although the energy surface in MM2 is too flat to determine the specific geometry. In any case, the energy difference between planar and optimum structures is less than 0.5 kcal/mol for each method, and hence our overall conclusion remains unchanged.

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The System Aluminum Chloride-Acetyl Chloride in Sulfur Dioxide Solvent

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Nuclear magnetic resonance studies of the system aluminum chloride-acetyl chloride in sulfur dioxide as solvent show the existence of complexes with two and one aluminum chloride per acetyl chloride. Equilibrium constants and exchange rates for these complexes were determined as a function of temperature and some conclusions were reached on the mechanism of the exchange reactions.

Introduction

The system aluminum chloride-acetyl chloride is one of the fundamental reagents of the Friedel-Crafts acylation reaction and is of some industrial importance.[2] From the first report of the aluminum chloride-acetyl chloride complex[3] until the present there have been many studies of it by infrared,[4-6] nuclear magnetic resonance[7-9] and X-ray crystallography,[10] and the subject has been reviewed.[11] The consensus of opinion is that this compound exists in solution as an equilibrium mixture of ionic and molecular forms whose relative concentrations depend on solvent and temperature. In fact, for antimony pentachloride and *p*-toluoyl chloride both forms have been isolated as crystalline solids.[12] Nevertheless we will show that, at least in sulfur dioxide as solvent, a solution of acetyl chloride and aluminum chloride contains only a one 1:1 complex, in addition to a complex with two aluminum chloride entities for each acetyl chloride and free acetyl chloride and aluminum chloride.

Experimental Section

Acetyl chloride was purified by fractional distillation. Aluminum chloride was purified by repeated vacuum sublimation. Sulfur dioxide was dried over P_2O_5 and stored over mercury.

Table I. ^{27}Al and ^1H Chemical Shifts and Line Widths for Species of Interest to the System $AlCl_3$-CH_3COCl in SO_2 as Solvent

sample	$\Xi(^{27}Al)$	$\Delta^{27}Al$, Hz	$\delta\,^1H$
$AlCl_3$	26 058 956	80	
$(CH_3)_4NAlCl_4$	26 059 270[14]	<10	
$(CH_3)_2OAlCl_3$	26 059 489[14]		
$3AlCl_3$ + CH_3COCl	26 059 275 (strong) 26 059 497 (weak)		
$2AlCl_3$ + CH_3COCl	26 059 256		3.20
	26 059 513		4.18
$AlCl_3$ + CH_3COCl	26 059 276 (weak)	120	3.20 4.18
	26 059 535 (strong)	15	2.70
$AlCl_3$ + $2CH_3COCl$	26 059 537	<40	3.20 (very weak) 4.18 (weak) 2.70 (strong)
CH_3COCl			2.70

Samples were prepared by quickly transferring, in a drybox, some aluminum trichloride to an NMR sample tube closed with a stopcock. Known quantities of vapor of the other two compounds were then transferred on a greaseless vacuum line onto the weighed quantity of aluminum chloride, and the sample was sealed under vacuum. All concentrations are reported as mole fractions and calculations of equilibrium and rate constants are made with this concentration unit.

Proton resonance spectra were obtained in the Fourier transform mode on a Varian Associates XL-100 spectrometer equipped with a Nicolet computer and its pulsing and power amplifier components operating at 100.1 MHz. The variable-temperature apparatus was calibrated via a methanol sample. Aluminum-27 spectra were obtained at 26.08 MHz with a Nicolet multinuclear probe and the associated mixing circuits. Proton chemical shifts are reported relative to tetramethylsilane signals as zero. Aluminum chemical shifts are reported as Ξ values, with Ξ for $Al(H_2O)_6^{3+}$ as 26 056 780 Hz.[13,14] Tetramethylsilane slowly reacts with aluminum trichloride, so those samples used for de-

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[1] Issued as NRCC No. 19970.

[2] Olah, G. A., Ed. "Friedel-Crafts and Related Reactions"; Interscience: New York, 1963; Vol. 1, p 91.

[3] Boeseken, J. *Recl. Trav. Chim. Pays-Bas* **1901**, *20*, 102.

[4] Cook, D. *Can. J. Chem.* **1959**, *37*, 48.

[5] Cassimatis, D.; Bonnin, J. P.; Theophanides, T. *Can. J. Chem.* **1970**, *48*, 3860.

[6] Germain, A.; Commeyras, A.; Casadevall, A. *Bull. Soc. Chim. Fr.* **1972**, *8*, 3177.

[7] Wilinski, J.; Kurland, R. J. *J. Am. Chem. Soc.* **1978**, *100*, 2233.

[8] Olah, G. A.; Moffatt, M. E.; Kuhn, S. J.; Hardie, B. A. *J. Am. Chem. Soc.* **1964**, *86*, 2198.

[9] Haraguchi, H.; Fujiwara, S. *J. Phys. Chem.* **1969**, *73*, 3467.

[10] Le Carpentier, J. M.; Weiss, R. *Acta Crystallogr., Sect. B* **1972**, *28*, 1421.

[11] Chevrier, B.; Weiss, R. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 1.

[12] Chevrier, B.; Le Carpentier, J. M.; Weiss, R. *J. Am. Chem. Soc.* **1972**, *94*, 5718.

[13] McFarlane, W. *Ann. Rev. NMR Spectrosc.* **1968**, *1*, 135.

[14] Glavincevski, B.; Brownstein, S. *Can. J. Chem.* **1981**, *59*, 3012.

0022-3263/82/1947-1005$01.25/0

Table II. Concentrations and Equilibrium Constants for the Species in $AlCl_3$-CH_3COCl Solutions in SO_2 at -54 °C

sample ratio	total $AlCl_3$, mmol	total CH_3COCl, mmol	$[AlCl_3]$	$[2AlCl_3\cdot CH_3COCl]$	$[AlCl_3\cdot CH_3COCl]$	$[CH_3COCl]$	K_1	K_2
1.5:1	0.265	0.199	0.0037	0.00311	0.00560	0.00289	524	150
1.5:1	0.232	0.174	0.0030	0.00303	0.00458	0.00259	589	220
1:1	0.146	0.147	~0	0.00197	0.00580	0.00373		$0.22K_1$
1:1	0.140	0.137	~0	0.00244	0.00533	0.00293		$0.25K_1$
1:1.5	0.306	0.459	~0	0.00672	0.00847	0.0111		$1.04K_1$
1:2	0.110	0.222	~0	0.00167	0.00558	0.0100		$0.54K_1$
1:3	0.115	0.344	~0	0.00075	0.0050	0.0144		

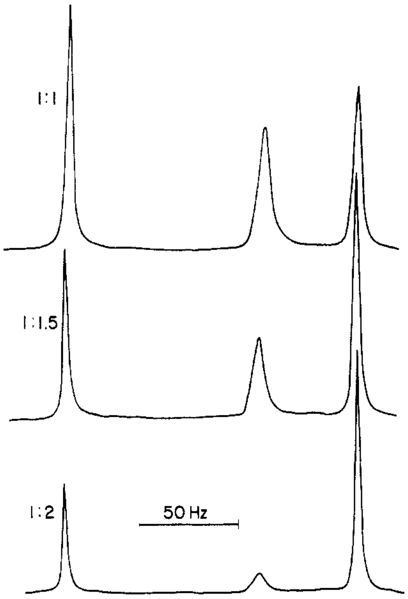


Figure 1. Proton resonance spectra of some $AlCl_3$–CH_3COCl samples in SO_2 at -54 °C.

termination of equilibrium and rate constants were prepared without tetramethylsilane. Peak areas were obtained by integration, using the software of the operating system, and line widths by direct measurement of the spectra. Theoretical spectra for rate studies were calculated by a stochastic method.[15]

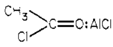
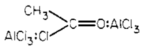
Results and Discussion

^{27}Al and ^1H chemical shifts and ^{27}Al line widths of some representative samples at low temperature are listed in Table I. The single aluminum resonance line with an excess of acetyl chloride suggests that under these conditions predominantly one $AlCl_3$ species is present and the similarity of its chemical shift to that of $(CH_3)_2OAlCl_3$ indicates that it is coordinated to oxygen. As the relative amount of $AlCl_3$ increases, a second resonance line appears and becomes more intense. It may be attributed to a second equivalent of $AlCl_3$ coordinated to the chlorine bonded to carbon of the original 1:1 complex. The similarity of its chemical shift to that of $AlCl_4^-$ is consistent with this assignment. There is rapid exchange of the $AlCl_3$ coordinated to chlorine and any excess of free $AlCl_3$. Under similar conditions there is no appreciable exchange between $AlCl_3$ and $AlCl_4^-$.[14] The spectra were obtained at temperatures from -64 °C for acetyl chloride rich samples to -24 °C for $AlCl_3$ rich samples. At room temperature only a single averaged line is observed for all samples. The ^{27}Al chemical shift of the 1:1 complex is consistent with that reported in CH_2Cl_2 as solvent[7] and the absence of the weak peak from $AlCl_3$ coordinated to chlorine may be due to a different equilibrium constant in the low dielectric constant solvent, CH_2Cl_2.

Table III. Effect of Temperature upon the Ratio of Equilibrium Constants

temp, °C	K_2/K_1
-64	0.8 ± 0.2
-54	0.5 ± 0.2
-44	0.2 ± 0.1

Table IV. Chemical Shift Assignments for Acetyl Chloride Aluminum Chloride Complexes

species	δ^1H	$\Xi(^{27}Al:O)$	$\Xi(^{27}Al:Cl)$
	4.18	26 059 528	
	3.20	26 059 524	26 059 266

The variation of the intensities of the proton resonance peaks with sample composition permits their assignment to the free and complexed species. This variation is shown for a few samples at -54 °C in Figure 1. The quantitative results are listed in Table II. From the known quantity of CH_3COCl in a given sample and from the relative areas of the peaks for the acetyl chloride species it is possible to calculate the concentrations of the acetyl chloride species. Given these concentrations one can calculate the amount of complexed $AlCl_3$, and by subtraction from the total $AlCl_3$, one can calculate the concentration of free $AlCl_3$. These concentrations then allow one to calculate the equilibrium constants, K_1 and K_2, for the formation of the 2:1 and 1:1 complexes.

$$CH_3COCl + AlCl_3 \rightleftharpoons AlCl_3\cdot CH_3COCl \qquad (1)$$

$$K_1 = \frac{[AlCl_3\cdot CH_3COCl]}{[AlCl_3][CH_3COCl]}$$

$$AlCl_3\cdot CH_3COCl + AlCl_3 \rightleftharpoons 2AlCl_3\cdot CH_3COCl \qquad (2)$$

$$K_2 = \frac{[2AlCl_3\cdot CH_3COCl]}{[AlCl_3][AlCl_3\cdot CH_3COCl]}$$

Since the concentration of free $AlCl_3$ is calculated as the difference of two numbers, it is not reliably known when it is small compared to these numbers. Such is the case for all the samples of this study except those with a ratio 1.5:1. Although it is not possible to calculate K_1 if the concentration of free $AlCl_3$ is not known, one can still calculate the ratio of K_2 to K_1 by substitution of the expression for $[AlCl_3]$ from eq 1 into eq 2:

$$K_2 = \frac{K_1[2AlCl_3\cdot CH_3COCl][CH_3COCl]}{[AlCl_3\cdot CH_3COCl]^2}$$

The average values for the ratios of K_2 to K_1 for all the samples at several temperatures are listed in Table III. As the temperature is raised the resonance lines broaden due to exchange amongst the acetyl chloride species. In acetyl chloride rich samples the concentration of 2:1 complex is small and at -44 °C its area cannot be measured, so K_2/K_1 is the average of only four samples. The assignments of

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[15] Sack, R. A. *Mol. Phys.* **1958**, *1*, 163.

Table V. Lifetimes as a Function of Temperature for Some Acetyl Chloride Species

sample ratio	temp, °C	$\tau(AlCl_3\cdot CH_3COCl)$, s	$\tau(CH_3COCl)$, s
1:1	−44	0.14	0.052
	−34	0.046	0.025
	−24	0.0093	0.0052
1:1	−44	0.12	0.052
	−34	0.046	0.024
	−24	0.012	0.007
1:1.5	−44	0.093	0.093
	−34	0.034	0.034
	−24	0.012	0.016
1:2	−44	0.15	0.26
	−34	0.040	0.059
	−24	0.014	0.019
1:3	−44	0.11	0.30
	−34	0.037	0.10
	−24	0.015	0.045

chemical shifts for the complexes, which are listed in Table IV, are derived from all the preceding arguments.

Lifetimes of the acetyl chloride species were obtained by comparison of theoretical spectra with those observed. In order to calculate theoretical spectra one must know or assume the populations of the species, their chemical shifts, and line widths in the absence of exchange and certain aspects of the exchange mechanism. If the various exchange rates differ significantly, it is possible to get qualitative information without a study of the effect of all the preceding variables. Near the slow exchange limit the lifetime for each species is inversely proportional to the increase in line width from the nonexchanging value. For two exchanging species A and B the relationship between lifetimes and concentrations is given by $[A]/\tau_A = [B]/\tau_B$. Exchange of one of these species, say A, with a third species C will broaden the line found for A beyond that given by the preceding expression. This extra broadening is a measure of the exchange rate with C.

For all of the samples in this study it was found that exchange broadening of the line from the 2:1 complex, at a given temperature, was significantly less than for the 1:1 complex or free acetyl chloride. Therefore, as an initial approximation one can ignore the involvement of the 2:1 complex in the exchange reaction. It was also found that broadening of the line for acetyl chloride was somewhat greater than could be accounted for by exchange with the 1:1 complex alone. Thus the exchange reactions can be approximately described by the ready exchange between acetyl chloride and the 1:1 complex and the slow exchange between acetyl chloride and the 2:1 complex, while there is negligible exchange between the 1:1 and 2:1 complexes. The exchange matrix can then be written as:

$$\begin{array}{ccc} -1 & 0 & 1 \\ 0 & -1 & 1 \\ {}^1/_2 & {}^1/_2 & -1 \end{array}$$

where the first row corresponds to the 2:1 complex, the second row to the 1:1 complex, and the third row to acetyl chloride. From spectra in the slow-exchange region it appeared that the change in chemical shift over the temperature range employed was negligible in comparison with the differences in chemical shifts of the three acetyl chloride species. Relative concentrations were estimated from the equilibrium expressions in those cases where areas of individual lines could not be measured.

Exchange lifetimes, obtained by comparison of theoretical and experimental spectra, are listed in Table V. A sample of matching theoretical and experimental spectra is shown in Figure 2 for a 1:1.5 sample at −34 °C. Once the lifetimes are obtained, the next step is to determine the rate constants for the exchange reaction. This requires a knowledge of the molecularity of the exchange reaction. In the present case the two most plausible exchange mechanisms are either via displacement of complexed acetyl chloride by free acetyl chloride or via dissociation and recombination of the complex. If the reaction occurs by a displacement mechanism the lifetime of the complex will be inversely proportional to the concentration of free acetyl chloride, i.e., $[CH_3COCl] \times \tau(AlCl_3\cdot CH_3COCl) =$ constant.[16] A consequence of this mechanism is that the activation enthalpy for exchange must be less than the enthalpy of dissociation of the complex. If exchange occurs by a dissociation mechanism, the lifetime of the complex is independent of the concentration of free acetyl chloride and the activation enthalpy for exchange equals the enthalpy of dissociation of the complex. It can be seen by inspection of Table IV that at each temperature $\tau(AlCl_3CH_3COCl)$ is independent of the concentration of CH_3COCl. Therefore, the exchange occurs by a dissociation mechanism and the rate constant for the exchange reaction is the reciprocal of the lifetime. From an Arrhenius plot of the temperature dependence of the rate constant for exchange, one obtains an activation enthalpy of 12.9 ± 0.4 kcal/mol and an activation entropy of 0 eu. This is in excellent agreement with the heats of formation of 10–15 kcal/mol for acyl halide–aluminum halide complexes.[17]

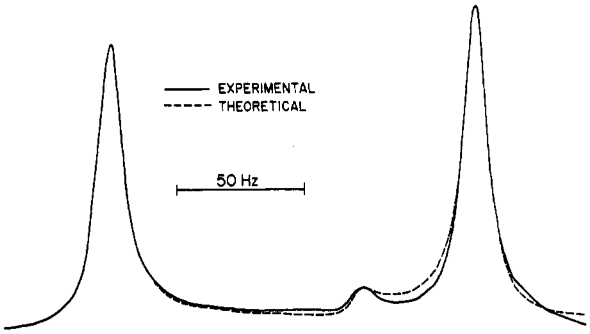

Figure 2. Experimental and theoretical proton resonance spectra for a 1:1.5 $AlCl_3$–CH_3COCl solution at −34 °C.

Because of the uncertainty in the concentration of the 2:1 complex, reliable lifetimes toward acetyl exchange could not be obtained for it. Since it only exchanges with free acetyl chloride and not with the 1:1 complex, the exchange must occur via a bimolecular mechanism with an aggregate of two acetyl chloride and two $AlCl_3$ species as an intermediate or activated complex. If the exchange were to occur by a dissociation of the 2:1 complex, then exchange with the 1:1 complex would be observed.

Conclusions

In the system aluminum chloride–acetyl chloride in sulfur dioxide as solvent there is an equilibrium between 2:1 and 1:1 complexes and the uncomplexed species. Exchange between free acetyl chloride and that in the 1:1 complex occurs readily by a dissociation mechanism, while other exchange reactions are slower. It is possible that these observations may have a bearing on the mechanism of the Friedel–Crafts reaction and this will be explored with various aromatic hydrocarbons and other metal halides.

Registry No. $AlCl_3$, 7446-70-0; $2AlCl_3$–CH_3COCl, 12385-46-5; $AlCl_3$–CH_3COCl, 10511-57-6; CH_3COCl, 75-36-5.

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[16] Brownstein, S.; Eastham, A. M.; Latremouille, G. A. *J. Phys. Chem.* **1963**, *67*, 1028.

[17] Reference 2, p 587.