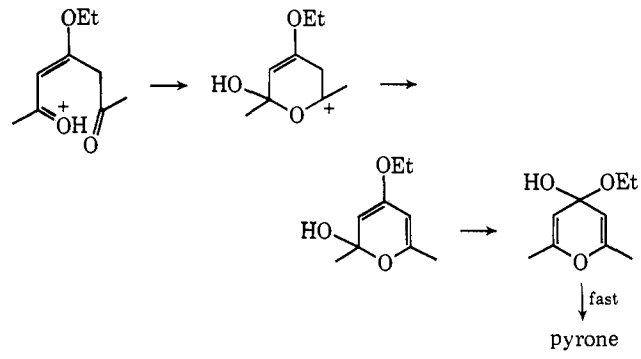
K_a^D = 1.7 for the 2,6-dimethylpyrylium salt is roughly that expected for an acid of comparable acidity,[14]

Formation of 4-Pyrone. The identity of the acid plateau rate constant ($k_a = k_0 \sim$ Figures 5 and 6) with the rate constant for the rate of formation of 4-pyrone (k_b) in the plateau region and the identity of the *pH-dependent* rate constant for the latter reaction with that for the hydrolysis of the isolated intermediate is good evidence for the changeover in rate-limiting step and mechanism. The plateau region for k_b corresponds to the direct reaction of water at the 4 position which is predominant because although the acid-catalyzed hydrolysis of the intermediate is larger than its rate of formation at this pH (Table IV) the latter is much less than the direct rate.

The hydrolysis of intermediate to give diacetylacetone which then cyclizes to 2,6-dimethyl-4-pyrone is not a valid mechanism since the bimolecular acid-catalyzed rate constant for the latter reaction is $1.36 \times 10^{-4}\ M^{-1}$ sec^{-1} (45°) which does not support the overall rate constant from intermediate (14 sec^{-1}, see Table IV). Mechanisms involving the intermediates shown are probably not valid since models of their dehydration[15]

also have rate constants ($\sim 10^{-5}\ M^{-1}$ sec^{-1} at 25°) insufficient to sustain the observed rate constant. The mechanism of Chart III is suggested as a possible can-

Chart III



didate and work of Pocker and Hill[16] on the rearrangement of 1-phenyl-3-methylallyl alcohol (an analog of the penultimate step) suggests that the rearrangement step could be rate controlling. The inverse deuterium isotope effect (Table IV) supports the preequilibrium protonation of the diketone.

(14) R. P. Bell, "The Proton in Chemistry," Methuen, London, 1959, p 188.
(15) S. Winstein and H. S. Lucas, *J. Amer. Chem. Soc.*, **59**, 1461 (1937); H. J. Lucas, W. T. Stewart, and D. Pressman, *ibid.*, **66**, 1818 (1944).
(16) Y. Pocker and M. J. Hill, *ibid.*, **91**, 3243 (1969).

The Hydrolysis of Pyrylium Salts. Kinetic Evidence for Hemiacetal Intermediates

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Contribution from the Chemical Laboratory, University of Kent, Canterbury, Kent, England. *Received September 14, 1970*

Abstract: The hydrolyses of 2,4,6-triphenylpyrylium tetrafluoroborate, 2,4,6-trimethylpyrylium perchlorate, and 2-methyl-4,6-diphenylpyrylium chloride (to yield diketones) were measured over a range of pH, buffer concentration, and in deuterium oxide solvent. The rate constant for the forward reaction in each case obeyed the empirical equation $k_f = k_{H_2O}/(1 + a_H/K_a) + k_{OH}[OH] + k_B[B]$. The titration term is judged to arise from the pH-dependent partitioning of a cyclic hemiacetal intermediate formed by reaction of water at the C_2 position. The attack of water on the 2-methyl-4,6-diphenylpyrylium cation proceeds at the 2 position and the product is shown to be the 1,3-diphenyl-2-hexene-1,5-dione.

The formation of pseudobases from pyrylium salts and aqueous media is a well-known phenomenon[1] and probably involves a cyclic hemiacetal intermediate but evidence for this mechanism is indirect.[2] The structures of the final hydrolysis products are now known not to include the hemiacetal adduct except where this or its vinylog cannot react further.[2c] Berson[1a] showed that the pseudobase from the 2,4,6-triphenylpyrylium cation was the diketone and not the keto enol.

(1) (a) J. A. Berson, *J. Amer. Chem. Soc.*, **74**, 358 (1952); (b) W. Dilthey, *J. Prakt. Chem.*, **94**, 53 (1916); **95**, 107 (1917); 101, 177 (1920); (c) W. Dilthey and T. Böttler, *Ber.*, **52**, 2040 (1919); (d) H. R. Hensel, *Justus Liebigs Ann. Chem.*, **611**, 97 (1958); (e) J. J. Basselier, *Ann. Chim. (Paris)*, **6**, 1131 (1961); (f) G. Rio and Y. Fellion, *Tetrahedron Lett.*, 1213 (1962).
(2) (a) K. Dimroth and K. H. Wolf, "Newer Methods of Preparative Organic Chemistry," W. Foerst, Ed., Academic Press, New York, N. Y., 1964, p 357; (b) M. Gomberg and L. H. Cone, *Justus Liebigs Ann. Chem.*, **370**, 142 (1909); (c) S. Wawzonek, "Heterocyclic Compounds," R. C. Elderfield, Ed., Wiley, New York, N. Y., 1951, p 463 ff; (d) see ref 2c, p 316 ff; (e) D. W. Hill and R. R. Melhuish, *J. Chem. Soc.*, 1163 (1935).

Experimental Section

Materials. Deuterium oxide (99.7%) was obtained from Prochem Ltd., U.K. Deuterium oxide buffers were prepared directly from heavy water and protium buffer. For example, 0.1 *M* disodium hydrogen phosphate will exchange in heavy water to give 0.05 *M* water, a dilution of the heavy water which is negligible for the purposes of our experiments. pD was calculated from the

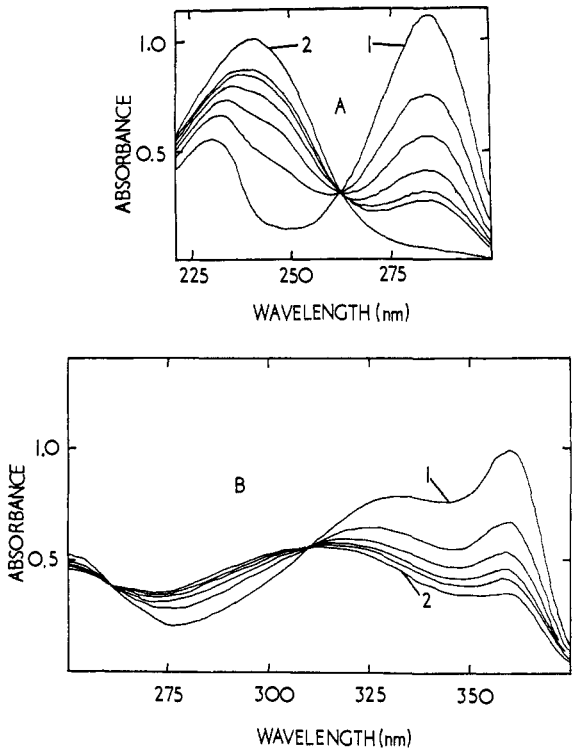


Figure 1. Spectrum scan of hydrolysis of A: 2,4,6-trimethylpyrylium perchlorate (1), substrate concentration 0.824×10^{-4} *M*, pH 5.68, 25°, 0.1 *M* ionic concentration, scanning interval 2 min (infinity scan, 2); B, 2-methyl-4,6-diphenylpyrylium chloride (1), substrate concentration 0.39×10^{-4} *M*, pH 4.36, 25°, 0.1 *M* ionic concentration, scanning intervals 1.5 min, infinity scan (2).

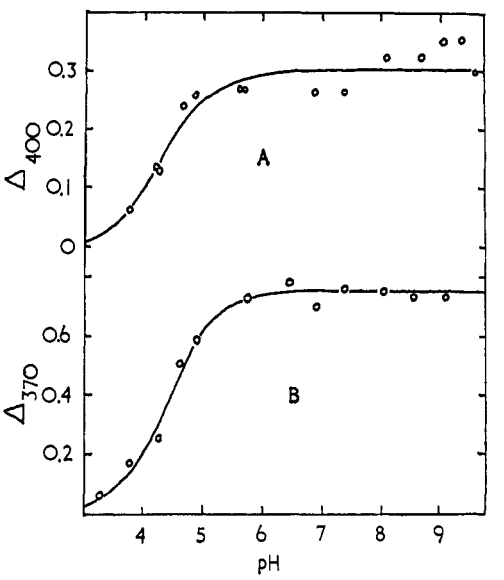


Figure 2. pH dependence of extent of pseudobase formation at equilibrium: A, 2,4,6-triphenylpyrylium cation; B, 2-methyl-4,6-diphenylpyrylium cation; 25°, 0.1 *M* ionic concentration. Lines are theoretical, see text.

equation[3] pD = pH meter reading + 0.4, and pOH and pOD were calculated from the autoprotolysis constants of water and deuterium oxide[4] using pH and pD, respectively. pH(D) was measured using a PYE Dynacap pH meter.

2,4,6-Trimethylpyrylium perchlorate was prepared according to the method of Diels and Alder[5] and had mp 246–247° (lit.[5] mp 245–247°). 2,4,6-Triphenylpyrylium tetrafluoroborate was prepared by boiling an acidified solution of the ferrichloride[6] with aqueous fluoroboric acid. The product crystallized as yellow needles, mp 214–215° (lit.[6] mp 214–215°). 2-Methyl-4,6-diphenylpyrylium chloride was prepared by dissolving the sulfoacetate[7] in a little hot acidified water and adding a saturated sodium chloride solution. Light yellow needles separated on cooling, mp 125–126° (lit.[7] mp 125–126°). The pseudobase of 2,4,6-trimethylpyrylium perchlorate was prepared by adding 2 g of the salt to a phosphate buffer solution of pH 7.5 (0.1 *M*, 100 ml). After standing at room temperature for 0.5 hr, the organic product was extracted with chloroform. The oil from the dried, evaporated chloroform was evacuated under high vacuum (0.01 mm) for 0.5 hr to remove traces of solvent. *Anal.* Calcd for $C_8H_{12}O_2$: C, 68.5; H, 8.6. Found: C, 68.3; H, 8.7. Ir (liquid film) showed 1720 (CH_3COCH_2), 1690 (=CH-$COCH_3$), 1620 cm^{-1} (C=C); $uv_{max}(CH_3CN)$ 237 nm (ϵ 1450); nmr ($COCl_3$) τ 3.6, 3.7 (s, 1, =CH-), 6.2, 6.7 (s, 2, $-CH_2-$), 7.8, 8.05 (m, 9, $-CH_3$). In the nmr spectrum the ratio of olefin peak areas equalled the ratio of methylene peak areas. The pseudobase of the 2,4,6-triphenylpyrylium cation was prepared according to Berson.[1a] It had mp 115–116° (lit.[1a] mp 119°); ir (Nujol) 1675 ($CH_2COC_6H_5$), 1645 (C=CH—COC_6H_5), 1570, and 1585 cm^{-1} (C=C); uv max (CH_3CN) 245 nm (ϵ 14,800), 300 nm (ϵ 13,400); nmr (DMSO) τ 1.7–1.26 (m, 16 aromatic + high field =CH-), 5.1 (s, 2, $-CH_2-$).

The pseudobase from 2-methyl-4,6-diphenylpyrylium chloride was isolated by shaking a mixture of the salt (2 g), phosphate buffer (100 ml, pH 6, 0.1 *M*), and ether (25 ml) for about 0.25 hr, separating the ether layer, drying, and evaporating. The thick purplish oil had ir (liquid film) 1720, 1680, 1650, 1590, and 1570 cm^{-1}. *Anal.* Calcd for $C_{18}H_{16}O_2$: C, 81.8; H, 6.1. Found: C, 81.6; H, 5.9.

Kinetics. Buffer (2.5 ml) was placed in a cuvet and equilibrated in the thermostated cell compartment of a Unican SP 800 recording spectrophotometer. Pyrylium salt in acetonitrile was then placed on the tip of a glass rod using a pipet and introduced into the buffer. The absorbance change was followed at the appropriate wavelength [2,4,6-trimethylpyrylium perchlorate, 287 nm ($\Delta\epsilon$ 14,900); 2,4,6-triphenylpyrylium tetrafluoroborate, 404 mn ($\Delta\epsilon$ 25,500); 2-methyl-4,6-diphenylpyrylium chloride, 370 nm ($\Delta\epsilon$ 29,000)]. Final concentrations of pyrylium cations were 4.12×10^{-5}*M* (2% CH_3CN), 0.736×10^{-5} *M* (0.02% CH_3CN), 0.39×10^{-4} *M* (1% CH_3CN), respectively. Product analysis studies were carried out by scanning the uv spectrum of the reacting solution at preset time intervals throughout the reaction. Kinetics in deuterium oxide solvent were carried out using 1 ml of buffer solution at the required pD in semimicro silica cells.

The fitting of kinetic data to theoretical functions of the hydrogen ion concentration was carried out using a computer program which chose the set of parameters which gave the best least-squares fit to the data. The method employed is essentially a computerized version of the method of Hansen.[8]

Results

The pseudobase from 2,4,6-trimethylpyrylium cation has uv, ir, and nmr data which suggest an equilibrium mixture of the cis and trans isomers of 4-methyl-4-heptene-2,6-dione. The ir, uv, and nmr data for the hydrolysis product of 2,4,6-triphenylpyrylium cation suggest a structure 1,3,5-triphenyl-3-pentene-1,5-dione. Structural isomerism is a complication in the hydrolysis product of 2-methyl-4,6-diphenylpyrylium cation and the ir spectrum of the product exhibits an absorption at 1720 cm^{-1} characteristic of a $-CH_2COCH_3$ group indicating that the hydrolysis product is 1,3-diphenyl-2-hexene-1,5-dione. Studies of the hydrolytic reactions carried out by scanning the uv spectrum at appropriate time intervals showed that the reactions had no side complications over the pH range studied

(3) P. K. Glasoe and F. A. Long, *J. Phys. Chem.*, **64**, 188 (1960).
(4) R. W. Kingerly and V. K. La Mer, *J. Amer. Chem. Soc.*, **63**, 3256 (1941).
(5) O. Diels and K. Alder, *Ber.*, **60**, 722 (1927).
(6) Reference 2a, p 411.
(7) W. Schneider and F. Seeback, *Ber.*, **54**, 2285 (1921).
(8) (a) B. Hansen, *Acta Chem. Scand.*, **16**, 1945 (1962); (b) A. Williams, "Introduction to the Chemistry of Enzyme Action," McGraw-Hill, London, 1969, p 123.

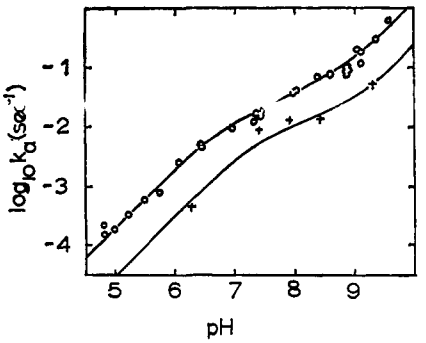
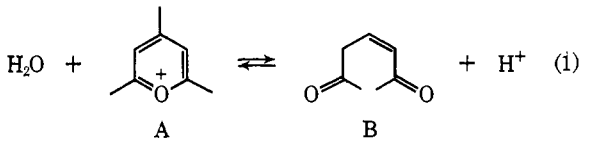


Figure 3. pH dependence of hydrolysis rate constant for 2,4,6-trimethylpyrylium perchlorate; 25°, 0.1 M ionic concentration; O, values for H_2O; +, values for D_2O. Lines are theoretical from eq 3 (k_f) and data from Table V.

and the stoichiometry was shown to be 100% by the presence of clean isosbestic wavelengths (see, *e.g.*, Figure 1) and by comparing the ratios of absorptions for product and reactant with those expected from the known extinction coefficients.

The stoichiometric equation (1) for the hydrolysis



reaction indicates that K (= [B]/[A]) must be pH dependent and the concentration of B is given by the ratio $A_0/(1 + a_H/K_a')$, where A_0 is the total of B and A. In the case of the trimethylpyrylium cation K_a' was sufficiently greater than a_H in the pH region studied for the reaction to yield 100% hydrolysis product. The phenyl-substituted salts did not hydrolyze completely (Figure 2); the apparent K_a' derived from these results ($10^{-4.4}$ and $10^{-4.3}$ for diphenyl and triphenyl salts, respectively) shows these pseudoacids to be as strong as acetic acid. Trimethylpyrylium cation is stronger than acetic acid since it is not titrated in the low pH region.

Table I. Hydrolysis of 2,4,6-Trimethylpyrylium Perchlorate[a]

pH[c]	k_{obsd} × 10^4, sec^{-1}	pH	k_{obsd} × 10^4, sec^{-1}
4.84	1.47	8.04	400
4.84	2.13	8.40	666
5.00	1.78	8.60	780
5.25	2.82	8.88	890
5.50	5.97	8.88	910
5.75	7.6	8.88	767
6.05	25.1	9.06	1900
6.43	44.7	9.11	1400
6.45	47.0	9.12	1160
6.97	92.5	9.36	2990
7.33	125	9.57	5350
7.35	168		
7.43	174		
7.43	162		
7.97	352	6.29[b]	4.11
		7.44[b]	98
		7.93[b]	133
		8.44[b]	133
		9.37[b]	523

[a] 25°, 0.1 M ionic concentration, other conditions as in Experimental Section. [b] pD. [c] Acetate buffer up to pH 5.75, phosphate to pH 7.43, and borate to pH 9.57.

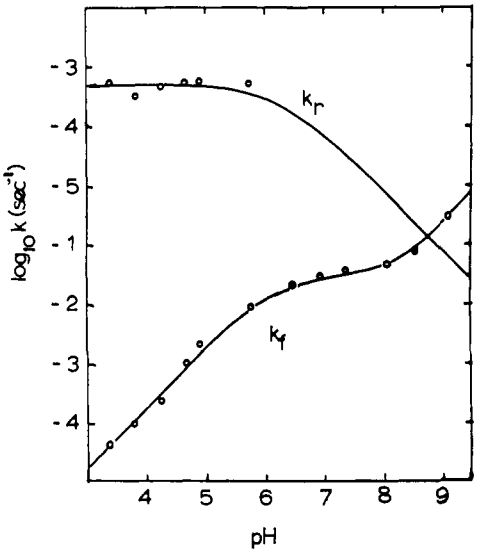


Figure 4. pH dependence of hydrolysis rate constant for 2-methyl-4,6-diphenylpyrylium chloride; 25°, 0.1 M ionic concentration. Lines are theoretical from eq 3 (k_f) and 4 (k_r) and data from Table V.

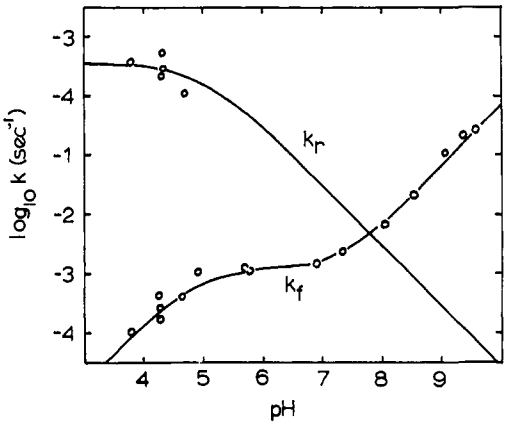


Figure 5. pH dependence of hydrolysis rate constant for 2,4,6-triphenylpyrylium tetrafluoroborate; 25°, 0.1 M ionic concentration. Lines are theoretical from eq 3 (k_f) and 4 (k_r) and data from Table V.

In a reaction involving an equilibrium the observed rate constant ($k_{obsd} = k_f + k_r$) can be transformed to

$$k_{obsd} = k_f[1 + (1/K)] \quad (2)$$

give eq 2. When K is large, the reaction proceeds completely to B and k_{obsd} is identical with k_f; if K is known, k_r and k_f can be calculated from k_{obsd} but in practice this is only possible when $10 > K > 0.1$.

The interconversion of pyrylium salt to pseudobase followed excellent first-order kinetics over 90% of the reaction. General base catalysis, ionic strength, and dielectric effects were observed. The effect of the last two was eliminated by the use of constant ionic strength (0.1 M) and no organic solvent (except acetonitrile used as the stock solvent, less than 2% final concentration). 0.1 M buffer concentration had negligible specific effect. The effect of deuterium oxide solvent was also studied for the trimethylpyrylium cation. Figures 3–5 illustrate the pH dependencies. The pH dependence of the forward reaction for the hydrolysis of all three salts (Tables I–III) followed eq 3 which also predicted the

$$k_f = k_{OH}[OH] + k_{H_2O}/(1 + a_H/K_a) \quad (3)$$

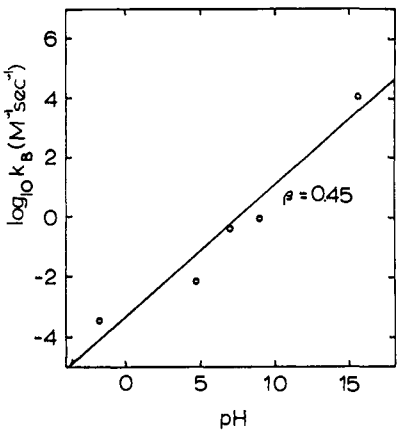


Figure 6. Brønsted relationship between k_B and pK_a of the conjugate acid of B. The data are from Table V and the line has an arbitrary slope of +0.45.

pH dependence of the forward reaction in D_2O (with appropriate substitution). The reverse rate constant (k_r) was determined for the two phenyl-substituted substrates and was only measured over a short pH range owing to the large K at higher pH's (Tables II and III).

Table II. Hydrolysis of 2,4,6-Triphenylpyrylium Tetrafluoroborate[a]

pH[e]	$k_{obsd} \times 10^4$, sec^{-1}	$k_f \times 10^4$, sec^{-1}	$k_r^b \times 10^4$, sec^{-1}	Δ_{400}[c]	K[d]
3.78	4.9	1.01	3.88	0.062	0.26
4.26	9.7	4.4	5.3	0.136	0.83
4.28	6.0	2.56	3.44	0.128	0.745
4.28	3.83	1.64	2.20	0.128	0.745
4.65	5.11	4.09	1.02	0.240	4.0
4.90	12.6	10.9		0.260	
5.69	12.6	12.6		0.270	
5.76	10.1	10.1		0.268	
6.91	14.7	14.7		0.264	
7.34	24.6	24.6		0.264	
8.04	65	65		0.324	
8.55	215	215		0.324	
9.06	1070	1070		0.354	
9.36	2190	2190		0.354	
9.57	2760	2760		0.300	

[a] 25°, 0.1 M ionic concentration, other conditions as in Experimental Section. [b] $k_r = k_f/K$. [c] Δ_{400} = total change in absorbance. [d] $K = \Delta_{400}/(0.3 - \Delta_{400})$. [e] Acetate buffer to pH 5.69, phosphate to pH 7.34, borate to pH 9.57.

Table III. Hydrolysis of 2-Methyl-4,6-diphenylpyrylium Chloride[a]

pH[e]	$k_{obsd} \times 10^4$, sec^{-1}	$k_f \times 10^4$, sec^{-1}	$k_r^b \times 10^4$, sec^{-1}	Δ_{350}[c]	K[d]
3.38	5.95	0.431	5.6	0.054	0.077
3.78	4.08	0.922	3.15	0.170	0.293
4.26	7.25	2.42	4.84	0.250	0.500
4.65	16.3	10.9	5.45	0.500	2.0
4.90	27.2	21	6.15	0.580	2.41
5.76	105	96.5	5.2	0.730	18.5
6.45	213	213		0.780	
6.91	284	284		0.700	
7.34	383	383		0.765	
8.04	480	480		0.770	
8.55	810	810		0.740	
9.06	3110	3110		0.730	

[a] 25°, 0.1 M ionic concentration, other conditions as in Experimental Section. [b] $k_r = k_f/K$. [c] Δ_{350} is the change in absorbance. [d] $K = \Delta_{350}/(0.75 - \Delta_{370})$. [e] Acetate buffer to pH 5.76, phosphate to pH 7.34, borate to pH 9.06.

The experimental values of k_r are fitted to the theoretical equation (4) as in Figures 4 and 5. K_a in eq 4 is not related to K_a'.

$$k_r = k_r^0(1 + K_a/a_H) \quad (4)$$

Catalysis by buffers was studied with the trimethylpyrylium cation using borate, phosphate, and acetate buffers at different pH's (Table IV). The close similarity of k_B (see Discussion for meaning of k_B) for each buffer (but different buffer ratio) indicates the absence of acid catalysis. The general base terms are collected in Table V and Figure 6 shows how k_B varies with the pK_a of the base catalyst.

Table IV. General Base Catalysis. Trimethylpyrylium Cation[a]

Buffer	pH	Concn, M	k, sec^{-1}	k_B, M^{-1} sec^{-1}
Borate	8.04	0.05	5.1×10^{-2}	
		0.025	4.65×10^{-2}	
		0.005	4.1×10^{-2}	9.3×10^{-1}
	Intercept = 4.0×10^{-2} sec^{-1}			
	8.60	0.05	1.2×10^{-2}	
		0.025	9.4×10^{-2}	
		0.005	7.95×10^{-2}	9.0×10^{-1}
	Intercept = 7.8×10^{-2} sec^{-1}			
Phosphate	6.45	0.04	0.99×10^{-2}	
		0.02	0.75×10^{-2}	
		0.004	0.5×10^{-2}	4.4×10^{-1}
	Intercept = 0.47×10^{-2} sec^{-1}			
	7.35	0.032	3.0×10^{-2}	
		0.016	2.25×10^{-2}	
		0.0032	1.84×10^{-2}	4.55×10^{-1}
	Intercept = 1.68×10^{-2} sec^{-1}			
Acetate	5.00	0.2	1.49×10^{-3}	
		0.1	0.80×10^{-3}	
		0.02	0.3×10^{-3}	0.91×10^{-2}
	Intercept = 1.8×10^{-4} sec^{-1}			
	5.75	0.2	2.38×10^{-3}	
		0.1	1.65×10^{-3}	
		0.02	0.87×10^{-3}	0.89×10^{-2}
	Intercept = 0.76×10^{-3} sec^{-1}			

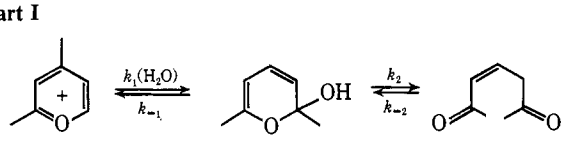
[a] 25°, 0.1 M ionic concentration.

Discussion

The pH dependence of k_f in the hydrolysis of pyrylium salts is expected to consist of a plateau region (attack of water) and a region where k_f increases linearly with pOH (hydroxide ion attack).

The existence of an apparent titration indicates that an intermediate deprotonates to give a reactive species or is formed with the simultaneous release of a proton. Overall, it is formally necessary that a proton is liberated in either a fast or slow step to yield a reactive intermediate. The simplest mechanism (see Chart I)

Chart I



$+ H_3O^+$

$$k_f = k_1k_2(H_2O)/(k_{-1}a_H + k_2)$$

$$k_r = k_{-1}k_{-2}a_H/(k_{-1}a_H + k_2)$$

conforming with these criteria involves attack of water on the pyrylium nucleus α to the ring oxygen (attack may be aided by general bases). The cyclic hemiacetal then decomposes *via* a pH-independent pathway (muta-

Table V. Collection of Kinetic and Thermodynamic Data[a]

Substrate cation	$k_r^0 \times 10^{-4}$, sec^{-1}	$k_{H_2O} \times 10^2$, sec^{-1}	$k_{OH} \times 10^{-4}$, $M^{-1}\ sec^{-1}$	K_a, M	K_a', M
Trimethyl-pyrylium		2.1 ± 0.1	1.3 ± 0.1	$10^{-6.7}$	
		1.3 ± 0.1[b]	1.4 ± 0.1[b]	$10^{-7.6}$ [b]	
Methyl-diphenyl-pyrylium	5 ± 0.2	3.2 ± 0.1	2.5 ± 0.1	$10^{-6.2}$	$10^{-4.4}$
Triphenyl-pyrylium	3 ± 0.2	0.13 ± 0.01	0.65 ± 0.05	$10^{-5.0}$	$10^{-3.3}$

General Base Terms for Trimethylpyrylium Cation[a]

Base	pK_a	k_B, $M^{-1}\ sec^{-1}$
Borate	8.0	9.2×10^{-1}
Phosphate	7.0	4.5×10^{-1}
Acetate	4.7	0.9×10^{-2}
Water	−1.7	3.78×10^{-4} [c]
Hydroxide	15.6	1.26×10^{4}

[a] 25°, 0.1 M ionic concentration. [b] Deuterium oxide term. [c] k_B for water equals $k_{H_2O}/55.5$.

rotation of glucose, an analogous reaction, is pH independent from 2 to 7.5[9]) to yield diketone or reacts with a proton to reconstitute pyrylium ion. The derived kinetic equations are included in the chart for the forward and reverse reactions. The mechanism is formally similar to that giving rise to the titration at acid pH's in the hydrolysis of other substrates not possessing an ionizable group[10] and is a special case of a general one where a base attracts a proton from the water attacking the pyrylium nucleus to form the conjugate acid.

Equation 5 governs the kinetics for this mechanism

$$k_f = \frac{k_1[\text{base}]}{\frac{k_{-1}}{k_2}[\text{acid}] + 1} \qquad (5)$$

and it is important to investigate this equation in order to assign the observed rate constants to reactions. In the case of bases other than water (acetate, phosphate, and borate) k_f should only be linear in base concentration at low buffer concentrations where (k_{-1}/k_2) [acid] < 1. The results on Table IV show k_f to be linear in [B], thus the calculated k_B is equivalent to k_1 in eq 5. Since k_{OH} fits the Brønsted relationship with these bases, it is probable that k_{OH} is also a true k_1. The Brønsted exponent (~0.45) for the action of general bases and the solvent deuterium isotope effects are in accord with the above general mechanism.

The decomposition of the hemiacetal should be pH independent within the range studied here in order to satisfy the pH dependence of k_1 (k_f) predicted from the mechanism. The pathway (for k_2) involving a protonated ether oxygen and an alcoholate anion (Chart II) can be eliminated since the microscopic reverse mechanism involves enolization of the ketone product. A value for this rate constant can be estimated (~10^{-6} sec^{-1} at pH 7) using data from Bell[11] which are too small to accommodate the observed reverse rate constant (~4.10^{-4} sec^{-1}, see Table V) for the methyldiphenyl derivative. The principle of microscopic reversibility rules out this mechanism for the forward path and we suggest the mechanism shown in Chart III

Chart II

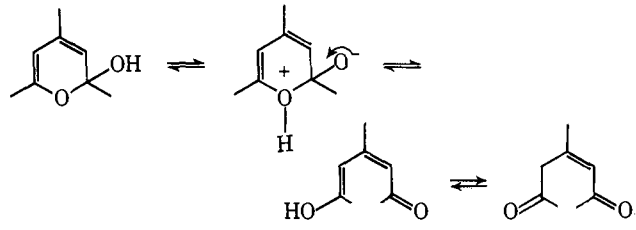
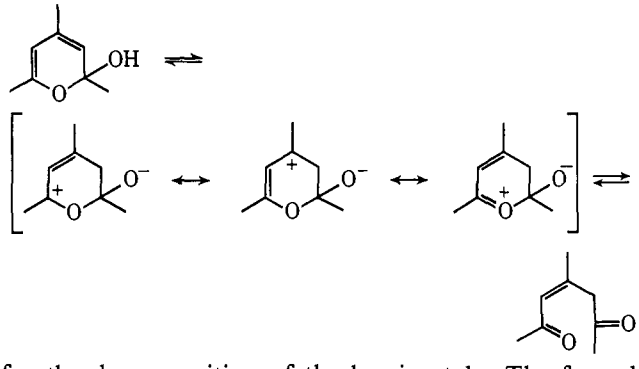


Chart III



for the decomposition of the hemiacetal. The formal similarity between the decomposition of the hemiacetal and the mutarotation of glucose is not reflected in the detailed mechanism which in the latter case involves a proton transfer to the ring oxygen.

Attack of water at the 2-methyl-4,6-diphenylpyrylium cation is at C_2 (adjacent to methyl) because comparison of the nucleophilic rate data (Table V) shows that the trimethyl- and methyldiphenylpyrylium salts react with nucleophiles with a similar rate constant about tenfold faster than the triphenyl salt. The selectivity of the reactions of water and hydroxide with the three pyrylium salts is similar in the methyldiphenyl- and trimethylpyrylium hydrolyses but is larger for the triphenyl case; this difference reflects the difference in reactivity of the pyrylium salts where the triphenylpyrylium cation is less reactive than the trimethyl one.

The phenyl-substituted pyrylium salts have acidities close to that of acetic acid and the relative values (trimethyl more acid than triphenyl) are in accord with the stabilization of the pyrylium nucleus rather than the diketone pseudobase by the phenyl substituents.

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