1068. *The Mechanism of Solvolysis of γ-Phenyltetronic Acid Enol Esters. Part I. A Conductometric Study of the Methanolysis of γ-Phenyltetronic Acid Enol Benzoate.*

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The methanolysis of γ-phenyltetronic acid enol benzoate under initially neutral or under basic conditions involves acyl–oxygen fission and is of the first order in ester. In the presence of pyridine and of its methyl derivatives, the first-order rate coefficients are linearly dependent on the concentration of base. The second-order rate constants obeyed the Brönsted relation, indicating general base catalysis.

γ-Phenyltetronic acid (I) is an αβ-unsaturated lactone. It has been shown that in the tautomeric equilibrium, the enol form (I) predominates in polar solvents. It is a stronger acid than acetic acid; its pK_a in water is approximately the same (3·76) as that of unsubstituted tetronic acid.[1] The primary interest in γ-phenyltetronic acid enol esters (cf. II) is that they can be considered as a type of mixed anhydride. Characteristic of the solvolysis of acetic anhydride is the catalysis by bases, such as tertiary amines,[2,3] carboxylic anions,[4] nitrite ions,[5] hydroxyl ions,[6] and methoxide ions.[3] It was of interest to examine first the neutral methanolysis of γ-phenyltetronic acid enol benzoate, and then the effect of bases, with a view to establishing the mechanism of solvolysis.

The Mode of Fission and the Products of Reaction.—The mode of fission can be established by the Cohen and Schneider criterion,[7] by which the position of bond fission in solvolysis is proved directly by the nature of the products. Acyl–oxygen fission (1) would lead to

[1] Haynes and Plimmer, *Quart. Rev.,* 1960, 292.
[2] Gold and Jefferson, *J.,* 1953, 1409, 1416; Bafna and Gold, *J.,* 1953, 1406.
[3] Koskikallio, *Suomen Kem.,* 1959, **32,** B, 41.
[4] Kilpatrick, *J. Amer. Chem. Soc.,* 1928, **50,** 2891; 1930, **52,** 1410, 1418.
[5] Lees and Saville, *J.,* 1958, 2262.
[6] Koskikallio, *Ann. Acad. Sci. Fennicae,* 1954, **11,** A, 57.
[7] Cohen and Schneider, *J. Amer. Chem. Soc.,* 1941, **63,** 3382.

methyl benzoate and γ-phenyltetronic acid, whereas alkyl–oxygen fission (2) would yield *O*-methyl-γ-phenyltetronic acid and benzoic acid. It was found that acyl–oxygen fission occurs during methanolysis of the ester under both initially neutral and basic conditions, at 55° and 95°, the former being the temperature at which all the kinetic work was done. Thus an 18·1mM-solution of ester gave on titration (Thymol Blue–Methyl Red mixed
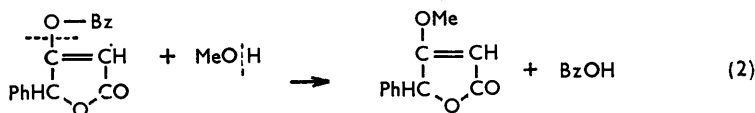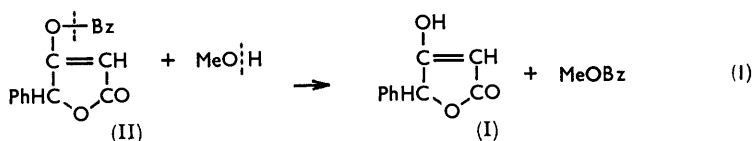
indicator at room temperature) the theoretical amount (99·5%) of γ-phenyltetronic acid. The methanol was removed from the titrated solution, and the residue extracted with ether. The oil recovered from the dried extract was hydrolysed with an excess of 0·1N-sodium hydroxide for 3 hours at 100°. From back-titration of the excess alkali it was found that the concentration of methyl benzoate was 17·5 mmoles l.$^{-1}$ (95·0%). Pure benzoic acid was recovered by acidification of the titrated solution. The methyl ether is stable to alkali and so the 95% of methyl benzoate and 99·5% of γ-phenyltetronic acid establishes acyl–oxygen fission on alkaline methanolysis.

The same procedure was adopted with runs under kinetic conditions, with a time of heating of the order of ten half-lives (see Table 1). These results and those given below show conclusively that under both initially neutral and initially basic conditions, acyl-oxygen fission occurs.

RESULTS

Kinetics of the Neutral Methanolysis.—Because of the methanolysis in the presence of alkali, direct titration could not be used for estimating the extent of reaction. Use was made of the solubilities of γ-phenyltetronic acid and its benzoate in water. To a methanolic solution (10 ml.) of γ-phenyltetronic acid and its benzoate, water (100 ml.) was added and the precipitated ester was filtered off. The filtrate was titrated with phenolphthalein as indicator. The precipitate was dissolved in methanol and titrated to the mixed indicator referred to above. Two experiments gave γ-phenyltetronic acid 98, 102%, and γ-phenyltetronic acid enol benzoate 107, 110%. This technique was then applied to a kinetic run at 55°. The results are shown in Table 2, concentrations being in mmole l.$^{-1}$. Analysis of these results by the first-order rate law gave $10^5 k_1 = 1\cdot91$ sec.$^{-1}$. There was no fall off in rate constant as the reaction proceeded.

The analytical method was not used in the comprehensive study, since it was tedious and not very accurate. As γ-phenyltetronic acid is a moderately strong acid, conductance was

TABLE 1.

Product analysis of reactions at 55°.

Base	Time of heating (hr.)	MeOBz (%)	Acid * (%)	Base	Time of heating (hr.)	MeOBz (%)	Acid * (%)
None	100	98·5	92·5	2-Picoline	12	—	52·5
	1200	68·5	27·0		21	106	36·3
Pyridine	6	82	—	2,6-Lutidine ...	6	88	106
	24	103	51·6	2,4,6-Collidine	6	97·5	87·5
				0·1N-NaOH ...	—	95·0	99·5

* γ-Phenyltetronic acid.

TABLE 2.

The rate of neutral methanolysis at 55°.

Time (hr.)	3·05	4·00	6·10	8·00	10·70	15·00	23·50
Concn. of ester	27·4	29·6	27·9	23·4	18·6	12·9	7·9
Concn. of ester (as acid)	—	29·4	28·0	23·4	18·2	14·3	7·7

TABLE 3.

Increase of specific conductance of methanolic γ-phenyltetronic acid with time.

Time (hr.)	0	25·5	49	97	144	164	189	213	240	264	312	408
λ_s (μmho cm.$^{-1}$)	17·8	18·2	18·8	20·2	20·8	21·4	22·1	22·6	23·0	23·7	24·3	26·3

measured instead. However, two difficulties occurred. First it was impossible to obtain reproducible calibration curves for γ-phenyltetronic acid in methanol, presumably because of traces of conducting impurity in the acid. Secondly, the specific conductance (λ_s) of methanolic solutions of the acid at 55° increases slowly with time (Table 3); the relation is approximately linear. This made λ_s at the completion of methanolysis difficult to determine.

From conductance measurements on the ester undergoing methanolysis it is found that the change in λ_s with time can be divided into two parts, the first fast, and the second slow (Fig. 1). The fast part lasts about a day, whereas the slow can be studied over weeks. The fast part is the neutral methanolysis of the ester; the slow part is due to some subsequent reaction of either or both of the products.

Arising from the initial attempts to obtain calibration curves of specific conductance against concentration of the acid it was found that the relation

$$c/\lambda_s = \alpha + \beta\lambda_s \tag{3}$$

was reasonably well obeyed, where α and β are constants and c is the concentration of γ-phenyltetronic acid. The following iterative method was devised to determine α and β, based on a trial value of k_1, namely, $k_1{}^0$.

Now

$$d\lambda_s/dt = (d\lambda_s/dc)(dc/dt) \tag{4}$$

and

$$d\lambda_s/dc = (\alpha + 2\beta\lambda_s)^{-1} \tag{5}$$

$$dc/dt = k_1(c_\infty - c)$$
$$= k_1[\alpha(\lambda_s{}^\infty - \lambda_s) + \beta\{(\lambda_s{}^\infty)^2 - \lambda_s{}^2\}] \tag{6}$$

Hence substituting (5) and (6) in (4) gives:

$$d\lambda_s/dt = k_1[\alpha(\lambda_s{}^\infty - \lambda_s) + \beta\{(\lambda_s{}^\infty)^2 - \lambda_s{}^2\}]/(\alpha + 2\beta\lambda_s). \tag{7}$$

If $\lambda_s = 0$ when $t = 0$, then

$$(d\lambda_s/dt)_0 = (k_1/\alpha)[\alpha\lambda_s{}^\infty + \beta(\lambda_s{}^\infty)^2] \tag{8}$$

$$= k_1[1 + \omega\lambda_s{}^\infty]\lambda_s{}^\infty \tag{9}$$

where $\omega = \beta/\alpha$. If now the observed conductance at time t, λ_s', is plotted against t for the first 60 minutes, $\lambda_s{}^0$ and $(d\lambda_s/dt)_0$ may be obtained. In this way, λ_s ($= \lambda_s' - \lambda_s{}^0$) may be obtained as a function of time. Further, from a plot of λ_s' against t for the first 300 hours, $(\lambda_s{}^\infty)'$ may be obtained by extrapolation to zero time, the points for the first 60 hours being neglected. Thus $\lambda_s{}^\infty$ [$= (\lambda_s{}^\infty)' - \lambda_s{}^0$] is obtained, and also a correction factor for the rate of change of the conductance of γ-phenyltetronic acid with time. The λ_s values are then corrected for this effect. Next an estimate of $k_1{}^0$ is made and equation (9) solved for ω^0. Superscripts 0, 1, 2, . . . refer to the zero, first, second . . . approximation. Equation (3) may be written as

$$c/\lambda_s = \alpha(1 + \omega\lambda_s) \tag{3'}$$

and, when c_∞ and $\lambda_s{}^\infty$ are known, it may be solved for α^0. β^0 is then obtained from $\beta^0/\alpha^0 = \omega^0$. From the values of λ_s at time t, c can be obtained from equation (3) or (3').

The next step is to calculate $k_1{}^1$ the second approximation from the c values, and repeat the procedure with this value of k_1. This will lead to ω^1, α^1, and β^1, and hence to a new set of c

values and thus $k_1{}^2$. The procedure may be repeated until successive values of k_1 do not differ by more than 2%. Three cycles are usually sufficient. Rate constants obtained in this fashion are shown in Table 4 and lead to the mean value $10^5 k_1 = 2\cdot25$ sec.$^{-1}$, in reasonable agreement with the value obtained from the analytical method reported earlier.

The possibility of catalysis by the platinum electrodes was investigated by using a cell with wire electrodes. The cell constant was $0\cdot671$ cm.$^{-1}$ compared with the usual $0\cdot03$—$0\cdot06$ cm.$^{-1}$.

TABLE 4.

k_1 for neutral methanolysis at 55°.

c_{ester} (mmole l.$^{-1}$)	73·8	36·3	36·7	24·6	22·2	21·3
$10^5 k_1$ (sec.$^{-1}$)	2·23	2·23	2·24	2·11	2·72	1·94

TABLE 5.

The lack of catalysis by platinum.

Time (hr.)	0	2	4	6	8	10	12
$\Delta\lambda_s$ (μmho cm.$^{-1}$)	0	3·61	5·29	6·52	7·54	8·33	9·00
$\Delta\lambda_s$ (μmho cm.$^{-1}$) for wire electrode cell	0	3·45	5·16	6·27	7·25	8·01	8·68

The results (Table 5) led to first-order rate constants of $2\cdot13 \times 10^{-5}$ sec.$^{-1}$ in each case and show that the electrode surface has no significant influence on the rate of reaction.

In assigning a mechanism to the reaction which has been shown to be of the first order in ester (Table 4) over the concentration range 20—70 mmole l.$^{-1}$, use is made of two general criteria. In the case of a bimolecular attack of the solvent molecule at the carbonyl centre of the ester, the rate of reaction would be affected by steric hindrance and subject to base catalysis.[8] The rate of initially neutral methanolysis of γ-phenyltetronic acid enol acetate is appreciably greater than that of the benzoate.[9] Again, methanolysis in the presence of 8·7 mmoles l.$^{-1}$ of sodium methoxide was found to be too fast to follow. The same was observed in the presence of 10 mmoles l.$^{-1}$ of piperidine. However, pyridine, 2-picoline, 2,6-lutidine, and 2,4,6-collidine were found to be of a convenient basic strength for their catalytic influence to be studied under the experimental conditions used for the neutral runs. This work is described in the next section, but, anticipating the results, it may be noted that the dependence of $k_1{}^B$ upon base is given by

$$k_1{}^B = k_1{}^N + k_2{}^B[B], \qquad (10)$$

and that $k_1{}^N$ is obtained in this fashion and agrees within the experimental error with that derived from the neutral runs.

Analysis of the concentration–time data for the neutral reaction shows that there is no fall-off in rate coefficient as the reaction proceeds. This eliminates the possibility that the methoxide ion is the attacking agent under initially neutral conditions, as the concentration of methoxide ions would be progressively reduced as the concentration of γ-phenyltetronic acid increases during reaction. The conclusion to be drawn from these experiments is that methanolysis proceeds by attack of methanol upon the ester, leading to first-order kinetics.

Kinetics of the Base-catalysed Methanolysis.—It was found that the conductance of γ-phenyl-tetronic acid in the presence of bases such as pyridine or its methyl derivatives is sufficiently high for traces of conducting impurities to be without noticeable effect, in contrast with the behaviour in the absence of base. Reproducible calibration curves were obtained for different samples of both acid and methanol. For fast reactions (in presence of high concentrations of base) λ_s for a given concentration of ester calculated from the calibration curve was equal to the observed value after ten half-lives. Moreover, infinity values in terms of acid concentrations obtained by the Swinbourne method [10] were in fair agreement with those calculated on the basis of the weight of ester taken (Table 6). In view of this, rate constants in the presence of bases were evaluated by use of a calibration curve in which specific conductance is plotted against concentration of acid (Fig. 2). Along with the calibration points are points representing the infinity values for a number of runs. That all fit on a common line further justifies the use of calibration curves. Similar curves were obtained for 1-picoline, 2,6-lutidine, and 2,4,6-collidine. Methanolysis in all cases followed first-order kinetics, the constant $k_1{}^B$

[8] Ingold, " Structure and Mechanism in Organic Chemistry," Bell, London, 1953, pp. 400, 321.
[9] Konasiewicz, *J.*, 1961, following paper.
[10] Swinbourne, *J.*, 1960, 2371.

being obtained from a plot of log $(c_\infty - c_t)$ against time. The c_t values were obtained from a smoothed curve of concentration values in turn obtained from the calibration curve. A typical plot is shown in Fig. 3. From each of the runs, $k_2{}^B$ was calculated from $k_2{}^B = (k_1{}^B - k_1{}^N)/[B]$, or from the slope of a plot of $k_1{}^B$ against [B]. The intercept gave $k_1{}^N$. Typical rate
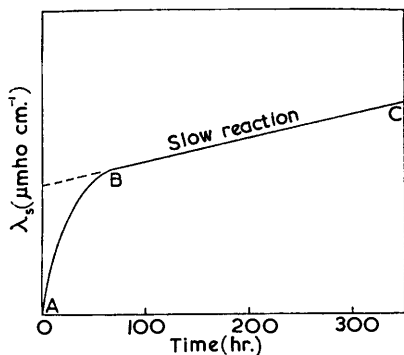

FIG. 1. Variation of conductance with time in the neutral methanolysis of γ-phenyltetronic acid enol benzoate.

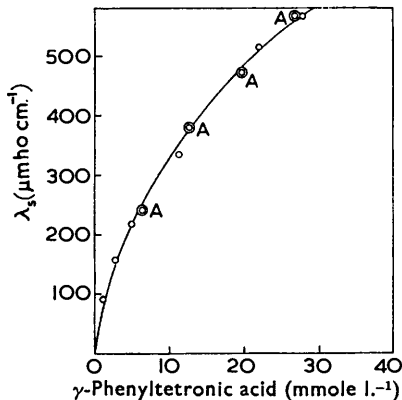The intercept give $\Lambda_s{}^\infty$. A—B = Methanolysis; B—C slow reaction.

FIG. 2. The specific conductance of γ-phenyltetronic acid in methanol containing 200 mmoles l.$^{-1}$ of pyridine.

A = Infinity points from kinetic runs; others are calibration points.
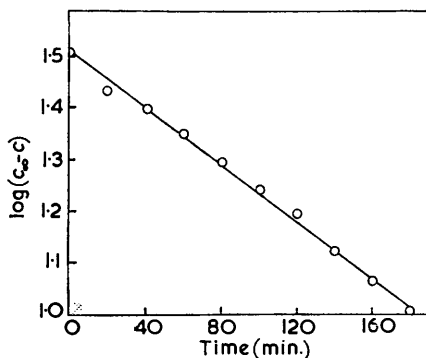

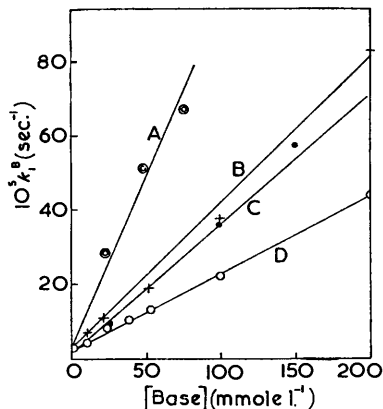FIG. 3. A typical first-order log plot.

FIG. 4. The dependence of first-order rate constants on the concentration of base.

A, 2,4,6-Collidine.   B, 2,6-Lutidine.
C, 2-Picoline.   D, Pyridine.

constants for reactions in methanol containing 51·7 mmoles l.$^{-1}$ of pyridine are shown in Table 7. The reaction is clearly of the first order. Two runs were done at an initial ester concentration of about 20 mmoles l.$^{-1}$, one in the wire electrode cell, the other in the presence of 19·0 mmoles l.$^{-1}$ of γ-phenyltetronic acid in methanol containing 200 mmoles l.$^{-1}$ of pyridine. The rate constants were $4·75 \times 10^{-4}$ and $4·51 \times 10^{-4}$ sec.$^{-1}$, to be compared with the mean of six determinations, namely, $4·49 \times 10^{-4}$ sec.$^{-1}$. Again there was no catalysis by platinum or inhibition by acid. The latter was also shown to be true for 2-picoline and collidine. The plots of $k_1{}^B$ against [B] for the four bases are shown in Fig. 4, the complete experimental results being recorded in the

experimental section. For pyridine, values were calculated from $k_2{}^B = (k_1{}^B - k_1{}^N)/[B]$ with $k_1{}^N$ taken as $2\cdot23 \times 10^{-5}$ sec.$^{-1}$, as shown in Table 8; these gave a mean value of $k_2{}^B$ of $2\cdot15 \times 10^{-6}$ l. mmole^{-1} sec.$^{-1}$ or $2\cdot15 \times 10^{-3}$ l. mmole^{-1} sec.$^{-1}$. Values of $k_2{}^B$ for the other bases, together with pK_b values in water are shown in Table 9.

Some runs were done in the presence of quinine (pK_b 6·66). Good first-order behaviour was observed, but in base concentrations of 10 and 16·4 mmoles l.$^{-1}$, the mean values of $k_2{}^B$ were $5\cdot6 \times 10^{-2}$ and $10\cdot4 \times 10^{-2}$ l. mole^{-1} sec.$^{-1}$, respectively. $k_1{}^B$ thus increases much more rapidly than [B]. This was thought to be associated with the diacidic character of the base, and the runs were not pursued further.

DISCUSSION

The Mechanism of the Reaction.—Base-catalysed methanolysis may involve (1) the nucleophilic attack of the base at the carbonyl centre, (2) specific base catalysis by methoxide ions formed by the interaction of the base with the solvent, or (3) general base

TABLE 6.

Infinity values of λ_s (concns. in mmole l.$^{-1}$).

Base	Pyridine	2-Picoline	2,6-Lutidine	2,4,6-Collidine	Quinine
Concn. (wt. of ester)	19·2	10·8	9·7	18·7	9·08
Concn. (Swinbourne)......	19·8	10·9	10·5	18·8	9·00

TABLE 7.

Rate constants for reaction in methanol containing 51·7 mmole l.$^{-1}$ of pyridine.

Concn. of ester (mmole l.$^{-1}$)	12·8	14·1	21·9	27·5	36·8	38·8	42·8
$10^5k_1{}^B$ (sec.$^{-1}$)	13·1	13·2	13·3	12·7	13·1	12·7	13·7

TABLE 8.

Values of $k_2{}^B$ for B = pyridine.

Concn. of base (mmole l.$^{-1}$)	10·1	24·4	39·5	51·7	100	200
$10^5k_1{}^B$ (sec.$^{-1}$)	4·39	8·50	10·1	13·1	22·2	44·9
$10^6k_2{}^B$ (l. mmole^{-1} sec.$^{-1}$)	2·12	2·57	1·99	2·10	2·00	2·13

TABLE 9.

Catalytic rate constants.

Base	Pyridine	2-Picoline	2,6-Lutidine	2,4,6-Collidine
pK_b	8·78 [11]	8·04 [11]	7·28 [11]	6·55 [12]
$10^3k_2{}^B$ (l. mmole^{-1} sec.$^{-1}$)	2·15	3·29	3·89	10·2

catalysis. Mechanism (1) can be eliminated by the fact that α-methylpyridines should be subject to steric hindrance, and so the rate of methanolysis should be depressed. This is not observed; in fact the rate of methanolysis increases, though not linearly, with the strength of the base. In the second case, methoxide ions would be formed by the inter-action of the base with the solvent

$$B + MeOH \rightleftharpoons BH^+ + MeO^- \qquad (11)$$

The methoxide ion concentration would thus be proportional to $[B]/[BH^+]$ and conse-quently the rate of reaction would be directly proportional to the basic strength of the catalyst. This is not observed. Also the equilibrium (11) would be affected both by the acid formed during the reaction, and by initially added acid. γ-Phenyltetronic acid (TH) is a stronger acid than methanol:

$$TH + B \rightleftharpoons T^- + BH^+ \qquad (12)$$

and thus the equilibrium (12) would be of much greater importance than (11). Under these conditions the methoxide ion concentration would become proportional to $[T^-]/[TH]$ and a decrease in rate, either as the reaction proceeds or in the presence of added acid,

[11] Andon, Cox, and Herrington, *Trans. Faraday Soc.*, 1954, **50**, 918.
[12] Golombic and Orchin, *J. Amer. Chem. Soc.*, 1957, **79**, 2365.

would be expected. Neither of these is observed, so mechanism (2) may be excluded. The methanolysis is thus unambiguously general-base catalysed.
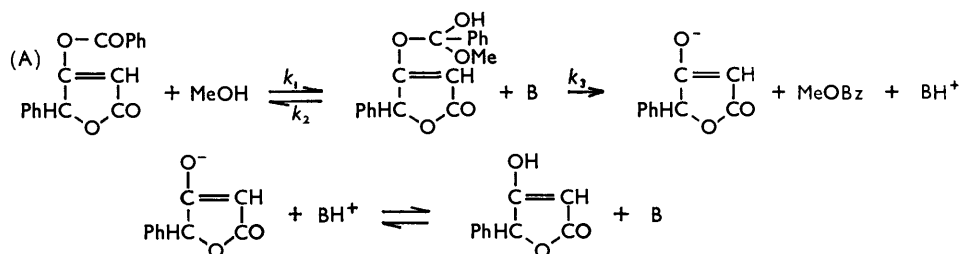
Either a bimolecular or a termolecular mechanism is consistent with the observed facts. Thus the bimolecular mechanism may be written as (A) and, for $k_2 \gg k_3[B]$, the kinetic equation is

$$d[P]/dt = k_1 k_3 [A][B][S]/k_2, \tag{13}$$

where [P], [A], and [S] represent the concentrations of products, ester, and methanol, respectively. This implies a pre-equilibrium, with the attack of the base on the complex rate-determining. Scheme (B) would also give the same kinetic behaviour, namely:

$$d[P]/dt = K_b k_3 k_5 [A][B][S]/k_4, \tag{14}$$

where K_b is the basic dissociation constant of the base B in methanol.

Alternatively a termolecular mechanism involving (C) or (D), namely synchronous attack by MeOH and B or by MeO⁻ and BH⁺, would give the same dependence of rate on reagent concentrations.
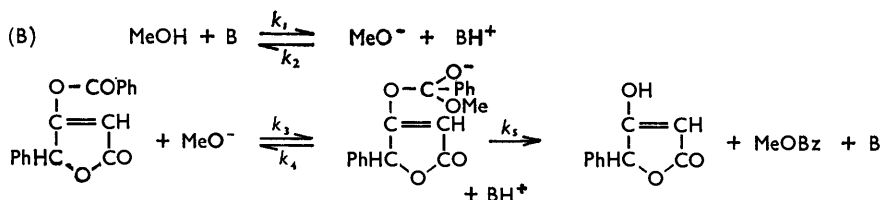
In the present work, a marked increase in rate constant (k_2) was observed as the basic strength of the catalyst increased, namely, collidine > lutidine > picoline > pyridine. This result, as has been shown, precludes the possibility of nucleophilic attack by the base, which *a priori* might have seemed the most probable mechanism. Preliminary results on γ-phenyltetronic acid enol acetate gave the k_2 sequence pyridine > collidine > lutidine > picoline, and it seems that in this case the smaller size of methyl than of phenyl permits nucleophilic attack.

Following Brönsted,[13] we write:

$$k_2^B = G K_b^\beta, \tag{15}$$

where G is a constant and K_b is the basic dissociation constant. Equation (15) may be written

$$\log k_2^B = \log G + \beta \log K_b = \log G - \beta.pK_b, \tag{16}$$

and hence a plot of log k_2^B against pK_b should yield a straight line. A difficulty occurs in that, while the kinetics were investigated in absolute methanol, pK_b values are obtainable only for aqueous solutions. However, Bell[14] has shown that for a series of similar bases $K_b(MeOH)/K_b(H_2O)$ is a constant, and expression (16) will still hold in these circumstances. There is also the temperature dependence of K_b to consider. The plot is shown in Fig. 5, the slope of the line yielding the value 0·3 for β. Such a relation has

[13] Brönsted, *Chem. Rev.*, 1928, **5**, 322.
[14] Bell, " The Proton in Chemistry," Methuen, London, 1959, p. 44.

been found in a number of cases, such as the mutarotation of glucose in aqueous solution,[15] the decomposition of nitramide in isopentyl alcohol [16] and *m*-cresol,[17] the reaction of acetic anhydride [18] with certain bases, and the hydrolysis of *p*-nitrophenol acetate.[19]

(C) (D)
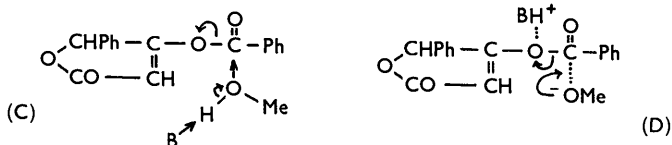
The same mechanistic ambiguity that exists for base catalysis also exists for the neutral reaction. The second-order rate constant, k_2^N, obtained by dividing k_1^N by the concentration of methanol, has the value 9.8×10^{-7} l. mole^{-1} sec.$^{-1}$. This fits roughly
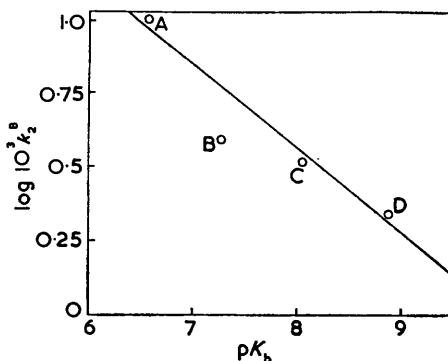

FIG. 5. The Brönsted relation between
log k_2^B and pK_b.

A, 2,4,6-Collidine. B, 2,6-Lutidine.
C, 2-Picoline. D, Pyridine.

on the Brönsted plot, when the value p$K_{auto.}$ = 16·7 is used for methanol.[20] Thus methanol takes the place of the base B in the mechanism proposed for basic catalysis. In this case the distinction between general base catalysis and nucleophilic catalysis [21] is lost. Since all mechanisms lead to a third-order rate law, the appropriate third-order constants are listed in Table 10. The value of k_3^{Py}/k_3^N is about 2000, which is of the same order of magnitude as that (1500) found by Koskikallio [3] for the methanolysis of acetic anhydride.

TABLE 10.

Third-order rate constants.

Base	Methanol	Pyridine	2-Picoline	2,6-Lutidine	2,4,6-Collidine
$10^5 k_3^B$ (l.^{2} mole^{-2} sec.$^{-1}$)	0·0041	9·0	14	16	43

EXPERIMENTAL

Preparation of Materials.—Methanol was purified by distillation through a 3-ft. column packed with glass helices. The specific conductance was 0·3—0·4 μmho cm.$^{-1}$. γ-Phenyl-tetronic acid was obtained from *O*-acetylmandelyl chloride and diethyl malonate.[22] A typical sample had m. p. 127°.

γ-Phenyltetronic acid enol benzoate was prepared by either of the following methods. The acid (I), dissolved in 2N-sodium carbonate, was shaken with a slight excess of benzoyl chloride until the product crystallised. The latter was suspended in an ice-cold solution of sodium hydrogen carbonate, filtered off, and twice recrystallised from light petroleum (b. p. 60—80°).[23]

[15] Brönsted and Guggenheim, *J. Amer. Chem. Soc.*, 1927, **49**, 2554.
[16] Brönsted and Vance, *Z. phys. Chem.*, 1933, *A*, **163**, 240.
[17] Brönsted, Nicholson, and Delbanco, *Z. phys. Chem.*, 1934, *A*, **169**, 379.
[18] Gold and Jefferson, *J.*, 1953, 1409.
[19] Jencks and Carriuolo, *J. Amer. Chem. Soc.*, 1960, **82**, 1778.
[20] Hammett, " Physical Organic Chemistry," McGraw-Hill, New York, 1940, p. 256.
[21] Bender, *Chem. Rev.*, 1960, **60**, 53.
[22] Haynes, Plimmer, and Stanners, *J.*, 1956, 4661.
[23] Jamieson, Ph.D. Thesis, Edinburgh, 1959.

Alternatively the acid was treated in cooled pyridine with an excess of benzoyl chloride. The solid was filtered off, washed with dilute hydrochloric acid and ice-cold sodium hydrogen carbonate solutions until free from pyridine and acid, then recrystallised as above. A typical specimen had m. p. 110° (Found: C, 72·9; H, 4·4. Calc. for $C_{17}H_{12}O_4$: C, 72·9; H, 4·3%) and no more than 0·6% of non-acid impurities as determined by titration of a methanolic solution with alkali, Thymol Blue–Cresol Red being used as indicator.

Pyridine was purified *via* the zinc chloride salt,[24] and other bases by distillation.

Kinetic Methods.—The conductance cells were of a conventional type with bright platinum electrodes. The cells used for most runs had constants in the range 0·03—0·06 cm.$^{-1}$; a cell with platinum wire electrodes had a cell constant of 0·671 cm.$^{-1}$. Conductance measurements were done with an a.c. bridge, the accuracy being about $\pm 0·2\%$. The thermostat temperature was 54·95° $\pm$ 0·01°. All basic solutions were made up volumetrically, by dissolving a given weight, in methanol. Solutions for the kinetic runs were prepared by dissolving a known weight of ester in 25 ml. of solvent that had been heated to 55°. The conductance cell was then filled by means of a pipette and λ_s was measured at intervals. From the appropriate calibration curve, in the case of the base-catalysed reaction, concentration was obtained as a function of time, and rate constants were calculated from the first-order law.

Kinetic Results.—The results are tabulated here (concentrations in mmole l.$^{-1}$).

Base: Pyridine.

[Base]	1·00 ^{a}	← 10·1 →				← 24·4 →				
[Ester]	36·1	15·1	16·9	22·4	32·1	15·7	20·8	21·7	21·6	21·7
10^5k_1 (sec.$^{-1}$)	2·38	4·25	4·58	4·42	4·30	8·31	8·13	8·39	8·85	8·82
10^5k_1 (sec.$^{-1}$ mean)	2·38			4·39				8·50		

[Base]	← 39·5 →				← 51·7 →						
[Ester]	16·8	17·7	22·4	32·9	12·8	14·1	21·9	27·5	36·8	38·8	42·8
10^5k_1 (sec.$^{-1}$)	9·98	9·44	10·70	10·30	13·1	13·2	13·3	12·7	13·1	12·7	13·7
10^5k_1 (sec.$^{-1}$) (mean)			10·1					13·1			

[Base]	← 100 →			← 200 →					
[Ester]	15·8	18·1	45·5	13·1	20·0	26·5	36·0	20·0 ^{b}	20·9 ^{c}
10^5k_1 (sec.$^{-1}$)	22·1	22·6	21·9	44·5	46·2	44·0	42·0	47·5	45·1
10^5k_1 (sec.$^{-1}$) (mean)		22·2				44·9			

Base: 2-Picoline.

[Base]	← 25 →		← 100 →					← 150 →	
[Ester]	7·80	14·8	7·33	13·10	19·00	18·6 ^{d}	23·1 ^{e}	10·8	21·7
10^5k_1 (sec.$^{-1}$)	8·74	8·64	35·8	34·5	37·5	34·1	38·3	57·6	57·9
10^5k_1 (sec.$^{-1}$ mean)	8·69				36·0				57·8

Base: 2,6-Lutidine.

[Base]	← 10·0 →			← 20·0 →				← 50 →	
[Ester]	4·88	7·83	9·70	6·69	7·74	13·7	12·8	18·8	20·9
10^5k_1 (sec.$^{-1}$)	6·87	6·90	6·85	10·7	9·60	10·4	18·8	18·6	18·4
10^5k_1 (sec.$^{-1}$) (mean)		6·87			10·2			18·6	

[Base]	← 100 →			← 200 →		
[Ester]	12·6	16·3	37·6	10·0	10·3	43·9
10^5k_1 (sec.$^{-1}$)	37·3	36·8	36·6	82·1	83·0	84·5
10^5k_1 (sec.$^{-1}$) (mean)		36·9			83·2	

Base: 2,4,6-Collidine.

[Base]	← 23·7 →			← 50·0 →				← 75 →	
[Ester]	6·99	10·7	13·7	8·1	11·6	9·13	9·71	18·7	35·0
10^5k_1 (sec.$^{-1}$)	28·3	28·6	28·1	55·8	56·3	55·8	65·8	66·0	70·5
10^5k_1 (sec.$^{-1}$) (mean)		28·3			55·9			67·4	

^{a} Rate calculated as for neutral reaction. ^{b} 19·0 mmoles l.$^{-1}$ γ-phenyltetronic acid initially added. ^{c} In cell with wire electrodes. ^{d} 9·13 mmoles l.$^{-1}$ of γ-phenyltetronic acid initially added. ^{e} 13·8 mmoles l.$^{-1}$ of γ-phenyltetronic acid initially added. ^{f} 8·1 mmoles l.$^{-1}$ of γ-phenyltetronic acid initially added.

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^{24} Vogel, " Practical Organic Chemistry," Longmans, London, 1948, p. 175.