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The Solution Behavior of Thenoyltrifluoroacetone in Alcoholic Solvents

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The solution behavior of thenoyltrifluoroacetone (TTA) has been investigated in a series of higher alcohols which are often used in solvent extraction by means of UV and NMR spectrometries. It was experimentally confirmed that TTA exists in the enol and hemiacetal forms in dehydrated alcohol, while in wet alcohol we should also take a hydrate form into consideration. The fractions of the species at equilibrium were determined, and their dependencies on the water concentration and on the solvent properties, *i.e.*, the dielectric constant and the solubility parameter, were examined. The interconversion rate between the enol and hemiacetal forms were also observed as a function of the water concentration.

The identification of the chemical form of a partitioning species is one of the most important problems in fundamental research into solvent extraction. TTA (4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione) has been extensively used as a powerful extractant for metal ions, especially for heavy metals.[1] The predominant form of TTA in the inert solvents commonly used in solvent extraction is known to be the enol form, and in aqueous solvents, the hydrate form.[2–4] In addition, it has been reported that TTA reacts with methanol.[5] However, there is no information on whether TTA reacts with the higher alcohols used in solvent extraction. Recently, Suzuki *et al.*[6] observed that the partition rate of TTA between higher alcohol and water is very slow compared to that between an inert solvent and water. This fact seems to suggest a specific interaction between TTA and higher alcohol.

In the present study, a quantitative investigation has been carried out on the chemical equilibrium and the kinetic behavior of TTA in eleven higher alcohols by means of UV and ^{19}F and ^{1}H NMR spectrometries.

Experimental

Materials. The TTA (Dojindo G. R.) was purified by vacuum sublimation. The purity was checked by mp measurement (43.2—43.8 °C, lit, 42.5—43.2 °C[1]). Commercially purchased alcohols were fractionally distilled over calcium oxide or calcium sulfate. The purified TTA and alcohols were stored in a silica-gel desiccator. The dioxane was purified by the ordinary method.[7] The deuterated methanol (CD_3OD, 99%), dehydrated methanol, and perchloric acid were all reagent-grade. Redistilled water was used throughout.

Determination of Water Concentration. The concentration of water in alcohol was determined by the Karl-Fischer method. Water-saturated alcohol was prepared by placing a diluted aqueous solution (pH=3.5) of perchloric acid in contact with purified alcohol for several days in a thermostated room at 25 °C. The determination was repeated three times for each sample.

NMR Measurement. A deuterated methanol solution of TTA (1M) was prepared one day before measurement. The ^{1}H NMR spectra of the solution were taken on a Varian A-60 NMR apparatus. An alcohol solution of TTA (0.3M) was prepared for each alcohol at 25±0.5 °C. In order to establish the equilibration, the solutions were allowed to stand for four days in the case of dehydrated solutions and for two or three days in the case of water-containing solutions. The ^{19}F NMR spectra of the solutions were taken on a JEOL-PS-100 NMR apparatus at 94 MHz and 25±2 °C. The signal integration of a resonance peak was repeated at least four times. As an internal standard of the chemical shift, tetramethylsilane was used for the ^{1}H NMR and fluorotrichloromethane for the ^{19}F NMR.

Kinetic Measurements. The interconversion rate among the species of TTA was measured by observing the decrease in the enol concentration photometrically; 50 μl of a dioxane solution of TTA (0.003 M) was spiked into 5 ml of alcohol in a quartz cell, and the subsequent decrease in the transmittance at 340 nm (absorption maximum of enol form) was recorded on a Hitachi 356 UV-VIS spectrophotometer at 25±0.2 °C.

Results and Discussion

Chemical Species of TTA in Alcoholic Solvents. The ^{1}H NMR spectra of the deuterated methanol solution of TTA are shown in Fig. 1. The two multiplets at 7.76 and 7.10 ppm are assigned to the thienyl group, and the singlet at 6.48 ppm, to the α-proton of the enol form. The quartet at 3.34 ppm with a coupling constant of

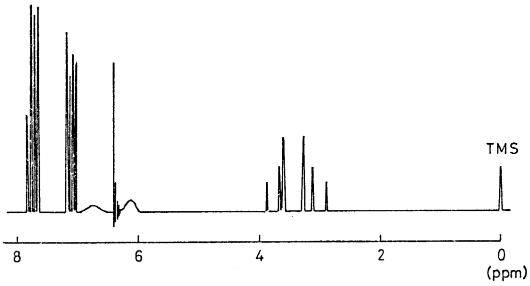


Fig. 1. ^{1}H NMR spectrum of the deuterated methanol solution of TTA.

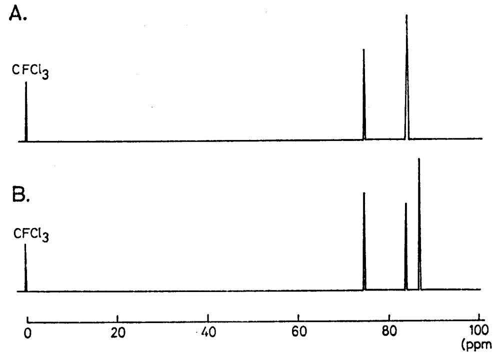
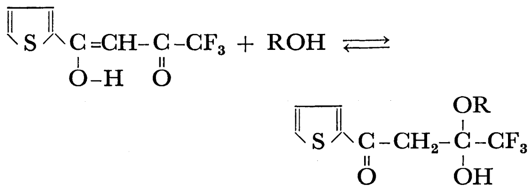
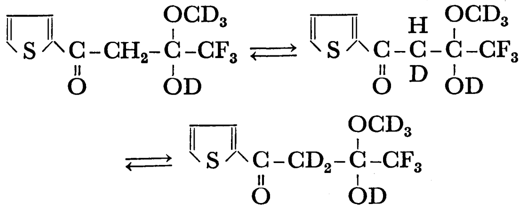


Fig. 2. ^{19}F NMR spectra of the alcoholic solution of TTA.
A: Dehydrated methanol solution,
B: water-saturated 1-hexanol solution.

J=15.7 cps and the doublet at 3.52 and 3.12 ppm are thought to be assignable to species other than the enol form. The ^{19}F NMR spectra of a dehydrated methanol solution of TTA is shown in Fig. 2(A). Two singlet signals were observed at 77.2 and 83.6 ppm. In the other dehydrated alcohols also, similar spectra were observed except for the cases of 2-octanol and 3-methyl-1-butanol. These results show that TTA is in two forms in dehydrated alcohols, *viz.*, enol and hemiacetal produced by a reaction with alcohol:


(1)

The hemiacetal form has two α-protons which are not equivalent because of the effect of the asymmetric carbon atom at the adjacent position. Since the α-protons belong to the AB-type group, they may be expected to show a quartet. Consequently, the quartet at 3.34 ppm can be assigned to the α-protons of the hemiacetal form. The doublet in Fig. 1 can be explained by considering a proton-deuteron exchange in one of the α-protons as follows:

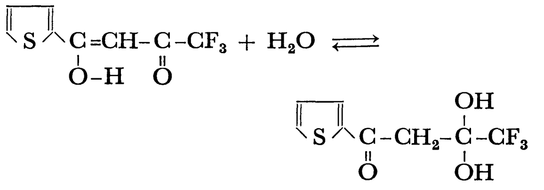

(2)

In this way, the NMR spectra of methanol solution of TTA can be thoroughly interpreted by considering the enol and the hemiacetal forms.

The ^{19}F NMR spectra of a water-saturated 1-hexanol solution of TTA are shown in Fig. 2(B). Three singlet signals, at 77.6, 84.1, and 88.2 ppm, were observed. In the other water-saturated alcohols, similar spectra were obtained except for the cases of 2-octanol and 3-methyl-1-butanol. The signal of 88.2 ppm, which appears only in wet alcohol, is assigned to the hydrate form, because the signal becomes progressively larger as the water concentration increases. The other two signals are consistent with the signals assigned to the enol and hemiacetal forms in dehydrated alcohol.

The equilibrium fraction of each species was determined from the integrated intensity of the corresponding signal of the ^{19}F spectra. In Table 1, the fractions of the TTA species in hydrated and water-saturated alcohols are listed, together with the solubility of water, the dielectric constant, and the solubility parameter.

Solvent Effect on the Equilibria among the Three Species. From the NMR spectra, it was found that TTA in dehydrated alcohol exists as an equilibrium mixture of the enol (E) and hemiacetal (A) forms. Furthermore, Table 1 shows that the ratio of E% to A% is not greatly affected by the solvent employed, while in water-saturated alcohols the fraction of the hydrate form (H) depends on the solvent. Since the hydration reaction is expressed by the following equation:


(3)

the fraction of the hydrate form can be expected to depend on the water concentration. In Table 2, the fractions of the three forms in 1-butanol containing water in various concentrations are listed. A linear correlation between ln [H]/[E] and ln X_W (mole fraction of water) was obtained in the mole-fraction range from 0.136 to 0.514, as is shown in Fig. 3. However, the plots for water-saturated alcohols are appreciably scattered from the line obtained for aqueous 1-butanol, hence, it is found that the water concentration is the primary, but not the only, factor governing the fraction of the hydrate form. It is considered that

TABLE 1. FRACTIONS (%) OF TTA SPECIES IN DEHYDRATED AND WATER-SATURATED ALCOHOLS[a]

No.	Solvent	Dehydrated		Water-saturated			Solubility[c] of water (mole fraction)	ε[c]	δ[f]
		Enol (%)	Hemiacetal (%)	Enol (%)	Hydrate (%)	Hemiacetal (%)			
1	1-Butanol	29.2	71.8	13.6	62.7	23.7	0.514	17.5	11.4
2	1-Pentanol	32.0	68.0	18.2	54.9	26.9	0.283	13.9	10.9
3	1-Hexanol	34.2	65.8	20.9	49.1	30.0	0.313	13.3	10.7
4	1-Heptanol	33.6	66.4	21.9	46.6	31.5	0.267[d]	11.5	10.9
5	1-Octanol	33.9	66.1	24.9	40.5	34.6	0.237[d]	10.3	10.3
6	2-Ethyl-1-hexanol	—	—	21.1	28.7	50.2	0.162	4.4	9.5
7	2-Octanol	93.4	3.5, 3.1[b]	34.1	59.4	3.6, 2.9[b]	0.228[d]	7.9	8.5
8	3-Methyl-1-butanol	30.3	19.4, 50.3[b]	17.0	51.9	8.3, 22.7[b]	0.343	14.7	11.0
9	Cyclohexanol	—	—	15.0	80.8	4.2	0.426[e]	15.0	11.4
10	2-Methyl-1-propanol	26.8	73.2	13.2	60.7	26.0	0.456	17.7	10.8
11	Benzyl alcohol	36.5	63.5	15.2	64.6	20.2	0.354[e]	13.1	11.1

a) Determined from the ^{19}F NMR spectra at 25±2 °C. b) The fraction for each of the two signals which appear at the chemical shift corresponds to the hemiacetal form. c) Data quoted from Ref. 7 (25 °C). d) This work (25 °C). e) At 20 °C. f) G. H. Morrison and H. Freiser, "Solvent Extraction in Analytical Chemistry," John Wiley & Sons, New York (1957), p. 249.

Table 2. Fractions (%) of the three species of TTA in aqueous butanol solutions

Mole fraction of water	Enol (%)	Hydrate (%)	Hemiacetal (%)
0.000	29.2	—	71.8
0.070	25.0	19.2	55.8
0.136	20.9	34.0	45.1
0.222	18.1	45.8	36.1
0.343	16.9	55.5	27.6
0.423	15.2	60.6	24.2
0.514	13.6	62.7	23.7

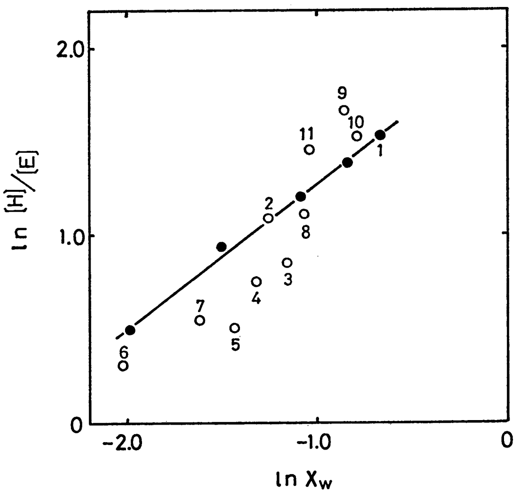


Fig. 3. Dependence of the enol-hydrate equilibrium constant on water mole fraction in alcohol; ●, aqueous 1-butanol, ○, water-saturated alcohols. The numbers in this figure correspond to those in Table 1.

alcohols affect the solubilities of both water and the hydrate form. Therefore, we also examined the influence of the physical properties of alcohols on the fraction ratio of [H]/[E].

Bernstein and Powling[8] have accounted for the influence of the solvent on the keto-enol tautomerism of β-diketones in terms of Onsager's model, which considers the different energies of the electrostatic interaction of each tautomer with its surroundings. According to the relationship established in their work, the enthalpy of hydration, ΔH, may be represented as follows:

$$\Delta H_{\text{gas}} = \Delta H_{\text{solution}} + \left(\frac{\varepsilon-1}{2\varepsilon+1}\,\frac{1}{V_0}\right)_{\text{solvent}}(\mu_H^2-\mu_E^2), \tag{4}$$

where μ_H and μ_E are the dipole moments of the hydrate form and the enol form respectively, and where V_0 and ε are the molar volume and the dielectric constant of alcohol respectively. Equation 4 suggests the correlation between the free energy of the hydration, which is equal to $-RT$ ln [H]/[E], and $(\varepsilon-1)/V_0(2\varepsilon+1)$. In Fig. 4, ln [H]/[E] is plotted against the solvent quantity $(\varepsilon-1)/V_0(2\varepsilon+1)$. The plots almost follow a straight line, and the positive sign of the slope means that $\mu_H > \mu_E$.

Recently, the solubility parameter concept has been applied to the interpretation of the solvent effect of alcohols on the partition equilibrium of TTA.[6] According to the solubility parameter theory, the equilibrium constant of the hydration reaction can be represented approximately by

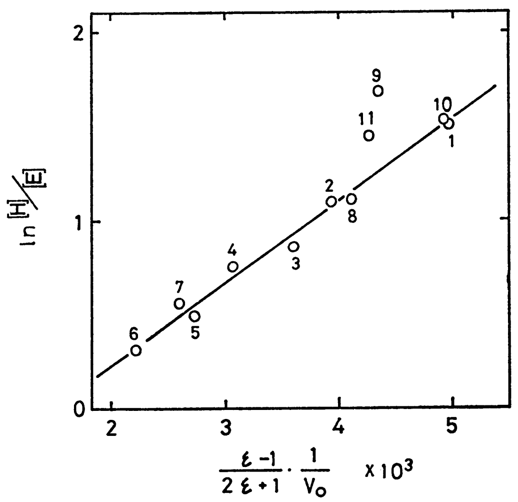


Fig. 4. Correlation between the enol-hydrate equilibrium constant and the solvent quantity $(\varepsilon-1)/V_0(2\varepsilon+1)$. The numbers in this figure correspond to those in Table 1.

$$\ln\,[\mathrm{H}]/[\mathrm{E}] = \frac{V_E}{RT}(\delta_H-\delta_E)(2\delta_0-\delta_E-\delta_H) + \text{const}, \tag{5}$$

where V_E is the molar volume of the enol form and where δ_H, δ_E, and δ_0 are the respective solubility parameters of the hydrate form, the enol form, and the water-saturated alcohol. The influence of water on the solubility parameter of the water-saturated alcohols is not serious in most alcohols, except for the cases of 1-butanol and 2-methyl-1-propanol, in which the next equation can be used for correction:

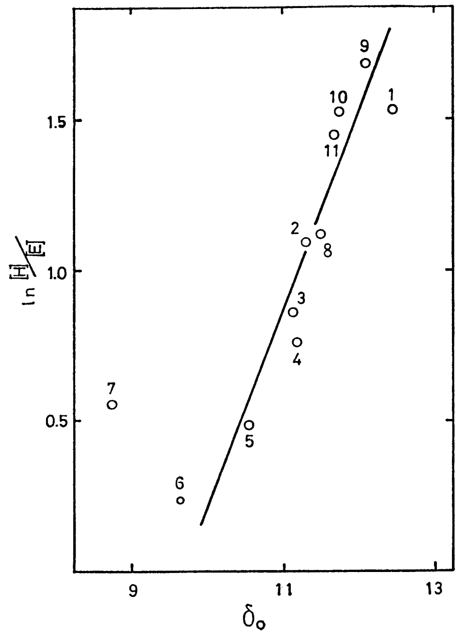


Fig. 5. Correlation between the enol-hydrate equilibrium constant and the solubility parameter of alcohol. The numbers correspond to those in Table 1.

$$\delta_0 = \phi_s\delta_s + \phi_a\delta_a, \qquad (6)$$

where ϕ_a and ϕ_s are the respective volume fractions of water and alcohol and where δ_a and δ_s are the respective solubility parameters of water (23.4 $\text{cal}^{1/2}$ $\text{cm}^{-3/2}$) and alcohol. In Fig. 5, ln [H]/[E] is plotted against the solubility parameter of the alcohol. In most alcohols, the plots follow a straight line. The positive sign of the slope means that $\delta_H > {}_E\delta$, which corresponds to the result of $\mu_H > \mu_E$. From above results, we can state that the fraction of the hydrate form increases with the solvent quantity, ε or δ.

Inversion Rate of the Hemiacetal Form. The observed first-order rate constant (k) in dehydrated alcohol is the sum of the forward rate constant (k_a) and the reverse rate constant (k_e) in Eq. 2, *i.e.*, $k = k_a + k_e$. The enolization rate constant is calculated by means of the following relation:

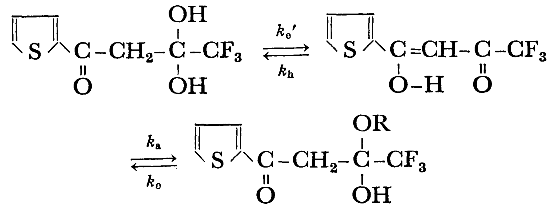
$$k_e = fk, \qquad (7)$$

where f is the enol fraction. The observed rate constant and the calculated enolization rate constant are listed in Table 3 for several alcoholic systems. The rate constant in 2-methyl-1-propanol is smaller than the others. This may be the result of the steric effect in the transition state.

TABLE 3. OBSERVED INTERCONVERSION RATE CONSTANT (k) BETWEEN THE ENOL AND HEMIACETAL FORMS AND THE ESTIMATED ENOLIZATION RATE CONSTANT (k_e) OF TTA IN ALCOHOLIC SOLUTIONS

Solvent	Mole fraction of water	$k \times 10^3$ (min^{-1})	$k_e \times 10^3$ (min^{-1})
1-Butanol	0.000	2.39	0.70
	0.025		2.31
	0.049		3.72
	0.133		8.96
	0.234		20.7
1-Pentanol	0.000	3.48	1.11
1-Hexanol	0.000	11.7	4.00
1-Octanol	0.000	3.96	1.34
2-Methyl-1-propanol	0.000	1.07	0.29

In the case of a water-containing alcoholic solution, the following reaction can be expected to occur:



(8)

The rate equation for the above reaction may be described as

$$-\frac{\mathrm{d}}{\mathrm{d}t}[\mathrm{E}] = (k_h + k_a)[\mathrm{E}] - k_e'[\mathrm{H}] - k_e[\mathrm{A}]. \qquad (9)$$

When the hydration rate is fast and the equilibrium between the enol form and the hydrate form is instantly established, Eq. 9 becomes

$$-\frac{\mathrm{d}}{\mathrm{d}t}[\mathrm{E}] = \left(\frac{k_a}{1+K} + k_e\right)([\mathrm{E}] - [\mathrm{E}]_{eq}), \qquad (10)$$

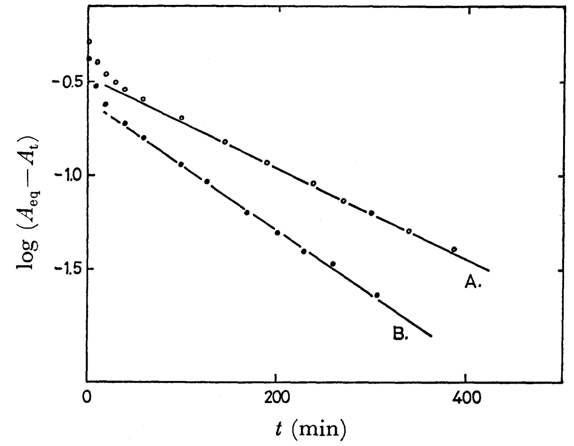


Fig. 6. Absorbance change of the enol form in aqueous 1-butanol solution; A, $X_w = 0.025$, B, $X_w = 0.049$.

where K is the equilibrium constant, $K = [\mathrm{H}]_{eq}/[\mathrm{E}]_{eq}$. The integration of Eq. 10 gives the final equation:

$$\log([\mathrm{E}]_{eq} - [\mathrm{E}]) = -\frac{k_a + (1+K)k_e}{2.30(1+K)}t + \text{const.} \qquad (11)$$

Typical absorbance changes of the enol form observed in the aqueous 1-butanol solutions are shown in Fig. 6. The fast-reaction part and the subsequent slow-reaction part are clearly seen. The fast-reaction is connected with the hydration reaction. From the slope of the slow-reaction part, the rate constant of the enol-hemiacetal reaction was obtained. The rate constant for the process from the hemiacetal form to the enol form was calculated from the following reaction:

$$k_e = (1+K)fk. \qquad (12)$$

The obtained values for k and k_e are listed in Table 3. The value of k_e increases with the water concentration. In Fig. 7, log ($k_e - k_e^\circ$) is plotted against the molar concentration of water, where k_e° denotes the enolization rate constant in dehydrated 1-butanol. A linear correlation with a slope of 0.92 was obtained. The result suggests that one water molecule participates in the

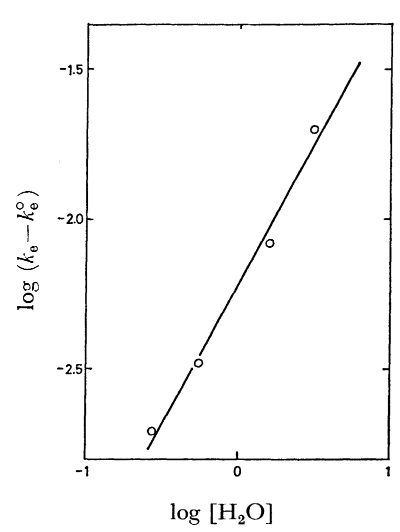


Fig. 7. Water concentration dependence of the enolization rate constant of the hemiacetal form in aqueous 1-butanol.

transformation from the hemiacetal form to the enol form. Takada *et al.*⁹⁾ examined the water-concentration dependence of the hydration rate of TTA in both dioxane and acetonitrile and suggested the third order in water. Bell *et al.*¹⁰⁾ have reported that three water molecules participate in the hydration of 1,3-dichloroacetone and that the water can be replaced by either carboxylic acid or 2,6-dichlorophenol. In the present system also, it can reasonably be expected that one water and some alcohol molecules participate cooperatively in the enolization process of the hemiacetal form.

From the results that the fraction of the hemiacetal forms is 20—30% for most water-saturated alcohols and that the inversion rate to the enol form is very slow, it can be expected that the hemiacetal form plays an important role in the kinetics and mechanism of metal extraction with TTA in an alcohol/water system.

References

1) A. K. De, S. M. Khopkar, and R. A. Chalmers, "Solvent Extraction of Metals," Van Nostrand Reinhold, London (1970), p. 56.

2) M. Yamazaki and T. Takeuchi, *Kogyo Kagaku Zasshi*, **72**, 2223 (1969).

3) J. C. Reid and M. Calvin, *J. Am. Chem. Soc.*, **72**, 2948 (1950).

4) M. R. Jaffe, D. P. Fay, M. Cefola, and Sutin, *J. Am. Chem. Soc.*, **93**, 2878 (1971).

5) Y. Kodama, K. Sato, and K. Arakawa, *Nippon Kagaku Zasshi*, **87**, 1092 (1966).

6) N. Suzuki, K. Akiba, T. Kanno, and T. Wakahayashi, *J. Inorg. Nucl. Chem.*, **26**, 2521 (1964).

7) A. Weissberger, E. S. Proskauer, J. A. Riddick, and E. E. Troops, Jr., "Technique of Organic Chemistry," Interscience, New York (1955), Vol. 7..

8) J. Powling and H. J. Bernstein, *J. Am. Chem. Soc.*, **73**, 4353 (1951).

9) H. Watarai, Y. Takada, and N. Suzuki, unpublished result.

10) R. P. Bell and J. E. Critchlow, *Proc. R. Soc. London, Ser. A*, **325**, 35 (1971).