680. *The Mechanism of the Pinacol–Pinacone Rearrangement. Part I. Catalysis by Strong Monobasic Acids.*

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The kinetics of the rearrangement of pinacol to pinacone, with perchloric, nitric, hydrochloric, and toluene-*p*-sulphonic acids in aqueous media, at concentrations between 0·01 and 1·5 molar, and temperatures between 67·8° and 113·5°, are in accordance with the reaction scheme

$$H^+ + P \underset{}{\overset{\text{Fast}}{\rightleftharpoons}} HP^+ \xrightarrow{\text{Slow}} \text{products}$$

where P represents the pinacol molecule. There is no evidence for any simultaneous alternative reaction route.

ALTHOUGH the mechanism of the pinacol–pinacone rearrangement has been often discussed[1] the reaction kinetics have been studied very little. Bartlett and Brown,[2] Sello,[3] and

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[1] See, for example, Bennett, *Ann. Reports*, 1930, **27**, 114; Wallis, "Organic Chemistry," Ed. Gilman, Wiley, New York, 1947, Vol. 1, p. 965; Ingold, "Structure and Mechanism in Organic Chemistry," Bell, London, 1953.

[2] Bartlett and Brown, *J. Amer. Chem. Soc.*, 1940, **62**, 2927.

[3] Sello, Ph.D. Thesis, Univ. of Missouri, 1940.

Criegee and Plate [4] studied the rearrangement of the geometric isomers of 7 : 8-diphenylacenaphthenediols, and the last authors also reported results with 1 : 2-dimethyl*cyclo*pentane-1 : 2-diols. Meerburg [5] studied tetra-*p*-chlorobenzpinacol, whilst Bergmann and Schuchardt [6] used various tetra-alkylpinacols. Recently the velocity of rearrangements of benzpinacol has been investigated.[7]

This earlier work was done in acetic acid or other non-aqueous solvents, and with one exception the results are difficult to interpret. Apparently the reaction is unimolecular with respect to the pinacol, and the velocity is proportional to the acid concentration. But it is remarkable that this important reaction has not yet been studied in detail in aqueous acids.

We have determined the rate of rearrangement of pinacol itself under a variety of conditions in aqueous media, and now describe the results of reaction with strong monobasic acids and discuss the evidence they provide for the mechanism of the rearrangement.

EXPERIMENTAL

Reagents.—The pinacol was prepared from acetone,[8] and the hexahydrate so obtained dehydrated.[9] The anhydrous pinacol was twice distilled in all-glass apparatus through a 40-cm. column [the fraction, b. p. 172°, was collected], and stored over calcium chloride.

Hydrochloric and nitric acids were prepared from analytical grade concentrated reagents. The perchloric acid, from A.R. 70% solution, was diluted and standardized with barium hydroxide.[10] The toluene-*p*-sulphonic acid was purified [11] to constant m. p. 107°.

Method.—Below 90° a constant-temperature water-bath with temperature control to better than ±0·1° was used. Aqueous solutions of pinacol were mixed with temperature-equilibrated acids, zero time being taken at half-addition of acid to the glycol. To follow the reaction, samples (5 ml.) were pipetted at various times from the stoppered reaction flasks into a cooled excess of a saturated sodium hydrogen carbonate solution for analysis.

Above 90°, a constant-temperature oil-bath (better than ±0·5°) was used. Cold samples (5 ml.) were pipetted into tubes which were sealed and immersed in the bath for reaction. Rates of reaction were always so slow at room temperature that zero time could be taken as the time when the tubes were immersed in the bath. Likewise, quenching the sample tubes in ice–water was effective for rapidly stopping the reaction. The tube contents were finally rinsed into a cold excess of saturated hydrogen carbonate solution for analysis.

Analysis for Pinacol.—The specific reaction of periodate with α-glycols [12] was employed. 10 ml. of 0·1M-periodic acid [12] were added to each sample in saturated hydrogen carbonate solution, and the mixture was left for 4 hr. at room temperature.[13] No attack by the periodate on the pinacone produced was detected. 10 ml. of 0·1N-sodium arsenite [12] and 1 ml. of 20% potassium iodide solution were then added, and after 10 min. the excess of arsenite was estimated with 0·1N-iodine, a starch indicator being used.

Analysis for Pinacone.—(*a*) For the estimation of pinacone after complete reaction (*i.e.*, ~0·1M-ketone), Smith and Mitchell's titrimetric method [14] was used. (*b*) In the study of pinacone production during reaction, method (*a*) was not sufficiently sensitive and an ultraviolet absorption technique was adopted. Measurements were made at 2800 Å with a 0·5 mm. slit on a Hilger " Uvispek " with 1-cm. quartz cells. The samples were rapidly chilled after the reaction, but not treated with bicarbonate solution. The percentage transmission was compared with that obtained under identical conditions with solutions containing 0·1M-pinacol, acid at the same strength as used in the reaction, and known amounts of pinacone. The degree of absorption obtained with 0·01M-pinacone solution was unaffected within experimental error by the presence of 0·1M-pinacol.

Side Reactions.—With concentrations above about 1·5N of hydrochloric, perchloric, and

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[4] Criegee and Plate, *Ber.*, 1939, **72**, 178.
[5] Meerburg, *Rec. Trav. chim.*, 1905, **24**, 131.
[6] Bergmann and Schuchardt, *Annalen*, 1931, **487**, 225.
[7] Gebhardt and Adams, *J. Amer. Chem. Soc.*, 1954, **76**, 3925.
[8] *Org. Synth.*, Coll. Vol. I, 1943, p. 459.
[9] King and Stewart, *Chem. Abs.*, 1931, **25**, 1799.
[10] Smith and Koch, *Ind. Eng. Chem. Anal.*, 1931, **3**, 53.
[11] Vogel, " Textbook of Practical Organic Chemistry," Longmans, London, 1948, p. 532.
[12] Jackman, *Org. Reactions*, 1947, **2**, 341.
[13] Price and Kroll, *J. Amer. Chem. Soc.*, 1938, **60**, 2726.
[14] Smith and Mitchell, *Analyt. Chem.*, 1950, **22**, 750.

nitric acids, a yellow coloration was frequently noticed in the reaction mixtures especially at high temperatures. At 50°, for instance, heating for 100 min. was sufficient to cause a pronounced coloration. Whenever the yield of pinacone was low, distinct coloration was obtained and the results were therefore discarded.

RESULTS

(a) *Single Acids.*—Kinetic runs have been made by following the pinacol loss with four strong monobasic acids, *viz.*, hydrochloric, perchloric, nitric, and toluene-*p*-sulphonic. The first-order rate was always dependent on the concentration of pinacol; the values of the rate constant are given in Table 1.

TABLE 1. *First-order rate constants* [concentrations in mole/l.; k_{exp} in 10^5 sec.$^{-1}$].

Concn.	k_{exp}	Concn.	k_{exp}	Concn.	k_{exp}	Concn.	k_{exp}
$HClO_4$ at 67·8°		$HClO_4$ at 100·0°		HCl at 78·0		p-$CH_3 \cdot C_6H_4 \cdot SO_3H$	
1·12	2·34	0·31	31·3	0·99	4·36	at 78·0	
0·95	2·07	0·19	14·8	0·73	2·31	0·93	3·79
0·55	0·96	0·14	13·3	0·46	1·61	0·64	1·92
0·51	0·90	0·09	6·69	0·30	0·89	0·54	1·57
		0·07	5·57	0·13	0·33	0·42	1·27
at 78·0°		0·05	3·48	0·05	0·16	0·17	0·54
1·41	13·9						
0·95	5·60	at 113·5°		at 90·0°		at 90·0°	
0·67	4·25	0·71	307	1·13	29·2	0·93	16·0
0·30	1·19	0·50	219	0·91	19·4	0·54	12·1
0·07	0·36	0·29	121	0·73	15·9	0·35	7·32
0·03	0·14	0·19	102	0·46	8·47	0·15	2·88
		0·07	39·4	0·11	1·65	0·14	2·42
at 90·0°		0·03	14·5	0·06	1·00	0·07	1·00
1·13	43·0						
0·76	22·9	HNO_3 at 100°		at 100·0°		at 100·0°	
0·50	13·2	0·40	34·5	0·42	33·9	0·34	27·6
0·39	9·54	0·31	25·0	0·29	22·5	0·18	13·4
0·35	8·56	0·30	23·5	0·21	16·8	0·14	10·1
0·07	1·15	0·10	7·69	0·10	7·86	0·07	5·02
				0·08	5·02		
				0·05	3·85		
				0·01	0·56		

TABLE 2. *Comparison of* (A) *rate of formation of pinacone with* (B) *rate of loss of pinacol, both at* 100° [rates are expressed as $a/(a - x)$; time in sec.].

	0·295M-*Hydrochloric acid*								
t	900	1500	2125	2915	3775	4390	5095	5815	9955
A	1·13	1·26	1·45	1·66	1·88	2·22	2·43	2·66	12·1
B	1·14	1·27	1·51	1·70	1·90	2·14	2·75	2·80	12·0
	0·339M-*Toluene*-p-*sulphonic acid*								
t	1080	1800	2580	4560	8340	8760			
A	1·51	1·77	2·28	3·50	8·35	12·0			
B	1·56	1·77	2·05	3·30	8·55	11·8			

(b) *Pinacone Production.*—The rate of formation of pinacone was sometimes determined at the same time as the rate of loss of pinacol (see Table 2); the two rates were identical within the limits of experimental error. It was, however, possible to check that these were the same only at concentrations above about 0·01M-pinacone because of instrumental limitations. In most of the kinetic runs followed by pinacol analysis, the initial concentration of pinacol was 0·01—0·1M.

(c) *Acid–Salt Mixtures.*—The reaction was also followed by determining the loss of pinacol with acid–salt mixtures of constant ionic strength and variable concentration either of hydrogen ion or of anion. The results for mixtures of either hydrochloric acid or perchloric acid and their sodium and potassium salts respectively are plotted in Fig. 1 (curve *F*). The full line is that obtained for the pure acids, the results for which were identical within the limits of error at such low ionic strengths. The points for pure nitric acid are also shown.

DISCUSSION

It is generally accepted that the first stage of this reaction is proton addition to the hydroxyl group, *viz.*,

$$H^+ + P \rightleftharpoons HP^+ \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where P represents the pinacol molecule. This equilibrium is believed to be set up very rapidly. Without detailing the final stage (concerning which the kinetics alone will provide no evidence), we may write the rearrangement as proceeding either by (*a*) unimolecular decomposition of the pinacol conjugate acid :

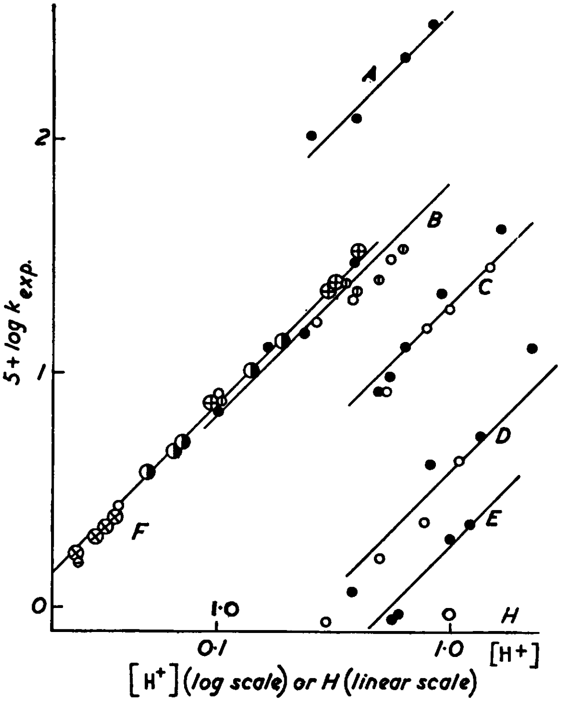

FIG. 1. log k_{exp} *plotted as a function of the acidity constant H.* ○, *Hydrochloric acid;* ●, *perchloric acid;* ⦶, *nitric acid. Curves A,* 113·6°; *B,* 100·0°; *C,* 90·0°; *D,* 78·0°; *E,* 67·8°. *In curve F,* log k_{exp} *at* 100° *is plotted as a logarithmic function of* [*acid*] *for mixtures of* (a) *hydrochloric acid and sodium chloride at ionic strength* 0·1 (*points* ⊙), (b) *perchloric acid and potassium perchlorate at an ionic strength of* 0·05 (*points* ⊗), (c) *pure nitric acid* (*points* ⊕), *and* (d) *toluene-*p*-sulphonic acid* (*points* ◑). *The points marked* ⊖ *were determined at* [NaCl] = 0·03M *and ionic strength* 0·13, *made up with mixtures of perchloric acid and potassium perchlorate. The lines for curves A—E are drawn with unit slope, and for curve F the line is that obtained for all pure monobasic strong acids below concentrations of* 0·1M.

$$HP^+ \xrightarrow{\text{Slow}} A \xrightarrow{\text{Fast}} \text{products} + H^+ \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

or (*b*) bimolecular reaction with the solvent :

$$HP^+ + H_2O \xrightarrow{\text{Slow}} A \xrightarrow{\text{Fast}} \text{products} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where A is the transition state. The reaction rate in mechanism (2) will clearly depend on the concentration of HP$^+$ in the steady state, and may be shown [15] to be

$$R = k[HP^+] = kK_a[H^+][P]\gamma_{H^+}\gamma_P/\gamma_{HP^+} \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where R is the reaction rate, K_a is the thermodynamic equilibrium constant of reaction (1), k is the rate constant, and the γ's are the appropriate activity coefficients of the various species in the mixture.

When $kK_a = k_1$ the experimentally determined rate constant k_{exp}, given in Table 1, is given by

$$k_{exp} = k_1[H^+]\gamma_{H^+}\gamma_P/\gamma_{HP^+} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

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[15] Bell, " Acid–Base Calalysis," Oxford Univ. Press, 1942.

By comparison, the reaction rate corresponding to eqn. (3) would be

$$R = k\{\mathrm{HP}\}\{\mathrm{H_2O}\}$$

$$= k_1[\mathrm{H}^+][\mathrm{P}]\{\mathrm{H_2O}\}\,\gamma_{\mathrm{H}^+}\gamma_{\mathrm{P}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

$$= k_{\mathrm{exp}}[\mathrm{P}]$$

where

$$k_{\mathrm{exp}} = k_1[\mathrm{H}^+]\gamma_{\mathrm{P}^+}\gamma_{\mathrm{H}}\{\mathrm{H_2O}\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Let us consider the experimental results in the light of eqns. (5) and (7).

(a) *Hydrogen-ion Concentration.*—When log k_{exp} was plotted against log [HX] (where X is the anion and [HX] is the stoicheiometric concentration of HX) all the monobasic acids, at low concentrations, gave good straight lines which were practically coincident. This would be expected if the hydrogen-ion concentration were assumed to be equal to the stoicheiometric acid concentration, which is reasonable. A typical plot, for nitric acid, is shown in Fig. 1 (curve *F*). Also shown are the rate constants obtained with mixtures of strong acids with their alkali-metal salts, for which the rate constants were also proportional to the acid concentration. Total ionic strength was always quite small and the activity coefficient variations would not be significant. This result therefore confirms that the hydrogen-ion concentration determines the rate of reaction, which is uninfluenced by the concentration or nature of the anion. This result would be expected from both eqns. (5) and (7).

(b) *Acidity Function.*—Although it is impossible to distinguish between eqns. (5) and (7) at very low concentrations, this can be done at high concentrations where the activity coefficient variations become significant. Variations in the activity coefficient ratio, $\gamma_{\mathrm{H}^+}\gamma_{\mathrm{P}}/\gamma_{\mathrm{HP}^+}$, can be accommodated by use of the Hammett acidity function [16]

$$H = (-\log[\mathrm{H}^+])\gamma_{\mathrm{H}^+}\gamma_{\mathrm{B}^-}/\gamma_{\mathrm{HB}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where HB may be, say, a coloured indicator which dissociates to give a conjugate base B of a different colour. Although there is no direct dependence of the right-hand expression of eqn. (8) on the product $-\log([\mathrm{H}^+]\gamma_{\mathrm{H}^+}\gamma_{\mathrm{P}}/\gamma_{\mathrm{PH}^+})$, use of *H* instead of this quantity in many acid-catalysed reactions indicates that the two expressions vary in like manner. The plot of log k_{exp} against *H* gives lines of almost unit slope in most H^+-ion catalysed reactions at room temperature and in reactions at higher temperatures [16] although *H* is determined [17] at 25°. We have therefore plotted log k_{exp} against *H*, as in Fig. 1 (curves *A*—*E*), for hydrochloric, perchloric, and nitric acids, the values of *H* quoted by Hammett and Paul [17] for these acids at 25° being used. The plots of the different acids are almost coincident, and nearly of unit slope. Long and McIntyre [18] have recently re-emphasized that the slope of the acidity function plot would be expected to be exactly unity only when the term $\gamma_{\mathrm{P}}/\gamma_{\mathrm{HP}^+}$ in eqn. (4) changes precisely as does the term $\gamma_{\mathrm{B}^-}/\gamma_{\mathrm{HB}}$ in eqn. (8). In general, the slopes will all differ slightly from unity and from one another. In the present experiments these differences are hardly greater than experimental error (which has a variable contribution because of the use of acidity function data at 25° for kinetic experiments made at 67·8—113·5°). This probably accounts for the fact that the slope for hydrochloric acid is less than that for perchloric acid, whereas it should be greater. Salt effects are therefore small in our system, and according to Long and McIntyre [18] these strong acids behave thus with a wide series of neutral molecules.

If eqn. (7) were obeyed, we should not expect plots such as Fig. 1 (curves *A*—*E*) to be obtained, since $\{\mathrm{H_2O}\}$ is not inversely proportional to γ_{HP^+}, but is a complicated function of the acid strength and the osmotic coefficient of the acid solution.[19] Insertion of tabulated data in eqn. (6) indicates that, were that equation obeyed, the highest acid concentration (~1·5M) is sufficient to cause deviations, of significant magnitude,

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[16] Hammett and Deyrup, *J. Amer. Chem. Soc.*, 1932, **54**, 2721.

[17] Hammett and Paul, *ibid.*, 1934, **56**, 827.

[18] Long and McIntyre, *ibid.*, 1954, **76**, 3240, 3243.

[19] Harned and Owen, " The Physical Chemistry of Electrolyte Solutions," Reinhold, New York, 1950.

in linearity and slope. Eqn. (6) is clearly not obeyed. Analogous results for sulphuric acid confirm this, for only small deviations from linearity and unit slope were evident over a much larger concentration range {$0\cdot1 < [H_2SO_4] < 5$ molar; see Fig. 1 of next paper}.

(c) *Calculation of Variation in Activity Coefficient Ratio.*—Although the kinetic effect of an acid in these reactions is dependent on the concentration and activity of the hydrogen ion alone, a thermodynamic evaluation of the activity of the hydrogen ion-anion pair ($\gamma^{\pm}{}_{\mathrm{HX}}$) only can be made (where X is the anion of the monobasic acid). But we may write

$$\log(\gamma_{\mathrm{H}^+}\gamma_{\mathrm{P}}/\gamma_{\mathrm{HP}^+}) = \log(\gamma_{\mathrm{H}^+}\gamma_{\mathrm{X}}/\gamma_{\mathrm{HP}^+}\gamma_{\mathrm{X}}) + \log\gamma_{\mathrm{P}} \quad . \quad . \quad . \quad (9)$$

$$= 2\log(\gamma^{\pm}{}_{\mathrm{HX}}/\gamma^{\pm}{}_{\mathrm{HPX}}) + \log\gamma_{\mathrm{P}} \quad . \quad . \quad . \quad (10)$$

where $\gamma^{\pm}{}_{\mathrm{HPX}}$ is the activity coefficient of the pinacol conjugate acid salt, which can of course be completely dissociated.

Now variations in the values of these activity coefficients can be safely predicted from the known trends of the activity coefficients of simple acids and salts, since the conditions of the experiment are such that simple approximations can reliably be made, thus:

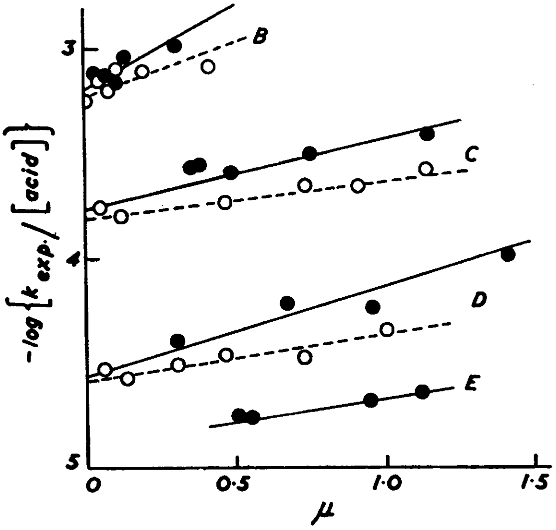

FIG. 2. log k_{exp}/[acid] *as a function of ionic strength* (μ). ○, *Hydrochloric acid*; ●, *perchloric acid. Curves* B, 100·0°; C, 90·0°; D, 78·0°; E, 67·8° c.

(i) Since the HP$^+$ concentration is very small compared with that of the acid, then

$$\gamma^{\pm}{}_{\mathrm{HX}} = \gamma^{\circ\pm}{}_{\mathrm{HX}}$$

where $\gamma^{\circ\pm}{}_{\mathrm{HX}}$ is the activity coefficient of the pure acid in solutions of the same ionic strength.

(ii) For a similar reason, the contribution to γ_{P} of terms involving interaction between pinacol molecules will be negligible, and we can write [20]

$$\log\gamma_{\mathrm{P}} = k_s[\mathrm{HX}] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

where k_s is a constant.

(iii) The value of $\gamma^{\pm}{}_{\mathrm{HPX}}$, the activity coefficient of HPX in solutions of low concentration of HPX in high concentrations of acid, can be evaluated in terms of $\gamma^{\pm}{}_{\mathrm{HX}}$ and $\gamma^{\pm}{}_{\mathrm{HPX}}$, the activity coefficient of pure HPX, by application of Harned's rule [19, 21] which will certainly be valid for such mixtures of a base with its conjugate acid. Hence,

$$\log\gamma^{\pm}{}_{\mathrm{HPX}} = \tfrac{1}{2}(\log\gamma^{\circ}{}_{\mathrm{HX}} - \log\gamma^{\circ}{}_{\mathrm{HPX}}) \quad . \quad . \quad . \quad . \quad . \quad (12)$$

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[20] Long and McDevitt, *Chem. Rev.*, 1952, **51**, 119.
[21] Glueckauf, *Nature*, 1949, **163**, 414.

from which

$$\begin{aligned}\log(\gamma_{\mathrm{H}^+}\gamma_{\mathrm{P}}/\gamma_{\mathrm{HP}^+}) &= 2\log\gamma^{\circ\pm}{}_{\mathrm{HX}} - (\log\gamma^{\circ}{}_{\mathrm{HX}} + \log\gamma^{\circ}{}_{\mathrm{HPX}}) + k_s[\mathrm{HX}]\\ &= \log\gamma^{\circ\pm}{}_{\mathrm{HX}} - \log\gamma^{\circ}{}_{\mathrm{HPX}} + k_s[\mathrm{HX}]\\ &= \alpha_{12}[\mathrm{HX}] + k_s[\mathrm{HX}]\\ &= [\mathrm{HX}](\alpha_{12} + k_s) \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (13)\end{aligned}$$

where α_{12} is the Harned coefficient, and is constant over wide changes of concentration.[19]

Hence we may conclude that, since

$$\begin{aligned}\log(k_{\mathrm{exp}}/[\mathrm{H}]) &= \log k_1 + \log(\gamma_{\mathrm{H}^+}\gamma_{\mathrm{P}}/\gamma_{\mathrm{HP}^+})\\ &= \log k_1 + [\mathrm{HX}](\alpha_{12} + k_s) \quad . \; . \; . \; . \; . \quad (14)\end{aligned}$$

then log $(k_{\mathrm{exp}}/[\mathrm{H}^+])$ should vary linearly with HX. Also, since α_{12} is generally positive and dependent on the nature of the acid HX, the slope of this plot will be positive, and vary for each acid. Fig. 2 shows the results for perchloric and hydrochloric acid, and as would be expected, the slope of the line for the latter acid is greater than that for the former. This result agrees with that obtained by the conventional approach of evaluating the activity coefficient ratio in eqn. (5) by use of the Debye–Hückel equation, for

$$\log k_{\mathrm{exp}} = \log k_1 + \log[\mathrm{H}^+] + 2Az_{\mathrm{H}}z_{\mathrm{P}}\mu^{\frac{1}{2}} + (B_{\mathrm{H}^+} + B_{\mathrm{P}} - B_{\mathrm{HP}^+}) \quad . \quad (15)$$

where z is the ionic charge of the indicated species, μ is the ionic strength, and B the Debye–Hückel constant referring to the species indicated. Since the pinacol molecule is uncharged we should expect the third term to be zero, and a linear plot to be obtained for log $k_{\mathrm{exp}}/[\mathrm{H}^+]$ against μ, of small slope, since $B_{\mathrm{H}} + B_{\mathrm{P}} - B_{\mathrm{HP}^+}$ is small (see Fig. 2). If the reaction had not involved an uncharged species in its first stage the minimum possible value for the third term on the right of eqn. (13) would have been $\mu^{\frac{1}{2}}$ (A being taken as 0·5 from Debye–Hückel theory). This would have led to a change in log k_{exp} by 1·5 units on the logarithmic scale for $\mu = 1{\cdot}5$, which is at least a factor of 5 more than that obtained in most cases (see Fig. 2). Clearly then, the kinetics are in accordance with equations (1), (2), and (5).

(d) *Rearrangements by Formation of Epoxide.*—In the rearrangement of benzpinacol, Gebhardt and Adams [7] have reported that 80% of the reaction proceeds at 75° by way of the formation of the epoxide. Evidence for this was adduced from the rate of production of benzpinacone from both the pinacol and the epoxide which was followed by spectrophotometric estimation of the benzpinacone. The same method used by us with pinacone itself gave the rate constants quoted in Table 3 which show that there is no significant difference between the rate of pinacol loss and the rate of pinacone production. It is therefore clear that we are concerned only with a single reaction route.

TABLE 3. *Rate constants calculated from data simultaneously from* (A) *the rate of loss of pinacol and* (B) *the rate of production of pinacone at* 100° [k_{exp} in 10^5 sec.$^{-1}$].

Acid	k_{exp} from A	k_{exp} from B	Acid	k_{exp} from A	k_{exp} from B
0·295M-HCl	20·2	21·9	0·339M-$\mathrm{Me{\cdot}C_6H_4{\cdot}SO_3H}$ ...	28·4	31·3

This conclusion does not exclude the possibility of the rearrangements' proceeding by the reaction

$$\begin{tikzcd} \mathrm{P} + \mathrm{H}^+ \arrow[r, shift left, "\text{Fast}"] & \mathrm{HP}^+ \arrow[l, shift left] \arrow[r, shift left, "\text{Fast}"] & \text{Epoxide} + \mathrm{H_3O^+} \arrow[l, shift left] \arrow[d] \\ & & \text{Pinacone} \end{tikzcd} \quad . \; . \; . \; . \quad (16)$$

but the second stage would have to be fast (compared with the rate of rearrangement) and the last stage would be the rate-determining step. For the epoxide, if present, would probably be oxidized by periodic acid (*via* conversion into pinacol) and included in the pinacol analysis. However, it is hardly possible for the epoxide mechanism to make any significant contribution to the mechanism since one would expect it to be completely converted into pinacol by the catalysing acid. It is also known [22] that dilute aqueous acids convert alicyclic epoxides into pinacols, and one would not have expected the tetramethyl pinacol to act differently. On the other hand, one might have expected that the tetraphenylpinacol carbonium ion [$Ph_2C(OH){\cdot}C^+Ph_2$] would be much more stable than the corresponding tetramethyl ion even in aqueous acid, but especially so in the non-aqueous solvent used by Gebhardt and Adams [7] for the former. This would explain satisfactorily these authors' finding that part of the rearrangement of the tetraphenylpinacol proceeds *via* the epoxide. But with the tetramethylpinacol, the evidence suggests that the epoxide mechanism is not significant.

TABLE 4. *Values of* k_1 (10^5 sec.$^{-1}$)

Temp.	$HClO_4$	HCl	HNO_3	p-Me·C_6H_4·SO_3H	Mean
67·8°	1·3 ± 0·1	—	—	—	1·3 ± 0·1
78·0	2·7 ± 0·2	2·6 ± 0·05	—	3·1 ± 0·1	2·8 ± 0·17 *
90·0	18·0 ± 1·0	16·0 ± 1·0	—	17·0 ± 1·0	17·0 ± 1·0 *
100·0	65·0 ± 2·0	61·0 ± 3·0	66·0 ± 2·0	68·0 ± 2·0	65·0 ± 2·3 *
113·5	450·0 ± 50·0	—	—	—	450·0 ± 50·0

* The limits quoted are standard deviations.

(e) *Arrhenius Plot.*—By extrapolation to zero concentration of plots similar to those in Fig. 2, values of k_1 in eqn. (5) can be evaluated. Table 4 gives the values.

A plot of log k_1 (mean values) against $1/T$ leads to a value of 32·7 kcals./mole for the energy of activation. This compares with a value of 31 kcals./mole calculated for the rearrangement of benzpinacol [7] by reactions analogous to (1) and (2).

The foregoing results are in accordance with reactions (1) and (2) and there is no evidence of any reaction involving any other intermediates.

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[22] Bartlett and Bayley, *J. Amer. Chem. Soc.*, 1938, **60**, 2416.