

Kinetic and spectral investigations were carried out using a Unicam SP 1800 spectrometer with cell block thermostated at  $25.0 \pm 0.1$  °C or a Durrum-Gibson stopped-flow spectrophotometer, also operating at  $25.0 \pm 0.1$  °C. The dead time of the latter was determined using a published procedure.<sup>26</sup> First-order rate constants were obtained from plots of  $\ln(A_t - A_\infty)$  or  $\ln(A_\infty - A_t)$  vs. time.

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## References and Notes

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## The Reactivity of Oxocarbenium Ions. 2. Hydrolysis in Sulfuric Acid Solutions and Estimates of Reactivity in Water

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**Abstract:** Rate constants have been obtained in sulfuric acid solutions for the hydrolysis of a number of oxocarbenium ions, one mercaptocarbenium ion, and a nitrilium ion. A common rate constant-acidity dependence is observed, with the exception of ions with considerable structural difference or with a different mechanism of hydrolysis. A general function ranging from 0 to 92% H<sub>2</sub>SO<sub>4</sub> has been generated which accurately describes the acidity dependence. Rate constants for hydrolysis of the oxocarbenium ions in water have been obtained by extrapolation of the rate constants in the sulfuric acid solutions, using the general function. The estimates for four ions of the type ArC<sup>+</sup>(OMe)Me have been compared with those recently reported for the same ions using a sulfite trapping technique, and show excellent agreement. The effect of structure on oxocarbenium ion reactivity is discussed. In the series (4-MeOC<sub>6</sub>H<sub>4</sub>)<sub>n</sub>C<sup>+</sup>(OMe)<sub>3-n</sub>, *n* = 0-3, the results suggest that a major contributing factor in the relative unreactivity of triarylcarbonium ions is steric hindrance to water attack. For the two ions ((4-MeOC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>C<sup>+</sup>XMe (X = O, S), it is the cation with sulfur which is less reactive (and considerably so). The results of this paper now permit an analysis of the substituent effects on rate and equilibrium constants for ArC(OMe)<sub>2</sub>R + H<sup>+</sup> ⇌ ArC<sup>+</sup>(OMe)R + MeOH, for both ortho esters (R = MeO) and ketals (R = Me). The comparison shows that (a) the transition state for the ortho esters is less advanced and (b) the ortho esters exhibit a smaller resonance interaction with the aromatic substituent.

In the previous paper<sup>1</sup> experiments are reported which show that the oxocarbenium ion can be observed during the hydrolysis of certain ketals and ortho esters, and the rate constant for hydrolysis of the ion measured. The substrates for which this proves to be possible are such that the ion has unusual stabilizing characteristics, either in the form of resonance stabilization or steric hindrance to nucleophilic attack. In this paper we consider the question of the rate constants for hydrolysis of less stabilized oxocarbenium ions, the type of ions more commonly involved in studies of ketal and ortho ester hydrolysis.

Our approach here is based upon the fact that oxocarbenium ions can be obtained as stable entities. For example, a solution of the ion in strongly acidic media can be prepared, simply by addition to the acid of the precursor acetal, ketal, or ortho ester.<sup>2-4</sup> Also, stable salts can be isolated where the counterions

are nonnucleophilic (e.g., BF<sub>4</sub><sup>-</sup> or SbCl<sub>6</sub><sup>-</sup>), by treatment of the precursor acetal, etc., with the appropriate Lewis acid.<sup>4-13</sup> Alternatively a carbonyl oxygen can be alkylated, for example, with a dialkoxycarbonium ion salt,<sup>10,11,14</sup> or in certain cases with a reaction with a trialkyloxonium ion salt<sup>5,15-19</sup> or an alkyl fluorosulfonate.<sup>20</sup> An excellent review of the preparation and properties of these ions has appeared.<sup>21</sup>

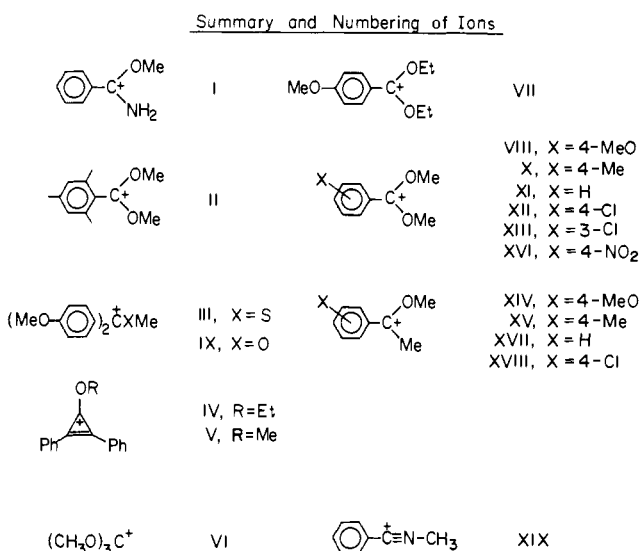
Conceivably then it is possible to study oxocarbenium ion hydrolysis directly, in a sense entering the ketal or ortho ester hydrolysis reaction after the normal rate-determining step. Practically this direct approach is not generally feasible for solutions in pure water because of very great reactivity. As we have recently shown, however,<sup>4</sup> the hydrolysis can be followed in aqueous sulfuric acid, solutions where a decreased reactivity arises because of substantially lowered water activity. This approach is suggested by the fact that many oxocarbeniums

are stable in concentrated sulfuric acid.<sup>2</sup> Obviously, if they are to have very high reactivity in water, there must be some region of acidity where the progress of the hydrolysis can be conveniently followed.

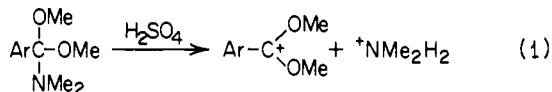
Our previous study<sup>4</sup> involved two dialkoxycarbonium ions. Reported here are rate constant data for a series of ions of varying structure, including species with one, two, and three oxygens attached to the central carbon. In addition, studies involving a mercaptocarbonium ion and a nitrilium ion (N-alkylated nitrile) are reported for comparison. Our original goal in this study was to obtain some evaluation of the effect on reactivity of (1) the structure of the ion and (2) the sulfuric acid medium. The results obtained show that a common acidity dependence characterizes the rate constant variation for the entire series. This makes it possible to obtain estimates of reactivity in water alone, estimates which can be compared in certain cases to those recently reported on the basis of sulfite trapping experiments.<sup>22</sup>

## Results

The ions of relevance to this paper, along with their numbering, are summarized below. The ions VII–XVIII were



generated from an appropriate precursor in 96% H<sub>2</sub>SO<sub>4</sub> or 100% H<sub>2</sub>SO<sub>4</sub>, and their identity was verified by the NMR spectrum obtained in that solution. In the case of the dialkoxycarbonium ions in this series, amide acetals proved more convenient precursors than ortho esters, principally since the synthesis of the former is generally accompanied by fewer problems. Interestingly, while NMR spectra of benzamide acetals showed only peaks in concentrated H<sub>2</sub>SO<sub>4</sub> attributable to dialkoxycarbonium ion and dimethylammonium ion (C–N cleavage,<sup>23</sup> eq 1), the NMR spectrum of *N,N*-dimethylform-



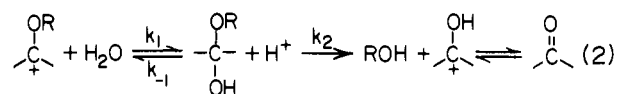
amide dimethyl acetal displays only peaks due to methanol and imidatonium ion (C–O cleavage<sup>23</sup>). The ions VIII and XI were also obtained in 100% H<sub>2</sub>SO<sub>4</sub> from the ortho ester, and as stable BF<sub>4</sub><sup>−</sup> salts. No difference outside of experimental error is observed when the ions are generated in these different ways. Ions IV–VI and XIX were used as salts. Ions I<sup>24</sup> and II<sup>4</sup> have been previously described. Ion III was used directly as a solution in methylene chloride obtained by treating 4,4'-dimethoxythiobenzophenone with methyl fluorosulfonate. This reagent appears (by NMR) to quantitatively alkylate this compound, although this is not the case with the oxygen analogue 4,4'-dimethoxybenzophenone, where an equilibrium slightly favoring the methyl on fluorosulfonate is set up.

The oxocarbonium ions hydrolyze cleanly in water and aqueous sulfuric acid solutions producing a molecule of methanol or ethanol and the appropriate carbonyl compound. Further hydrolysis of ester products does sometimes occur in more concentrated acids, where this hydrolysis, which is probably proceeding by an A<sub>Ac</sub>1 mechanism,<sup>25</sup> occurs at a faster rate than the dialkoxycarbonium ion hydrolysis. Ion III hydrolyzes below 45% H<sub>2</sub>SO<sub>4</sub> to give 4,4'-dimethoxybenzophenone as the only apparent aromatic product. Above this acidity some 4,4'-dimethoxythiobenzophenone is also produced, although this compound is itself not stable in these more concentrated acids but is slowly converted to the benzophenone (the thio ketone is stable in the more dilute acids). The nitrilium ion XIX hydrolyzes at all acidities up to 95% H<sub>2</sub>SO<sub>4</sub> to produce *N*-methylbenzamide as the only detectable product.

Kinetic studies were carried out in general by following the disappearance of the ion using UV spectroscopy, with NMR being used in the case of VI. Strict first-order kinetics were adhered to, with one exception. That was ion III, which above 50% H<sub>2</sub>SO<sub>4</sub> showed curved first-order plots, because of the further decomposition of the product thiobenzophenone which has a UV spectrum similar to that of the ion in these solutions. In general rate constants were obtained over an acidity region such that the half-life ranged from 2 s to 2–10 h. The upper limit is imposed for many of the ions because of further decomposition of the products, a problem which arises because these slower runs involve more concentrated acids. The lower limit is imposed by the problem of mixing solutions when using conventional UV spectrophotometry.

## Discussion

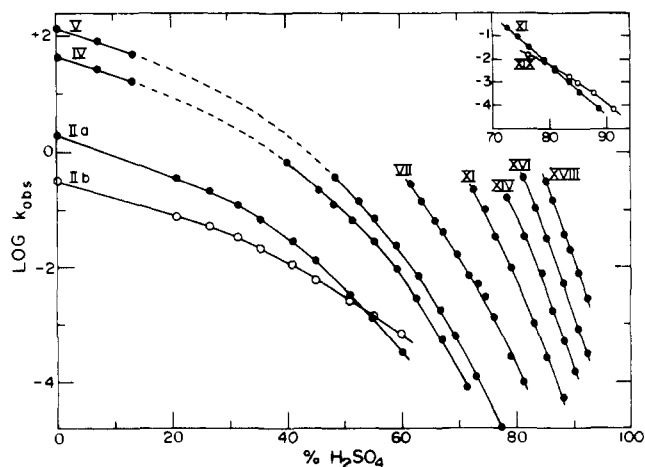
**Mechanism.** In the ensuing discussion it will be assumed that the reaction being observed is that of the oxocarbonium ion with a water molecule (eq 2, where proton transfer steps have



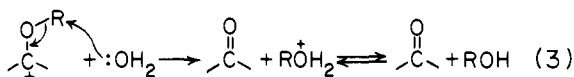
not been explicitly included in the reactions involving the tetrahedral adduct). The following comments can be made regarding this mechanism.

(1) In terms of eq 2 the observed rate constant is a composite of several rate constants, for example,  $k_{\text{obsd}} = k_1 k_2 / (k_{-1} + k_2)$  if the steady-state assumption can be made for the tetrahedral species. The question then arises as to the relative leaving tendencies of OH and OR from the adduct, that is, the relative magnitudes of  $k_{-1}$  and  $k_2$ . Although a definitive statement is not possible, it is likely that for the ions of this study  $k_2$  is somewhat greater than  $k_{-1}$ . This is due to the fact that the protonated carbonyl and the transition state leading to it are stabilized by hydrogen bonding to solvent water molecules, a type of solvation not present in the starting oxocarbonium ions. Certain evidence is in accord with this suggestion. In the tetrahedral intermediate formed during acid-catalyzed ester hydrolysis, carbonyl oxygen experiments<sup>26–28</sup> suggest that the alkoxy group has a preference to leave, over a hydroxy group, by a factor of 5 or greater after accounting statistically for the fact that there are two OH groups. In addition there is one example in which the acid-catalyzed decomposition of a hemiacetal and a structurally analogous acetal are compared.<sup>29</sup> The former, which produces on cleavage the protonated carbonyl, reacts at a rate 500 times greater. In summary, it is probably not completely correct to ignore the reversibility of the hydration process, but we feel that it is not terribly important in the ions under concern here, so that the values of  $k_{\text{obsd}}$  do fairly accurately reflect values of  $k_1$ .

(2) A second concern is the possibility that the hydrolysis may be occurring via a dealkylation reaction (eq 3). This



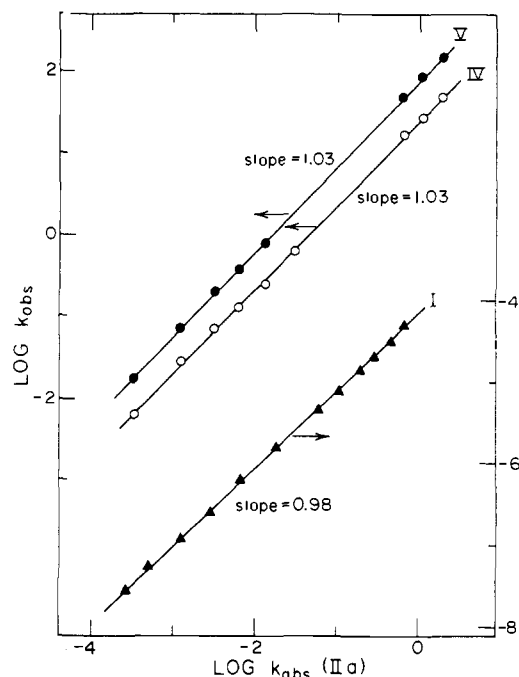
**Figure 1.** Dependence on sulfuric acid concentration of the observed rate constants for the hydrolysis of oxocarbenium ions at 25 °C. The rate constants plotted in water and dilute sulfuric acid solution for II, IV, and V are based on stopped-flow measurements described in the previous paper. Plotted for IIa are rate constants for pro-acyl carbon-oxygen bond cleavage; plotted for IIb are rate constants for alkyl carbon-oxygen bond cleavage.<sup>4</sup>



question was examined in our previous study for two dialkoxycarbonium ions, where it was demonstrated using appropriate <sup>18</sup>O labeling that XI hydrolysis with only cleavage of the pro-acyl carbon-oxygen bond (eq 2) at all acidities, while the sterically hindered II shows a significant amount of dealkylation. This latter behavior is exceptional; as summarized in a recent review,<sup>31</sup> previous labeling and stereochemical studies of acetal or ketal hydrolysis (or their formation) provide no evidence of alkyl carbon-oxygen cleavage. Generally we conclude that this is also true for the oxocarbenium ions of this study, other than II. Some indirect evidence for a common mechanistic behavior comes from the observation to be discussed of a very similar rate-acidity dependence for all the ions, including II when only the pro-acyl carbon-oxygen bond cleavage pathway is considered.

**Rate-Acidity Dependence.** With these reservations then we will consider that the rate data refer to the rate constants for reaction of a water molecule with the various ions, forming a tetrahedral adduct. One of the striking features of these data, as shown for selected cases in Figure 1, is that the curves of log  $k_{\text{obsd}}$  vs. acid concentration are reasonably parallel, with two exceptions. This parallelism is not surprising perhaps when considering those ions whose data extend only over a limited range of acidity. However, the parallelism is apparently maintained over fairly large ranges of acidity, as seen with ions I, II, IV, and V where data are available from water to at least 60%  $\text{H}_2\text{SO}_4$  (using in the case of the latter three the stopped-flow measurements described in the previous paper for water and the dilute acids). Figure 2 depicts plots of rate constants for I, III, and V as a function of rate constants for II. Although the absolute reactivity difference within this series is approximately  $10^6$ , the plots are linear with, more importantly, a slope very near unity. It is particularly surprising in this comparison to see the excellent correlation for the imidatonium ion I, since this ion might be construed to be structurally different.

The reactivity-selectivity principle (RSP)<sup>32</sup> would predict that the curves of Figure 1 would not be parallel, but would converge in the more dilute acids, as the selectivity decreases with increasing reactivity. A number of cases which fail to obey the RSP have now arisen.<sup>32</sup> Particularly relevant to this study



**Figure 2.** Correlation of oxocarbenium rate constants. The data for II refer to pro-acyl carbon-oxygen bond cleavage only.

are cation-anion combination reactions<sup>33</sup> and various acid-catalyzed reactions.<sup>32</sup> Our system resembles the former except that here the reactivity of the nucleophile is varied by changing its activity and not its structure. The similarity with the latter is that reactivity is varied in the same way, namely, by changing acid concentration. The difference is that the effect of increasing acid concentration is opposite in the two cases; the failure of the RSP is revealed in both types of systems by the parallel rate-acidity curves.

Equation 4 gives the acidity dependence of  $k_{\text{obsd}}$

$$k_{\text{obsd}} = k_{\text{H}_2\text{O}} \left\{ \frac{f_{\text{R}^+} a_{\text{H}_2\text{O}}}{f_{\ddagger}} \right\} \quad (4)$$

The term  $k_{\text{H}_2\text{O}}$  is the first-order rate constant for hydrolysis in pure water,  $a_{\text{H}_2\text{O}}$  is the water activity, and  $f_{\text{R}^+}$  and  $f_{\ddagger}$  are the activity coefficients for the cation and transition states, the latter three terms all being referred to water as the standard state. In terms of this equation the parallelism implies that the variation with acidity of the term in brackets is independent of the structure of the ion. This dependence of an activity coefficient term is of course the basis of acidity functions. Although the use of these functions has received much criticism, it must be concluded that it is a reasonably viable approach for species of similar structure.<sup>34,35</sup> We claim no more for our system. Obviously the constraint of similarity must apply here as well. Both the nitrilium ion hydrolysis and the hydrolysis reaction of II proceeding via dealkylation show significantly different rate-activity variations (Figure 1).

Applying the same approach that is used to derive an acidity function from parallel ionization ratio curves,<sup>34,35</sup> a general function for the term in brackets in eq 4 can be calculated, and is given in Table I. The applicability of this function can be tested by plotting the rate constants for the various ions against it. Excellent straight lines are obtained with slopes all close to unity (Table II).

**Reactivity in Water.** The intercepts listed in Table II can be taken as values of  $k_{\text{H}_2\text{O}}$ , the rate constants for hydrolysis of the ions in water. An alternate method of estimating these numbers is as the average of values obtained by applying

**Table I.** A General Function Describing Oxocarbenium Ion Reactivity in Sulfuric Acid Solutions<sup>a</sup>

| % H <sub>2</sub> SO <sub>4</sub> | log (f <sub>R+aH<sub>2</sub>O</sub> /f <sub>±</sub> ) | % H <sub>2</sub> SO <sub>4</sub> | log (f <sub>R+aH<sub>2</sub>O</sub> /f <sub>±</sub> ) |
|----------------------------------|---|----------------------------------|---|
| 0                                | 0   | 68                               | -4.98   |
| 10                               | -0.36   | 72                               | -5.65   |
| 20                               | -0.72   | 76                               | -6.41   |
| 28                               | -1.05   | 80                               | -7.25   |
| 35                               | -1.43   | 82                               | -7.71   |
| 41                               | -1.86   | 84                               | -8.24   |
| 47                               | -2.39   | 86                               | -8.79   |
| 52                               | -2.88   | 88                               | -9.33   |
| 56                               | -3.30   | 90                               | -9.93   |
| 60                               | -3.79   | 92                               | -10.53  |
| 64                               | -4.36   |                                  |   |

<sup>a</sup> For a summary of the ions used over various acidity ranges in constructing this function see Table II under heading "acid range".

$$\log k_{\text{H}_2\text{O}} = \log k_{\text{obsd}} - \log \left[ \frac{f_{\text{R}+\text{aH}_2\text{O}}}{f_{\pm}} \right] \quad (5)$$

where  $k_{\text{obsd}}$  are the measured rate constants. Numbers obtained in this way are also given in Table II, and show in general good agreement with the intercept values, as they should. Differences can be observed where the slopes deviate from unity. We will use in our later discussions the values obtained from eq 5. These values, in a sense, represent the average vertical difference in rate-acidity curves such as in Figure 1, anchored to the  $k_{\text{H}_2\text{O}}$  values actually measured for II, IV, and V.

Whatever method is used our approach can be described as an extrapolation from acid solutions where rate constants are actually measured, based on the assumption that the rate constant-acidity curves remain parallel. Young and Jencks<sup>22</sup> have recently described a different approach for estimating the reactivity of oxocarbenium ions derived from acetophenone dimethyl ketals. Their method is based on the competitive trapping with added sulfite of the ion when formed as an intermediate during the ketal hydrolysis in aqueous solutions. The experimental numbers in this case are ratios of reactivities,  $k_{\text{H}_2\text{O}}/k_{\text{SO}_3^{2-}}$ , with values of  $k_{\text{H}_2\text{O}}$  being obtained on setting  $k_{\text{SO}_3^{2-}}$  equal to the diffusion limit, as was argued to be the case. Our series now includes four ions studied by Young and Jencks. These ions are incidentally the most reactive of our investi-

**Table III.** Evaluation of the Effect of Aromatic Substituent on Rate Constants and Equilibrium Constants for Oxocarbenium Ion Formation from Substituted Acetophenone Dimethyl Ketals and Trimethyl Orthobenzoates (eq 6)

|   | Yukawa-Tsuno <sup>a</sup> |      | Young-Jencks <sup>b</sup> |          |
|---|---------------------------|------|---------------------------|----------|
|   | $\rho$                    | $r$  | $\rho$                    | $\rho^r$ |
| Acetophenone Dimethyl Ketals <sup>c</sup> |                           |      |                           |          |
| $k_f$                                     | -2.0                      | 0.18 | -2.0                      | -0.7     |
| $k_r$                                     | 1.6                       | 1.00 | 1.6                       | 1.6      |
| $K_{\text{eq}}$                           | -3.6                      | 0.50 | -3.6                      | -2.2     |
| Trimethyl Orthobenzoates                  |                           |      |                           |          |
| $k_f^d$                                   | -1.1                      | 0.06 | -1.1                      | -0.2     |
| $k_r^e$                                   | 2.6                       | 0.24 | 2.7                       | 1.1      |
| $K_{\text{eq}}$                           | -3.7                      | 0.19 | -3.7                      | -1.3     |

<sup>a</sup> Log ( $k/k_0$ ) or ( $K/K_0$ ) =  $\rho\sigma + \rho r(\sigma^+ - \sigma)$ . <sup>b</sup> Log ( $k/k_0$ ) =  $\rho\sigma_n + \rho^r(\sigma^+ - \sigma_n)$ . <sup>c</sup> All numbers taken from ref 22. <sup>d</sup> Calculated from data in ref 59. <sup>e</sup> Calculated from log  $k_{\text{H}_2\text{O}}$  data in Table II.

gation and as such require the greatest extrapolation and have the greatest uncertainty. The numbers obtained with the two approaches are compared in Table III. Considering the different assumptions on which the methods are based, the agreement must be regarded as acceptable, if not remarkable. It certainly provides confidence that the estimates of reactivity provided by the two approaches are meaningful.

This agreement also strengthens the conclusion of Young and Jencks that less stable oxocarbenium ions (e.g.,  $\text{CH}_3\text{OCH}_2^+$ ) must react at diffusion-controlled rates in water so that in the hydrolysis of a corresponding acetal the water might be regarded as to have attacked before the alcohol has completely departed. It is noteworthy in this connection that we (and others<sup>2</sup>) find that such ions cannot be obtained in 100% H<sub>2</sub>SO<sub>4</sub> on dissolving the acetal, although they have been obtained in even more acidic solutions.<sup>3,36</sup>

**Structural Effects on Oxocarbenium Ion Reactivity.** In general one can conclude that the relative reactivities, as seen either in the  $k_{\text{H}_2\text{O}}$  estimates of Table II or in the simple positions of the rate-acidity curves, are much as one might have expected. A few specific observations follow.

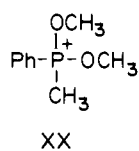
(1) Particularly striking, as we have noted previously,<sup>4</sup> is the 10<sup>9</sup> difference in reactivity between XI and I, in which one MeO group is replaced by NH<sub>2</sub>. Replacing the MeO by Me to give XVII on the other hand results in only about a 10<sup>2.7</sup>

**Table II.** Slope, Intercept, and Correlation Coefficient of Plots of Log  $k_{\text{obsd}}$  vs. Log (f<sub>R+aH<sub>2</sub>O</sub>/f<sub>±</sub>)

| ion             | acid range<br>% H <sub>2</sub> SO <sub>4</sub> | slope | intercept | correlation<br>coefficient | (log $k_{\text{H}_2\text{O}}$ ) <sub>av</sub> <sup>b</sup> |
|-----------------|--|-------|-----------|----------------------------|--|
| I               | 12-63  | 0.97  | -3.85     | 0.999                      | -3.77  |
| II <sup>a</sup> | 0-60   | 0.99  | 0.29      | 0.999                      | 0.30   |
| III             | 24-53  | 0.97  | 0.60      | 0.998                      | 0.66   |
| IV              | 0-71   | 1.02  | 1.67      | 0.999                      | 1.64   |
| V               | 0-78   | 1.03  | 2.17      | 0.999                      | 2.07   |
| VI              | 72-84  | 0.97  | 2.46      | 0.997                      | 2.67   |
| VII             | 62-81  | 0.98  | 3.38      | 0.999                      | 3.50   |
| VIII            | 66-83  | 0.97  | 4.04      | 0.999                      | 4.22   |
| IX              | 74-84  | 1.00  | 4.38      | 0.996                      | 4.36   |
| X               | 70-83  | 1.00  | 4.57      | 0.999                      | 4.54   |
| XI              | 73-88  | 1.01  | 5.10      | 0.999                      | 5.06   |
| XII             | 74-88  | 1.03  | 5.86      | 0.999                      | 5.65   |
| XIII            | 76-88  | 1.02  | 6.10      | 0.999                      | 6.02   |
| XIV             | 78-90  | 0.99  | 6.14      | 0.999                      | 6.15 (6.85) <sup>c</sup>                                   |
| XV              | 81-92  | 1.03  | 7.30      | 0.999                      | 7.02 (7.70) <sup>c</sup>                                   |
| XVI             | 81-92  | 0.97  | 6.80      | 0.999                      | 7.10   |
| XVII            | 84-92  | 0.96  | 7.34      | 0.998                      | 7.74 (7.98) <sup>c</sup>                                   |
| XVIII           | 85-92  | 0.99  | 8.05      | 0.999                      | 8.10 (8.32) <sup>c</sup>                                   |

<sup>a</sup> For pro-acyl carbon-oxygen bond cleavage. <sup>b</sup> Average value of quantity  $\log k_{\text{obsd}} - \log (f_{\text{R}+\text{aH}_2\text{O}}/f_{\pm})$ . <sup>c</sup> Values of log  $k_{\text{H}_2\text{O}}$  based on sulfite trapping experiments.<sup>22</sup>

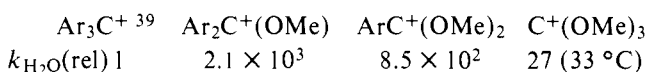
increase in reactivity. A further comparison which we might note here is with the phosphonium ion XXV, an ion which might be considered a phosphorus analogue of a dialkoxy-carbonium ion. The hydrolysis of XXV can be easily followed



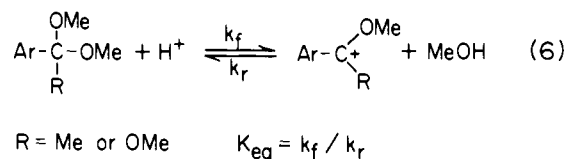
in aqueous solutions, with a  $k_{\text{H}_2\text{O}}$  value of  $0.0002 \text{ s}^{-1}$ ; <sup>37</sup> it is then also  $10^9$  less reactive than the carbon analogue XI.

(2) Ions III and IX furnish a comparison of species which differ only in the replacement of oxygen for sulfur. The considerably greater reactivity of the oxygen compound implies that of this pair it is the sulfur heteroatom which is more efficient at stabilizing the adjacent carbonium ion center. This observation is not consistent with that of other systems.<sup>38</sup> A number of explanations for the difference comes to mind. We will defer a discussion of these, since further studies of sulfur-stabilized cations are currently underway. The comparison here demonstrates again that this question of oxygen vs. sulfur is far from simple.

(3) The series below shows a comparison of ions where 4-methoxyphenyl groups (Ar) are replaced by methoxy. The trends can be explained by a counterbalancing of resonance and steric effects. A directly bonded methoxy group is obviously conjugatively more stabilizing,<sup>40</sup> but the presence of the aryl group, particularly a number of these, results in steric hindrance<sup>41</sup> to attack by water. Our study indicates that carbonium ions are highly reactive. The relative stability of tri-arylcarbonium ions is probably due as much to the steric effect as to a conjugative effect.



(4) As described by Young and Jencks,<sup>22</sup> the value of the equilibrium constant for eq 6 can be estimated from the ratio

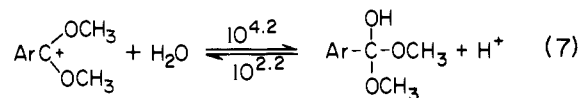


of rate constants  $k_f$  and  $k_r$ , making the assumption that the second-order rate constant for the addition of methanol is the same as that for addition of water ( $k_{\text{H}_2\text{O}}/55.5$ ). This approach allows an evaluation of the effect of aromatic substituents on the various rate and equilibrium constants. We are in a position here to compare series of ketals and ortho esters. This is provided in Table III, in terms of both the Yukawa-Tsuno treatment<sup>42</sup> and the alternate treatment proposed by Young and Jencks,<sup>22</sup> these modified forms of the Hammett equation being required since some of the sets of data do not correlate well with either  $\sigma$  or  $\sigma^+$ . The data of Table III for the ketal system are those of Young and Jencks. The four  $k_{\text{H}_2\text{O}}$  values that we have obtained in this system produce a  $\rho$  value of 2.1 (vs.  $\sigma^+$ ), as compared to the value of 1.6 of the above authors, again satisfactory agreement considering the difference in the two approaches.

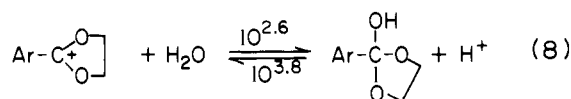
Two points arise from the comparison. Firstly, the data are fully consistent with the previous conclusion<sup>43</sup> that the ortho ester system has a considerably earlier transition state (more closely resembles substrate) than the ketal system. Thus, although the  $\rho$  values for the overall equilibrium are very close, the  $\rho$  value for the forward reaction is greater in absolute magnitude for the ketals, but in the reverse direction the value of  $\rho$  is greater in the ortho ester series. Secondly, the data in-

dicate that resonance with the aromatic substituent is less important in the ortho ester system (see, for example, the values of  $r$  or  $\rho/\hat{\rho}'$ ). This can be accounted for simply on the basis that in this system there are two oxygens available to stabilize the positive charge on the ion. It has also been suggested that there is a considerable steric hindrance to conjugation with the aromatic ring in an aryl dialkoxy-carbonium ion,<sup>44,45</sup> and this may well be a contributing factor also.

That this latter factor is indeed important is seen by considering the equilibria below (with  $\text{Ar} \equiv 4\text{-methoxyphenyl}$ ). The equilibrium of eq 8 can actually be observed,<sup>46</sup> while the assumption is made for that of eq 7 that the  $k_{\text{H}^+}$  value for ex-



$$pK_{\text{R}^+} = -2.0$$



$$pK_{\text{R}^+} = 1.2$$

pulsion of OH from the hydrogen ortho ester is the same as that for expulsion of OMe from the ortho ester,<sup>47</sup> the value for which has been taken from the literature.<sup>43</sup> It has been suggested that the steric inhibition to resonance is substantially, if not completely, removed in the cyclic case.<sup>44,45</sup> The numbers certainly attest to the fact that the cyclic ion is more stable. It is hydrated more slowly and forms from the hydrogen ortho ester more quickly, these effects combining to produce a difference of greater than 3 in the  $pK_{\text{R}^+}$  values.

## Experimental Section

**Materials.** Aqueous sulfuric acid solutions were prepared and standardized as previously described.<sup>46</sup> III was prepared as a solution in methylene chloride by treatment of 4,4'-dimethoxythiobenzophenone with an equimolar amount of methyl fluorosulfonate. The transfer of the methyl group could be followed in the NMR and was complete in approximately 1 h. Attempts to precipitate III as the salt by addition of diethyl ether or carbon tetrachloride resulted only in the formation of a dark-colored, pungent oil. IV and V were prepared as their  $\text{BF}_4^-$  salts<sup>49</sup> by alkylation with the appropriate trialkyloxonium borofluorate salt. VI was prepared as its  $\text{BF}_4^-$  salt by treatment of the orthocarbonate with boron fluoride.<sup>7</sup> VII, VIII, X, XI, XII, XIII, and XVI were prepared as solutions in 100%  $\text{H}_2\text{SO}_4$  on dissolving the appropriate amide acetal.<sup>23</sup> VIII and XI were also prepared as their  $\text{BF}_4^-$  salts,<sup>7</sup> and as solutions in 100%  $\text{H}_2\text{SO}_4$  obtained by dissolving the appropriate ortho ester. IX, XIV, XV, XVII, and XVIII were prepared as solutions in 100%  $\text{H}_2\text{SO}_4$  by addition of the appropriate ketal. The NMR spectra of all ions prepared in 100%  $\text{H}_2\text{SO}_4$  exhibited only peaks due to the ion, and the leaving group, methanol or dimethylamine. XIX was obtained commercially as its  $\text{PF}_6^-$  salt and used directly.

**Kinetics.** With the exception of VI, hydrolyses were followed by UV spectroscopy on a Unicam SP1800 spectrophotometer, observing the decrease in the peak due to the ion. These runs were initiated in general by addition of approximately 0.01 mL of a solution in 100%  $\text{H}_2\text{SO}_4$  directly to the preequilibrated UV cell (25 °C) containing the acid solution. Rate constants ( $k_{\text{obsd}}$ ) were obtained from the slopes of plots of  $\ln(A - A_\infty)$  vs. time. These plots were excellently linear for several half-lives, and rate constants obtained from duplicate runs agreed to within better than 2%. In the case of VIII and XI three sources of the ion were employed, including direct addition of the salt to the solution of interest. No difference outside of experimental error was observed in the rate constants so obtained. Product analysis was carried out by comparison of the UV spectrum after complete hydrolysis with that of an authentic sample of the expected carbonyl product.

In the case of VI, the salt was dissolved in the acid solution of interest to give an approximately 0.5 M solution. This was placed in an

NMR tube and the progress of the hydrolysis followed directly in the NMR spectrophotometer by monitoring the relative peak intensities of ion, and products, methanol and methyl carbonate.

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**Supplementary Material Available:** First-order rate constants for hydrolysis of ions in acid solutions (3 pages). Ordering information is given on any current masthead page.

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