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The Solvent Effects in the Acylation of Alcohol. The Effects of Liquid Sulfur Dioxide on the Dissociation of Hydrogen-bonded Alcohol

Toshikazu NAGAI, Hironobu ABE and Niichiro TOKURA

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka

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The reason for the rate-enhancing effect of liquid sulfur dioxide on the rate of the benzoylation of methanol has been studied. The observation of the NMR spectra revealed that the amount of the hydrogen-bonded methanol is decreased (but not completely eliminated) by sulfur dioxide in the liquid SO_2-CCl_4 system. The existence of a correlation between the rates of esterification and the dissociation of the associated alcohol accounts for the role of the sulfur dioxide as the agent for the dissociation of the methanol-hydrogen bonding during the esterification.

In continuation of our work on the solvent effect of the acylation of alcohol, the obvious effect of liquid sulfur dioxide has aroused the interest of the present authors since the reaction proceeds very rapidly in both first- and second-order-rate reactions.[1]

Liquid sulfur dioxide is an electrophilic solvent, the reaction in which the ρ value in the Hammett's equation is negative, *viz.*, in which a cation plays a predominant role, being favored in this solvent.[2]

The first-order acylation where the reaction rate is described as: Rate$=k$[RCOCl] can be well elucidated by the above interpretation because the rate-determining formation of the RCO^+ cation should be favored in liquid sulfur dioxide. However, the enhanced acylation by the second-order-rate law, first order both in alcohol and in acyl halide, is difficult to understand. An alternative explanation is that the association of alcohol by the hydrogen bonding may be disrupted in the presence of liquid sulfur dioxide, as was indicated by Hoyer,[3] and the alcohol may be increased when the solvent is replaced by liquid sulfur dioxide.

In the present communication the effect of the sulfur dioxide concentration on the hydrogen bonding of methanol and the effect of that solvent on the reaction rate of the acylation have been compared with each other. The correlation between the two effects may be useful as evidence for the role of sulfur dioxide.

As for the effect of hydrogen-bonding on the rate of a reaction, the inhibition of phenol alkylation by ethers has been reported on by Hart *et al.*;[4] they accounted for the quantitative decrease in the rate by assuming the formation of a 2 : 1 phenol-dioxane complex.

The dissociation of the hydrogen bonding which may be brought about by sulfur dioxide has been measured by means of the proton magnetic resonance spectra in liquid sulfur dioxide-carbon tetrachloride systems. The reaction rates of the esterification of benzoyl chloride with methanol, which follow the second-order rate law, have been followed by GLC analysis.

Experimental

Apparatus. The chemical shift data were determined from the proton magnetic resonance spectra obtained on a Nihondenshi spectrometer at 60 Mc. The reaction rates were measured by pressure vessels equipped with needle valves.

Materials. The methanol was dehydrated over magnesium and distilled. The liquid sulfur dioxide was purified by distillation over phosphorus pentoxide. The carbon tetrachloride was purified by washing it with alkali and sulfuric acid; it was distilled after dehydration over calcium chloride. The benzoyl chloride was purified by an ordinary method.

Procedure. *Proton Magnetic Resonance.* The solutions to be studied were prepared in NMR tubes as follows. After weighing the reagents in the tube and after adding methylsilane, the tube was connected with a pressure vessel containing liquid sulfur dioxide; then there was added a definite amount of sulfur dioxide by distillation under cooling in a liquid nitrogen bath. Finally, the tube was sealed and submitted to NMR analysis. The chemical shifts were all determined relative to the internal standard, tetramethylsilane. A dilution study of methanol in carbon tetrachloride was undertaken in order to determine the chemical shift associated with

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[1] a) N. Tokura and F. Akiyama, This Bulletin, **37**, 1723 (1964). b) F. Akiyama and N. Tokura, *ibid.*, **39**, 131 (1966). c) F. Akiyama and N. Tokura, *ibid.*, **41**, 2690 (1968).

[2] a) N. Tokura, T. Kawahara and S. Ikeda, *ibid.*, **37**, 138 (1964). b) N. Tokura, M. Matsuda and M. Iino, *ibid.*, **36**, 278 (1963). c) R. Asami and N. Tokura, *J. Polymer Sci.*, **42**, 545 (1963).

[3] H. Hoyer, *Angew. Chem.*, **72**, 269 (1960).

[4] H. Hart, F. A. Cassis and J. J. Bordeaux, *J. Am. Chem. Soc.*, **76**, 1639 (1954).

monomeric methanol. This study covered the concentration range of 1.193—0.019 wt% methanol and was done at a constant temperature of 20°C. To establish complete hydrogen bonding, a measurement was carried out at around the melting point of methanol. For the purpose of detecting the dissociation of the hydrogen bonding, the molar ratios of the SO_2-CCl_4 mixtures were varied from 0 to 100%, while the methanol concentration was kept constant at about 6 mol/*l*.

Kinetic Procedure. The procedure used to follow the kinetics was as follows. Into a pressure vessel there were introduced 0.6164 mol/*l* of benzoyl chloride and 2.8829 mol/*l* of methanol in a liquid SO_2-CCl_4 mixture (SO_2: 0—92 mol%); then, after a definite period of time at 0°C, the reaction mixtures were added to a large amount of water. The solution was then introduced into a separatory funnel including a definite amount of nitrobenzene in CCl_4 and then washed seven times with pure water in order to remove any unreacted methanol and benzoyl chloride. The solvent of the CCl_4 solution thus obtained was distilled out under reduced pressure after drying over $MgSO_4$. The residual solution was submitted to GLC analysis. The concentration of methyl benzoate formed was determined by measuring the area of the gas chromatograms and by applying a previously-determined calibration factor, which was obtained from the area of methyl benzoate relative to that of a definite amount of nitrobenzene added as a standard. GLC was carried out under the following conditions: column; P.E.G. 6000, 4 m, 132°C; carrier; H_2 70 m*l*/min. The retention times were 9.5 min for methyl benzoate and 16.5 min for nitrobenzene.

Results and Discussion

The Hydrogen Bonding of the Methanol Molecules Themselves. The results of the dilution study of methanol in carbon tetrachloride are presented in Fig. 1. This study suggests that, below a concentration of 0.117 wt%, the methanol in carbon tetrachloride exists in only one state, probably the monomeric form. Assuming this to be the case, the value of δ_1, the chemical shift of monomeric methanol relative to tetramethylsilane, is 2.08 ppm.

The value of δ_A, the chemical shift of associated methanol, was determined to be δ 5.84 ppm by measuring the value for pure methanol around its melting point, −93°C.

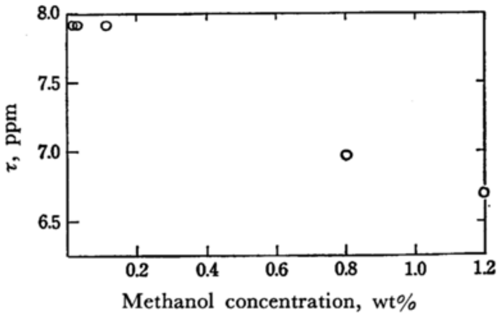

Fig. 1. Dilution study of methanol in carbon tetrachloride.

The chemical shift data, δ_{obs}, for the hydroxylic hydrogen atom of methanol measured at 20, 0, and −20°C at a definite concentration of about 6 mol/*l* in the SO_2-CCl_4 solvent mixture, together with those for the methyl, δ_{CH_3}, are listed in Table 1.

As may be seen in Table 1, upon an increase in the relative amount of SO_2, the hydroxylic hydrogen atom shifts to a higher magnetic field. This could be attributed to the change in the molecular complexation of alcohol, possibly owing to a weak interaction of the oxygen atoms of methanol with the sulfur atoms of sulfur dioxide, as is shown in Fig. 2, I, rather than that visualized in Fig. 2, II, which would result in a shift to a lower field, a shift contrary to the facts.

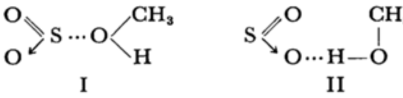

Fig. 2

The neighbor anisotropy effect of SO_2 on the shift will be omitted here since the shifts of the methyl protons remain constant throughout the various compositions of the solvent mixtures used.

TABLE 1. THE VALUES (ppm) OF δ_{CH_3} AND δ_{obs} OF THE HYDROXYLIC HYDROGEN ATOM RELATIVE TO TMS FOR METHANOL

Methanol (mol/*l*)	Solvent (molar ratio) SO_2 : CCl_4	20°C		0°C		−20°C	
		δ_{CH_3}	δ_{obs}	δ_{CH_3}	δ_{obs}	δ_{CH_3}	δ_{obs}
5.98	0 : 100	3.36	4.77	3.40	5.25	3.34	5.32
5.93	15.64 : 84.36	3.43	4.70	3.40	5.17	3.25	5.28
5.69	38.83 : 61.17	3.36	4.30	3.39	4.71	3.37	4.98
6.68	59.77 : 40.23	3.36	4.15	3.39	4.67	3.37	4.93
7.45	72.36 : 27.64	3.38	4.08	3.38	4.56	3.40	4.82
6.47	79.53 : 20.47	3.35	3.88	3.39	4.43	3.38	4.70
6.37	90.77 : 9.23	3.36	3.63	3.38	4.20	3.37	4.52
5.98	100 : 0	3.38	3.70	3.38	3.96	3.40	4.47

Comprehensive studies[5-7] have been made of the nuclear magnetic resonance on the molecular complexation of alcohol or on hydrogen bonding between proton-donating acids and bases. In these studies, the shifts of the NMR signals have been considered from the standpoint of dilution or enthalpy change upon the formation of a hydrogen bond. Meanwhile, Hoyer[3] has observed in his IR studies that sulfur dioxide molecule can neither permit a hydrogen bond among alcohol molecules themselves nor make hydrogen bridges with the hydrogen atoms of the alcohols by using oxygen atoms of the sulfur dioxide molecule.

Saunders and Hyne[6] have interpreted their data by making the simplifying assumption that the methanol molecule exists in carbon tetrachloride in equilibrium with the monomer and the tetramer as follows:

$$4CH_3OH \overset{K_4}{\rightleftharpoons} (CH_3OH)_4 \tag{1}$$

Assuming this to be the case in the present system, the following value, K_4, will be a parameter of the complexation in this system:

$$K_4 = \frac{M_4}{M_1{}^4} = \frac{C-M_1}{4M_1{}^4} \tag{2}$$

$$C = M_1 + 4M_4 \tag{3}$$

where M_1 and M_4 are the molar concentrations of the monomer and the tetramer respectively.

On the other hand, the observed chemical shift, δ_{obs}, follows Eq. (4):

$$\delta_{obs} = \frac{\delta_1 M_1 + \delta_A (C-M_1)}{C} \tag{4}$$

where δ_1 and δ_A are the chemical shifts of the hydroxylic protons of the noncomplexed and complexed states respectively.

The K_4 values derived from Eqs. (2) and (4), together with the values of M_1/C, are listed in Table 2.

These results indicate that the association of methanol is possible in an appreciable amount in liquid SO_2 alone; this is somewhat different from the observation made by IR.[3]

TABLE 2. THE VALUES OF M_1/C AND K_4 AT 0°C

Methanol (mol/l)	SO_2 (mol%)	M_1/C	K_4 (l^3mol^{-3})
5.98	0	0.157	1.630
5.93	15.64	0.178	0.980
5.69	38.83	0.301	0.120
6.68	59.77	0.311	0.061
7.45	72.36	0.341	0.030
6.47	79.53	0.376	0.029
6.37	90.77	0.436	0.015
5.98	100	0.500	0.0094

When a smaller concentration of methanol (1.8 mol/l) was used, the hydroxylic hydrogen atom shifted to a higher field, δ 2.67 ppm relative to the TMS in liquid SO_2 at 20°C, thus affording larger M_1/C value; this is further evidence of the presence of the complexation of methanol in liquid SO_2.

Rate of S_N2-type Esterification. Benzoyl chloride was submitted to reaction with methanol in liquid sulfur dioxide-carbon tetrachloride mixtures. The reaction obeyed the second-order-rate law at the initial stage of the reaction, indicating that methanol acts in the rate-determining step of

TABLE 3. THE SECOND-ORDER-RATE CONSTANTS (k_2, min^{-1} mol^{-1} l) OF THE BENZOYLATION OF METHANOL IN VARIOUS LIQ. SO_2-CCl_4 MIXTURES AT 0°C

SO_2 (mol%)	$k_2\times10^4$
0	5.31
51.02	6.10
70.37	8.60
81.37	11.86
91.68	16.30

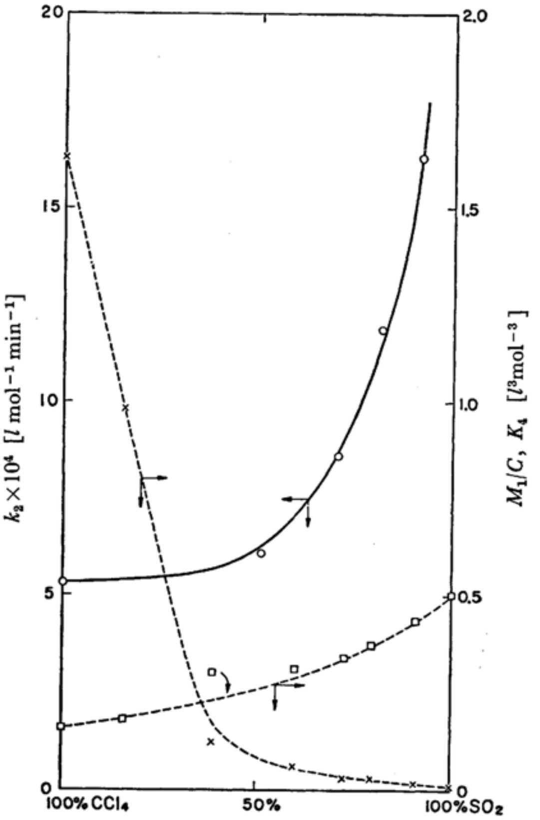

Fig. 3. Effect of added SO_2 on the values of the k_2, K_4, and M_1/C.

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[5] C. M. Huggins, G. C. Pimental and J. N. Shoolery, *J. Phys. Chem.*, **60**, 1311 (1956).

[6] M. Saunders and J. B. Hyne, *J. Chem. Phys.*, **29**, 1319 (1958).

[7] D. P. Eyman and R. S. Drago, *J. Am. Chem. Soc.*, **88**, 1617 (1966).

TABLE 4. THE RATE CONSTANTS, k'_2 DERIVED USING THE MONOMERIC METHANOL CONCENTRATION AS THE METHANOL CONCENTRATION

SO_2 mol %	K_4* l^3 mol^{-3}	C mol l^{-1}	M** mol l^{-1}	k'_2 l mol^{-1} min^{-1} $\times 10^3$
0	1.630	2.8829	0.76	2.02
51.02	0.080	2.8829	1.46	1.36
70.37	0.038	2.8829	1.68	1.48
81.37	0.028	2.8829	1.78	1.92
91.68	0.014	2.8829	2.00	2.35
				Mean = 1.83

* K_4: obtained from the K_4 *vs.* SO_2 % curve in Fig. 3.

** M_1: the unassociated monomer concentration derived from the equation: $4[M_1]^4K_4+[M_1]=C$.

the reaction. Another support for this was given by the fact that a small isotope effect was observed when CH_3OD was used in this esterification reaction. Consequently, the rate constant, k_2, should afford some information regarding the effect of the complexation of methanol on the S_N2-type reaction.

The k_2 values, together with the M_1/C and K_1 values, are visualized in Fig. 3.

The k_2 values increase as the amount of sulfur dioxide added is greater; however, the k_2' values, defined as is indicated in Eq. (5), were nearly constant, as is shown in Table 4.

$$\begin{aligned}\text{Rate} &= k_2[\text{benzoyl chloride}][C]\\ &= k'_2[\text{benzoyl chloride}][M_1]\end{aligned} \tag{5}$$

$$k'_2 = k_2\frac{[C]}{[M_1]} \tag{6}$$

The increase in the reaction rate of the esterification of benzoyl chloride by methanol, brought about by the addition of sulfur dioxide, may adequately be accounted for by assuming that the dissociated methanol monomer rather than the associated methanol participates in the esterification reaction and also by assuming that sulfur dioxide acts as the hydrogen bond-disrupting agent in the reaction.

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