Hydrolysis of Ortho Esters: Further Investigation of the Factors Which Control the Rate-Determining Step

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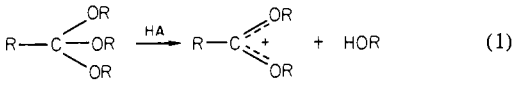
Abstract: Comparison of rates of hydronium ion catalyzed hydrolysis measured at low and at high pH reveals that the cyclic ortho ester 2-methyl-2-methoxy-1,3-dioxolane undergoes a change in reaction mechanism from rate-determining generation of a dialkoxycarbonium ion (stage 1) to rate-determining decomposition of a hydrogen ortho ester intermediate (stage 3), but it shows that its acyclic counterpart, trimethyl orthoacetate, does not. This difference is not caused by the dimethyleneoxy structure of the cyclic ortho ester, inasmuch as an acyclic ortho ester with a similar structure, tris(2-methoxyethyl) orthoacetate, also does not undergo a change in rate-determining step. This difference in behavior is inconsistent with a hypothesis advanced before involving differential substituent effects on stage 1 and stage 3, and analysis of previously published data shows that the substituent effects on these two stages are in fact quite similar. Two other effects, (1) entropic disadvantage of ring-opening processes and (2) solvational stabilization of hydrogen ortho ester intermediates, are suggested as possible factors which control the rate-determining step in these reactions.

The acid-catalyzed hydrolysis of ortho esters is known to be a three-stage reaction process: (1) generation of an alkoxycarbonium ion (eq 1) is followed by (2) hydration of this ion to



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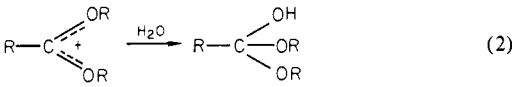

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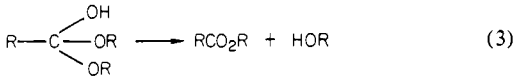
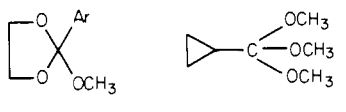


(3)

a hydrogen ortho ester intermediate (eq 2) and that, by (3) conversion of this intermediate to the ultimate carboxylic acid ester plus alcohol products (eq 3). Stage 1 is generally the rate-determining step of this sequence, especially in neutral or basic solution where very efficient base catalysis of stage 3 makes this step much faster than stage 1, which is not catalyzed by bases at all. For some ortho esters, however, acid catalysis of stage 3 is less effective than acid catalysis of stage 1, and for these substances the rate-determining step switches from stage 1 at high pH to stage 3 at low pH.

We first observed this change in rate-determining step for certain cyclic ortho esters substituted with cation-stabilizing groups at the *pro*-acyl carbon atom, such as 2-aryl-2-methoxy-1,3-dioxolanes (**1**), and we attributed the phenomenon to a differential



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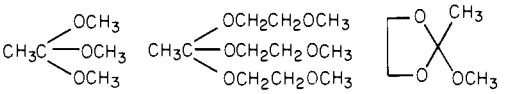
substituent effect which raised the rate of stage 1 but left that of stage 3 relatively unchanged.[2] This explanation makes no use of the cyclic nature of these substrates, and it suggested that a similar change in rate-determining step might be found with appropriately substituted acyclic ortho esters. We consequently investigated the hydrolysis of trimethyl orthocyclopropanecarboxylate (**2**) and found that this acyclic substrate underwent a change in rate-determining step as well.[3]

This discovery has prompted us to examine the hydrolysis of other acyclic ortho esters, and we now report that we have been unable to detect a change in rate-determining step for two methyl-substituted ortho esters trimethyl orthoacetate (**3**) and



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tris(2-methoxyethyl) orthoacetate (**4**). We have also redetermined the rate constants for the corresponding cyclic ortho ester 2-methyl-2-methoxy-1,3-dioxolane (**5**) and have confirmed that this substance does undergo a change in rate-determining step.

Experimental Section

Materials. Tris(2-methoxyethyl) orthoacetate was prepared by acid-catalyzed alcohol exchange of triethyl orthoacetate with 2-methoxyethanol; the product had a boiling point that agreed with the literature value[4] and gave a proton NMR spectrum consistent with its structure. A sample for kinetic measurements was purified by fractional distillation from sodium metal.

2-Methyl-2-methoxy-1,3-dioxolane was a sample that had been prepared before,[2b] and trimethyl orthoacetate was obtained commercially; these two substrates were purified for kinetic measurements by gas chromatography. All other materials were the best available commercial grades and were used as such. Solutions were prepared with deionized water purified further by distillation from alkaline permanganate.

Kinetics. Rate measurements were made spectrophotometrically by monitoring the appearance of acetic acid ester absorbance in the region 210-220 nm. A Cary Model 118C spectrometer was used for the slow runs in biphosphate buffer solutions, and a Durrum-Gibson Stopped-Flow spectrometer was used for the faster runs in hydrochloric acid solution. The output from the Durrum-Gibson instrument was fed directly through an analog-to-digital converter into a transient recorder; the information was then transferred into a Tektronix Model 4051 minicomputer, which calculated observed first-order rate constants by linear least-squares analysis. This system also provided visual displays on a cathode-ray tube and hard-copy output via a Tektronix Model 4662 Interactive Digital Plotter. This plotter could be operated in reverse as a digitizer, and it was used in this way to feed strip-chart recorder data from the slow runs measured on the Cary instrument into the minicomputer; rate constants were therefore obtained from these data by the same kind of mathematical analysis as was used for the fast runs. The runs performed with tris(2-methoxyethyl) orthoacetate in biphosphate buffers, however, were

(1) On sabbatical leave from Seton Hall University, South Orange, NJ.

(2) (a) Ahmad, M.; Bergstrom, R. G.; Cashen, M. J.; Kresge, A. J.; McClelland, R. A.; Powell, M. F. *J. Am. Chem. Soc.* **1977**, *99*, 4827-4829. (b) Ahmad, M.; Bergstrom, R. G.; Cashen, M. J.; Chiang, Y.; Kresge, A. J.; McClelland, R. A.; Powell, M. F. *Ibid.* **1979**, *101*, 2669-2677; (c) *Ibid.* **1982**, *104*, 1156-1157.

(3) Burt, R. A.; Chiang, Y.; Kresge, A. J.; McKinney, M. A. *J. Am. Chem. Soc.* **1982**, *104*, 3685-3687.

(4) Kuryla, W. C. U.S. Patent 3419580, 1968; *Chem. Abstr.* **1969**, *70*, 57154C.

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Table I. Catalytic Constants for the Hydrolysis of Ortho Esters Determined in This Study[a]

substrate	$10^{-3}k_{H^+}$, M^{-1} s^{-1}		k_0, s^{-1}		$k_{H_3PO_4}$, M^{-1} s^{-1}	$10^3 k_{H_2PO_4^-}$, M^{-1}
	HCl	buffer	HCl	buffer × 10^3		
trimethyl orthoacetate	9.69 ± 0.53	13.7 ± 0.2[b]	3.90 ± 7.27	−0.41 ± 0.13[b]	81.6 ± 3.5[b]	37.0 ± 0.2[b,e]
tri(2-methoxyethyl) orthoacetate	1.40 ± 0.02	1.60 ± 0.07[c]	5.37 ± 4.73	−0.13 ± 0.06[c]		2.76 ± 0.23[e,f]
2-methyl-2-methoxy-1,3-dioxolane	1.24 ± 0.02	22.0 ± 0.6[d]	2.02 ± 0.80	−0.42 ± 0.44[d]	28.9 ± 3.4[d,e]	22.3 ± 2.1[d,e]

[a] In wholly aqueous solution at 25.0 °C and 0.10 M ionic strength. [b] Based on data obtained at $[H_2PO_4^-]/[HPO_4^{2-}] = 7$, 3, and 2. [c] Based on data obtained at $[H_2PO_4^-]/[HPO_4^{2-}] = 7$ and 5. [d] Based on data obtained at $[H_2PO_4^-]/[HPO_4^{2-}] = 7$, 3, and 1. [e] Obtained by using eq 6. [f] Average of two values.

too slow to permit convenient measurement of the infinite-time absorbances required for analysis by minicomputer, and the data here were therefore reduced to observed first-order rate constants by the Swinbourne method.[5]

Results

An ortho ester whose hydrolysis reaction undergoes a change in rate-determining step will give a different hydronium ion catalytic coefficient at low than at high pH, and this difference can be used to detect this mechanistic change. We therefore measured rates of hydrolysis of the presently investigated ortho esters in dilute HCl solutions of pH 1–3 and in biphosphate buffers of pH ca. 6; the data are summarized in Tables S1 and S2.[6]

Observed first-order rate constants determined in HCl solutions were accurately proportional to acid concentration, and bimolecular hydronium ion catalytic coefficients were therefore evaluated by linear least-squares analysis. The resulting values are listed in Table I together with the intercepts, k_0, obtained in these analyses; the latter represent the "uncatalyzed" or solvent-catalyzed portion of the hydrolysis reaction in this medium.

The kinetic measurements in biphosphate buffers were performed in series of solutions of constant buffer ratio but varying total buffer concentration. Observed first-order rate constants showed a weak dependence upon buffer concentration, consistent with the mild general-acid catalysis usually found for ortho ester hydrolysis under these conditions.[2b,3,7] Systems of this kind generally follow the rate law shown as eq 4. Since $[H^+]$ is

$$k_{obsd} = k_0 + k_H + [H^+] + k_{H_2PO_4^-}[H_2PO_4^-] \quad (4)$$

constant along a series of buffer solutions of constant buffer ratio, values of the general-acid catalytic coefficient, $k_{H_2PO_4^-}$ can be obtained by least-squares analysis of the relationship between k_{obsd} and $[H_2PO_4^-]$. This treatment, however, produced constant values of $k_{H_2PO_4^-}$ for only one of the substrates examined here [tris(2-methoxyethyl) orthoacetate]; for the other two, $k_{H_2PO_4^-}$ obtained in this way varied systematically with buffer ratio, increasing with increasing $[H^+]$. This is the sort of behavior expected of systems in which a significant amount of reaction occurs through catalysis by H_3PO_4: though the concentration of this species in $H_2PO_4^-/HPO_4^{2-}$ buffers is quite small, this substance is a much stronger acid than $H_2PO_4^-$ and thus a more effective catalyst, and it can therefore sometimes make an important contribution to the overall rate of reaction.[8]

The rate law that applies when this is so is given as eq 5. The

$$k_{obsd} = k_0 + k_H + [H^+] + k_{H_2PO_4^-}[H_2PO_4^-] + k_{H_3PO_4}[H_3PO_4] \quad (5)$$

concentration variable $[H_3PO_4]$ can be expressed in terms of $[H_2PO_4^-]$ and $[H^+]$ through K_1, the first acid dissociation constant of phosphoric acid. This leads to eq 6, which shows that the

$$k_{obsd} = k_0 + k_H + [H^+] + (k_{H_2PO_4^-} + k_{H_3PO_4}[H^+]/K_1)[H_2PO_4^-] \quad (6)$$

proportionality constant between k_{obsd} and $[H_2PO_4^-]$ will increase with $[H^+]$, as noted above, if $k_{H_3PO_4}[H^+]/K_1$ is sufficiently large compared to $k_{H_2PO_4^-}$. This rate law was used to analyze the data for trimethyl orthoacetate and 2-methyl-2-methoxy-1,3-dioxolane obtained here, and the coefficient of $[H_2PO_4^-]$ was separated into its $k_{H_2P_{O_4}}$- and $k_{H_3PO_4}$- constituents through its dependence on $[H^+]$. Hydronium ion concentrations required for this purpose were calculated using the acidity constants $K_a = 7.52 \times 10^{-3}$ M for H_3PO_4[9] and $K_a = 6.31 \times 10^{-8}$ M for $H_2PO_4^-$[10] and activity coefficients for H_3O^+, $H_2PO_4^-$, and HPO_4^{2-} recommended by Bates;[11] the activity coefficient of H_3PO_4 was taken to be unity. Results obtained in this way are summarized in Table I.

Hydronium ion catalytic coefficients were obtained from the buffer solution data by analyzing the dependence upon $[H^+]$ of the intercepts $k_0 + k_H + [H^+]$, obtained by applying eq 4 [for tris(2-methoxyethyl) orthoacetate] or eq 6 (for trimethyl orthoacetate and 2-methyl-2-methoxy-1,3-dioxolane). In all three cases the value of k_0 proved to be negligibly small; the results are summarized in Table I.

The value of k_{H^+} determined here for 2-methyl-2-methoxy-1,3-dioxolane i biphosphate buffers, $k_{H^+} = (2.20 \pm 0.06) \times 10^4$ M^{-1} s^{-1}, is somewhat different from the result we first reported, $k_{H^+} = 1.5 \times 10^3$ M^{-1} s^{-1},[2b] and later amended to $k_{H^+} = 1.5 \times 10^4$ M^{-1} s^{-1},[2c] when we discovered a power of 10 error in the calculation. But our previous measurements were somewhat crude, and the present result should be taken as a better indication of the true value. Our current result for this substrate in HCl solutions, $k_{H^+} = (1.24 \pm 0.02) \times 10^3$ M^{-1} s^{-1}, is also to be preferred over the value, $k_{H^+} = 1.4 \times 10^3$ M^{-1} s^{-1}, we reported before.[2b]

Discussion

The data of Table I show that the hydronium ion catalytic coefficient measured for the hydrolysis of 2-methyl-2-methoxy-1,3-dioxolane (**5**) in hydrochloric acid solutions, $k_{H^+} = 1240$ M^{-1} s^{-1}, is decidedly different from that determined at higher pH in biphosphate buffers, $k_{H^+} = 22\,000$ M^{-1} s^{-1}. The same quantity is therefore not being measured under the two sets of reaction conditions, and there must thus be a change in rate-determining step. We have shown before[2] that when this occurs, the rate-determining step at high pH is stage 1 of the hydrolysis reaction, generation of a dialkoxycarbonium ion (eq 1), while the rate-determining step at low pH in stage 3, decomposition of the hydrogen ortho ester intermediate (eq 3).

The other two ortho esters investigated here, on the other hand, give values of k_{H^+} in hydrochloric acid solution that are similar to those measured in biphosphate buffers. For tris(2-methoxyethyl) orthoacetate, the agreement is reasonably good, $k_{H^+} = 1400$ and 1600 M^{-1} s^{-1}, but for trimethyl orthoacetate it is less so, $k_{H^+} = 9700$ as opposed to 13 700 M^{-1} s^{-1}.[12] However, the fact that appearance of carboxylic acid ester product in the latter case obeyed the first-order rate law well, and in particular showed no initial lag, indicates that these two rate constants do refer to the same reaction step (stage 1). Calculations simulating a two-step reaction process with $k = 13\,000$ M^{-1} s^{-1} for the first step and

(5) Swinbourne, E. S. *J. Chem. Soc.* **1969**, 2371–2372.
(6) Tables S1 and S2 are available as supplementary material; see paragraph at the end of this paper.
(7) (a) Chiang, Y.; Kresge, A. J.; Salomaa, P.; Young, C. I. *J. Am. Chem. Soc.* **1974**, *96*, 4494–4499. (b) Chiang, Y. Kresge, A. J.; Young, C. I. *Finn. Chem. Lett.* **1978**, 13–18. (c) Bergstrom, R. G.; Cashen, M. J.; Chiang, Y.; Kresge, A. J. *J. Org. Chem.* **1979**, *44*, 1639–1642. (d) Burt, R. A.; Chiang, Y.; Hall, H. K., Jr.; Kresge, A. J. *J. Am. Chem. Soc.* **1982**, *104*, 3687–3690.
(8) Loudon, G. M; Ryono, D. E. *J. Org. Chem.* **1975**, *40*, 3574–3577. Kresge, A. J.; Weeks, D. P., unpublished results.
(9) Mims, L. F. *J. Am. Chem. Soc.* **1983**, *56*, 1110–1112.
(10) Grybowski, A. J. *J. Phys. Chem.* **1958**, *62*, 555–559.
(11) Bates, R. G. "Determination of pH"; Wiley-Interscience: New York, 1973; p 49.
(12) For this substrate the absorbance change used to monitor the reaction was small and rates in HCl solutions were fast; the results are therefore of poorer quality than in the other cases.

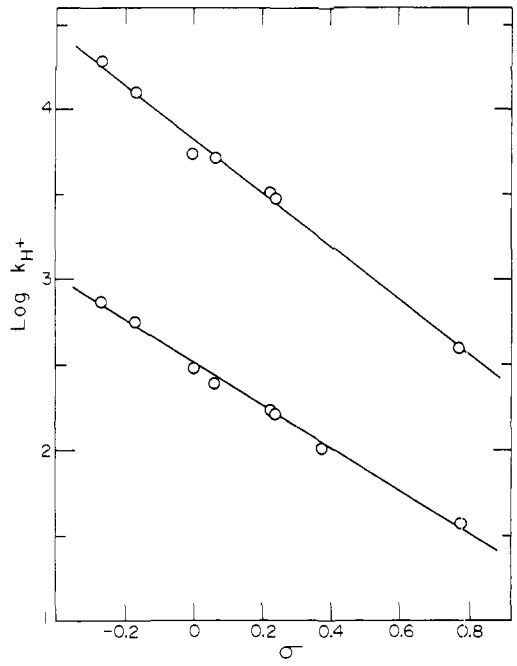


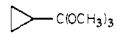
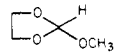
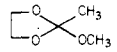
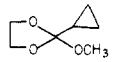
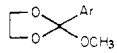
Figure 1. Hammett $\sigma-\rho$ correlations for the hydrolysis of 2-aryl-2-methoxy-1,3-dioxolanes using the data of ref 1. Top line, $k^1_{H^+}$; bottom line, $k^3_{H^+}$.

k = 9700 M^{-1} s^{-1} for the second give data that show a clearly discernable induction period, and such an induction period has in fact been observed in the hydrolysis of another ortho ester, 2,6,7-trioxabicyclo[2.2.1]heptane, for which the specific rates of stages 1 and 3 happen to be quite similar.[7d] An induction period was also not observed here in the hydrolysis of tris(2-methoxyethyl) orthoacetate, and the possibility that the two closely similar values of k_{H^+} measured for this substrate in hydrochloric acid and buffer solutions are an accidentally degenerate pair of rate constants for stages 3 and 1, respectively, can thus be ruled out.

These results indicate that methyl substitution at the *pro*-acyl carbon atom affects the course of ortho ester hydrolysis quite differently in the cyclic 2-methoxy-1,3-dioxolane series (**5**) than in acyclic substrates such as trimethyl orthoacetate (**3**): in the former case there is a change in rate-determining step between high and low pH whereas in the latter case there is not. That this difference is not caused by the dimethyleneoxy structure of the cyclic substance is shown by the fact that tris(2-methoxyethyl) orthoacetate (**4**), an acyclic substrate with a similar dimethyleneoxy structure, also does not undergo a change in rate-determining step.

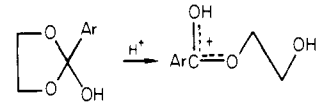
This difference in behavior of methyl-substituted ortho esters is not consistent with the hypothesis we advanced earlier that the change in rate-determining step is produced by a differential substituent effect on stages 1 and 3,[2,3] and in fact, examination of previously published data for the hydrolysis of 2-aryl-2-methoxy-1,3-dioxolanes (**1**),[2] indicates that the substituent effects on the rates of these two stages, at least for this series, are quite similar. We showed before that specific rate constants for stage 1 catalyzed by the hydronium ion, $k^1_{H^+}$, in the hydrolysis of a series of substrates of this kind where the aryl groups are meta- and para-substituted phenyl derivatives, give a good Hammett $\sigma-\rho$ correlation.[7b] This correlation is reproduced in Figure 1 (top line) along with an equally good correlation (bottom line) using hydronium ion catalytic coefficients for stage 3, $k^3_{H^+}$, of these same hydrolysis reactions. It may be seen that the slopes of these two lines are rather similar; least-squares analysis gives $\rho = -1.58 \pm 0.06$[13] for the correlation using $k^1_{H^+}$ and $\rho = -1.24 \pm 0.04$ for that using $k^+_{H^+}$. The ratio of these two slopes is 0.78, which indicates that stage 3 of the hydrolysis reaction responds to substituent changes at the *pro*-acyl carbon atom only some 20% less strongly than does stage 1.

Table II. Comparison of Hydronium Ion Catalytic Coefficients for Stages 1 and 3 of Some Ortho Ester Hydrolysis Reactions

substrate	$k^1_{H^+}$, M^{-1} s^{-1}	$k^3_{H^+}$, M^{-1} s^{-1}	$k^3_{H^+}/k^1_{H^+}$
$HC(OCH_3)_3$	263[a]	70000[b]	270
$CH_3C(OCH_3)_3$	11 700[c]	>66000[d]	>5
	81 000[e]	5300[e]	0.065
	175[a]	1200[b]	6.9
	22 000[c]	1240[c]	0.057
	50 000[f]	1100[f]	0.022
	400–20 000	40–1000	0.1–0.05

[a] Reference 7a. [b] Estimated from rate constant measured in aqueous acetonitrile at 15 °C (ref 17) as suggested in ref 17. [c] This work. [d] Lower limit based on absence of induction period in product appearance; this requires $k^3_{H^+}$ to be at least 5 times $k^1_{H^+}$; see ref 2b. [e] Reference 3. [f] Reference 2b.

The similarity of these ρ values suggests a similarity of reaction mechanism, which implies that stage 3 involves generation of a cationic intermediate just as does stage 1. This means that the hydrogen ortho ester reactant of stage 3 is probably converted to a hydroxyalkoxycarbonium ion (eq 7), which then loses a proton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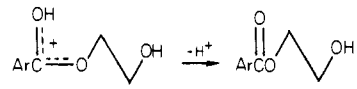

(8)

in a fast but discrete step (eq 8), as opposed to a concerted process in which both of these changes occur at the same time and the cationic intermediate is avoided. There would seem to be little reason to avoid this intermediate, for it is unlikely to be too unstable: pK_R values of the corresponding dialkoxycations, i.e., dioxolenium ions, range from 1.1 to −2.4 and average −0.8,[2b] and the present ions are apt to be even more stable inasmuch as hydroxy groups are more effective than alkoxy groups at stabilizing adjacent positive charge in dilute aqueous solution.[14] It has recently been shown, moreover, that a hydroxy cationic intermediate is not avoided in the ketonization of isobutyraldehyde enol (eq 9)[15] despite the fact that, unlike in the present situation,

$$(CH_3)_2C{=}CHOH \xrightarrow{H^+} (CH_3)_2CHCHOH^+ \xrightarrow{-H^+} (CH_3)_2CHCHO \quad (9)$$

this intermediate is not stabilized further by an additional alkoxy group.

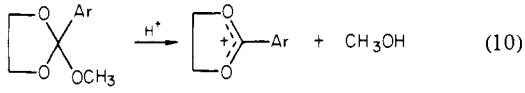
Since the cationic intermediate generated in stage 3 is likely to be more stable than that formed in stage 1, the transition state leading to this intermediate in stage 3 should be of lower free energy than the transition state in stage 1. This suggests that stage 3 should take place more rapidly than stage 1, but as the distance between the two lines of Figure 1 indicates, stage 3 is the slower process by at least an order of magnitude. Stage 3 is also slower than stage 1 in the hydrolysis of other orthoesters for which a change in rate-determining step has been observed, such as 2-methyl- and 2-cyclopropyl-2-methoxy-1,3-dioxolane and trimethyl

(13) The difference between this value and the result given in ref 7b, $\rho = -1.60 \pm 0.03$, is due to a revised value of $k^1_{H^+}$ for 2-phenyl-2-methoxy-1,3-dioxolane.[7c]

(14) Kresge, A. J.; Chen, H. J.; Hakka, L. E.; Kouba, J. E. *J. Am. Chem. Soc.* **1971**, *93*, 6174–6181.
(15) Chiang, Y.; Kresge, A. J.; Walsh, P. A. *J. Am. Chem. Soc.* **1982**, *104*, 6122–6123.

orthocyclopropanecarboxylate (see Table II for a listing of the relevant rate constants); indeed a change in rate-determining step cannot occur unless $k^3_{H^+}$ is less than $k^1_{H^+}$.

Other factors must be operative, and one of these could be the ring-opening nature of stage 3 in most of these cases. There is evidence that the exocyclic group is lost first in the hydrolysis of monocylic ortho esters such as 2-aryl-2-methoxy-1,3-dioxolanes (eq 10)[2b,7a] and that gives this reaction, and therefore stage 1, the



(10)

entropic advantage afforded by incipient generation of two particles from one. Stage 3, on the other hand, is a ring-opening process (see eq 7 and 8) from which this entropic benefit is absent because the two separating parts of the molecule are still held together by the remaining ring atoms. Effects of this kind have been observed, for example, in the hydrolysis of cyclic acetals and ketals, which react more slowly than do the corresponding acyclic substrates; the retardation, moreover, appears largely as a more negative entropy of activation.[16]

This factor, of course, cannot operate to slow the rate of stage 3 for acylic ortho esters such as the first three entries in Table II, and it is significant, therefore, that the ratio of $k^+_{H^+}$ to $k^1_{H^+}$ for each of these substrates is greater than that for its similarily substituted cyclic counterpart, e.g., $k^+_{H^+}/k^1_{H^+}$ = 270 for trimethyl orthoformate whereas this ratio is only 6.9 for 2-methoxy-1,3-dioxolane. Another factor must be functioning here, and that could be an initial state effect which lowers the free energy of the hydrogen ortho ester reactant of stage 3 and thus slows the rate of reaction in this way. For example, hydrogen ortho esters, because of their hydroxy functional groups, will be better solvated than ortho esters themselves in the aqueous medium used for these reactions, and this additional stabilization will add an increment to the free energy of activation for reactions of hydrogen ortho esters which will be absent from that for the ortho esters. This solvation effect should be relatively more important for hydrogen ortho esters with large hydrophobic substituents such as aryl or cyclopropyl at their *pro*-acyl carbon atoms than for substrates with small groups such as hydrogen at this position, and it is significant, therefore, that the $k^+_{H^3}/k^1_{H^3}$ ratio drops from hydrogen through methyl to cyclopropyl (and aryl) substituents along both the acyclic and cyclic series listed in Table II.

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Registry No. 2, 54917-76-9; **3**, 1445-45-0; **4**, 20006-56-8; **5**, 19798-71-1; HCl, 7647-01-0; H^+, 12408-02-5; H_3PO_4, 7664-38-2; $H_2PO_4^-$, 14066-20-7; $HC(OCH_3)_3$, 149-73-5; 2-methoxy-1,3-dioxolane, 19693-75-5.

Supplementary Material Available: Tables of rate constants (5 pages). Ordering information is given on any current masthead page.

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The Strain Energy of Diphenylcyclopropenone: A Reexamination

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Abstract: The published value for $\Delta H_f°(g)$ of diphenylcyclopropenone and its attendant strain energy have been reinvestigated. Conceptual and calculational schemes indicate that the published value is too high by as much as 50 kcal/mol. Preliminary heat of combustion studies support this conclusion. On the basis of isodesmic equations employing the 4-31G and 6-31G* basis sets, significant aromatic stabilization is found in cyclopropenone.

Almost 25 years of cyclopropenone chemistry[1-5] have failed to decide the issue of whether or not this molecule is, in fact, the smallest neutral aromatic specie. The stabilities of derivatives (e.g. diphenylcyclopropenone is thermally stable to 130 °C)[1-5] and their high dipole moments (ca. 4.7–5.1 D[5]), low infrared carbonyl frequencies (1640 cm^{-1} which may be compared with 1815 cm^{-1} for cyclopropanone), and low pK_b values[5] have all been cited as proof for aromatic stabilization. Gas-phase structural studies of cyclopropene, cyclopropanone, and cyclopropenone[6] suggest a lengthening of the carbonyl bond and a shortening of C_1–C_2 compatible with extensive π delocalization. Similar parameters have been found for solid-state diphenylcyclopropenone hydrate.[7] Admittedly primitive, Hückel calculations obtain a resonance stabilization of 1.36β in cyclopropenone,[8] which may be compared with values of 2β in benzene, 0.96β in methylenecyclopropene, and 0.47β in 1,3-butadiene. Using the criterion of resonance energy per π electron (REPE), Hess and Schaad concluded that cyclopropenone is aromatic while tropone is not.[9]

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