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$E_2^{\neq} = 14.4$ kcal/mole

$\Delta S_2^{\neq} = -10.7$ cal/mole·deg

$\Delta V_2^{\neq} = +5$ cc/mole

Although the results are somewhat obscure, it is assumed that the distance between two nitrogen atoms will stretch in the transition state considering the positive value of $\Delta V_2^{\neq}$. Anyway, the reaction mechanism of disproportionation has been little studied and is quite ambiguous, although the investigation of the pressure effects would be expected to light some aspects on elucidating the reaction mechanism.

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The Acid-Catalyzed Rearrangement of Pinacol

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The effect of pressures up to 1,447 bar on the rate of the acid-catalyzed rearrangement of pinacol has been measured at 60~70°C in dilute hydrochloric acid and at 25°C in concentrated sulfuric acid. The volumes of activation in the former at 1 bar are in the range from 6.8 to 8.4 cm^3/mole, and decrease as the temperature rises. The energy and entropy of activation at 1 bar are 36.1 kcal/mole and 22.3 cal/deg·mole, respectively, and both increase with increasing pressure. On the other hand, the volume of activation in the latter at 1 bar is 6.1 cm^3/mole in 47.5 wt% and 5.6 cm^3/mole in 55.8 wt% sulfuric acid. A modified mechanism for the rearrangement has been discussed in the light of these results. Consequently, it is suggested that the slow step is the migration of the methyl group of the intermediate ion $(R\cdots OH_2)^+$ formed from the protonated pinacol and is not probably varied with the acidity of the solution.

Introduction

The acid-catalyzed rearrangement of pinacol has been thought to proceed according to the A–1 mechanism on the basis of the Zucker-Hammett hypothesis[1] from the evidence that the rate is proportional to the Hammett acidity function h_0. But the explanations about the mechanisms proposed for the rearrangement are not necessarily the same in details. For instance, Duncan *et al.*[2] and Deno *et al.*[3] concluded that the reaction proceeded directly from the conjugate acid of pinacol to pinacolone, and it was not through the carbonium ion as an intermediate. On the other hand, Bunton *et al.*[4] reported from the evidence of O^{18} exchange experiments on pinacol that solvent water captures *ca.* 70% of carbonium ions, regenerating the pinacol enriched in O^{18} at relatively low acidities and in such an acid concentration the slow step should be the conversion of carbonium ion into pinacolone, possibly synchronizing with proton removal. Furthermore, they considered that at higher acidities, such as 50 wt% sulfuric acid, more than 90% of carbonium ions would be rearranged to pinacolone and the rate of rearrangement becomes similar to that of formation of carbonium ions. The result of 2-methylpropane-1,2-diol[5] as a related reaction is also consistent with the conclusion that the slow step is the

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* Paper which appeared in this journal, **38**, 50 (1968) is numbered as Part I in this series.

[1] L. M. Zucker and L. P. Hammett, *J. Am. Chem. Soc.*, **61**, 2791 (1939)

[2] J. F. Duncan and K. R. Lynn, *J. Chem. Soc.*, **1956**, 3512, 3519, 3674

[3] N. C. Deno and C. Perizzolo, *J. Org. Chem.*, **22**, 836 (1957)

[4] C. A. Bunton, T. Hadwick, D. R. Llewellyn and Y. Pocker, *J. Chem. Soc.*, **1958**, 403

[5] J. B. Ley and C. A. Vernon, *ibid.*, **1957**, 2987

formation of carbonium ion from the conjugate acid of the glycol.

Recently, Stiles and Mayer[6] has proposed a new mechanism that involves the formation of a "carbonium hydrate" structurally analogous to an "intimate ion pair" and is relatively close to the concerted process in which the elimination of a water molecule from the protonated pinacol is accompanied rather than followed by the migration of the alkyl group.

In many organic reactions it is well-known that the volume of activation helps to reveal the mechanism and gives frequently a useful information about the structural details of the transion state. Thus, in order to examine the mechanism by means of the volume of activation, the effect of pressure on the rate of rearrangement of pinacol has been measured. In addition, an attempt to seek evidence on the question whether the rate-controlling step varies with the acidity of solution has been also made by measuring the volume of activation in concentrated sulfuric acid.

Experimentals

Materials

Pinacol was prepared from acetone[7], and recrystallized from benzene as the hexahydrate, mp. 47°C. The solution of hydrochloric acid used as a catalyst was made by diluting the analytical grade concentrated acid and standardized with sodium carbonate solution. The concentrated solutions of sulfuric acid as a solvent were prepared by the volume method and the exact composition was determined by the density measurement. All other chemicals used were of reagent grade and were not further purified.

Analytical methods

The rate of rearrangement in dilute aqueous hydrochloric acid was followed by the conventional periodate titration for unchanged pinacol; 5 m*l* of the reaction mixture was added to a mixture containing 10 m*l* of saturated sodium hydrogencarbonate solution and 10 m*l* of 0.02 mole/*l* periodic acid, and the resulting solution was allowed to stand for over night at room temperature. Then 10 m*l* of 2N hydrochloric acid and 10 m*l* of 1.2 mole/*l* potassium iodide solution were added, and the iodine liberated was titrated with 0.1N sodium thiosulfate solution using starch as indicator.

On the other hand, for the reaction in concentrated sulfuric acid the rate was determined by measuring the optical density of the reaction mixture with a Hitachi Model-139 spectrophotometer. The measurements were done at 271 mμ in 47.5 wt% sulfuric acid and at 267 mμ in 55.8 wt%, at which an absorption maximum of pinacolone exists.

Apparatus and procedure

The runs at atmospheric pressure were carried out under nitrogen atmosphere in a glass vessel immersed in a thermostat controlled within ± 0.05°C of the setting temperature.

Under high pressure, the apparatus shown in Fig. 1 was used. The reaction mixture was enclosed

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6) M. Stiles and R. P. Mayer, *J. Am. Chem. Soc.*, **81**, 1497 (1959)

7) R. Adams and E. W. Adams, "Org. Synth.," Vol. 5, p. 87, ed. by C. S. Marvel, John Wiley and Sons, Inc., London (1925)

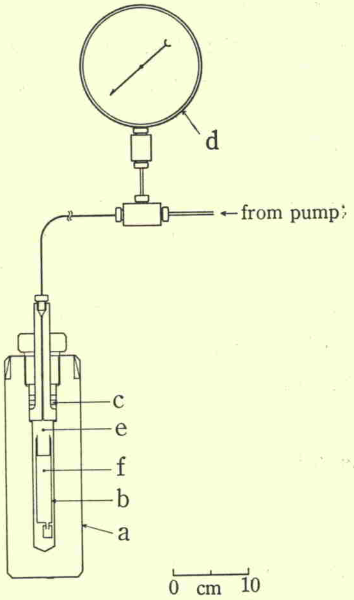

Fig. 1 High pressure apparatus

a: pressure vessel
b: glass syringe
c: packing
d: Bourdon gauge
e: silicone oil
f: reaction mixture

in a glass syringe with a teflon cap, put in the pressure vessel which was filled with silicone oil as pressure-transmitting fluid and placed in the thermostat. The pressure vessel was sealed by "unsupported area" packing of teflon and neoprene rubber rings. The pressure was generated by means of a high-pressure hand pump connected with the apparatus and was measured directly by a Bourdon tube gauge, which was calibrated against a pressure balance made by the American Instrument Co. Inc.

The reaction mixture was prepared by the volume method using acid and pinacol solutions of known concentrations at room temperature, and was quickly poured into the reaction vessel.

Results

The rate was measured usually over a range of 0∼50% of complete reaction. Each solution was measured at least twice under a given condition.

Since the reaction was kinetically of first order in pinacol, the first order rate constants k_{a1} for runs with dilute solution of hydrochloric acid were obtained graphically in usual way. The kinetical results are listed in Table 1. The second order rate constants k_{a2} given were obtained by dividing the first order constants k_{a1} by the concentration of acid corrected for the compression and thermal expansion of the reaction mixture, which were assumed to be the same as that of water[8].

For reactions in concentrated acid, 55.8% sulfuric acid solution, first order rate constants were

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8) P. W. Bridgman, *Proc. Am. Acad. Arts Sci.*, **48**, 309 (1912)

Table 1 Rate constants for the rearrangement of pinacol catalyzed by hydrochloric acid

T,°C	P, bar	[C_{HCl}], mole·l^{-1}	$10^6\ k_{n1}$, sec^{-1}	$10^6\ k_{n2}$, l·mole^{-1}·sec^{-1}
60	1	0.885	2.58	2.96
	467	0.885	2.12	2.38
	955	0.871	1.87	2.06
	1447	0.885	1.64	1.78
65	1	0.871	5.65	6.61
	467	0.871	4.90	5.62
	955	0.871	4.45	5.02
	1447	0.871	4.13	4.58
70	1	0.871	12.4	14.5
	467	0.871	11.0	12.6
	955	0.871	9.97	11.3
	1447	0.871	9.08	10.1

The reaction mixture was initially about 0.03 mole/l in pinacol at room temperature and pressure. The concentration of hydrochloric acid shows the value at room temperature and pressure.

obtained graphically by plotting $\ln(D_\infty - D_t)$ against time t, where D_∞ and D_t are the optical densities of the reaction mixture after the completion of reaction (practically, 98% of complete reaction) and after time t, respectively. In 47.5 wt% solution the rate was fairly slow, so that a long time was required for the estimation of D_∞. Therefore, in this case the first order rate constants were determined conveniently from the slope of a graph of $\ln(D_{t+\Delta t} - D_t)$ against time t by the application of Guggenheim's method[9], where the interval of time Δt was about two fold of the half-life. The kinetical

Table 2 Rate constants for the rearrangement of pinacol in concentrated sulfuric acid at 25°C

H_2SO_4, wt%	P, bar	$10^6\ k_{n1}$, sec^{-1}
47.5 (3.10)	1	9.68
	216	9.15
	467	8.73
	955	7.62
	1,447	6.77
55.8 (4.00)	1	67.7
	216	65.5
	467	60.7
	955	55.2
	1,447	48.9

Initial concentrations of pinacol at room temperature and pressure were 2.49×10^{-2} mole/l in 47.5 wt% sulfuric acid and 2.19×10^{-2} mole/l in 55.8 wt%. The number in parenthesis denotes the value of $-H_0$.

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[9] E. A. Guggenheim, *Phil. Mag.*, **2**, 538 (1926)

results in both solutions are listed in Table 2, in which the rate constants are not converted to the second order constants because neither the compressibility nor the pressure dependence on the acidity of concentrated sulfuric acid is available in the literatures and in addition the rate at higher acid concentrations as the present conditions are unlikely of first order in acid.

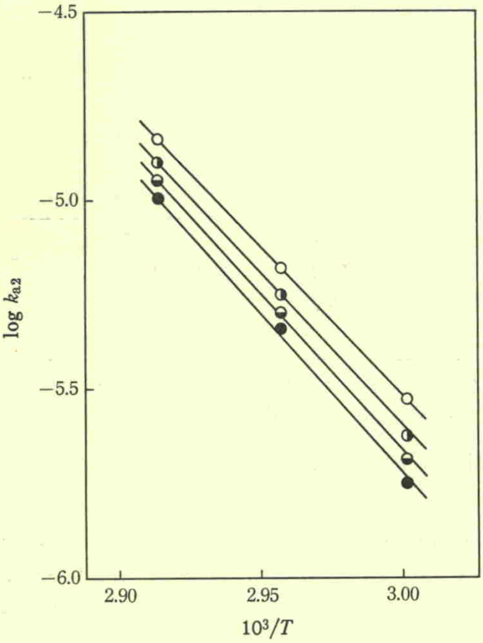

Fig. 2 Arrhenius plot for the rearrangement of pinacol catalyzed by hydrochloric acid

○: 1 bar ◑: 467 bar

◒: 955 bar ●: 1,447 bar

Table 3 Energies and entropies of activation for the rearrangement of pinacol

P, bar	E, kcal·mole^{-1}	$\Delta S^{\ddagger}$, cal·deg^{-1}·mole^{-1}
1	36.1	22.3
467	37.0	24.6
955	37.9	27.0
1,447	38.7	29.1

An Arrhenius plot for the reaction catalyzed by hydrochloric acid is given in Fig. 2, and shows fairly better straight lines at each pressure. Table 3 shows the values of activation parameters calculated from these plots. The activation energy obtained at 1 bar is in fairly good agreement with the values of 32.7 kcal/mole determened by Duncan *et al.*[2] and 33.7 kcal/mole by Bunton *et al.*[4] Also this is comparable to the value 31 kcal/mole estimated for the rearrangement of benzopinacol[10] by an analogous reaction process. The second order rate constants as a function of pressure at each temperature are shown in Fig. 3. Similary the first order rate constants in concentrated acid are also plotted against pressure in Fig. 4.

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[10] H. J. Gebhart, Jr. and K. H. Adams, *J. Am. Chem. Soc.*, **76**, 3925 (1954)

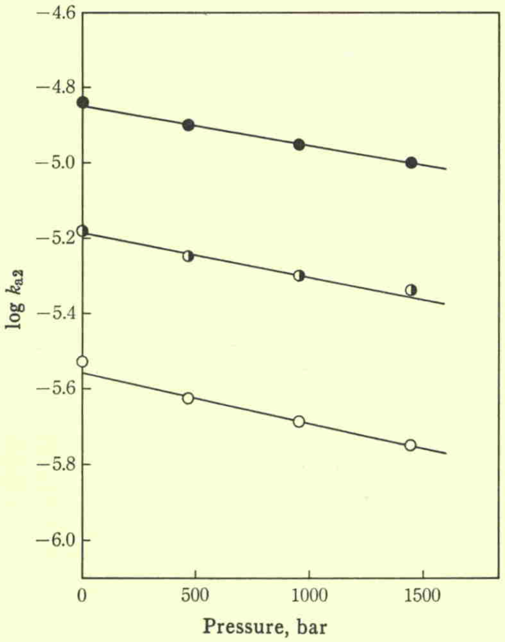

Fig. 3 Effect of pressure on the rate of the rearrangement of pinacol catalyzed by hydrochloric acid

○: 60°C ◑: 65°C ●: 70°C

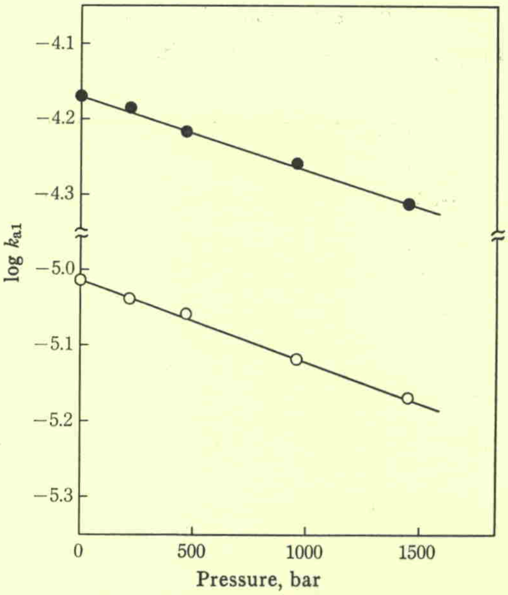

Fig. 4 Effect of pressure on the rate of the rearrangement of pinacol in concentrated sulfuric acid at 25°C

○: 47.5 wt% ●: 55.8 wt%

All of them were fitted graphically to the equation,

$$\log k = a + bP,$$

and the volume of activation at 1 bar was calculated from those slopes using the equation,

$$\left(\frac{\partial \ln k}{\partial P}\right)_T = -\frac{\Delta V^{\neq}}{\boldsymbol{R}T} = 2.303b.$$

The results are summarized in Table 4.

Table 4 Volumes of activation for the rearrangement of pinacol

T, °C	$\Delta V^{\neq}$, cm^3·mole^{-1}	T, °C	H_2SO_4, wt %	$\Delta V^{\neq}$, cm^3·mole^{-1}
60	8.4	25	47.5	6.1
65	7.6	25	55.8	5.6
70	6.8			

For comparison with values measured by Deno *et al.*[3] and Stiles *et al.*[6], the rate constants in sulfuric acid at 25°C and 1 bar were plotted against the Hammett acidity function H_o The values of H_o used were taken by interpolating the data of Long and Paul[11]. The result is given in Fig. 5, in which our values lie on the best straight line through the points and the agreement with acidity dependence

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[11] M. A. Paul and F. A. Long, *Chem. Rev.*, **57**, 1 (1957)

is shown to be satisfactory. The ρ-value given by the equation,

$$\log k_{a1} = -\rho H_{\circ} + \text{constant}\,,$$

is found to be 0.95 from the graph.

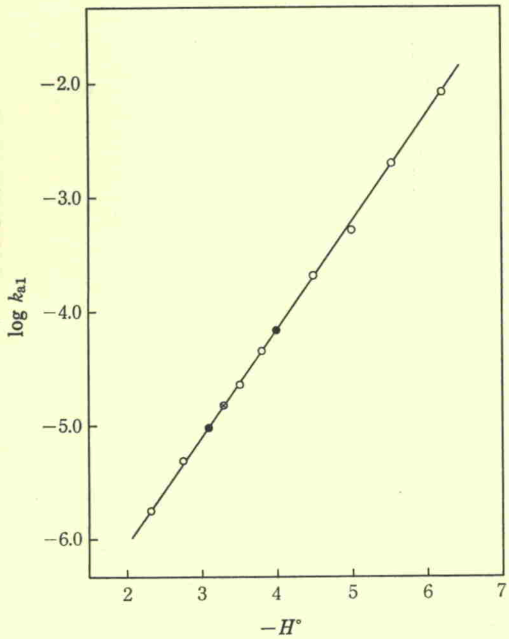

Fig. 5 Dependence of $-H_{\circ}$ on the rate of the rearrangement of pinacol at 25°C and 1 bar

○: Deno *et al.*[3]
⊗: Stiles *et al.*[6]
●: this work

Discussion

Reaction mechanism

The carbonium ion mechanism[4][5][12], in which the carbonium ion formation is rate-determining and the so-called concerted mechanism[2][3] involving the direct decomposition of the protonated pinacol into pinacolone, has been so far proposed for the rearrangement of pinacol. However, to account for the recent evidences related to the oxygen exchange[4][13] and the migration tendencies of alkyl groups[6] in the rearrangement, both remain somewhat in doubt and are inadequate. So some modifications are possible on the grounds of the consideration by Stiles *et al.*[6] and the inference from analogy with alcohol dehydration[14]. It becomes apparent from the detailed discussion presented later that a possible mechanism for the rearrangement of pinacol in strong acid solution may be envisaged as follows:

$$\mathrm{POH} + \mathrm{H_3O^+} \overset{K_1}{\rightleftarrows} \mathrm{POH_2^+} + \mathrm{H_2O}\,, \qquad \text{(i)}$$

$$\mathrm{POH_2^+} \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} (\mathrm{P{-}{-}{-}OH_2})^+\,, \qquad \text{(ii)}$$

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12) F. A. Long and M. A. Paul, *Chem. Rev.*, **57**, 974 (1957)

13) Y. Pocker, *Chem. Ind.*, **1959**, 332

14) R. H. Boyd, R. W. Taft, Jr., A. P. Wolf and D. R. Christman, *J. Am. Chem. Soc.*, **82**, 4729 (1960)

$$(P{-}{-}{-}OH_2)^+ \xrightarrow{k_3} KH^+ + H_2O\,, \tag{iii}$$

$$KH^+ + H_2O \xrightarrow{\text{fast}} K + H_3O^+\ , \tag{iv}$$

where POH represents the pinacol, K the pinacolone and $(P{-}{-}{-}OH_2)^+$ an intermediate ion, similar to the "carbonium hydrate" named by Stiles *et al*[6].

If one assumes a steady state concentration of the intermediate ion $(P{-}{-}{-}OH_2)^+$, the overall rate of rearrangement can be expressed by the equation,

$$\text{rate} = \frac{K_1 \cdot k_2 \cdot k_3 \cdot h_\circ \cdot [\text{POH}]}{k_{-2} + k_3}\ , \tag{1}$$

where k's are the rate constants, K_1 the equilibrium constant for the first step (i), $h_\circ$ the Hammett acidity function and the brackets denote the concentration terms.

Assuming the limiting case where $k_{-2} \gg k_3$, the rate equation reduces to

$$\text{rate} = K_1 \cdot K_2 \cdot k_3 \cdot h_\circ \cdot [\text{POH}]\ , \tag{2}$$

where K_2 is the equilibrium constant for the second step (ii). In agreement with observed kinetic results, the rearrangement is found to be first order in pinacol and the rate to be proportional to the Hammett acidity function $h_\circ$.

Volumes of activation

The measured volumes of activation are positive, and decrease with increasing temperature, which implies evidently that the initial state is thermally more expansible than the transition state as expected also from the results of the entropy of activation. Further detailed consideration about the volume of activation will be given below.

The apparent second order rate constant k_{a2} obtained experimentally in dilute aqueous hydrochloric acid is given by the equation,

$$\text{rate} = k_{a2}\,[C_{HCl}]\,[\text{POH}]\ . \tag{3}$$

By comparison of equations (2) and (3),

$$k_{a2} = K_1 \cdot K_2 \cdot k_3 \cdot h_\circ \,/\, [C_{HCl}] \tag{4}$$

Therefore, the measured volume of activation $\Delta V^{\neq}$ is actually represented as a composite quantity as follows :

$$\Delta V^{\neq} = \Delta V_1 + \Delta V_2 + \Delta V_3^{\neq} + \frac{\boldsymbol{RT}\ \partial \ln([C_{HCl}]/h_\circ)}{\partial P}\ , \tag{5}$$

where ΔV_1 and ΔV_2 represent the volume changes for the steps (i) and (ii), respectively, and $\Delta V_3^{\neq}$ the volume of activation for the slow step (iii). The fourth term on the right hand side in equation (5) can be estimated approximately in the following way : if the change of $h_\circ$ with pressure could be assumed to be due to only the change of the concentration of acid with pressure[15], then

$$\frac{\boldsymbol{RT}\ \mathrm{d} \ln([C_{HCl}]/h_\circ)}{\mathrm{d}\,P} = \boldsymbol{RT}\,\kappa \left[1 - \frac{\mathrm{d} \ln h_\circ}{\mathrm{d} \ln [C_{HCl}]} \right], \tag{6}$$

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[15] R. J. Withey and E. Whalley, *Trans. Faraday Soc.*, **56**, 901 (1963)

where κ is the compressibility of the solution.

In $[C_{HCl}]=0.871\sim0.885$ mole/l, $d\ln h_o/d\ln[C_{HCl}]=1.36$ from the variation of h_o with the concentration of hydrochloric acid at 25°C[11]. Using the compressibilities of water[8] or aqueous hydrochloric acid taken by interpolating the data from the literature[16],

$$\frac{RT\, d\ln([C_{HCl}]/h_o)}{dP} \cong 0.40\sim0.42\ \mathrm{cm^3/mole}$$

Evidently, the variation of h_o with pressure is small and insignificant in the case of so dilute acid as in this work, and then it follows from the observed values of $\Delta V^{\ne}$ that

$$\Delta V_1+\Delta V_2+\Delta V_3^{\ne} \cong 7.2\sim8.8\ \mathrm{cm^3/mole}$$

in the experimental temperature range.

In the pre-equilibrium proton transfer (i), there is no change in the number of molecules and probably little change in the electrostriction of the solvent, so that the volume change ΔV_1 should be slightly positive and not so different from zero[17]. Hence, it follows that the measured volume of activation is mainly determined by the sum of ΔV_2 and $\Delta V_3^{\ne}$.

In order to elucidate the location of the transition state on the reaction coordinate, we determined the volume change for the complete reaction from the density measurement, and found to be 30±0.5 cm^3/mole at 65°C and 1 bar. The partial molar volume of pinacol is less than that of pinacolone by 12 cm^3/mole, and this results from strong hydrophilic character of the hydroxyl group of pinacol. From these results, the volume of activation $\Delta V^{\ne}$ is about one third the volume change of complete reaction ΔV, and so the transition state can be located closely to the initial state in volume and seems to have the character similar to pinacol. The present mechanism may be also valid on the view of these.

The conversion of a van der Waals bond between a molecule and the conjugate acid of substrate to a partial valence bond in the transition state results in the decrease of volume of about 10 cm^3/mole, as found in most acid-catalyzed hydrolysis[18]. On the basis of this evidence, if the intermediate ion $(P{-}{-}{-}OH_2)^+$ is structurally similar to the transition state in which a molecule of water takes part in the A–2 mechanism, then the volume change ΔV_2 of step (ii) becomes about 8 cm^3/mole. This value is little differenct from that of $\Delta V_1+\Delta V_2+\Delta V_3^{\ne}$ estimated above. Consequently, the volume of activation for the slow step (iii) seems to be near to zero or slightly negative, which is not hard to understand because there is an intramolecular migration of the methyl group to the α–C atom without further appreciable elongation of the $C{-}{-}{-}OH_2$ bond and there will be more diffusion of the positive charge in the transition state than in the original ion $(P{-}{-}{-}OH_2)^+$.

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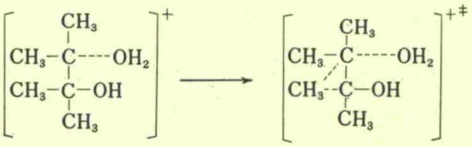
16) J. Timmermans, "The Physico-Chemical Constants of Binary Systems in Concentrated Solutions", Vol. 4, p. 453, Interscience Publishers Inc., New York (1960)

17) E. Whalley, *Trans. Faraday Soc.*, **55**, 798 (1959)

18) E. Whalley, "Advances in Physical Organic Chemistry", Vol. 2, p. 93, ed. by V. Gold, Academic Press, London (1964)



The effect of pressure on the rearrangement in concentrated sulfuric acid could be also discussed in the same manner. Since the apparent first order rate constant obtained is expressed by

$$k_{a1} = K_1 \cdot K_2 \cdot k_3 \cdot h_o \quad , \qquad (7)$$

the volume of activation is given by

$$\Delta V^{\ddagger} = \Delta V_1 + \Delta V_2 + \Delta V_3^{\ddagger} - \frac{RT\,\partial \ln h_o}{\partial P} \quad . \qquad (8)$$

Since the variation of h_o with the concentration of acid at 25°C[11], that is,

$$\frac{d \ln h_o}{d \ln [C_{H_2SO_4}]} = 8.5 \, , \qquad \text{(at 47.5 wt\%)}$$

$$\frac{d \ln h_o}{d \ln [C_{H_2SO_4}]} = 10.3 \, , \qquad \text{(at 55.8 wt\%)}$$

by using the compressibility data of Gibson[19], the dependences of h_o on pressure are found to be

$$\frac{RT\,\partial \ln h_o}{\partial P} = 6.2 \text{ cm}^3/\text{mole} \quad ,$$

$$\frac{RT\,\partial \ln h_o}{\partial P} = 7.1 \text{ cm}^3/\text{mole} \quad ,$$

respectively. Hence, the value of $\Delta V_1 + \Delta V_2 + \Delta V_3^{\ddagger}$ becomes actually 12.3 cm^3/mole in the former and 12.7 cm^3/mole in the latter, and is likely to be little different in these acid concentrations. According to the foregoing discussion, these values may be regarded as being close to ΔV_2 itself that arises mainly from the elongation of a covalent bond C–OH$_2^+$. For comparison, the value of $\Delta V_1 + \Delta V_2 + \Delta V_3^{\ddagger}$ at 25°C obtained by extrapolating the results in dilute hydrochloric acid is 14.4 cm^3/mole compared with that obtained in concentrated acid. The agreement between this value and the corresponding values in concentrated acid is satisfactory, and the small difference is probably due to special properties of the solvent systems. Thus, it may be certainly expected from these evidences that no change of mechanism has essentially occurred with the acidity of solution.

Energies and entropies of activation

The activation process in the rearrangement seems to closely resemble that in the dehydration of alcohol to olefin. Boyd *et al.*[14] have recently proposed a new mechanism proceeding through an encumbered carbonium ion intermediate to the transition state as follows ;

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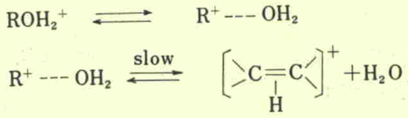
[19] R. E. Gibson, *J. Am. Chem. Soc.*, **56**, 4, 865 (1934)



$$ROH_2^+ \rightleftarrows R^+ \text{---} OH_2$$

$$R^+ \text{---} OH_2 \overset{\text{slow}}{\rightleftarrows} \left[\gt C \overset{}{\underset{|\atop H}{=}} C \lt \right]^+ + H_2O$$

They estimated the enthalpies and entropies of activation for alcohol dehydration, that is, $\varDelta H^{\neq} = 33.9 \pm 0.3$ kcal/mole and $\varDelta S^{\neq} = 19 \pm 2$ cal/deg·mole for *t*-butyl alcohol, and $\varDelta H^{\neq} = 29.1 \pm 0.5$ kcal/mole and $\varDelta S^{\neq} = 12 \pm 2$ cal/deg·mole for *t*-amyl alcohol, respectively. From the thermodynamic and activation parameters for the hydration of dissolved isobutene[20] are also derived the values of 32.7 ± 0.2 kcal/ mole and 13.3 ± 0.7 cal/deg·mole for the corresponding values for dehydration of *t*-butyl alcohol. Comparing these values with the present results for the rearrangement of pinacol, the enthalpies of activation for both reactions are found to be nearly the same, but the entropies to be less than that of the rearrangement by about 10 cal/deg·mole. This appears to be probably due to the substantial difference between the change of entropy accompanied by the migration of the methyl group in the activation process and that by formation of "π-complex" in the dehydration.

On the basis of these considerations, it is supposed that the mechanism for the rearrangement of pinacol does not essentially differ from that for the dehydration and further the oxygen exchange of alcohol. Accordingly, the intermediate ion $(P\text{---}OH_2)^+$ presented in the proposed mechanism seems to be almost analogous to the encumbered carbonium ion[14] in character.

Although any definitive evidence that a modified carbonium ion is favored over the classical one has not been obtained in this work, it may be concluded from the above discussions that the rearrangement mechanism involving such a reaction intermediate is reasonable in the light of the present results. The character of the intermediate should be argued in more detail with further extensive data.

The authors would like to express their thanks to Professor J. Osugi of Kyoto University for his advice and encouragement.

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[20] E. L. Purlee, R. W. Taft, Jr. and C. A. DeFazio, *J. Am. Chem. Soc.*, **77**, 837 (1955); R. W. Taft, Jr. and P. Riesz, *ibid.*, **77**, 902 (1955)