165

Flash photolytic generation and study of ketenes: acid-catalysed hydration in aqueous solution[†]

J. Andraos and **A. J. Kresge**[††]

Department of Chemistry, University of Toronto, Toronto, Ontario M5S 1A1 (Canada)

Abstract

Flash photolysis was used to generate $CH_2=C=O$ by fragmentation of cyclobutanone and $(CH_3)_3CCH=C=O$, $(CH_2)_5C=C=O$ and $PhC(CH_3)=C=O$ by the photo-Wolff reaction of the corresponding diazoketones; the rates of hydration of these ketenes were measured in wholly aqueous solutions of sodium perchlorate, perchloric acid and phosphoric and acetic acid buffers. Uncatalysed and acid-catalysed reactions were observed for the aliphatic ketenes, but only an uncatalysed reaction was observed for the aromatic derivative. A mechanism for the acid-catalysed process, involving rate-determining proton transfer from the catalyst to the terminal carbon atom of the ketene functional group, is indicated by the occurrence of general acid catalysis and hydronium ion isotope effects in the range $k_{H^+}/k_{D^+}=2.7$–3.3. The absence of acid catalysis in the hydration of $PhC(CH_3)=C=O$ is explained in terms of a phenyl-substituent effect that retards the acid-catalysed process but accelerates the uncatalysed reaction.

1. Introduction

Flash photolysis has played an important role in elucidating the chemistry of ketenes in aqueous solution. Ketenes are useful substances that undergo a wide variety of important reactions [1]. They are also quite reactive, and kinetic studies of their hydration to produce carboxylic acids

$$R_2C=C=O + H_2O \longrightarrow R_2CHCO_2H \tag{1}$$

have usually been carried out in non-hydroxylic solvents containing only small concentrations of water; this has had the effect of slowing the hydration reaction and rendering it observable by conventional kinetic methods [2]. With flash photolytic techniques, however, direct observation of the reaction in wholly aqueous solution is possible.
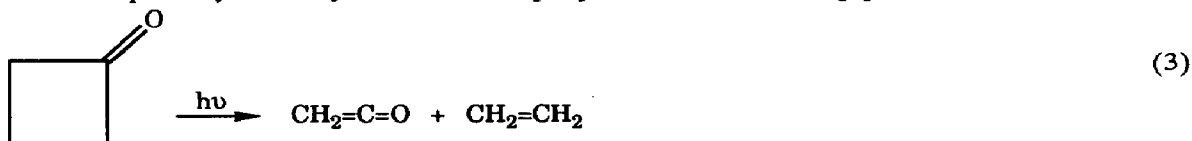
The first flash photolytic investigations of ketene hydration in wholly aqueous solution used the photo-Wolff reaction of diazoketones to generate a series of aryl ketenes [3]
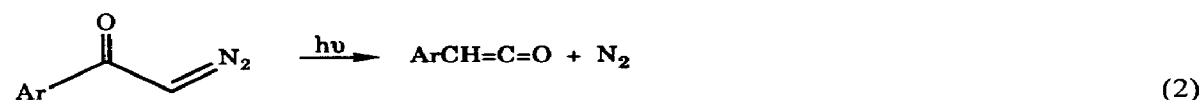
$$\tag{2}$$

---

and the photolysis of cyclobutane to prepare ketene itself [4]

$$\text{cyclobutanone} \xrightarrow{\ h\upsilon\ } CH_2{=}C{=}O \ + \ CH_2{=}CH_2 \tag{3}$$

These studies employed conductimetric detection to monitor the hydration reaction: the carboxylic acid products are partly ionized in aqueous solution and the process is consequently accompanied by an increase in solution conductivity. This technique is limited to media which themselves do not conduct strongly, and it could not be applied to solutions more acidic than pH 4 or more basic than pH 11. It consequently established the presence of an uncatalysed ketene hydration reaction, but it did not pick up either acid or base catalysis of the process.

A more recent flash photolytic investigation of this reaction in aqueous solution used spectrophotometric detection, based on the strong UV absorbance of ketenes, to monitor the process [5]. This method has no pH range limitations, and both acid and base catalysis were detected.

The present study extends this work, focusing its attention on acid catalysis in the reactions of four ketenes: ketene itself (**1**), *t*-butylketene (**2**), pentamethyleneketene (**3**) and phenylmethylketene (**4**).

$$CH_2{=}C{=}O \qquad (CH_3)_3CCH{=}C{=}O \qquad \text{[cyclohexylidene]}{=}C{=}O \qquad PhC(CH_3){=}C{=}O$$

$$\textbf{1} \qquad\qquad\qquad \textbf{2} \qquad\qquad\qquad\qquad \textbf{3} \qquad\qquad\qquad\qquad \textbf{4}$$
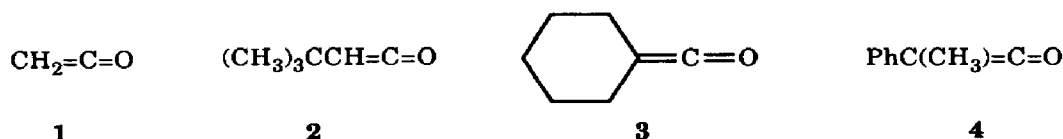
2. Experimental details

2.1. Materials

Ketene was generated by the photofragmentation of cyclobutanone (eqn. (3)) [3]. *t*-Butylketene, pentamethyleneketene and phenylmethylketene were prepared by the photo-Wolff reaction of the corresponding diazoketones (α-diazopinacolone [6], α-diazocyclohexanone [7] and α-diazopropiophenone [8] respectively). All other materials were best available commercial grades and were used as received.

2.2. Kinetics

Flash photolysis was carried out using a system of conventional design described previously [5]. Measurements were recorded at 25.0 ± 0.05 °C on wholly aqueous solutions, using the decrease in absorbance which accompanies ketene hydration to monitor the reaction; the wavelengths employed were $\lambda = 210$–215 nm for the aliphatic ketenes and $\lambda = 260$ nm for the aromatic derivative. The concentration of diazoketone used to prepare the substituted ketenes was 0.0004–0.001 M and the concentration of cyclobutanone used to produce ketene itself was 0.03 M. The kinetic data conformed accurately to the first-order rate law, and observed first-order rate constants were evaluated by least-squares fitting to an exponential function.

3. Results

The rates of hydration of the four ketenes were determined in aqueous solutions whose ionic strength was maintained at 0.10 M through the addition of sodium

perchlorate as required. Measurements were made using solutions with no other additives and also with solutions containing various acid catalysts. The results obtained in the absence of acids are summarized in Table 1; each of the rate constants listed is the average of 10–20 separate determinations. The value for ketene itself ($k = 37$ s^{-1}) is consistent with $k = 44$ s^{-1} reported earlier for this substance [4], but the value determined here for t-butylketene ($k = 15$ s^{-1}) is considerably less than the rate constant ($k = 38$ s^{-1}) estimated for this ketene by extrapolation of measurements made in acetonitrile–water mixtures [9].

The rates of hydration of the four ketenes were also determined in dilute perchloric acid solutions. Acid concentrations were varied for each substrate by factors of 5–50. The rates of reaction of three of the ketenes proved to be sensitive to acid concentration, with first-order rate constants increasing in direct proportion to acid concentration (see Fig. 1). Linear least-squares analysis provided the catalytic coefficients listed in Table 2 and gave zero acid concentration intercepts which agreed well with the rate constants for uncatalysed hydration measured directly in the absence of added acid (Table 1).
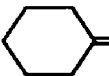
First-order rate constants for the fourth substrate, phenylmethylketene, were independent of acid concentration over the range investigated (Fig. 2); linear least-squares analysis gave a catalytic coefficient whose uncertainty exceeded its value by a considerable margin: $k_{H^+} = -34 \pm 139$ M^{-1} s^{-1}. The intercept of this relationship, $k = 51.0 \pm 0.9$ s^{-1}, is consistent with the directly-measured uncatalysed rate constant for this substrate ($k = 55.7 \pm 0.6$ s^{-1}).

The rates of hydration of two ketenes were also measured in buffer solutions: t-butylketene in phosphoric acid buffer and pentamethyleneketene in acetic acid buffer. A series of solutions of constant buffer ratio and constant ionic strength, but varying buffer concentration, was used. This served to hold the hydronium ion concentrations constant along a series of solutions for the acetic acid buffers, but not for the phosphoric acid buffer; significant buffer failure [10] occurred in the latter case causing hydronium ion concentrations to drop systematically as the buffer was diluted; this produced corresponding changes in the hydronium ion contributions to the observed rate constants. These changes were compensated for by adjusting the observed rate constants for a given series of solutions to a common hydronium ion concentration; this was performed using the known hydronium ion catalytic coefficient (Table 2) plus the hydronium ion concentrations obtained by calculation (employing $pK_a = 2.146$ for H$_3$PO$_4$ [11] and activity coefficients recommended by Bates [12]).

The observed rate constants adjusted in this way proved to be linear functions of phosphoric acid concentration (see Fig. 3), and least-squares analysis gave the

TABLE 1

Summary of rate data for the uncatalysed hydration of ketenes in aqueous solution at 25 °C[a]

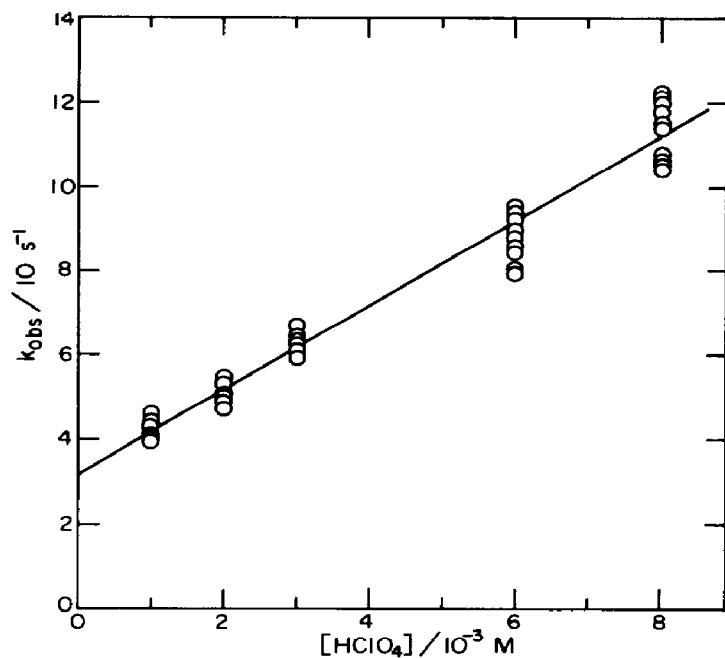| Substrate	k_{H_2O} (s^{-1})	k_{D_2O} (s^{-1})	k_{H_2O}/k_{D_2O}
CH$_2$=C=O	36.5 ± 0.4	23.0 ± 0.3	1.59 ± 0.02
(CH$_3$)$_3$CCH=C=O	14.6 ± 0.1	7.28 ± 0.09	2.01 ± 0.03
⬡=C=O	23.0 ± 0.5	11.3 ± 0.2	2.04 ± 0.06
PhC(CH$_3$)=C=O	55.7 ± 0.6	36.0 ± 1.3	1.55 ± 0.06

[a]Ionic strength $= 0.10$ M.

Fig. 1. Relationship between perchloric acid concentration and the observed first-order rate constants for the hydration of $CH_2=C=O$ in aqueous solution at 25 °C.
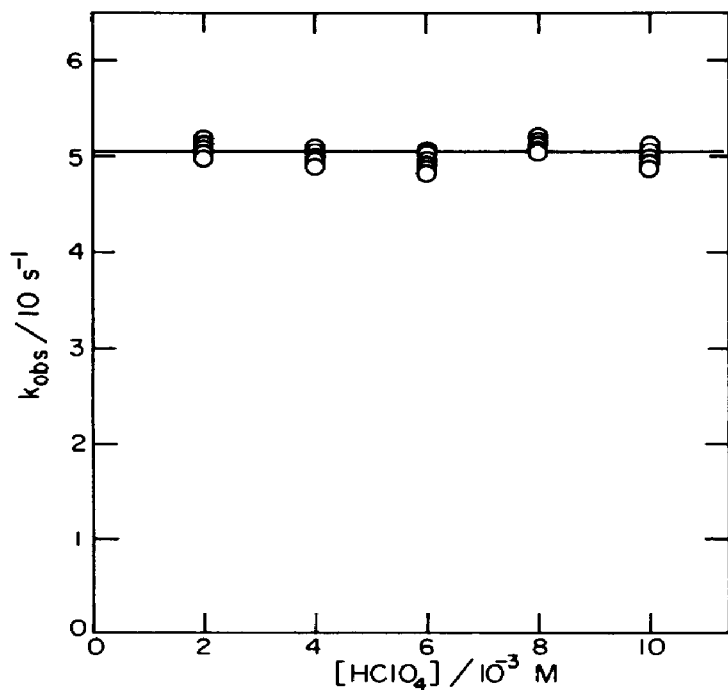

Fig. 2. Relationship between perchloric acid concentration and the observed first-order rate constants for the hydration of $PhC(CH_3)=C=O$ in aqueous solution at 25 °C.

TABLE 2

Summary of rate data for the hydration of ketenes in dilute aqueous perchloric acid solutions at 25 °C[a]

Substrate	k_{H^+} (10^3 M^{-1} s^{-1})	k_{D^+} (10^3 M^{-1} s^{-1})	k_{H^+}/k_{D^+}
$CH_2=C=O$	10.1 ± 0.3	3.11 ± 0.10	3.25 ± 0.14
$(CH_3)_3CCH=C=O$	4.77 ± 0.04	1.80 ± 0.03	2.65 ± 0.05
⬡=C=O	2.78 ± 0.09	0.997 ± 0.043	2.79 ± 0.15
$PhC(CH_3)=C=O$	–	–	–

[a]Ionic strength = 0.10 M.
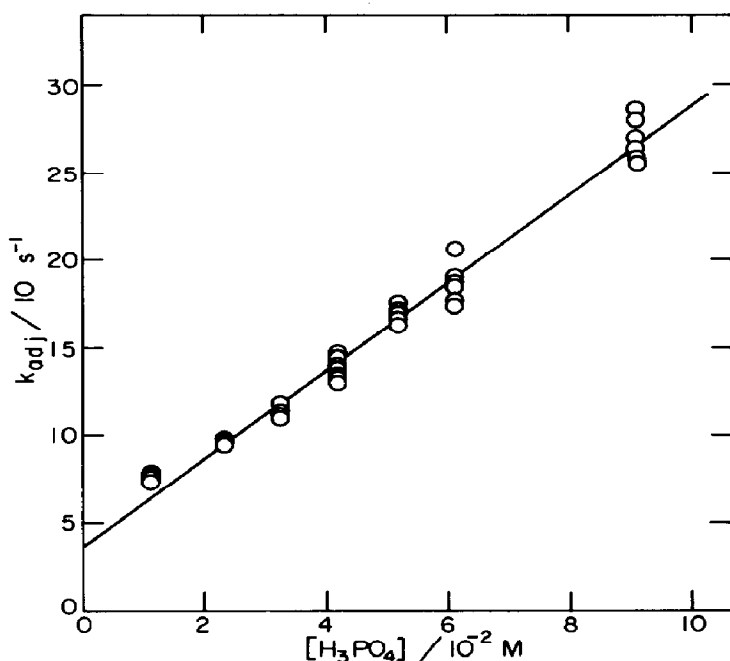

Fig. 3. Relationship between phosphoric acid concentration and the adjusted first-order rate constants for the hydration of $(CH_3)_3CCH=C=O$ in aqueous $H_3PO_4/H_2PO_4^-$ buffer solutions at 25 °C.

catalytic coefficients listed in Table 3. It may be seen that these catalytic coefficients remain reasonably constant as the buffer ratio is varied; this indicates that the catalysis is of the general acid type. In contrast, the analysis of the data on the assumption of general base catalysis produced catalytic coefficients which changed with buffer ratio.

In contrast with this behaviour in phosphoric acid buffers, no buffer catalysis was observed in acetic acid buffer solutions; the rates of hydration of pentamethyleneketene remained constant as the buffer concentration was varied. Moreover, the magnitude of these rates was consistent with expectation for the operation of hydronium ion catalysis plus an uncatalysed reaction.

TABLE 3

Phosphoric acid catalytic coefficients for the hydration of t-butylketene in aqueous $H_3PO_4/H_2PO_4^-$ buffer solutions at 25 °C[a]

| $[H_3PO_4]/[H_2PO_4^-]$	k_{HA} (10^3 M^{-1} s^{-1})
5.03	2.73 ± 0.08
2.01	2.53 ± 0.08
1.00	2.52 ± 0.05

[a]Ionic strength $= 0.10$ M.

4. Discussion

4.1. Reaction mechanism

Two different reaction mechanisms can be postulated for the acid-catalysed hydration of ketenes, each derived from the different mechanisms by which the constituents of the ketene functional group (the carbon–carbon double bond and the carbonyl group) undergo acid-catalysed reactions. The first of these mechanisms involves rate-determining proton transfer from the catalyst to the terminal carbon atom of the ketene group, followed by rapid hydration of the ensuing cationic intermediate

$$CH_2=C=O+HA \xrightarrow{\text{r.d.}} CH_3C^+=O+A^-$$
$$CH_3C^+=O+H_2O \xrightarrow{\text{fast}} CH_3CO_2H+H^+ \tag{4}$$
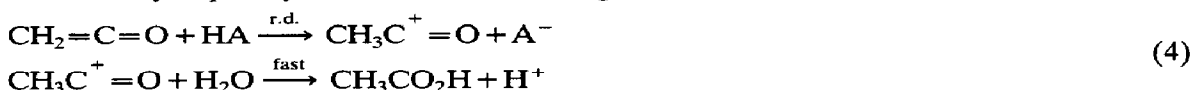
This is the analogue of the acid-catalysed hydration of simple carbon–carbon double bonds. The other mechanism begins with rapid pre-equilibrium protonation of the oxygen atom of the carbonyl group, followed by the addition of water to the central carbon of the ketene

$$CH_2=C=O+HA \xrightleftharpoons{\text{fast}} CH_2=C=OH^+ +A^-$$
$$CH_2=C=OH^+ +H_2O \xrightarrow{\text{r.d.}} CH_2=C(OH)_2+H^+ \tag{5}$$
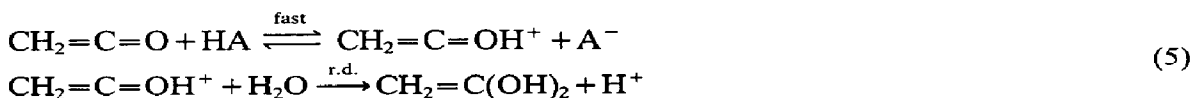
This produces a carboxylic acid enol, which will then ketonize rapidly

$$CH_2=C(OH)_2 \longrightarrow CH_2CO_2H \tag{6}$$

The first part of this second mechanism, production of the enol (eqn. (5)), is the analogue of the acid-catalysed addition of nucleophiles to carbonyl groups.

These two mechanisms may be distinguished by the form of their acid catalysis. The rate-determining transition state of the first mechanism (eqn. (4)) contains the substrate plus a general acid; reaction by this mechanism will therefore show general acid catalysis. However, the rate-determining transition state of the second mechanism (eqn. (5)) contains the substrate and only a proton (in addition to a water molecule); rates of reaction by this route will therefore be proportional to hydronium ion concentration only, and the process will consequently show specific hydronium ion catalysis.

The two mechanisms of eqns. (4) and (5) plus (6) may also be distinguished by the direction of their hydronium ion isotope effects: rate-determining proton transfer reactions, such as that of eqn. (4), generally give hydronium ion isotope effects in the normal direction ($k_{H^+}/k_{D^+} > 1$), whereas those involving pre-equilibrium proton transfer, such as eqn. (5), usually give inverse isotope effects ($k_{H^+}/k_{D^+} < 1$) [10, 13].

Both of these criteria, on the basis of the evidence obtained here, point to the operation of the first mechanism (eqn. (4)) for the acid-catalysed hydration of ketenes: general acid catalysis, not specific hydronium ion catalysis, was observed in the hydration of t-butylketene, and all of the hydronium ion isotope effects determined here are normal (see Table 2). This mechanistic assignment is consistent with previous observations of general acid catalysis and normal hydronium ion isotope effects in the hydration of other ketenes [14], and it is supported by theoretical calculations [15].

4.2. Occurrence of acid catalysis

The hydration of one of the ketenes investigated (phenylmethylketene (4)) was not catalysed by acids. A similar lack of acid catalysis has been observed previously in the aqueous solution hydration of phenylketene (5) and diphenylketene (6) [5]. This behaviour contrasts with the acid catalysis found for hydration of ketenes without phenyl substituents, such as the other ketenes examined here and other aliphatic ketenes [5, 9, 14].
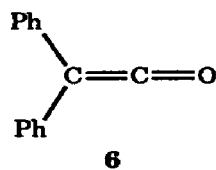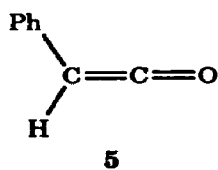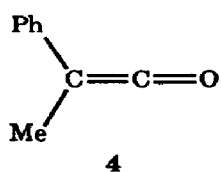
The lack of acid catalysis in the hydration of phenyl-substituted ketenes may be understood in terms of a differential effect of the phenyl substituent on the rates of the acid-catalysed and uncatalysed reactions. This substituent retards the acid-catalysed process, but speeds up the uncatalysed reaction, and as a result acid catalysis is no longer visible against a background of uncatalysed hydration.

It is well known that phenyl groups stabilize carbon–carbon double bonds appreciably; the effect has been estimated at 4.9 kcal mol^{-1} per phenyl group [16]. This effect will lower the free energies of the initial and transition states of the acid-catalysed hydration reactions of phenyl-substituted ketenes; however, its influence on the initial state will be greater than on the transition state because, in the initial state the substrate has a full carbon–carbon double bond, whereas in the transition state this bond is on its way to becoming a single bond. This difference will have the effect of increasing the free energy of activation and retarding the reaction rate. Rate retardations of this kind have been observed previously in the acid-catalysed hydration of olefins [17], the acid-catalysed hydrolysis of vinyl ethers [18] and the acid-catalysed ketonization of enols [19]; all of these occur by a reaction mechanism (rate-determining proton transfer from catalyst to substrate) which is similar to that established for acid-catalysed ketene hydration.

The uncatalysed hydration of ketenes occurs by a different mechanism: the rate-determining conversion of the ketene to a carboxylic acid enol followed by rapid ketonization of the enol [2, 5, 9, 14, 20]

$$CH_2=C=O + H_2O \xrightarrow{\text{r.d.}} CH_2=C(OH)_2 \xrightarrow{\text{fast}} CH_3CO_2H \qquad (7)$$
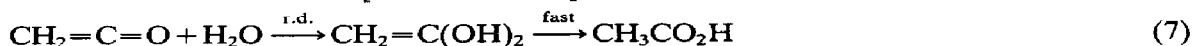
The carbon–carbon double bond remains intact in the rate-determining stage of this process, and phenyl substitution will consequently not have a retarding effect on its rate. A phenyl substituent will have an accelerating effect, since the attack of water on the carbonyl carbon atom of the ketene in the rate-determining stage of this process gives negative charge to the substrate, and this charge can be stabilized by phenyl substitution [2, 3].

These arguments can be put on a quantitative basis to show that the differential effect of phenyl substitution on acid-catalysed and uncatalysed ketene hydration is sufficiently large to render the acid-catalysed reaction invisible. β-Phenyl substitution retards the rate of vinyl ether hydrolysis by a factor of 285 in the case of cis-β-methoxystryene (7) and by a factor of 1090 in the case of trans-β-methoxystyrene (8) [18]. By applying the average of these rate reductions to the rate constant determined here for ketene ($k_{H+} = 1.01 \times 10^4$ M^{-1} s^{-1}) leads to a prediction of $k_{H+} = 15$ M^{-1} s^{-1} for phenylketene. A similar calculation based on the β-phenyl effects shown by the ketonization of the cis and trans enols of phenylacetaldehyde [19] (9 and 10) gives $k_{H+} = 33$ M^{-1} s^{-1}. Both of these estimates are sufficiently small to make the rate of hydronium ion catalysed hydration of phenylketene, even in moderately concentrated acid solutions, considerably less than the rate of the uncatalysed process, for which $k = 4770$ s^{-1} [5]. Similar conclusions concerning the non-observability of acid catalysis may be reached for phenylmethylketene, using the additional rate retardation observed for β-methyl substitution in vinyl ether hydrolysis [21], and also for diphenylketene, using the rate retardation observed for β,β-diphenyl substitution in the enol of diphenylacetaldehyde (11) [19].
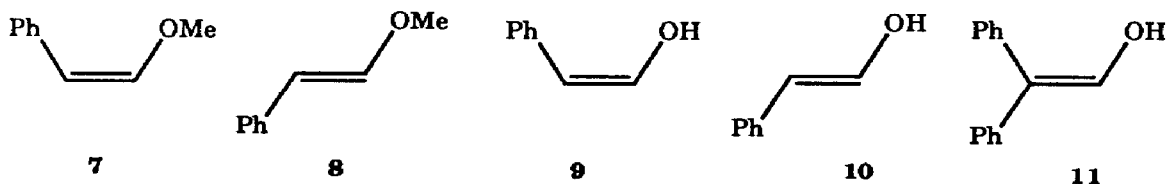
Although the hydration of the aliphatic ketenes investigated here showed acid catalysis in perchloric acid solutions, and t-butylketene gave acid catalysis in phosphoric acid buffer, no acid catalysis was found for pentamethyleneketene in acetic acid buffer. This is the consequence of an overwhelming uncatalysed reaction. Acid catalysis occurred in phosphoric acid buffer because phosphoric acid is a fairly strong acid and its buffer has a fairly high hydronium ion concentration. Acetic acid buffer, on the other hand, is much more weakly acidic, and it consequently cannot provide sufficiently large acid-catalysed rates to compete successfully with a strong uncatalysed reaction.

Acknowledgments

References

1 S. Patai (ed.), The Chemistry of Ketenes, Allenes, and Related Substances, Parts I and II, Wiley, New York, 1980.
2 H. R. Seikaly and T. T. Tidwell, Tetrahedron, 42 (1986) 2587.
   D. P. N. Satchell and R. S. Satchell, Chem. Soc. Rev., 4 (1975) 231.
3 E. Bothe, H. Meier, D. Schulte-Frohlinde and C. von Sonntag, Angew. Chem. Int. Ed. Engl., 15 (1976) 380.
4 E. Bothe, A. M. Dessouki and D. Schulte-Frohlinde, J. Phys. Chem., 84 (1980) 3270.
5 A. D. Allen, A. J. Kresge, N. P. Schepp and T. T. Tidwell, Can. J. Chem., 65 (1987) 1719.

6 M. Regitz and F. Menz, *Chem. Ber.*, *101* (1968) 2622.

7 M. Regitz, J. Ruter and A. Leidhegener, *Org. Synth.*, *51* (1971) 86.

8 D. F. Taber, R. E. Ruckle, Jr. and M. J. Hennessy, *J. Org. Chem.*, *51* (1986) 4077.

9 A. D. Allen and T. T. Tidwell, *J. Am. Chem. Soc.*, *109* (1987) 2774.

10 J. R. Keeffe and A. J. Kresge, in C. F. Bernasconi (ed.), *Techniques of Chemistry, Vol. VI, Investigation of Rates and Mechanisms of Reactions*, Wiley-Interscience, New York, Part I, Chapter XI.

11 K. S. Pitzer and L. F. Silvester, *J. Solution Chem.*, *5* (1976) 269.

12 R. G. Bates, *Determination of pH. Theory and Practise*, Wiley-Interscience, New York, 1973, p. 49.

13 A. J. Kresge, R. A. More O'Ferrall and M. F. Powell, in E. Buncel and C. C. Lee (eds.), *Isotopes in Organic Chemistry*, Elsevier, New York, 1987, Chapter 4.

14 S. H. Kabir, H. R. Seikaly and T. T. Tidwell, *J. Am. Chem. Soc.*, *101* (1979) 1059.
A. D. Allen, A. Stevenson and T. T. Tidwell, *J. Org. Chem.*, *54* (1989) 2843.

15 R. H. Nobes, W. J. Bouma and L. Radom, *J. Am. Chem. Soc.*, *105* (1983) 309.
M. T. Nguyen and A. F. Hegarty, *J. Am. Chem. Soc.*, *106* (1984) 1552.
R. Leung-Toung, M. R. Peterson, T. T. Tidwell and I. G. Csizmadia, *J. Mol. Struct. (Theochem)*, *183* (1989) 319.

16 J. Hine, *Structural Effects on Equilibria in Organic Chemistry*, Wiley-Interscience, New York, 1975, p. 273.

17 P. Knittel and T. T. Tidwell, *J. Am. Chem. Soc.*, *99* (1977) 3408.

18 A. J. Kresge and H. J. Chen, *J. Am. Chem. Soc.*, *94* (1972) 2818.
Y. Chiang, A. J. Kresge and C. I. Young, *Can. J. Chem.*, *56* (1978) 461.

19 Y. Chiang, A. J. Kresge and E. T. Krogh, *J. Am. Chem. Soc.*, *110* (1988) 2600.
Y. Chiang, A. J. Kresge, P. A. Walsh and Y. Yin, *J. Chem. Soc., Chem. Commun.*, (1989) 869.

20 J. Andraos, unpublished work, 1990.

21 Y. Chiang, W. K. Chwang, A. J. Kresge and S. Szilagyi, *Can. J. Chem.*, *58* (1980) 124.