5 equiv) was added dropwise, and the cooling bath was removed. After the solution was stirred for 40 min at room temperature, a solution of tetra-*n*-butylammonium fluoride trihydrate (338 mg, 1.07 mmol, 6.0 equiv) in THF (2 mL) was added. The mixture was stirred for 30 min, diluted with CH_2Cl_2, poured into brine, and thoroughly extracted with CH_2Cl_2. The combined extracts were dried over anhydrous sodium sulfate, filtered, evaporated, and separated on a silica gel column (eluted with Et_2O, then 10% acetone in Et_2O) to afford 39 mg (64%, 82% based on recovered **2**) of the aldols **13**. The major diastereoisomer (56% yield) was separated from two minor, inseparable isomers on PTLC silica gel (33% acetone in Et_2O). Major diastereoisomer mp 195-196 °C (recrystallized from hexane/CH_2Cl_2).

^1H NMR (100 MHz) ($CDCl_3$) δ ($CHCl_3$) 1.16 (3 H, s), 1.33 (3 H, s), 1.38 (3 H, s), 1.48-2.25 (4 H, m), 2.94 (3 H, s), 3.04 (3 H, s), 3.12-4.16 (5 H, m), 4.11 (1 H, d, J = 10 Hz), 6.45 (1 H, d, J = 10 Hz, D_2O exchange); IR (NaCl, neat) 3380 (broad), 1670, 1210, 750 cm^{-1}; mass spectrum, m/e 327 ($M^+ - CH_3$, 8.0%), 227 (65.4), 198 (8.3), 115 (100). Anal. ($C_{16}H_{26}N_2O_6$) C, H, N.

Regioselective Synthesis of 13 (n = 1, R = $CH_2CH{=}CH_2$; Table IV, Entry 4). The same procedure as described above for **13** (n = 1, R = CH_3), starting from **12** (n = 1, R = $SiMe_3$) and allyl bromide, was used. From 13 mg (0.05 mmol) of **12**, 3.5 mg (24%, 74% based on recovered **12**) of **20** (R′ = $SiMe_3$, R = $CH_2CH{=}CH_2$) was obtained (chromtographed on PTLC silica gel eluted with 20% hexanes in Et_2O) (oil). ^1H NMR (100 MHz) ($CDCl_3$) δ ($CHCl_3$) 0.16 (9 H, s), 1.83-2.13 (2 H, m), 2.27 (2 H, m), 2.51 (3 H, s), 3.81 (3 H, s), 3.88-4.22 (2 H, m), 4.9-6.4 (3 H, m). From 3 mg (0.01 mmol) of **20**, 1 mg (46%, 70% based on recovered **19**) of **13** (n = 1, R = $CH_2CH{=}CH_2$) was obtained (chromatographed on PTLC silica gel eluted with 20% acetone in Et_2O) (oil).

^1H NMR (100 MHz) ($CDCl_3$) δ ($CHCl_3$) 1.74-2.27 (4 H, m), 2.45 (3 H, s), 3.17 (3 H, s), 3.56 (1 H, m), 3.88 (2 H, m), 4.95-6.09 (3 H, m); IR (NaCl, neat) 1650, 1480, 1330, 1270, 1110, 1095, 910 cm^{-1}; mass spectrum, m/e 224 (M^+, 3.4%), 195 (2), 188 (2.3), 157 (41.4), 110 (100).

Acknowledgment. Acknowledgement is made to the National Institutes of Health Grant 1 R01 AIGM 18957-01, the donors of the Petroleum Research Fund administered by the American Chemical Society (No. 12786-G1), Research Corp., and the Colorado State University Biomedical Research Support Grant 537276 for support of this work. NMR measurements at 360 and 90.54 MHz were obtained at the Colorado State University Regional NMR Center, funded by the National Science foundation Grant CHE 78-18581.

Registry No. 2, 78877-97-1; **3**, 85168-14-5; **8**, 5076-82-4; **9**, 85168-15-6; **10**, 85168-16-7; **11**, 85168-17-8; **12** (n = 1, R = $SiMe_3$), 85168-18-9; **12** (n = 1, R = $CH_2CH{=}CH_2$), 85168-19-0; **12** (n = 1, R = SCH_3), 85168-20-3; **12** (n = 1, R = COPh), 85168-21-4; **12** (n = 1, R = CH_3), 85168-22-5; **12** (n = 2, R = CH_3), 78878-06-5; **12** (n = 2, R = SCH_3), 85168-23-6; **12** (n = 2, R = CHOHPh) (isomer 1), 85168-24-7; **12** (n = 2, R = CHOHPh) (isomer 2), 85201-87-2; **12** (n = 2, R = $CH_2CH{=}CH_2$), 85168-25-8; **12** (n = 2, R = COPh), 85168-26-9; **12** (n = 2, R = $SiMe_3$), 85168-27-0; **13** (n = 1 R = $CH_2CH{=}CH_2$), 85185-14-4; **13** (n = 1, R = CH_3), 85185-15-5; **13** (n = 2, R = CH_3), 78878-02-1; **13** (n 2, R = CHOHPh) (isomer 1), 85168-28-1; **13** (n = 2, R = CHOHPh) (isomer 2), 85201-88-3; **13** (n = 2, R = $CH_2CH{=}CH_2$), 85168-29-2; **13** (n = 2, R = COPh), 85168-30-5; **13** (n = 2, R = $CHOHC(Me)CH_2OC(Me)_2O$), 85168-31-6; **14** (n = 1, R = $SiMe_3$), 85185-16-6; **14** (n = 1, R = SCH_3), 85185-17-7; **14** (n = 1, R = CH_3), 85185-18-8; **14** (n = 2, R = CH_3), 85168-32-7; **18**, 85168-33-8; **19**, 85168-34-9; **20** (n = 1, R = CH_3; R′ = $SiMe_3$), 85185-19-9; pySSpy, 2127-03-9; ethylene oxide, 75-21-8; 2-methyl-2,3-*O*-isopropylidenepropionaldehyde, 68691-67-8; allyl bromide, 106-95-6.

Acid-Catalyzed Hydrolysis of 1,1-Bis(methylthio)ethene. Buffer- and Thiol-Dependent Changes in the Rate-Determining Step

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Abstract: Acid-catalyzed hydrolysis of 1,1-bis(methylthio)ethene has been studied kinetically in 10% aqueous acetonitrile at 30 °C. The rate increased with buffer concentration, showing saturation at higher concentrations. Addition of 2-mercaptoethanol had little influence on the rate at the limiting zero buffer concentration, but it greatly accelerated the reaction in buffer solutions and followed a saturation curve. It was concluded that the rate-determining step is largely the protonation of the double bond at zero buffer concentration (k_2/k_{-1} = 3.13) but it changes to the attack of water on the intermediate carbenium ion as the buffer concentration increases. The ^1H NMR spectral analysis of the reaction products in 80% CH_3CN-D_2O showed that the H-D isotope exchange at the 2-position of the substrate occurred extensively in a formate buffer but only moderately in a DCl solution during the hydrolysis.

Acid-catalyzed hydrolyses of vinyl ethers,[1-3] vinyl sulfides,[4-6] and ketene acetals[7-12] occur through hydration of the carbon-carbon double bond; a hemiacetal, or a hydrogen ortho ester, thus formed rapidly decomposes to the ultimate reaction products (eq 1). It is known that ketene dithioacetals undergo hydrolysis similarly to give thiolesters.[13-15]

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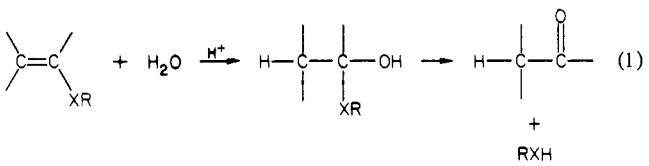
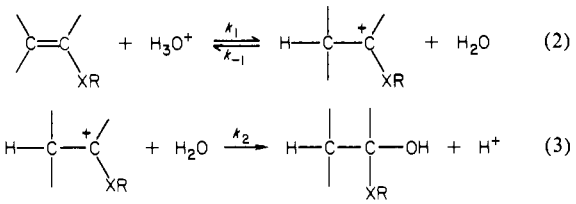


(1)

X = O or S

The hydration takes place through the initial carbon protonation (eq 2) followed by the water attack on the carbenium ion inter-



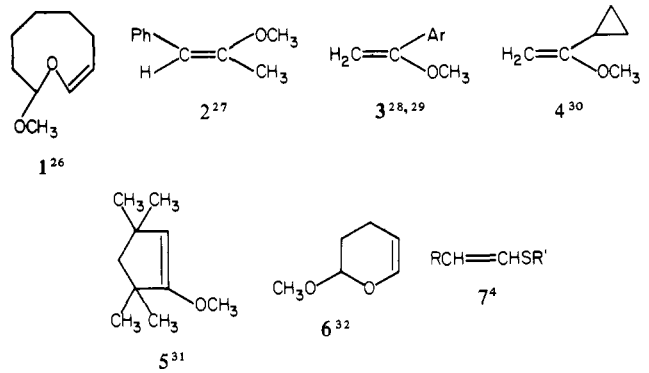
(2)

(3)

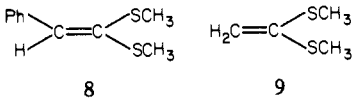
mediate (eq 3). The carbon protonation is usually rate determining ($k_{-1} < k_2$), as is the case for simple alkenes.[16-19] However, the margin of the difference between k_{-1} and k_2 is not very large. Tertiary alcohols were found to undergo ^{18}O exchange only 1–2 orders of magnitude more rapidly than they dehydrate to give alkenes.[20-22]

Some enamines undergo hydrolysis with rate-determining attack of water on the iminium ion intermediate in acid solutions where the iminium ion is built up.[23-25] The rate constant k_2 was however evaluated to be about 7 times greater than k_{-1} for the hydrolysis of piperidine enamines of propiophenone.[25]

In 1971 Cooper et al.[26] claimed in their short communication that a vinyl ether of somewhat unusual structure **1** underwent hydrolysis through a rapid and reversible protonation in acetate buffers. Since then such a change in the rate-determining step of the hydrolysis has been searched for with several vinyl ethers **2–6** and vinyl sulfides **7**.



All these substrates were however found to undergo hydrolysis by the conventional mechanism involving rate-determining protonation. Structural modifications designed to stabilize the initial state relative to the carbenium ion might lower the free energy of the protonation transition state while not affecting very much the transition state for subsequent hydration of this ion, and this might thereby effect a mechanistic change. However, it was found that phenyl conjugation was not enough to induce such a change (**2**).[27] A single alkylthio group was also found to be insufficient to change the rate-determining step (**7**).[7] Two alkylthio groups coupled with a phenyl group, however, were found to effect the mechanistic change when the hydrolysis of 1,1-bis(methylthio)-2-phenylethane (**8**) proved to proceed through a rapid and



8 **9**

reversible protonation followed by a rate-dtermining decay of the carbenium ion intermediate.[33] Similar reversibility of the carbon protonation has recently been found in the hydrolysis of vinyl selenides.[34,35]

The present communication deals with hydrolysis of a simple ketene dithioacetal, 1,1-bis(methylthio)ethene (**9**). The hydrolysis of this thioacetal takes place through predominantly rate-determining protonation in mineral acid solutions. However, the hydration of the resultant carbenium ion becomes rate determining as buffer concentration increases. Moreover, addition of thiol to the reaction mixture accelerates the decay of the intermediate cation and makes the initial protonation step rate determining again even in buffer solutions at higher concentrations of thiol.

Experimental Section

Materials. 1,1-Bis(methylthio)ethene (**9**) was prepared from 1,1,1-tris(methylthio)ethane according to the literature:[36] bp 54.5–55.0 °C (13 mmHg) [lit.[37] bp 54–55 °C (10 mmHg)]; ^1H NMR (CCl_4) δ 2.30 (s, 6 H), 5.15 (s, 2 H).

2-Mercaptoethanol and acetonitrile were distilled before use. Sodium formate and acetate and potassium chloride of reagent grade were used without further purification. Deuterium oxide (99.75%) was supplied by Merck. Glass-distilled water was used throughout.

Kinetic Measurements. Buffer solutions containing 10 vol % acetonitrile were prepared by bringing 10 parts by volume of CH_3CN and necessary amounts of chemicals to 100 parts with added water in a volumetric flask. Thiol-containing solutions were obtained in the same way as above except for the use of a 2-mercaptoethanol solution in CH_3CN instead of pure CH_3CN. The ionic strength was adjusted usually at 0.45 with KCl. Deuterium oxide solutions were prepared similarly. Solutions containing 90 vol % organic components were obtained by bringing 10 parts of aqueous hydrochloric acid, and an appropriate amount of 2-mercaptoethanol (usually as a solution in CH_3CN) when necessary, to 100 parts by volume with CH_3CN in a volumetric flask. Solutions of intermediate compositions were obtained similarly by adding CH_3CN to an appropriate amount of aqueous solution to fill a volumetric flask. A stock solution of **9** in CH_3CN was prepared by weighing ($\sim$2.5 $\times$ 10^{-2} M).

The reaction was started by introducing 30 μL of the stock solution of **9** from a microsyringe into 3-mL of buffer solution equilibrated thermally at 30 $\pm$ 0.1 °C in a Teflon-stoppered cuvette in a water-jacketed cell holder. The reaction was monitored by following the decrease in absorbance at 250 nm (or 260 nm for the thiol reactions) on

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Table I. Buffer Effects on the Hydrolysis Rate of 9 in 10% CH_3CN-H_2O at the Ionic Strength of 0.45 and 30 °C

buffer	pH	10^3k_0, s^{-1}	10^2K_{app}, M	10^3k_{max}, s^{-1}	$10^2k_{max}/K_{app}$, M^{-1} s^{-1}	$1/K_{app}$, M^{-1}
formate	2.99	33.9	29.0 ± 2.3	114.1 ± 4.5	39.3	3.45
formate	3.16	22.9	13.9 ± 0.6	77.9 ± 1.4	56.0	7.19
formate	3.64	8.0	11.3 ± 1.3	32.0 ± 2.2	28.3	8.85
formate	4.24	1.91	8.53 ± 0.20	9.02 ± 0.09	10.6	11.7
acetate	4.04	3.02	9.65 ± 1.51	10.65 ± 0.86	11.0	10.4
acetate	4.19	2.15	9.91 ± 0.42	8.36 ± 0.17	8.44	10.1
acetate	4.69	0.72	4.76 ± 0.66	3.04 ± 0.19	6.39	21.0
acetate	5.36	0.14	3.19 ± 0.29	0.817 ± 0.043	2.56	31.6

a Shimadzu UV 200 spectrophotometer.

The pH values of 10% aqueous acetonitrile solutions were measured on a Hitachi-Horiba F-7 pH meter calibrated with aqueous buffers and corrected by subtracting 0.06 from the pH meter readings. The correction factor was obtained from the difference between the readings and -log [HCl] for dilute HCl solutions (0.001–0.01 M).

Isotope Exchange. To 10 mL of a 0.01 M DCl solution in 80 vol % CH_3CN-D_2O was added 0.15 mL of **9**; this mixture was shaken and left standing at room temperature for 1.5 h. The mixture was extracted with 3 mL of CCl_4, washed with 10% $NaHCO_3$ and 4 times with water, and dried over $MgSO_4$. The ^1H NMR spectrum of the extract was recorded on a JNM-4H-100 spectrometer. The spectrum showed singlets at 1.80 and 2.08 ppm and poorly resolved peaks at 2.23 and 2.27 ppm. Relative intensity of the signals at 1.80, 2.08, and 2.23–2.27 was 1:6:6.

The reaction was also carried out in a formate buffer solution in 80% CH_3CN-D_2O in the same way as above but at 30 °C. A sample of 0.3 mL of **9** was added to 20 mL of the buffer solution (0.1 M HCO_2D/0.1 M HCO_2Na) prepared from 4 mmol of sodium formate, 4 mL of 0.5 M DCl, and a necessary amount of CH_3CN. A 10-mL portion of the reaction mixture was extracted with CCl_4 (3 mL) after 22 h of reaction and the other portion after 90 h of reaction. The spectra showed singlets at 2.08, 2.23, 2.30, and 5.15 ppm in relative intensities about 3:2:18:1 and 10:7:6:0 for the reaction times 22 and 90 h, respectively. A signal at 1.8 ppm was only slightly perceived.

Results

Acid-catalyzed hydrolysis of the ketene dithioacetal **9** gives a thioacetate **10** as anticipated; the absorption at 250 nm diminishes with the accompanying development of a new absorption of λ_{max} 233 nm (**10**). ^1H NMR spectra of the products showed also the formation of **10**.

$$\underset{\mathbf{9}}{H_2C{=}C(SCH_3)_2} + H_2O \xrightarrow{H^+} \underset{\mathbf{10}}{CH_3COSCH_3} + CH_3SH \quad (4)$$

Rates of the hydrolysis were measured at 30 °C usually in aqueous solutions containing 10 vol % acetonitrile, the ionic strength being maintained at 0.45 with KCl. The reaction was followed by the decrease in absorbance at 250 nm; reactions in the presence of thiol were monitored at a longer wavelength. All the runs followed pseudo-first-order kinetics and the observed first-order rate constants k_{obsd} were proportional to the acid concentrations [HCl]: k_H = 31.6 (±0.7) M^{-1} s^{-1}. The rate constants were also obtained in deuterium media: k_D = 8.49 (±0.24) M^{-1} s^{-1} and k_H/k_D = 3.72 (±0.18). Data are given in Table S1 (supplementary material).

At a constant concentration of acid, [HCl] = 0.01 M, and without any added salt, rates were measured in solutions containing varying amounts of CH_3CN. As Figure 1 shows, the rate sharply decreases with increasing fraction of CH_3CN and levels off at about 50 vol %.

The rate constants k_{obsd} increased with buffer concentrations $[B]_t$ (Table S2) showing a saturation at higher $[B]_t$ as illustrated in Figure 2. The nonlinear buffer dependence fits eq 5, where

$$k_{obsd} - k_0 = \frac{(k_{max} - k_0)[B]_t}{K_{app} + [B]_t} \quad (5)$$

k_0 and k_{max} are the rate constants extrapolated to zero and infinite concentrations of the buffer, respectively. The parameter K_{app} is equal to $[B]_t$ when k_{obsd} attains a half-maximum increase in rate (i.e., $k_{obsd} - k_0 = (k_{max} - k_0)/2$). These parameters were calculated by the least-squares treatments of $1/(k_{obsd} - k_0)$ vs. $1/[B]_t$ and are summarized in Table I. The k_0 values were

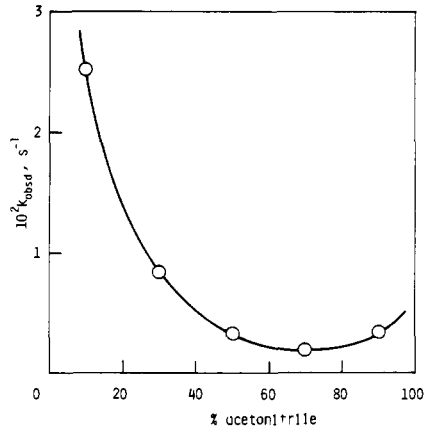


Figure 1. Effects of solvent composition on the hydrolysis rate of **9** in aqueous acetonitrile solutions at [HCl] = 0.01 M and 30 °C. The abscissa refers to vol % of acetonitrile.

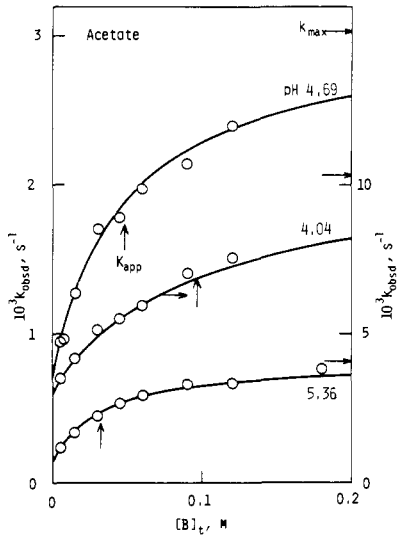


Figure 2. Dependences of the hydrolysis rate of **9** on buffer concentration in acetate buffers at pH indicated and 30 °C. Plots for pH 4.04 refer to the right ordinate. Curves are based on eq 5 with parameters given in Table I.

determined by extrapolation and trial calculations to give the best correlation. The logarithms of the rate constants k_0 (and k_{obsd} in HCl solutions) and k_{max} are plotted against pH in Figure 3, both being linear with a slope of −1.

Rates of disappearance of **9** were determined in the presence of 2-mercaptoethanol by keeping the total organic components (CH_3CN + $HOCH_2CH_2SH$) of the solution constant at 10 vol % (or 90 vol % in some cases). The rates measured in HCl solutions or formate buffers of low concentration were barely affected by the addition of thiol as summarized in Table II. By contrast, the disappearance of **9** was greatly accelerated by thiol addition in formate and acetate buffer solutions (of higher concentrations) (Table S3). The acceleration levels off at high concentrations of thiol [RSH] as seen in Figure 4. The higher

Table II. Effects of 2-Mercaptoethanol on the Rate Constants ($10^3 k_{obsd}$, s^{-1}) for the Hydrolysis of **9** at 30 °C

			[RSH], M					
pH	buffer	$10^2[B]_t$, M	0	0.05	0.10	0.15	0.20	0.30
3.00	HCl[a]	0.10	31.6		30.5		31.8	34.0
3.71	formate[a]	0.90	8.29	8.22	8.02	8.18	8.03	
3.68	formate[a]	4.5	13.2	14.4	14.7	14.8	14.7	
	HCl[b]	0.10	3.35		3.36		3.54	3.34

[a] In 10 vol % organic components (CH_3CN + $HOCH_2CH_2SH$) at the ionic strength of 0.45 (KCl). [b] In 90 vol % organic components without added salt.

Table III. Effects of 2-Mercaptoethanol on the Hydrolysis Rate of **9** in Buffer Solutions[a]

pH	buffer	$[B]_t$, M	$10^3 k_0^T$, s^{-1}	$10^2 K_{app}^T$, M	$10^3 k_{max}^T$, s^{-1}	$10^3 k_{max}^{T,b}$, s^{-1}	k_t/k_2, M^{-1}
3.64	formate	0.10	20.5	149 ± 31	82 ± 12	47.9	2.7
4.22	formate	0.045	4.37	11.8 ± 0.6	8.41 ± 0.11	6.05	16.3
4.21	formate	0.10	5.82	10.7 ± 0.5	14.2 ± 0.2	17.7	22.8
4.21	formate	0.18	7.12	16.3 ± 1.0	24.4 ± 0.7	29.7	21.0
4.04	acetate	0.10	7.51	16.9 ± 2.1	16.8 ± 1.3	17.4	13.3
4.06	acetate	0.18	9.65	18.7 ± 3.0	24.6 ± 1.9	27.9	13.7
4.70	acetate	0.045	1.87	5.66 ± 0.83	4.60 ± 0.15	4.65	43.5
4.68	acetate	0.10	2.51	6.37 ± 0.69	8.53 ± 0.24	9.28	53.4
5.69	acetate	0.18	2.74	8.56 ± 0.64	14.4 ± 0.4	15.9	61.4
5.38	acetate	0.045	0.574	3.32 ± 0.87	2.11 ± 0.16	1.69	111
5.34	acetate	0.10	0.668	2.89 ± 0.29	3.52 ± 0.11	3.54	182
5.29	acetate	0.18	0.780	3.83 ± 0.35	6.09 ± 0.19	6.29	204

[a] In aqueous solutions containing 10 vol % organic components (CH_3CN + $HOCH_2CH_2SH$), at the ionic strength of 0.45 (KCl) and 30 °C. [b] Calculated from k_1 and k_1' given in Table IV.

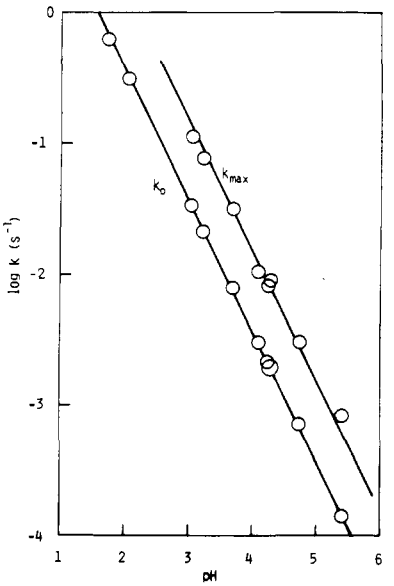


Figure 3. pH dependences of logarithms of k_0 and k_{max}.

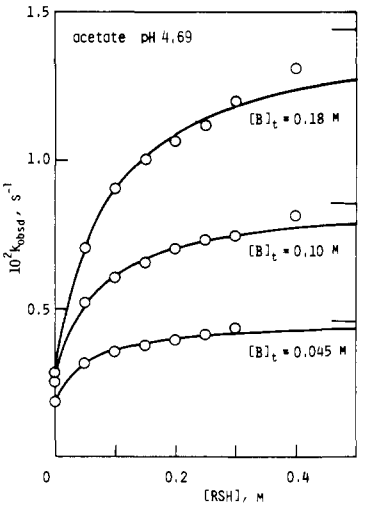


Figure 4. Effects of added 2-mercaptoethanol on the rate of disappearance of **9** in acetate buffer solutions of given concentrations at pH 4.69. Curves are based on eq 6 with parameters given in Table III.

the buffer concentrations, the greater are the apparent effects of the thiol. The curved dependence of the rate on [RSH] follows eq 6, similar to eq 5. The parameters k_0^T, k_{max}^T, and K_{app}^T have

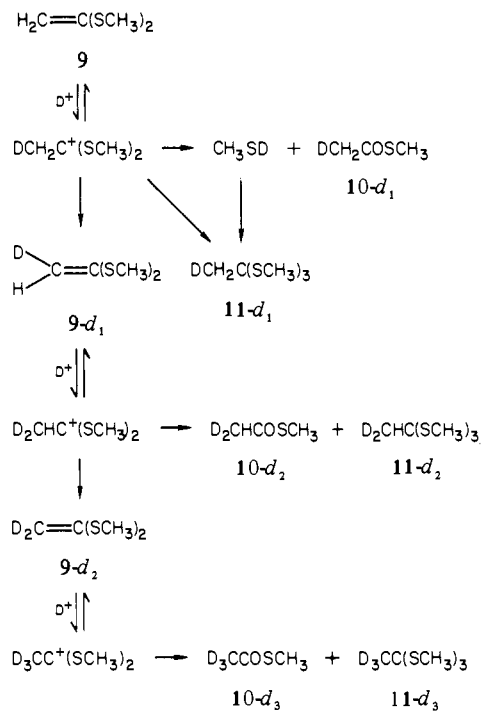
$$k_{obsd} - k_0^T = \frac{(k_{max}^T - k_0^T)[RSH]}{K_{app}^T + [RSH]} \quad (6)$$

meanings similar to those for eq 5. These parameters were obtained in the same way as those for the buffer dependence and are summarized in Table III.

Products from the reactions in DCl and formate buffer solutions in 80 vol % CH_3CN–D_2O were subjected to ^1H NMR analysis to search for possible isotope exchange as shown in Scheme I. In the spectra obtained, signals for methyl groups of the orthothioester **11** were found at 1.80 and 2.08 ppm in addition to the closely positioned singlets for the thiolester **10** (2.23 and 2.27 ppm). The former product must come from the reaction of the carbenium ion intermediate with methanethiol liberated on the formation of **10**. This occurs because the concentration of the substrate **9**, and so methanethiol formed, is high enough (~0.13 M) in the product analysis experiments. The product ratio of **10** to **11** was about 2:1.

In the case of the reaction products in 0.01 M DCl, the relative intensity of the signals for methyl groups of **11** (SCH_3:DCH_2 ≃ 9:1.5) showed that about 25% of the 2 hydrogen was lost during the reaction. The signals for methyl groups of **10** are too closely positioned to evaluate separately their intensities from the integral curve. Much slower reaction in a 0.2 M formate buffer solution resulted in about 25% conversion in 22 h and 75% in 90 h. The spectrum for the 22-h reaction showed signals for the remaining substrate **9**, but the intensity of the signal for the olefinic hydrogen (5.15 ppm) was only 17% of that expected from the SCH_3 intensity (2.30 ppm). Furthermore, the spectrum for the 90-h reaction did not show any trace of the peak at 5.15 ppm for the 2-hydrogen of **9** although the SCH_3 signal for **9** remained in nearly 25% of the initial intensity. The signal for the 2-hydrogen of the product **11** (1.8 ppm) was also only slightly observed (a few percents of the expected intensity). That is, most of the 2-hydrogen was lost during the reaction owing to the H–D isotope exchange.

Scheme I



Discussion

Buffer Dependence. The nonlinear dependence of rate on buffer concentration is often associated with a change in the rate-determining step.[8,11,12,26,30,38,39] In the present reaction, the rate-determining step may change from the protonation of the double bond at low $[B]_t$ to the hydration of the intermediate carbenium ion at higher $[B]_t$ (eq 7).

$$\underset{\mathbf{9}}{H_2C{=}C(SCH_3)_2} \underset{k_{-1}'[B]}{\overset{k_1[H^+]}{\underset{k_{-1}(H_2O)}{\overset{k_1'[BH^+]}{\rightleftharpoons}}}} \overset{+}{C}H_3C(SCH_3)_2 \xrightarrow{k_2(H_2O)} \underset{\mathbf{10}}{CH_3COSCH_3} \quad (7)$$

According to the reaction sequence of eq 7 and by use of rate constants given, the empirical parameters of eq 5 are described by eq 8–10, where α stands for the base fraction of the buffer.

$$k_0 = k_1k_2[H^+]/(k_{-1} + k_2) \quad (8)$$

$$k_{max} = k_1'k_2(1 - \alpha)/k_{-1}'\alpha = k_1k_2[H^+]/k_{-1} \quad (9)$$

$$K_{app} = (k_{-1} + k_2)/k_{-1}'\alpha \quad (10)$$

Both limiting rate constants at zero and infinite buffer concentrations, k_0 and k_{max}, are proportional to $[H^+]$ as was found in Figure 3, and the proportionality constants are $k_1k_2/(k_{-1} + k_2) = 33.4\ M^{-1}\ s^{-1}$ and $k_1k_2/k_{-1} = 138\ M^{-1}\ s^{-1}$: k_{max} is about 4 times as great as k_0 at any pH and in any buffer. The values obtained above give the rate constant $k_1 = 44.1\ M^{-1}\ s^{-1}$ and $k_2/k_{-1} = 3.13$. That is, the protonation is about 76% $[k_2/(k_{-1} + k_2)]$ rate determining without buffer catalysis. The kinetic isotope effect observed in hydrochloric acid solutions, $k_H/k_D = 3.72$, is consistent with a mechanism involving mainly rate-determining protonation.[40]

Equations 9 and 10 lead to eq 11 and 12 by using the calculated

$$k_{max}/K_{app} = k_1'k_2(1 - \alpha)/(k_{-1} + k_2) = 0.76k_1'(1 - \alpha) \quad (11)$$

$$1/K_{app} = k_{-1}'\alpha/(k_{-1} + k_2) = 0.76k_{-1}'\alpha/k_2 \quad (12)$$

value of $k_2/(k_{-1} + k_2) = 0.76$. These values calculated are given in Table I and plotted against the base fractions of the buffers in Figures 5 and 6. Reasonable linearities found demonstrate the validity of the mechanism of eq 7 and the kinetic analyses. That is, the protonation is catalyzed by general acids and the deprotonation by general bases. Catalytic constants are summarized in Table IV. The constants for formic and acetic acids give a rough value of the Brønsted coefficient α of 0.65, which is in the range of α (0.6–0.7) found for the vinyl ether hydrolysis.[41]

The nonlinear dependence of rate on buffer concentration is satisfactorily accommodated by the mechanism given in eq 7. The relative value of $k_2/k_{-1} = 3.13$ obtained indicates that the protonation is largely rate determining at the limiting zero buffer concentration. Since general bases catalyze the deprotonation (k_{-1}), the initial protonation process becomes reversible and the hydration of the intermediate cation takes over the rate-deter-

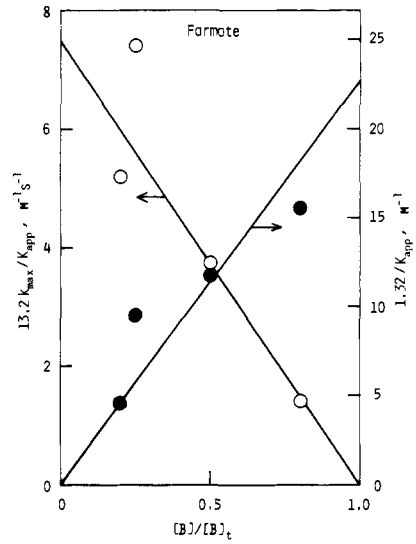


Figure 5. Correlations of buffer-dependent rate constants with the base fraction of formate buffers.

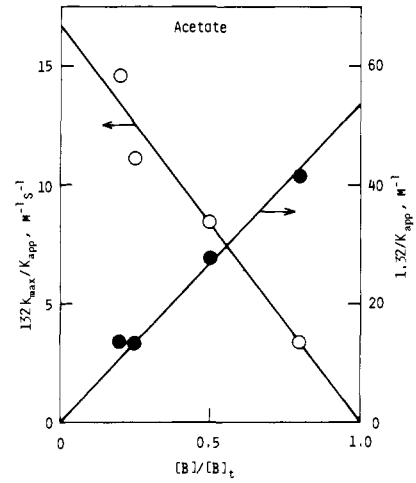


Figure 6. Correlations of buffer-dependent rate constants with the base fraction of acetate buffers.

Table IV. Catalytic Constants for the Hydrolysis of 9 in 10% CH_3CN-H_2O at 30 °C

acid	k_1', $M^{-1}\ s^{-1}$	base	k_{-1}'/k_2
H_3O^+	44.1	H_2O	0.32
HCO_2H	0.75	HCO_2^-	22.7[a]
CH_3CO_2H	0.167	$CH_3CO_2^-$	53.5[a]

[a] M^{-1}.

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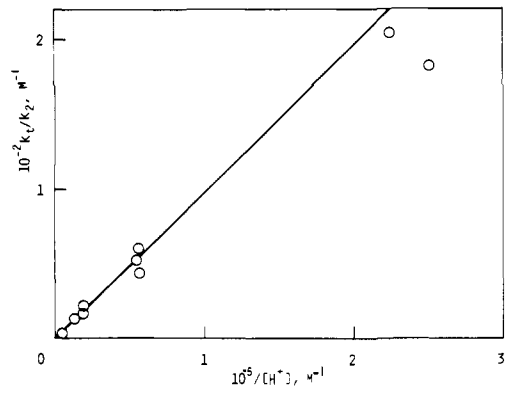


Figure 7. Correlation of rate constants for the thiol reaction with the reciprocal concentrations of hydronium ion.

mining step in buffer solutions of high concentration. This was confirmed by the observations on the effects of added thiol on the reaction rates and the isotope exchange experiments.

Effect of Thiol. Thiols are strongly nucleophilic and can compete with water[42] even in acidic aqueous solutions. If a nucleophilic attack by water on the carbenium ion intermediate is involved in the rate-determining step of the reaction, added thiols should accelerate the reaction (disappearance of the substrate). They can however hardly affect the rate of the reaction, the rate-determining step of which is the formation of the intermediate (protonation).

$$CH_3C^+(SCH_3)_2 + RSH \xrightarrow{k_t} CH_3C(SR)(SCH_3)_2 \quad (13)$$

In practice, the rates of the reaction in aqueous HCl solutions and formate buffer solutions of very low concentration were little influenced by the addition of 2-mercaptoethanol (Table II), while the reaction was greatly accelerated by the thiol in other buffer solutions (Figure 4). These observations confirm the conclusion deduced from the buffer experiments: The rate-determining step is the protonation in mineral acid solutions or at the limiting zero buffer concentration while it changes to the nucleophilic attack by water on the carbenium ion intermediate as the buffer concentration increases.

The acceleration arises from a nucleophilic reaction of eq 13 in addition to the reactions given in eq 7. The kinetic parameters of eq 6 are described by eq 14–16. The value of k_0^T is k_{obsd} at

$$k_0^T = \frac{k_2(k_1[H^+] + k_1'[BH^+])}{k_{-1} + k_2 + k_{-1}'[B]} \quad (14)$$

$$k_{max}^T = k_1[H^+] + k_1'[BH^+] \quad (15)$$

$$K_{app}^T = (k_{-1} + k_2 + k_{-1}'[B])/k_t \quad (16)$$

$[RSH] = 0$ and k_t is the apparent second-order rate constant for the thiol reaction. The maximum rate constant k_{max}^T, a limiting value when the initial protonation step becomes rate determining, can also be calculated from the rate constants obtained from the buffer experiments (eq 15). The k_{max}^T values thus calculated independently from the thiol and buffer experiments show reasonable agreement (Table III).

Equations 14 and 15 imply that even at the zero buffer concentration thiol can increase the rate from $(k_1k_2[H^+])/(k_{-1} + k_2) = 0.76k_1[H^+]$ to $k_1[H^+]$; the amount of the increase easily detectable. However, the large value of K_{app}^T may make the observation of the increase difficult at lower pH.

The relative rate constants k_t/k_2 can be evaluated by eq 17 and

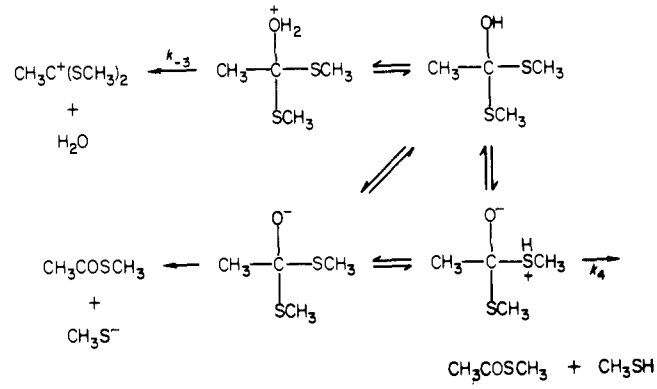
$$k_t/k_2 = k_{max}^T/k_0^T K_{app}^T \quad (17)$$

are given in the last column of Table III. These values appear to be independent of buffer concentrations (with rather large deviations probably due to accumulated experimental uncertainties) but increase with increasing pH. The k_t values seem to be inversely proportional to $[H^+]$ as shown in Figure 7. The reactive species must be essentially thiolate ion in the pH region examined, and the contribution from neutral thiol (k_t^0 in eq 18)

$$k_t = (k_t^0[RSH] + k_t^-[RS^-])/[RSH]_t = k_t^0 + k_t^- K_{RSH}/[H^+] \quad (18)$$

is negligible as compared with that from the thiolate (k_t^- term): $k_t^-/k_2 = 4.9 \times 10^6\ M^{-1}$ (using $pK_{RSH} = 9.7$).

Scheme II



Isotope Exchange. Kinetic observations demonstrate that the initial protonation of the double bond is more or less reversible during the hydrolysis of **9**. This must result in the H–D isotope exchange of the olefinic hydrogen if the reaction is carried out in deuterium media (Scheme I). This is actually the case as observed by the ^1H NMR spectroscopy. The ^1H NMR spectrum of the products obtained from the reaction in a 0.01 M DCl solution in 80% CH_3CN–D_2O shows that about 25% of the 2-hydrogen was exchanged by solvent deuteron during the reaction. In a formate buffer solution (0.2 M) in the same medium the isotope exchange was almost complete. More than 80% of the olefinic hydrogen of the unreacted substrate **9** was lost within the progress of 25% reaction. This tendency that the buffer (general base) promotes the exchange is in accord with the kinetic results. We chose here the reaction medium containing more organic component to avoid the solubility problem. Since we now know that the reversibility of the protonation is greatly affected by the reaction medium,[33b] quantitative kinetic analysis of the exchange was not undertaken.

Decay of Dithiocarbenium Ion. The decay of the carbenium ion intermediate to form a thiol ester should take place at least in two steps (eq 19). The rate-determining step of this reaction

$$CH_3C^+(SCH_3)_2 + H_2O \underset{k_{-3}[H^+]}{\overset{k_3}{\rightleftharpoons}} CH_3C(OH)(SCH_3)_2 \xrightarrow{k_4} CH_3COSCH_3 + CH_3SH \quad (19)$$

may be another problem to be solved. In the case of 2-aryl-1,3-dioxolanyl cations, the decay of a hydrogen ortho ester (the k_4 step) was found to be rate determining; this step is catalyzed by both acid and base.[43] Cyclic thio analogues, 2-aryl-1,3-dithiolanyl cations, have however been found to decompose differently.[44] The hydration (k_3) is rate determining at higher pH (>3) while the decay of a hydrogen ortho thio ester is rate determining at pH <2. In the present reaction, k_2 was found to be constant over the pH range 2–6. The hydration step (k_3) is likely to be rate determining in the pH range examined. The difference in nucleophilic reactivities between the thiolate ion and water ($k_t^-/k_2 = 5 \times 10^6\ M^{-1}$) found here is somewhat smaller than those obtained for triarylmethyl and other stable cations ($\sim 10^8\ M^{-1}$)[42] but not inconsistent with the mechanism proposed.

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The conclusion that the k_3 step is rate determining can be represented in another way in terms of Scheme II. In the pH range 2–6, a thiol is more easily released from the hydrogen ortho thio ester, a tetrahedral intermediate, than water is. This agrees with the results of hydrolyses of thiol esters and ketene *O,S*-acetals.[11,45] Contribution from the protonated tetrahedral intermediate, which gives away water more easily, becomes appreciable only below pH 2.[45] That is, the explusion of water should be slower than that of thiol at pH >2.

General base catalysis of the hydration of carbenium ion is a problem of recent interest.[46-49] The less stable the carbenium ion, the less likely is its hydration subject to general base catalysis. The k_2 value was found to be seemingly independent of buffer concentrations. The catalysis must be weak, if the hydration of 1,1-bis(methylthio)ethyl cation is subject to general base catalysis. Furthermore, possible inverse solvent effects of the buffer component (carboxylic acid) on the rate (see solvent effects presented in Figure 1) may cancel the potential buffer catalysis. As a result k_{obsd} became approximately constant at limiting concentrations of buffer to give the constant k_{max}.

As a whole, the present observations indicate that the initial protonation of the ketene thioacetal is mostly rate determining at the zero buffer concentrations but is accelerated by the buffer to make the protonation reversible and the second step rate determining; furthermore, the addition of a thiol accelerates the second step to force the first step to be the slower step again. The rate-determining step of the reaction can thus be controlled by the addition of either buffer or thiol.

Acknowledgment. We are grateful to Professor A. J. Kresge for helpful discussions and examination of the manuscript.

Registry No. 9, 51102-74-0; 2-mercaptoethanol, 60-24-2.

Supplementary Material Available: Tables of observed first-order rate constants for the hydrolysis (Tables S1–S3) (3 pages). Ordering information is given on any current masthead page.

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Photochemical Transformations. 33. Some Studies of the Photorearrangements of Dibenzobarrelenes. A Novel Excitation-Transfer Relay Mechanism[1]

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Abstract: The unsensitized and sensitized photorearrangements of 1-methyldibenzobarrelene (**4**) and 7-methyldibenzobarrelene (**5**) to 3-methyldibenzocyclooctatetraene (**12**) and, for the former case, mixtures of 2-methyldibenzosemibullvalene (**9**) and 5-methyldibenzosemibullvalene (**10**), and for the latter case, mixtures of 1-methyldibenzosemibullvalene (**11**) and 2-methyldibenzosemibullvalene (**9**), are reported. The unsensitized reactions gave largely cyclooctatetraene, while the triplet-sensitized reactions gave the semibullvalenes via di-π-methane rearrangements. The regioselectivity of the di-π-methane rearrangements did not vary with sensitizer, although the quantum yields did. The lack of dependence of product ratio upon sensitizer suggests that the product-determining step occurs after excitation transfer, rather than during it or in an exciplex containing triplet sensitizer and reactant. A similar conclusion may be tentatively reached by the fact that the quenchable triplet intermediate has the same lifetime (4 ± 1 ns) whether produced by acetone, acetophenone, or benzophenone sensitization of dibenzobarrelene (**1**), although the excitation-transfer rates from each of these sensitizer triplets to **1** vary substantially. In solutions of acetone and of **1** and **5** in acetonitrile, the ratio of dibenzocyclooctatetraene products to dibenzosemibullvalene products is much smaller than one would calculate from the fraction of the light absorbed by the dibenzobarrelene, when the solutions are irradiated at 254 nm. These results are rationalized by the assumption that an excitation-transfer relay mechanism exists, in which reactant absorbs light to give an excited singlet. This is followed by quenching by "sensitizer" to give its singlet. That singlet intersystem crosses to give a sensitizer triplet, which then delivers triplet excitation to reactant.

Since the first report[2a] of the photosensitizer-induced transformation of barrelene to semibullvalene and of the photoinduced transformation[2b] of polyphenyl-substituted propenes to cyclopropanes, there has been much interest in this class of reactions, now dubbed "di-π-methane reactions".[3] Study of dibenzobarrelene (**1**) and certain of its derivatives is particularly interesting, as Ciganek[4] showed that irradiation through Pyrex of an acetone solution of **1** gave dibenzosemibullvalene (**2**), while Friedman and co-workers[5] showed that irradiation of **1** in cy-

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