) as well as an intramolecular pathway (k_i), which conceivably might play a role.

Our results can be interpreted on the basis of Scheme I, with different rate-limiting steps for different pH ranges, as follows.

(1) Extrapolation of $\tau_1^{-1} = k_1^{OH}[OH^-]$ to the pH range of 11–12 (Figure 1) shows that in this range k_{obsd} of the hydrolysis reaction coincides with $k_1^{OH}[OH^-]$, indicating that nucleophilic attack by hydroxide ion is the rate-limiting step in this range. This implies that $k_1^{OH}[OH^-]$ and k_{-1} are much lower than the rate terms of the reactions that lead from T_{OH}^- to products, i.e., T_{OH}^- is a steady-state intermediate in this pH range.

(2) As the pH is lowered (<10) k_{obsd} becomes pH independent (Figure 1) and levels off at a value of $1.05 \times 10^{-4}\ s^{-1}$. Since in this range $k_{obsd} > k_1^{OH}[OH^-]$, the rate-limiting step can not possibly be one that is later than the first step and hence must be nucleophilic attack by water, i.e., $k_1^{H_2O} = 1.05 \times 10^{-4}\ s^{-1}$.

(3) As the pH is increased above 12, the rate of formation of T_{OH}^- ($k_1^{OH}[OH^-]$) becomes faster than the reactions leading from T_{OH}^- to products. This leads to an accumulation of T_{OH}^- to

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[9] Hibbert, F.; Robbins, H. J. *J. Am. Chem. Soc.* **1978**, *101*, 8239.

[10] The $k_B[OH^-][BH]$ term in eq 4 corresponds to general base catalysis and is equivalent to $k_BK_w[B^-]/K_a^{BH}$.

[11] For reviews, see (a) Patai, S.; Rappoport, Z. In "The Chemistry of Alkenes"; Patai, S., Ed.; Interscience: New York, 1964; p 496; (b) Fyfe, C. A. In "The Chemistry of the Hydroxyl Group"; Patai, S., Ed.; Interscience: New York, 1971; p 51.

detectable levels, which is observed as a separate kinetic process (τ_1), while k_{obsd} becomes pH independent (plateau in pH profile, Figure 1); the plateau indicates that T_{OH}^- is now the ground state for the hydrolysis reaction. This is confirmed by spectral data that show that absorption at 450 nm due to T_{OH}^- increases and reaches a plateau in the same pH range where the transition from the pH-dependent to the pH-independent k_{obsd} occurs (Figure 3).

(4) In principle, the pH-independent plateau at pH ~12.5 to ~13.5 is consistent with k_4, $k_2^{H_2O}$, or k_i being rate limiting. However, observation of general acid catalysis by 2,4,6-trimethylphenol (k_{BH}, eq 4 and Table II) and of solvent kinetic isotope effects both for the water reaction [$k_0(H_2O)/k_0(D_2O)$ = 4.5–5.5] and for the buffer reaction [$k_{BH}(H_2O)/k_{BD}(D_2O) = 4.0$, which are in the order of magnitude for a primary isotope effect, is inconsistent with k_4 being rate limiting. The results are consistent with rate-limiting carbon protonation of T_{OH}^- ($k_2^{H_2O}$, k_2^{BH}), with a possible contribution by the k_i pathway. Hence, the operational rate constants k_o and k_{BH} defined in eq 4 and Table II have the meaning $k_o = k_2^{H_2O} + k_i$ and $k_{BH} = k_2^{BH}$; in the Discussion section it will be shown that k_i is negligible, i.e., $k_o \approx k_2^{H_2O}$.

(5) Above pH 13.5 k_{obsd} again increases with pH (Figure 1 and k_{OH} term in eq 4), indicating that a new OH⁻-catalyzed pathway becomes dominant. There is also general base catalysis by 2,4,6-trimethylphenoxide ion (or the equivalent of OH⁻ catalysis followed by general acid catalysis as described by the k_B term in eq 4). Interestingly the general base-catalyzed pathway shows a kinetic solvent isotope effect $k_B(H_2O)/k_B(D_2O) = 2.5$, while the OH⁻-catalyzed reaction shows an *inverse* isotope effect $k_{OH}(H_2O)/k_{OD}(D_2O) \approx 0.8$ (Table II).

The results for the general base-catalyzed pathway are most easily interpreted in terms of a rapid equilibrium between T_{OH}^- and T_{OH}^{2-} followed by rate-limiting carbon protonation of T_{OH}^{2-} by 2,4,6-trimethylphenol to form T_{OH}^{0-}.[12] Thus k_B in eq 4 has the meaning of $K_5^{OH}k_6^{BH}$ with K_5^{OH} being the equilibrium constant for the reaction $T_{OH}^- + OH^- \rightleftharpoons T_{OH}^{2-}$. The solvent isotope effect is then given by $k_B(H_2O)/k_B(D_2O) = (K_5^{OH}/K_5^{OD})(k_6^{BH}/k_6^{BD})$; K_5^{OH}/K_5^{OD} is estimated to lie between 0.5 and 0.8,[14] which implies a k_6^{BH}/k_6^{BD} ratio of 3–5. This value for k_6^{BH}/k_6^{BD} is thus very similar to that found for carbon protonation of T_{OH}^- (k_2^{BH}/k_2^{BD} = 5) by the same buffer acid and supports our interpretation in terms of rate-limiting carbon protonation of T_{OH}^{2-}.

Interpretation of the results for the k_{OH} pathway is less straightforward. Assuming rate limiting C protonation of T_{OH}^{2-} by water as with 2,4,6-trimethylphenol, k_{OH} takes on the meaning of $K_5^{OH}k_6^{H_2O}$ and $k_{OH}(H_2O)/k_{OD}(D_2O) = (K_5^{OH}/K_5^{OD})(k_6^{H_2O}/k_6^{D_2O})$, thus implying a value for $k_6^{H_2O}/k_6^{D_2O}$ between 0.8 and 1.7. This result would indicate that there is at best a small and perhaps no primary isotope effect at all, which is inconsistent with rate-limiting carbon protonation;[15] it implies that the k_{OH} pathway has a different mechanism, as will be further elaborated upon in the Discussion section.

Kinetics in Acidic Solution. The experiments in acidic solution had three main objectives.

(a) To obtain the rate constant for the hydronium ion catalyzed reversion of T_{OH}^- to the olefin (k_{-1}^H step in Scheme I). In combination with $k_1^{H_2O}$ and k_1^{OH}, this would allow us to obtain k_{-1}, an important rate constant which is inaccessible by any other method.

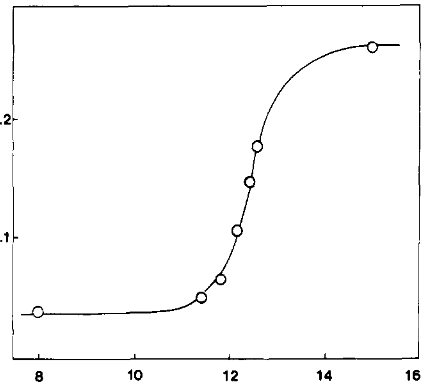

Figure 3. Absorption at 450 nm due to $T_{OH'}^-$ measured immediately after buildup of T_{OH}^- but before further reaction has made significant progress.

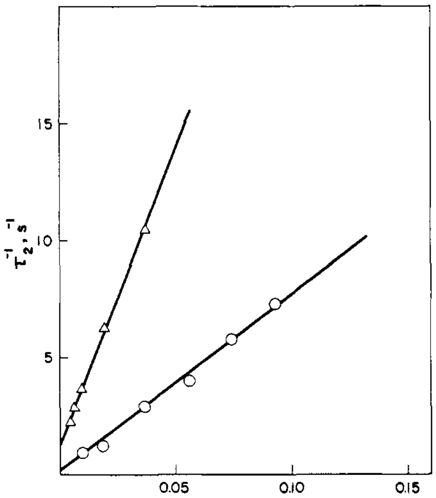

Figure 4. General acid catalysis of fast process (τ_2^{-1}) in pH-jump experiments, representative plots. (▲) $ClCH_2COOH$, pH 3.76; (○) AcOH, pH 4.70.

(b) To obtain the rate constants of carbon protonation of T_{OH}^- by acids other than water and 2,4,6-trimethylphenol, including the hydronium ion.

(c) To obtain kinetic information on the rates of the conversion of $T_{OH}^0 \rightarrow T_{OH}^{0-}$, and of $T_{OH}^{0-} \rightarrow P$, information that is not obtainable in basic solution since neither of these steps is rate limiting at high pH.

The experiments were carried out in the following way. T_{OH}^- was first generated by mixing the substrate with just enough base to convert as much olefin into T_{OH}^- as possible without inducing too much base-catalyzed hydrolysis, i.e., the $k_1^{OH}[OH^-]/k_{obsd}$ ratio was maximized. KOH (0.005 M) solutions of the substrate, incubated for about 2 min, gave the best results. These incubated solutions were then mixed with an acidic buffer or an HCl solution in the stopped-flow apparatus ("pH-jump" experiments).

At 450 nm where T_{OH}^- is the only absorbing species we observed one kinetic process with the relaxation time τ_2; it corresponds to the loss of T_{OH}^-. At 280 nm where S, T_{OH}^-, and benzophenone (but not $\bar{C}H(NO_2)_2$) absorb, two kinetic processes were observed: the first has the same relaxation time (τ_2) as the one observed at 450 nm; the second is slower and its relaxation time will be called τ_3.

Between 310 and ~410 nm where S, T_{OH}^-, and $\bar{C}H(NO_2)_2$ (but not benzophenone) absorb, three kinetic processes were detected: the slowest one corresponds to τ_3 observed at 280 nm and the other two are seen in the time range of τ_2 but are not well separated. The additional relaxation time can be attributed to the carbon

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[12] The alternative assumption that the reaction $T_{OH}^- \rightarrow T_{OH}^{2-}$ is rate limiting is totally inconsistent with the values obtained for k_{OH} and k_B; for example, $k_{OH} = 0.21\ M^{-1}\ s^{-1}$ is 9–10 orders of magnitude smaller than expected for the deprotonation of an alcohol by OH⁻.[13] However, deprotonation of T_{OH}^0 to form T_{OH}^{0-} *is* rate limiting in acidic solution as shown below.

[13] (a) Eigen, M. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 1; (b) Eigen, M.; Kruse, W.; Maass, G.; DeMayer, L. *Progr. React. Kinet.* **1964**, *2*, 287.

[14] Loughton, P. M.; Robertson, R. E. In "Solute-Solvent Interactions"; Coetzee, J. F.; Ritchie, C. D., Eds.; Marcel Dekker: New York, 1969; p 400.

[15] The argument that the smaller isotope effect than in the protonation of T_{OH}^- might be due to a change in transition-state structure caused by the additional negative charge is not a satisfactory one for two reasons. (1) The additional negative charge is expected to enhance the basicity of the carbanion (pK_a of T_{OH}^0 ~ 13.5, see below), which would reduce the pK difference between proton donor (H_2O, pK_w = 15.93) and acceptor (carbanion), thereby potentially increasing the symmetry of the transition state. This would tend to increase rather than decrease the kinetic isotope effect.[16] (2) A similar reduction in isotope effect would be expected for the 2,4,6-trimethylphenol reaction, but none is observed.

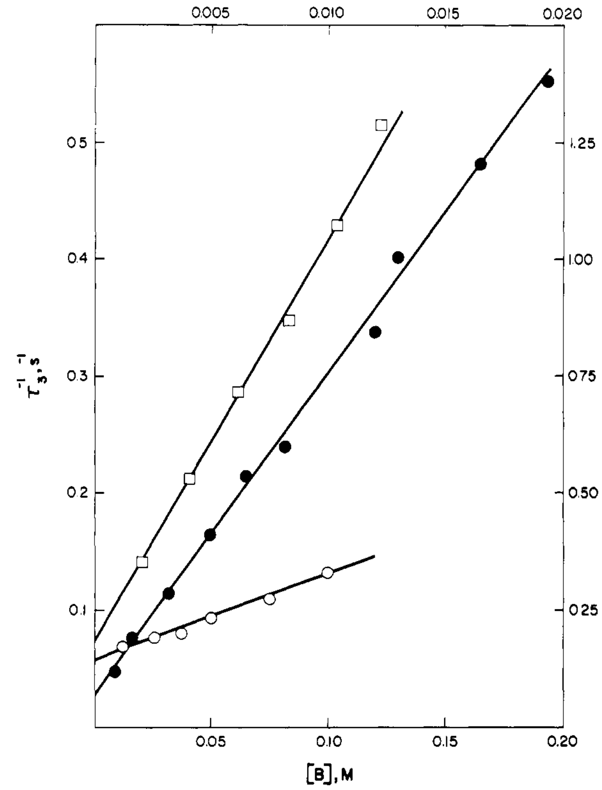


Figure 5. General base catalysis of slow process (τ_3^{-1}) in pH-jump experiments, representative plots. (□) $HCOO^-$, pH 5.51 (left and bottom axes); (○) $ClCH_2COO^-$, pH 3.71 (left and bottom axes); (●) 4-picoline, pH 4.14–4.23 (right and top axes).

protonation of $\bar{C}H(NO_2)_2$,[17] which is present in significant amounts owing to partial hydrolysis during incubation before performance of the pH-jump.

The kinetic analysis was carried out at 450, 363, or 280 nm as follows. τ_2^{-1} was measured at 450 nm in HCl solution at pH 1.56, 1.70, 1.97, and 2.27 and in chloroacetic (pH 3.76), formic (pH 4.47 and 5.11), and acetic acid solutions (pH 4.49 and 4.71). The results are summarized in Table S6.[5] The τ_2^{-1} process is subject to general acid catalysis. Two representative buffer plots are shown in Figure 4; the data in HCl solutions show τ_2^{-1} to be proportional to a_{H^+}. Hence τ_2^{-1} obeys an equation of the form

$$\tau_2^{-1} = k_H a_{H^+} + k_{BH}[BH] \qquad (6)$$

At pH >5 the addition of a small $k_B[B]$ term to eq 6 slightly improves the fit although the improvement is barely outside the experimental error. As discussed below, the proposed mechanism does call for such a $k_B[B]$ term.

τ_2^{-1} was also measured in 50% Me_2SO–50% D_2O in DCl solutions at pD 1.66, 1.75, 1.87, 2.04, 2.39, and 2.87. The data are included in Table S6;[5] they can be described by $\tau_2^{-1} = k_D a_{D^+}$.

τ_3^{-1} was determined at 280 nm in HCl solution at pH 1.37, 1.55, 1.70, and 2.27, in chloroacetic (pH 3.71), formic (pH 4.47, 5.11, 5.37, and 5.76), and acetic acid solutions (pH 4.71) and at 363 nm in nicotinamide (pH 3.14 and 3.20), pyridine (pH 4.51), and 4-picoline (pH 4.14) solutions. The results are included in Table S6.[5] The τ_3^{-1} process is subject to general base catalysis. Three representative buffer plots are shown in Figure 5; in HCl solutions τ_3^{-1} is pH independent ($\tau_3^{-1} = 7.0 \times 10^{-2}$ s^{-1}) and refers to a "water reaction". Thus τ_3^{-1} obeys an equation of the form

$$\tau_3^{-1} = k_0' + k_B'[B] + k_{OH}'[OH^-] \qquad (7)$$

Table III. Determination of pK_a^0 (C-H of T_{OH}^0)

pH^a	OD_{res}^b	OD_0^c-OD_{res}^b	$\frac{OD_{res}}{OD_0\text{-}OD_{res}} = \frac{[T_{OH}^-]}{[T_{OH}^0]}$	pK_a^0 = pH − log $[T_{OH}^-]/T_{OH}^0]$
5.37	16	23	0.695	5.53
5.49	19.5	21.5	0.907	5.53
5.76	21	12	1.75	5.52

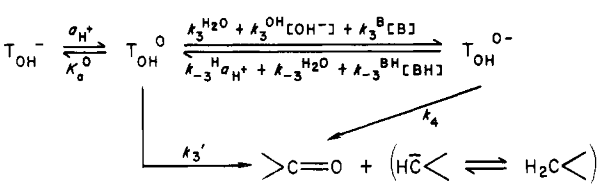
^{a} Formate buffers. ^{b} Residual absorption at $\tau_3 >> t >> \tau_2$ in arbitrary units as determined from oscilloscope trace in stopped-flow apparatus; see text. ^{c} Initial absorption in same units as OD_{res}; see text.

At pH >4.8 the rate constants in eq 7 start to decrease with increasing pH as discussed in more detail below.

τ_3^{-1} was also measured in 50% Me_2SO–50% D_2O in DCl solutions at pD 1.87, 2.04, and 2.39 (Table S6); τ_3^{-1} is independent of pD with an average value of 3.03 ± 0.06 × 10^{-2} s^{-1}.

Mechanism in Acidic Solution. In this section we report a number of additional observations and show that the τ_2^{-1} process refers to reaction 8, while the τ_3^{-1} process is associated with reaction 9. In this latter reaction the $T_{OH}^- \rightleftharpoons T_{OH}^0$ step is at

$$S \xleftarrow{k_{-1}^{H}a_{H^+} + k_{-1}^{BH}[BH]} T_{OH}^- \underset{k_{-2}^{H_2O} + k_{-2}^{B}[B]}{\overset{k_2^{H}a_{H^+} + k_2^{BH}[BH]}{\rightleftharpoons}} T_{OH}^0 \qquad (8)$$



(9)

equilibrium, while oxygen deprotonation ($T_{OH}^0 \rightarrow T_{OH}^{0-}$) is rate limiting. Note that at very low pH the product carbanion ends up in its protonated form. Note also that in reaction 9 we have allowed for a direct pathway from T_{OH}^0 to products (k_3'); as shown in the Discussion section, this pathway does play a significant role at low pH.

In order to simplify the discussion we shall mention that the pK_a^0 (C-H) of T_{OH}^0 was determined to be 5.5 as described below. This means that below pH 4.5 the $k_{-2}^{H_2O}$ and $k_{-2}^{B}[B]$ terms in eq 8 are negligible compared to the $k_2^{H}a_{H^+}$ and $k_2^{BH}[BH]$ terms.

The mechanistic assignments are based on the following observations.

(1) τ_2^{-1} is associated with a decrease in absorption at 450 nm, which must refer to the disappearance of T_{OH}^- since it is the only species that absorbs at 450 nm.

(2) The spectrum taken in an HCl solution in the stopped-flow apparatus immediately after the τ_2 process ($t >> \tau_2$) but before the τ_3 process has made significant progress ($t << \tau_3$) corresponds essentially to the spectrum of the substrate (S) but with an absorption that is much smaller than that expected for 100% conversion of T_{OH}^- into S. The absence of any other spectral contribution implies that a significant fraction of T_{OH}^- must have been converted into a species that does not absorb in the spectral range studied (250–450 nm). This species must therefore be the saturated compound T_{OH}^0. From the spectrophotometrically determined yield of S in pH-jump experiments with HCl at pH ≤2 where reaction 8 reduces to eq 10, one obtains $k_{-1}^{H}/k_2^{H} = 0.026$

$$S \xleftarrow{k_{-1}^{H}a_{H^+}} T_{OH}^- \xrightarrow{k_2^{H}a_{H^+}} T_{OH}^0 \qquad (10)$$

± 0.005;[20] in 50% Me_3O–50% D_2O this ratio is $k_{-1}^{D}/k_2^{D} = 0.115$ ± 0.015.

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(16) (a) Westheimer, F. H. *Chem. Rev.* **1961**, *61*, 265; (b) Bell, R. P. "The Proton in Chemistry", Cornell University Press: Ithaca, NY, 1973; p 250; (c) More O'Ferrall, R. A. In "Proton Transfer Reactions"; Caldin, E. F.; Gold, V., Eds.; Wiley: New York, 1975; p 201.

(17) The rate constant for protonation of $\bar{C}H(NO_2)_2$ in water is 2.1 × 10^3 M^{-1} s^{-1}.[18] Assuming that the rate in 50% Me_2SO–50% water is similar to that in water or slightly higher[19] would indeed make ka_{H^+} comparable to τ_2^{-1}.

(18) Dronov, V. N.; Tselinski, I. V. *Org. React.* **1970**, *7*, 277.

(19) Bernasconi, C. F.; Kanavarioti, A. *J. Org. Chem.* **1979**, *44*, 4829.

(20) The relatively high experimental error is due to complications in evaluating this ratio which arise from a nonquantitative conversion of S into T_{OH}^- *prior* to the pH-jump. More details are given in the Experimental Section.

Table IV. Rate Constants for the Carbon Protonation–Deprotonation Reaction $T_{OH}^- + BH \rightleftharpoons T_{OH}^0 + B$

BH	pK_a^{BH}	$\Delta pK = pK_a^{0\,a} - pK_a^{BH}$	k_2^{BH} or k_2^{BD}, $M^{-1}\,s^{-1}$	k_2^{BH}/k_2^{BD}	k_{-2}^{B},[e] $M^{-1}\,s^{-1}$
H_3O^+	-1.44[b]	6.94	$4.82 \pm 0.20 \times 10^3$	1.85 ± 0.12	1.53×10^{-2}[f]
D_3O^+			$2.60 \pm 0.10 \times 10^3$		
$ClCH_2COOH$	3.71[c]	1.82	$2.62 \pm 0.20 \times 10^2$		3.97
HCOOH	4.46[c]	1.07	$2.33 \pm 0.20 \times 10^2$		1.99×10^1
CH_3COOH	5.78[c]	-0.25	81 ± 8		1.44×10^2
$2,4,6\text{-}Me_3C_6H_2OH$	12.44[c]	-6.94	0.32 ± 0.02	4.0 ± 0.7	2.80×10^6
$2,4,6\text{-}Me_3C_6H_2OD$			0.08 ± 0.01		
H_2O	17.34[d]	-11.84	$2.80 \pm 0.14 \times 10^{-3}$[g]	5.5 ± 0.6	7.08×10^7
D_2O			$5.10 \pm 0.25 \times 10^{-4}$		

[a] pK_a^0 (C–H of T_{OH}^0) = 5.53; see text. [b] $-\log [H_2O] = -\log 27.7$. [c] Determined potentiometrically. [d] $pK_s + \log [H_2O]$ with pK_s = 15.9; ref 8a. [e] k_{-2}^B calculated as $k_2^{BH}K_a^0/K_a^{BH}$. [f] In units of s^{-1}; $k_{-2}^{H_2O}/[H_2O] = 2.77 \times 10^{-4}\ M^{-1}\,s^{-1}$. [g] In units of s^{-1}; $k_2^{H_2O}/[H_2O] = 1.01 \times 10^{-4}\ M^{-1}\,s^{-1}$.

(3) The infinity spectrum ($t >> \tau_3$) shows essentially quantitative conversion into final products,[21] i.e., benzophenone and dinitromethane (or its anion).

(4) In contrast to the situation in highly acidic solutions where T_{OH}^- completely disappears during the τ_2 process, some residual absorption at 450 nm remains at pH ≥4.5 which only disappears with the τ_3 process. This indicates that the equilibrium $T_{OH}^- \rightleftharpoons T_{OH}^0$ is no longer completely on the T_{OH}^0 side and allows the pK_a^0 of T_{OH}^0 to be determined spectrophotometrically. The results are summarized in Table III; they yield $pK_a^0 = 5.53$.[22]

(5) The proportionality between τ_2^{-1} and a_{H^+} in HCl solution ($k_H a_{H^+}$ term in eq 6) is consistent with the simplified scheme of eq 10 for which $\tau_2^{-1} = k_H a_{H^+} = (k_{-1}^H + k_2^H)a_{H^+}$. From $k_H = k_{-1}^H + k_2^H = 4.95 \pm 0.15 \times 10^3\ M^{-1}\,s^{-1}$ and $k_{-1}^H/k_2^H = 0.026 \pm 0.005$ (see above), one obtains $k_{-1}^H = 125 \pm 30\ M^{-1}\,s^{-1}$ and $k_2^H = 4.82 \pm 0.15 \times 10^3\ M^{-1}\,s^{-1}$. In 50% Me_2SO–50% D_2O, $k_{-1}^D + k_2^D = 2.90 \pm 0.10 \times 10^3\ M^{-1}\,s^{-1}$, which in combination with $k_{-1}^D/k_2^D = 0.115 \pm 0.015$ yields $k_{-1}^D = 300 \pm 50\ M^{-1}\,s^{-1}$ and $k_2^D = 2.60 \pm 0.10 \times 10^3\ M^{-1}\,s^{-1}$; thus the kinetic solvent isotope effects are $k_{-1}^H/k_{-1}^D = 0.42 \pm 0.16$ and $k_2^H/k_2^D = 1.85 \pm 0.12$.

The value for k_{-1}^H/k_{-1}^D falls within the range that is typical for an A1 mechanism for the loss of the OH group from T_{OH}^-.[14,23] The low value for k_2^H/k_2^D which contrasts with the much higher isotope effects for the protonation of T_{OH}^- by water ($k_2^{H_2O}/k_2^{D_2O}$ = 4.5–5.5) or by 2,4,6-trimethylphenol ($k_2^{BH}/k_2^{BD} = 4.0$) is a well-established phenomenon[14,24] for carbon protonation by the hydronium ion, especially for protonation of delocalized carbanions.[25]

(6) The rate constants for buffer catalysis can now be obtained as follows. k_{BH} in eq 6 is equivalent to $k_{-1}^{BH} + k_2^{BH}$ in eq 8. However, since the k_{-1}^H/k_2^H ratio is very small (0.026), the k_{-1}^{BH}/k_2^{BH} ratio is also expected to be very small (although not necessarily identical with the k_{-1}^H/k_2^H ratio).[26] Thus we can set $k_{BH} \approx k_2^{BH}$. For chloroacetic acid one obtains $k_2^{BH} = 262 \pm 20\ M^{-1}\,s^{-1}$ from this analysis. In formic and acetic acid buffers the $k_{-2}^B[B]$ term of eq 8 is no longer negligible. Here τ_2^{-1} is best approximated by

$$\tau_2^{-1} \approx k_2^{BH}[BH] + k_{-2}^B[B] \qquad (11)$$

In view of the smallness of the $k_{-2}^B[B]$ term, we preferred to calculate k_{-2}^B as $k_2^{BH}K_a^0/K_a^{BH}$, where K_a^{BH} is the acidity constant of the buffer and k_2^{BH} is obtained from k_{BH} at pH ≤4.71. The various rate constants are summarized in Table IV.

Table V. Rate Constants for the Oxygen Deprotonation–Protonation Reaction $T_{OH}^0 + B \rightleftharpoons T_{OH}^{0-} + BH$

B	pK_a^{BH}	$\Delta pK = pK_a^{BH} - pK_a^{OH\,a}$	k_3^B, $M^{-1}\,s^{-1}$	k_{-3}^{BH}, $M^{-1}\,s^{-1}$
H_2O	-1.44[b]	-14.74	$7.00 \pm 0.1 \times 10^{-2}$[f]	(1.37×10^{12})[g]
$ClCH_2COO^-$	3.71[c]	-9.59	0.70 ± 0.07	$\sim 2.0 \times 10^9$[h]
$HCOO^-$	4.46[c]	-8.84	5.00 ± 0.30	$\sim 2.0 \times 10^9$[h]
CH_3COO^-	5.78[c]	-7.52	29.5 ± 2.0	$\sim 2.0 \times 10^9$[h]
nicotinamide	2.69[c]	-10.61	0.31 ± 0.03	1.26×10^{10}[i]
pyridine	4.51[c]	-8.79	14.7 ± 0.1	9.1×10^9[i]
4-picoline	5.25[c]	-8.05	70.7 ± 3.5	7.9×10^9[i]
OH^-	17.34[d]	4.04	$1.3 \pm 0.2 \times 10^9$	3.2×10^6[j]

[a] pK_a^{OH} (OH of T_{OH}^0) = 13.3; see text. [b–e] See Table IV. [f] In units of s^{-1}; $k_3^{H_2O}/[H_2O] = 2.6 \times 10^{-3}\ M^{-1}\,s^{-1}$; see text for meaning of $k_3^{H_2O} \approx k_3'$. [g] Calculated from k_3^B ($B = H_2O$) and pK_a^{OH}, assuming $k_3^{H_2O} + k_3' \approx k_3^{H_2O}$; see text. [h] Assumed value for a diffusion-controlled reaction; see ref 27. [i] Calculated from k_3^B and pK_a^0. [j] Calculated from k_3^B ($B = OH^-$) and pK_a^{OH}; $k_{-3}^{H_2O}$ in units of s^{-1}; $k_{-3}^{H_2O}/[H_2O] = 1.15 \times 10^5\ M^{-1}\,s^{-1}$.

(7) In HCl solution τ_3^{-1} is concentration independent, which means that in eq 7 k_0' is the only significant term. Since at these pH values T_{OH}^0 is the ground state for reaction 9, k_0' is equivalent to $k_3^{H_2O} + k_3'$; its value is $7.00 \pm 0.1 \times 10^{-2}\ s^{-1}$. In 50% Me_2SO–50% D_2O $k_0' = 3.03 \pm 0.06 \times 10^{-2}\ s^{-1}$; thus the isotope effect is $k_0'(H_2O)/k_0'(D_2O) = 2.38 \pm 0.24$.

In chloroacetate and nicotinamide buffers eq 7 still holds with k_B' being equivalent to k_3^B in eq 9. In the other buffers the equilibrium between T_{OH}^- and T_{OH}^0 is not completely on the side of T_{OH}^0; here τ_3^{-1} is given by

$$\tau_3^{-1} = \frac{a_{H^+}}{K_a^0 + a_{H^+}}(k_3^{H_2O} + k_3' + k_3^B[B^-] + k_3^{OH}[OH^-]) \qquad (12)$$

i.e., k_B' in eq 7 becomes $k_3^B a_{H^+}/(K_a^0 + a_{H^+})$, etc. Four different buffer ratios, corresponding to pH 4.47, 5.11, 5.37, and 5.76, were used with formate buffer. The slopes of the plots of τ_3^{-1} vs. $[HCOO^-]$ obey the equation

$$(\text{slope})^{-1} = \frac{K_a^0}{k_3^B a_{H^+}} + \frac{1}{k_3^B} \qquad (13)$$

from which $k_3^B = 5.0 \pm 0.5\ M^{-1}\,s^{-1}$ and $K_a^0 = 2.78 \pm 0.70 \times 10^{-6}$ ($pK_a^0 = 5.55 \pm 0.10$) was obtained. The pK_a^0 thus obtained is in excellent agreement with the value of 5.53 determined spectrophotometrically (see point 4). For the remaining buffers k_3^B was calculated from eq 12, using the spectrophotometric pK_a^0.

$k_3^{OH} = 1.3 \pm 0.2 \times 10^9\ M^{-1}\,s^{-1}$ was obtained via eq 12 from the intercepts of the formate buffer plots. The various rate constants are summarized in Table V.

(8) A Brønsted plot for k_3^B for nicotinamide, pyridine, 4-picoline, chloroacetate, formate, and acetate ion, including $k_3^{H_2O}$

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(21) Conversion is about 97 ± 1% complete; the balance consists of the small amount of S formed during the τ_2 process (eq 8 or 10).

(22) In principle the formation of S in competition with the formation of T_{OH}^0 needs to be taken into account in determining pK_a^0. However, since only a few percent of S is formed,[21] this factor can be neglected.

(23) Cordes, E. H.; Bull, H. G. *Chem. Rev.* **1974**, *74*, 581.

(24) (a) Kresge, A. J.; Onwood, D. P. *J. Am. Chem. Soc.* **1964**, *86*, 5014; (b) Bunton, C. A.; Shiner, V. J., Jr. *Ibid.* **1961**, *83*, 3214.

(25) (a) Riley, T.; Long, F. A.; *J. Am. Chem. Soc.* **1962**, *84*, 522; (b) Long, F. A.; Watson, D. *J. Chem. Soc.* **1958**, 2019; (c) Maron, S. H.; LaMer, V. K. *J. Am. Chem. Soc.* **1938**, *60*, 2588.

(26) k_{-1}^{BH} may in fact be zero if the acid-catalyzed OH departure from T_{OH}^- proceeds by an A1 mechanism, as seems likely based on the isotope effect k_{-1}^H/k_{-1}^D.

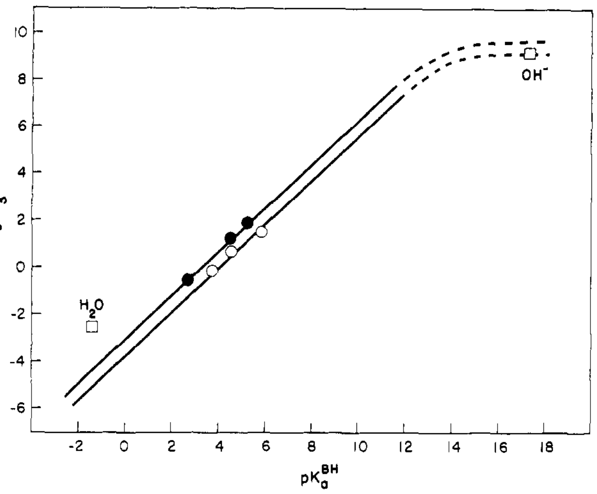


Figure 6. Brønsted plot for oxygen deprotonation of T_{OH}^0. Data from Table V. (○) Carboxylate ions, (●) pyridine bases, (□) H_2O and OH^-.

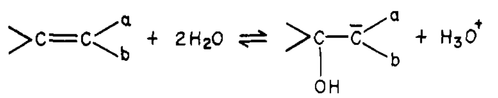
$+ k_3'$ and k_3^{OH}, is shown in Figure 6. The three pyridine bases define an excellent straight line of slope $\beta = 0.93 \pm 0.02$. The points for the carboxylate ions show some scatter but can be described by a straight line of equal slope which is displaced by 0.6 log unit downward from the line defined by the pyridines. The β value close to unity is characteristic of a diffusion-controlled proton-transfer reaction between normal acids and bases[13] in the thermodynamically disfavored direction. Equally characteristic is the change in slope from approximately 1 to zero as the reaction becomes thermodynamically favored and encounter controlled, which is the case for OH^-.[27] Our results are therefore consistent with k_3^B and k_3^{OH} referring to the deprotonation of the OH group in T_{OH}^0, implying that oxygen deprotonation of T_{OH}^0 is rate limiting in reaction 9.

The fact that the Brønsted line for the pyridine bases is displaced upward by a factor of about 4 from the one defined by the carboxylate ions is best understood in terms of an electrostatic acceleration of the encounter-controlled reverse reaction (k_{-3}^{BH}), which involves the recombination of an anion with a cation:[13] since $\log k_3^B = \log k_{-3}^{BH} + \Delta pK$, k_3^B for the forward reaction is also enhanced.

The point for the water reaction ($k_3^{H_2O} + k_3'$) deviates positively 80- and 320-fold, respectively, from the two Brønsted lines. These are much larger deviations than can be accounted for by the usually enhanced rate constants for diffusion-controlled proton transfer involving H_3O^+[13] ($k_{-3}^{H^+}$). As will be shown in the Discussion section, this deviation as well as the solvent isotope effect of 2.4 indicates that it is k_3' rather than $k_3^{H_2O}$ (eq 9) that dominates the water reaction.

Discussion

Formation of T_{OH}^-. Table VI summarizes the rate and equilibrium constants of the reversible addition of OH^- (k_1^{OH}, k_{-1}, K_1^{OH}) and of water ($k_1^{H_2O}$, $k_{-1}^{H^+}$, $K_1^{H_2O}$) to 1,1-dinitro-2,2-diphenylethylene (**2**); the table includes similar data for benzylidene Meldrum's acid (**1**). The Lewis acidities of the two compounds ($pK_1 = 5.43$ for **1**, 6.09 for **2**) are seen to be very close, just as the Brønsted acidities of Meldrum's acid ($pK_a = 4.83$)[30] and of dinitromethane ($pK_a = 3.57$)[4] are quite similar to each other. Inasmuch as the addition of a base to an olefin produces the same type of carbanion as the abstraction of a proton from a correspondingly activated carbon acid (eq 14 and 15), this parallelism


(14)


(15)

of the effect of a and b on Lewis and Brønsted acidities is not surprising.[31]

In contrast to the equilibrium constants for nucleophilic addition, the *rate* constants are vastly different for the two olefins. This is best appreciated by considering the ratios of constants in the last column of Table VI. For water addition to the two olefins

Table VI. Rate and Equilibrium Constants for Reversible Addition of OH^- and H_2O to 1,1-Dinitro-2,2-diphenylethylene (**2**) and to Benzylidene Meldrum's Acid (**1**)

	2[a]	**1**[b]	1/2[c]
k_1^{OH}, $M^{-1}\ s^{-1}$	12.2 ± 0.6	7.45×10^2	6.1
k_{-1},[d] s^{-1}	$1.9 \pm 0.8 \times 10^{-9}$	3.73×10^{-6}	1.96×10^3
K_1^{OH},[e] M^{-1}	$6.4 \pm 2.7 \times 10^9$	2.00×10^8	3.13×10^{-2}
$k_1^{H_2O}$, s^{-1}	$1.05 \pm 0.05 \times 10^{-4}$	0.55	5.25×10^3
$k_1^{H_2O}/[H_2O]$, $M^{-1}\ s^{-1}$	$3.81 \pm 0.20 \times 10^{-6}$	9.9×10^{-3}	2.60×10^3
$k_{-1}^{H^+}$, $M^{-1}\ s^{-1}$	$1.3 \pm 0.5 \times 10^2$	1.47×10^5	1.13×10^3
$K_1^{H_2O}$ (pK_1), M	$8.1 \pm 3.5 \times 10^{-7}$ (6.09)	3.75×10^{-6} (5.43)	4.63
$K_1^{H_2O}/[H_2O]$	$2.9 \pm 1.2 \times 10^{-8}$	6.75×10^{-8}	2.33

[a] This work, in 50% Me_2SO–50% H_2O at 20 °C. [b] Reference 2, in H_2O at 25 °C. [c] $k_1^{OH}(1)/k_1^{OH}(2)$, $k_{-1}^{H_2O}(1)/k_{-1}^{H_2O}(2)$, $K_1^{OH}(1)/K_1^{OH}(2)$, etc. [d] $k_{-1}^{H_2O}$ obtained as k_1^{OH}/K_1^{OH}. [e] K_{-1}^{OH} obtained as $K_1^{H_2O}/K_w$ with $K_w = 1.26 \times 10^{-16}$ ($pK_w = 15.9$) taken from ref 8a.

Table VII.[37] Rate and Equilibrium Constants for the Ionization of 1,1-Dintroethane[a] (Revised from ref 19)

rate constant, $M^{-1}\ s^{-1}$	pK_a^{BH} [c]	$\Delta pK = pK_a^{NO_2}$ [e] $- pK_a^{BH}$
$k_1^{w}/[H_2O] = 4.66 \times 10^{-3}/27.6$	-1.44[b]	6.44
$k_{-1}^{H} = 4.66 \times 10^2$	-1.44[b]	6.44
$k_1^{Cl_2CHCOO^-} = 0.39$	2.15	2.85
$k_{-1}^{Cl_2CHCOOH} = 2.75 \times 10^2$	2.15	2.85
$k_1^{ClCH_2COO^-} = 4.97$	3.71	1.29
$k_{-1}^{ClCH_2COOH} = 97$	3.71	1.29
$k_1^{HCOO^-} = 12.2$	4.46	0.54
$k_{-1}^{HCOOH} = 37.8$	4.46	0.54
$k_1^{AcO^-} = 91.3$	5.78	-0.78
$k_{-1}^{AcOH} = 14.0$	5.78	-0.78
$k_1^{p\text{-}CNC_6H_4O^-} = 1.22 \times 10^4$	8.75	-3.75
$k_{-1}^{p\text{-}CNC_6H_4OH} = 2.17$	8.75	-3.75
$k_1^{C_6H_5O^-} = 3.55 \times 10^5$	11.45	-6.45
$k_{-1}^{C_6H_5OH} = 0.12$	11.45	-6.45
$k_1^{OH} = 7.33 \times 10^6$	17.34[d]	-12.34
$k_{-1}^{w}/[H_2O] = 9.2 \times 10^{-5}/27.6$	17.34[d]	-12.34

[a] $CH_3CH(NO_2)_2$ $(k_1^{w} + k_1^{B}[B] + k_1^{OH}a_{OH}) \rightleftharpoons (k_{-1}^{H}a_{H^+} + k_{-1}^{BH}[BH] + k_{-1}^{w})$ $CH_3\bar{C}(NO_2)_2$. [b–d] See Table IV. [e] pK_a of $CH_3CH(NO_2)_2 = 5.00$, determined spectrophotometrically.

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[27] On the basis of the Smoluchowski–Einstein–Stokes[28] expression, $k_{diff} = 8RT/3000\eta$, the diffusion-controlled limit in 50% Me_2SO–50% water which has a viscosity of 3.45 cp[29] is $1.96 \times 10^9\ M^{-1}\ s^{-1}$. $k_3^{OH} = 1.3 \times 10^9\ M^{-1}\ s^{-1}$ is seen to be very close to this limit.

[28] (a) Caldin, E. F. "Fast Reactions in Solution"; Wiley-Interscience: New York, 1964; p 10; (b) Hague, D. N. "Fast Reactions"; Wiley-Interscience: New York, 1971; p 13.

[29] Janz, G. J.; Tomkins, R. P. T. "Nonaqueous Electrolyte Handbook", Vol. 1; Academic Press: New York, 1972; p 1043.

[30] Eigen, M.; Ilgenfritz, G.; Kruse, W. *Chem. Ber.* **1965**, *98*, 1623.

[31] Whether one should expect a perfect paralellism between the two types of acidities is hard to tell in the absence of a body of systematic data. The fact that the Lewis acidity of **1** is slightly higher than that for **2** while the Brønsted acidity of Meldrum's acid is somewhat lower than that of dinitroethane shows that the parallelism is not perfect in this case. Possible reasons for this reversal of the relative acidities are a solvent effect on the pK_1 of **2** and, probably more importantly, a steric effect by the second phenyl group of **2**. This steric effect could be a direct one, hindering the attack by the base, or/and it could be an effect on the resonance stabilization of T_{OH}^- by hindering the coplanarity of the two nitro groups. Our data on the rates of carbon protonation of T_{OH}^- discussed below indicate that steric hindrance of resonance probably occurs.

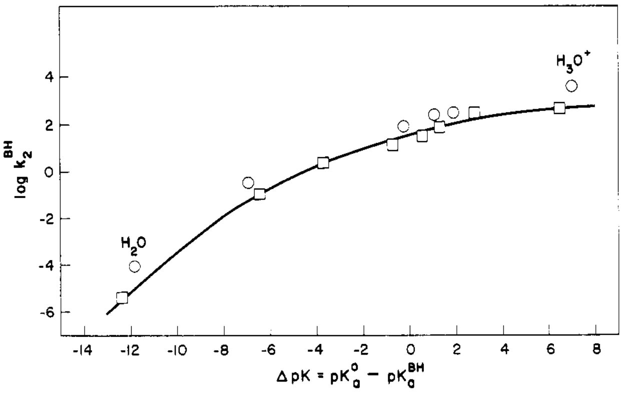


Figure 7. Eigen plot for carbon protonation of T_{OH}^- (○) and of 1,1-dinitroethane anion (□). Data from Table IV (T_{OH}^-) and Table VII [$CH_3C(NO_2)_2^-$].

the equilibrium constants, corrected for the different water concentrations in the two solvents ($K_1/[H_2O]$), differ by a factor of only 2.33, yet the rate constants in both directions are more than 10^3-fold lower for the nitro compound. This indicates that the intrinsic rate constant[32] for water addition to **2** is about 10^3 lower than for **1** (or the kinetic barrier for **2** is higher than for **1**). A similar conclusion is reached for the OH^- reaction: even though the equilibrium constant for OH^- addition to **2** is 32 times larger than for **1**, the rate constant is 6.1 times *smaller*. Or in the reverse direction **1** is favored thermodynamically compared to **2** by a factor of 32, but kinetically it is favored much more, namely by a factor of 1.96×10^3.

Recently we reported that the intrinsic rate constants for addition of amine nucleophiles to activated olefins decrease (or the kinetic barriers increase) as the activating substituents become more effective in delocalizing negative charge, e.g., k(cyano) > k(alkoxycarbonyl) > k(nitro).[34] We pointed out that this is the same trend that is generally observed in the deprotonation of carbon acids activated by the same substituents (see eq 14 and 15). The present results provide additional support for this proposition. The intrinsic rate constant for deprotonation (k when $\Delta pK = 0$) of Meldrum's acid in water is $\approx 4 \times 10^3$ M^{-1} s^{-1}[30], while for the deprotonation of 1,1-dinitroethane it is ~ 7 M^{-1} s^{-1} in water[35] and ≈ 40 M^{-1} s^{-1} in 50% Me_2SO–50% water[19] (see also Figure 7). It appears from these numbers that the difference in the intrinsic rate constants for nucleophilic addition to **1** and **2** is in the same order of magnitude (10^2–10^3) as the difference in the intrinsic rate constants for deprotonation of Meldrum's acid and 1,1-dinitroethane, respectively.[36]

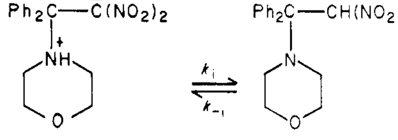
Carbon Protonation of T_{OH}^-. Rate constants for protonation of T_{OH}^- on carbon by the hydronium ion, chloroacetic acid, formic acid, acetic acid, 2,4,6-trimethylphenol, and water have been determined. In conjunction with the pK_a of T_{OH}^0 (5.5) the corresponding rate constants for the deprotonation of T_{OH}^0 were also obtained. The results are summarized in Table IV. Figure 7 shows an Eigen[13] plot of log k_2^{BH} vs. ΔpK along with a similar plot for the protonation of 1,1-dinitroethane anion ($pK_a = 5.00$) in the same solvent.[37] It is noteworthy that all points for the protonation of T_{OH}^- deviate positively from the Eigen plot defined by the 1,1-dinitroethane anion, implying a higher intrinsic rate of proton transfer for T_{OH}^-. The deviations amount to 0.4–0.6 log unit for the buffer acids, 0.9 unit for water, and 1.0 unit for H_3O^+.[38]

These deviations can be understood in the following terms. The Ph_2COH moiety in T_{OH}^- hinders the establishment of coplanarity of the two nitro groups in the anion to a greater extent than the methyl group in 1,1-dinitroethane anion, as is clearly apparent from molecular models. As a consequence there is less delocalization of charge into the nitro groups and more negative charge remaining on carbon. This has two effects.

(a) The basicity of the anion increases,[39] as is borne out by the higher pK_a of T_{OH}^0 (5.5) compared to that of 1,1-dinitroethane (5.00). The basicity enhancing effect is probably much larger than suggested by this pK_a difference because the Ph_2COH moiety is electron withdrawing compared to a methyl[40] group and thus, in absence of a steric effect, T_{OH}^- should be *less* rather than more basic than the 1,1-dinitroethane anion.

(b) The increased negative charge which is localized on carbon lowers the intrinsic barrier for the proton transfer in the same way as the change to a less delocalizing substituent[42,43] does and thus enhances the intrinsic rate, as observed. The fact that the deviations from the Eigen plot for 1,1-dinitroethane anion (Figure 7) are relatively larger for the small acids H_3O^+ and water and smaller for the larger buffer acids shows that there is also a *direct* steric effect that hinders the approach of the acid to the carbanionic site of T_{OH}^-, but apparently it is not large enough to compensate for the rate enhancement due to steric hindrance of charge delocalization.

Our data on the carbon protonation of T_{OH}^- allow a further conclusion. They show that the intramolecular pathway (k_i–k_{-i} in Scheme I) is insignificant; if it were significant the rate constant for protonation of T_{OH}^- by water ($k_2^{H_2O}$) would have to show an abnormally large positive deviation from the Eigen plot of the 1,1-dinitroethane anion (Figure 7). This is an interesting conclusion because in the case of **3** the intramolecular proton switch is a very significant pathway.[8a] As is discussed in a forthcoming



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paper,[44] the incidence or absence of a significant intramolecular pathway in the proton transfer between carbon and nitrogen or oxygen depends primarily on the pK_a of the oxygen or nitrogen group, and on the pH range investigated. The intramolecular pathway becomes generally more important when this pK_a is close to neutrality (as in **3** whose $pK_a^{NH^+} \sim 4$[8a]); when the pK_a is at an extreme of the pH scale (as for T_{OH}^- where $pK_a^{OH} > 16$[45]) the *inter*molecular pathway is faster.

Base-Catalyzed Breakdown of T_{OH}^0. The results for τ_3^{-1}, which refers to reaction 9 and in particular the Brønsted plot in Figure

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[32] In the Marcus[33] sense the intrinsic rate constant is defined as the rate constant when $K_1 = 1$ ($\Delta G^\circ = 0$).

[33] (a) Marcus, R. A. *J. Phys. Chem.* **1968**, *72*, 891; (b) Cohen, A. O.; Marcus, R. A. *Ibid.* **1968**, *72*, 4249; (c) Marcus, R. A. *J. Am. Chem. Soc.* **1969**, *91*, 7224; (d) Hine, J. *Adv. Phys. Org. Chem.* **1977**, *15*, 1.

[34] Bernasconi, C. F.; Fox, J. P.; Fornarini, S. *J. Am. Chem. Soc.* **1980**, *102*, 2810.

[35] Bell, R. P.; Tranter, R. L. *Proc. R. Soc. London, Ser. A* **1974**, *337*, 518.

[36] It should be noted that the lower intrinsic rate constant for the nitro compound is *not* due to the different solvent since the addition of 50% Me_2SO tends to *increase* rather than decrease the intrinsic rate (Bernasconi, C. F.; Grodzinski, L. J., unpublished observations), just as in proton transfers.[19]

[37] Some of the rate constants and pK_a values for the protonation of 1,1-dinitroethane anion reported earlier[19] have been redetermined. In a few instances the new values were found to differ slightly from the published ones, typically 20–50%. The revised data are summarized in Table VII. None of the conclusions reached earlier[19] are changed in any way.

[38] The manner by which the plots in Figure 7 are presented implies that we interpret them as curved. They could also be interpreted as straight lines defined by the buffer catalysts with the water and H_3O^+ points deviating negatively.[35] The two interpretations have vastly different theoretical implications, but in the present context a choice between the two is not necessary.

[39] The pronounced sensitivity of the pK_a of 1,1-dinitroalkanes to steric effects has been noted by several authors; see, e.g., (a) Sitzmann, M. E.; Adolph, H. G.; Kamlet, M. J. *J. Am. Chem. Soc.* **1968**, *90*, 2815; (b) Tselinskii, I. V.; Kosmynina, A. S.; Dronov, V. N.; Shokor, I. N., *Org. React.* **1970**, *7*, 20; (c) ref 18.

[40] σ^* for Ph_2COH does not appear to be known, but σ^* for Ph_2CH is 0.40 and σ^* for CH_2OH is 0.56;[41] in contrast σ^* for CH_3 is 0.[41]

[41] Taft, R. W. In "Steric Effects in Organic Chemistry"; Newman, M. S., Ed.; Wiley: New York, 1956; Chapter 13.

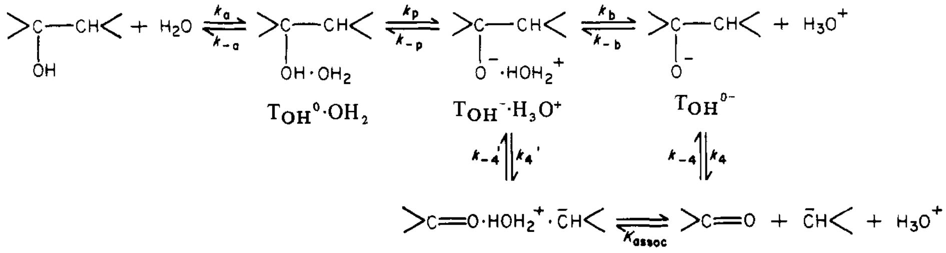
[42] Bell, R. P. "The Proton in Chemistry"; Cornell University Press: Ithaca, NY, 1973; p 212.

[43] Kresge, A. J. *Acc. Chem. Res.* **1975**, *8*, 354.

[44] Bernasconi, C. F.; Hibdon, S. A.; McMurry, S. E., manuscript in preparation.

[45] Estimated.

Scheme II



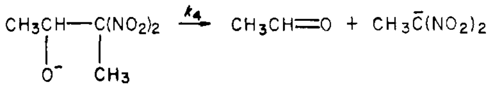
6, were shown in the Results section to be consistent with rate-limiting deprotonation of the OH group of $T_{OH}{}^0$ by OH^- ($k_3{}^{OH}$) and by buffer bases ($k_3{}^B$). The rate constants are summarized in Table V.

The $pK_a{}^{OH}$ of the OH group of $T_{OH}{}^0$ can now be estimated as follows. The reactions $T_{OH}{}^{0-} + BH \rightarrow T_{OH}{}^0 + B^-$ with acetic, formic, and chloroacetic acids are expected to be diffusion controlled, each with a rate constant $k_{-3}{}^{BH}$ in the order of $\sim 2 \times 10^9$ $M^{-1}\ s^{-1}$ in our solvent.[27] Thus $K_a{}^{OH}$ can be calculated as $K_a{}^{OH} = K_a{}^{BH}k_3{}^B/k_{-3}{}^{BH} = K_a{}^{BH}k_3{}^B/2 \times 10^9$, where $K_a{}^{BH}$ is the acidity constant of the buffer. One obtains $K_a{}^{OH} = 6.0 \times 10^{-14}$, 7.0×10^{-14}, and 2.4×10^{-14} based on chloroacetic, formic, and acetic acids, respectively, with an average value of 5.1×10^{-14} ($pK_a{}^{OH} = 13.3$).[46] Combining $pK_a{}^{OH}$ with $k_3{}^{OH}$ and $k_3{}^B$ (B = pyridine bases) now affords $k_{-3}{}^{H_2O}$ and $k_{-3}{}^{BH}$ (BH = pyridinium ions), as reported in Table V. The higher $k_{-3}{}^{BH}$ values (7.9×10^9 to $1.26 \times 10^{10}\ M^{-1}\ s^{-1}$) for the pyridinium ions compared to $k_{-3}{}^{BH}$ for the carboxylic acids are expected on electrostatic grounds.[13]

The fact that oxygen deprotonation of $T_{OH}{}^0$ is rate limiting implies $k_4 >> k_{-3}{}^{H^+}a_{H^+} + k_{-3}{}^{H_2O} + k_{-3}{}^{BH}[BH]$ (eq 9). Since the buffer plots of $\tau_3{}^{-1}$ (Figure 5) do not shown any curvature, this inequality must hold up to the highest concentration of BH used, which was 0.25 M in the case of 4-picoline. With $k_{-3}{}^{BH} \approx 8 \times 10^9\ M^{-1}\ s^{-1}$ for 4-picoline we thus have $k_{-3}{}^{BH}[BH] \approx 2 \times 10^9\ s^{-1}$ and therefore $k_4 >> 2 \times 10^9\ s^{-1}$.

This then confirms earlier findings that tetrahedral addition complexes between weakly basic carbanions and aldehydes or ketones can break down very rapidly, sometimes approaching and perhaps surpassing the limit for diffusional separation.[2,3] For comparison, ammonia departure from $Ph_2C(O^-)NH_3{}^+$ has an estimated rate constant of 10^6–$10^7\ s^{-1}$;[49] using Sayer's[49] method one can estimate a rate constant of 10^9–$10^{10}\ s^{-1}$ for the departure of an amine of the same basicity as $CH(NO_2)_2{}^-$. This comparison suggests that in this carbonyl-forming elimination a carbanion and an amine of the same pK_a leave at comparable rates. More work is in progress to test the possible generality of this behavior, which is in dramatic contrast to that of olefin-forming elimination reactions (ElcB).[50]

It should be noted that not all reactions of tetrahedral intermediates are quite as fast as those of $T_{OH}{}^{0-}$ derived from **1** and **2**. For example, for the reaction shown in eq 17 $k_4 \approx 2 \times 10^5$



$$CH_3CH(O^-){-}C(NO_2)_2(CH_3) \xrightarrow{k_4} CH_3CH{=}O + CH_3\bar{C}(NO_2)_2 \quad (17)$$

7

s^{-1} in water,[48] which is more than 4 orders of magnitude lower than for $T_{OH}{}^{0-}$ derived from **2**. There are several factors that probably all contribute to this large difference in rates. (a) 1,1-Dinitroethane anion is a more basic leaving group than dinitromethane by almost 2 pK units. (b) The interaction of two phenyl groups with two nitro groups in $T_{OH}{}^{0-}$ leads to a steric acceleration that is likely to be larger than the steric acceleration provided by the interaction of one methyl group with the bulkier leaving group in **7**; the phenyl groups are also likely to increase the rate by an increased "push" owing to the developing resonance with the C=O bond being formed.[51] (c) Just as the intrinsic rate of carbon proton transfer for dinitromethane is higher than for 1,1-dinitroethane,[52] the same is probably true for the intrinsic leaving group reactivities.

Water-Catalyzed Breakdown of $T_{OH}{}^0$. That the water-catalyzed breakdown of $T_{OH}{}^0$ must proceed by a different mechanism (k_3' in eq 9) is best seen by considering the reaction in the reverse direction. If the water reaction were a simple deprotonation of $T_{OH}{}^0$ ($k_3{}^{H_2O}$), $k_{-3}{}^{H^+}$ in the reverse direction would have to be $1.41 \times 10^{12}\ M^{-1}\ s^{-1}$ based on the pK_a of $T_{OH}{}^0$. This value is about 2 orders of magnitude higher than the expected rate constant for diffusion-controlled protonation of an alkoxide ion by the hydronium ion in our solvent.[53,55]

The solvent isotope effect, $k_0'(H_2O)/k_0'(D_2O) = 2.4$ is also inconsistent with simple deprotonation because in such a case the isotope effect would take on the meaning $k_3{}^{H_2O}/k_3{}^{D_2O}$, which is equivalent to $(K_a{}^{OH}/K_a{}^{OD})(k_{-3}{}^H/k_{-3}{}^D)$. $K_a{}^{OH}/K_a{}^{OD}$, the ratio of the acidity constant of $T_{OH}{}^0$ in the two isotopic solvents, is expected to be between 4 and 6,[14] while $k_{-3}{}^H/k_{-3}{}^D$ must be ≈ 1.23, the value expected for a diffusion-controlled reaction.[56] Hence one calculates $k_3{}^{H_2O}/k_3{}^{D_2O} \sim 5$–$7.5$, which is much higher than the experimental value of 2.4.

There are several mechanistic possibilities for the k_3' step. The solvent isotope effect of 2.4 suggests that motion of the proton is involved in the transition state and thus excludes a simple rate-limiting breakdown of $T_{OH}{}^0$ into $CH(NO_2)_2{}^-$ and $Ph_2C{=}OH^+$.[57] One reasonable possibility is that oxygen deprotonation of $T_{OH}{}^0$ by water is concerted with C–C bond cleavage (**8**), possibly with simultaneous, or nearly simultaneous, carbon protonation (**9**). Transition state **8** is analogous to the one postulated for

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(46) A different method for estimating $pK_a{}^{OH}$ is based on a Taft correlation, which in water is given by $pK_a = 17.03 - 1.32\ (\sigma^*{}_R + \sigma^*{}_{R'} + \sigma^*{}_{R''})$ for alcohols of the type RR′R″COH.[47] Using 0.6 for $\sigma^*{}_{Ph}$[41] and 2.76 as σ^* for the 1,1-dinitromethyl group,[48] one obtains $pK_a = 11.8$. Assuming that the pK_a in 50% Me_2SO–50% water increases by nearly the same amount as pK_w, one then obtains a $pK_a{}^{OH}$ value close to the kinetic one of 13.3.

(47) Guthrie, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 5892.

(48) Hine, J. *J. Am. Chem. Soc.* **1971**, *93*, 3701.

(49) Sayer, J. M.; Conlon, P. *J. Am. Chem. Soc.* **1980**, *102*, 3592.

(50) Stirling, C. J. M. *Acc. Chem. Res.* **1979**, *12*, 198.

(51) That the effect of the two phenyl groups may be quite large is suggested by the fact that the equilibrium constant for water addition to the carbonyl group of benzophenone is 10^7 smaller than for acetaldehyde; Guthrie, J. P., *Can. J. Chem.* **1978**, *56*, 962.

(52) For $RCH(NO_2)_2 + H_2O\ (k_{H_2O}) \rightleftharpoons (k_{H^+})\ R\bar{C}(NO_2)_2 + H_3O^+$, $k_{H_2O} = 7.1 \times 10^{-1}\ s^{-1}$ and $k_{H^+} = 2.1 \times 10^3\ M^{-1}\ s^{-1}$ for R = H,[18] $k_{H_2O} = 1.33 \times 10^{-3}\ s^{-1}$ and $k_{H^+} = 2.31 \times 10^2\ M^{-1}\ s^{-1}$ for R = CH_3.[35] That is, k_{H_2O} for R = H is 530 times faster than for R = CH_3 even though the acidity constant is only 78 times higher, while k_{H^+} for R = H is 9.1 times higher than for R = CH_3 despite the lower basicity of the anion with R = H.

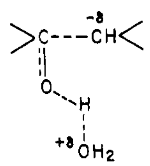
(53) In water at 25 °C ($\eta = 0.89$)[54] this is about 3–$5 \times 10^{10}\ M^{-1}\ s^{-1}$;[13] in 50% Me_2SO–50% water at 20 °C ($\eta = 3.45$ cp)[29] this reduces to $\sim 10^{10}\ M^{-1}\ s^{-1}$.

(54) Riddick, J. A.; Bunger, W. B. In "Techniques of Chemistry", Vol. 2; Wiley-Interscience: New York, 1970; p 67.

(55) For the water reaction of $T_{OH}{}^0$ derived from **1** a similar deviation from the Brønsted line was observed and several possible interpretations were offered.[2] Since here $k_{-3}{}^H$ calculated on the assumption that $k_3' = 0$ gives a value of $\sim 2 \times 10^{13}\ M^{-1}\ s^{-1}$, which again is much larger than the rate constant for a diffusion-controlled reaction, it is now clear that the correct explanation is in terms of the k_3' mechanism, just as for the reaction of **2**.

(56) Corresponds to ratio of diffusion coefficients in H_2O and D_2O, respectively; Mills, R. "Molecular Motions in Liquids"; Lascombe, J., Ed.; Reidel: Dordrecht, Holland, 1974; p 391.

(57) The secondary isotope effect for such a breakdown is expected to be ≤ 1.5.[58]



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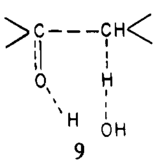

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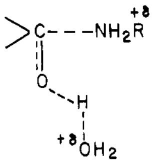

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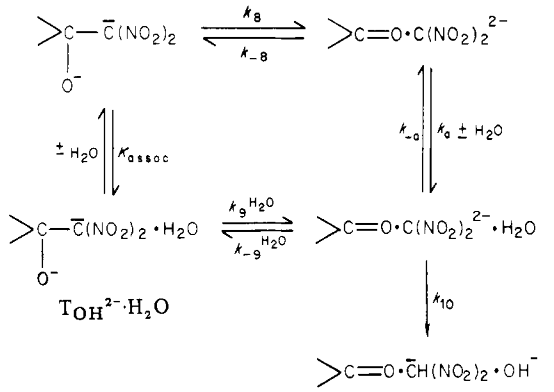
water-catalyzed breakdown of nitrogen protonated carbinolamines (**10**).[59]

Another mechanism is shown in Scheme II. Here deprotonation and C–C bond cleavage occur in separate steps but with $k_4' > k_b$ so that C–C bond cleavage takes place before H_3O^+ has diffused away from the encounter complex (k_b).[60] Since this mechanism requires that in the reverse direction there is a preassociation between the ketone, the carbanion, and the acid before nucleophilic addition (k_{-4}') occurs, this is known as "preassociation mechanism";[60b] note that the top horizontal line is simply the Eigen[13] mechanism for proton transfer. It should be noted that since this mechanism implies $k_4' >(>>) k_b$ it should not only prevail for the water reaction but for the buffer-catalyzed pathways (H_3O^+ replaced by HB in Scheme II) as well. The fact that the Brønsted β value for buffer catalysis is 0.93 instead of 1.0 would be consistent with k_4' being rate limiting and with a transition state that is stabilized by hydrogen bonding.[61]

There are three problems with this mechanism. (1) The large positive deviation of the water point from the Brønsted plots (Figure 6) would have to be accounted for by an exceptionally strong hydrogen bonding stabilization by H_3O^+ compared to that provided by the buffer acids. The nature of this extra stabilization is obscure; if it were of electrostatic origin, the water point should be on, or close to, the Brønsted line defined by the pyridine bases.[62a] (2) The condition $k_4' >(>>) k_b$ requires k_4' to be at least of the order of 10^{11} s^{-1}[13] and k_4 even higher. This would represent a $>10^6$-fold acceleration over reaction 17, which seems too high. (3) If one assumes that the k_4' step is rate limiting ($k_4' << k_{-p}$, Scheme II), the solvent isotope effect of 2.4 appears to be significantly larger than what has been observed in similar situations.[62] The isotope effect would, however, possibly be consistent with k_p being (partially) rate limiting, but this would require $k_4' \gtrsim k_{-p}$, where k_{-p} may be as high as 10^{12}–10^{13} s^{-1},[13b,63] which makes point 2 even more compelling.

We therefore prefer the concerted mechanism with transition state **8**, or possibly **9**. It should be noted that, just as in the case of carbinolamine breakdown,[59] this mechanism is *not* "enforced" by a lifetime of an intermediate (T_{OH}^-) too short for it to exist.[60] The fact that the water-catalyzed and base-catalyzed pathways proceed by two different mechanisms is best understood in terms of a competition between two reactions that are available to T_{OH}^0: oxygen deprotonation and (concerted) breakdown. If the base is sufficiently strong, deprotonation is faster than breakdown and it will be the major pathway, as is the case for the buffer bases and hydroxide ion. If the base is very weak, deprotonation is too slow and breakdown becomes favorable, as is the case when water is the only available base. It should be noted that breakdown will only become competitive with deprotonation by a weak base if there is a large driving force for breakdown. In the case of T_{OH}^0 derived from **2** the driving force comes from a combination of a good leaving group and a strong push by the two phenyl groups; in T_{OH}^0 derived from **1**[2] it appears to be mainly the good leaving group.

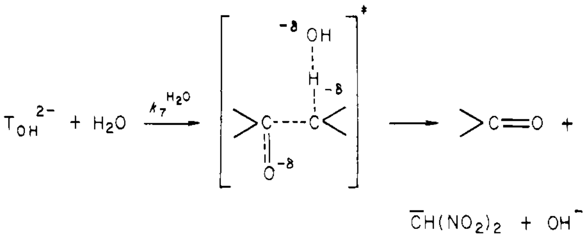
Scheme III



Breakdown of T_{OH}^{2-}. The solvent isotope effect for the 2,4,6-trimethylphenol-catalyzed breakdown of T_{OH}^{2-}, k_6^{BH}/k_6^{BD} = 3–5, was shown (see the Results section) to be consistent with rate-limiting carbon protonation of T_{OH}^{2-} followed by rapid breakdown of T_{OH}^{0-} into $Ph_2C{=}O$ and $CH(NO_2)_2^-$. On the other hand, the water-catalyzed breakdown does not seem to involve rate-limiting carbon protonation, as is indicated by the much smaller solvent isotope effect estimated to be between 0.8 and 1.7.

Four possible mechanisms for the water-catalyzed breakdown suggest thermselves. (1) T_{OH}^{2-} breaks down unimolecularly into $Ph_2C{=}O$ and $C(NO_2)_2^{2-}$ followed by rapid protonation of $C(NO_2)_2^{2-}$. No significant isotope effect is expected for this mechanism, which may or may not be consistent with our data. It should be noted, though, that $C(NO_2)_2^{2-}$ is likely to be a very unstable species, which may not have a long enough lifetime to exist as a discrete intermediate under the experimental conditions.[64]

(2) T_{OH}^{2-} forms products by a concerted process thereby avoiding the creation of the unstable $C(NO_2)_2^{2-}$. A $k_7^{H_2O}/k_7^{D_2O}$ value close to the lower limit of 0.8 would be difficult to reconcile with this mechanism, but if $k_7^{H_2O}/k_7^{D_2O}$ was close to the upper limit of 1.7, a concerted reaction with an asymmetric transition state (or one where there is strong coupling between motions of the protons and heavy atoms)[16] is a real possibility. For example, the cleavage of the 1-phenylcyclopropanolate ion, a reaction very similar to eq 18, is almost certainly concerted and has an isotope effect of 1.9.[65]



(18)

(3) A third possibility is that T_{OH}^{2-} breaks down by a preassociation mechanism.[60b,65] This mechanism, which in Scheme III is represented by the pathway going through $T_{OH}^{2-}{\cdot}H_2O$, would prevail if $C(NO_2)_2^{2-}$ can exist as a discrete species, but the rates of its reaction with $Ph_2C{=}O$ to form T_{OH}^{2-} (k_{-8}) or $T_{OH}^{2-}{\cdot}H_2O$ ($k_{-9}^{H_2O}$) and of its protonation by water (k_{10}) are faster than the diffusional processes k_a and k_{-a}.[60] That this mechanism is "enforced"[60b] under the stated conditions is best appreciated by considering the reaction in the reverse direction. If $k_{-9}^{H_2O} >> k_{-a}$, the encounter complex $>C{=}O{\cdot}C(NO_2)_2^{2-}{\cdot}H_2O$ must revert preferentially to $T_{OH}^{2-}{\cdot}H_2O$ ($k_{-9}^{H_2O}$). By virtue of the principle of microscopic reversibility the same pathway will then be followed

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[58] Schowen, R. L. *Progr. Phys. Org. Chem.* **1972**, *9*, 275.

[59] (a) Rosenberg, S.; Silver, S. M.; Sayer, S. M.; Jencks, W. P. *J. Am. Chem. Soc.* **1974**, *96*, 7986; (b) Sayer, S. M.; Pinsky, B.; Schonbrunn, A.; Washtien, W. *Ibid.* **1974**, *96*, 7998.

[60] (a) k_a and k_{-a} refer to diffusional steps, but since they involve the solvent which is already part of the solvation shell, this diffusion is more aptly described as a reorientation of the solvent than a translational motion. The same considerations apply to K_{assoc} in Scheme III. (b) Jencks, W. P. *Acc. Chem. Res.* **1976**, *9*, 425; **1980**, *13*, 161.

[61] This hydrogen bonding stabilization must be understood as relative to the $T_{OH}^0{\cdot}OH_2$ state (Scheme II), i.e., it is the result of a small destabilization of the transition state of the k_4' step relative to $T_{OH}^{0-}{\cdot}H_3O^+$ (slight lowering of k_4') compensated for by a larger stabilization of the $T_{OH}^{0-}{\cdot}H_3O^+$ state relative to $T_{OH}^0{\cdot}OH_2$ (large enhancement of $K_p = k_p/k_{-p}$).

[62] (a) Ewing, S. P.; Lockshon, D.; Jencks, W. P. *J. Am. Chem. Soc.* **1980**, *102*, 3072; (b) Gilbert, H. F.; Jencks, W. P. *Ibid.* **1977**, *99*, 7931.

[63] Kreevoy, M. M.; Mead, C. A. *Discuss. Faraday Soc.* **1965**, *39*, 166.

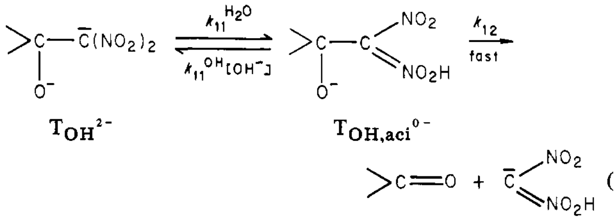
[64] Dilithium salts of nitroalkane dianions have been prepared from nitroalkanes and *n*-butyllithium; Seebach, D.; Lehr, F. *Helv. Chim. Acta* **1979**, *62*, 2239.

[65] Thibblin, A.; Jencks, W. P. *J. Am. Chem. Soc.* **1979**, *101*, 4963.

in the forward direction ($k_9^{H_2O}$).

With $k_9^{H_2O}$ as the rate-limiting step and assuming a negligible solvent isotope effect on K_{assoc}, the estimated isotope effect of 0.8–1.7 would refer to $k_9^{H_2O}/k_9^{D_2O}$. A value of the isotope effect close to unity would in fact be consistent with a rate-limiting $k_9^{H_2O}$ step in which there is some transition-state stabilization by hydrogen bonding to the negative carbon. This situation would resemble one suggested for the cleavage of the 1,2-diphenylcyclopropanolate ion.[65] A referee has suggested that the k_{10} step could possibly be rate limiting. It seems to us that the observed isotope effect is too small to be consistent with such a proposition.

(4) A fourth possibility, suggested by Hoz,[66] is that rate-limiting protonation by water occurs on the oxygen of a nitro group. Even though the solvent isotope effect is compatible with this mechanism, it can be rejected on the following grounds. (a) From the value of 0.21 for k_{OH} (Table II) (which takes on the meaning $k_{OH} = K_5^{OH}k_{11}^{H_2O}$) and an estimated value of <1 for K_5^{OH}[67] (Scheme I), one obtains $k_{11}^{H_2O} > 0.2\ s^{-1}$, while deprotonation of $T_{OH,aci}^{0-}$ is expected to be diffusion controlled with $k_{-11}^{OH} \sim 2 \times 10^9\ M^{-1}\ s^{-1}$.[27] Hence from $k_{-11}^{OH}/k_{11}^{H_2O} < 10^9\ M^{-1}$, one obtains a p$K_a$ value for $T_{OH,aci}^{0-} > 7$. The pK_a of the aci form of 1,1-dinitroethane is <1;[68] the pK_a of the aci form of T_{OH}^0 [$Ph_2C(OH)C(NO_2)NO_2H$] is likely to be lower still because the negative charge in the anion (T_{OH}^-) appears to be more localized on carbon than is the case for the anion of 1,1-dinitroethane (see under "Carbon Protonation of T_{OH}^-"). Thus the estimated lower limit of the pK_a value for $T_{OH,aci}^{0-}$ of 7 implies that conversion of the OH group into O^- raises the pK_a of the aci form by more than 6 units. This is unlikely considering that there are four atoms separating the substituent from the reaction site.



T_{OH}^{2-} $T_{OH,aci}^{0-}$ (19)

(b) The mechanism of eq 19 requires that $k_{12} >> k_{-11}^{OH}[OH^-]$; since the highest [$OH^-$] used was nearly 1 M, this requires $k_{12} >> 10^9\ s^{-1}$. This would imply that the k_{12} process (eq 19) is about as favorable as the k_4 process (Scheme I or eq 9) even though in the latter a much more stable form of the dinitromethane anion is produced. This is again unlikely.

On the basis of the available evidence, mechanism 4 can therefore be excluded but a definite choice between mechanisms 1–3 cannot be made, although we slightly favor the preassociation mechanism. Regardless of the exact mechanism it is noteworthy that, just as the water-catalyzed breakdown of T_{OH}^0 (k_3' in eq 9) appears to proceed by a different mechanism than the base-catalyzed reactions, the water-catalyzed breakdown of T_{OH}^{2-} seems to follow a different pathway than the acid-catalyzed process. Again this dichotomy is best understood as a competition between two possible reactions that are available to T_{OH}^{2-}: carbon protonation and breakdown. If an acid of sufficiently high acidity is available, carbon protonation will be faster than breakdown and thus will be the major pathway, as is the case with 2,4,6-trimethylphenol. If the only available acid is very weak (water), protonation is slow and breakdown competes favorably with protonation.

Experimental Section

Materials. 1,1-Dinitro-2,2-diphenylethylene was a gift from Professor Zvi Rappoport. Phenol, K_2HPO_4, nicotinamide, and acetic, formic, and chloroacetic acids were reagent grade and were used without further purification. 2,4,6-Trimethylphenol (Aldrich purum) was decolorized by boiling with charcoal in ether. After filtration and evaporation of the ether, petroleum ether (30–60 °C) was added, and the mixture was heated until complete solution occurred and cooled to ice temperature. 2,4,6-Trimethylphenol crystals were obtained with mp 71.5 °C (lit. mp 72 °C[69]); fresh 0.1–0.5 M stock solutions in pure Me_2SO were prepared every other day. Reagent grade dimethyl sulfoxide was stored over 4A molecular sieves prior to use. D_2O used contained 99.8% deuterium.

Reaction Solutions, pH and pK_a Determinations. The procedures described earlier[8a] were used.

Spectra. The spectrum of 1,1-dinitro-2,2-diphenylethylene (**2**) was known.[8a] The spectra of benzophenone and of the hydrolysis products (benzophenone plus dinitromethane anion) were obtained on a Cary 14 spectrophotometer. The spectrum of T_{OH}^- was measured in a Gilford kinetic spectrophotometer after injecting 15 μL of a 2.4×10^{-2} M Me_2SO–solution of **2** into a cuvette containing 3 mL of a 4×10^{-3} M KOH solution in 50% Me_2SO–50% water. By suitable extrapolation of the OD vs. time curve (correction for loss of T_{OH}^- due to hydrolysis) $\epsilon_{T_{OH}^-}$ at a given wavelength was thus obtained. This procedure was repeated at various wavelengths from 260 to 360 nm at 5-nm intervals and from 360 to 500 nm at 10-nm intervals.

The spectrum of T_{OH}^0 could not be measured directly because under no experimental conditions could a solution be obtained that contained T_{OH}^0 as the exclusive or major species. T_{OH}^0 is produced in pH-jump experments in competition with small amounts of **2** (eq 10). However, the solution contains additional amounts of **2** because of nonquantitative conversion of **2** into T_{OH}^- during "incubation" in basic solution and also significant amounts of benzophenone and dinitromethane because during incubation part of T_{OH}^- is converted into these products. By performing the pH-jump under carefully controlled conditions (known time of incubation before jump), the concentration of the various species could be calculated both immediately before and after the pH-jump from the known rate constants. The OD after the pH-jump was then measured in the stopped-flow spectrophotometer at various wavelengths from 280 to 450 nm at 10-nm intervals. It could be shown that the entire absorption can be attributed to **2** and benzophenone [$CH_2(NO_2)_2$ does not absorb in this range] even though these species accounted for less than 50% of the material balance. This indicates that T_{OH}^0 does not absorb between 280 and 450 nm as would be expected.

Rate Measurements. The slow rates were measured in a Gilford kinetic spectrophotometer and the fast rates in a Durrum-Gibson stopped-flow spectrophotometer. The general procedures were the same as the ones used previously.[8a]

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Supplementary Material Available: Kinetics of hydrolysis (Table S1), kinetics of adduct formation (Table S2), 2,4,6-trimethylphenol buffer catalysis in 50% Me_2SO–50% H_2O (Table S3), 2,4,6-trimethylphenol buffer catalysis in 50% Me_2SO–50% D_2O (Table S4), kinetics of 2,4,6-trimethylphenoxide ion addition (Table S5), pH-jump kinetic experiments (Table S6) (8 pages). Ordering information is given on any current masthead page.

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[66] Hoz, S., personal communication.

[67] k_{obsd} does not significantly level off even at [OH^-] of 0.5 and 0.7 M, indicating $K_5^{OH} < 1$.

[68] See footnote 11 in ref 19.

[69] Lange, N. A., Ed. "Lange's Handbook of Chemistry", McGraw-Hill: New York, 1967.