J. Am. Chem. Soc. **1991**, *113*, 4937-4946

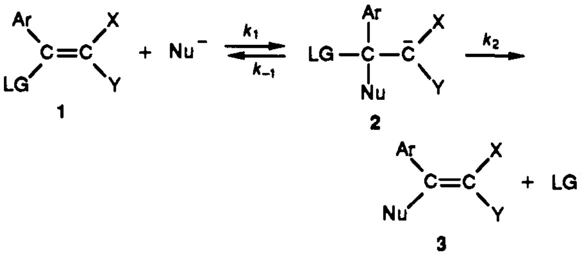
Kinetics of Reactions of Hydroxide Ion and Water with β-X-Substituted α-Nitrostilbenes (X = Cl, I, SEt, OMe, SCH_2CH_2OH) in 50% Me_2SO–50% Water. Search for the Intermediate in Nucleophilic Vinylic Substitution

Claude F. Bernasconi,*[1a] Julianne Fassberg,[1a] Robert B. Killion, Jr.,[1a] David F. Schuck,[1a] and Zvi Rappoport[1b]

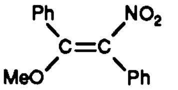
Contribution from Thimann Laboratories, Chemistry Department, University of California, Santa Cruz, California 95064, and the Department of Organic Chemistry, The Hebrew University, Jerusalem 91904, Israel. Received November 15, 1990

Abstract: The hydrolysis of $Ph(LG)C{=}CPh(NO_2)$ (**4-LG**, LG = Cl, I, SEt, OMe) in basic solution yields the anion of 1,2-diphenyl-2-nitroethanone, $PhC({=}O)C({=}NO_2^-)Ph$ (**8⁻**), by the addition–elimination mechanism of nucleophilic vinylic substitution (Scheme I), while the reaction of base with $Ph(SCH_2CH_2OH)C{=}CPh(NO_2)$ (**4-SCH₂CH₂OH**) leads to a cyclic intermediate (**7⁻**) by intramolecular nucleophilic attack by the ionized OH group (eq 6). The intermediate **4-(LG,OH)⁻** along the substitution path of **4-LG** could not be observed, irrespective of LG. With the good leaving groups of Cl, I, and SEt this is not surprising, but with OMe one would anticipate that formation of the intermediate **4-(OMe,OH)⁻** is much faster than its conversion to products by loss of MeO^-. It is concluded that **4-(OMe,OH)⁻** does not accumulate to detectable levels due to pathways other than unimolecular loss of MeO^- from **4-(OMe,OH)⁻** that lead to products. These pathways are deprotonation of the OH group, followed by collapse of the much more reactive dianion **4-(OMe,O⁻)⁻** to products and/or intramolecular acid catalysis of MeO^- departure from **4-(OMe,OH)⁻** by the OH group (Scheme IV). Our conclusions are applicable to S_NAr reactions and shed new light on why the anionic σ-complex intermediate in the reaction of 2,4,6-trinitroanisole with OH^- has never been observed. When the cyclic intermediate 7^- is treated with acid, protonation on carbon occurs (**7-CH**) which at low pH is preceded by a fast protonation on the nitro group to form the nitronic acid **7-NOH**; **7-CH** is subsequently transformed into $Ph(OCH_2CH_2SH)C{=}CPh(NO_2)$ (**4-OCH₂CH₂SH**) via 7^- by acid-catalyzed C–S bond cleavage (Scheme III).

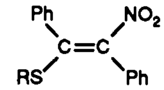
The most common mechanism for nucleophilic vinylic substitution reactions is the addition–elimination mechanism shown in eq 1 for an anionic nucleophile. It is favored by strongly electron withdrawing groups X and/or Y. Until recently, there was no *direct* evidence for the existence of the intermediate **2**, although numerous pieces of *indirect* evidence left little doubt regarding the stepwise nature of the reaction, at least for strongly activated systems.[2,3] Recently we reported the first examples where **2** is not a steady-state intermediate but is directly observable spectrophotometrically, and for which the k_1, k_{-1}, and k_2 were measured separately.[4] They are the reactions of alkanethiolate ions with **4-OMe** and **4-SR** (R = $CH_3CH_2CH_2$ and $HOCH_2CH_2$) in 50% Me_2SO–50% water at 20 °C. So far these are the only reactions that meet the following three necessary conditions for the detectability of the intermediate. (1) The equilibrium of the first step must be favorable, i.e., $k_1[Nu^-]/k_{-1} = K_1[Nu^-] >(\gg) 1$.[5] (2) The formation of the intermediate must be faster than its conversion to products, i.e., $k_1[Nu^-]/k_2 >(\gg) 1$.[5] (3) The absolute magnitude of k_2 must be low enough to allow the detection of **2** by a suitable technique, e.g., by conventional or stopped-flow spectrometry.



(1)



4-OMe



4-SR

In the reactions of alkanethiolate ions with **4-OMe** and **4-SR** a combination of factors contribute to meeting these conditions: The high thermodynamic affinity (high K_1) and nucleophilicity (high k_1) of thiolate ions toward olefins,[3d,6] the low nucleofugality of thiolate ions and especially of methoxide ion[7] (low k_2), the strong stabilization of the negative charge by X, Y = Ph, NO_2[6b] (high K_1, low k_2), and the low intrinsic rate of nitronate ion forming/consuming reactions[8] (low k_2). In fact, in the reaction of $HOCH_2CH_2S^-$ with **4-OMe**[4] ($K_1 = 7.65 \times 10^3$ M^{-1}, $k_1 = 3.90 \times 10^2$ M^{-1} s^{-1}, $k_2 = 9.6 \times 10^{-6}$ s^{-1}) the three conditions are so amply met, even at low nucleophile concentrations (e.g., for $[HOCH_2CH_2S^-] = 10^{-3}$ M, $K_1[Nu^-] = 7.65$ and $k_1[Nu^-]/k_2 = 4.06 \times 10^4$), that one might anticipate the observation of an intermediate in the reaction of **4-OMe** with weaker nucleophiles.

Consequently we recently studied the reaction of **4-OMe** with aliphatic amines hoping to detect an intermediate.[9] The considerably lower nucleophilicity and thermodynamic affinity of amines than thiolate ions[6b] toward olefins should make detection of an intermediate more difficult. However, with piperidine as the nucleophile, $k_1 = 1.01$ M^{-1} s^{-1}[9] is only 386-fold lower than $k_1 = 3.90 \times 10^2$ M^{-1} s^{-1} for $HOCH_2CH_2S^-$,[4] so the $k_1[Nu]/k_2$ ratio could still be $\gg 1$ if k_2 did not change significantly. K_1 for piperidine addition was estimated to be $\leq 7.44 \times 10^{-4}$ M^{-1},[9] which would make $K_1[Nu] \ll 1$ under any conditions. However, because

---

[1] (a) University of California. (b) The Hebrew University.

[2] (a) Rappoport, Z. *Adv. Phys. Org. Chem.* **1969**, *7*, 1. (b) Modena, G. *Acc. Chem. Res.* **1971**, *4*, 73. (c) Miller, S. I. *Tetrahedron* **1977**, *33*, 1211. (d) Rappoport, Z. *Acc. Chem. Res.* **1981**, *14*, 7. (e) Rappoport, Z. *Recl. Trav. Chim. Pays-Bas* **1985**, *104*, 309. (f) Shainyan, B. A. *Usp. Khim.* **1986**, *55*, 942.

[3] (a) Rappoport, Z.; Gazit, A. *J. Am. Chem. Soc.* **1987**, *109*, 6698. (b) Rappoport, Z.; Avramovitch, B. *J. Am. Chem. Soc.* **1988**, *110*, 911. (c) Lodder, G.; van Dorp, J. W. J.; Avramovitch, B.; Rappoport, Z. *J. Org. Chem.* **1989**, *54*, 2574. (d) Rappoport, Z.; Topol, A. *J. Org. Chem.* **1989**, *54*, 5967.

[4] Bernasconi, C. F.; Fassberg, J.; Killion, R. B., Jr.; Rappoport, Z. *J. Am. Chem. Soc.* **1989**, *111*, 6862; **1990**, *112*, 3169.

[5] It is assumed that $[Nu^-]_0 \gg [\mathbf{1}]_0$.

[6] (a) Rappoport, Z.; Ladkani, D. *Chem. Scr.* **1974**, *5*, 124. (b) Bernasconi, C. F. *Tetrahedron* **1989**, *45*, 4017. (c) Rappoport, Z. In *Nucleophilicity*; Harris, J. M., McManus, S. P., Eds.; Advances in Chemistry 215; American Chemical Society: Washington, D.C., 1987; p 399.

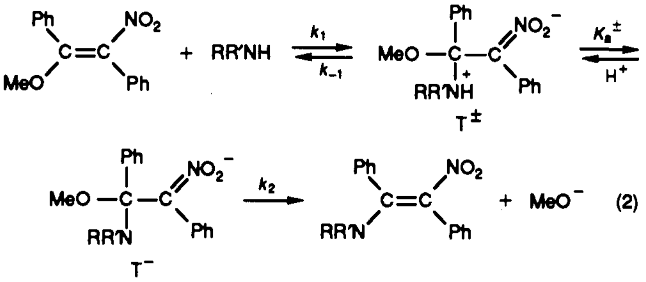
[7] Stirling, C. J. M. *Acc. Chem. Res.* **1979**, *12*, 198.

[8] (a) Bernasconi, C. F. *Tetrahedron* **1985**, *41*, 349. (b) Bernasconi, C. F. *Acc. Chem. Res.* **1987**, *20*, 301.

[9] Bernasconi, C. F.; Fassberg, J.; Killion, R. B., Jr.; Rappoport, Z. *J. Org. Chem.* **1990**, *55*, 4568.

0002-7863/91/1513-4937$02.50/0

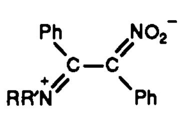
the amine reactions involve a proton-transfer equilibrium ($T^{\pm} \rightleftarrows T^-$, eq 2) the first condition for the T^--form of the intermediate to accumulate is not $K_1[RR'NH] \gg 1$ but $K_1K_a^{\pm}[RR'NH]/a_{H^+} \gg 1$. With $pK_a^{\pm} \approx 7.73$[9] for the acidity of $T^{\pm}$ and assuming K_1



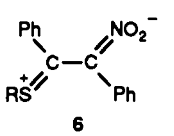
(2)

$\approx 7.44 \times 10^{-4}$ M^{-1} one would obtain $K_1K_a^{\pm}[RR'NH]/a_{H^+} \approx 7.44 \times 10^2$ at pH 14.73 (0.05 M KOH in 50% Me_2SO–50% water) and [piperidine] = 0.1 M. This amply meets the first requirement for detectability of T^-.

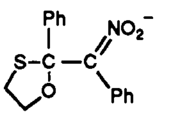
Nevertheless we were unable to detect T^- which remained at steady state levels under all reaction conditions. This was attributed to a large increase in k_2 compared with the thiolate ion reaction, making $k_1[RR'NH]/k_2 < (\ll)$ 1 even at high [RR'NH]. The major factor believed to be responsible for the large increase in k_2 is the strong "push" exerted by the amine, due to the developing product resonance (**5**) which is more pronounced for amine products than the corresponding effect in the thiolate products (**6**). There is evidence that the resonance effect (**5**) is almost completely developed in the transition state of the k_2 step in eq 2.[9] A steric factor of the larger piperidine moiety compared to $HOCH_2CH_2S^-$ moiety may also enhance k_2.



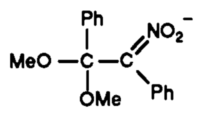
5



6

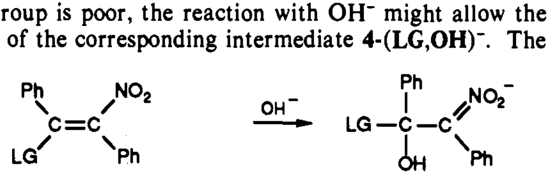


7⁻



4-(OMe,OMe)⁻

We report here on our kinetic studies of the reactions of water and OH^- with several **4-LG** substrates. We hoped that when the leaving group is poor, the reaction with OH^- might allow the detection of the corresponding intermediate **4-(LG,OH)⁻**. The most promising candidate is **4-(OMe,OH)⁻** since, owing to the high basicity of OH^-, K_1 for nucleophilic addition can be expected to be $\gg$1 while k_2 should not be as high as in the reaction of **4-OMe** with amines, due to a smaller push. Surprisingly, **4-(OMe,OH)⁻** could not be detected, but two other intermediates, i.e., **7⁻**, formed by cyclization of **4-SCH₂CH₂OH**, and **4-(OMe,OMe)⁻**, formed by reaction of **4-OMe** with MeO^- in methanol, were easily observed.



4-OMe: LG = OMe	**4-(OMe,OH)⁻**
4-Cl: LG = Cl	**4-(Cl,OH)⁻**
4-I: LG = I	**4-(I,OH)⁻**
4-SEt: LG = SEt	**4-(SEt,OH)⁻**
4-SCH₂CH₂OH: LG = SCH₂CH₂OH	**4-(SCH₂CH₂OH,OH)⁻**

Results

General Features. All results were obtained in 50% Me_2SO–50% water (v/v) at 20 °C. The ionic strength was maintained at 0.5 M with KCl. The kinetic runs were conducted in KOH solutions or in the presence of buffers, thereby assuring pseudo-first-order conditions. With the exception of **4-SCH₂CH₂OH** which leads to the stable cyclic adduct **7⁻**, all substrates are converted to the anion of 1,2-diphenyl-2-nitroethanone, **8⁻**. This anion probably arises from the deprotonation of the nucleophilic substitution product, **4-OH** (eq 3).

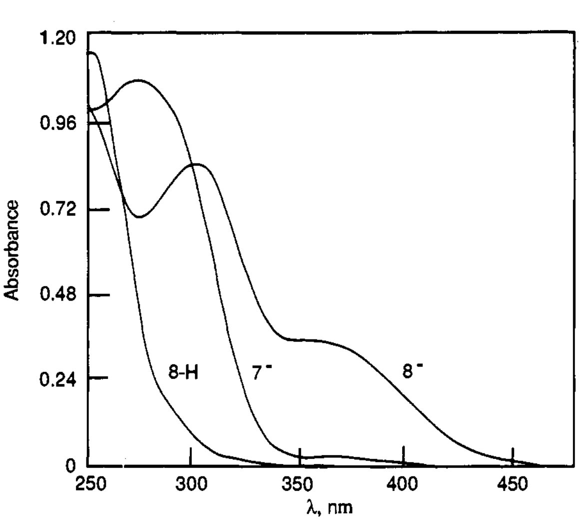
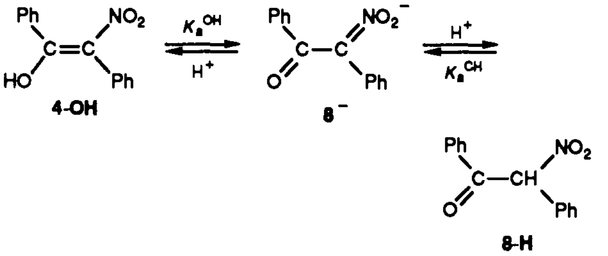


Figure 1. UV-vis spectra of 1,2-diphenyl-2-nitroethanone (**8**-H) in 0.01 M HCl, its anion (**8⁻**) in 0.01 M KOH, and the cyclic complex (**7⁻**) formed by cyclization of **4-SCH₂CH₂OH**. All spectra at 8.33×10^{-5} M substrate, 1 cm path length.



(3)

Absorption spectra of **8**-H and **8⁻** are displayed in Figure 1. The spectrum of **8**-H is very different from that of **4-OMe**, our model for the spectrum of **4-OH**. This shows that the protonated form of **8⁻** is indeed the keto form **8**-H which is much more stable than the enol form **4-OH**. The structure of **8**-H was confirmed by NMR, IR, and mass spectroscopy of an independently synthesized sample, as detailed in the Experimental Section. The absorption spectrum of **8⁻** (Figure 1) generated by deprotonation of the authentic sample of **8-H** was identical with that of product solutions of kinetic runs of the hydrolyses of the various **4-LG**'s. A pK_a^{CH} of 5.21 ± 0.10 for **8**-H was determined by classical photometric procedures, implying that the pK_a of **4-OH** (pK_a^{OH}) must be $\ll$5.21.

Reactions of 4-Cl, 4-I, and 4-SEt. The rates were measured by monitoring the reaction at 300 nm which is close to λ_{max} of the product **8⁻**. The reactions were quite slow and had to be studied at relatively high KOH concentrations (0.1–0.5 M) to get reasonable reaction times. Under these conditions no water reactions were observed and the kinetics are strictly second order, first order each in substrate and in hydroxide ion. The simplest mechanism (for a more elaborate one see Discussion) consistent with these results is that of Scheme I in which **4-(LG,OH)⁻** is a steady-state intermediate and nucleophilic attack by OH^- is rate limiting. Hence the k_{obsd} values (Table S1 of the supplementary material[10]) shown in Figure 2 are given by eq 4. An alternative

$$k_{obsd} = k_1^{OH}a_{OH^-} \quad (4)$$

interpretation in terms of rate-limiting nucleofuge departure is consistent with the rate law ($k_{obsd} = K_1^{OH}k_2a_{OH^-}$ with $K_1^{OH} = k_1^{OH}/k_{-1}^{H_2O}$) but is unattractive because it requires $k_{-1}^{H_2O} \gg k_2$

---

(10) See paragraph concerning supplementary material at the end of this paper.

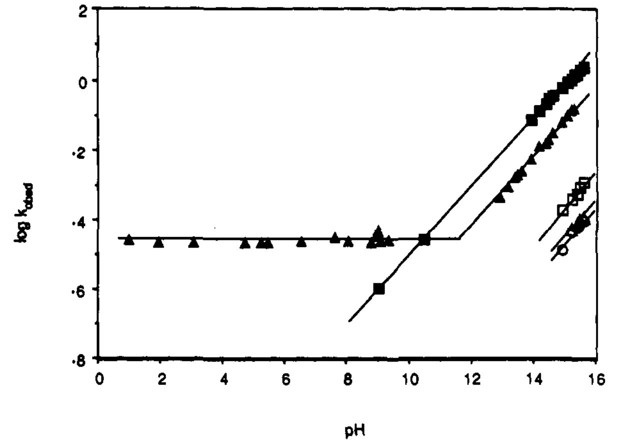


Figure 2. pH–rate profile for the hydrolysis reactions of Ph(LG)C═CPh(NO$_2$) (**4-LG**) with LG = HOCH$_2$CH$_2$S (■), MeO (▲), Cl (□), EtS (△), and I (○).

Scheme I

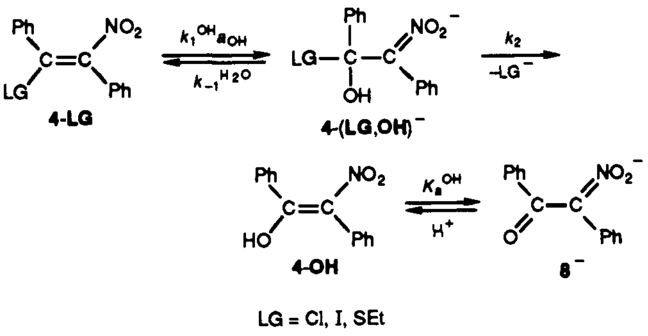


Table I. Summary of Rate Constants for Attack by Various Nucleophiles on Ph(LG)C═CPh(NO$_2$) (**4-LG**) in 50% Me$_2$SO–50% Water at 20 °C, μ = 0.5 M (KCl)

LG	k_1^{OH},[a] M^{-1} s^{-1}	$k_1^{H_2O}$,[a] s^{-1}	$k_1^{HOCH_2CH_2S^-}$,[b] M^{-1} s^{-1}	k_1^{Pip},[c] M^{-1} s^{-1}
H	0.219[d]	5.88×10^{-7}[d]	5.81×10^{4}[e]	1.17×10^{2}[f]
OMe	0.691	2.37×10^{-5}[h]	3.90×10^{2}	1.01
Cl	2.53×10^{-3}		37.8	1.81×10^{-2}
SEt	2.55×10^{-4}		≈4.74[g]	9.08×10^{-5}
I	2.01×10^{-4}		7.78	7.40×10^{-4}

[a] This work. [b] Reference 4. [c] Reference 9. [d] Reference 21. [e] Reference 22. [f] Reference 23. [g] Based on LG = CH$_3$CH$_2$CH$_2$S. [h] k_1^B = 8.5×10^{-5} M^{-1} s^{-1} (B = Dabco).

which is very unlikely (see Discussion). The k_1^{OH} values are given in Table I.

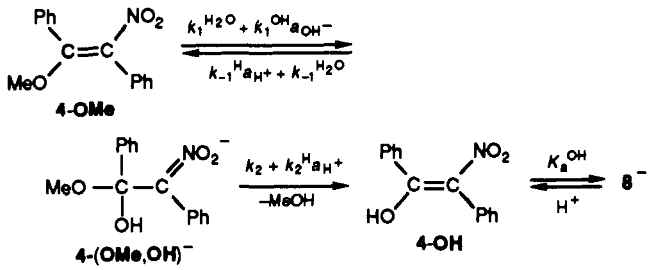
Reaction of 4-OMe. Hydrolysis of **4-OMe** is much faster than that of **4-Cl**, **4-I**, and **4-SEt**, enabling measurements over a much wider pH range (pH 1.00–15.30). Our data, again obtained at 300 nm, are summarized in Tables S2 (KOH solutions), S3 (Dabco buffer), and S4 (HCl solution and acetate buffers) of the supplementary material.[10] Figure 2 shows the dependence of log k_{obsd} on pH. The question of which step is rate limiting in this system is not simple and is discussed below. The simplest interpretation of our results is in terms of Scheme II (for a more elaborate mechanism, see Discussion) with rate-limiting nucleophilic attack by OH$^-$ and water, respectively, i.e., k_{obsd} is given by eq 5 with $k_1^{H_2O}$ = (2.37 ± 0.20) × 10^{-5} s^{-1} and k_1^{OH} = 0.69 ± 0.03 M^{-1} s^{-1}.

$$k_{obsd} = k_1^{H_2O} + k_1^{OH}a_{OH^-} \qquad (5)$$

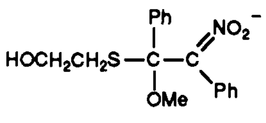
We included in Scheme II a step for the acid catalyzed leaving group departure ($k_2^Ha_{H^+}$) which may be important at the low end of the pH range used, just as the importance of the k_{-1}^H step can be inferred from the need to include $k_1^{H_2O}$ into eq 5 at pH ≲ 11.5.

There is slight buffer catalysis of water addition by Dabco which we attribute to concerted removal of a proton from the attacking water by the base (n-type mechanism). A plot of k_{obsd} vs [Dabco] (not shown) gives k_1^B = (8.5 ± 2.5) × 10^{-5} M^{-1} s^{-1}. The points on the pH–rate profile of Figure 2 were obtained at 0.01 M Dabco where catalysis is negligible.

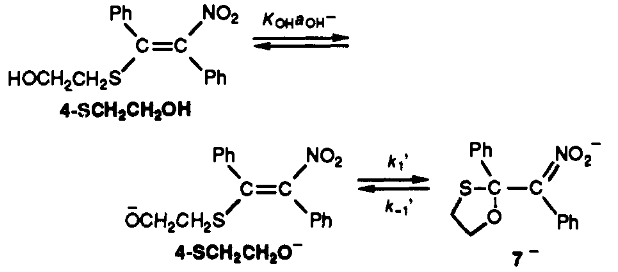
Scheme II



Reaction of 4-SCH$_2$CH$_2$OH. The reaction of **4-SCH$_2$CH$_2$OH** with base does not lead to **8$^-$** but to a species whose spectrum (Figure 1) closely resembles the spectrum of **9**.[4] We hence attribute it to the cyclic adduct **7$^-$** which is formed as shown in eq 6.



9



(6)

The reaction was monitored at 360 nm (λ_{max} of **4-SCH$_2$CH$_2$OH**). k_{obsd} values are collected in Table S5[10] while the pH–rate profile of k_{obsd} is given in Figure 2. It is apparent that k_{obsd} is much higher than that for any of the other substrates studied, further supporting a different mechanism. The results are consistent with eq 7 derived from eq 6; k_{-1}' is too small to be measurable. From the data at low base concentrations we obtain $K_{OH}k_1'$ = 5.09 ± 0.16 M^{-1} s^{-1}.

$$k_{obsd} = \frac{K_{OH}a_{OH^-}}{1 + K_{OH}a_{OH^-}}k_1' \qquad (7)$$

The slight curvature in the plot in strongly basic solution suggests that $K_{OH}a_{OH^-}$ becomes comparable to unity at high pH although, in view of the relatively high [KOH] used, a medium or salt effect could be partially responsible for the curvature. However, since no such curvature was detected in the reactions of OH$^-$ with **4-Cl**, **4-I**, **4-SEt**, and **4-OMe**, medium or salt effects may be excluded as a major cause for the curvature. From an inversion plot according to eq 8 (not shown) one obtains k_1' = 5.4 ± 0.5 s^{-1} and K_{OH} = 0.95 ± 0.25 M^{-1} (pK_a of **4-SCH$_2$CH$_2$OH** = 15.9 ± 0.1).

$$\frac{1}{k_{obsd}} = \frac{1}{k_1'} + \frac{1}{k_1'K_{OH}a_{OH^-}} \qquad (8)$$

7$^-$ is stable to product formation in basic solution but it forms products in an acidic solution. The following observations are consistent with the mechanism shown in Scheme III. When **7$^-$** is mixed with an HCl solution (10^{-3} to 0.5 M) there is an "instantaneous" change in the spectrum from that of **7$^-$** to one that is characteristic of nitronic acids (**7-NOH**), as shown in Figure 3. This spectrum changes gradually to one of generally low absorption (Figure 3), consistent with **7-CH** or perhaps a mixture of **7-CH** with small amounts of **4-OCH$_2$CH$_2$SH**. HPLC experiments described below indicated that the amounts of **4-**

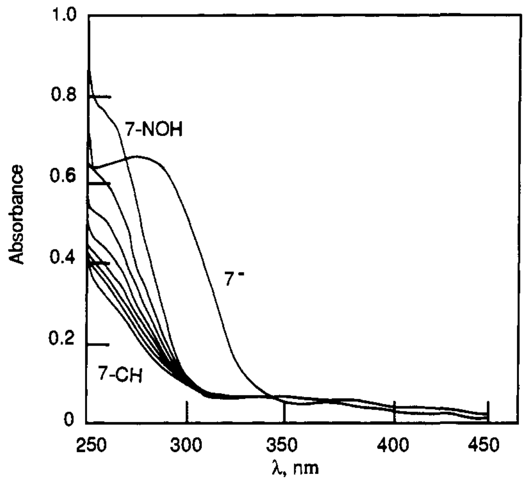


Figure 3. Repetitive UV–vis spectra of a solution of 7^- which is mixed with HCl. The spectra were taken at 6-min intervals.

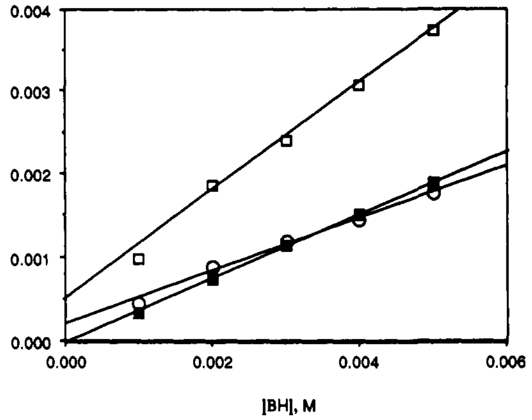
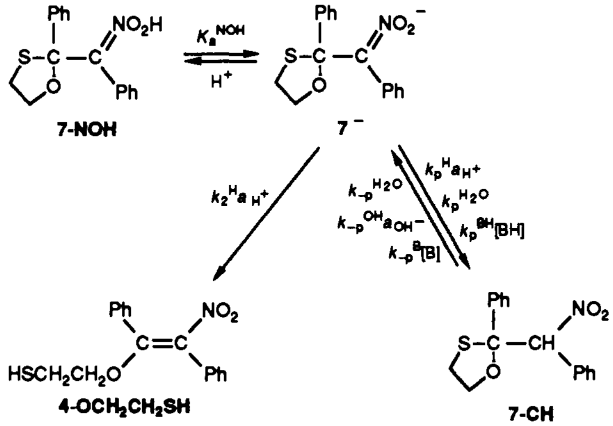


Figure 4. Reaction of 7^- with carboxylic acid buffers: □, methoxyacetic acid at 4.86; ○, acetic acid buffer at pH 5.23; ■, acetic acid buffer at pH 6.26.

Scheme III



OCH$_2$CH$_2$SH, if formed during this process, are too small to be measurable.

The kinetics of this process (k_{obsd}^{I}) was followed at 270 nm, and the results are in Table S6.[10] We also measured k_{obsd}^{I} in various methoxyacetate and acetate buffers at pH up to 6.26. The data (Table S6)[10] indicate strong buffer catalysis, which is consistent with protonation on carbon ($7^- \rightarrow$ **7-CH**); some representative buffer plots are shown in Figure 4.

The results can be fitted to eq 9 which in HCl solution, or after extrapolation to zero buffer concentration, simplifies to eq 10. A pH–rate profile according to eq 10 is shown in Figure 5. It yields $k_p^H = 47.2 \pm 1.6$ M^{-1} s^{-1} and p$K_a^{NOH} = 4.52 \pm 0.04$.

$$k_{obsd}^{I} = \frac{K_a^{NOH}}{K_a^{NOH} + a_{H^+}}(k_p^H a_{H^+} + k_p^{BH}[BH]) \qquad (9)$$

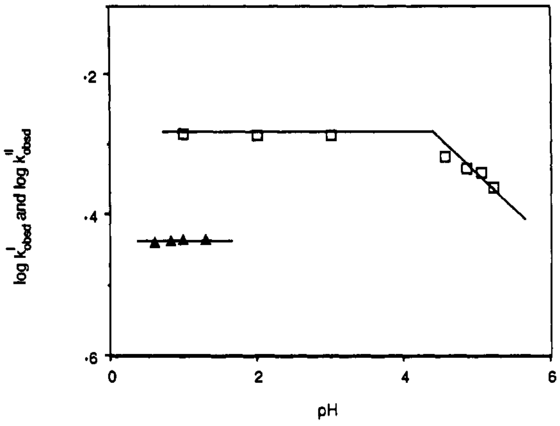


Figure 5. pH–rate profiles of k_{obsd}^{I} (□) and k_{obsd}^{II} (▲) for the reaction of 7^- with acid.

Table II. Slopes and Intercepts of Buffer Plots According to Equations 11 and 12 for the Reaction of 7^- with Methoxyacetic and Acetic Acids in 50% Me$_2$SO–50% Water at 20 °C, μ = 0.5 M (KCl)

pH	BH	slope, M^{-1} s^{-1}	intercept, s^{-1}
4.56	CH$_3$OCH$_2$COOH	0.440 ± 0.035	(6.55 ± 0.97) × 10^{-4}
4.86		0.603 ± 0.026	(4.44 ± 0.88) × 10^{-4}
5.06		0.675 ± 0.027	(3.89 ± 0.90) × 10^{-4}
5.23	AcOH	0.317 ± 0.016	(1.88 ± 0.53) × 10^{-4}
5.78		0.384 ± 0.008	*a*
6.26		0.384 ± 0.003	*a*

[a] Too small to measure.

$$k_{obsd}^{I}(\text{HCl}) \text{ or } k_{obsd}^{I}([\text{BH}] = 0) = \frac{K_a^{NOH}}{K_a^{NOH} + a_{H^+}} k_p^H a_{H^+} \qquad (10)$$

The slopes of the buffer plots (Table II) are given by eq 11 and yield p$K_a^{NOH} = 4.59 \pm 0.04$ and $k_p^{BH} = 0.917 \pm 0.030$ M^{-1} s^{-1} for MeOCH$_2$CO$_2$H and $k_p^{BH} = 0.384 \pm 0.010$ M^{-1} s^{-1} for AcOH.

$$\text{slope} = \frac{K_a^{NOH}}{K_a^{NOH} + a_{H^+}} k_p^{BH} \qquad (11)$$

The close agreement between the pK_a^{NOH} values obtained from the slopes and from eq 10 shows excellent internal consistency. We shall adopt the average of the two numbers (4.55) as the pK_a^{NOH} value of **7-NOH**.

The reaction mixture in HCl solution was subjected to an HPLC analysis. After about 1 half-life three species with retention times of 1.74, 5.44, and 6.31 min (for details see Experimental Section) were detected. The spectrum of the first species matched the spectrum of **7-NOH**, in Figure 3, while the second (large area) and third (small area) species had quite similar but not identical spectra that approximately matched the spectrum of **7-CH** in Figure 3. We attribute these two species to a mixture of the threo and erythro isomers of **7-CH**.

After two or more half-lives a new species appeared with a retention time of 2.41 min and a spectrum very different from that of **4-SCH$_2$CH$_2$OH** but similar although not identical with that of **4-OMe** (small λ_{max} at 270 nm, large λ_{max} at ≈215 nm). We shall assume that this is **4-OCH$_2$CH$_2$SH** even though the evidence is not conclusive; the kinetics of its appearance was followed by HPLC at various HCl concentrations. The results are reported in Table S5[10] (k_{obsd}^{II}) and displayed in Figure 5. The pH independence of k_{obsd}^{II} is consistent with conversion of **7-CH** to **4-OCH$_2$CH$_2$SH** via 7^- as the steady-state intermediate according to Scheme III, i.e., k_{obsd}^{II} is given by eq 12.

$$k_{obsd}^{II} = \frac{k_{-p}^{H_2O} k_2^H}{k_p^H + k_2^H} \qquad (12)$$

Table III. Slopes and Intercepts of Buffer Plots According to Equation 15 for the Reaction of **4-(OMe,OMe)**$^-$ with Methoxyacetic and Acetic Acids in 50% Me_2SO–50% Water at 20 °C, $\mu = 0.5$ M (KCl)

pH	BH	slope,[a] $M^{-1}\ s^{-1}$	intercept,[b] s^{-1}
4.56	CH_3OCH_2COOH	*c*	$(3.75 \pm 0.14) \times 10^{-3}$
5.23	AcOH	*c*	$(1.81 \pm 0.11) \times 10^{-3}$
5.78		*c*	$(1.00 \pm 0.07) \times 10^{-3}$
6.26		$(6.66 \pm 0.42) \times 10^{-2}$	$(4.22 \pm 0.14) \times 10^{-4}$
6.48		$(6.04 \pm 0.63) \times 10^{-2}$	$(2.53 \pm 0.21) \times 10^{-4}$
6.78		*c*	1.25×10^{-4}

[a] Slope = $K_a^{NOH}k_{-1}^{BH}/(K_a^{NOH} + a_{H^+})$. [b] Intercept = $K_a^{NOH}k_{-1}^{H}a_{H^+}/(K_a^{NOH} + a_{H^+})$. [c] Negligible slope.

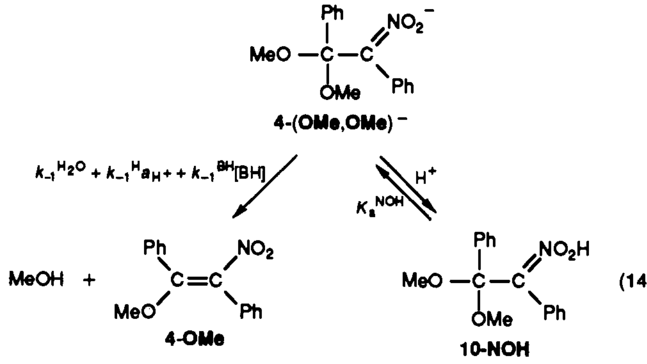
4-OCH$_2$CH$_2$SH itself is not stable but decomposes within 12 h to a new species with a retention time of 9.93 min and a spectrum that is nearly identical with that of **4-OCH$_2$CH$_2$SH**. No attempt was made to determine its structure; we suspect it to be an oxidation product of **4-OCH$_2$CH$_2$SH** since thiols are known to be oxidized by air and Me_2SO.

Equation 12 may be simplified to eq 13 since the lack of formation of **4-OCH$_2$CH$_2$SH** during the k_{obsd}^{I} process indicates that

$$k_{obsd}^{II} \approx \frac{k_{-p}^{H_2O}}{k_p^{H}}k_2^{H} = K_a^{CH}k_2^{H} \qquad (13)$$

$k_2^H \ll k_p^H = 47.2\ M^{-1}\ s^{-1}$; since our HPLC analysis would have detected a ≥5% formation of **4-OCH$_2$CH$_2$SH** we can set k_2^H at $\leq 2.36\ M^{-1}\ s^{-1}$. Our results thus yield $K_a^{CH}k_2^H = (4.22 \pm 0.15) \times 10^{-5}\ s^{-1}$ from the average of four k_{obsd}^{II} values. From $K_a^{CH} = 4.22 \times 10^{-5}/k_2^H$ and $k_2^H < 2.36\ M^{-1}\ s^{-1}$ we obtain $K_a^{CH} \geq 1.80 \times 10^{-5}$ or $pK_a^{CH} \leq 4.74$.

Reaction of 4-(OMe,OMe)$^-$. The methoxide ion adduct of **4-OMe**, **4-(OMe,OMe)**$^-$, was generated in a solution of NaOMe in MeOH. In one type of experiment 1 mL of the methanolic adduct solution (~5 × 10^{-3} M) was diluted 100-fold with an HCl or carboxylic acid buffer solution in 50% Me_2SO–50% water. A quantitative conversion to **4-OMe** was indicated by HPLC. The rate of this process was monitored at 280 nm (**4-OMe**). The results (Table S7[10]) show general acid catalysis at pH > 4.5 but in HCl solution there is no pH dependence. A pH–rate profile including k_{obsd} in HCl and k_{obsd} extrapolated to zero buffer concentration (Table III) is displayed in Figure 6. The results are consistent with eq 14, with k_{obsd} given by eq 15 ($k_{-1}^{H_2O}$ is negligible in acidic solution). From the pH–rate profile one calculates $k_{-1}^{H} = (7.46 \pm 0.20) \times 10^2\ M^{-1}\ s^{-1}$ and $pK_a^{NOH} = 5.2 \pm 0.1$. From the buffer slopes in acetate buffers (Table III) we obtain $k_{-1}^{AcOH} = (6.8 \pm 0.5) \times 10^{-2}\ M^{-1}\ s^{-1}$; catalysis by $MeOCH_2CO_2H$ was too weak to yield a reliable k_{-1}^{BH} value. The weaker catalysis by the stronger acid is a consequence of the fact that even though the k_{-1}^{BH}-step is acid catalyzed, due to the preequilibrium with **10-NOH**, the reaction is overall general base catalyzed at pH ≪ pK_a^{NOH}.



(14)

$$k_{obsd} = \frac{K_a^{NOH}}{K_a^{NOH} + a_{H^+}}(k_{-1}^{H}a_{H^+} + k_{-1}^{BH}[BH]) \qquad (15)$$

An approximate $k_{-1}^{H_2O}$ value was obtained by reacting **4-(OMe,OMe)**$^-$ in MeOH with KOH solutions in 50% Me_2SO–50% water. The $k_{-1}^{H_2O}$ process is very slow so that **4-OMe** cannot be observed since it is rapidly converted to **8**$^-$. The slow buildup of **8**$^-$, followed by HPLC, amounted to ca. 5% conversion after 30 days. Treating **4-OMe** as a steady-state intermediate in the conversion of **4-(OMe,OMe)**$^-$ to **8**$^-$, with the $k_{-1}^{H_2O}$ being rate limiting, affords $k_{-1}^{H_2O} \approx 1.8 \times 10^{-8}\ s^{-1}$.

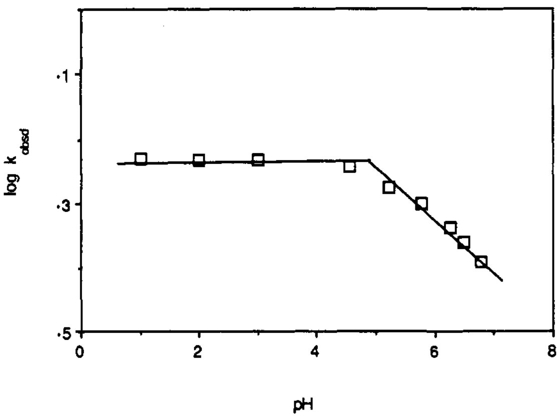


Figure 6. pH–rate profile for the reaction of **4-(OMe,OMe)**$^-$ with acid.

Table IV. Rate Constants for Departure of Leaving Groups from Intermediates of the Type $Ph(RG)(LG)CCPh(NO_2)^-$ in 50% Me_2SO–50% Water at 20 °C

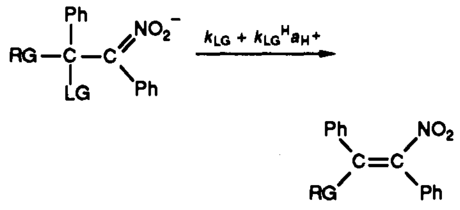
no.	RG	LG	k_{LG}, s^{-1}	k_{LG}^{H}, $M^{-1}\ s^{-1}$	ref
1	H	EtS^-	3.49×10^{-3}		22
2	H	$HOCH_2CH_2S^-$	7.02×10^{-2}		22
3	MeO	MeO^-	$\approx 1.8 \times 10^{-8}$	7.46×10^2	this work
4	MeO	EtS^-	7.85×10^{-3}		4
5	MeO	$HOCH_2CH_2S^-$	5.10×10^{-2}		4
6	$HOCH_2CH_2S$	MeO^-	9.60×10^{-6}		4
7	$HOCH_2CH_2S$	$HOCH_2CH_2S^-$	2.52×10^{-1}		4

Discussion

The hydrolysis of **4-Cl**, **4-I**, **4-SEt**, and **4-OMe** yields **8**$^-$ but **4-SCH$_2$CH$_2$OH** leads in basic solution to cyclic complex **7**$^-$, which, after acidification, is converted to **4-OCH$_2$CH$_2$SH**. The simplest mechanism consistent with the results for the reactions of **4-Cl**, **4-I**, and **4-SEt** is shown in Scheme I, that for the reaction of **4-OMe** in Scheme II, and that for the reaction of **4-SCH$_2$CH$_2$OH** in eq 6 and Scheme III. There is no detectable intermediate in the reactions of **4-Cl**, **4-I**, **4-SEt**, and **4-OMe**, and the kinetics are consistent with rate-limiting nucleophilic attack. The k_1^{OH} and $k_{-1}^{H_2O}$ (**4-OMe**) values are summarized in Table I, along with previously determined corresponding values for $HOCH_2CH_2S^-$ and piperidine.

In terms of Scheme I, the absence of direct evidence for the intermediate **4-(LG,OH)**$^-$ implies $K_1^{H_2O}/a_{H^+} = K_1^{OH}a_{OH^-} \ll 1$ ($K_1^{H_2O} = k_1^{H_2O}/k_{-1}^{H}$, $K_1^{OH} = k_1^{OH}/k_{-1}^{H_2O}$) and/or $k_1^{OH}a_{OH^-} \ll k_2$ even at the highest base concentration (0.25 M for **4-OMe**, 0.5 M for **4-Cl**, **4-I**, **4-SEt**), while rate-limiting nucleophilic attack requires $k_2 \gg k_{-1}^{H_2O}$. In terms of Scheme II the implication of the non-observance of **4-(OMe,OH)**$^-$ is that $k_1^{OH}a_{OH^-} + k_1^{H_2O} \ll k_2 + k_2^{H}a_{H^+}$ and rate-limiting nucleophilic attack means $k_2 + k_2^{H}a_{H^+} \gg k_{-1}^{H_2O} + k_{-1}^{H}a_{H^+}$.

In an attempt to understand our results it is instructive to estimate the relevant rate constants in Schemes I and II from model systems for which they are known. A summary of such kinetic parameters which refer to eq 16 (RG = remaining group) is provided in Table IV.



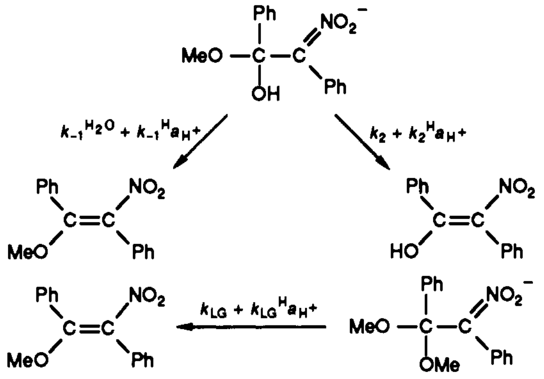
(16)

Table V. Measured and Estimated[a] Rate and Equilibrium Constants for the Hydrolysis of **4-OMe** According to Schemes II and IV

parameter	value	parameter	value
k_1^{OH}, $M^{-1}\ s^{-1}$	0.69	$k_{-1}^{H_2O}$, s^{-1}	$<(\ll)0.9 \times 10^{-8}$
$k_1^{H_2O}$, s^{-1}	2.15×10^{-5}	k_{-1}^{H}, $M^{-1}\ s^{-1}$	$<(\ll)3.7 \times 10^{2}$
$K_1^{H_2O}$, M	$>(\gg)5.8 \times 10^{-8}$	k_2, s^{-1}	$\approx 0.9 \times 10^{-8}$
K_1^{OH}, M^{-1}	$>(\gg)4.6 \times 10^{8}$[b]	k_2^{H}, $M^{-1}\ s^{-1}$	$\approx 3.7 \times 10^{2}$
		$k_3K_a^{OH'}$, $M\ s^{-1}$	$\gg 8.69 \times 10^{-17}$
pK_a^{CH}(**8-H**)	5.21 ± 0.1	k_3, s^{-1}	$\gg 0.03$
pK_a^{OH}(**4-OH**)	$\ll 5.21$	k_{2i}, s^{-1}	$\gg 2.15 \times 10^{-5}$
$pK_a^{OH'}$-(**4-OMe,OH**)$^-$	≈ 14.55		

[a] See text. [b] From $K_1^{H_2O}/K_w$ with $K_w = 1.26 \times 10^{-16}\ M^2$.

Hydrolysis of 4-OMe. We may assume that k_2 and k_2^H for **4-OMe** (eq 17) are about the same as the respective k_{LG} and k_{LG}^H in eq 18 (entry 3 in Table IV), except for a statistical correction.



(17)

(18)

This is because they refer to the loss of the same nucleofuge (MeO^-), and the "push" exerted by the remaining HO group should be similar to that exerted by a remaining MeO group. Hence we estimate $k_2 \approx 0.9 \times 10^{-8}\ s^{-1}$ and $k_2^H \approx 3.7 \times 10^2\ M^{-1}\ s^{-1}$ (Table V).

OH^- is a poorer leaving group than MeO^- from Meisenheimer complexes,[11] suggesting that $k_{-1}^{H_2O} <(\ll)\ k_2$. If $k_{-1}^{H_2O}$ is only slightly smaller than k_2, the latter would become co-rate limiting and k_{obsd} in basic solution would be given by the steady state eq 19. On the other hand, if $k_{-1}^{H_2O} \ll k_2$, then eq 19 simplifies to eq 5, i.e., nucleophilic attack is solely rate limiting.

$$k_{obsd} = \frac{(k_1^{H_2O} + k_1^{OH}a_{OH^-})k_2}{k_{-1}^{H_2O} + k_2} \tag{19}$$

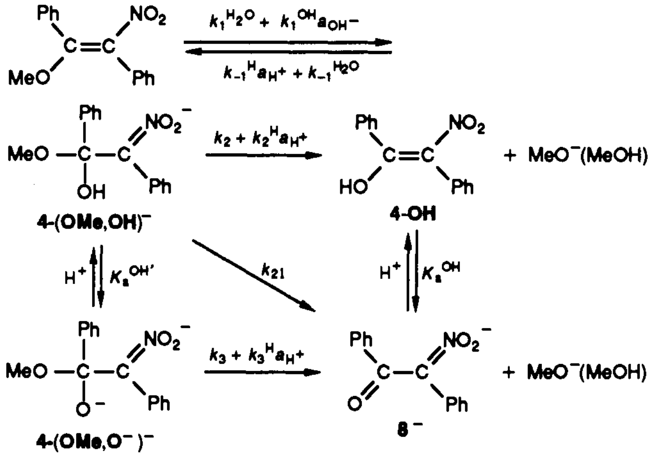
Two lines of arguments indicate that this latter situation is more likely. First, at low pH, the steady-state expression is given by eq 20. The fact that k_{obsd} is constant over the range from pH 1.0

$$k_{obsd} = \frac{k_1^{H_2O}k_2^{H}}{k_{-1}^{H} + k_2^{H}} \tag{20}$$

to 11.5 (Figure 2) requires that either $k_{-1}^{H_2O} \ll k_2$ and $k_{-1}^H \ll k_2^H$ so that $k_{obsd} = k_1^{H_2O}$ over the entire range from pH 1.0 to 11.5 or $k_2/(k_{-1}^{H_2O} + k_2) = k_2^H/(k_{-1}^H + k_2^H)$. This latter condition can only be met if $k_2/k_{-1}^{H_2O} = k_2^H/k_{-1}^H$, which seems rather unlikely.

A second argrument is based on some numerical estimates. From $k_1^{H_2O} = 2.15 \times 10^{-5}\ s^{-1}$ (Table I) and $k_{-1}^H < k_2^H \approx 3.7 \times 10^2$ one estimates $K_1^{H_2O} = k_1^{H_2O}/k_{-1}^H > 5.8 \times 10^{-8}$ M and $K_1^{OH} = K_1^{H_2O}/K_w > 4.6 \times 10^8\ M^{-1}$ (Table V). With this K_1^{OH} value, the first necessary condition ($K_1^{OH}a_{OH^-} \gg 1$) for the detection of the intermediate **4-(OMe,OH)**$^-$ is easily met at pH > 8.2 ($K_1^{OH}a_{OH^-} \geq 10$ at pH 8.2). Consequently, the reason why the intermediate was not observed cannot be insufficient thermodynamic stability relative to reactants but must be that $k_1^{OH}a_{OH^-} + k_1^{H_2O} \ll k_2 + k_2^Ha_{H^+}$. However, on the basis of the various rate constants (see Table V), the opposite relation, $k_1^{OH}a_{OH^-} + k_1^{H_2O} \gg k_2 + k_2^Ha_{H^+}$, should hold. For example, at pH ≥ 12.0

Scheme IV



where the k_1^{OH} and k_2 terms dominate, we have $k_1^{OH}a_{OH^-}/k_2 \gtrsim 9.65 \times 10^3$. Even at pH 8.0 where the $k_1^{H_2O}$ and $k_2^Ha_{H^+}$ terms are dominant, we still have $k_1^{H_2O}/k_2^Ha_{H^+} \approx 5.8$.

These considerations demonstrate that although within the framework of Scheme II all necessary conditions for the detection of the intermediate **4-(OMe,OH)**$^-$ in the hydrolysis of **4-OMe** are amply met, the intermediate has not been detected. We do not ascribe this contradiction to grossly inaccurate estimates of K_1^{OH} and/or k_2; even if our estimates for the various k's were off in the direction of reducing K_1^{OH} and the k_1^{OH}/k_2 ratio by one or two orders of magnitude there would still be ample room to easily meet the criteria for detectability of the intermediate. Hence, **4-(OMe,OH)**$^-$ has not been observed because there must be one or several much faster pathways leading to products. One such pathway may involve the deprotonated form of the intermediate, **4-(OMe,O**$^-$**)**$^-$ (Scheme IV), and another is the direct conversion of **4-(OMe,OH)**$^-$ to **8**$^-$ by intramolecular acid catalysis of nucleofuge departure.

The requirement for neither intermediate to be observable is that $(k_3 + k_3^Ha_{H^+})K_a^{OH'}/a_{H^+} + k_{2i} \gg k_1^{OH}a_{OH^-} + k_1^{H_2O}$. In strongly basic solution it simplifies to $k_3K_a^{OH'}/a_{H^+} \gg k_1^{OH}a_{OH^-}$ which is equivalent to $k_3K_a^{OH'}/K_w \gg k_1^{OH}$ or $k_3K_a^{OH'} \gg k_1^{OH}K_w = 8.69 \times 10^{-17}\ M\ s^{-1}$.[12] From the Taft equation[13] (eq 21) we estimate $pK_a^{OH'} \approx 12.75$ (loss of OH proton in **4-(OMe,OH)**$^-$) in water using $\sigma^*_{Ph} = 0.75$,[13] $\sigma^*_{OMe} = 1.81$[13] and $\sigma^*_{CPh(NO_2)^-} \approx -0.34$;[14] in 50% Me_2SO–50% water we add 1.8 units[36] which yields $pK_a^{OH'} \approx 14.55$.

$$pK_a = 15.9 - 1.42\sum\sigma^* \tag{21}$$

This means $k_3 \gg 0.03\ s^{-1}$ and, if our estimate of $k_2 \approx 0.9 \times 10^{-8}\ s^{-1}$ is accepted, a k_3/k_2 ratio of $\gg 3.4 \times 10^6$. This large ratio implies that the k_3 pathway dominates over the k_2 pathway in strongly basic solution and at pH values as low as 8.90. The fast breakdown of **4-(OMe,O**$^-$**)**$^-$ may be understood in terms of a transition state that derives substantial stabilization from the development of resonance in **8**$^-$; judging from the high acidity of **4-OH** ($pK_a^{OH} \ll 5.21$) this resonance effect is quite large. By way of comparison, pK_a^{OH} of $PhC(OH){=}CH_2$ in water is 10.34.[15]

In the pH range where $k_1^{H_2O} \gg k_1^{OH}a_{OH^-}$ (pH ≤ 10.4; $k_1^{OH}a_{OH^-} = k_1^{H_2O}$ at pH 11.4) and $k_3^HK_a^{OH'} + k_{2i} \gg k_3K_a^{OH'}/a_{H^+}$ (pH unknown), the rate of conversion of the intermediate to products is much faster than its formation when $k_3^HK_a^{OH'} + k_{2i} \gg k_1^{H_2O} = 2.15 \times 10^{-5}\ s^{-1}$. Our results suggest that $k_{2i} \gg k_3^HK_a^{OH'}$ and hence $k_{2i} \gg 2.15 \times 10^{-5}\ s^{-1}$; if the $k_3^HK_a^{OH'}$ term were dominant instead, $k_3^HK_a^{OH'} \gg 2.15 \times 10^{-5}\ s^{-1}$ would imply $k_3^H \gg 7.6 \times$

---

(11) Terrier, F. *Chem. Rev.* **1982**, *82*, 78.

(12) $pK_w = 15.9$ in 50% Me_2SO–50% water, 20 °C, $\mu = 0.5$ (KCl).

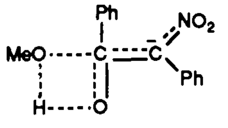
(13) Perrin, D. D.; Dempsey, B.; Serjeant, E. P. *pK_a Prediction for Organic Acids and Bases*; Chapman and Hall: New York, 1981; p 109.

(14) Bernasconi, C. F.; Fassberg, J.; Killion, R. B., Jr.; Rappoport, Z. To be published.

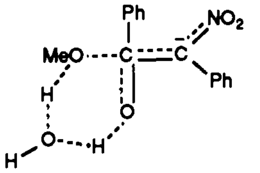
(15) Chiang, Y.; Kresge, A. J.; Santaballa, J. A.; Wirz, J. *J. Am. Chem. Soc.* **1988**, *110*, 5506.

10^9 M^{-1} s^{-1} ($pK_a^{OH'} \approx 14.55$) which would make the k_3^H step faster than diffusion controlled.

With $k_{2i} \gg 2.15 \times 10^{-5}$ s^{-1} the k_{2i}/k_2 ratio is $\gg 2.4 \times 10^3$, showing strong intramolecular acid catalysis of methoxide ion departure. Since the pK_a of the OH group changes from ≈ 14.55 in **4-(OMe,OH)**$^-$ to $\ll 5.21$ in **4-OH** (**8**$^-$), such strong catalysis is not unexpected.[16] The transition state for the k_{2i} step may be visualized as **11** or **12**.



11



12

What is the rate-limiting step of the hydrolysis reaction? With reference to Scheme IV the condition for rate-limiting nucleophilic attack is given by the inequality shown in eq 22. The relevant rate constants (or lower limits for k_{2i} and k_3) are summarized in Table V. At very high pH, $k_{-1}^{H_2O} \gg k_{-1}^H a_{H^+}$ and $k_2 \gg k_2^H a_{H^+}$;

$$k_2^H a_{H^+} + k_2 + k_{2i} + k_3 K_a^{OH'}/a_{H^+} \gg k_{-1}^H a_{H^+} + k_{-1}^{H_2O} \quad (22)$$

since k_2 is also negligible irrespective of pH, eq 22 simplifies to eq 23. Inspection of the k_{2i}, $k_3K_a^{OH'}$, and $k_{-1}^{H_2O}$ values demonstrates that the inequality of eq 23 indeed holds by a large margin.

$$k_{2i} + k_3 K_a^{OH'}/a_{H^+} \gg k_{-1}^{H_2O} \quad (23)$$

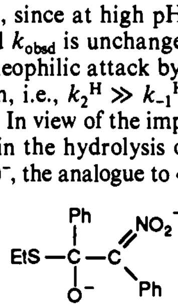
Hence, even if k_2 were only marginally larger than $k_{-1}^{H_2O}$, nucleophilic attack is solely rate limiting at high pH because of the k_{2i} and $k_3K_a^{OH'}/a_{H^+}$ terms.

Between pH ~10.0 and ~7.2, $k_{-1}^H a_{H^+} \gtrsim 10k_{-1}^{H_2O}$, $k_{2i} \gg k_3K_a^{OH'}/a_{H^+}$, and the $k_2a_{H^+}$ term is still negligible. Here eq 22 becomes eq 24, and at very low pH, it eventually simplifies to k_2^H

$$k_{2i} \gg k_{-1}^H a_{H^+} \quad (24)$$

$\gg k_{-1}^H$. In conclusion, since at high pH nucleophilic attack is solely rate limiting and k_{obsd} is unchanged between pH 1.0 and 11.5, rate-limiting nucleophilic attack by water must also occur in highy acidic solution, i.e., $k_2^H \gg k_{-1}^H$ must indeed hold.

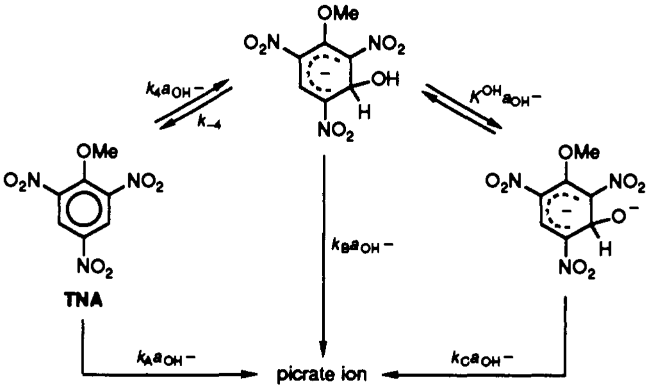
Hydrolysis of 4-SEt. In view of the importance of the pathway through **4-(OMe,O**$^-$**)**$^-$ in the hydrolysis of **4-OMe** it is difficult to argue that **4-(SEt,O**$^-$**)**$^-$, the analogue to **4-(OMe,O**$^-$**)**$^-$ in Scheme IV, is not a significant intermediate in the hydrolysis of **4-SEt**. However, let us examine whether reaction via **4-(SEt,O**$^-$**)** and/or by the k_{2i} step is essential for explaining why **4-(SEt,OH)**$^-$ could not be detected or whether the k_2 and $k_2^Ha_{H^+}$ steps are sufficiently fast to turn **4-(SEt,OH)**$^-$ into a steady-state intermediate. From entry 4 in Table IV we shall assume that k_2 in Scheme IV (OMe replaced by SEt) is $\approx 7.85 \times 10^{-3}$ s^{-1}. $k_{-1}^{H_2O}$ is estimated at $\approx 4 \times 10^{-6}$ s^{-1}, based on entry 6 in Table IV (9.6×10^{-6}) and a correction factor of 0.42 which corresponds to the $k_{-1}^{H_2O}/k_2$ ratio for the **4-OMe** system and corrects for the fact that OH^- is a poorer nucleofuge than MeO^-. No relevant data are available to estimate k_{-1}^H and k_2^H.



4-(SEt, O$^-$**)**$^-$

From $k_1^{OH} = 2.55 \times 10^{-4}$ M^{-1} s^{-1} and $k_{-1}^{H_2O} \approx 4 \times 10^{-6}$ s^{-1} we calculate $K_1^{OH} \approx 6.4 \times 10^1$ M^{-1}, while for k_1^{OH}/k_2 we obtain $\approx 3.2 \times 10^{-2}$ M^{-1}. These parameters suggest that the condition $K_1^{OH}a_{OH^-} \gg 1$ is met at the high end of the pH range used, e.g., $K_1^{OH}a_{OH^-} \approx 6.4$ at pH 14.9. *However the condition $k_1^{OH}a_{OH^-} \gg k_2$ is never met.* Hence, even though the reaction undoubtedly follows all the pathways shown in Scheme IV, the k_2 step alone is fast enough to account for the lack of detection of the intermediate. Our estimates indicate that $k_2 \approx 7.85 \times 10^{-3}$ $s^{-1} \gg k_{-1}^{H_2O} \approx 4 \times 10^{-6}$ s^{-1}, confirming our initial conclusion that k_1^{OH} is rate limiting.

Scheme V



Hydrolysis of 4-Cl and 4-I. In view of the well-known high nucleofugality of Cl^- and I^-[7,17] the same conclusions as for the hydrolysis of **4-SEt** can be drawn: k_1^{OH} is definitely rate limiting and the k_2 step is sufficiently fast to explain why no intermediate could be detected. Again, this conclusion does not exclude **4-(LG,O**$^-$**)**$^-$ from being an important intermediate, but the analogue to Scheme IV undoubtedly simplifies to one in which there are no acid-catalyzed steps since such catalysis would violate a basic principle.[16]

Regarding the role played by the deprotonated intermediate **4-(LG,O**$^-$**)**$^-$, an interesting question is whether the k_2 step might be so fast as to bypass **4-(LG,O**$^-$**)**$^-$. For example, if k_2 approaches the diffusion-controlled limit, k_3 could not be significantly higher than k_2 and hence the pathway through the dianionic intermediate would become unimportant except at pH > $pK_a^{OH'}$. Its importance could be further reduced because the establishment of the acid-base equilibrium between **4-(LG,OH)** and **4-(LG,O**$^-$**)**$^-$ would no longer be fast on the time scale of the k_2 step, i.e., deprotonation of **4-(LG,OH)** by OH^- could become slower than k_2, especially as the pH is decreased. In such an event **4-(LG,O**$^-$**)**$^-$ would actually not be formed.

Implications for S_NAr Reactions. Our results and conclusions regarding the hydrolysis of **4-OMe** shed an interesting light on the analogous reaction of 2,4,6-trinitroanisole (TNA). Gibson and Crampton[18] studied the reaction of TNA with NaOH in aqueous solution. They observed a rapid color forming reaction by stopped-flow spectrometry followed by a slower decomposition to picrate ion and suggested a rapid formation of a 1,3-Meisenheimer complex and its ionized form and slow conversion of **TNA** as well as of the 1,3-complexes into picrate ion (Scheme V). The kinetics were consistent with $k_A = 1.4$ M^{-1} s^{-1}, $k_B = 0.8$ M^{-1} s^{-1}, $k_C = 0.1$ M^{-1} s^{-1}, $k_4 = 12$ M^{-1} s^{-1}, $k_{-4} = 8.4$ s^{-1} ($K_4 = 1.4$ M^{-1}), $K^{OH} = 6.0$ M^{-1} ($pK_a = 13.22$).

The 1,1-Meisenheimer complex on the reaction path of the k_A process was not observed, implying that $K_1^{OH}a_{OH^-} \ll 1$ and/or $k_2 \gg k_1^{OH}a_{OH^-}$ (top line of Scheme VI). The possibility that the reaction could proceed through **(TNA,O**$^-$**)**$^-$ or the k_{2i} step was not considered. From the following estimates of k_2 and $k_{-1}^{H_2O}$ in Scheme VI one can show, however, that if it were only for the k_2 step, **(TNA,OH)**$^-$ should have been observed more easily than the 1,3-complexes in Scheme V! In estimating $k_{-1}^{H_2O}$ and k_2 we start with the equilibrium constant, K_1^{MeO}, for MeO^- addition to

---

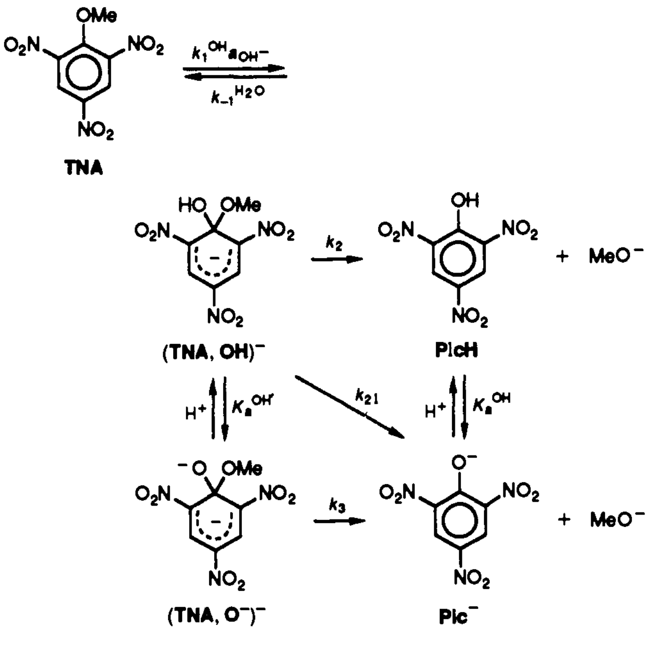
(16) Jencks, W. P. *J. Am. Chem. Soc.* **1972**, *94*, 4731.

(17) (a) Marshall, D. R.; Thomas, P. J.; Stirling, C. J. M. *J. Chem. Soc., Perkin Trans. 2* **1977**, 1898. (b) Thomas, P. J.; Stirling, C. J. M. *J. Chem. Soc., Perkin Trans. 2* **1978**, 1130. (c) Issari, B.; Stirling, C. J. M. *J. Chem. Soc., Chem. Commun.* **1982**, 684.

(18) Gibson, B.; Crampton, M. R. *J. Chem. Soc., Perkin Trans. 2* **1979**, 648.

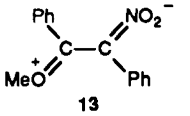
(19) An estimate for $pK_a^{OH'}$ is obtained as follows. The pK_a of the OH^- adduct of 1,3,5-trinitrobenzene is ≈ 13.0.[20] Assuming a Taft $\rho^* = 1.42$ (see eq 19), the replacement of H ($\sigma^*_H = 0.49$) with MeO ($\sigma^*_{OMe} = 1.81$) leads to $pK_a \approx 13.0 - 1.42(1.81 - 0.49) = 11.1$

Scheme VI



TNA in methanol at 25 °C, to form (TNA,OMe)⁻, the methoxy analogue of (TNA,OH)⁻. An average from four different laboratories gives $K_1^{MeO} = 1.45 \times 10^4$ M^{-1}.[11] K_1^{OH} for OH⁻ addition to TNA in water should be somewhat lower as found for the reactions of 1,3,5-trinitrobenzene (TNB): with TNB the equilibrium constant for OH⁻ addition in water is about 6-fold smaller than that for MeO⁻ addition ion methanol.[11] Using this factor and taking into account that K_1^{OH} in Scheme VI is favored by a statistical factor of 2 over K_1^{MeO} yields $K_1^{OH} \approx {}^2/_6 K_1^{MeO} = 4.8 \times 10^3$ M^{-1}. With $k_1^{OH} = 1.4$ M^{-1} s^{-1} we obtain $k_{-1}^{H_2O} \approx 2.9 \times 10^{-4}$ s^{-1}. Assuming that k_2 exceeds $k_{-1}^{H_2O}$ about 10-fold[21] affords $k_2 \approx 2.9 \times 10^{-3}$ s^{-1} and hence $k_1^{OH}/k_2 \approx 4.8 \times 10^2$ M^{-1}. These estimates show that even at 0.1 M NaOH (the reaction was studied at [NaOH] up to 0.8 M),[18] we have $K_1^{OH}a_{OH^-} \approx 480$ and $k_1^{OH}a_{OH^-}/k_2 \approx 48$, i.e., (TNA,OH)⁻ should have been easily detected. We conclude that the pathway through (TNA,O⁻)⁻[19] and/or the k_{2i} step must be more important than the k_2 step.

Structure–Reactivity Relationships. A. OH⁻ and Water Attack on 4-LG. Table I provides a summary of k_1^{OH} and $k_1^{H_2O}$ values for the reactions of **4-LG** and rate constants for nucleophilic attack by $HOCH_2CH_2S^-$[4] and piperidine[9] determined earlier and relevant data for **4-H**.[22,23] Previously we have identified steric crowding in the transition state leading to the adduct as the most important factor affecting the rate constants for nucleophilic attack although polar effects by the leaving group surely play a role.[4,9] Thus the reactivity order H ≫ OMe ≫ Cl ≫ I > SEt for addition of $HOCH_2CH_2S^-$ and piperidine reflects the relative size of the nucleofuges as well as their polar effects quite well except perhaps for I vs SEt. It was suggested that resonance stabilization of **4-OMe** (**13**) may contribute to the large reactivity difference between 4-H and **4-OMe**.[4]



13

A comparison of the k_1^{OH} values for OH⁻ attack on the same substrates shows a similar trend as with the $k_1^{HOCH_2CH_2S^-}$ and k_1^{Pip} values, suggesting that the same factors determine the relative reactivities of the various substrates. However, k_1^{OH} for **4-OMe** no longer fits the trend: the ratio k_1^{OH}(**4-OMe**)/k_1^{OH}(**4-Cl**) of 273 is much larger than $k_1^{HOCH_2CH_2S^-}$(**4-OMe**)/$k_1^{HOCH_2CH_2S^-}$(**4-Cl**) = 10.3 and k_1^{Pip}(**4-OMe**)/k_1^{Pip}(**4-Cl**) = 56. More dramatically, k_1^{OH} for **4-OMe** is actually 3-fold larger than k_1^{OH} for **4-H** while with the other nucleophiles **4-OMe** is more than 100-fold less reactive than 4-H. Similarly, $k_1^{H_2O}$ for **4-OMe** is 40-fold larger than that for **4-H**. Apparently a new factor, probably the well-documented mutual stabilization exerted by geminal oxygen atoms,[24] also known as the anomeric effect,[25] overrides the steric and resonance effects in **4-OMe**. It should render **4-(OMe,OH)⁻** particularly stable and would also be expected to lower the transition-state energy of the k_1^{OH} and $k_1^{H_2O}$ steps. That $k_1^{H_2O}$ is even more enhanced than k_1^{OH} may indicate a transition state in which C–O bond formation has progressed more in the water reaction than in the OH⁻ reaction. We note, however, that a late transition state may also require greater loss of resonance stabilization (**11**) which would tend to reduce the gain from the enhanced anomeric effect.

Table VI. Rate and Equilibrium Constants for the Reactions of **4-SCH₂CH₂OH** in Basic Solution (Equation 6) and for the Reactions of 7⁻ in Acidic Solutions (Scheme III) in 50% Me₂SO–50% Water at 20 °C, μ = 0.5 M (KCl)

equation 6		Scheme III	
parameter	value	parameter	value
K_{OH}, M^{-1}	0.95 ± 0.15	pK_a^{NOH}	4.55 ± 0.04
pK_a^{OH}	15.9 ± 0.1	k_p^H, M^{-1} s^{-1}	47.2 ± 1.6
k_1', s^{-1}	5.4 ± 0.5	$k_p^{MeOAcOH}$, M^{-1} s^{-1}	0.92 ± 0.03
k_{-1}', s^{-1}	≪1.1 × 10⁻⁶	k_p^{AcOH}, M^{-1} s^{-1}	0.384 ± 0.010
K_1'	≫4.9 × 10⁶	$K_a^{CH}k_2^H$, s^{-1}	(4.22 ± 0.15) × 10⁻⁵
		k_2^H, M^{-1} s^{-1}	≤2.36
		pK_a^{CH}	≤4.74

B. Reaction of 4-SCH₂CH₂OH. Rate and equilibrium constants for the processes shown in eq 6 and Scheme III are summarized in Table VI. k_1' for intramolecular nucleophilic attack is approximately (2 × 10⁴)-fold larger than k_1^{OH} for OH⁻ attack on **4-SEt**. This enhancement is probably mainly the result of the intramolecularity of the reaction.[26]

The pK_a^{CH} ≤ 4.74 of **7-CH** (Scheme III) is substantially lower than the pK_a of $PhCH_2NO_2$ in the same solvent (7.93),[27] due to the strongly electron withdrawing effect of the $\mathrm{Ph}\overline{\mathrm{CSCH_2CH_2O}}$ moiety. This contrasts with the rather minor reduction in the pK_a^{NOH} of **7-NOH** (4.55) relative to that of PhCH=NO₂H (4.75). This strong dependence of pK_a^{CH} on substituents but relative insensitivity of the pK_a^{NOH} appears to be typical for nitroalkanes. For example, in water the pK_a^{CH} of $PhCH_2NO_2$ (6.77) is 3.51 units lower than the pK_a^{CH} of CH_3NO_2 (10.28) yet the pK_a^{NOH} is about the same for both compounds, with that of PhCH=NO₂H (3.64) being actually slightly higher than that of CH₂=NO₂H (3.25).[27]

For carbon protonation of 7⁻ by the hydronium ion, $k_p^H = 4.72$ M^{-1} s^{-1} compares with 209 M^{-1} s^{-1} for carbon protonation of PhCH=NO₂⁻ by the hydronium ion.[27] This 44-fold reduction in k_p^H, which corresponds to a Brønsted $\beta \leq 0.52$, seems rather large since β values for the protonation of phenylnitronate ions are typically very small or even negative.[28] This result suggests that k_p^H for 7⁻ is depressed by a steric effect due to the bulky

---

(20) Crampton, M. R.; Davis, A. B.; Greenhalgh, C.; Stevens, J. A. *J. Chem. Soc., Perkin Trans. 2* **1989**, 675.

(21) Bernasconi, C. F.; Bergstrom, R. G. *J. Am. Chem. Soc.* **1974**, *96*, 2397.

(22) Bernasconi, C. F.; Killion, R. B., Jr. *J. Am. Chem. Soc.* **1988**, *110*, 7506.

(23) Bernasconi, C. F.; Renfrow, R. A. *J. Org. Chem.* **1987**, *52*, 3035.

(24) (a) Hine, J.; Klueppl, A. W. *J. Am. Chem. Soc.* **1974**, *96*, 2924. (b) Wiberg, K. B.; Squires, R. R. *J. Chem. Thermodyn.* **1979**, *11*, 773. (c) Harcourt, M. P.; More O'Ferrall, R. A. *J. Chem. Soc., Chem. Commun.* **1987**, 823; (d) Harcourt, M. P.; More O'Ferrall, R. A. *Bull. Soc. Chim. Fr.* **1988**, 407.

(25) (a) Kirby, A. G. *The Anomeric Effect and Related Stereoelectronic Effects of Oxygen*; Springer Verlag: Berlin, 1983. (b) Schleyer, P. v. R.; Jemmis, E. D.; Spitznagel, G. W. *J. Am. Chem. Soc.* **1985**, *107*, 6393.

(26) Kirby, A. G. *Adv. Phys. Org. Chem.* **1980**, *17*, 183.

(27) Bernasconi, C. F.; Kliner, D. A. V.; Mullin, A. S.; Ni, J. X. *J. Org. Chem.* **1988**, *53*, 3342.

(28) (a) Fukuyama, M.; Flanagan, P. W. K.; Williams, F. T.; Frainer, L.; Miller, S. A.; Schechter, H. *J. Am. Chem. Soc.* **1970**, *92*, 4689. (b) Bordwell, F. G.; Boyle, W. J., Jr. *J. Am. Chem. Soc.* **1972**, *94*, 3907. (c) Bordwell, F. G.; Bartmess, J. E.; Hautala, J. A. *J. Org. Chem.* **1978**, *43*, 3107.

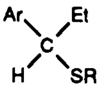
Table VII. Rate and Equilibrium Constants for the Reactions of **4-(OMe,OMe)**$^-$ (Equation 14) in 50% Me_2SO–50% Water at 20 °C, μ = 0.5 M (KCl)

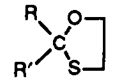
parameter	value
k_{-1}^{H}, $M^{-1}\ s^{-1}$	$(7.46 \pm 0.20) \times 10^2$
$k_{-1}^{H_2O}$, s^{-1}	$\approx 1.8 \times 10^{-8}\ s^{-1}$
k_{-1}^{AcOH}, $M^{-1}\ s^{-1}$	0.37 ± 0.06
pK_a^{NOH}	5.2 ± 0.1

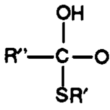
$\mathrm{Ph\overline{CSCH_2CH_2O}}$ moiety.

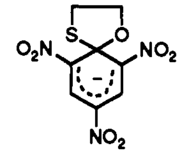
As mentioned above, we have assumed that the k_2^H process refers to the formation of **4-OCH$_2$CH$_2$SH** by C–S bond cleavage even though our HPLC spectra were not entirely conclusive; the alternative formation of **4-SCH$_2$CH$_2$OH** by C–O bond cleavage was definitely ruled out, though, since the spectrum of **4-SCH$_2$CH$_2$OH** would have been recognized very easily.

If the k_2^H process indeed refers to such formation of **4-OCH$_2$CH$_2$SH**, this would mean that acid-catalyzed C–S bond cleavage is faster than acid-catalyzed C–O bond cleavage. Both preferential C–S and preferential C–O bond cleavage have been reported in similar situations. For example, with the O,S-acetals **14**, acid-catalyzed C–O bond cleavage is faster than C–S bond cleavage when R = Et, but with R = Ph, C–S cleavage is dominant.[29] For 1,3-oxothiolanes (**15**), Fife[30] has postulated C–S cleavage, but other authors have reported C–O cleavage.[31,32] For more examples of O,S-acetal reactions, see ref 33. Similar competition between C–O and C–S bond cleavage occurs in the hydrolysis of ketene O,S-acetals[34] where products are formed by acid-catalyzed ROH or R'SH departure from **16**. For example, with R = R' = CH_3 and R'' = $PhCH_2$ methanol and methanethiol depart at comparable rates.[34a] More pertinent to the reaction of **7**$^-$ is the favored C–S bond cleavage over C–O bond cleavage in the *non*-catalyzed ring opening of **17**.[35]


14


15


16


17

C. Reaction of 4-(OMe,OMe)$^-$. The rate and equilibrium constants are summarized in Table VII. There is an interesting contrast in how **4-(OMe,OMe)**$^-$ (eq 14) and **7**$^-$ (Scheme III) behave in strongly acidic solution. In both cases there is "instantaneous" formation of the nitronic acid with comparable pK_a^{NOH} values (5.2 for **4-(OMe,OMe)**$^-$, 4.55 for **7**$^-$). With **7**$^-$ this is followed by rapid conversion to the carbon-protonated form (**7-CH**) which then slowly collapses to the product (**4-OCH$_2$CH$_2$SH**) via **7**$^-$ as a steady-state intermediate. With **4-(OMe,OMe)**$^-$, carbon protonation is not observed; it is the nitronic acid (**10-NOH**) that collapses to products (**4-OMe** + MeOH) via **4-(OMe,OMe)**$^-$, even though the pK_a of the carbon in **4-(OMe,OMe)**$^-$ is not expected to be substantially different from that in **7**$^-$. The reason for this difference in behavior is that $k_{-1}^H = 7.46 \times 10^2\ M^{-1}\ s^{-1}$ in eq 14 is much larger than $k_2^H \leq 2.36$ in Scheme III and favorably competes with protonation on carbon. We may assume that the rate constant for carbon protonation of **4-(OMe,OMe)**$^-$ is similar to $k_p^H = 47.2\ M^{-1}\ s^{-1}$ in Scheme III. This makes the ratio $k_{-1}^H/k_p^H \approx 15.8$, i.e., collapse of **4-(OMe,OMe)**$^-$ to **4-OMe** is indeed strongly favored over carbon protonation.

Conclusions

(1) Hydrolysis of **4-Cl**, **4-I**, **4-SEt**, and **4-OMe** is likely to occur by the addition–elimination mechanism. Our results are consistent with rate-limiting nucleophilic attack by OH$^-$ (or water) to form the intermediate **4-(LG,OH)**$^-$, which, however, cannot be observed directly.

(2) The mechanism of Scheme II cannot explain the failure to detect the intermediate, **4-(OMe,OH)**$^-$, in the hydrolysis of **4-OMe**. This conclusion is based on estimates for k_2 and k_2^H which show that $k_1^{OH}a_{OH^-} + k_1^{H_2O} \gg k_2 + k_2^H a_{H^+}$ by a wide margin. However, the results can be explained by the mechanism displayed in Scheme IV. A similarly expanded mechanism (Scheme VI) is needed to explain why the Meisenheimer complex (**TNA,OH**)$^-$ has never been observed in the S_NAr reaction of OH$^-$ with 2,4,6-trinitroanisole.

(3) A mechanism analogous to Scheme IV probably also operates in the hydrolysis of **4-SEt**, although the data do not require it. With **4-Cl** and **4-I** our simplest mechanism, Scheme I, is sufficient to account for the results even though the dianionic intermediate, **4-(LG,O**$^-$**)**$^-$, may also be involved in the conversion of the first intermediate to products, unless the k_2 step approaches a diffusion-controlled rate.

(4) The dependence of k_1^{OH} on the leaving group is determined by steric and polar effects except for the reaction of **4-OMe** where anomeric stabilization of the transition state leads to an unusually large k_1^{OH} value. $k_1^{H_2O}$ for water attack appears to be even more dramatically enhanced by this effect, presumably because of a later transition state.

(5) The reaction of **4-SCH$_2$CH$_2$OH** with OH$^-$ is much faster than that of the other substrates. This is because the reaction does not involve nucleophilic attack by OH$^-$ but intramolecular attack by the O$^-$ group to form the cyclic adduct **7**$^-$. Acid-catalyzed breakdown of **7**$^-$ leads to C–S rather than C–O bond cleavage.

Experimental Section

Materials. Ph(LG)C=CPh(NO_2) (LG = I, Cl, $HOCH_2CH_2S$, MeO) were available from a previous study.[4] Ph(SEt)C=CPh(NO_2) (**4-SEt**) was synthesized by adding 94 μL (1.27 mmoles) of ethanethiol to a solution of 0.038 g (0.127 mmoles) of **4-Cl** in 5 mL of acetonitrile. After addition of 177 μL (1.27 mmol) of triethylamine the reaction mixture was stirred for 1.5 h, poured into 25 mL of water, and extracted with 2 × 15 mL of dichloromethane. After the extract was washed with 5 × 25 mL of water and dried over Na_2SO_4 the solvent was evaporated. Recrystallization from 95% ethanol gave 15.5 mg (36% yield) of **4-SEt**: mp 84–86 °C; ^{1}H NMR (60 MHz, $CDCl_3$) δ 1.10 (t, 3 H, J = 7.2 Hz), 2.27 (q, 2 H, J = 7.2 Hz), 7.13 (s, 10 H); MS, m/e 285 (M$^+$); UV, λ_{max} = 365 nm (ϵ 1.08×10^4).

1,2-Diphenyl-2-nitroethanone (**8H**) was prepared by hydrolyzing 72 mg (0.31 mmol) of **4-Cl** in a solution of 1 mL of 1 N KOH in 5 mL of Me_2SO. The bright yellow solution was acidifed with 2 mL of 1 N HCl, and the resulting colorless solution was poured into 30 mL of CH_2Cl_2, washed with 5 × 30 mL of water, dried (Na_2SO_4), and evaporated under reduced pressure, to yield a thick oil. The oil was dissolved in 0.2 mL of ethyl acetate and chromatographed over a silica gel column equilibrated in hexane. With use of a 5:1 hexane–ethyl acetate eluant, the thick, yellow oil obtained after evaporation of the solvent at reduced pressure solidified after refrigeration for 7 days to give 0.0449 g (73% yield) of **8H**: mp 62.5–63.5 °C; ^{1}H NMR (60 MHz, $CDCl_3$) δ 7.96–7.20 (Ar-H, m); ^{13}C NMR (25 MHz, $CDCl_3$) δ 187.7 (C=O), 134.5, 130.8, 130.4, 129.2 (Ar), 94.4 (C–NO_2); IR, 1694 cm^{-1} (C=O); MS, m/e 241 (M$^+$).

Dimethyl sulfoxide (Fisher Scientific, reagent grade) was purified by vacuum distillation. Methoxyacetic acid, acetic acid, and KCl were reagent grade and were used without further purification. Dabco (1,4-diazabicyclo[2.2.2]octane) was purified by sublimation. KOH and HCl solutions were "Dilute-it" (Baker) diluted to appropriate volumes with distilled water.

Solutions and Kinetics. Our procedures were similar to the ones used earlier.[4,9] The fast reactions were measured in a Durrum-Gibson stopped-flow spectrophotometer and the slow ones in a Perkin-Elmer 559A

---

(29) Jensen, J. L.; Jencks, W. P. *J. Am. Chem. Soc.* **1979**, *101*, 1476.

(30) Fife, T. H.; Jao, L. K. *J. Am. Chem. Soc.* **1969**, *91*, 4217.

(31) (a) Guinot, F.; Lamaty, G.; Münsch, H. *Bull. Soc. Chim. Fr.* **1971**, 541. (b) Guinot, F.; Lamaty, G. *Tetrahedron Lett.* **1972**, 2569.

(32) Pihlaja, K. *J. Am. Chem. Soc.* **1972**, *94*, 3330.

(33) Satchell, D. P. N.; Satchell, R. S. *Chem. Soc. Rev.* **1990**, *19*, 55.

(34) (a) Hershfield, R.; Schmir, G. L. *J. Am. Chem. Soc.* **1972**, *94*, 1263. (b) Hershfield, R.; Yeager, M. J.; Schmir, G. L. *J. Org. Chem.* **1975**, *40*, 2940.

(35) Crampton, M. R.; Willison, M. J. *J. Chem. Soc., Perkin Trans. 2* **1976**, 901.

(36) Hallé, J. C.; Gaboriaud, R.; Schaal, R. *Bull. Soc. Chim. Fr.* **1970**, 2047.

UV-vis spectrophotometer, both thermostated and equipped with computerized data acqusition and analysis. All pH measurements were performed with an Orion Research 611 digital pH meter calibrated for 50% Me_2SO-50% water (v/v) with buffers described by Hallé et al.[32]

The kinetics of the conversion of **7**-CH to **4**-OCH_2CH_2SH in acidic solution (Scheme III) was followed by HPLC by using a reverse-phase ODS Hypersil (4.6 × 100 mm) column and a Hewlett-Packard 1090M LC instrument. This instrument is equipped with a diode array detector which allows recording of the spectra of each eluting species. The peak area corresponding to **7**-CH was measured as a function of time at 230 nm; the retention time of this peak was 5.4 min at 40 °C, 1.5 mL/min in 50% acetonitrile-50% water. A plot of ln (peak area) vs time was linear over at least 2.5 half-lives and its slope was equated with k_{obsd}[11]. All other HPLC experiments were performed under the same conditions.

Acknowledgment. This research was supported by Grants No. CHE-8617370 and No. CHE-8921739 from the National Science Foundation (C.F.B.) and a grant from the US-Israel Binational Science Foundation, Jerusalem, Israel (Z.R.).

Supplementary Material Available: Tables S1-S6 containing pseudo-first-order rate constants (k_{obsd}) for the hydrolysis of Ph(LG)=$CPh(NO_2)$ and the reaction of 7^- and **4-(OMe,OMe)**$^-$ with acid (9 pages). Ordering information is given on any current masthead page.

Chemistry of Hydrotrioxides.[1] Preparation, Characterization, and Reactivity of Dimethylphenylsilyl Hydrotrioxides. Hydrogen Trioxide (HOOOH), a Reactive Intermediate in Their Thermal Decomposition?

Božo Plesničar,*,† Janez Cerkovnik,† Jože Koller,†,‡ and Franci Kovač†

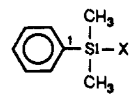
Contribution from the Department of Chemistry, University of Ljubljana, P.O. Box 537, 61000 Ljubljana, Yugoslavia, and "Boris Kidrič" Institute, 61000 Ljubljana, Yugoslavia.
Received December 3, 1990

Abstract: The preparation and ^1H, ^{13}C, and ^{29}Si NMR spectroscopic characterization of dimethylphenylsilyl hydrotrioxides (**2**), produced by the low temperature (−78 °C) ozonation of dimethylphenylsilanes (**1**) in acetone-d_6, methyl acetate, and dimethyl ether, is reported. ^1H NMR spectroscopic evidence for the involvement of a transient polyoxide, tentatively assigned to hydrogen trioxide (HOOOH), in the decomposition of **2** is given. All attempts to characterize both types of hydrotrioxides by ^{17}O NMR spectroscopy failed. The calculated relatively strong binding energy for the intermolecularly hydrogen-bonded cyclic dimer of HOOOH (BE = 7.7 kcal/mol, 6-31G**//6-31G) support the belief that self-association is, similarly to previously studied hydrotrioxides, $H_3SiOOOH$ and CH_3OOOH, the characteristic structural feature of this species. Kinetic and activation parameters for the decomposition of **2**, i.e., large negative activation entropies, a rather significant substituent effect on the decomposition of **2a** in methyl acetate (Hammett ρ value 1.2 ± 0.1) as well as the observed dependence of the rate of the decomposition of **2a** on solvent polarity, indicate the importance of polar decomposition pathways. The results of ESR spin trapping experiments are, together with product studies, discussed in terms of possible contributions of homolytic processes to the overall mechanism of the decomposition of **2**. The negative Hammett ρ values for the oxidation of phenyl methyl sulfides to sulfoxides and the latter to the corresponding sulfones with **2** as well as the reactivity order 4-XPhSMe ≫ 4-XPhSOMe indicate an electrophilic nature of the oxidant.

Introduction

Considerable interest has been devoted in recent years to the studies of ozonation of various saturated organic substrates.[2] Although the involvement of hydrotrioxides, ROOOH, in the reaction of ozone with C-H bonds has already been documented,[3,4] there have been no reports in the literature on the spectroscopic characterization of silyl hydrotrioxides.[5] However, these polyoxides have already been proposed as transient intermediates in the reaction of ozone with various silanes.[6] Very recently, triethylsilyl hydrotrioxide has been shown to be an excellent source of $^1O_2$[7] as well as an efficient reagent for direct conversion of electron-rich olefins to 1,2-dioxetanes and for the conversion of unactivated olefins to oxidatively fragmented carbonyl products.[8] As a part of our continuous interest in polyoxides, we wish to report the preparation, characterization, and thermal decomposition of dimethylphenylsilyl hydrotrioxides. Evidence for the involvement of still another polyoxide species, tentatively assigned to hydrogen trioxide (HOOOH), in the decomposition of these hydrotrioxides is given. Ab initio calculations have been carried out to predict the equilibrium structures of monomeric and cyclic dimeric HOOOH. The importance of polar decomposition pathways in the decomposition of these polyoxides is stressed. Attempts have also been made to elucidate possible contributions of homolytic processes to the overall decomposition mechanism of **2**. We also

Table I. Selected ^1H, ^{13}C, and ^{29}Si NMR Chemical Shifts (δ) of Dimethylphenylsilyl Hydrotrioxide and Some Other Organosilicon Analogues in Acetone-d_6 at −78 °C[a]



	^1H NMR		^{13}C NMR		^{29}Si NMR
X	δCH_3	δSi-X	δCH_3	δC(1)	δSi
H	0.30	4.40	−1.1	140.6	−16.95
OH	0.32	4.5-5.5	3.1	143.5	3.30
OOH	0.43	11.2	2.8	139.6	14.31
OOOH	0.55	13.96[c,d] 13.76 (−50 °C)	2.7	138.5	17.31
$OSi(CH_3)_2Ph$	0.33		3.9	143.1	−0.96
$OOSi(CH_3)_2Ph$	0.40		2.8	139.5	16.6

[a] Values in parts per million downfield from the internal standard Me_4Si. [b] Area ratio of peaks δSi-X:δCH_3 (X = H, OH, OOH, OOOH) was in all cases 1:6. [c] δOOOH, methyl acetate, 13.62; ethyl acetate, 13.64; dimethyl ether, 13.40. [d] δOOOH, 4-$CH_3PhSi(CH_3)_2O_3H$, 13.78; 4-$CH_3OPhSi(CH_3)_2O_3H$, 13.78; 4-$ClPhSi(CH_3)_2O_3H$, 13.70.

---

† University of Ljubljana.

‡ "Boris Kidrič" Institute.

0002-7863/91/1513-4946$02.50/0