THE REVIEW OF PHYSICAL CHEMISTRY OF JAPAN, VOL. 40, NO. 2, 1970

EFFECTS OF PRESSURE ON ORGANIC REACTIONS IV

The Base-Catalyzed Decomposition of Diacetone Alcohol in Aqueous Ethanol Mixtures

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The effects of solvent and pressure on the rate of the base-catalyzed decomposition of diacetone alcohol in aqueous ethanol mixtures have been measured at 20.00~40.00°C and at 30.00~40.00°C, respectively. The variation with solvent composition of the activation parameters $\Delta G_P^{\neq}$, $\Delta H_P^{\neq}$ and $\Delta S_P^{\neq}$ at constant pressure indicates that $\Delta G_P^{\neq}$ gives only a slight solvent dependence compared with $\Delta H_P^{\neq}$ and $\Delta S_P^{\neq}$, so that the latter two parameters vary with solvent composition in a compensating manner given by $\delta\Delta H_P^{\neq}=\beta\delta\Delta S_P^{\neq}$. The β-value seems to be strongly dependent on the acidity of organic cosolvent. The small minima observed in $\Delta H_P^{\neq}$ and $\Delta S_P^{\neq}$ in highly aqueous region may be mainly attributed to relatively large change of internal pressure in the solvent system, which will reflect an increase in its structuredness by small addition of organic cosolvent to water. The activation volume exhibits also the minimum behavior similar to those in $\Delta H_P^{\neq}$ and $\Delta S_P^{\neq}$, and changes the sign from negative to positive as the temperature rises. From these results, it is reasonably suggested that in highly aqueous solvents a water molecule at least is incorporated into the transition state and that the cleavage of carbon-carbon bond of the reaction species in the slow step is accompanied rather than followed by the hydrogen abstraction from a water molecule leading to the formation of products.

Introduction

The base-catalyzed decomposition of diacetone alcohol has been extensively investigated at atmospheric pressure for a long time[1)~4)]. It was first found by Åkerlöf[2)] in 1928 that this reaction was strongly dependent upon the medium. He measured the variation of the rate with solvent composition in aqueous mixtures of a number of different aliphatic alcohols at 25°C and found very interesting results that in the systems involving ethanol and *n*-propanol the rate changed through a minimum as the content of alcohol increased, whereas it increased monotonically in isopropanol system

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(*Received April 10, 1971*)

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2) G. Åkerlöf, *ibid.*, **50**, 1272 (1928)
3) G. M. Murphy, *ibid.*, **53**, 977 (1931)
4) V. K. LaMer and M .L. Miller, *ibid.*, **57**, 2674 (1935)

and decreased in methanol, ethylene glycol and glycerol systems. Amis *et al.*[5] attempted to examine the behavior of reaction in mixed solvents using the data of Åkerlöf on the basis of a theoretical equation proposed by them for the reaction between ions and dipolar molecules, and claimed to agree reasonably with their theory only for the results in ethanol and *n*-propanol solvent systems, but such a solvent dependence of the rate is almost unknown in exact nature of it. Thus the solvent effect observed in aqueous binary solvents is mysterious from the viewpoint of solute-solvent interaction and any explanation about it has been not yet established.

As is well known, the effect of pressure on the rate of ionic reactions varies with the characters of solvents, and therefore the activation volume measured in such solvent as aqueous alcohol mixture should be sufficiently expected to vary profoundly, reflecting the change of structure and nature[6][7] of the medium with composition. Recently the analysis of such a variation of the pressure dependence with binary solvent composition has been powerfully made on some reactions, especially the solvolysis of organic halides[8]~[13] and the other compounds[14] in aqueous alcohol mixtures, and the specific nature of the substrate-solvent interaction has been discussed.

Now, the mechanism for the decomposition of diacetone alcohol catalyzed by strong bases in aqueous solution has been proposed on the grounds analogous to aldol condensation, in which the rate-controlling step is thought to be the cleavage of the conjugate anion of reactant into acetone and carbanion[15]. However, there is a significant question whether a solvent molecule is incorporated into the transision state. Therefore, it is necessary to elucidate the structural detail about the transition state with a view to understanding the complicated effect of solvent on the rate process. As emphasized by Whalley[16][17], the activation volume is more useful for the determination of reaction mechanism than any other activation parameters and serves as a tool for estimating the structure of the transion state. Therefore, it is worthwhile to measure the activation volume of the reaction concerned in the variation of solvent composition in connection with the present problems.

Thus, in this paper the author gives the descriptions about the effects of solvent and pressure on

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the rate of the base-catalyzed decomposition of diacetone alcohol in aqueous ethanol mixtures. The observed results have been examined in terms of the changes in activation parameters with solvent composition, temperature and pressure, and also considered on the question, what kind of isokinetic condition[14)18)] will be found in the studied reaction. In addition, a reasonable mechanism for the decomposition has been discussed in the light of their results.

Experimental

Materials

Commercial diacetone alcohol was redistilled twice under reduced pressure, and the middle fraction (bp. 69~70°C/20 mm) was retained. Ethanol was purified by the Lund-Bjerrum magnesium method and distilled. Water was obtained by distilling that which was passed through the deionizing resin. Stock solutions of mixed solvents were prepared by the weight method. The alkaline solution used as catalyst was prepared by dissolving the required amount of commercial guaranteed reagent of sodium hydroxide in desired solvent mixtures.

Reagents for analysis of the carbonyl group, which were used in the rate measurement with an analytical method, were prepared according to the method of Smith and Mitchell[19)].

The other chemicals used were of reagent grade and were purified by conventional means when necessary.

Apparatus and kinetic procedure

The rate at atmospheric pressure was measured by an analytical method based on the oximation of carbonyl group in early runs and by a dilatometric method in late ones. Runs with the former method were done in a glass vessel, which was connected through a glass tube with a gas reservoir combined with a glass syringe, and the whole system was replaced with nitrogen to avoid carbon dioxide. The samples for analysis were slowly taken out through a capillary tube mounted in the vessel by pushing the syringe. The latter measurements were made in dilatometers of about 40 m*l* capacity, and with the capillary of from 65 to 90 cm long and 0.8 mm in inner diameter, according to the usual way. The reaction mixture was heated to drive out the dissolved gases just before its use. The thermostat used in both methods was controlled within ± 0.01°C.

Runs under pressures were carried out with two kinds of high pessure apparatus. One of them is shown in Fig. 1, being capable of continuous sampling from the pressure vessel, which is essentially similar to those used by Gibson *et al.*[20)] and recently Whalley *et al.*[17)]. In this apparatus a glass syringe served as the reaction vessel is attached to one end of high pressure capillary tube, which is screwed into the plug and connected at the other end with a sampling valve. The pressure vessel is sealed by

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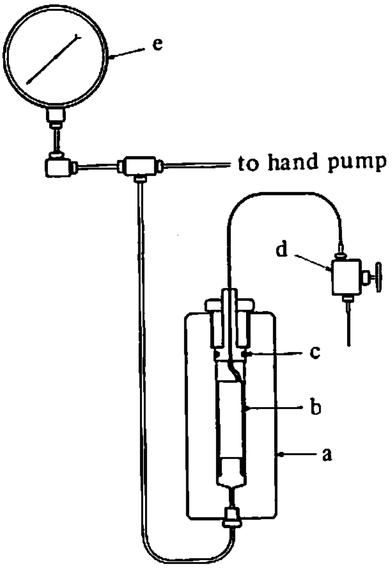

Fig 1 High pressure apparatus
a: Pressure vessel
b: Reaction vessel
c: O-ring
d: Sampling valve
e: Bourdon gauge

means of an O-ring, and the whole system of the apparatus is filled with silicone oil as the pressure-transmitting fluid. The pressure was generated by means of a high-pressure hand pump connected with the system and was measured by means of a Bourdon gauge, which was calibrated against a pressure balance made by the American Instrument Co., Inc. The glass vessel and the pressure vessel were both immersed in a thermostat controlled within ± 0.05°C. In doing a run, the glass syringe filled with the reaction mixture was attached to the capillary tube jutted out inside the plug, and then the pressure vessel was assembled quickly and pressurized. After the desired time, the solution for analysis was carefully taken out in a suitable vessel by opening the valve, and then the pressure was maintained by pumping oil into the system. About 6~8 samples were taken during kinetic runs under pressure. Another apparatus is what is able to measure piezometrically without ang sampling the rate of reaction which proceeds with a change of pressure in a closed vessel by using a manganin-resistance gauge. It had been designed and constructed in the course of the present investigation, and was effectively employed in place of the analytical method in the rest of run. The details of its constitution and the technique for measurement have been described elsewhere[21]. The thermostat capable of ±0.001°C control was used in this method.

The reaction mixtures in all runs were made up by the weight method from diacetone alcohol, sodium hydroxide solution of known concentration and mixed solvent, and the concentrations were expressed in terms of their molalities. The solution was initially about 0.4~0.5 mole/kg·solvent with respect to diacetone alcohol. The initial and the final solutions of reaction were titrated with standard oxalic acid. but there was no appreciable change in the concentration of alkaline as catalyst. The actual concentration of catalyst is approximately in the range $10^{-3}\sim 2\times10^{-2}$ mole/kg·solvent.

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21) *Bull. Chem. Soc. Japan*, in press

Analysis

In the sampling-type method, the decomposition of diacetone alcohol was mainly followed by determining the concentration of carbonyl group by the oximation with hydroxylamine hydrochloride[19]. The procedure is as follows.

About 2 m*l* of the reaction mixture was pipetted into a stoppered flask containing the weighed amount (8 m*l*) of 0.5 N-hydroxylamine hydrochloride including thymol blue as indicator and then weighed. After allowing to stand for about 5 hours at room temperature, the solution was titrated with 0.5 N-standard sodium hydroxide in 90 per cent methanol until the hue of solution matched that of the reference solution at the same volume adjusted by using 90 per cent methanol as diluent. The reference solution was made up by mixing 2 m*l* of the reaction mixture including no catalyst with 8 m*l* of hydroxylamine reagent and by adding the calculated quantity of 0.5 N-standard sodium hydroxide in 90 per cent methanol, which was required for neutralization of liberated hydrochloride. Analytical error for pure reactant in this method was within ±0.1 per cent. In practice, small correction for alkaline in the reaction mixture was made to calculate the net amount consumed for the determination of carbonyl group.

Gas chromatographic technique as another method for analysis was also temporarily employed in some runs. The amount of acetone produced was estimated from chromatogram by the application of the internal standardization method with methanol as the standard substance. The analysis was performed by a Shimazu gas chromatograph, model GC-1C fitted with a glass column (3.375 m) of polyethylene glycol 1,000 at 76°C with 40 m*l*/min of helium carrier gas. The sample removed from the vessel was pipetted into the weighed solution containing the required amount of hydrochloric acid to quench the catalyst and an appropriate amount of methanol, and then the total mixture was weighed. After the solution was completely neutralized using acid solution, it was dried with anhydrous sodium sulfate and the supernatant solution was chromatographed. The extent of conversion was determined from the chromatogram of the reaction mixture using a calibration curve obtained between the weight ratio of acetone to methanol and the ratio of their peak heights.

Results

Since the decomposition was kinetically of first order in diacetone alcohol, almost all of the first order rate constants k_1 were obtained graphically by the application of Guggenheim's method[22],

$$\begin{aligned} k_1 t + \ln(V_{t+\Delta t} - V_t) &= \ln[(V_0 - V_\infty)(e^{-k_1 \Delta t} - 1)] \\ &= \text{constant}, \end{aligned} \tag{1}$$

where V_t and $V_{t+\Delta t}$ represent the values of a variable corresponded to the conversions at time t and $t + \Delta t$, respectively. That is, they are dependent on the method used in the rate measurement and refer to m*l* of sodium hydroxide reagent consumed to titrate the reaction mixture of unit weight, the height of

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22) E. A. Guggenheim, *Phil. Mag.*, **2**, 538 (1926)

the meniscus of dilatometer and the unbalanced potential in the piezometric measurement. Only the data with the gas chromatographic determination were analyzed according to the usual first order rate equation. The time interval Δt during the kinetic run was actually about 2 times of half-lives of the reaction. The second order rate constants k_a were obtained for convenience by dividing the measured first order constants by the concentration of alkaline used over the whole range of solvent composition.

The second order rate constants obtained at various conditions of temperature, pressure and solvent composition are summarized in Tables 1～3. The rate constants at atmospheric pressure as a

Table 1 Rate constants for the base-catalyzed decomposition of diacetone alcohol in water at various pressures

Pressure atm	$10^2 \cdot k_a$, $kg \cdot mole^{-1} \cdot sec^{-1}$ 20.00°C	 30.00°C	 35.00°C	 40.00°C
1	0.625[a]	1.50[a]	2.43[b]	4.01[a]
	0.617[b]	1.50[b]		4.00[b]
100		1.55		
500		1.73[a]	2.51	3.78
		1.71		
1,000		1.93[a]	2.60	3.41
		1.97		
1,500		2.11[a]	2.68	3.15
		2.21		

[a] From runs with an analytical method based on the oximation of carbonyl group
[b] From usual dilatometric measurements
All the unspecified values are those obtained from piezometric measurements and those at 30.00°C are from the previous paper[31].

Table 2 Rate constants for the base-catalyzed decomposition of diacetone alcohol in aqueous ethanol at 1 atm

X[a]	$10^2 \cdot k_a$, $kg \cdot mole^{-1} \cdot sec^{-1}$ 20.00°C	 30.00°C	 35.00°C	 40.00°C
0.10	0.592[b]	1.43	2.30	3.73
		1.42[b]		
0.20		1.44	2.21	3.65
0.24	0.558[b]	1.38[b]		3.58
0.42	0.501	1.29		4.49
0.63	0.505	1.70		5.53
0.76	0.509	1.96		5.85
0.98	0.634	2.44[b]		7.30

[a] Mole fraction of ethanol
[b] From runs with an analytical method based on the oximation of carbonyl group
All the unspecified values are those obtained from usual dilatometric measurements.

Table 3 Rate constants for the base-catalyzed decomposition of diacetone alcohol in aqueous ethanol at various pressures

X[a]	$10^2 \cdot k_a$, kg·mole^{-1}·sec^{-1}			
	Pressure, atm			
	1	500	1,000	1,500
30.00°C				
0.10	1.42[b] 1.43[c]	1.71	2.05	2.32
0.20	1.44[c]	1.66	1.84	2.15
0.24	1.38[b]	1.61[b]	1.82[b]	1.91[b]
0.42	1.29[c]	1.34[b]	1.41[b]	1.49[b]
0.51	1.41[c]	1.43[d]	1.46[d]	1.49[d]
0.63	1.70[c]	1.60	1.57[d]	1.51[d]
0.76	1.96[c]	1.82[d]	1.71[d]	1.61[d]
0.98	2.44[b]	2.16[b]	1.96[b]	1.74[b]
35.00°C				
0.10	2.30[c]	2.47	2.65	2.69
0.20	2.21[c]	2.40	2.51	
40.00°C				
0.10	3.73[c]	3.57	3.33	3.04
0.20	3.65[c]	3.42	3.17	2.99
0.63	5.53[c]	4.78	4.08	3.52

[a] Mole fraction of ethanol

[b] From runs with an analytical method based on the oximation of carbonyl group

[c] From usual dilatometric measurements

[d] From runs with an analytical method using gas chromatographic technique

All the unspecified values are those obtained from piezometric measurements.

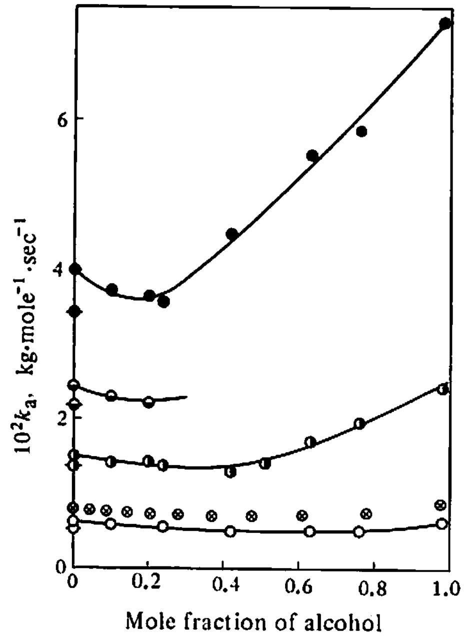

Fig. 2 Variation of the rate constants with solvent composition for the decomposition of diacetone alcohol at 1 atm

LaMer *et al.*[4]:
○--- 20°C, ◐--- 30°C,
◒--- 35°C, ●--- 40°C
Åkerlöf[2]:
⊗--- 25°C
this work:
○--- 20.00°C, ◐--- 30.00°C,
◒--- 35.00°C, ●--- 40.00°C

function of the solvent composition are shown in Fig. 2, in which they are plotted for comparison together with those calculated from the data in the literatures. The values of LaMer *et al.*[4)] in water, in which the concentrations of alkaline are expressed in terms of normality, are all less than those observed, and the differences between both ralues at four temperatures are in the range of 10~20 per cent. Those of Murphy[3)], 5.13×10^{-3} kg/mole·sec at 20°C and 1.34×10^{-2} kg/mole·sec at 30°C, are also low in the same degree. The observed effect of solvent composition on the rate in mixed solvents are similar to the result of Åkerlöf[2)] at 25°C, but his values are also a little less than those expected from the present data. The reason for these discrepancy is not clear at present.

The activation energies E_a for the decomposition under various solvent and pressure conditions were graphically obtained by using the usual equation

$$E_a = -2.303\cdot RT\left(\frac{\partial \log ka}{\partial T}\right)_P , \tag{2}$$

Table 4 Constant-pressure activation parameters for the decomposition of diacetone alcohol in aqueous ethanol at 30.00°C and various pressures

X^a	P, atm	$\Delta G_P^{\ddagger}$, kcal·mole^{-1}	$\Delta H_P^{\ddagger}$, kcal·mole^{-1}	$\Delta S_P^{\ddagger}$, cal·deg^{-1}·mole^{-1}
0.00	1[b]	20.4	16.6 (17.2)	−12.4
	1[c]	20.4	16.7 (17.3)	−12.1
	1	20.3	16.6 (17.2)	−12.2
	500	20.2	13.2 (13.8)	−23.1
	1,000	20.1	9.9 (10.5)	−33.7
	1,500	20.0	6.1 (6.7)	−46.0
0.10	1	20.3	16.4 (17.0)	−13.0
	500	20.2	13.0 (13.6)	−23.8
	1,000	20.1	8.5 (9.1)	−38.3
	1,500	20.0	4.5 (5.1)	−51.2
0.20	1	20.3	17.3 (17.9)	− 9.9
	500	20.2	12.9 (13.5)	−24.2
	1,000	20.1	9.5 (10.1)	−35.0
	1,500	20.1	5.6 (6.2)	−47.7
0.24	1	20.3	17.7 (18.3)	− 8.7
0.42	1	20.4	19.3 (19.9)	− 3.6
0.63	1	20.2	21.0 (21.6)	+ 2.6
	500	20.3	19.9 (20.5)	− 1.2
	1,000	20.3	17.3 (17.9)	− 9.8
	1,500	20.3	15.3 (15.9)	−16.4
0.76	1	20.1	21.6 (22.2)	+ 4.8
0.98	1	20.0	22.0 (22.6)	+ 6.6

The numbers in parenthesis denote the values of activation energy

[a] Mole fraction of ethanol

[b] Calculated from the data of LaMer *et al.*[4)]

[c] Calculated from the data of Murphy[3)]

where R is the gas constant and T is the absolute temperature. The activation enthalpies $\varDelta H_P^{\neq}$, entropies $\varDelta S_P^{\neq}$ and Gibbs free energies $\varDelta G_P^{\neq}$ at constant pressure were calculated from the values of k_a and E_a using the equations,

$$\varDelta H_P^{\neq} = E_a - RT\,, \tag{3}$$

$$\varDelta S_P^{\neq} = 2.303\cdot R\cdot\left\{\log ka - \log\left(\frac{k_B T}{h}\right) + \frac{\varDelta H_P^{\neq}}{2.303\cdot RT}\right\} \tag{4}$$

and

$$\varDelta G_P^{\neq} = \varDelta H_P^{\neq} - T\varDelta S_P^{\neq}, \tag{5}$$

where k_B is Boltzmann's constant and h is Plank's constant. The values obtained at a mean temperature of 30.00°C are summarized in Table 4, in which the results calculated from the data at atmosperic pressure in the literatures are included for comparion. The activation energy had been found to be a function of temperature by the detailed study of LaMer *et al.*[4]. Their value is 17.2 kcal/mole in water at 30°C, being identical with the observed one. The agreement with 17.3 kcal/mole obtained from the data of Murphy[3] is also well satisfactory.

The effect of pressure on the rate constants in water and aqueous alcohol mixtures was graphically examined in the usual manner. Consequently, it was found that all of them were approximately fitted to the relation,

$$\log k_a = a + bP\,, \tag{6}$$

where a and b are the constants, and P is the pressure. Therefore, the activation volumes $\varDelta V^{\neq}$ at 1

Table 5 Activation volumes for the decomposition of diacetone alcohol in aqueous ethanol at various temperatures

Temp., °C	X^a	$\varDelta V^{\neq}$, cm^3·mole^{-1}
30.00	0.00	−6.6
	0.10	−9.0
	0.20	−6.8
	0.24	−6.9
	0.42	−2.3
	0.51	−0.8
	0.63	+1.9
	0.76	+3.4
	0.98	+5.7
35.00	0.00	−1.6
	0.10	−3.6
	0.20	−3.5
40.00	0.00	+3.8
	0.10	+3.0
	0.20	+3.5
	0.63	+7.7

[a] Mole fraction of ethanol

atm were calculated from the slopes b by the equation

$$\Delta V^{\neq} = -\,2.303 \cdot \boldsymbol{RT} \left(\frac{\partial \log ka}{\partial P} \right)_T$$

$$= -\,2.303 \cdot b \cdot \boldsymbol{RT}\,. \qquad (7)$$

The values obtained at three temperatures are summarized in Table 5.

Discussion

Solvent dependence of the rate

The effect of solvent on the rate of decomposition at atmospheric pressure is shown in Fig. 2. The rate varies with the increase of the content of alcohol through a small minimum,of which the position tends to shift toward the highly aqueous region of the solvent as the temperature rises. For the solvent dependence of the rate of this reaction, Amis *et al.*[5] attempted to explain from the change of dielectric constant of the medium, using their kinetic equation derived for ion-dipole reaction. From the examination for the data of Åkerlöf[2] in various kinds of aqueous alcohol mixtures, it had been pronounced that only the results in ethanol and *n*-propanol systems were in reasonable agreement with their theory. However, the abnormal effects in methanol and isopropanol systems could not been explained.

The hydroxide ion OH^- in aqueous alcohol mixtures can be thought to be in equilibrium with alcohol ROH as organic cosolvent, as given by the equation[15]

$$OH^- + ROH \rightleftharpoons RO^- + H_2O\,. \qquad (8)$$

Hence, the actual concentration of OH^- varies with the change of acidity of alcohol coexisted. By Hine *et al.*[21], from the results of measurement on the relative acidity of various substances in isopropanol solution, the acidity of lower aliphatic alcohols is found to increase in the order of isopropyl $<$ ethyl $<$ water $<$ methyl. Therefore, most of the marked lowering effect on the rate in methanol system[2][24] can be explained on the basis of the more acidic nature of alcohol. Howeve, in the solvent system involving alcohol which is in acidity comparable to or less than water, the bulk dielectric property of the medium rather than the acidity will contribute significantly to the solvent dependence of the rate. The increasing effect in the rate by addition of ethanol and *iso*propanol[24] agrees with the direction expected from the decrease of the bulk dielectric constant of mixed solvent on the basis of simple electrostatic grounds, if it could be assumed that the dispersal of electrostatic charge occurs in the activation process of the studied reaction. Also, the dielectric constant of the aqueous mixture decreases as the temperature rises[25] and so the rate increases in agreement with the present results, especially in alcoholrich region. The mild decrease of the rate in less alcoholic solvent range suggests partly the

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[24] Unpublished work

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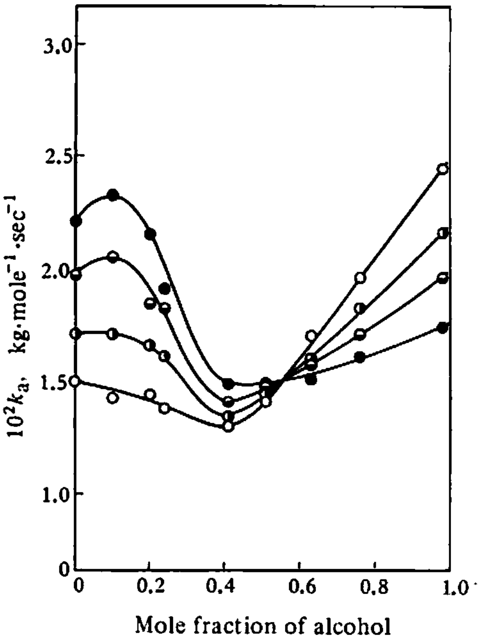

Fig. 3 Variation of the rate constants with solvent composition for the decomposition of diacetone alcohol at 30.00°C and various pressures

○--- 1 atm, ◑--- 500 atm,
◒--- 1,000 atm, ●--- 1,500 atm

existence of an equilibrium given by equation (8) because the acidity of ethanol is almost comparable to that of water[23], but the exact cause cannot be immediately proved.

The effect of solvent on the rate under pressures is shown in Fig. 3. The rate as a function of solvent composition changes in a profound manner with pressure, and particularly interesting view can be taken in highly aqueous solvents. The rate in this region is accelerated by pressure and the effect of pressure reaches a maximum in 0.1 mole fraction of alcohol. Such a feature in the pressure effect cannot be explained in terms of simple ion-dielectric theory[26], but it must be attributed to the changes of specific interactions between the reactants and the solvent. Of course, it seems to reflect the significant changes in structuredness and the nature of aqueous binary solvent with composition, as is pointed out from the results for the solvolysis of organic halides[7,8,10,13].

The description of the effect of pressure on the solvent effect is essentially the same as that of the effect of solvent on the activation volume $\Delta V^{\neq}$ as represented by the equation[27]

$$\frac{\partial}{\partial P}\left(\frac{\partial \ln k}{\partial X}\right)_T = \frac{\partial}{\partial X}\left(\frac{\partial \ln k}{\partial P}\right)_T = -\frac{1}{RT}\left(\frac{\partial \Delta V^{\neq}}{\partial X}\right)_T, \qquad (9)$$

where X is a parameter denoting the composition of solvent mixture, and the latter will be in some detail later.

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26) S. D. Hamann, "Physico-Chemical Effects of Pressure", p. 52, Butterworths Scientific Publications, London (1957)

27) B. T. Baliga and E. Whalley, *Can. J. Chem.*, **42**, 1835 (1964)

Effect of solvent on the activation parameters

The activation parameters at constant pressure and the activation volume as a function of solvent composition are illustrated in Figs. 4 and 5, respectively. The activation free energy $\Delta G_P^{\ddagger}$ exhibits only a slight solvent dependence compared with the activation enthalpy $\Delta H_P^{\ddagger}$ and entropy $\Delta S_P^{\ddagger}$, so that the latter two parameters increase in a complementary manner with solvent composition. The small minima in $\Delta H_P^{\ddagger}$ and $\Delta S_P^{\ddagger}$ appear in near 0.1 mole fraction of alcohol, which coincide in position with that of the activation volume $\Delta V^{\ddagger}$. Such a minimum behavior observed in highly aqueous solvent is similar in the character to the well-known results obtained for solvolysis of organic halides[28]. However, it is supposed from the difference of reaction type that the reason for these observations must appreciably differ from that in the latter reactions in which the change of a dipole-solvent interaction plays the most important part in the rate process. Since the present reaction is an ion-dipole reaction between diacetone alcohol and hydroxide ion, all the changes of ion-dipole, ion-solvent and dipole-solvent interactions in the activation process will probably exert more complicated effects on the kinetics in aqueous solvent mixture. Then, it is necessary to examine whether the observed

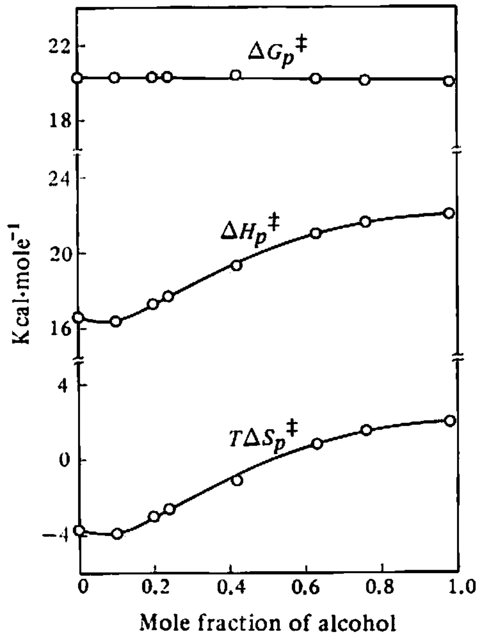

Fig. 4 Solvent composition dependence of the activation parameters at constant pressure for the decomposition of diacetone alcohol at 30.00°C

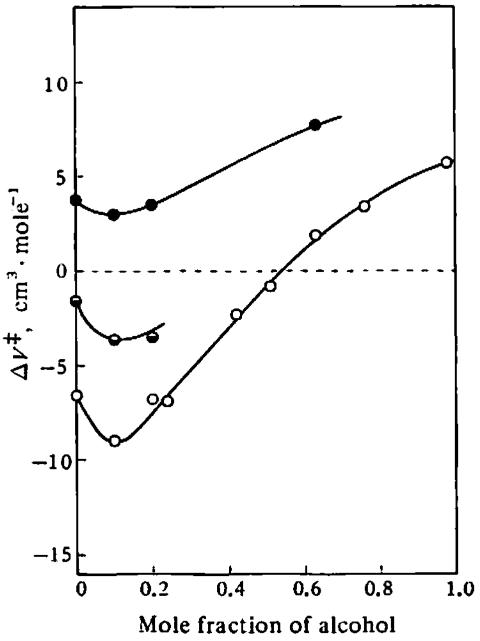

Fig. 5 Solvent composition dependence of the activation volume for the decomposition of diacetone alcohol at various temperatures

○--- 30.00°C, ◒--- 35.00°C,
●--- 40.00°C

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[28] S. Winstein and A. H. Fainberg, *J. Am. Chem. Soc.*, 79, 5937 (1957); J. B. Hyne, *ibid.*, 82, 5129 (1960); J. B. Hyne, R. Wills and R. E. Wonkka, *ibid.*, 84, 2914 (1962); J. B. Hyne and R. Wills, *ibid.*, 85, 3650 (1963); R. E. Robertson and S. E. Sugamori, *ibid.*, 91, 7254 (1969)

minimum behavior may be also regarded as an appearance caused by them. Whalley *et al.*9)12)14) pointed out from their results for solvolysis in aqueous alcohol mixtures that the complexity of the variation in the constant-pressure parameters may be ascribed mainly to the large change of thermal expansivity of solvent with composition and so the constant-volume parameters are undoubtedly the simpler functions of the solvent composition. Thus, it is of interest to argue the solvent dependence in the studied reaction in terms of the constant-volume parameters.

The activation internal energy $\Delta U_V^{\ddagger}$ and entropy $\Delta S_V^{\ddagger}$ at constant volume are obtained from the relations17)

Table 6 Constant-volume activation parameters for the decomposition of diacetone alcohol in aqueous ethanol at 30.00°C

X^a	$10^6 \cdot \alpha^b$, deg^{-1}	$10^6 \cdot \kappa^c$, atm^{-1}	$T\alpha/\kappa$, atm	$T\alpha\Delta V^{\ddagger}/\kappa$, $cal \cdot mole^{-1}$	$\Delta U_V^{\ddagger}/\kappa$ $kcal \cdot mole^{-1}$	$T\Delta S_V^{\ddagger}$, $kcal \cdot mole^{-1}$
0.00	303	44.5	2060	−329	16.9	−3.4
0.10	563	40.3	4240	−924	17.3	−3.0
0.20	813	46.0	5360	−883	18.2	−2.1
0.24	863	49.3	5310	−887	18.6	−1.7
0.42	987	65.0	4600	−256	19.6	−0.8
0.63	1064	80.8	3990	+184	20.8	+0.6
0.76	1089	88.6	3730	+307	21.3	+1.2
0.98	1108	98.8	3400	+469	21.5	+1.5

[a] Mole fraction of ethanol

[b] From the data in the literature29)

[c] From the data of Moesveld at 25°C30)

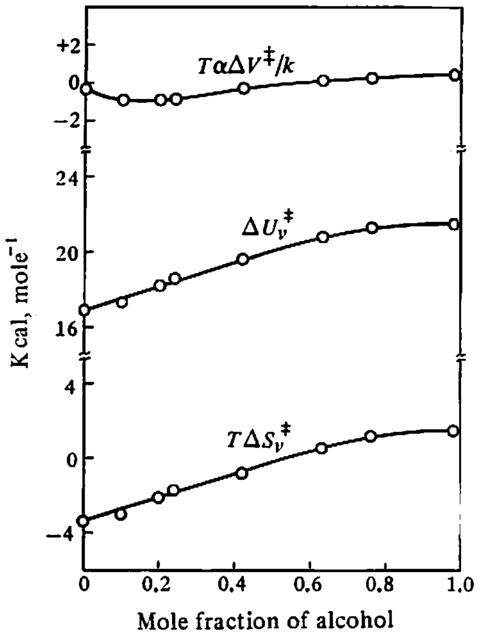

Fig. 6 Solvent composition dependence of the activation parameters at constant volume for the decomposition of diacetone alcohol at 30.00°C

$$\Delta U_V^{\neq} = \Delta H_P^{\neq} - T\alpha\Delta V^{\neq}/\kappa\,, \tag{10}$$

$$T\cdot\Delta S_V^{\neq} = T\cdot\Delta S_P^{\neq} - T\alpha\Delta V^{\neq}/\kappa\,, \tag{11}$$

where α and κ are the isopiestic thermal expansivity and the isothermal compressibility of reaction mixture respectively, and they can be assumed without any significant error to be the same as those of the pure solvent. The results obtained for the present reaction are listed in Table 6 and the solvent dependences of $\Delta U_V^{\neq}$, $T\Delta S_V^{\neq}$ and $T\alpha\Delta V^{\neq}/\kappa$ are shown in Fig. 6. There are no minima in both $\Delta U_V^{\neq}$ and $T\Delta S_V^{\neq}$, which vary with solvent composition in apparently simpler manner than $\Delta H_p^{\neq}$ and $T\Delta S_p^{\neq}$ because of the absence of the $T\alpha\Delta V^{\neq}/\kappa$ profoundly dependent on the solvent. From the values in Tables 5 and 6, it is evident that the change of $T\alpha\Delta V^{\neq}/\kappa$ with solvent is due to both the change of $T\alpha/\kappa$ as a character of solvent mixture and that of $\Delta V^{\neq}$ subjected chiefly to the change of reacting solute-solvent interaction, but is largely due to the former rather than the latter in highly aqueous region. The term $T\alpha/\kappa$ can be also thermodynamically related to the external pressure P and the so-called internal pressure of the reaction mixture $(\partial U/\partial V)_T$ as follows:

$$\begin{aligned}\frac{T\alpha}{\kappa} &= T\left(\frac{\partial P}{\partial T}\right)_V \\ &= P + \left(\frac{\partial U}{\partial V}\right)_T.\end{aligned} \tag{12}$$

Hence, such a solvent dependence of this term reflects essentially that of the internal pressure in the medium. The value of $T\alpha\Delta V^{\neq}/\kappa$ is eventually given as the sum of two terms $P\Delta V^{\neq}$ and $(\partial U/\partial V)_T\cdot\Delta V^{\neq}$, referring to the works of expansion against the external pressure and against the internal pressure respectively[14], and therefore it follows that the activation parameters at constant pressure vary in more responsible manner for the nature of the solvent system than those at constant volume do. From these considerations, it may be concluded that the small minima in $\Delta H_p^{\neq}$ and $\Delta S_p^{\neq}$ observed in highly aqueous region of solvent composition are mainly attributed to the relatively large change of the internal pressure in the solvent system which will reflect the significant change of structuredness in the medium by small addition of organic cosolvent. In connection with this, recently Macdonald *et al.*[31] have found experimentally that the maximum in $(\partial U/\partial V)_T$ occurs in three alcohol-water mixtures at 30.0°C and in the mixtures of such more hydrophobic alcohol as *n*-propanol and *t*-butanol appears more sharply at lower contents (near 0.1 mole fraction) than in methanol-water system.

Isokinetic condition

The condition at which the rate virtually comes to be not affected at all by the change of a parameter is called the isokinetic condition and has been found in a large number of reactions[18]. However, the existence of isokinetic solvent with respect to pressure has been predicted only in the isotope

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29) International Critical Tables, vol. 3, p. 116, McGraw-Hill Book Company, Inc., New York (1928)

30) A. L. Th. Moesveld, *Z. Physik. Chem.* (Leipzig), **105**, 450 (1923)

31) D. D. Macdonald, J. B. Hyne and F. L. Swinton, *J. Am. Chem. Soc.*, **92**, 6355 (1970)

exchange reaction[14], and it has not been still proved experimentally. As shown in Fig. 3, there is no effect of pressure on the rate in near 0.55 mole fraction of alcohol. The solvent mixture in this region in which the activation volume becomes zero is exactly the isokinetic solvent with respect to pressure and is given by the condition[14]

$$\left(\frac{\partial \ln k}{\partial P}\right)_{T,S,\cdots} = 0\,, \tag{13}$$

where S denotes the parameter with respect to solvent. This expression indicates also the isokinetic temperature with respect to pressure in a given solvent system. It is found in the results in Fig. 5 that the activation volume in highly aqueous solvents changes the sign from negative to positive between 35°C and 40°C. This implies evidently that there will be the temperature at which the rate is independent on the pressure, that is, the isokinetic temperature with respect to pressure. It is supposed that the grounds of these observations may be ascribed in large part to the changes of more specific interactions between the reactants and the solvent which cannot be explained on the basis of simple ion-dielectric theory.

The parallel behavior observed between the variations of $\Delta H_p^{\ddagger}$ and $\Delta S_p^{\ddagger}$ with solvent composition in Fig. 4 is more clearly demonstrated in Fig. 7, in which their values under pressures are also plotted together. It shows that the well-known compensation relationship $\delta\Delta H_p^{\ddagger}=\beta\delta\Delta S_p^{\ddagger}$, where the symbol δ denotes the change of parameters with solvent composition and β is a constant given in

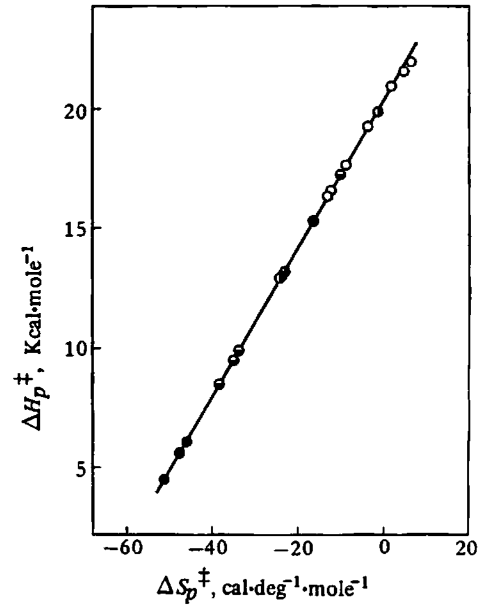


Fig. 7 Correlation of $\Delta H_P^{\ddagger}$ and $\Delta S_P^{\ddagger}$ for the decomposition of diacetone alcohol at various pressures

○--- 1 atm, ◑--- 500 atm,
◒--- 1,000 atm, ●--- 1,500 atm

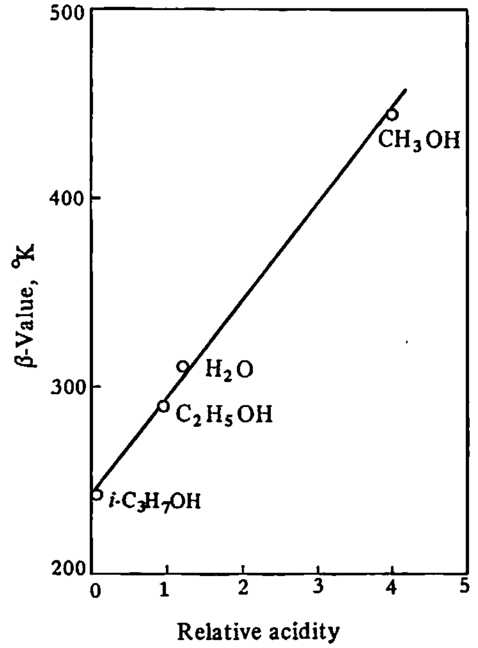


Fig. 8 Relationship between β-value and the relative acidity[23]

terms of absolute temperature, is satisfactorily found in all of the studied solvent systems. The β-value is exactly calculated by the method of least-squares from the result in each solvent system, and is found to be 311°K for pure water, 290°K for mixed solvent and 307°K for all the results plotted in Fig. 7. In addition, it has been found that the values in aqueous methanol and isopropanol systems are 445°K and 243°K, respectively[24]. The solvent dependence of the activation parameters in the system exhibiting the compensation effect can be represented by the equation[18]

$$\begin{aligned}\delta\Delta G_P^{\ddagger} &= \delta\Delta H_P^{\ddagger} - T\delta\Delta S_P^{\ddagger}\\ &= (\beta-T)\,\delta\Delta S_P^{\ddagger}\,. \end{aligned}\tag{14}$$

When $T=\beta$°K, $\delta\Delta G_P^{\ddagger}=0$. That is, this temperature is the isokinetic one with respect to solvent, and the condition is also given as follows[14]:

$$\left(\frac{\partial \ln k}{\partial S}\right)_{T,P,\cdots} = 0\,. \tag{15}$$

The β-value obtained appears to be significantly dependent on the nature of alcohol as organic cosolvent. The details of the solvent dependence are illustrated in Fig. 8, in which the β-value is plotted for convenience against the relative acidity of water and alcohols measured by Hine *et al.*[23]. From the fact that there is a surprisingly good correlation between both values, it is strongly suggested that the degree of compensation effect seems to be closely responsible for the acidity of organic cosolvent rather than for the dielectric constant of it and so this is probably associated with the extent of the stabilization of reacting anion by the acidic nature of the medium.

Activation volume and reaction mechanism

The activation volume $\Delta V^{\ddagger}$ for the decomposition of diacetone alcohol in water is -6.6 cm^3/mole at 30.00°C and increases as the temperature rises, giving $+3.5$ cm^3/mole at 40.00°C. As shown in Fig. 5, the effect of temperature on $\Delta V^{\ddagger}$ is significantly affected by solvent composition and is exerted maximally at 0.1 mole fraction of alcohol, at which the extremum behavior in $\Delta V^{\ddagger}$ appears in a similar manner as in $\Delta H_p^{\ddagger}$ and $\Delta S_p^{\ddagger}$. This large temperature dependence in highly aqueous region of the solvent composition is quite surprising in comparison with those observed in the usual reactions, and it implies obviously that the thermal expansion of the transition state is much larger than that of the initial state as predicted also from the results of the activation entropy satisfying the thermodynamic relationship

$$\left(\frac{\partial \Delta V^{\ddagger}}{\partial T}\right)_P = -\left(\frac{\partial \Delta S^{\ddagger}}{\partial P}\right)_T\,. \tag{16}$$

The major source of such a dependence in volume must be undoubtedly sought in the structure of the solvent environment around the reaction species rather than in that of them, which may be also supported by the effect of solvent on $\Delta V^{\ddagger}$.

The variations of three activation parameters with pressure in some solvents are shown in Fig. 9, in which $\Delta G_p^{\ddagger}$ varies little with pressure, so that $\Delta H_p^{\ddagger}$ and $\Delta S_p^{\ddagger}$ decrease largely in a compensating manner, being in character similar to their behaviors with solvent composition. Since $\Delta V^{\ddagger}$ can be given thermodynamically by two partial derivatives with respect to pressure as follows:

$$\Delta V^{\ddagger} = \left(\frac{\partial \Delta G_P^{\ddagger}}{\partial P}\right)_T$$

$$= \left(\frac{\partial \Delta H_P^{\ddagger}}{\partial P}\right)_T - T\left(\frac{\partial \Delta S_P^{\ddagger}}{\partial P}\right)_T . \tag{17}$$

It is found that in the solvent range up to 0.1 mole fraction of alcohol the change of $(\partial \Delta H_P^{\ddagger}/\partial P)_T$ with solvent composition outweighs that of $(\partial \Delta S_P^{\ddagger}/\partial P)_T$, leading to more negative value of $\Delta V^{\ddagger}$, whereas in less aqueous region above that composition the situation reverses, $\Delta V^{\ddagger}$ increasing as the organic content in the solvent increases. In other words, it may be stated that the solvent dependence of $\Delta V^{\ddagger}$ is of enthalpy-controlling in the former solvent region and of entropy-controlling in the latter. In agreement with this, it is found that there is a distinct difference in correlation between $\Delta V^{\ddagger}$ and $\Delta S_P^{\ddagger}$ as shown in Fig. 10.

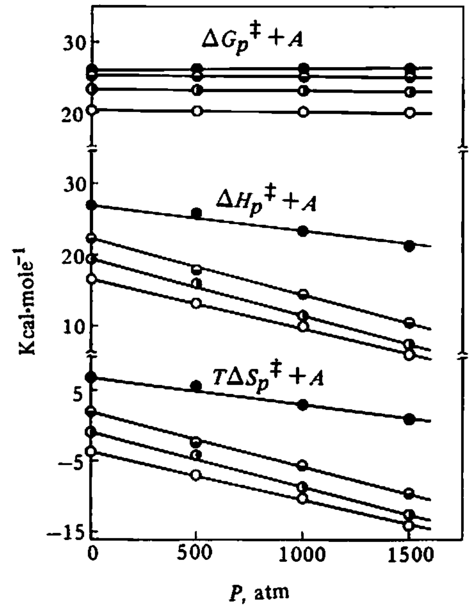


Fig. 9 Pressure dependence of the activation parameters for the decomposition of diacetone alcohol at 30.00°C

○--- (X=0, A=0)
◐--- (X=0.10, A=3)
◒--- (X=0.20, A=5)
●--- (X=0.63, A=6)
X: mole fraction of alcohol

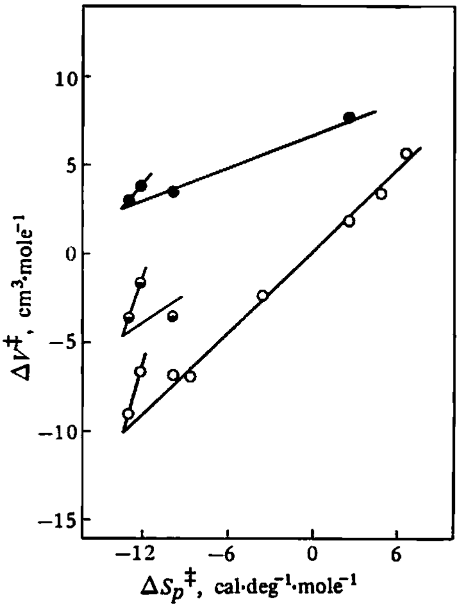
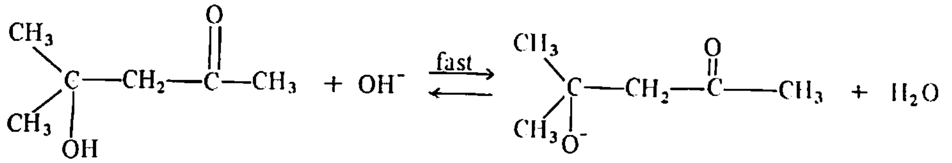


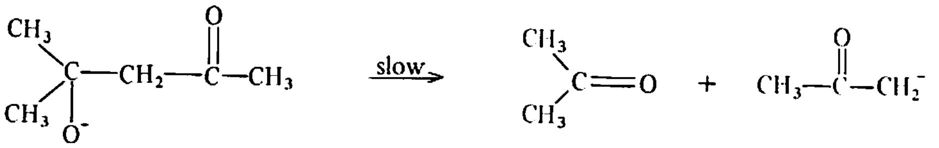
Fig. 10 Relationship between $\Delta V^{\ddagger}$ and $\Delta S_P^{\ddagger}$ for the decomposition of diacetone alcohol

○--- 30.00°C, ◒--- 35.00°C,
●--- 40.00°C

In the mechanism generally accepted[15], the formation of a conjugate anion by the proton removal of hydroxide ion rapidly attains equilibrium and is followed by the unimolecular decomposition of slow step (B-1 mechanism).



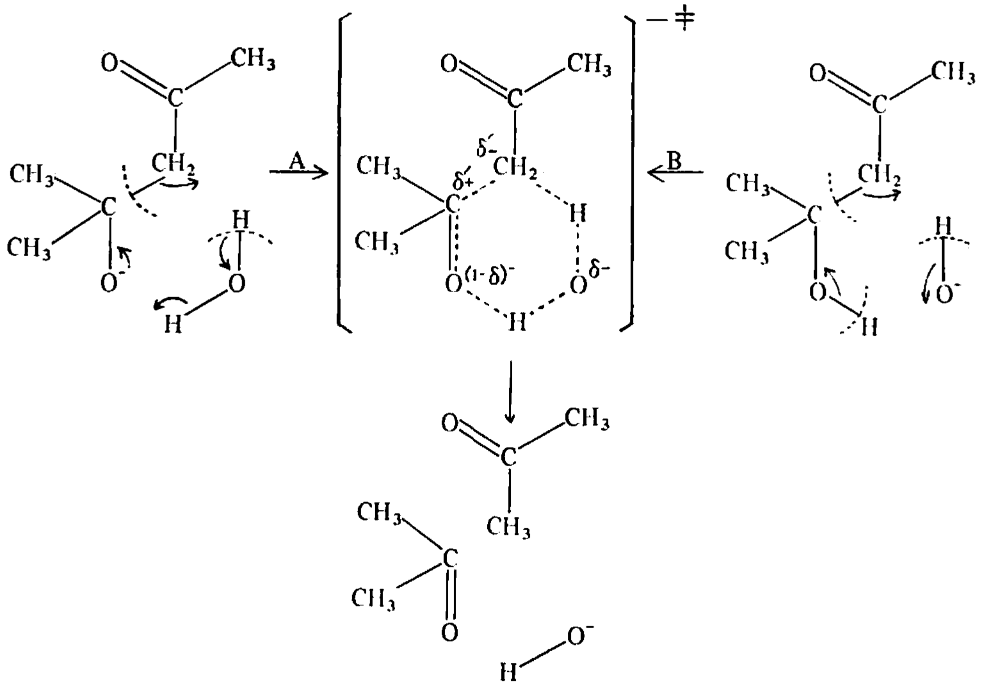
(i)



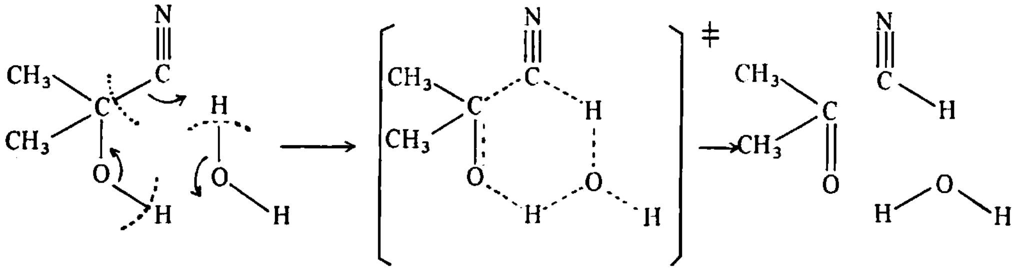
(ii)

From this reaction scheme, the volume change due to only the structural change of reaction species may be apparently assumed to be positive. Therefore, the activation volume observed as a whole should be positive, if there is no large increase in the electric dipole moment in the transition state or no other effect swamping enough the increase in volume due to the partial cleavage of the C-C bond in the slow step. Similar consideration can be also taken for the activation entropy. These predictions, however, are evidently in conflict with the present results.

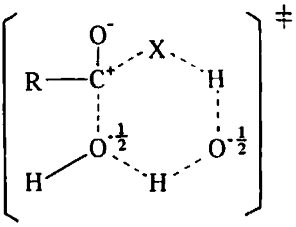
From the large dependence of $\Delta V^{\neq}$ on the temperature and the solvent composition described above, it is suggested that in highly aqueous solvents one molecule of water at least is presumably incorporated into the transition state to make a ring structure linked loosely in which the cleavage of C_{α}-C_{β} bond leading to the formation of products is accompanied rather than followed by the hydrogen abstraction from the water molecule.



Such a transition state may be thought to be formed by the direct process B other than by the process A, but it is impossible at present from the lack of the available informations to decide through which process the reaction proceeds preferably. A similar mechanism may be also proposed for the spontaneous decomposition of acetonecyanohydrin as the related reaction, which has been partly investigated in the same solvent mixtures by the present author, who finds that $\Delta V^{\ddagger}$ for this reaction is positive in water but behaves in a similar manner with varying solvent composition.

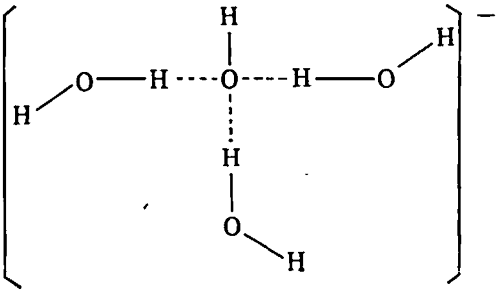


Further details of this reaction will be reported in a subsequent paper. Moreover, the transition state represented above is also structurally analogous to that proposed by Laidler and Chen[32] for the base-catalyzed hydrolysis of esters and amides.



X: -OR′, -NH$_2$

The hydroxide ion in aqueous solution exists in the hydrated form ($H_7O_4^-$) as proved by Yagil and Anbar[33],



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[32] K. J. Laidler and D. Chen. *Trans. Faraday Soc.*, **54**, 1026 (1958)

[33] G. Yagil and M. Anbar, *J. Am. Chem. Soc.*, **85**, 2376 (1963)

therefore, in the process B, a water molecule of hydration at least must be presumably replaced by substrate in the activation process, resulting in the breaking of some hydrogen bonds with the surrounding water structure. In any process described above, the formation of such a transition state must substantially require the reorientation of solvent environment which will result in the local collapse of inherent water structure to a configuration most favorable for the interaction with reaction species and probably causes the decrease in volume. This effect of structure-breaking in the activation process appears more greatly in highly structured solvent than in less structured one and consequently will lead to a largely negative activation volume in the former. As the temperature rises, the structuredness of the medium is reduced and so this effect will become smaller, producing less negative value in $\Delta V^{\ast}$. Since the volume change due to the structural change of reaction species itself can be assumed to be not so largely dependent on the temperature and little on the solvent composition, most of the observed effects of temperature and solvent on $\Delta V^{\ast}$ may be ascribed to such a contribution to the solvent structure.

Acknowledgments

The author wishes to thank Professor J. Osugi of Kyoto University for helpful discussions and suggestions, and Dr. T. Kume for his continued interest and encouragement.

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