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The Reactivity of Oxocarbonium Ions. 1. Detection as Transient Intermediates in the Hydrolysis of Ketals and Ortho Esters

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Abstract: Experiments are described in which oxocarbonium ion intermediates are detected spectroscopically in the hydrolysis of certain ketals and ortho esters, by arranging conditions such that the formation of the ion is more rapid than its decay. The compounds for which this is possible include tropone diethyl ketal, trimethyl orthomesitoate, and the dimethyl and diethyl ketals of 2,3-diphenylcyclopropenone. The intermediate ions from trimethyl 4-methoxyorthobenzoate and trimethyl orthobenzoate cannot be detected in water alone, but are observed in experiments in 1.0 M $HClO_4$ and 5.5 M $NaClO_4$. No ion can be detected in any of these solutions from 4-methoxyacetophenone dimethyl ketal. These experiments, where successful, furnish rate constants for the hydrolysis of the intermediate ion.

There is a substantial body of evidence consistent with the general mechanism of Scheme I for the acid-catalyzed hydrolysis of acetals, ketals, and ortho esters,[1-3] with few apparent exceptions.[1-6] Numerous kinetic studies also reveal, again with few exceptions,[7,8] that the rate-determining step is step (i), the formation of the oxocarbonium ion intermediate. With this step being rate determining, no direct kinetic study of the later steps has been possible, although indirect investigations of step (ii) have been reported, based on competition experiments.[9-11] We have initiated recently a search for ways of following directly the kinetics of these later steps (see, for example, ref 8). These experiments not only provide direct evidence of the validity of the general mechanism, but further our detailed understanding of the overall reaction.

In this paper cases are reported where conditions can be arranged such that the oxocarbonium ion is detectable as a transient intermediate during the hydrolysis of a ketal or ortho ester. This corresponds to a changeover in rate-determining step in the overall hydrolysis and permits, in these cases, the direct measurement of the rate constant for the capture of the intermediate ion by water.

Our approach is based on the idea that at some acidity the rate constant for step (i) will exceed that of step (ii), so that the oxocarbonium ion forms more rapidly then it decays. This changeover will occur at some acidity since the rate of step (i) is first order in hydronium ion concentration, whereas the rate of step (ii) is pH independent.[12] A changeover of this type is in principle observable with every acetal, ketal, or ortho ester, but for most substrates such a high acidity is required that the experiments to be described are not practical. There are, however, several cases characterized by relatively stable oxocarbonium ion intermediates where the changeover can be detected, and these are the subject of this report. The problem of the less stable oxocarbonium ions is considered in the following paper.
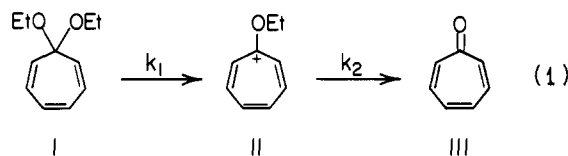
Results and Discussion

Tropone Diethyl Ketal. Of the large number of acetals, ketals, and ortho esters which have been now studied, those which

Scheme I
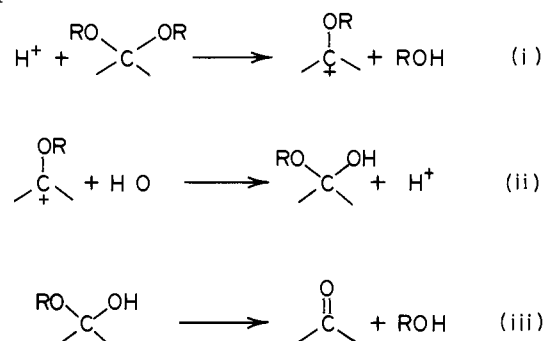
produce perhaps the most stable oxocarbonium ions during hydrolyses are the ketals of tropone.[13,14] This statement can

be justified on consideration of the pK_{R^+} values for the equilibrium hydration of related carbonium ions.[14] Moreover, the hydrolysis of these ketals is subject to general acid catalysis,[13,14] while such catalysis is not detectable with other acetals or ketals derived from alcohols with high pK_a values.[2,14] This observation can be accounted for in terms of the extreme stability of the intermediate ions.[2]

In accord with this stability we find that such ions have sufficient lifetime to be detected in water even by conventional UV spectroscopy, the only oxocarbonium ions of this study and the next for which this is possible. In Figure 1 are shown the initial and final spectra obtained on dissolving in water the borofluorate salt of the ethoxytropylium ion (II), a salt obtained on treatment of tropone with triethyloxonium borofluorate. As expected the final spectrum is identical with that
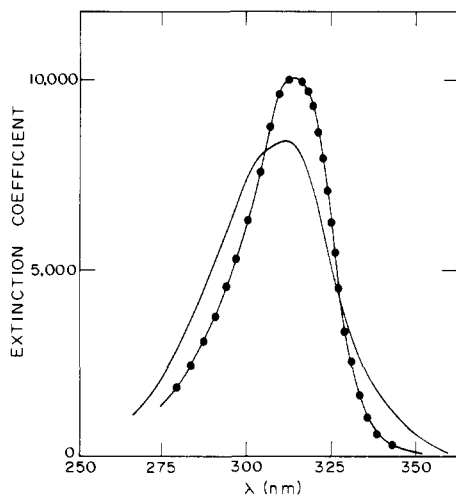
Figure 1. Ultraviolet spectra of ethoxytropylium borofluorate (—●—●—) and tropone (—) in water (0.001 N HCl). The spectrum of the salt is based on extrapolation to zero time.

Table I. Rate Constants for the Hydrolysis of the Ethoxytropylium Ion and for Its Formation from Tropone Diethyl Ketal[a]

rate constant	$\mu = 0.1$	$\mu = 0.5$
k_{H_2O}, s^{-1} [b]	0.017	0.014
k_{OH^-}, M^{-1} s^{-1} [b]	1.0×10^4	
k_{HCOO^-}, M^{-1} s^{-1} [b]	0.01–0.02	0.014
$k_{CH_3COO^-}$, M^{-1} s^{-1} [b]	0.03	0.026
$k_{HPO_4^{2-}}$, M^{-1} s^{-1} [b]	0.13	
k_0, s^{-1} [c]	0.0086	
$k_{H_3O^+}$, M^{-1} s^{-1} [c]	2.2×10^5	
$k_{H_2PO_4^-}$, M^{-1} s^{-1} [c]	0.4	

[a] At 25 °C, ionic strength maintained with NaCl. [b] Hydrolysis of ion. [c] Formation of ion.

of tropone, and, although the initial spectrum is somewhat similar to this, the difference is significant.

We propose that the initial spectrum does correspond to that of the ethoxytropylium ion itself. As confirmation, it can be noted that this spectrum is very similar to that obtained on dissolving the salt in strongly acidic media (90% H_2SO_4, for example). In such solutions the ion is stable, a fact which can be verified by NMR spectroscopy. The initial spectrum also resembles closely the spectrum of protonated tropone (e.g., tropone in 3 N HCl).

With the relative stability of this ion in water, a detailed kinetic investigation of its hydrolysis to tropone is possible. This study is most conveniently carried out by following the increase in absorbance at 345 nm. Strict first-order kinetics are observed under all conditions. The observed first-order rate constants, which will be referred to throughout this paper as k_2, show the variation of eq 2 with changing pH and buffer concentration (see also Figure 2)

$$k_2 = k_{H_2O} + k_{OH^-}[OH^-] + k_B[B] \qquad (2)$$

where B refers to the base component of the buffer used to maintain pH. The various rate constants are given in Table I. The contributions due to the last term are quite small, and particularly at the lower ionic strength the k_B values listed in the table cannot be regarded as being very precise.

The rate variation expressed in eq 2 is much as expected for the hydrolysis of an oxocarbonium ion. The first two terms refer to reaction of the ion with water and hydroxide, respectively. The reactivity of II can be compared with that of the tropylium ion itself and with various aryl-substituted deriva-
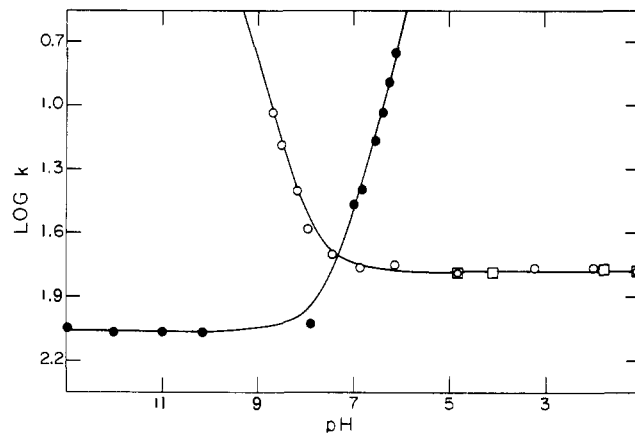
Figure 2. Rate-pH profiles in the hydrolysis of tropone diethyl ketal. The symbols (●) represent k_1, rate constants for the formation of the ethoxytropylium ion from the ketal. The symbols (O, □) represent k_2, rate constants for the hydrolysis of the ion, (O) referring to experiments starting with the ketal. Rate constants in buffer solutions are based on extrapolation to zero buffer concentration. Conditions: 25 °C, $\mu = 0.1$, maintained with NaCl.

tives.[15] The unsubstituted ion has a water rate constant of 2.6 s^{-1}, so that the presence of the ethoxy group results in a 150-fold decrease in reactivity. The oxocarbonium ion in fact resembles more closely the *p*-dimethylaminophenyltropylium ion ($k_{H_2O} = 0.020$ s^{-1}).

The last term of eq 2 corresponds to general base catalysis of water attack. The presence of such a process is not unexpected in this system. If the departure of ethanol from tropone diethyl ketal to produce this ion is general acid catalyzed, the hydration of the ion ought to be general base catalyzed, since this is essentially the same process in reverse, with water in place of ethanol. We can note that the Brønsted coefficient for this base catalysis is quite small, a β value of 0.26 being obtained from the two carboxylate rates at $\mu = 0.5$.

Starting with tropone diethyl ketal, we find that in solutions with a pH value less than about 5, the only UV spectral change which is observed (using conventional UV spectroscopy) is that of Figure 1. The rate constants obtained following this change (at λ 345 nm) are the same within experimental error as those obtained starting from the ethoxytropylium salt (Figure 2). This suggests that in this pH region the conversion of the ketal to the intermediate ion is very rapid, and what is being observed in the overall hydrolysis to tropone is the hydrolysis of this ion, i.e., the second step.

To obtain kinetic data for the first step, the increase in UV absorbance has been followed at 306 nm, a wavelength corresponding to an isosbestic point of the second step. First-order constants so obtained, defined now as k_1, follow

$$k_1 = k_{H^+}[H^+] + k_0 + k_{HA}[HA] \qquad (3)$$

This rate dependency is identical with that observed by Anderson and Fife for the hydrolysis of this ketal.[12] Rate constants obtained in our study are reported in Table I; these differ slightly from those of Anderson and Fife, who worked at a different temperature and ionic strength.[16]

In considering now the overall hydrolysis of tropone diethyl ketal to tropone examination of Figure 2 reveals that only in solutions with a pH value greater than about 8.5 is k_1 much smaller than k_2, so that the formation of the ion is fully rate determining. These two rate constants are equal at a pH of about 7.3. In acidic solutions, $k_1 \gg k_2$, and the limiting step in the formation of tropone is the hydrolysis of the oxocarbonium ion.

Trimethyl Orthomesitoate. An ion which is also stabilized, but now for steric reasons, is the dialkoxycarbonium ion V
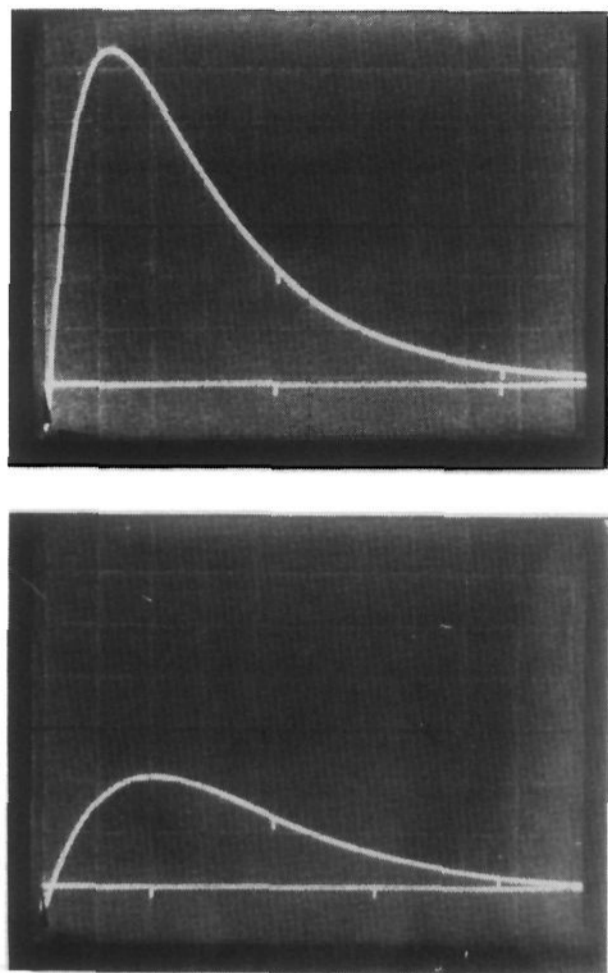
Figure 3. Oscilloscope traces obtained at 280 nm in the hydrolysis of trimethyl orthomesitoate. One horizontal division refers to 0.2 s; one vertical division to 0.02 absorbance units. The top trace refers to 0.1 N HCl, the bottom trace to 0.05 N HCl, both concentrations after mixing. The concentration of substrate in each run is identical.
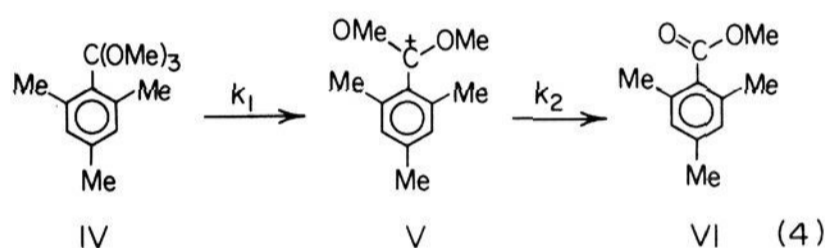

derived from trimethyl orthomesitoate (IV), this steric stabilization being apparent from the observation that this ion hydrolyzes with water attack at the O-methyl as well as the central carbon.[17] In Figure 3 are depicted oscilloscope traces obtained at 280 nm when IV, dissolved in 0.001 N NaOH, is mixed with aqueous hydrochloric acid in a stopped-flow spectrophotometer. These traces show the rapid formation and decay of some transient. The UV spectrum of this transient in 0.5 N HCl was constructed and is provided in Figure 4, along with spectra of the ortho ester and ultimate product of the hydrolysis, methyl mesitoate (VI). This transient signal was suspected as being due to the intermediate ion V. This ion can be isolated as its borofluoride salt,[17,18] and its UV spectrum in 70% H_2SO_4, where it is relatively stable,[17] is virtually identical with that of the transient (Figure 4).

The curves traced out in Figure 3 take the form expected[18] for the variation with time of the intermediate species B of two consecutive first-order reactions

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

with values of the two rate constants which fit the data presented in Table II. The values of k_1 are linear in hydronium ion concentration, and yield a second-order rate constant k_{H^+} of about 100 M^{-1} s^{-1}. This rate constant refers to the formation of the ion from the ortho ester, that is, the "normal" rate-determining step. The same value of k_{H^+}, within experimental error, is obtained in much less acidic solutions, where no intermediate ion accumulates, and the appearance of
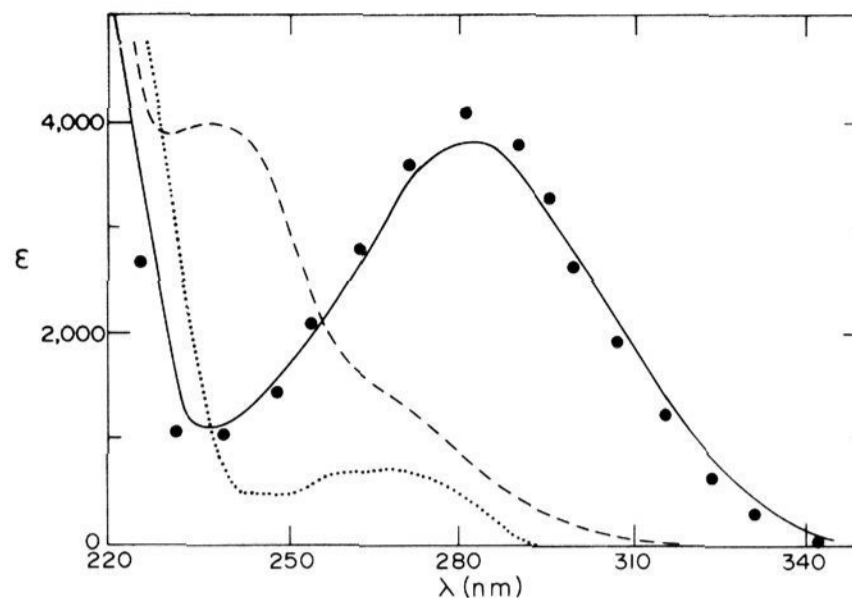
Figure 4. Ultraviolet spectra of trimethyl orthomesitoate in H_2O ($\cdots$), methyl mesitoate in H_2O (- - -), and dimethoxy-2,4,6-trimethylphenylcarbonium borofluorate in 70% H_2SO_4 (—). (●) Extinction coefficient of transient (after 10 ms elapsed time) observed in hydrolysis of trimethyl orthomesitoate in 0.5 N HCl.

Table II. Rates Constants in the Hydrolysis of Trimethyl Orthomesitoate[a]

pH	k_1, s^{-1}	$k_1/[H^+]$, M^{-1} s^{-1}	k_2, s^{-1}
1.00[b]	9.79[f]	98	2.33[g]
1.10[b]	7.78[f]	98	2.26[g]
1.23[b]	6.02[f]	102	2.31[g]
1.41[b]	4.16[f]	107	2.37[g]
1.00[c]	23[f]		1.02[g]
1.00[d]	17[f]		1.78[g]
5.64[e]	2.5×10^{-4}	109	
5.88[e]	1.5×10^{-4}	114	
6.04[e]	9.9×10^{-5}	109	
6.24[e]	6.5×10^{-5}	113	
6.41[e]	3.9×10^{-5}	100	

[a] 25 °C and $\mu = 0.1$ (NaCl) unless otherwise noted. [b] HCl solutions. [c] Solution contained 0.10 M $HClO_4$, plus 1.0 M $NaClO_4$. [d] Solution contained 0.10 M HCl, plus 1.0 M NaCl. [e] Phosphate buffer; rate constants were obtained at 240 nm, and are values extrapolated to zero buffer concentration. [f] λ 256 nm. [g] λ 280 nm.

product at 240 nm is followed. The rate constant k_2 refers to the reaction of the ion with water (k_{H_2O} of eq 2). The values for this are independent of acid concentration with $k_2 = 2.3$ s^{-1} ($\mu = 0.1$). The pH where $k_1 = k_2$ in this case is approximately 1.6.

2,3-Diphenylcyclopropenone Ketals. One of the other ketals considered by Fife and Anderson[14] as a candidate for undergoing general-acid-catalyzed hydrolysis is VII (R = Et). The
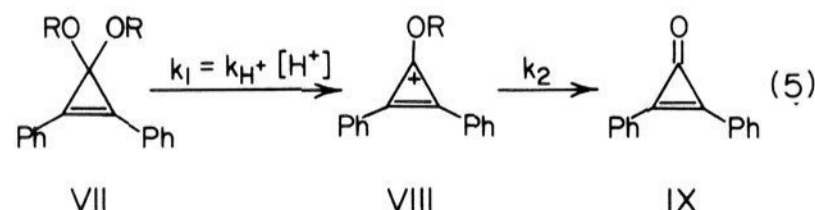
ion derived from this ketal, although stabilized, was suggested by Fife and Anderson to be less so than the ethoxytropylium ion, and the hydrolysis in fact fails to show detectable catalysis by added buffer.[14] Our findings are in accord with these stability considerations, with the ion being of sufficient stability to be just detectable in acidic solutions.

With this system the values of k_{H^+} (measured at pH ~7) are such that in acid solutions as concentrated as 0.1 N HCl the oxocarbonium ion is essentially completely formed within the mixing time of a stopped-flow spectrophotometer. For VII,

Table III. Rate Constants for the Hydrolysis of Oxocarbonium Ions VIII (25 °C)

solution	k_2, s^{-1}	
	R = Me	R = Et
0.1 M HCl	1.3×10^2	45
7.0% H_2SO_4	88	28
13.0% H_2SO_4	50	17
2.6 M ClO_4^- [a]	14	
5.2 M ClO_4^- [a]	3.9	
6.5 M ClO_4^- [a]	1.3	

[a] 0.20 M $HClO_4$, plus $NaClO_4$.

Table IV. Rate Constants Obtained Following the Appearance of Methyl 4-Methoxybenzoate in the Hydrolysis of Trimethyl 4-Methoxyorthobenzoate (25 °C)

solution	k_{obsd}^{255}, s^{-1}	$k_{obsd}^{255}/[H^+]$, M^{-1} s^{-1}
pH 2.8–5.3		161[a]
$\mu = 0.5$		
0.1 M HCl	15	150
0.5 M HCl	88	176
1.2 M HCl	3×10^2	250
1.6 M HCl	5×10^2	310

[a] Reference 20.

R = Et, k_{H^+} = 1.7×10^4 M^{-1} s^{-1} (in 20% dioxane);[14] for VII, R = Me, we find k_{H^+} = 2.2×10^4 M^{-1} s^{-1}. In 0.1 N HCl the half-life of the ketals is then of the order of 0.3 ms; the dead time of the spectrophotometer used in our experiments is 2 ms. The oxocarbonium ions will be detectable in the stopped-flow spectrophotometer, provided that they themselves have sufficient lifetime. This is the case. Mixing the ketals into acidic solutions reveals transients, the spectra of which closely correspond to those of the ions VIII which can again be obtained as stable salts and their spectra recorded in concentrated acid.

Rate constants for the decomposition of the two ions are presented in Table III. The values of k_2 are large here, approaching the limit beyond which the ions would not be detected using stopped-flow spectroscopy. As compared to the mesitoate system the values of k_{H^+} for the first step are also much larger, and in fact the changeover occurs in slightly less acidic solutions for this system. For example, for R = Me, the pH value where $k_1 = k_2$ is approximately 2.3.

Trimethyl 4-Methoxyorthobenzoate. The three previous cases all have unusual stabilizing features in the intermediate ion undoubtedly responsible for its detectability. We now turn to what might be considered a more normal substrate, the ortho ester X. With this system the UV spectra are such that it is

X   XI   XII
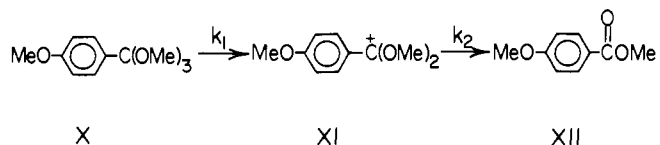
possible to follow separately the appearance of the product ester XII (at 255 nm), and search for the intermediate ion XI (at 305 nm).

Stopped-flow experiments in HCl solutions up to 1.6 M in concentration, and in H_2SO_4 solutions up to 13.0%, reveal *no* transient signal at this latter wavelength. The increase in absorbance at the former wavelength is first order throughout. The first-order rate constants (k_{obsd}^{255}, Table IV) increase with increasing acid concentration, and have the values anticipated on the basis of the literature k_{H^+} value for X, obtained in less acidic solutions.[20] (It should be noted here that in nondilute acid solutions, the rate constant is expected to increase more rapidly then the hydronium ion concentration.[1]) Therefore, in these solutions there is no change in rate-determining step, $k_{obsd}^{255} = k_1$ throughout, and $k_2 > k_1$. It can be shown using the appropriate equation[19] for two consecutive first-order reactions that some signal due to the intermediate would be apparent even for $k_2 = 5k_1$. Since solutions were employed where k_1 was of the order 300–500 s^{-1}, this places a lower limit on k_2 of 2000 s^{-1}.

An approach which is successful in revealing the transient ion in this case is suggested by results in salt solutions. Maintaining the [H$^+$] concentration constant, and increasing the concentration of added salt, increases k_1 (see Table II, and also ref 19), but has the effect of decreasing k_2 (Tables II and III).

Increasing the acid concentration outside the dilute acid region also has the same effect (see Table III), but obviously there is a practical limit to the extent to which this can be done in our experiments where water and acids must be mixed in a stopped-flow apparatus. Using salts, the ortho ester can be dissolved in a neutral or very slightly basic salt solution, and mixed with a solution of acid and salt, such that the ionic strength in both is identical. This setting up of equal ionic strength in each chamber avoids mixing problems in the stopped-flow apparatus. Sodium perchlorate was chosen for our studies since the kinetic salt effects associated with it are pronounced, and fairly concentrated solutions can be prepared. Indeed, when X is dissolved in 6.5 M $NaClO_4$ and mixed (equally) with 2.0 M $HClO_4$ and 4.5 M $NaClO_4$, there is produced a short-lived transient with a spectrum corresponding to the dialkoxycarbonium ion. On decreasing the total perchlorate concentration the lifetime of this transient decreases; the limit of detectability occurs around 4–5 M perchlorate. The disappearance of the transient is first order; the rate constant in the 6.5 M perchlorate solution is 1.4×10^2 s^{-1}. The same rate constant, within experimental error, is obtained by following the increase in absorbance at 255 nm. Because of the positive salt effect on k_{H^+}, the value of k_1 in this solution is probably considerably greater than this. In other words, we feel that a change in rate-determining step has been achieved for this system using these salt-rich solutions.

This incidentally illustrates why the experiments in more aqueous solutions fail to show the changeover. Some idea of the effect of these high salt concentrations is provided by the results for ion VIII, R = Me (Table III), which show a 100-fold decrease in reactivity between 0.1 M HCl and 6.5 M perchlorate. The following paper suggests that solvent-induced changes in reactivity of this type are parallel. If a similar factor then applies to XI, the rate constant for its hydrolysis in 0.1 M HCl is of the order of 10^4 s^{-1}, and the ion would not be detected, even if k_1 were greater than this.

Trimethyl Orthobenzoate. In a similar experiment in 6.5 M perchlorate, trimethyl orthobenzoate shows an extremely short-lived signal at a wavelength corresponding to the intermediate ion (265 nm). If this is indeed real, the half-life of the dialkoxycarbonium ion is of the order of 1 ms. This places an estimate of 10^5 s^{-1} on the rate constant for hydrolysis of the ion in water.

4-Methoxyacetophenone Dimethyl Ketal. This ketal displays *no* transient at a wavelength corresponding to the oxocarbonium ion (330 nm) even in the 6.5 M perchlorate solution, under conditions in which the overall hydrolysis is complete within mixing. This places a lower limit of 10^5 s^{-1} on the rate constant of hydrolysis of the ion in water alone.

Experimental Section

All compounds were prepared using published procedures: I,[13] II-BF$_4^-$ salt,[21] III,[22] IV,[17] V-BF$_4^-$ salt,[17] VII,[14] VIII-BF$_4^-$ salts,[21] X,[20] XI,[23] dimethoxyphenylcarbonium borofluorate,[23] 4-methoxyacetophenone dimethyl ketal,[24] and the methylmethoxy-4-methoxyphenylcarbonium ion as a solution in 100% H_2SO_4.[25]

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

Acknowledgment. Financial support from the National Research Council of Canada is gratefully acknowledged.

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verse of step (i), and the rate-determining step would then be controlled by the relative rates of the reverse of step (i) and step (ii). However in experiments in aqueous solution the reverse of step (i) will always be slower than step (ii) since the concentration of water far exceeds that of alcohol.
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The Reactivity of Oxocarbonium 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 oxocarbonium ions, one mercaptocarbonium 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_2SO_4 has been generated which accurately describes the acidity dependence. Rate constants for hydrolysis of the oxocarbonium 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 $ArC^+(OMe)Me$ 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 oxocarbonium ion reactivity is discussed. In the series $(4\text{-}MeOC_6H_4)_nC^+(OMe)_{3-n}$, $n = 0$–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 $((4\text{-}MeOC_6H_4)_2C^+XMe$ $(X = O, S)$, 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 $ArC(OMe)_2R + H^+ \rightleftharpoons ArC^+(OMe)R + MeOH$, 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[1] experiments are reported which show that the oxocarbonium 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 oxocarbonium 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 oxocarbonium 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.[2-4] Also, stable salts can be isolated where the counterions

are nonnucleophilic (e.g., BF_4^- or $SbCl_6^-$), by treatment of the precursor acetal, etc., with the appropriate Lewis acid.[4-13] Alternatively a carbonyl oxygen can be alkylated, for example, with a dialkoxycarbonium ion salt,[10,11,14] or in certain cases by reaction with a trialkyloxonium ion salt[5,15-19] or an alkyl fluorosulfonate.[20] An excellent review of the preparation and properties of these ions has appeared.[21]

Conceivably then it is possible to study oxocarbonium 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,[4] 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 oxocarboniums