# Kinetics of Hydrolysis of Some Sterically Hindered Ketene Acetals

## A. Jerry Kresge*[†] and Thomas S. Straub

*Contribution from the Department of Chemistry, University of Toronto, Scarborough College, West Hill, Ontario M1C 1A4, Canada, and the Department of Chemistry, Illinois Institute of Technology, Chicago, Illinois 60616. Received August 17, 1982*

**Abstract:** The kinetics of hyrolysis of five ketene acetals with reduced reactivity was studied in aqueous perchloric acid ($H_2O$ and $D_2O$) and carboxylic acid buffer solutions. All of the data point to a reaction mechanism involving rate-determining proton transfer from the catalyzing acid to the $\beta$-carbon atom of the ketene double-bond system. The reduced reactivity of these substrates may be attributed to steric interference of positive charge delocalization in the rate-determining transition states of these reactions, which is induced by bulky substituents at the $\beta$-positions of these substrates.

The acid-catalyzed addition of water to the carbon–carbon double bond of simple olefins is a relatively slow reaction whose rate can be measured conveniently only in concentrated acid solutions. Introduction of electron-donating substituents such as alkoxy groups, however, greatly speeds up this process, and the hydration of such carbon–carbon double bonds can usually be investigated in dilute aqueous acids where intrepretation of the kinetic data is more straightforward. The acid-catalyzed hydrolysis of vinyl ethers, eq I, has therefore been extensively employed by

$$CH_2=CHOR \xrightarrow[H_2O]{HA} CH_3CH(OH)OR \rightarrow CH_3CHO + HOR$$

(I)
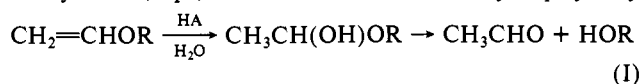
us and by others in order to gain information on electrophilic addition to carbon–carbon double bonds and also on the details of acid–base catalysis.

It would be of interest to extend these studies to even more reactive substrtes, and to this end ketene acetals, $CH_2=C(OR)_2$ (1) are potentially very useful substances. They suffer, however, from being too reactive. Ketene diethyl acetal, for example, is hydrolyzed so rapidly even by water containing no acid that useful kinetic data cannot be obtained at temperatures greater than 15 °C.[1] The introduction of chloro or cyano substituents at the $\beta$-carbon atom of ketene acetals, however, slows the rate of hydroxysis markedly, and some very interesting information has been obtained from the investigation of such substances.[2] In this paper we describe a further study of such less reactive ketene acetals; our results indicate that the decreased reactivity of these substances is the result of an interesting steric interaction in addition to the expected electronic effects of the chloro and cyano groups.

## Experimental Section

**Materials.** Ketene acetals were prepared by standard methods: dimethylketene dimethyl acetal, **2**, and methylbromoketene diethyl acetal,
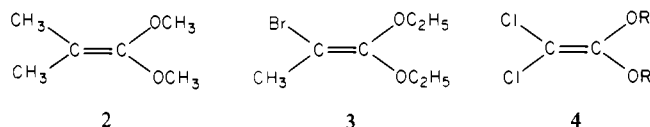


3, by eliminating 1 equiv of alcohol from the corresponding ortho ester through treatment with aluminum *tert*-butoxide,[3] and dichloroketene dimethyl, **4** (R = $CH_3$), diethyl, **4** (R = $C_2H_5$), and di-*n*-propyl, **4** (R = $C_3H_7$), acetals by dehydrohalogenating the corresponding trichloroacetaldehyde acetals with potassium *tert*-butoxide.[4] These substances and their precursors were identified by their proton NMR spectra and by comparison of physical properties with literature values whenever the latter were available. Three of these ketene acetals were new substances (**3**, **4** (R = $CH_3$, $C_3H_7$)), and satisfactory elemental analyses were obtained for these materials.[5] Samples for kinetic measurements were purified by fractional distillation.

All other materials were best available commercial grades. Solutions were prepared by using deionized $H_2O$ purified further by distillation

from alkaline permanganate or $D_2O$ (Merck, Sharp and Dohme) as received.

**Kinetics.** Rates of hydrolysis were measured spectroscopically by monitoring the disappearance of the strong UV absorption band that all of the present ketene acetals displayed at ca. 200 nm. Measurements were made on the shoulder of this band, at 220–230 nm, by using a Cary Model 11 PM spectrometer with a thermostated cell compartment. Reactions studied at 25 °C were conducted in standard 1-cm quartz cuvettes, but at temperatures other than this, additional control was obtained by using jacketed cells; water from a constant-temperature bath was circulated through the jackets, and reaction temperatures were measured directly inside the cells.

Reactions were initiated by adding a small amount of ketene acetal to an acid or buffer solution that had come to temperature equilibrium by standing in the cell or cuvette, in the spectrometer cell compartment for a sufficient length of time (15–30 min). The cell and its contents were shaken vigorously and were replaced in the spectrometer, and absorbance readings were then recorded continuously. Reactions were followed for approximately 4 half-lives, and infinite time readings were taken after at least 10 half-lives. Rate constants were obtained as slopes of plots of log $(A_t - A_\infty)$ vs. time; the first-order rate law was obeyed within experimental accuracy.

## Results

The hydrolyses of five ketene acetals, dimethylketene dimethyl acetal (**2**), methylbromoketene diethyl acetal (**3**), and the dimehyl, diethyl, and di-*n*-propyl acetals of dichloroketene (**4**), were studied in the present work. For none of these substrates could a significant spontaneous or base-catalyzed reaction be detected in dilute aqueous alkali, but the hydrolysis of all five substances was strongly accelerated by acids. These acid-catalyzed reactions were studied in perchloric acid solutions, both in $H_2O$ and in $D_2O$ and as a function of temperature, and also in a number of carboxylic acid buffers. The data are summarized in Tables S1–S8.[6]

First-order rates of hydrolysis in dilute perchloric acid were found to be exactly proportional to acid concentration. Since no uncatalyzed reactions took place, second-order catalytic coefficients, $k_{H^+}$, were evaluated by linear least-squares analysis with the intercept parameter set equal to zero. These results are listed in Table I. The value for dimethylketene dimethyl acetal at 25 °C refers to a variable ionic strength, equal to the perchloric acid concentration (0.0001–0.001 M); all other results are for a constant ionic strength, 0.02 M in the case of methylbromoketene diethyl acetal and 0.04 M for all other substrates. The effect of changing

---

(1) Kankaanpera, A.; Touminen, H. *Suom. Kemistil. B* **1967**, *40*, 271–276.

(2) (a) Gold, V.; Waterman, D. D. A. *J. Chem. Soc. B* **1968**, 839–855. (b) Hershfield, R.; Yeager, M. J.; Schmir, G. L. *J. Org. Chem.* **1975**, *40*, 2940–2946.

(3) McElvain, S. M.; Davie, W. R. *J. Am. Chem. Soc.* **1951**, *73*, 1400–1402.

(4) Beyerstedt, F.; McElvain, S. M. *J. Am. Chem. Soc.* **1937**, *59*, 1273–1275.

(5) For further experimental details, see: Straub, T. S., Ph.D Thesis, Illinois Institute of Technology, Chicago, IL, 1970.

(6) Supplementary material. See paragraph at the end of this paper.

---

[†] University of Toronto.

3958 *J. Am. Chem. Soc., Vol. 105, No. 12, 1983*

*Kresge and Straub*

**Table I.** Summary of Rate Constants for Ketene Acetal Hydrolysis

| temp, °C | acid catalyst | p$K_a$ | $k$, M$^{-1}$ s$^{-1}$ | | | | |
|---|---|---|---|---|---|---|---|
| | | | dimethyl-ketene dimethyl acetal | methyl-bromoketene diethyl acetal | dichloro-ketene dimethyl acetal | dichloro-ketene diethyl acetal | dichloro-ketene di-*n*-propyl acetal |
| 25.0 | H$_3$O$^+$ | | 28.9 | 6.52 | 5.19 | 3.38 | 4.24 |
| | D$_3$O$^+$ | | 10.1 | 2.43 | 2.29 | 1.31 | 1.67 |
| | CNCH$_2$CO$_2$H | 2.47 | 2.81 | 1.63 | 0.860 | 0.965 | |
| | CH$_2$ClCO$_2$H | 2.87 | 2.93 | 1.59 | 0.955 | 0.992 | |
| | CH$_3$OCH$_2$CO$_2$H | 3.57 | 1.54 | 0.940 | 0.438 | 0.477 | |
| | HCO$_2$H | 3.75 | 0.865 | 0.448 | 0.205 | 0.229 | |
| | CH$_2$OHCO$_2$H | 3.83 | | | 0.316 | 0.357 | |
| | CH$_3$CO$_2$H | 4.76 | 0.392 | 0.295 | 0.141 | 0.169 | |
| 9.7 | H$_3$O$^+$ | | | | 1.57 | 1.15 | 1.46 |
| 44.2 | H$_3$O$^+$ | | | | 21.3 | 14.7 | 16.6 |
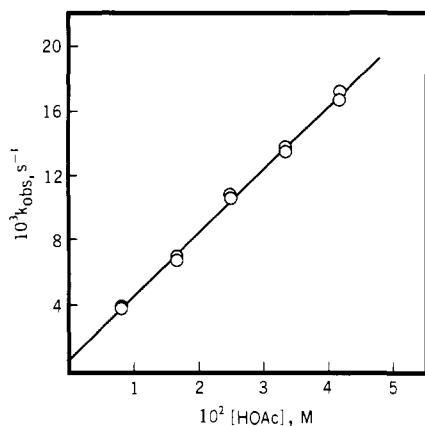
**Figure 1.** Relationship between observed first-order rate constants and buffer acid concentration for the hydrolysis of dimethylketene dimethyl acetal in acetic acid buffers; buffer ratio = 1.0 and ionic strength = 0.04 M.

ionic strength on the rate of hydrolysis of cyanoketene dimethyl acetal is known to be small;[2a] this was corroborated here by experiments with dimethylketene dimethyl acetal (Table S2).

Rates of hydrolysis in carboxylic acid buffers were measured in series of solutions of constant buffer ratio but varying total buffer concentration. The first-order rate constants determined in these solutions were accurately proportional to undissociated acid concentration (Figure 1) and obeyed the rate law shown in eq 1. Second-order catalytic coefficients, $k_{HA}$, were therefore

$$k_{obsd} = k_{H^+}[H^+] + k_{HA}[HA] \tag{1}$$

determined by linear least-squares fitting to this expression. The intercepts so obtained, which represent the hydronium ion contributions to the observed rates, $k_{H^+}[H^+]$, though significant, were generally quite small. This is the expected situation for systems such as this which obey the Brønsted relation with small values of the exponent $\alpha$ (see below). Because the intercepts were small, they could not be fixed with good precision, and accurate values of $k_{H^+}$ could therefore not be calculated from them. Nevertheless, the results obtained were not inconsistent with $k_{H^+}$ values measured directly in perchloric acid solutions. In some of the buffer solutions of the stronger carboxylic acids, significant ionization of the undissociated acid took place, and the extent of this ionization changed as the buffer concentration was varied. This "buffer failure" was corrected for by adjusting observed rate constants to constant hydronium ion concentrations with $k_{H^+}$ values measured in perchloric acid solution and [H$^+$] values calculated from the carboxylic acid p$K_a$'s and activity coefficients estimated by the Debye–Hückel equation with ion size parameters of 9.0, 4.5, and 3.5 Å for H$_3$O$^+$, RCO$_2^-$, and HCO$_2^-$, respectively.[7] The

**Table II.** Brønsted Exponents for the Hydrolysis of Ketene Acetals Catalyzed by Carboxylic Acids

| substrate | $\alpha^a$ | substrate | $\alpha^a$ |
|---|---|---|---|
| dimethylketene dimethyl acetal | 0.41 ± 0.06 | dichloroketene dimethyl acetal | 0.39 ± 0.07 |
| methylbromoketene diethyl acetal | 0.36 ± 0.07 | dichloroketene diethyl acetal | 0.37 ± 0.07 |

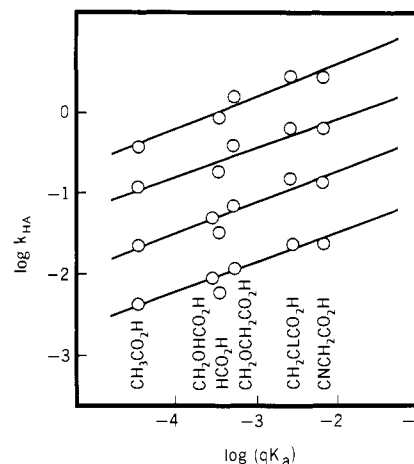$^a$ Error estimates are standard deviations.

**Figure 2.** Brønsted relations for the hydrolysis of ketene acetals. From top to bottom: dimethylketene dimethyl acetal, methylbromoketene diethyl acetal, dichloroketene dimethyl acetal, and dichloroketene diethyl acetal. The vertical scale refers to dimethylketene dimethyl acetal; for the subsequent substrates it is lowered by 0.4, 0.8, and 1.6 log units, respectively.

carboxylic acid catalytic coefficients obtained by this analysis are listed in Table I.

These catalytic coefficients obey the Brønsted relation, eq 2.[8]

$$k_{HA} = G(K_{HA})^\alpha \tag{2}$$

The dependence of $k_{HA}$ upon the acidity constant of the catalyzing acid $K_{HA}$, however, is not strong, and the Brønsted exponents, $\alpha$, are consequently rather small (Table II). The average value for the four substrates investigated is $\alpha = 0.38 \pm 0.02$. The data also show quite regular systematic variations from the overall linear relationships (Figure 2). For example, the formic and cyanoacetic acid points are consistently low, whereas the chloro- and methoxyacetic acid points are consistently high. Systematic variations of this kind have been noticed before in the hydrolysis of a number of vinyl ethers, though in previous cases they have not been as consistent nor as pronounced. This may be due to the fact that Brønsted exponents are unusually low in the present systems and

(7) Bates, R. G. "Determination of pH. Theory and Practice"; Wiley: New York, 1973; p 49.
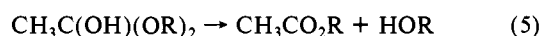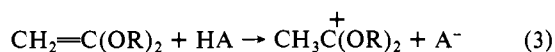
(8) Brønsted, J. N.; Pedersen, K. J. *Z. Phys. Chem., Stoechiom. Verwandtschaftsl.* **1924**, *108*, 185–235.

general acid catalysis is consequently quite strong; undissociated acid catalytic coefficients may therefore be measured with unusual precision, and idiosyncratic differences may be especially well characterized.

It is difficult to say what is the cause of these systematic differences. They seem to be related to the size of the catalyzing acids: formic acid, which is small, is always too slow, and chloroacetic acid, which is large, is always fast. This trend is consistent with the fact that pivalic acid often shows positive deviations from Brønsted relations.[2a,9a,10] This suggests that the variations may be produced by London dispersion interactions between substrate and catalyst, which serve to lower the free energy of the hydrolysis transition state.[11]

## Discussion

**Reaction Mechanism.** The commonly accepted reaction mechanism for acid-catalyzed hydrolysis of ketene acetals involves protonation of the $\beta$-carbon atom of the double-bond system, eq 3, hydration of the ensuing cation to form a hydrogen ortho ester

$$CH_2{=}C(OR)_2 + HA \rightarrow CH_3\overset{+}{C}(OR)_2 + A^- \qquad (3)$$

$$CH_3\overset{+}{C}(OR)_2 + H_2O \rightarrow CH_3C(OH)(OR)_2 + H^+ \qquad (4)$$

$$CH_3C(OH)(OR)_2 \rightarrow CH_3CO_2R + HOR \qquad (5)$$

intermediate, eq 4, and breakdown of the latter to carboxylic acid ester and alcohol products, eq 5. This reaction scheme is based upon the observation of general acid catalysis and the occurrence of sizable kinetic isotope effects; it is also consistent with magnitude of the entropies of activation generally found for these systems.[1,2,12] This mechanism received striking confirmation very recently when hydrogen ortho ester intermediates were detected in the hydrolysis of two ketene acetals.[13]

The carbon protonation step in the acid-catalyzed addition of water to simple olefinic double bonds is generally rate determining and not reversible, but the introduction of heteroatom substituents sometimes changes this situation. In the hydrolysis of enamines, for example, rapid and reversible carbon protonation is not uncommon under some conditions,[14] and the hydrolysis of certain vinyl selenides has lately been shown to involve reversible protonation of the double bond.[15] Of particular relevance to the present study is the recent discovery of reversible carbon protonation in the hydrolysis of some ketene dithioacetals and diselenoacetals.[16] There is no definitive evidence for reversal of the carbon protonation step in the hydrolysis of ketene acetals themselves, and the detection of only one deuterium atom in the hydrogen ortho ester intermediates produced in the hydrolysis of certain cyclic ketene acetals[13] indicates that carbon protonation is not reversible here. It has been suggested,[17] however, that the incursion of reversibility might be responsible for the nonlinear dependence of hydrolysis rate upon buffer acid concentration

Table III. Activation Parameters for the Hydrolysis of Ketene Acetals by Aqueous ($H_2O$) Perchloric Acid[a]

| substrate | $\Delta H^\ddagger$, kcal mol$^{-1}$ | $\Delta S^\ddagger$, cal K$^{-1}$ mol$^{-1}$ |
|---|---|---|
| dichloroketene dimethyl acetal | 13.0 ± 0.2 | −11.5 ± 0.7 |
| dichloroketene diethyl acetal | 12.7 ± 0.8 | −13.3 ± 2.6 |
| dichloroketene di-*n*-propyl acetal | 12.1 ± 0.5 | −15.0 ± 1.7 |

[a] Error estimates are standard deviations.

Table IV. Kinetic Isotope Effects on the Hydrolysis of Some Deactivated Ketene Acetals Catalyzed by the Hydronium Ion

| substrate | $k_{H^+}/k_{D^+}$ obsd | $k_{H^+}/k_{D^+}$ calcd |
|---|---|---|
| dimethylketene dimethyl acetal | 2.86 | 3.41 |
| methylbromoketene diethyl acetal | 2.68 | 3.18 |
| dichloroketene dimethyl acetal | 2.27 | 3.14 |
| dichloroketene diethyl acetal | 2.54 | 3.11 |
| dichloroketene di-*n*-propyl acetal | 2.59 | 3.08 |
| cyanoketene dimethyl acetal[a] | 2.96 | 3.38 |
| 2-dichloromethylene-1,3-dioxolane[a] | 2.46 | 3.58 |

[a] Reference 2a.

observed in the reaction of cyanoketene dimethyl acetal and 2-dichloromethylene-1,3-dioxolane in carboxylic acid buffers and originally attributed to association between carboxylic acid and carboxylate ion.[2a] Reversible carbon protonation, moreover, has been demonstrated in the reaction of simple ketene acetals with phosphorus acids in the aprotic solvents benzene and carbon tetrachloride,[18] and there is evidence that suggests that carbon protonation is reversible in the hydrolysis of a rather unusual vinyl ether.[19]

Completely reversible carbon protonation followed by unassisted attack of water on the ensuing cation would give specific hydrogen ion catalysis, which is contrary to the general acid catalysis observed for ketene acetal hydrolysis here and in other studies of this reaction. General acid catalysis would result if the attack of water were assisted by proton transfer to a general base, but it is doubtful whether such a scheme could give rise to Brønsted exponents as low as the $\alpha = 0.4$ observed here. Reaction of water with the cationic intermediate (eq 4) is likely to be an exoergonic process with a reactant-like transition state and a near-zero Brønsted exponent; the exponent $\beta = 0.09$ has in fact been found for the closely similar reaction of water with the 1-methoxy-1-(4-methoxyphenyl)ethyl cation, eq 6.[20] This low exponent, when

$$CH_3OC_6H_4\overset{+}{C}(CH_3)OCH_3 \xrightarrow[B]{H_2O} CH_3OC_6H_4C(OH)(CH_3)OCH_3 \qquad (6)$$
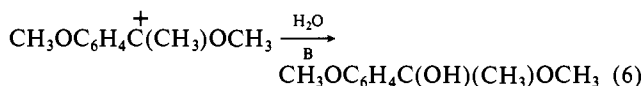
coupled with an exonent of unity for a preceding reversible carbon-protonation step, would produce a value of $\alpha$ for the overall reaction that would be close to unity itself.

Partly reversible carbon protonation, on the other hand, would lead to a nonlinear dependence of observed rate constants on buffer acid concentration for hydrolyses conducted in buffer solutions. As Figure 1 demonstrates, the relationship between these two variables observed here is accurately linear, and partial reversibility of the carbon protonation step can therefore be excluded as a mechanistic possibility.

These arguments suggest that carbon protonation is fully rate determining in the present reactions under the conditions investigated. This conclusion is supported by a close similarity between the activation parameters for the present hydrolyses, Table III, and those for the hydrolysis of ethyl vinyl ether,[21] a process

(9) (a) Lienhard, G. E.; Wang, T. C. *J. Am. Chem. Soc.* **1969**, *91*, 308–322. Kresge, A. J.; Chen, H. L.; Chiang, Y.; Murrill, E.; Payne, M. A.; Sagatys, D. S. *Ibid.* **1971**, *93*, 413–423. (b) Kresge, A. J.; Chen, H. J. *Ibid.* **1972**, *94*, 2818–2822. Chwang, W. K.; Eliason, R.; Kresge, A. J. *Ibid.* **1977**, *99*, 805–808. Kresge, A. J.; Chwang, W. K. *Ibid.* **1978**, *100*, 1249–1253.

(10) Bell, R. P.; Gelles, E.; Moeller, E. *Proc. R. Soc. London, Ser. A* **1949**, *198*, 308–322.

(11) Grunwald, E.; Ralph, E. K. *J. Am. Chem. Soc.* **1967**, *89*, 4405–4411.

(12) Kankaanpera, A.; Aaltonen, R. *Acta Chem. Scand.* **1972**, *26*, 1698–1706. Huurdeman, P. G. J.; Engberts, B. F. N. *J. Org. Chem.* **1979**, *44*, 297–300. Okuyama, T.; Kawao, S.; Fueno, T. *Ibid.* **1981**, *46*, 4372–4375.

(13) Capon, B.; Ghosh, A. K. *J. Am. Chem. Soc.* **1981**, *103*, 1765–1768.

(14) Maas, W.; Janssen, M. J.; Stamhuis, E. J.; Wynberg, H. *J. Org. Chem.* **1967**, *32*, 1111–1115. Sollenberger, P. Y.; Martin, R. B. *J. Am. Chem. Soc.* **1970**, *92*, 4261–4270.

(15) Hevesi, L.; Piquard, J. L.; Wautier, H. *J. Am. Chem. Soc.* **1981**, *103*, 870–875.

(16) Okuyama, T.; Fueno, T. *J. Am. Chem. Soc.* **1980**, *102*, 6590–6591. Okuyama, T.; Kawao, S.; Fueno, T. *Ibid.*, in press. Wautier, H.; Desauvage, S.; Hevesi, L. *J. Chem. Soc., Chem. Commun.* **1981**, 738–739.

(17) Albery, W. J.; Curran, J. S.; Campbell-Crawford, A. N. *J. Chem. Soc., Perkin Trans. 2* **1972**, 2185–2189.

(18) Dyer, R. L.; Hall, C. D. *Chem. Ind. (London)* **1973**, 1109–1110.

(19) Cooper, J. D.; Vitullo, V. P.; Whalen, D. L. *J. Am. Chem. Soc.* **1971**, *93*, 6294–6296.

(20) Young, P. R.; Jencks, W. P. *J. Am. Chem. Soc.* **1977**, *99*, 8238–8248.

well-known to proceed by fully rate-determining protonation on carbon. For the hydrolysis of ethyl vinyl ether catalyzed by the hydronium ion, $\Delta H^* = 13.8 \pm 0.2$ kcal mol$^{-1}$ and $\Delta S^* = -11.1 \pm 0.5$ cal K$^{-1}$ mol$^{-1}$; these do not differ significantly from the values of Table III.

It is interesting, in the light of this similarity, to extend the comparison of ketene acetal and vinyl ether hydrolyses to an examination of kinetic isotope effects. As the data of Table IV show, isotope effects on the present ketene acetal hydrolyses catalyzed by the hydronium ion, plus two others for similarly deactivated ketene acetals,[22] are all in the normal direction and of appreciable magnitude, as expected for rate-determining proton transfer from this acid. They are, however, consistently less than isotope effects expected for the hydrolysis of vinyl ethers of the same reactivity. The last column of Table IV lists isotope effects predicted from an expression based on Marcus rate theory that was found to correlate hydronium ion isotope effects with free energies of activation for the hydrolysis of some 30 vinyl ethers.[23] Observed isotope effects for ketene acetal hydrolysis are all significantly lower than those predicted from this correlation; the average difference is 25%.

The reason for this difference is not clear. The additional alkoxy group of ketene acetals allows more extensive delocalization of the positive charge in the cation formed in the rate-determining proton-transfer step; this will raise the intrinsic barrier for this reaction step,[24] and that should broaden the isotope effect maximum,[25] leading to larger rather than smaller isotope effects. The observed differences could be the result of steric effects, for most of these ketene acetals have bulky groups, Cl or CH$_3$, attached to the carbon atom to which the proton is being transferred; the presence of these groups might stiffen transition-state bending vibrations involving the atom being transferred, and that would have the effect of contributing additional isotopically sensitive zero-point energy to offset that of the initial state. A similar stiffening of bending vibrations upon introduction of bulky groups is known to affect isotopic fractionation factors of hydrogens attached to carbon.[26] Some additional support for this idea comes from the fact that the least bulky of the substrates listed in Table IV, cyanoketene dimethyl acetal, shows the smallest difference between observed and predicted isotope effects. Small isotope effects have also been observed in the hydrolyses of some vinyl ethers with bulky substituents at the $\beta$-position, notably the two cyclic substrates **5** and **6**[27] and methyl isobutenyl ether **7**.[23]
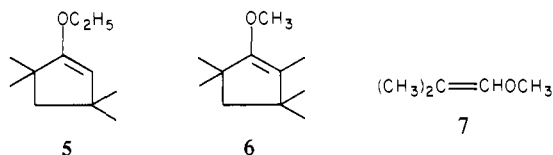


**Reactivity.** The bulk of the substituents at the $\beta$-positions of the ketene acetals studied here seems also to be responsible, at least in part, for their reduced reactivity. Quantitative examination of this matter requires knowledge of the rate constant for hy-

drolysis of the parent member of the series, unsubstituted ketene dimethyl acetal, but reaction of this substance unfortunately proved to be too fast to measure by the methods we had at our disposal. An estimate, however, can be made by using an expression, eq 7, that successfully correlates the rates of protonation of a large

$$\log k_{H^+} = -8.92 - 10.5 = \sum \sigma_p^+ \tag{7}$$

number of variously substituted carbon–carbon double bonds.[28] This relationship gives $k_{H^+} = 2.6 \times 10^7$ M$^{-1}$ s$^{-1}$ for the hydrolysis of ketene dimethyl acetal, which is consistent with a rough estimate for the closely similar ketene diethyl acetal, $k_{H^+} = 10^6$–$10^7$ M$^{-1}$ s$^{-1}$, made by extrapolating a Brønsted relation based on catalytic coefficients for several very weak acids measured at a low temperature.[1]
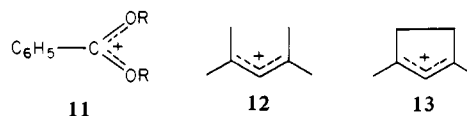
This value of $k_{H^+}$ gives the two methyl groups at the $\beta$-position of dimethylketene dimethyl acetal a rate-retarding effect of $(2.6 \times 10^7)/29 = 9 \times 10^5$, which is surprisingly large in view of the fact that similar substitution reduces the rate of vinyl ether hydrolysis by only a factor of 30: $k_{H^+} = 0.76$ M$^{-1}$ s$^{-1}$ for CH$_2$=C-HOCH$_3$[23] and $k_{H^+} = 0.025$ M$^{-1}$ s$^{-1}$ for (CH$_3$)$_2$C=CHOCH$_3$.[29] A plausible explanation of this difference involves steric interaction between the $\beta$-methyl groups and the alkoxy functions of the ketene acetal, which prevents the alkoxy groups from exerting their full accelerative effect.

The dialkoxy cation intermediate formed in the rate-determining step of ketene acetal hydrolysis will be most stable, and the rate of hydrolysis will therefore be the greatest, when the positive charge is able to delocalize freely onto both oxygen atoms. This requires a planar arrangement of the O–C–O triad and the atoms directly attached to it, and that restricts the geometry of the system to either a cis–cis (**8**), a cis–trans (**9**), or a trans–trans (**10**)
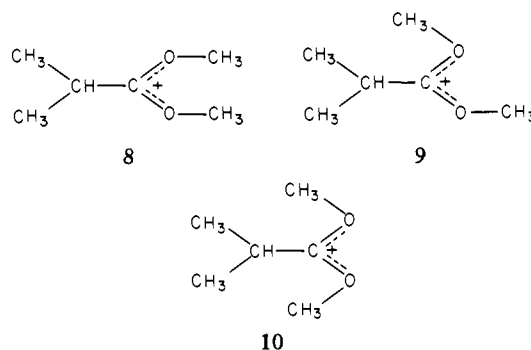


conformation. Each of these structures, however, will be strained, **8** by interference between the methoxy methyl groups and **9** and **10** by interference between methoxy methyl and $\beta$-methyl groups. The system will therefore be forced to adopt a compromise nonplanar conformation in which delocalization of positive charge onto the oxygen atoms is reduced and the stability of the cation, and that of the transition state leading to it, is correspondingly decreased.

Such steric inhibition of resonance is known to operate in the dialkoxy cation formed in the hydrolysis of benzoate ortho esters, **11**,[30] and it is also responsible for the reduced stability of meth-



yl-substituted acyclic alkyl cations such as **12** when compared to that of their cyclic counterparts, **13**.[31] In cyclic structures such as **13**, the strain present in the cis–cis conformation of acyclic

(21) Kresge, A. J.; Chiang, Y. *J. Chem. Soc. B* 1967, 58–61.

(22) These additional ketene acetals are ones for which it has been suggested carbon protonation might be reversible in carboxylic acid buffers.[17] Reversibility, however, is much less probable in strong mineral acid solutions such as those used to measure these isotope effects, where no basic species are present to effect deprotonation.

(23) Kresge, A. J.; Sagatys, D. S.; Chen, H. L. *J. Am. Chem. Soc.* 1977, 99, 7228–7233.

(24) Bell, R. P. "The Proton in Chemistry"; Cornell University Press: Ithaca, NY, 1973; pp 208–212. Kresge, A. J. *Acc. Chem. Res.* 1975, 8, 354–360.

(25) Kresge, A. J. In "Isotope Effects on Enzyme Catalyzed Reactions"; Cleland, W. W., O'Leary, M. H., Northrup, D. B., Eds.; University Park Press: Baltimore, MD, 1977; pp 37–63.

(26) Hartshorn, S. R.; Shiner, V. J., Jr. *J. Am. Chem. Soc.* 1972, 94, 9002–9012. Shiner, V. J., Jr. In "Isotope Effects on Enzyme Catalyzed Reactions"; Cleland, W. W., O'Leary, M. H., Northrup, D. B., Eds.; University Park Press: Baltimore, MD, 1977; pp 1–36. Cleland, W. W. *Methods Enzymol.* 1980, 64B, 104–125.

(27) Chiang, Y.; Chwang, W. K.; Kresge, A. J.; Szilagyi, S. *Can. J. Chem.* 1988, 58, 124–129.

(28) Csizmadia, V. M.; Koshy, K. M.; Law, K. C. M.; McClelland, R. A.; Nowlan, V. J.; Tidwell, T. T. *J. Am. Chem. Soc.* 1979, 101, 974–979 and references therein.

(29) Salomaa, P.; Nissi, P. *Acta Chem. Scand.* 1967, 21, 1386–1389.

(30) Chiang, Y.; Kresge, A. J.; Salomaa, P.; Young, C. I. *J. Am. Chem. Soc.* 1974, 96, 4494–4499.

(31) Deno, N. C.; Scholl, P. C. *J. Am. Chem. Soc.* 1971, 93, 2702–2704. Deno, N. C.; Haddon, R. C.; Nowak, E. *Ibid.* 1970, 92, 6691–6693.

systems such as **8** is relieved by formation of a small ring. It follows from this that the 2-dichloromethyl-1,3-dioxolenium ion, **14**, should be more stable than its acyclic counterparts, **15**, and
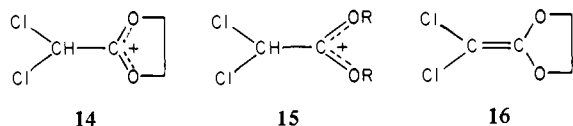


that the rate of hydrolysis of 2-dichloromethylene-1,3-dioxolane should be greater than those of corresponding acyclic dichloroketene dialkyl acetals such as those studied here. This is in fact

the case: $k_{H^+}$ for **16** is reported as 104 M$^{-1}$ s$^{-1}$,[2a] which is 20–30 times greater than the rate constants for the acyclic dichloroketene acetals determined here.

# Protonation of Diazomethane in Superacid Media[1]

**John F. McGarrity\* and D. Phillip Cox**

*Contribution from the Institut de Chimie Organique, Université de Lausanne, CH-1005 Lausanne, Switzerland. Received October 25, 1982*

**Abstract:** Diazomethane is protonated by HOSO$_2$F in SO$_2$ClF at -120 °C to yield exclusively methanediazonium ion (**1**), which decomposes at -85 °C to yield methyl fluorosulfate. When the more acidic HOSO$_2$F/SbF$_5$ system is used, both **1** and the isomeric methylenediazenium ion (**2**) are formed. These structures are confirmed by experiments using diazomethane labeled with $^{15}$N in each position. The compound **2**, the first example of its class, can be converted into **1** by lowering the acidity of the medium and may be stabilized in the less acidic medium by complexation with SO$_2$. The displacement of nitrogen from **1** is nucleophile assisted even in the system HOSO$_2$F/SbF$_5$/SO$_2$ClF.

The existence of alkanediazonium ions as intermediates has been well established in a variety of organic reactions.[2] In particular the methanediazonium ion (**1**) is sufficiently stable in the gas phase under ion cyclotron resonance conditions to allow direct investigation of its deprotonation and nucleophilic substitution reactions.[3] In a recent study of the acid-catalyzed hydrolysis of diazomethane, we were able to generate a protonated diazomethane species at concentrations up to 10$^{-4}$ M in THF/water.[4] However on the basis of the kinetic data alone we could not distinguish between structure **1** and that of the isomeric methylenediazenium ion (**2**). Indeed the formation of N-protonated diazoalkanes, such as **2**, has been occasionally proposed to explain anomalous reactions of diazoalkanes with weak acids[5,6] and the role of diazoalkanes as mildly basic catalysts,[7] but the existence of such species has never been proven.

In his pioneering study of protonated diazoalkanes in superacid media, Mohrig was able to examine trifluoroethanediazonium ion and hexafluoropropane-2-diazonium ion, but could not detect any of the N-protonated isomers.[8,9] Similarly, protonation of 1-phenyl-2,2,2-trifluorodiazoethane with fluorosulfuric acid yielded only one species, presumed to be the diazonium ion.[10] In contrast α-diazo ketones are protonated exclusively on oxygen in superacid media.[11-13]

In a preliminary communication on the reaction of diazomethane with fluorosulfuric acid in sulfuryl chlorofluoride, we described two reactive intermediates that decomposed to methyl fluorosulfate **3** on heating.[14] Structure **1** was attributed to the major species and structure **2** was assigned to the minor one. In this paper we correct the latter assignment and describe the conditions necessary for the observation of **2** as well as **1**. Structures **1** and **2** are unequivocally established by use of $^{15}$N-labeled diazomethane.

## Experimental Section

**Materials.** Sulfuryl chlorofluoride was supplied by Aldrich and was purified by refluxing over antimony pentafluoride prior to distillation.[15] Fluorosulfuric acid and [$^2$H]fluorosulfuric acid were supplied by Fluka AG (Buchs) and were purified by trap-to-trap distillation on the vacuum line with back distillation of 10% of the distillate. Antimony pentafluoride and hexafluoroantimonic acid were supplied by Aldrich; the former was purified as described for fluorosulfuric acid, and the latter was used as supplied. $^{15}$N-Labeled sodium nitrite and acetamide were used as supplied by Stohler Isotopes (Waltham MA). *N*-Nitroso-*N*-methylurea was prepared as described by Vogel.[16]

**Apparatus.** The vacuum line was fitted with Teflon stopcocks lubricated with Kel-F nonvolatile Teflon oil, and Kel-F Teflon grease was used on ground glass joints; both products were supplied by Roth KG (Karlsruhe). $^1$H and $^{13}$C NMR spectra were recorded on a Bruker WP-60 spectrometer in the FT mode with an internal $^{19}$F lock at 60 and 15.8 MHz, respectively. Chemical shifts (δ) are reported relative to Me$_4$Si *internal* reference.[17] $^{13}$C proton-decoupled spectra were measured

(1) Presented in part: "Abstracts of Papers", Second Chemical Congress of the North American Continent, Las Vegas, 1980; ORGN 036.
(2) Kirmse, W. *Angew. Chem., Int. Ed.* **1976**, *15*, 251–261.
(3) Foster, M. S.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1972**, *94*, 2425–2431.
(4) McGarrity, J. F.; Smyth, T. *J. Am. Chem. Soc.* **1980**, *102*, 7303–7308.
(5) Closs, G. L.; Goh, S. H. *J. Org. Chem.* **1974**, *39*, 1717–1723.
(6) Griengl, H.; Janoschek, R. *Tetrahedron* **1977**, *33*, 445–448.
(7) Clinging, R.; Dean, F. M. *J. Chem. Soc. C* **1971**, 3668–3671.
(8) Mohrig, J. R.; Keegstra, K. *J. Am. Chem. Soc.* **1967**, *89*, 5492–5493.
(9) Mohrig, J. R.; Keegstra, K.; Maverick, A.; Roberts, R.; Wells, S. *J. Chem. Soc., Chem. Comm.* **1974**, 780–781.
(10) Diderich, G. *Helv. Chim. Acta* **1972**, *55*, 2103–2112.

(11) Wentrup, C.; Dahn, H. *Helv. Chim. Acta* **1970**, *53*, 1637–1645.
(12) Avaro, M.; Levisalles, J.; Sommer, J. M. *Chem. Commun.* **1968**, 410–412.
(13) Malherbe, R.; Dahn, H. *Helv. Chim. Acta* **1974**, *57*, 2492–2503.
(14) Berner, D.; McGarrity, J. F. *J. Am. Chem. Soc.* **1979**, *101*, 3135–3136.
(15) Calves, J-Y.; Gillespie, R. J. *J. Am. Chem. Soc.* **1977**, *99*, 1788–1792.
(16) Vogel, A. I. "A Text-book of Practical Organic Chemistry", 3rd ed.; Longmans, Green and Co.: New York, 1956; p 696.