J. Org. Chem. **1984**, *49*, 89–93

Reversibility of the Protonation in the Hydrolysis of 2-Methylene-1,3-dithiane and Its Derivatives

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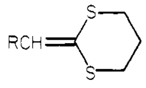
Received June 7, 1983

Acid-catalyzed hydrolyses of 2-methylene- (**1a**), 2-ethylidene- (**1b**), and 2-benzylidene-1,3-dithiane (**1c**) were studied kinetically in 10 vol % aqueous acetonitrile at 30 °C. The reaction takes place stepwise: protonation to form a carbocation **2** (k_1), hydration of **2** to give a 2-hydroxy-1,3-dithiane **3** (k_2), and decay of **3** to lead to a thiol ester. The effects of buffer and thiol on the rate indicate that the hydrolysis of **1a** and **1b** occurs through a mainly rate-determining protonation (k_2/k_{-1} = 45 for **1a** and 12 for **1b**), but the protonation is not solely rate determining for the hydrolysis of **1c** (k_2/k_{-1} = 1.6). The rate-determining step of the decay of **2** changes from formation of **3** above pH 2–3 to its breakdown at higher acidities. The hydrolysis reactivity of **1** is similar to that of the acyclic analogue, but the reversibility of the protonation of **1** is much smaller than that of the acyclic one. This is ascribed to the ease of hydration of **2** which may be due to the relief of the ring strain.

We have recently found that ketene dithioacetals undergo acid-catalyzed hydrolysis accompanying (partially) reversible protonation of the double bond.[1-3] This is in

$$RCH{=}C(SR')_2 + H_3O^+ \rightleftharpoons RCH_2C^+(SR')_2 + H_2O \rightarrow RCH_2C(OH)(SR')_2 \rightarrow RCH_2COSR' \quad (1)$$

marked contrast to closely related hydrolyses of ketene acetals,[4-9] vinyl ethers,[10-19] and vinyl sulfides,[20-22] all of which take place through rate-determining protonation. The present paper describes kinetic results of the hydrolysis of three cyclic ketene dithioacetals, 2-methylene-1,3-dithiane (**1a**) and its methyl- and phenyl-substituted derivatives (**1b** and **1c**), and presents discussion on the effects of the cyclic structure of the acetal on the reversibility of the protonation.



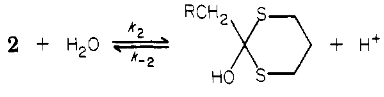
1a, R = H
b, R = CH_3
c, R = C_6H_5

Results

Hydrolysis of dithianes **1** occurs stepwise through two intermediates, a carbocation, **2**, and a hydrogen ortho thio esters, **3**, to lead to a thiol ester, **4** (eq 2–4) as an ultimate product under the reaction conditions employed. Further hydrolysis of **4** is slow enough in acid solutions. The final spectra of the reaction mixture showed an absorption maximum at 232–235 nm in accord with the formation of the thiol ester **4**. At higher acidities, however, formation of **4** monitored at this wavelength was delayed after the disappearance of **1** (followed at 250–260 nm for **1a** and **1b** and at 300 nm for **1c**). In strongly acidic solutions formation of the carbocation **2** was also observed (λ_{max} 310 nm).

(2)

1 **2**



(3)

3

$$\mathbf{3} \xrightarrow{k_3} RCH_2COS(CH_2)_3SH \quad (4)$$

4

The progress of the reaction was monitored spectrophotometrically as a function of time at 30 °C usually in an aqueous solution containing 10 vol % of acetonitrile (the ionic strength maintained at 0.45 M with KCl) but in almost wholly aqueous solutions (0.5% CH_3CN) of $HClO_4$ at higher acidities ($H_0 < 0$). In dilute HCl solutions ([HCl] < 0.01 M), disappearance of **1** followed pseudo-first-order kinetics, and the observed rate constants k_{obsd} are proportional to acid concentration (Figure 1); catalytic constants k_{H^+} are summarized in Table I.

Disappearance of **1a** monitored at 260 nm is faster than formation of the product **4a** (232 nm) at pH <2.5. The rate constants for the formation of **4a** change in a complicated manner with pH(H_0) as shown with open circles in Figure 1. The acidity functions H_0 of $HClO_4$ solutions were calculated by polynominal formulas presented by Kresge et al.[23] In strongly acidic solutions ([$HClO_4$] > 1.7 M), development of the absorption at 310 nm due to **2a** was instantaneous, and the subsequent decrease followed first-order kinetics, giving a k_{obsd} identical with that obtained from the formation of **4a** (232 nm). Similar spectral

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Table I. Rate Constants for the Hydrolysis of 1

no.	R	k_{H^+},[a] M^{-1} s^{-1}	k_{H^+}/k_{D^+}	k_1,[a] M^{-1} s^{-1}	k_2/k_{-1}[a]
1a	H	35.6 (33.4)[b]	3.36[c]	36 (44.1)[b]	45 (3.13)[b]
1b	CH_3	0.764 (1.28)[e]	3.44[d]	0.83 (1.9)[e]	12 (2.0)[e]
1c	C_6H_5	0.0897 (0.0939)[f]		0.15 (0.35)[f]	1.6 (0.36)[f]

[a] Obtained in 10 vol % CH_3CN-H_2O at $\mu = 0.45$ (KCl) and 30 °C. Values in parentheses are those determined for the acyclic analogues $RCH{=}C(SCH_3)_2$. [b] Reference 2. [c] $k_{obsd} = 3.76 \times 10^{-2}$ s^{-1} in a DCl solution (10% CH_3CN-D_2O, $\mu = 0.45$, [DCl] $= 3.55 \times 10^{-3}$ M). [d] $k_{obsd} = 7.87 \times 10^{-4}$ s^{-1} under the same conditions as described in footnote *c*. [e] Reference 3. [f] Reference 1.

Table II. Buffer Effects on the Hydrolysis Rates of 1

substrate	buffer	pH	$[B]_t$,[a] M	K_{app}, M	$\Delta k_{max}/k_0$
1a	formate	3.62	0.50	2.2 ± 3.2	56 ± 80
	acetate	4.33	0.40	0.34 ± 0.04	33 ± 3
	acetate	4.71	0.40	0.37 ± 0.14	53 ± 18
	acetate	5.04	0.45	0.21 ± 0.06	50 ± 12
1b	formate	3.11	0.80	1.10 ± 0.49	9.2 ± 3.8
	formate	3.62	0.80	0.87 ± 0.57	14.5 ± 4.2
1c	chloroacetate	2.82	0.50	0.19 ± 0.04	1.66 ± 0.21

[a] The highest concentration used.

behavior was apparent also with the methyl-substituted derivative **1b**, but detailed kinetic analysis was not undertaken.

The reaction of the phenyl-substituted derivative **1c** was much slower than that of the other two, and the apparent kinetic behavior seemed to be somewhat different. In the pH(H_0) range −0.5 to +2, induction periods were observed for the decrease in absorbance at 300 nm (both **1c** and **2c** absorb light at this wavelength), and k_{obsd} values obtained after the induction period are smaller than those extrapolated from higher pH. At still higher acidities ($H_0 < -0.5$), k_{obsd} decreases with increasing acidity (Figure 1).

The rates were also measured in a deuterium solution containing 10 vol % of acetonitrile. First-order kinetics held for both **1a** and **1b** and an kinetic isotope effect k_{H^+}/k_{D^+} of about 3.4 was estimated as given in Table I. For the reaction of **1c** at [DCl] = 4.97×10^{-2} M, the pseudo-first-order plots curved, probably owing to the isotope exchange[1] as well as the induction period. The approximate initial slope was 7.7×10^{-4} s^{-1}, and the ultimate slope was 9.96×10^{-4} s^{-1}.

Hydrolysis rates of 1 were measured in buffer solutions of carboxylates. Rate constants k_{obsd} are given in Table S1 (supplementary material). They increase with buffer concentration following eq 5 as observed before with other

$$\Delta k = \Delta k_{max}[B]_t/(K_{app} + [B]_t) \qquad (5)$$

ketene dithioacetals.[1-3] In eq 5, $\Delta k = k_{obsd} - k_0$ and $\Delta k_{max} = k_{max} - k_0$. This occurs because the rate-determining step changes with buffer concentration. The limiting rate constants k_0 and k_{max} at the zero and infinite concentrations of the buffer and the parameter K_{app} are described by eq 6–8[2] by using rate constants k_1 and k_{-1} given in eq

$$k_0 = k_{H^+}[H^+] = k_1\bar{k}_2[H^+]/(k_{-1} + \bar{k}_2) \qquad (6)$$

$$k_{max} = k_1\bar{k}_2[H^+]/k_{-1} \qquad (7)$$

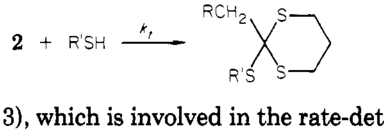
$$K_{app} = (k_{-1} + \bar{k}_2)/k_{-1}'\alpha \qquad (8)$$

2, the apparent rate constant $\bar{k}_2$ for the decay of the carbocation intermediate **2**, and the catalytic constant k_{-1}' for general-base-catalyzed deprotonation of **2**. The parameter α denotes the fraction of conjugate base of the buffer. The rate constants k_0 were calculated from k_{H^+} obtained in HCl solutions. The parameters Δk_{max} and K_{app} were evaluated by least-squares treatments of $1/\Delta k$ vs. $1/[B]_t$ and are summarized in Table II.

The effects of added 2-mercaptoethanol on the rate of disappearance of the substrate 1 were examined, while keeping the total amount of organic components (CH_3CN + $HOCH_2CH_2SH$) in the solution constant at 10% by volume. Rate constants are given in Table S2 (supplementary material). In HCl solutions the rate was hardly affected by the addition of thiol for **1a** ([HCl] = 0.001 and 0.002 M and [RSH] < 0.71 M) and for **1b** ([HCl] = 0.01 M and [RSH] = 0.12 M). However, the disappearance of **1c** was greatly accelerated by added thiol ([HCl] = 0.005–0.4 M). The nonlinear dependence of the rate increase Δk^T ($= k_{obsd} - k_0$) on thiol concentration [RSH] is described by eq 9 as before.[2] This occurs undoubtedly

$$\Delta k^T = \Delta k_{max}{}^T[RSH]/(K_{app} + [RSH]) \qquad (9)$$

because an additional pathway of disappearance of the intermediate carbocation **2** (eq 10) can compete with the



(10)

hydration (eq 3), which is involved in the rate-determining

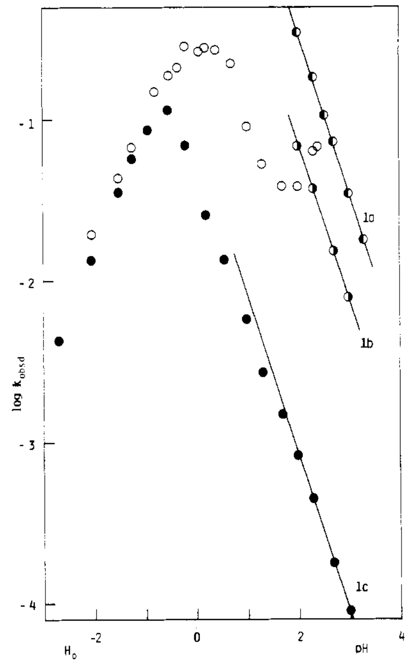


Figure 1. pH(H_0) − log k_{obsd} profiles for the hydrolysis of **1a** (◐, disappearance; ○, formation of **4a** or disappearance of **2a**), **1b** (◑), and **1c** (●).

Table III. Effects of Added 2-Mercaptoethanol on the Rate of Disappearance of 1c

[HCl], M	[RSH],[a] M	10^3k_0, s^{-1}	K_{app}^T, M	$10^3k_{max}^T$, s^{-1}	$k_0/\Delta k_{max}^T$	$k_{max}^T/K_{app}^T k_0$, M^{-1}
0.40	0.50	20.3	0.20 ± 0.03	60.7 ± 3.4	0.50 ± 0.05	14.6
0.10	0.50	5.76	0.18 ± 0.01	15.2 ± 0.2	0.61 ± 0.12	14.3
0.05	0.355	2.90	0.26 ± 0.09	6.65 ± 0.80	0.78 ± 0.17	8.9
0.01	0.50	0.994	0.27 ± 0.03	1.563 ± 0.034	1.75 ± 0.11	5.9
0.005	0.50	0.452	0.26 ± 0.07	0.732 ± 0.046	1.61 ± 0.27	6.1

[a] The highest concentration used.

step of the hydrolysis. The limiting rate constant k_{max}^T at the infinite concentration of thiol and the parameter K_{app}^T are expressed by eq 11 and 12.[2] These parameters

$$k_{max}^T = k_1[H^+] \tag{11}$$

$$K_{app}^T = (k_{-1} + \bar{k}_2)/k_t \tag{12}$$

were calculated by least-squares treatments of $1/\Delta k^T$ vs. $1/[RSH]$ and are given in Table III. In acetate buffer solutions ($[B]_t = 0.20$ and 0.45 M at pH 4.7), the rate of disappearance of **1a** increased markedly by added thiol in contrast to the results obtained in HCl solutions. Some results are included in Table S2 but further examinations were not undertaken.

Discussion

Effects of Buffer and Thiol. The nonlinear dependence of the rate on buffer concentration is undoubtedly ascribed to a change in the rate-determining step as discussed previously.[1-3] This comes from the fact that buffer components catalyze only the protonation step (eq 2) but not the subsequent steps (eq 3). The kinetic parameters of eq 5 are thus described by eq 6–8 by using rate constants k_1, k_{-1}, and $\bar{k}_2$. The rate constant $\bar{k}_2$ refers to the overall reaction of breakdown of the imediate intermediate **2** formed by the protonation. Although the hydration of **2** (eq 3) does not seem always to be the rate-determining step of the breakdown, we have reasonable evidence that this is the case at the pH values (>2.8) where the buffer effects were examined; hence $\bar{k}_2 = k_2$. Equation 13 can be derived

$$k_2/k_{-1} = \Delta k_{max}/k_0 \tag{13}$$

from eq 6 and 7. Values of $\Delta k_{max}/k_0$ are given in the last column of Table II, and average values are recorded in Table I as k_2/k_{-1}.

For the disappearance of **1a** and **1b** the protonation is largely rate determining at pH >3, but added buffers accelerate this step to make the subsequent step rate-determinig at high buffer concentrations. In accord with this behavior, 2-mercaptoethanol barely affects rate of the reaction of both **1a** and **1b** in HCl solutions but accelerates the reaction of **1a** (**1b** not examined) in acetate buffer solutions.

At higher acidities, the appearance of **4a** is delayed significantly after the disappearance of **1a**. That is, the intermediate **3** (or **2** at still higher acidities) accumulates, and the rate-determining step of the overall hydrolysis must be the decomposition of **3** (eq 4) as will be discussed below.

For the reaction of **1c**, the value k_2/k_{-1} evaluated from the buffer experiment is 1.66. Both steps, the protonation and hydration, are partially rate determining. Added 2-mercaptoethanol accelerates the reaction even in HCl solutions in this case. The curved dependences of rate on thiol concentration gave the kinetic parameters of eq 9 as summarized in Table III. Since the value k_{max}^T is described by eq 11, k_1 is calculated to be 0.148 M^{-1} s^{-1} as an average. From the values of k_1 and k_{H^+}, k_2/k_{-1} is evaluated to be 1.54, which is in fair agreement with that obtained from the buffer experiment. The value $\bar{k}_2/k_{-1}$ is also evaluated according to eq 14. The calculated values of $k_0/\Delta k_{max}^T$

$$\bar{k}_2/k_{-1} = k_0/\Delta k_{max}^T \tag{14}$$

vary with [HCl] as listed in Table III, but they seem to approach the constant value of 1.6 at lower acidity (pH >2) in good agreement with the value k_2/k_{-1} evaluated above. That is, above pH 2 the hydration becomes essentially the rate-determining step of the breakdown of the carbocationic intermediate **2c**: $\bar{k}_2 = k_2$. Below this pH the hydration step is no more solely rate determining, and finally the decomposition of **3** may become the slow step. The overall rate constant $\bar{k}_2$ would diminish with increasing acid concentration, and hence $\bar{k}_2/k_{-1}$ becomes smaller. A steady-state approximation to **2** results in eq 15.

$$\bar{k}_2 = k_2k_3/(k_{-2}[H^+] + k_3) \tag{15}$$

On the other hand, the relative rate constant $k_t/\bar{k}_2$ is calculated by eq 16. Such values are listed in the last

$$k_t/\bar{k}_2 = k_{max}^T/K_{app}^T k_0 \tag{16}$$

column of Table III. These values seem also to vary with [HCl] approaching the constant value $k_t/k_2 = 6$ M^{-1} above pH 2. This observation is also compatible with the changeover of the rate-determining step of the breakdown of **2c**, the hydration being rate determining at pH >2. The increase in $k_t/\bar{k}_2$ with acid concentration must be due to the decrease in $\bar{k}_2$ (eq 15). At higher acidities, however, the reaction of thiol with **2** (eq 10) would also become reversible and situations may be more complicated.

Decay of the Carbocation Intermediate. During the reaction of **1a**, formation of the thiol ester product **4a** was delayed significantly after the disappearance of the starting substrate **1a** below pH 2.5 and showed a complex pH–rate profile (Figure 1). Some intermediate must accumulate in this acidity range. Above pH 0 the hydrogen ortho thio ester **3a** should be such an intermediate, since the carbocation **2a** cannot be stable. The cation **2a** can be spectrophotometrically observed (310 nm) in strong acid, and both **2a** and **3a** must exist as an equilibrium mixture at certain acidities. The rates of formation of **4a** were found to be identical with those of decay of **2a** at such acidities ($[HClO_4]$ > 1.7 M) where the latter reaction can be observed. The complex acidity–rate profile thus refers to the decay of **2a**, with the breakdown of **3a** (k_3) being rate determining. Formation of **2a** from **1a** is much faster than the subsequent reactions at pH <2.5.

The observed rate constant for the formation of **4a** is described by eq 17, where K_2 and h_R are the equilibrium

$$k_{obsd} = k_3K_2/(K_2 + h_R) \tag{17}$$

constant for reaction 3 ($K_2 = k_2/k_{-2}$) and the acidity function ($h_R = 10^{-H_R}$),[23,24] respectively. Since the equilibrium 3 should depend on the H_R acidity function, the equilibrium fraction of **3a** decreases with increasing acidity

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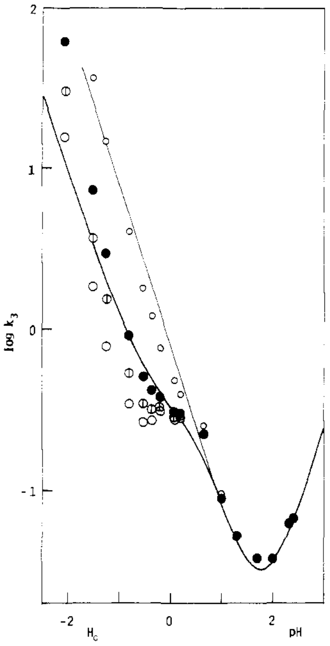


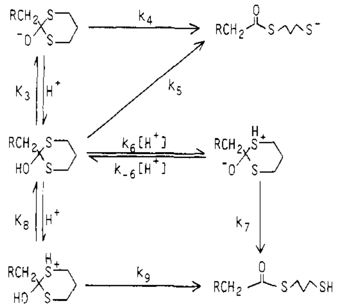
Figure 2. pH(H_0) − log k_3 profiles for the breakdown of **3a**. The values of k_3 are calculated by assuming K_2 = 1 (small circles), 10 (●), 20 (circles with vertical bar), and 40 (○). The solid curve is calculated by eq 18 with parameters given in text.

according to $K_2/(K_2 + h_R)$. This decrease in concentration of **3a** results in the decrese in observed rate. With the assumption of an appropriate K_2 value, k_3 can be calculated by eq 17. The k_3 values calculated with K_2 = 2–40 are logarithmically plotted against H_0 (pH) in Figure 2. The values k_3 obtained with K_2 = 2 seem to reflect simply acid- and hydroxide-ion-catalyzed reactions, but those calculated with $K_2 \geq 10$ are characteristic in that there is a plateau region around H_0 = 0. Since the appearance of the absorption of the cation **2a** was found only at $[\mathrm{HClO_4}] > 1$ M ($H_R < -0.8$), K_2 would not be smaller than 10. The profile obtained with K_2 = 40 (or greater values) has a second minimum near $H_0 = -0.5$, which is hard to be accommodated by any reasonable mechanism. Thus, the value of K_2 must be 10–40, *and the reaction does involve* a water-catalyzed (uncatalyzed) reaction as a rate-determining step around H_0 = 0.

The acidity–rate profile for the breakdown of 2-hydroxy-1,3-dithiane **3a**, that is characterized by two regions of acid catalysis, an uncatalyzed one in between, and a hydroxide ion catalyzed one at higher pH, may be accounted for by the mechanism given in Scheme I. A similar pH–rate profile was previously found for the decomposition of 2-hydroxy-1,3-dithiolane during the reaction of 2-(*p*-methoxyphenyl)-1,3-dithiolan-2-yl cation and accommodated by a similar mechanism.[25] The hydroxide ion reaction at pH >2 corresponds to the breakdown of an anionic intermediate (k_4). Of the two acid-catalyzed reactions, the one at higher acidities ($H_0 < -1$) must involve a cationic intermediate (k_9), and the other in the region of pH 1 would be due to an acid-catalyzed proton switch to form a zwitterionic intermediate (k_6). The uncatalyzed reaction must then be the breakdown of the zwitterion (k_7). The apparent rate constant k_3 is described by eq 18 according to Scheme I. The solid curve of Figure 2 is calculated by eq 18 with the following kinetic parameters: $K_3k_4 = 2.5 \times 10^{-4}$ M s^{-1}, $k_5 = 0$, $k_6 = 1$ M^{-1}s^{-1}, k_6k_7/k_{-6} = 0.3 s^{-1}, $k_9/K_8 = 0.1$ M^{-1} s^{-1}. The pH-dependent change of k_3 obtained with K_2 = 10 (closed points) resembles the curve although points at higher acidities deviate upward, probably owing to improper choice of the acidity function. The pK_2 value of −1 is not unreasonable as compared with p$K_2 \simeq 0$ for the 2-methyl-1,3-dithiolan-2-yl cation.[26] Direct breakdown of the neutral intermediate **3a** (k_5), a contribution from which might be found at the minimum near pH 2, was not appreciably observed in the present reaction.

$$k_3 = K_3k_4/[\mathrm{H}^+] + k_5 + k_6k_7[\mathrm{H}^+]/(k_{-6}[\mathrm{H}^+] + k_7) + k_9[\mathrm{H}^+]/K_8 \quad (18)$$

Scheme I



The reaction of the phenyl derivative **1c** was followed only by the decrease in absorbance at 300 nm, where **1c** and **2c** absorb light. The rate constants deviate from the line of slope −1 in the log k_{obsd}–pH plot below pH 2 and decrease at $H_0 < -0.5$ (Figure 1). The deviation must be due to the change in the rate-determining step around pH 2 as discussed above. The decrease in rate at high acidity is ascribed to the decreasing fraction of the hydroxydithiane intermediate **3c**, with its breakdown being rate determining as is the case with **1a**. Observed rates for **1a** and **1c** in this acidity region are approximately equal to each other. The β-phenyl group affects little the rate of decay of the carbocation **2**.

The observed rate constant in strong acid is described by $k_{\mathrm{obsd}} = (K_2k_9/K_8)(h_0/h_R)$ according to Scheme I (eq 18). The equilibrium fraction of **3** decreases with the acidity function H_R, but the breakdown of **3** may follow another acidity function, H_0. Since H_R decreases more rapidly than does H_0 with increasing acid concentration,[24] k_{obsd} decreases with acidity. For certain acid concentrations the H_R function is approximately given by $2H_0$ ($h_R = h_0^2$);[24] thus, the slope of log k_{obsd}–H_0 line is nearly unity. The behavior of the intermediate **3** might be of interest in view of closely related tetrahedral intermediates of an important reaction, thiol ester hydrolysis.[27-30]

Reactivity. Rate constants for the acid-catalyzed hydrolysis of **1** are summarized in Table I together with those for the acyclic analogues. Hydrolysis rates of the three substrates **1** are all close to those of the corresponding acyclic compounds, ketene dimethyl dithioacetals.[1-3] More specifically, the rate of protonation (k_1) of **1** is slightly (∼2-fold) smaller than that of the acyclic acetal.

The barrier against protonation is not affected by the cyclic structure of dithiane (six-membered ring), but the subsequent hydration of the carbocation **2** seems to be accelerated by the cyclic structure. This difference be-

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tween the effects on the two steps may be related to the fact that the latter reaction accompanies the hybridization changes (sp^2 to sp^3) of the 2-carbon involved in the dithiane ring, but the former does not undergo such a change. The 2-carbon is sp^2 hybridized in both states of **1** and **2** and so are the two adjacent sulfur atoms. However, these three atoms become sp^3 hybridized in **3**. As a result, the forced planarity involving the S–C–S triad induces a considerable strain to the dithiane ring of **1** and **2**, but such a strain does not occur in **3**. The strain does not change during the first step, but it is largely relieved during the second step of the hydrolysis of **1**. This would make the hydration of **2** faster than that of the acyclic analogue.

Experimental Section

Materials. 2-Methylene- (**1a**), 2-ethylidene- (**1b**), and 2-benzylidene-1,3-dithiane (**1c**) were prepared from 2-lithio-2-(trimethylsilyl)-1,3-dithiane and an appropriate aldehyde by the method of Seebach.[31] Boiling points were as follows: **1a**, 105 °C (22 mmHg) [lit.[31] 100 °C (20 mmHg)]; **1b**, 83 °C (2.5 mmHg) [lit.[31] 83 °C (2.5 mmHg)]; **1c**, 133–135 °C (0.1 mmHg) [lit.[31] 148 °C (0.2 mmHg)]. Other materials were obtained as described previously.[2]

Kinetic Measurements. Rate constants were determined in the same way as before.[2] Reactions at low acidities were carried out in aqueous HCl and buffer solutions containing 10 vol % of acetanitrile at 30 °C, the ionic strength being maintained at 0.45 M with KCl. Wholly aqueous HClO$_4$ solutions were used without any added salt for the reactions at higher acidities. Acid concentrations were determined by titration with a standard NaOH solution. Reactions were followed spectrophotometrically at an appropriate wavelength on a Shimadzu UV 200 spectrophotometer. The pH values of 10% CH$_3$CN–H$_2$O solutions were measured on a Hitachi-Horiba F-7 pH meter and corrected by subtracting 0.06 from the pH meter readings.[2]

Registry No. **1a**, 21777-31-1; **1b**, 51102-62-6; **1c**, 17590-58-8; deuterium, 7782-39-0; 2-mercaptoethanol, 60-24-2.

Supplementary Material Available: Tables S1 and S2 consisting of rate constants for the hydrolysis of **1** in buffer solutions and in the presence of 2-mercaptoethanol (2 pages). Ordering information is given on any current masthead page.

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Aromatic Nucleophilic Substitution. 19.[1] Kinetics of the Formation and Decomposition of 1,1-Disubstituted Naphthalene Meisenheimer Complexes in the Reactions of 1-Methoxy-2-cyano-4-nitronaphthalene with Various Metal Methoxides in Methanol. Evidence for Absence of Ion Pairing of Meisenheimer Complexes with Counterions

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Received May 10, 1983

The reactions of 1-methoxy-2-cyano-4-nitronaphthalene (**2**) with various metal methoxides have been studied. In the reactions of **2** with sodium, potassium, and lithium methoxides there are no minima in the relationships between k_ψ (pseudo-first-order rate constant) and alkoxide concentrations, which shows the absence of ion pairing of an anionic σ complex with a counterion. Furthermore, the K_c value (apparent equilibrium constant) increases slightly with increasing alkoxide concentration. Replacement of a cyano group at C-2 destabilized $\mathbf{2}^-$ (1,1-dimethoxy-substituted anionic σ complex of **2**) in comparison with $\mathbf{1}^-$ [1,1-dimethoxy-substituted anionic σ complex of 1-methoxy-2-nitro-4-cyanonaphthalene (**1**)].

Anionic σ complexes (Meisenheimer complexes) have been synthesized by attack of nucleophiles on polynitro aromatic compounds.[2] Furthermore, much evidence has accumulated for many nucleophilic aromatic substitution reactions that involve such complexes as intermediates.[3] Accordingly, much attention is concentrated on the stabilities and rates of formation and decomposition of such complexes. Naphthalene anionic σ complexes have been investigated in the reactions of several nitronaphthalenes with metal alkoxides.[2,4–10]

We previously reported the kinetics of formation and decomposition of the 1,1-disubstituted naphthalene anionic σ complexes (hereafter called complexes) in the reactions of 1-methoxy-2-nitro-4-cyanonaphthalene (**1**) with metal alkoxides in methanol, in which ion pairing took place between a complex and a counterion (Na$^+$ or K$^+$), as a result of the 2-nitro group in some cases.[3] In order to make sure of these results, we have carried out the reactions of 1-methoxy-2-cyano-4-nitronaphthalene (**2**) with three

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