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TETRAHEDRAL INTERMEDIATES 3.[1] THE KINETICS AND MECHANISM OF THE BREAKDOWN OF SOME HEMIORTHOESTERS

BRIAN CAPON* and MARIA DE NAZARE DE MATOS SANCHEZ

Department of Chemistry, University of Glasgow,
Glasgow G12 8QQ, Scotland, U.K.

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Abstract - The kinetics of the breakdown of hemiorthoesters generated from dialkoxyalkyl acetates or ketene acetals have been investigated. The following compounds were studied: dimethyl hemiorthoformate (*1b*), diethyl hemiorthoformate (*2b*), 2-hydroxy-1,3-dioxolane (*3b*), 2-hydroxy-4,4,5,5-tetramethyl-1, 3-dioxolane, (*4b*), 2-hydroxy-2-methyl-1,3-dioxolane (*5b*), and 2-hydroxy-2,4,4,5,5-pentamethyl-1,3-dioxolane (*6b*). The whole series was studied in aqueous acetonitrile (c_{H_2O} = 8.33 M); *4b*, *5b*, and *6b* were studied in aqueous acetonitrile (c_{H_2O} = 2.22 M) and *4b* and *6b* in water. Complete pc_H-rate or pH-rate profiles were obtained for each reaction. The mechanisms of the hydronium-ion, hydroxide-ion and "water" catalysed reactions are discussed and compared to those for the breakdown of hemiacetals and the hydrolysis of orthoesters.

We have recently shown that the tetrahedral intermediates of *O,O*-acyl transfer reactions (hemiorthoesters) can be generated by hydrolysis of dialkoxy-alkyl acetates and hydration of ketene acetals and detected by NMR spectroscopy.[1-4] We now report a kinetic investigation of the breakdown of these species generated in this way. This work, in which the hemiorthoesters are derived from formic and acetic acids, is complementary to that of McClelland and his co-workers in which the hemiorthoesters are derived from benzoic and substituted benzoic acids.[5]

EXPERIMENTAL

Materials. Dimethoxymethyl acetate (*1a*), 2-acetoxy-1,3-dioxolane (*3a*), 2-acetoxy-4,4,5,5-tetramethyl-1,3-dioxolane (*4a*), 2-methylene-1,3-dioxolane (*5a*), and 2-methylene-4,4,5,5-1, 3-dioxolane (*6a*) were prepared as described previously.[1,3] Diethoxyethyl acetate (*2a*), trimethyl orthoformate and triethyl orthoformate were purchased from Aldrich, purified by distillation, and their purity was checked by their ^{1}H NMR spectra. The acetonitrile used was BDH "Special for Spectroscopy" grade.

Kinetic Measurements. The following solvents were used for kinetic experiments: water, water : acetonitrile (c_{H_2O} = 2.22 M), water :acetonitrile (c_{H_2O} = 8.33 M). With water the ionic strength was maintained at 0.1 M with potassium chloride. The required pHs were obtained by the addition of small amounts of acids and bases too small to provide appreciable catalysis and were measured with glass and calomel electrodes and a pH-meter. (Radiometer PHM 64) in the usual way. For the acetonitrile-water mixtures no attempt was made to keep the ionic strength constant but this was always less than 10^{-2} M. The acidity of the medium was adjusted by the addition of small amounts of acids and bases and measured with glass and calomel electrodes and a pH-meter. Calibration curves were constructed for each acetonitrile-water mixture by plotting the millivolt readings against concentration of acid for a series of solutions of HCl of known concentrations. The readings for 10^{-2} M HCl were set arbitrarily at -289.2 and -264.3 mv respectively with the solvents with c_{H_2O} = 2.22 M and 8.33 M and the relationships between pa_{H^+} and mV were found to be those given in eqs. 1 and 2. These equations were then

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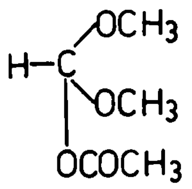
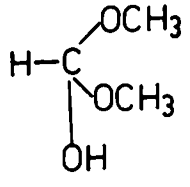
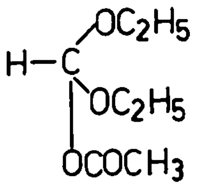
*Present address:Chemistry Department, University of Hong Kong, Pokfulam Road Hong Kong.



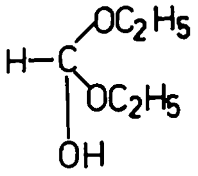
1a



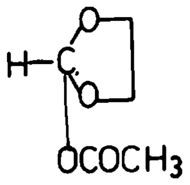
1b



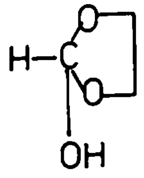
2a



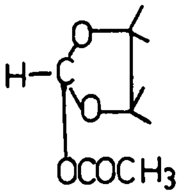
2b



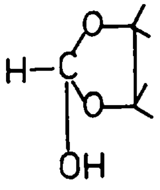
3a



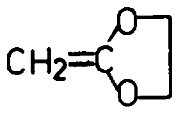
3b



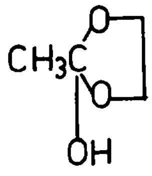
4a



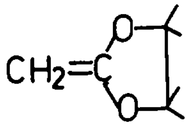
4b



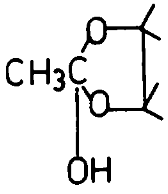
5a



5b



6a



6b

$$pc_H = 0.02201 \times mV + 8.2134 \quad (1)$$

$$pc_H = 0.02228 \times mV + 8.0649 \quad (2)$$

used to yield the values of pc_H for the reaction solutions from their millivolt readings. This procedure involves two assumptions. The first is that the liquid-liquid junction potential is constant throughout the acidity range used. This appears to be well established for many mixtures of water with organic solvents.[6] The second assumption is that pc_H is linearly related to the potential over the acidity range studied. A linear relationship of this type has been established for acetonitrile solutions[7] and such a relationship is also valid for water. It therefore appears reasonable that it should also be valid for aqueous acetonitrile. However if it is not the relative rate constants for a series of compounds determined under the same conditions should still have the correct values as they would all be affected in the same way.

Values of pK_w were obtained for the two mixtures of acetonitrile and water by using a procedure similar to that reported by McClelland.[5f] The potential of the glasselectrode/ calomel-electrode for a solution of 0.01 M sodium hydroxide was obtained in the same way as for the other solutions and a value of pc_H was calculated from the appropriate calibration curve. The following values of pK_w were then calculated from the equation:

$$pK_w = pc_H + pc_{HO}$$

H_2O : CH_3CN (c_{H_2O} 2.22 M), 21.79;

H_2O : CH_3CN (c_{H_2O} 8.33 M), 20.15.

The kinetics of breakdown of the tetrahedral intermediates, *1b* - *6b*, were measured by generating them from the precursors *1a* - *6a* by following the formation of the ester products at 205 nm as described previously.[1] NMR experiments were carried out under conditons as close as possible to those used in the kinetic experiments in order to check that the rate determining step in formation of the ester from the precursor was the breakdown of the intermediate. With some precursors breakdown of the intermediate was rate determining in acidic solutions but its formation started to become rate-determining as the solutions were made more basic, as demonstrated by the observation of non-first-order kinetics. When this happened the "pH-jump" method was used.[8] The tetrahedral intermediate was generated in acidic solution and sodium hydroxide solution in the appropriate solvent was added to change the pH or pc_H to that required, which was measured after the run.

RESULTS

The plots of k_{obs} versus pH or pc_H for all the hemiorthoesters studied were U-shaped curves and were fitted to the appropriate equation (3 or 4) by a generalized least squares method.[9]

$$k = k_O + k_{H^+} \times 10^{-pH} + k_{HO^-} \times K_w/10^{-pH} \qquad (3)$$

$$k = k_O + k_{H^+} \times 10^{-pc_H} + k_{HO^-} \times K_w/10^{-pc_H} \qquad (4)$$

When the solvent was water or water-acetonitrile (c_{H_2O} = 8.33 M) the three rate constants k_O, k_{H^+}, and k_{HO^-} were evaluated but when it was water-acetonitrile (c_{H_2O} = 2.22 M) the contribution of k_O to the total rate was so small that it could not be evaluated accurately (see Tables I-III).

The kinetics of hydrolysis of trimethyl and triethyl orthoformate were studied in order to compare them with those for the corresponding hemiorthoesters, *1b* and *2b*. The reactions were just acid-catalysed and the values of k_{H^+} in CH_3CN-H_2O (c_{H_2O} = 8.33 M) are given in Table III.

Table I Rate constants for the breakdown of tetrahedral intermediates in water at 15.00 ±0.05°, I = 0.100 M.

Tetrahedral Intermediate	k_O/s^{-1}(sd)	$k_{H^+}/M^{-1}s^{-1}$(sd)	$10^{-6} \times k_{HO^-}/M^{-1}s^{-1}$
2-Hydroxy-4,4,5,5-tetramethyl-1-3-dioxolane (*4b*)	0.191(0.0086)	285(17)	1020(28)
2-Hydroxy-2,4,4,5,5-pentamethyl-1-3-dioxolane (*6b*)	0.0180(0.0011)	29.1(0.25)	2.87(0.08)

Table II Rate constants for the breakdown of tetrahedral intermediates in CH_3CN-H_2O (c_{H_2O} = 2.22 M) at 15.00 ±0.05°

Tetrahedral Intermediate	$10^{-4} \times k_{H^+}/M^{-1}s^{-1}$(sd)	$10^{-5} \times k_{HO^-}/M^{-1}s^{-1}$(sd)
2-Hydroxy-4,4,5,5-tetramethyl-1,3-dioxolane (*4b*)	5.86(0.24)	1700(190)
2-Hydroxy-2,4,4,5,5-pentamethyl-1,3-dioxolane(a) (*6b*)	1.24(0.037)	3.7(0.46)
2-Hydroxy-2-methyl-1,3-dioxolane(b) (*5b*)	25.8(0.29)	899(43)

(a) k_{H^+} for hydration of ketene acetal = $1.71 \times 10^{11} M^{-1}s^{-1}$

(b) k_{H^+} for hydration of ketene acetal = $9.36 \times 10^{10} M^{-1}s^{-1}$

Table III Rate constants for the breakdown of tetrahedral intermediates in CH_3CN-H_2O (a_{H_2O} = 8.33 M) at 15.00 ±0.05°

Tetrahedral Intermediate	$10^2 k_0/s^{-1}$(sd)	$10^{-3} \times k_{H^+}/M^{-1}s^{-1}$(sd)	$10^{-9} \times k_{HO^-}/M^{-1}s^{-1}$(sd)
2-Hydroxy-4,4,5,5-tetramethyl-1,3-dioxolane (*4b*)	0.783(0.094)	2.03(0.066)	8.39(0.49)
2-Hydroxy-2,4,4,5,5-pentamethyl-1,3-dioxolane (*6b*)	0.149(0.063)	0.310(0.015)	0.00395(0.00045)
2-Hydroxy-1,3-dioxolane (*3b*)	2.70(0.13)	3.94(0.094)	600(12)
2-Hydroxy-2-methyl-1,3-dioxolane (*5b*)	1.53(0.24)	5.50(0.15)	19.7(1.9)
Dimethyl hemiorthoformate (*1b*)	2.57(0.34)	240(7.3)	32.1(2.1)
Diethyl hemiorthoformate (*2b*)	4.36(0.18)	186(18)	6.53(0.48)
Trimethyl orthoformate	-	0.121(0.0043)	-
Triethyl orthoformate	-	0.800(0.027)	-

DISCUSSION

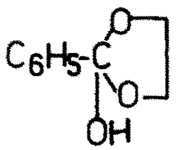
In order to compare the catalytic constants obtained in this investigation for the breakdown of the hemiorthoesters derived from formic and acetic acid with those obtained by McClelland and his co-workers[5] for the breakdown of hemiorthoesters derived from benzoic acid some extrapolations were necessary. This was done by converting the latter for 25° to 15° by dividing them by 2.5 and by extrapolating the former from acetonitrile-water ([H_2O] = 8.33 M) to water by multiplying by the averages of the ratios of the catalytic constants for the two hemiorthoesters, *4b* and *6b*, studied in both media. These factors were 0.117 for k_{H^+}, 0.42 for k_{HO^-}, and 28.25 for k_{H_2O}. The extrapolated values are given in Table IV. It was possible to check the validity of this procedure by comparing values of k_{H^+} for the breakdown of 2-hydroxy-1,3-dioxolane obtained by both methods since it has recently been indicated[5g] that the rate-limiting step in the hydrolysis of 2-methoxy-1,3-dioxolan in dilute HCl is breakdown of this hemiorthoester with k_{H^+} = 1.40 $M^{-1}s^{-1}$ at 25°. If this is extrapolated to 15° as before a value of 5.6 x $10^2 M^{-1}s^{-1}$ is obtained compared to the value obtained from extrapolation from aqueous acetonitrile, 6.4 x $10^2 M^{-1}s^{-1}$. Unfortunately at present we have no good means of comparing McClelland's rate constants[5f] for the breakdown of the acyclic hemiorthobenzoates in aqueous dioxan with our constants for the breakdown of acyclic hemiorthoformates in aqueous acetonitrile.

Also included in Table IV are rate constants for the breakdown of formaldehyde hemiacetals extrapolated from the values at 25° of Funderburk, Aldwin, and Jencks[10] by dividing by 2.5.

Table IV Extrapolated rate constants for the breakdown of hemiorthoesters and hemiacetals in water at 15° and rate constants estimated on the basis of different mechanisms

Compound	k_{H^+}[a,b]	k_{H_2O}[a,c]	k_{HO^-}[a,b]	pK_a[d]	$k_2/$[e,c]	k_{-1}[j,b]	$k_1/$[f,c]	k_2^*[g,b]
1b	2.81×10^4	7.26×10^{-1}	1.35×10^{10}	11.79	3.7×10^7	2.8×10^8	1.6×10^{-1}	4.5×10^{12}
2b	2.18×10^4	12.3×10^{-1}	2.74×10^9	11.48	3.7×10^6	1.4×10^8	3.3×10^{-1}	3.7×10^{11}
3b	4.61×10^2	7.63×10^{-1}	2.52×10^{11}	11.48	3.4×10^8	1.4×10^8	3.3×10^{-1}	2.3×10^{11}
5b	6.44×10^2	4.32×10^{-1}	8.3×10^9	12.12	4.9×10^7	5.9×10^8	7.6×10^{-2}	5.7×10^{11}
7	1.2×10^2	6.0×10^{-1}	2.4×10^{10}	11.33[i]	2.3×10^7	9.6×10^7	4.7×10^{-1}	1.3×10^{11}
4b	2.85×10^2	1.92×10^{-1}	1.02×10^9	11.37	1.9×10^6	1.1×10^8	4.3×10^{-1}	4.3×10^{10}
6b	2.92×10^1	1.80×10^{-1}	2.87×10^6	12.02	1.3×10^4	4.7×10^8	9.5×10^{-2}	1.8×10^{10}
8	5.2	3×10^{-2}	8×10^6	11.23	6.0×10^3	7.6×10^7	5.9×10^{-1}	5.1×10^9
Formaldehyde methylhemiacetal	0.23	7.24×10^{-2}	9.3×10^2	13.20	6.7×10^1	7.1×10^9	6.3×10^{-3}	1.1×10^{10}
Formaldehyde ethylhemiacetal	0.30	6.52×10^{-2}	5.2×10^2	13.04	2.6×10^1	5.0×10^9	9.1×10^{-3}	7.1×10^9
9	10.6	1.84	6.2×10^9	7.5	2.0×10^3	3.96×10^4	3.2×10^3	5.9×10^7

[a] Extrapolated as described in the text.
[b] Units $M^{-1}s^{-1}$.
[c] Units s^{-1}.
[d] Estimated as described in ref. 1.
[e] Estimated on the basis of the mechanism of eqs. 7 and 8.
[f] Estimated on the basis of the mechanism of eq. 10 on the assumption that the rate constant for recombination of the anion with H_3O^+ is 1×10^{11} $M^{-1}s^{-1}$.
[g] Estimated on the basis of the mechanism of eq. 9.
[h] Measured, not extrapolated, rate constants.
[i] At 25°.
[j] Estimated from the K_a and an assumed value of $k_1 = 10^{11}$ $M^{-1}s^{-1}$ (cf.eq.7).



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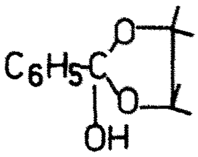

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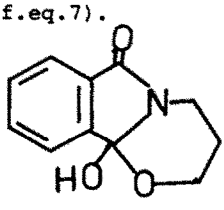

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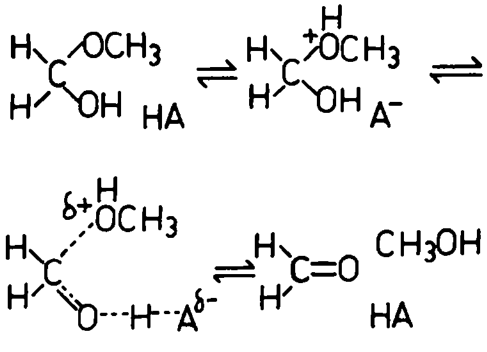
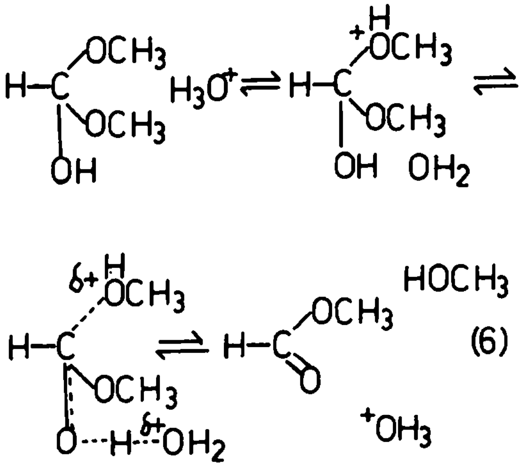
Hydronium-ion-catalysed reaction. The two acyclic hemiorthoesters, *1b* and *2b*, breakdown into the corresponding esters with rate constants 30 to 120 times greater than those for the cyclic hemiorthoesters *3b* - *5b* and these react more than 10 times faster than the cyclic hemiorthoester *6b* in which the three carbons of the dioxolane ring are fully substituted (see Table III). The breakdown of the acyclic hemiorthoesters, *1b* and *2b*, is also much faster than the hydrolysis of the corresponding orthoesters (Table III). Thus dimethyl hemiorthoformate reacts 1980 times faster than trimethyl orthoformate and diethyl hemiorthoformate reacts 233 times faster than triethyl orthoformate. A similar result has been reported by McClelland and Patel[5f] who found that dimethyl hemiorthobenzoate reacted 2700 times faster than trimethyl orthobenzoate. It therefore seems necessary to postulate that O-H bond breaking plays a role in facilitating the hydronium-ion-catalysed breakdown of these hemiorthoesters. This conclusion is similar to that reached by Jencks and co-workers[10] for the mechanism of breakdown of formaldehyde methyl hemiacetal on the basis that k_{H^+} for this reaction is 2600 times greater than for the hydrolysis of formaldehyde dimethyl acetal. On the basis of this and other evidence the mechanism of equation 5 was preferred.


(5)

A similar mechanism was considered for the breakdown of dimethyl hemiorthobenzoate but rejected on the basis that when the catalyst was formic acid the rate constant for the reaction of the conjugate acid of the substrate (assumed pK_a = -6) with formate would have to have a value of $10^{10}M^{-1}s^{-1}$.[5f] The possibility was considered of a "1-encounter" mechanism "in which the acid that donates the proton to the departing alkoxy group also acts as a general base to remove the OH proton before diffusional separation can occur". However, for the substrates studied in the present investigation the value for the rate constant for the reaction of the conjuate acid of the substrate with water would not have to be so large as $10^{12}M^{-1}s^{-1}$. Thus for dimethyl hemiorthoformate, the fastest reacting compound, this constant would have to be 5 x $10^{8}M^{-1}s^{-1}$ in water on the assumption that the pK_a of the conjugate acid was -6. A mechanism of this type (eq.6) is therefore a valid one.

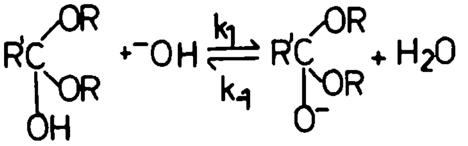


Dimethyl hemiorthoformate and diethyl hemiorthoformate breakdown about 10^5 times faster than the corresponding hemiacetals (Table IV). This can be explained on the mechanism of eq.6 by saying that the additional conjugation of the extra methoxyl group with the developing carbonyl group stabilizes the transition state. It has been estimated that the delocalization energy of an ester which results from conjugation of the alkoxy group with the carbonyl group is approximately 17 kcal. mole^{-1}.[11]

The value of k_{H^+} for the breakdown of the cyclic hemiorthoester, 2-hydroxy-1,3-dioxolan is 60 times less than that for dimethyl hemiorthoformate. This difference is similar to that found in the rate of hydrolysis of acetals. Thus benzaldehyde diethyl acetals are hydrolysed 30 to 35 times faster than the corresponding dioxolane.[12] In the reactions of the dioxolans (hemiorthoester or acetal) the leaving group is a β-alkoxyalcohol rather than methanol or ethanol in the acyclic compounds and part of the rate decrease may be due to the unfavourable electron withdrawing effect of the β-alkoxy group on the positively charged oxygen in the transition state. There may also be an unfavourable steric effect when the leaving group forms part of a five-membered ring.[12]

The introduction of a 2-methyl substituent into 2-hydroxy-1,3-dioxolan to give 2-hydroxy-2-methyl-1,3-dioxolane has a very small effect on k_{H^+}. This contrasts with what is found in the hydrolysis of acetals where even with 1,3-dioxolan where the effect is much reduced, the introduction of one and two 2-methyl substituents causes successive 6000 and 10.6 fold rate increases.[13] The effect of introducing a 2-phenyl substituent into 2-hydroxy-1,3-dioxolane also has a very small effect on k_{H^+}. This again contrasts with what is found in the hydrolysis of acetals where introduction of a 2-phenyl substituent into 1,3-dioxolane causes an increase in k_{H^+} of 2.7×10^5.[14] Even in the hydrolysis of the cyclic orthoester 2-methoxy-1,3-dioxolane, with fission of the exocyclic C-O bond, the introduction of a 2-phenyl substituent causes an increase of 42 in k_{H^+}.[15] This lack of sensitivity of k_{H^+} for the breakdown of hemiorthoesters to the introduction of both methyl and phenyl substituents suggests that C-2 bears little positive charge in the transition state and that this is being dispersed by conjugation with the attached oxygens.

Hydroxide-ion-catalysed reaction. Funderburk, Aldwin, and Jencks[10] proposed a mechanism for the breakdown of hemiacetals catalysed by hydroxide-ion which consists of the reversible formation of the anion followed by its unimolecular breakdown. A similar mechanism can be written for the breakdown of hemiorthoesters (eqs.7,8).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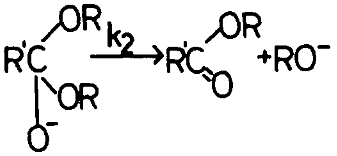

(8)

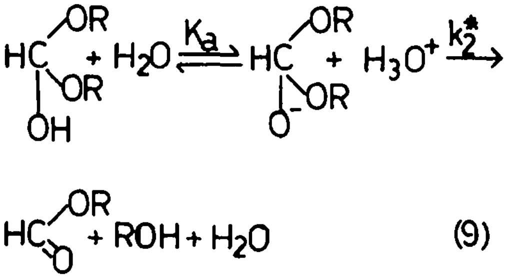
For the mechanism to be a valid one the value of k_2 calculated from the relationship $k_{HO^-} = K_1 k_2$ must be (i) less than the time constant for a molecular vibration ($10^{12} - 10^{14}s^{-1}$) (ii) less than the value of k_{-1} based on the estimated K_a and the assumption that the ionization equilibrium (eq.7) is diffusion controlled in the thermodynamically favourable direction; i.e. $k_1 = 10^{11}M^{-1}s^{-1}$. These two conditions are easily fulfilled with the hemiacetals but with the hemiorthoesters the calculated value of k_2 lies close to (or in one instance is greater than) the calculated value of k_{-1}. Therefore this mechanism may no longer be a valid one for the hydroxide-ion catalysed breakdown of the more reactive hemiorthoesters and the experimental results may be explained better by a mechanism in which there is a rate-limiting ionization or one in which there is concerted breaking of O-H and C-O bonds.

The much greater values of k_{HO^-} for the breakdown of the hemiorthoester compared to the hemioacetals may be attributed partly to the more favourable pK_a of the former, but must be mainly due to conjugation of the additional alkoxy group with the developing carbonyl group in the transition state.

The value of k_{HO^-} for the breakdown of 2-hydroxy-1,3-dioxolane, *3b*, is more than 10 times greater than for the breakdown of the acyclic hemiorthoesters *1b* and *2b*. This may be due to a more favourable pK_a as the more rigid structure of the dioxolane ring may lead to the dipoles of the C-O bonds being oriented more favourably to stabilize the anion. Our method for the estimation of the pK_a does not allow for an effect of this type and so the acceleration is shown in Table IV as arising from an effect on k_2. Alternatively it is possible that a more favourable k_2 for the dioxolane may arise from the leaving group being a β-alkoxyalkoxide rather than an alkoxide. Unfortunately a more definite explanation cannot be given at present.

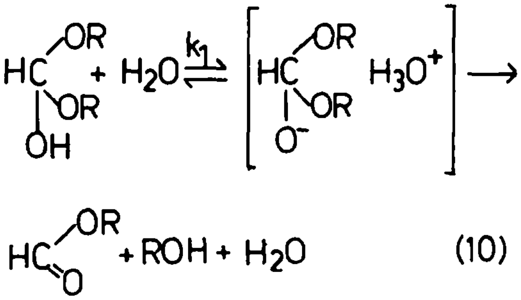
The presence of four methyl groups causes a large decrease on k_2. This effect is much larger than that found in the acid catalysed reaction. It is possible that in the hydroxide-ion catalysed reaction there is superimposed on the steric effect an electronic effect of the methyl groups which cause a decrease in the leaving group ability of the alkoxide ion due to their electronreleasing inductive effect. A similar effect is observed in the hydroxide-ion catalysed breakdown of benzaldehyde t-butyl and methyl hemiacetals for which $k_{HO^-}(Me)/k_{HO^-}(Bu^t) = 37.$[16] The introduction of a phenyl group into 2-hydroxy-1,3-dioxolane causes a decrease in the rate constant for the breakdown of the anion (k_2) of about 10. This may arise for its electron-withdrawing inductive effect which stabilizes the anion more than the transition state for its breakdown.

Spontaneous Reaction. There are at least three possible mechanisms for the spontaneous breakdown of hemiorthoesters, hemiacetals, and related species. Firstly, there may be a rapid and reversible ionization equilibrium followed by hydronium ion catalysed breakdown of the anion (eq. 9).[17] A necessary condition for this mechanism to be valid is that k_2^* calculated from k_{H_2O} and K_a should



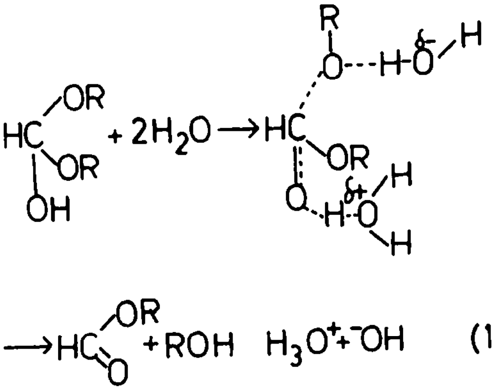
(9)

fall below the diffusion-controlled limit of ca $10^{10}M^{-1}s^{-1}$. The second mechanism is similar to this (eq.10) but



(10)

involves formation of the anion and hydronium ion in an encounter pair which react to give products faster than they diffuse apart.[1] With this mechanism therefore the ionization equilibrium is not established and the rate constant for reaction, k_{H_2O}, should be equal to the rate of ionization, k_1, which may be calculated from the K_a if it is assumed that the rate constant for the recombination of the anion and H_3O^+ has a rate constant of $10^{11}M^{-1}s^{-1}$. The third possibility is that the reaction is concerted (eq.11).[5f] This mechanism, unlike the other two, would explain a value of k_{H_2O} greater than the rate constant for ionization of the hydroxyl group, k_1. Therefore in principle one should be able to decide which mechanism explains the experimental results best by making estimates of k_1 and k_2^* and finding how they obey the above criteria. Such estimates are given in Table IV for a series of orthoesters, hemiacetals, and compound *9* studied by Gravitz and Jencks[17] but unfortunately owing to the number of assumptions made they are not very accurate, and so a definite decision can only be made concerning the best mechanism when the difference between the rate constants being compared is large. Thus with compound *9* the estimated value of k_2^* is well below the diffusion controlled limit and the estimated value of k_1 is three powers of ten greater than k_{H_2O}. The mechanism of equation 9 is therefore reasonable as concluded by Gravitz and Jencks.[17] With the other compounds listed in Table IV however the estimated values of k_2^* all lie close to or above the diffusion controlled limit of 10^{10} $M^{-1}s^{-1}$. Therefore if the reaction involves initial ionization it is necessary to postulate breakdown of the encounter complex immediately it is formed as in equation 10. With some of the compounds the estimated value of k_1 is less than k_{H_2O} so probably a concerted mechanism[5f] (eq.11) explains the results better.



(11)

Concluding Remarks. Our results and the complementary ones of McClelland and his co-workers[5] show clearly that the tetrahedral intermediates of *O,O*-acyl transfer reactions are definite molecular species capable of finite existence. The kinetic investigation reported in this paper and that already reported by McClelland[5] should lay the founation for a better understanding of acyl transfer reactions.

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