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EFFECTS OF PRESSURE ON ORGANIC REACTIONS V

The Base-Catalyzed Decomposition of Diacetone

Alcohol in Two Aqueous Alcohol Mixtures

BY TAKASHI MORIYOSHI

The effects of solvent and pressure on the rate of the base-catalyzed decomposition of diacetone alcohol have been measured in two aqueous mixtures involving methanol and isopropanol at 20.00~40.00°C, and in aqueous methanol at 30.00°C, respectively. The constant-pressure activation parameters for the decomposition in various compositions of solvent exhibit that $\Delta G_P^\ddagger$ is slightly dependent on the solvent composition but oppositely in the direction due to the solvent system, whereas $\Delta H_P^\ddagger$ and $\Delta S_P^\ddagger$ in both systems increase in a compensating manner as the content of alcohol rises, having no minima. The activation volume obtained in the methanol system increases also simply without any minimum against the solvent axis. These results are discussed in comparison with those of the ethanol system studied previously.

Introduction

In the previous paper¹⁾, the effects of solvent and pressure on the rate of the base-catalyzed decomposition of diacetone alcohol in aqueous ethanol mixtures were discussed from the viewpoints of the nature and structuredness of the binary solvent, and of the specific solute-solvent interaction. The constant-pressure activation parameters as a function of solvent composition indicated that $\Delta G_P^\ddagger$ was almost independent of solvent, whereas $\Delta H_P^\ddagger$ and $\Delta S_P^\ddagger$ changed through a faint minimum which coincided in position with that of $\Delta V^\ddagger$ as the organic content in the solvent increased. However, such minimum behaviors similar in character to the well-known results for solvolysis of organic halides²⁾³⁾ disappeared completely in the corresponding constant-volume parameters $\Delta U_V^\ddagger$ and $\Delta S_V^\ddagger$ in agreement with the direction pronounced by Baliga *et al.*⁴⁾⁵⁾. These observations led to the suggestion that the complexity of the solvent dependence observed in the constant-pressure parameters arose mainly from the change of $T\alpha\Delta V^\ddagger/\kappa$ with solvent composition, and that especially in highly aqueous region in which the minima appeared, it was strongly subjected to the change of $T\alpha/\kappa$ as a character of the

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- 1) T. Moriyoshi, *This Journal*, **40**, 102 (1970)
- 2) S. Winstein and A. H. Fainberg, *J. Am. Chem. Soc.*, **79**, 5937 (1957)
- 3) H. S. Golinkin and J. B. Hyne, *Can. J. Chem.*, **46**, 125 (1968)
- 4) B. T. Baliga, R. J. Withey, D. Poulton and E. Whalley, *Trans. Faraday Soc.*, **61**, 517 (1965)
- 5) B. T. Baliga and E. Whalley, *J. Phys. Chem.*, **71**, 1166 (1967)

solvent mixture itself rather than that of $\Delta V^\ddagger$ associated with the reacting solute-solvent interaction.

In general the properties and structuredness of aqueous binary mixture⁶⁾ may be appreciably affected by the nature of added alcohol. Therefore, some variations reflecting the effect of cosolvent would be probably observed in kinetics for varying solvent system. In this connection, it is of interest to examine what change in the solvent and pressure dependences of the concerned reaction will appear in any system of alcohol other than ethanol.

In the present work, thus some measurements have been made of the effects of solvent on the base-catalyzed decomposition of diacetone alcohol in two aqueous systems involving methanol and isopropanol, and of pressure in aqueous methanol. The results are examined in a similar manner to that in the previous ethanol system.

Experimental

Materials

The reagents were the same as those used in the previous work¹⁾, except for methanol and isopropanol which were purified by the Lund-Bjerrum magnesium method and by distilling the commercial guaranteed reagent three times, respectively. The check for impurities in these reagents was made by a gas chromatography.

Kinetics

The rates at atmospheric pressure were measured by the dilatometric method and those at pressures by the piezometric one⁷⁾. The descriptions of the apparatus and technique employed, and of the preparation of reaction mixture, were given previously¹⁾. The reaction mixture used was initially about 0.4~0.5 mole/kg-solvent in diacetone alcohol, and the concentration of sodium hydroxide as a catalyst was determined by titration with the standard oxalic acid, being in the range 10^{-2} ~ 5×10^{-1} mole/kg-solvent for the methanol solvent system and in the range 10^{-3} ~ 10^{-2} mole/kg-solvent for the isopropanol one. For the analysis of the rate of reaction, two sets of measurement were taken in each run so that all the time intervals between both series were equal to about two times of half-lives.

Results

All the first order rate constants were obtained by analyzing graphically the kinetic readings according to the Guggenheim method⁸⁾, and then they were divided by the concentration of alkaline to convert to the second order rate constants k_n . The obtained results are given in Table 1 for two solvent systems at atmospheric pressure and in Table 2 for methanol one at various pressures. The rate constants at atmospheric pressure as a function of solvent composition are shown in Figs. 1 and

6) F. Franks and D. J. G. Ives, *Quart. Rev.* (London), **20**, 1 (1966)

7) T. Moriyoshi, *Bull. Chem. Soc. Japan*, **44**, 2532 (1971)

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

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

X^a	$10^3 k_a$ (kg·mole ⁻¹ ·sec ⁻¹)		
	20.00°C	30.00°C	40.00°C
Methanol			
0.20	2.35	6.77	17.8
0.40	1.12	3.29	9.95
0.60	0.570	1.84	5.52
0.80	0.377	1.17	3.97
1.00	0.246	0.873	2.86
Isopropanol			
0.10	6.40	17.2	43.6
0.20	7.10	19.7	49.7
0.30	8.38	24.9	62.8
0.40	10.3	33.8	87.4

^a Mole fraction of alcohol

Table 2 Rate constants for the base-catalyzed decomposition of diacetone alcohol in aqueous methanol at 30.00°C and various pressures

X^a	$10^3 k_a$ (kg·mole ⁻¹ ·sec ⁻¹)			
	Pressure (atm)			
	1	500	1,000	1,500
0.10	11.2	11.4	11.5	11.7
0.20	6.77	6.40	6.12	5.49
0.40	3.29	2.77	2.41	2.00

^a Mole fraction of methanol

2, together with those obtained from data in the literatures for comparison. The observed effects of solvent on the rate constant are similar to the results of Åkerlöf⁹⁾ in two solvent systems at 25°C and of Murphy¹⁰⁾ in methanol one at 20°C and 30°C, but all the values from these literatures are somewhat less than those measured, as is noticed in ethanol system. It is unlikely that these discrepancies arise from the difference in concentration of alkaline between the present measurements and those ones (0.1 mole/kg·solvent in the literatures), and there is no reasonable explanation for this cause at present. The value of LaMer *et al.*¹¹⁾ in 18.5 volume per cent of methanol (corresponding to about 0.092 mole fraction of alcohol) lies closely on the best curve through the points obtained at 30.00°C, and the agreement is satisfactory. Since the reaction in the isopropanol system becomes very fast as the organic content of solvent rises, especially at higher temperatures, and so the measurements in the region more than 0.4 of alcohol mole fraction are given up. The effect of solvent on the rate constant

9) G. Åkerlöf, *J. Am. Chem. Soc.*, **50**, 1272 (1928)10) G. M. Murphy, *ibid.*, **53**, 977 (1931)11) V. K. LaMer and M. L. Miller, *ibid.*, **57**, 2674 (1935)

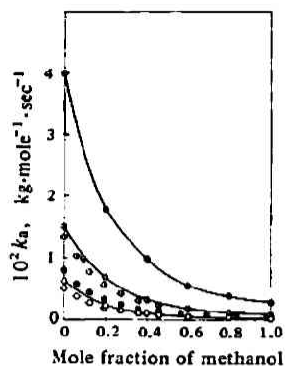


Fig. 1 Variation of the rate constants for the decomposition of diacetone alcohol in aqueous methanol at 1 atm
 Åkerlöf⁽⁹⁾: $\otimes$...25°C
 Murphy⁽¹⁰⁾: $\circ$...20°C,
 $\circ$...30°C
 LaMer *et al.*⁽¹¹⁾: $\odot$...30°C
 This work: $\circ$...20.00°C,
 $\odot$...30.00°C,
 $\bullet$...40.00°C

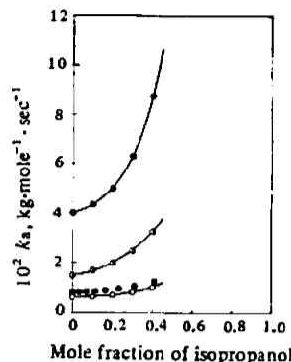


Fig. 2 Variation of the rate constants for the decomposition of diacetone alcohol in aqueous isopropanol at 1 atm
 Åkerlöf⁽⁹⁾: $\otimes$...25°C
 This work: $\circ$...20.00°C,
 $\odot$...30.00°C,
 $\bullet$...40.00°C

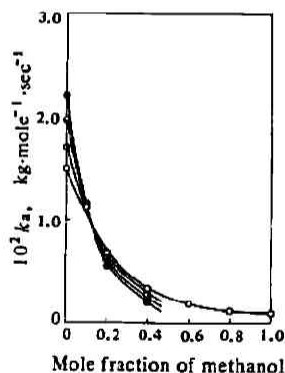


Fig. 3 Variation of the rate constants for the decomposition of diacetone alcohol at 30.00°C and various pressures
 $\circ$...1 atm, $\odot$...500 atm,
 $\bullet$...1,000 atm, $\bullet$...1,500 atm

at various pressures is shown in Fig. 3.

The constant-pressure activation parameters $\Delta G_P^\ddagger$, $\Delta H_P^\ddagger$ and $\Delta S_P^\ddagger$ for the decomposition in each of the two systems were obtained from the rate constants in Table 1 using the usual equations. The results obtained at a mean temperature of 30.00°C are given in Tables 3 and 4, and for the methanol system are compared with those from the literatures. The value of the activation energy by LaMer *et al.*⁽¹¹⁾ in 0.092 mole fraction of methanol is 18.9 kcal/mole, being in good agreement with 18.3 kcal/mole obtained by interpolating the values of Table 3 along the solvent axis. The values obtained from the data of Murphy⁽¹⁰⁾ in some mixed solvents agree also well with those estimated from the measured results, but there is a slight increase in the positive discrepancy from the latter ones in the alcohol-rich region.

Table 3 Constant-pressure activation parameters for the decomposition of diacetone alcohol in aqueous methanol at 30.00°C and 1 atm

X^a	$\Delta G_P^\ddagger$ (kcal·mole ⁻¹)	$\Delta H_P^\ddagger$ (kcal·mole ⁻¹)	$\Delta S_P^\ddagger$ (cal·deg ⁻¹ ·mole ⁻¹)
0.00 ^b	20.3	16.6 (17.2)	-12.2
0.059 ^a	20.5	17.1 (17.7)	-11.3
0.092 ^c	20.5	18.3 (18.9)	-7.4
0.123 ^d	20.7	18.1 (18.7)	-8.6
0.194 ^d	20.9	18.7 (19.3)	-7.2
0.20	20.8	18.3 (18.9)	-8.2
0.273 ^d	21.0	19.3 (19.9)	-5.7
0.360 ^d	21.2	19.7 (20.3)	-5.0
0.40	21.2	19.1 (19.7)	-7.0
0.458 ^d	21.4	20.3 (20.9)	-3.6
0.60	21.6	20.1 (20.7)	-4.8
0.80	21.8	21.0 (21.6)	-2.7
1.00	22.0	21.8 (22.4)	-0.7

The numbers in parenthesis denote the values of activation energy.

^a Mole fraction of methanol

^b From the previous paper¹⁾

^c Calculated from the data of LaMer *et al.*¹¹⁾

^d Calculated from the data of Murphy¹⁰⁾

Table 4 Constant-pressure activation parameters for the decomposition of diacetone alcohol in aqueous isopropanol at 30.00°C and 1 atm

X^a	$\Delta G_P^\ddagger$ (kcal·mole ⁻¹)	$\Delta H_P^\ddagger$ (kcal·mole ⁻¹)	$\Delta S_P^\ddagger$ (cal·deg ⁻¹ ·mole ⁻¹)
0.10	20.2	17.0 (17.6)	-10.6
0.20	20.1	17.4 (18.0)	-9.0
0.30	20.0	17.9 (18.5)	-6.9
0.40	19.8	18.6 (19.2)	-4.0

The numbers in parenthesis denote the values of activation energy.

^a Mole fraction of isopropanol

The activation volumes at 1 atm were determined graphically using the usual equation which expressed the pressure dependence of the rate constant. The obtained values are given in Table 5.

Discussion

As is shown in Figs. 1 and 2, and in the results by Åkerlöf⁹⁾, the rate of decomposition at atmospheric pressure yields a definite difference in the direction of solvent dependence between the two solvent systems. The reason must be evidently sought in the effect due to the nature of added alcohol as described previously¹⁾. The decrease of the rate with the increase of the content of methanol may

Table 5 Activation volumes for the decomposition of diacetone alcohol in aqueous methanol at 30.00°C

X^a	$\Delta V^\ddagger$, cm ³ ·mole ⁻¹
0.00 ^b	-6.6
0.10	-0.8
0.20	+3.1
0.40	+8.0

^a Mole fraction of methanol^b From the previous paper¹⁾

be mainly ascribed to the decreased concentration of OH⁻ ion caused by the more acidic nature of the organic cosolvent than that of water, as represented by the equilibrium¹²⁾,



On the contrary, most of the increasing effect on the rate observed in the isopropanol system will probably result from the decrease of the bulk dielectric constant of solvent by the addition of organic component, as might be expected from simple dielectric grounds rather than from the acidity of added alcohol.

The dependences of the constant-pressure activation parameters on the solvent in the two systems are illustrated in Figs. 4 and 5, and that of the activation volume in methanol one in Fig. 6. All the parameters vary with the solvent composition in a fairly simple manner compared with the results observed in the ethanol system. In both systems, $\Delta G_P^\ddagger$ slightly depends upon the solvent but oppositely in the direction due to the solvent system, whereas $\Delta H_P^\ddagger$ and $\Delta S_P^\ddagger$ increase monotonically in a compensating manner with increasing organic content in the solvent, and neither of them shows any minimum in their solvent dependences and also the situation is so for $\Delta V^\ddagger$ in the methanol system. As is well known, the nature of aqueous alcohol mixtures is dependent on the hydrophobic character of added organic component⁶⁾¹³⁾. In reflecting this, it is found that the depth in the minimum observed in the three activation parameters ($\Delta H_P^\ddagger$, $\Delta S_P^\ddagger$ and $\Delta V^\ddagger$) for solvolysis of benzyl chloride³⁾¹⁴⁾ increases, and further its position is shifted toward more highly aqueous region of solvent, in the order of methyl, ethyl, isopropyl and *tert*-butyl in a series of the alcohol used as cosolvent. The concerned decomposition involves much larger number of complicated factors in the effect of solvent than the solvolysis does, because of the difference of reaction type. Therefore, a reasoning similar to that for the latter reaction may not be readily made, but some of the simplicity in the solvent dependence of the activation parameters in the methanol system seems to be related to less hydrophobic character of the cosolvent. However, the similar consideration cannot be taken for the results in the isopropanol system, and there is no acceptable explanation for them at present. The decrease in $\Delta G_P^\ddagger$ observed in this system is evidently due to much larger increase in $\Delta S_P^\ddagger$ than that in $\Delta H_P^\ddagger$ as the organic

12) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism", p. 335, John Wiley & Sons, Inc., New York and London (1961)

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

14) H. S. Golinkin, I. Lee and J. B. Hyne, *ibid.*, **89**, 1307 (1967)

content rises, and it is suggested that more substantial increase in $\Delta S_P^\ddagger$, compared with the cases of methanol and ethanol systems, may be ascribed to the specific contribution of isopropanol to the geometry in the activation process.

The variation of the activation parameters at constant pressure with solvent composition frequently becomes simpler in the corresponding ones at constant volume, and it has been noticed in the results for the studied reaction in aqueous ethanol system. In order to verify this observation, the examination was made of the results obtained in the methanol system. The constant-volume parameters $\Delta U_V^\ddagger$ and $\Delta S_V^\ddagger$ are calculated from the values of $\Delta H_P^\ddagger$, $\Delta S_P^\ddagger$ and $\Delta V^\ddagger$ using the equations¹⁵⁾

$$\Delta U_V^\ddagger = \Delta H_P^\ddagger - T\alpha\Delta V^\ddagger/\kappa, \quad (2)$$

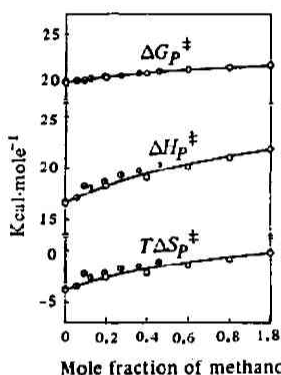


Fig. 4 Solvent composition dependence of the constant-pressure activation parameters for the decomposition of diacetone alcohol in aqueous methanol at 30.00°C
 ●...Murphy¹⁰⁾,
 ◐...LaMer *et al.*¹¹⁾,
 ○...This work

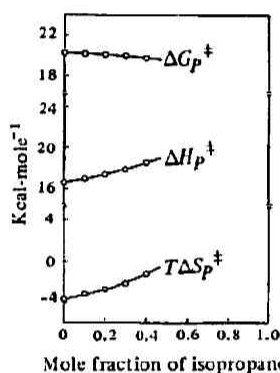


Fig. 5 Solvent composition dependence of the constant-pressure activation parameters for the decomposition of diacetone alcohol in aqueous isopropanol at 30.00°C

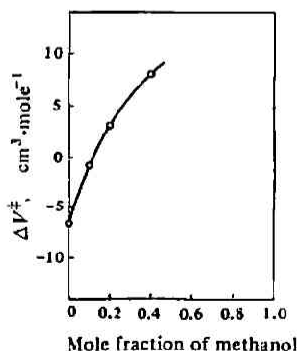


Fig. 6 Solvent composition dependence of the activation volume for the decomposition of diacetone alcohol in aqueous methanol at 30.00°C

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

$$T \cdot \Delta S_V^\ddagger = T \cdot \Delta S_P^\ddagger - T \alpha \Delta V^\ddagger / \kappa, \quad (3)$$

where α and κ are the thermal expansivity and compressibility of the reaction mixture, and they can be assumed to be approximately the same as those of the solvent. The results obtained for the methanol system are given in Table 6, and the variations with the solvent composition of $\Delta U_V^\ddagger$, $T \Delta S_V^\ddagger$ and $T \alpha \Delta V^\ddagger / \kappa$ are shown in Fig. 7.

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

χ^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·mole ⁻¹)	$\Delta U_V^\ddagger$ (kcal·mole ⁻¹)	$T\Delta S_V^\ddagger$ (kcal·mole ⁻¹)
0.00 ^d	303	44.5	2060	-329	16.9	-3.4
0.10	465	38.7	3640	-71	17.4 ^e	-3.1 ^e
0.20	635	39.6	4860	+365	17.9	-2.9
0.40	856	46.6	5570	+1079	18.0	-3.2

^a Mole fraction of methanol

^b Calculated from the data of density at 30°C in the literature¹⁶⁾

^c Obtained by interpolating the data of compression at 25°C by Gibson¹⁷⁾, and assumed for 30°C

^d From the previous paper¹⁾

^e Obtained from the values of $\Delta H_P^\ddagger$ estimated by interpolating the measured values in Table 3

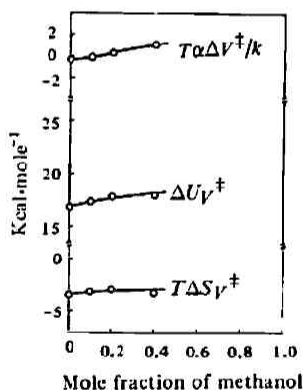


Fig. 7 Solvent composition dependence of the constant-volume activation parameters for the decomposition of diacetone alcohol in aqueous methanol at 30.00°C

The curves of $\Delta U_V^\ddagger$ and $T \cdot \Delta S_V^\ddagger$ are almost parallel to the solvent axis, and no significant change may be found in their parameters as a function of solvent composition. Such a simplicity observed in the constant-volume parameters is in agreement with the direction which is first pronounced by Baliga *et al.*⁴⁾ and is found for the results in the ethanol system, and it is evidently due to the absence of the quantity $T \alpha \Delta V^\ddagger / \kappa$ sensitive to solvent composition. The quantity $T \alpha \Delta V^\ddagger / \kappa$ depends essentially on the values of $T \alpha / \kappa$ (in other words, the internal pressure $(\partial U / \partial V)_T$) and of $\Delta V^\ddagger$, but it is impossible to decide which of them contributes more largely to it in this solvent system, as is apparent from the results in Tables 5 and 6.

16) J. Timmermans, "The Physico-Chemical Constants of Binary Systems in Concentrated Solutions", Vol. 4, p. 161, Interscience Publishers, Inc., New York (1960)

17) R. E. Gibson, *J. Am. Chem. Soc.*, **57**, 1551 (1935)

As shown in Fig. 6, $\Delta V^\ddagger$ changes the sign in highly aqueous region of solvent, and it is supposed to become zero in near 0.12 mole fraction of methanol. The solvent mixture of this composition is apparently the isokinetic solvent with respect to pressure, and the condition is given by the equation⁴⁾,

$$\left(\frac{\partial \ln k}{\partial P}\right)_{T, s, \dots} = 0. \quad (4)$$

where s is a parameter with respect to solvent. The same condition is found in fairly alcohol-rich region of ethanol system. The observations in $\Delta V^\ddagger$ that there is no minimum in the solvent dependence and the isokinetic solvent with respect to pressure appears in highly aqueous region of solvent may be ascribed considerably to more acidic nature of methanol as organic cosolvent, except for the specific solute-solvent interaction in the mixed solvents which cannot be explained in terms of simple ion-dielectric theory¹⁸⁾. That is, the substantial decrease of the concentration of OH^- ion, represented by the equation (1), will result in a lowering of its contribution to the activation process, so that a situation similar to that appearing in alcohol-rich region of the ethanol system seems to be probably caused by the small addition of methanol.

The correlations between $\Delta H_P^\ddagger$ and $\Delta S_P^\ddagger$, in the present two systems are shown in Fig. 8.

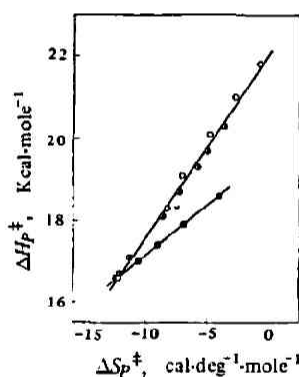


Fig. 8 Correlation of $\Delta H_P^\ddagger$ and $\Delta S_P^\ddagger$ for the decomposition of diacetone alcohol in aqueous methanol and isopropanol at 1 atm
Methanol system: ●...Murphy¹⁰⁾,
●...LaMer *et al.*¹¹⁾,
○...This work
Isopropanol system: ●

The slope β given as a constant by the relation $\partial \Delta H_P^\ddagger = \beta \partial \Delta S_P^\ddagger$, where ∂ denotes the solvent dependence of parameters, is calculated by the method of least squares, and is found to be 445°K for the methanol system and 243°K for the isopropanol one. As is represented by the equation¹⁹⁾,

$$\begin{aligned} \partial \Delta G_P^\ddagger &= \partial \Delta H_P^\ddagger - T \partial \Delta S_P^\ddagger \\ &= (\beta - T) \partial \Delta S_P^\ddagger, \end{aligned} \quad (5)$$

at the temperature which is equal to $\beta^\circ\text{K}$, $\partial \Delta G_P^\ddagger = 0$, that is, the activation Gibbs free energy is exactly independent of solvent. In other words, this temperature is the isokinetic one with respect to solvent and the condition is given by the equation⁴⁾,

18) S. D. Hamann, "Physico-Chemical Effects of Pressure", p. 55, Butterworths Scientific Publications, London (1957)

19) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions", p. 324, John Wiley & Sons, Inc., New York and London (1963)

$$\left(\frac{\partial \ln k}{\partial S}\right)_{T,P,\dots} = 0. \quad (6)$$

The constant β is likely to be closely related to the acidity of alcohol as cosolvent, as described previously¹³.

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*Department of Chemical Engineering
Faculty of Engineering
Tokushima University
Tokushima, Japan*