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[1956] *Mechanism of Pinacol–Pinacone Rearrangement. Part II.* 3519

681. *The Mechanism of the Pinacol–Pinacone Rearrangement. Part II.* Catalysis by Sulphuric Acid.*

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The rearrangement of pinacol to pinacone has been followed in sulphuric acid and in mixtures of hydrochloric acid, sulphuric acid, sodium hydrogen sulphate, and sodium sulphate at different ionic strengths; it is catalysed solely by the hydrogen ion, and the kinetic results generally confirm the conclusions of the preceding paper. The bisulphate ion does not significantly catalyse the reaction, but the sulphate ion retards it.

EXPERIMENTAL

THE experimental procedures were as described in the preceding paper.

(a) *Pinacol Loss.*—The reaction was studied with 0.001M—6.33M sulphuric acid solutions within the temperature range 72.6—$154°$ c. The first-order rate constants obtained are given in Table 1.

TABLE 1. *First-order rate constants for catalysis by sulphuric acid (k_{exp} in 10^5 sec.$^{-1}$).*

	72.6°					103.0°						
Molarity ...	6.33	4.83	1.14	0.67		0.910	0.850	0.660	0.300	0.157	0.078	0.010	0.001
k_{exp}	25.4	10.5	2.01	1.56		69.3	67.6	46.0	27.2	14.5	7.03	0.95	0.072

	124.5°					154.0°			
Molarity ...	0.157	0.085	0.077	0.036	0.018	0.018	0.005	0.002	0.001
k_{exp}	222	113	106	34.7	21.9	484	133	67.4	33.9

* Part I, preceding paper.

(b) *Pinacone Production.*—Table 2 shows the formation of pinacone and the simultaneous loss of pinacol. The values of k_{exp} calculated from these results were respectively, $11 \cdot 81 \times 10^{-5}$ sec.$^{-1}$ and $11 \cdot 40 \times 10^{-5}$ sec.$^{-1}$, which, like the results of the previous paper, are in accordance with a single reaction route.

TABLE 2. *Comparison of* (A) *rate of formation of pinacone with* (B) *rate of loss of pinacol in* $0 \cdot 14$M-*sulphuric acid at* $103°$ [rates expressed as $a/(a - x)$; t in sec.].

t	5000	7500	11,000	14,750	23,000	25,400
A	1·88	2·24	3·23	4·80	16·30	31·71
B	1·95	2·13	3·34	4·90	15·60	30·86

(c) *Acid–Salt Mixtures.*—The results are given in Table 3 of several experiments with mixtures of hydrochloric acid with either sodium sulphate or sodium hydrogen sulphate and of sulphuric acid with sodium sulphate. Frequently sodium chloride was also added to adjust the ionic strength.

TABLE 3. *First-order rate constants* (in 10^5 sec.$^{-1}$) *with acid–salt mixtures at* $100°$.

Molarity						
H_2SO_4	$NaHSO_4$	Na_2SO_4	NaCl	HCl	k_{exp}	Fig.
—	—	0·025	0·025	0·04	1·65	1
—	—	0·020	0·04 *	0·04	1·54	
—	—	0·010	0·07	0·04	2·10	
—	—	0·009	0·058	0·04	2·00	
—	—	0·005	0·095	0·04	2·25	
—	—	0·0014	0·095	0·04	2·43	
—	—	0·001	0·097	0·04	2·80	
0·005	—	0·045	—	—	0·06	2
0·01	—	0·04	—	—	0·14	
0·02	—	0·03	—	—	0·50	
0·03	—	0·02	—	—	0·89	
0·04	—	0·01	—	—	2·42	
—	0·01	—	0·09	0·03	2·12	3
—	0·02	—	0·07	0·02	1·26	
—	0·03	—	0·05	0·01	0·87	
—	0·04	—	0·03	—	0·58	

* LiCl.

DISCUSSION

(a) *Sulphuric Acid.*—In aqueous sulphuric acid, even if the rearrangement is catalysed solely by hydrogen ions, we may expect the variation of rate constant to be a complicated function of the stoicheiometric H_2SO_4 concentration quite apart from variations in ionic activity which are also serious in solutions containing multivalent ions.

We may, however, calculate with reasonable accuracy the hydrogen-ion concentration in dilute solutions by using the values of the mass products, $K_1 = [H^+][HSO_4^-]/[H_2SO_4]$ and $K_2 = [H^+][SO_4^{2-}]/[HSO_4^-]$, interpolated from Young and Blatz's data.[1] These values may be in error by 10%, due to uncertainty in the interpolation at low concentration, but this would not cause an error in the calculated hydrogen-ion concentration of more than 5%. Fig. 1 (curves *A—D*), in which the rate constants are plotted, shows that the reaction is dependent on the first power of $[H^+]$ over a very wide range of concentration, although there are some deviations at high concentrations as might be expected from activity effects.

Use of the acidity function [2] for sulphuric acid confirms this conclusion. The plots of rate constant against acidity function shown in Fig. 1 (curves *a—d*) are straight lines of nearly unit slope. In Fig. 1 (curves *C, c*) the lines (at $103°$) are those expected from the results with strong monobasic acids (see preceding paper), allowance being made in each case for a small difference between the temperatures at which these and the previous results were determined. There can be no doubt that the principal catalysing species is the hydrogen ion.

(b) *Catalysis by Solutions of Different Ionic Composition.*—The ionic composition of

¹ Young and Blatz, *Chem. Rev.*, 1949, **44**, 102.
² Hammett and Deyrup, *J. Amer. Chem. Soc.*, 1932, **54**, 2721.

sulphuric acid varies [1] with concentration from solutions which contain practically no bisulphate ions to solutions containing practically no sulphate ions. Systematic variation of the relative concentration of these ions at constant ionic strength is thus difficult, especially because of the low dissociation constant of bisulphate ion and the presence of bivalent as well as univalent ions. A reasonably wide variation in the relative concentrations of these ions at different ionic strengths was, however, studied by carrying out the reaction at 100° in the following mixtures : (i) sodium sulphate–hydrochloric acid, sometimes with sodium or lithium chloride (Fig. 1), (ii) sodium sulphate–sulphuric acid (Fig. 2), (iii) sodium hydrogen sulphate–sodium chloride–hydrochloric acid (Fig. 3).

A value of 10^{-2} being assumed for the dissociation constant of HSO_4^- the concentrations of the H^+, SO_4^{2-}, and HSO_4^- ions can be calculated. As this calculation takes no account of the activity coefficients of the mixtures there must be some inaccuracy. The estimated errors for an error in K_2 of twofold are given in Table 4. The relative errors reported are

TABLE 4. *Estimated errors (factor of 2 in the value of K_2) (concentrations in g.-ions/l.).*

Mixture Fig.	Absolute errors				Relative errors			
	H^+	SO_4^{2-}	HSO_4^-	μ	H^+	SO_4^{2-}	HSO_4^-	μ
1	0·003	0·0028	0·0025	0·005	0·0025	0·0017	0·0012	0·003
2	0·006	0·007	0·006	0·025	0·007	0·013	0·007	0·037
3	0·008	0·008	0·010	0·014	0·005	0·006	0·007	0·009

the changes in the differences between concentrations at the opposite ends of the plots of Figs. 1—3. The general shape of the curves cannot therefore be open to question even though there are relatively large errors in the absolute concentrations.

In Table 5, the values of $[H^+]$, $[HSO_4^-]$, $[SO_4^{2-}]$, and μ are given, for a series of mixtures, calculated from the results given in Table 3 (Fig. 1). In all mixtures the concentrations of bisulphate and sulphate ions are respectively less than 0·017M and 0·008M, even though the ionic strength varies by about 40%. At such low concentrations the presence of neutral electrolyte *per se* would not be expected to influence the rate constant (see previous paper), and it is not therefore surprising that in the mixtures in which the concentrations

TABLE 5.

$[H^+]$	$[HSO_4']$	$[SO_4^{2-}]$	μ	k_{exp} (10^5 sec.$^{-1}$)	$[H^+]$	$[HSO_4']$	$[SO_4^{2-}]$	μ	k_{exp} (10^5 sec.$^{-1}$)
0·023	0·017	0·008	0·105	1·65	0·036	0·004	0·001	0·142	2·25
0·026	0·015	0·006	0·112	1·54	0·039	0·001	0·0003	0·137	2·43
0·033	0·008	0·002	0·125	2·10	0·039	0·0008	0·0002	0·138	2·80
0·034	0·007	0·004	0·108	2·00					

of bisulphate and sulphate ions are low, the rate constants agree within experimental error with those obtained both with pure sulphuric acid and with strong monobasic acids. This is seen in Fig. 1 *C*.

When, however, the concentration of either bisulphate or sulphate ions becomes large a pronounced lowering of the reaction rate occurs, as the results with mixtures (ii) and (iii) (Table 3) show. These results were determined by systematically varying the stoicheiometric concentration of one or more of the constituent salts or acids, in each case with sufficient predetermined conditions to make the ionic composition dependent on only one variable. Thus, in Fig. 2 we have that $[Na_2SO_4] + [H_2SO_4] = 0.05$, whilst for Fig. 3, $3[NaHSO_4] + [HCl] + [NaCl] = 0.15$ and $[HCl] + [NaHSO_4] = 0.04$. We can therefore plot curves of the ionic concentrations of bisulphate, sulphate, and hydrogen ions, and of the ionic strength (μ) as functions of the observed rate constant, $k_{exp}/[H^+]$. These plots are shown in Figs. 2 and 3. They were calculated from smoothed plots of $k_{exp}/[H^+]$ against one of the systematically varied concentrations.

(c) *Effect of Ionic Strength.*—We may now interpolate values for $[H^+]$, $[HSO_4^-]$, $[SO_4^{2-}]$, and $k_{exp}/[H^+]$ for constant values of μ by using Figs. 2 and 3. The data are given in Table 6; $k_{exp}/[H^+]$ is obviously not constant at a given ionic strength, as is frequently obtained with reactions, catalysed by hydrogen ions, in mixtures in which only univalent ions are present. This variation is undoubtedly due to the presence of variable and relatively large amounts of bivalent ions.
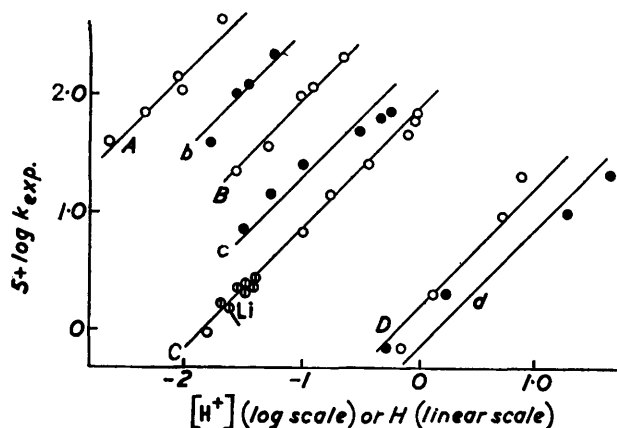
FIG. 1. log k_{exp} plotted as (a) a log-arithmic function of [H⁺] (capital letters, ○) and (b) as a linear function of the acidity function H (lower case letters, ●), both for pure sulphuric acid; (c) the calculated [H⁺] for [Na₂SO₄] + [NaCl] + [HCl] = 0·14 (◐). Curves Aa, 154°; Bb, 124·5°; Cc, 103°; Dd, 72·6° C. The lines at 103° are those obtained with strong monobasic acids (see previous paper), allowance being made for the small difference in temperature. The point marked Li indicates that lithium chloride was substituted for sodium chloride in mixture (c). The acidity function scale is negative and displaced by 0·3 unit.

FIG. 2. Calculated variation in [H⁺], [HSO₄⁻], [SO₄²⁻] (scale A), and μ (scale B) for a series of mixtures in which [H₂SO₄] + [Na₂SO₄] = 0·05M at 100° for different values of k_{exp}/[H⁺]. The latter values were obtained from smoothed curves of k_{exp}/[H⁺] plotted against [H₂SO₄]. The points ○ are those obtained for [Na₂SO₄] = 0.
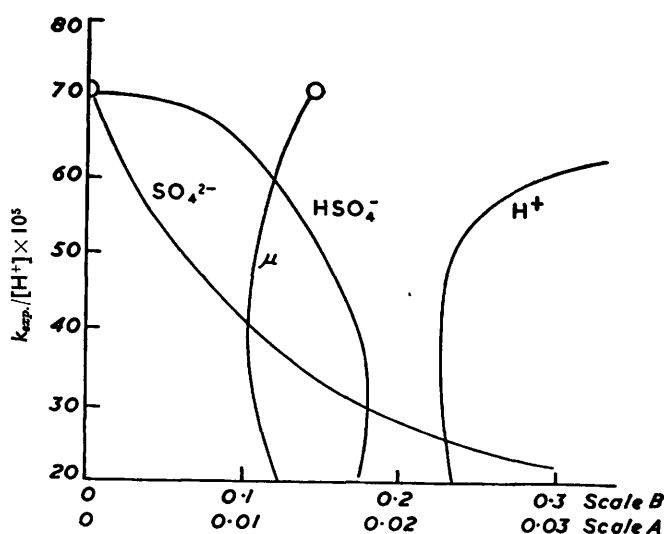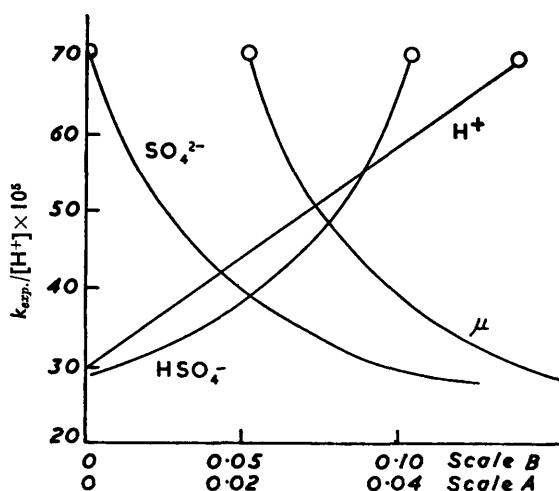
FIG. 3. Calculated variation in [H⁺], [HSO₄⁻], [SO₄²⁻] (scale A), and μ (scale B) for a series of mixtures in which 3[NaHSO₄] + [HCl] + [NaCl] = 0·15M and [NaHSO₄] + [HCl] = 0·04M at 100° for different values of k_{exp}/[H⁺]. The latter values were obtained from smoothed curves of k_{exp}/[H⁺] plotted against [HCl]. The points ○ are those obtained for pure hydrochloride acid at [HCl] = 0·04M, μ = 0·15, for which it is known that the presence of sodium chloride has no effect (see previous paper).

TABLE 6. *Values of $k_{exp}/[H^+]$ at constant ionic strength* (concns. in g.-ions/l.).

μ	H^+	HSO_4	SO_4^{2-}	$10^5 k_{exp}/[H^+]$	Fig. used.
0·11	0·003	0·024	0·027	35	2
0·11	0·023	0·018	0·009	39	3
0·12	0·006	0·020	0·031	33	2
0·12	0·023	0·015	0·0041	52	3
0·13	0·003	0·014	0·036	31	2
0·13	0·036	0·011	0·0011	63	3

(d) *Effect of Sulphate Ion.*—Table 6 suggests that the effect of the sulphate ion in lowering the rate constant is much larger than that of the bisulphate ion. This is more clearly seen in Figs. 2 and 3. In both Figs., low values of $k_{exp}/[H^+]$ correspond to very large concentrations of sulphate ion. Likewise in Fig. 2, $k_{exp}/[H^+]$ approaches the value obtained in pure sulphuric acid and in all strong monobasic acids (68 $\pm$ 2·3)* at the same hydrogen-ion concentration when $[SO_4^{2-}] < 0.01$M; whilst in Fig. 3, $k_{exp}/[H^+]$ approaches the value obtained in 0·04M hydrochloric acid (70 $\pm$ 2) in the presence or absence of neutral

FIG. 4. log $k_{exp}/[H^+]$ *plotted as a function of* $[SO_4^{2-}]$ *for* $\mu = 0.115$.
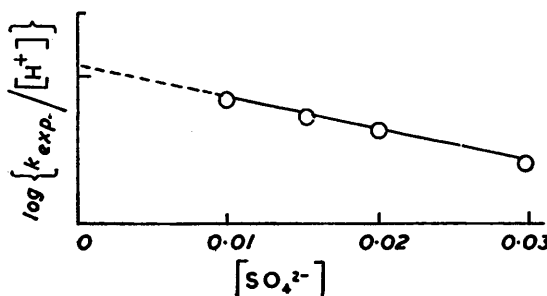
salt (see previous paper) when $[SO_4^{2-}] < 0.05$. In both cases the concentration of bisulphate ion is large, and we may conclude from these figures that it does not significantly depress or accelerate the reaction at these concentrations. It cannot be more than a tenth as effective as the sulphate ion in depressing the reaction rate. This agrees with the results of Fig. 1 C, in which $[SO_4^{2-}] < 0.008$M.

The solutions used to obtain the results recorded in Fig. 3 were made up so that the sulphate-ion concentration changed as much as possible with only small changes in the concentrations of the other constituents. There is clearly a wide range ($20 < k_{exp}/[H^+] < 50$) in which μ, $[HSO_4^-]$, and $[H^+]$ are sensibly constant. The values for these quantities obtained by interpolation at various points in this range are given in Table 7. (The absolute accuracy is probably not better than $\pm 10\%$ but the relative values are significant to the number of figures indicated.)

TABLE 7. *Variation of $k_{exp}/[H^+]$ with $[SO_4^{2-}]$* (concentration in g.-ions/l.).

$[SO_4^{-2}]$	$[H^+]$	$[HSO_4^-]$	μ	$10^5 k_{exp}/[H^+]$
0·01	0·0232	0·180	0·110	37·5
0·015	0·0230	0·185	0·112	37·0
0·02	0·0245	0·185	0·115	27·0
0·03	0·0248	0·180	0·121	21·0

Although there is some variation in μ, this is not large enough to give the nearly twofold change in $k_{exp}/[H^+]$, nor is the change obtained in the sense expected for $k_{exp}/[H^+]$ frequently increases as μ increases.[3] When the values of log ($k_{exp}/[H^+]$) are plotted against $[SO_4^{2-}]$, however, a straight line is obtained (Fig. 4). This reflects a variation in log ($\gamma_{H^+}/\gamma_{HP^+}$), since changes in γ_P will be smaller in comparison. Although such a result would probably not have been obtained at higher ionic strengths and sulphate-ion concentrations, it is satisfying that the dependence on sulphate-ion concentration follows a Harned type expression for γ_{H^+} and γ_{HP^+}, viz., log $(\gamma_{H^+}/\gamma_{HP^+})_\mu = $ log $(\gamma^\circ_{H^+}/\gamma^\circ_{HP^+})_\mu + A[SO_4^{2-}]$,

* The factor 10^5 is omitted through the discussion, for brevity.

[3] See, for example, Brönsted and Wynne-Jones, *Trans. Faraday Soc.*, 1929, **25**, 59.

where $\gamma^{\circ}{}_{H}$ and $\gamma^{\circ}{}_{HP^{+}}$ refer to the same mixture with zero concentration of sulphate ion, and A is a constant. For, when $[SO_4{}^{2-}]$ is zero, $\log(\gamma^{\circ}{}_{H^{+}}/\gamma^{\circ}{}_{HP^{+}}) = \log(k_{exp}/[H^{+}])$ (at $\mu = 0\cdot11$) $= 53$ (obtained by extrapolation) which compares with the value of $68 \pm 2\cdot3$, obtained with strong monobasic acids when $\mu < 0\cdot15$.

(e) *Effect of Bisulphate Ion.*—From the previous results we can conclude that the effect of the concentration of sulphate ion in lowering the reaction rate is small for $[SO_4{}^{2-}]$ $< 0\cdot008$, and $\mu < 0\cdot15$. In this region (Fig. 2), however, the rate constant, $k_{exp}/[H^{+}]$, is lower than that expected for pure sulphuric acid even though the concentration of bisulphate ion is greater than $0\cdot04$M. If there were any significant catalysis by the bisulphate ion, we should have expected a maximum or at least a hump in the bisulphate concentration curve. It is, of course, true that the lowering effect of the sulphate ion might mask any catalysis by bisulphate ion but the latter would require a specific rate constant of less than 2% of that for the hydrogen ion. We therefore conclude that there is no evidence for general acid catalysis by the bisulphate ion. This conclusion is confirmed by Fig. 4. For if the bisulphate ion significantly catalyses the reaction, the value of $k_{exp}/[H^{+}]$, at $[SO_4{}^{2-}] = 0$ and $\mu = 0\cdot11$, would exceed the value, at $\mu = 0$, obtained for strong monobasic acids (65). This could not be masked by ionic-strength effects at low concentrations which are known to be very small (see previous paper).

(f) *Conclusions.*—These results confirm those of the previous paper, that the kinetics of the pinacol–pinacone rearrangement in aqueous acid solutions are in accordance with the mechanism :

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

which is not complicated by any secondary reaction. The reaction is not catalysed by the bisulphate ion.

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