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Complexes of Ketones with Aluminum Chloride in Sulfur Dioxide as Solvent

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Nuclear magnetic resonance studies of the systems acetophenone–aluminum chloride and acetone–aluminum chloride in sulfur dioxide as solvent show the existence of complexes with two and one molecules of ketone per aluminum chloride. Cis and trans structures are proposed for the 2:1 complexes of acetophenone. Equilibrium constants and some details of exchange for the complexes were determined as a function of temperature.

Introduction

In the aluminum chloride catalyzed Friedel–Crafts reaction the end products are frequently aromatic ketones. Since these may complex with the aluminum chloride there will be a competition for it between the products and the carbonyl-containing reactants. Thus, the complexing behavior of ketones may affect the later course of the Friedel–Crafts reaction.

Complexes of $AlCl_3$ with oxygen-containing organic compounds, such as ethers, aldehydes, ketones, and esters, have frequently been reported.[2] The complexing of 2 equiv of oxygen-containing Lewis base per $AlCl_3$ has only been observed with dimethyl ether and tetrahydrofuran.[3-7] In nitrobenzene as solvent, only a 1:1 complex between $AlCl_3$ and acetone was observed by conductivity methods.[8] The infrared spectrum of the solid 1:1 complex between $AlCl_3$ and acetophenone has been reported.[9] Details of the structures of $AlCl_3$–acetonitrile complexes in acetonitrile as solvent have also been thoroughly discussed.[10]

Experimental Section

^1H, ^{13}C and ^{27}Al resonance spectra were obtained on a Varian Associates XL-100 spectrometer equipped with Nicolet Fourier Transform and multinuclear attachments. All spectra are reported with respect to tetramethylsilane, although neopentane was used as internal reference. Corrections applied were 0.92 ppm for protons and 31.4 ppm for ^{13}C. Ξ values are used for ^{27}Al. Variable-temperature measurements were calibrated against a methanol sample. Peak areas were obtained either by integration using the software of the operating system or by measurement with a planimeter.

Aluminum chloride was purified by repeated vacuum sublimation and used shortly thereafter. Acetone was dried with Drierite and fractionally distilled through a Vigreux column, and the middle fraction was collected and stored over 4A molecular sieves. After purification by fractional distillation, acetophenone and diethyl ketone were also stored over 4A molecular sieves. Neopentane and sulfur dioxide were transferred directly from the suppliers' cylinder to storage containers on the vacuum line with the SO_2 stored over P_2O_5. Samples were prepared by transferring, in a dry box, some $AlCl_3$ into an NMR tube closed by a Teflon high-vacuum stopcock. After the $AlCl_3$ was weighed, the appropriate quantities of neopentane, sulfur dioxide, and acetone or diethyl ketone, measured as a vapor, were condensed into the sample container, and the tube was sealed under vacuum. The vapor pressure of acetophenone was not high enough for accurate measurements by this procedure. Acetophenone was added to a side arm separated from the main container by a second Teflon high-vacuum stopcock. After it had been weighed, the procedure continued as with the more voltaile ketones. The samples were quickly thawed, mixed, and then stored at −80 °C.

All concentrations are presented as mole fractions, and equilibrium constants are calculated in this unit.

Results and Discussion

Typical proton resonance spectra of the aliphatic region of acetophenone-rich solutions in SO_2 containing $AlCl_3$ at −74 °C are shown in Figure 1. Neopentane is used as an internal reference, since it is reasonably inert in the $AlCl_3$-containing solutions.

There are two signals from 2:1 complexes of acetophenone with $AlCl_3$ at 3.25 and 3.14 ppm and a third signal, which is the weighted average of the rapidly exchanging 1:1 complex and free acetophenone. The methyl signal from the 1:1 complex alone is found at 3.32 ppm in a solution containing an excess of $AlCl_3$ and from free acetophenone at 2.66 ppm. Signals were assigned to particular complexed species on the basis of changes in relative areas with changes in sample composition. The following discussion will be based on these assignments. An alternate description will be presented and rejected subsequently.

The equilibria in these systems may be described by eq 1–5. Dividing eq 5 by eq 4 shows that the ratio of the concentrations of the two different 2:1 complexes at a given temperature should be independent of the overall composition of the solution. The results shown in Table I are a confirmation of this interpretation. The samples in Table I are ordered in increasing ratio of acetophenone to $AlCl_3$, but the ratio [cis]/[trans] is random. Average values at −74, −64, and −54 °C are 0.30 ± 0.08, 0.31 ± 0.08, and

$$PhCOCH_3 + AlCl_3 \rightleftharpoons PhCOCH_3{\cdot}AlCl_3 \qquad (1)$$

$$K_1 = \frac{[PhCOCH_3{\cdot}AlCl_3]}{[PhCOCH_3][AlCl_3]} \qquad (2)$$

$$PhCOCH_3 + PhCOCH_3{\cdot}AlCl_3 \rightleftharpoons (PhCOCH_3)_2{\cdot}AlCl_3 \text{ (trans and cis)} \qquad (3)$$

$$K_{2(\mathrm{trans})} = \frac{[(PhCOCH_3)_2{\cdot}AlCl_3]_{\mathrm{trans}}}{[PhCOCH_3{\cdot}AlCl_3][PhCOCH_3]} \qquad (4)$$

$$K_{2(\mathrm{cis})} = \frac{[(PhCOCH_3)_2{\cdot}AlCl_3]_{\mathrm{cis}}}{[PhCOCH_3{\cdot}AlCl_3][PhCOCH_3]} \qquad (5)$$

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Table I. Concentrations of the 2:1 Adducts in Solutions of Acetophenone and $AlCl_3$

sample	T, °C	$[AlCl_3]$[a]	$[PhCOCH_3]$[a]	[cis 2:1]	[trans 2:1]	[cis]/[trans]
A	−74	0.0103	0.0119	0.00124	0.00351	0.352
A	−64	0.0103	0.0119	0.00105	0.00346	0.303
A	−54	0.0103	0.0119	0.00105	0.00317	0.330
B	−74	0.0191	0.0227	0.00214	0.00453	0.472
B	−64	0.0191	0.0227	0.00200	0.00427	0.468
B	−54	0.0191	0.0227	0.00194	0.00486	0.399
C	−74	0.0176	0.0274	0.00447	0.0198	0.226
C	−64	0.0176	0.0274	0.00488	0.0196	0.249
C	−54	0.0176	0.0274	0.00421	0.0227	0.185
D	−74	0.0119	0.0229	0.00364	0.0152	0.239
D	−64	0.0119	0.0229	0.00335	0.0147	0.228
D	−54	0.0119	0.0229	0.00275	0.0138	0.199
E	−74	0.0151	0.0300	0.00549	0.0172	0.319
E	−64	0.0151	0.0300	0.00291	0.0172	0.169[b]
E	−54	0.0151	0.0300	0.00536	0.0164	0.327
F	−74	0.0105	0.0388	0.00314	0.0156	0.201
F	−64	0.0105	0.0388	0.00732	0.00948	0.772[b]
F	−54	0.0105	0.0388	0.00183	0.0109	0.168

[a] Mole fraction of reagent originally added. [b] This value is discarded in averaging the results.

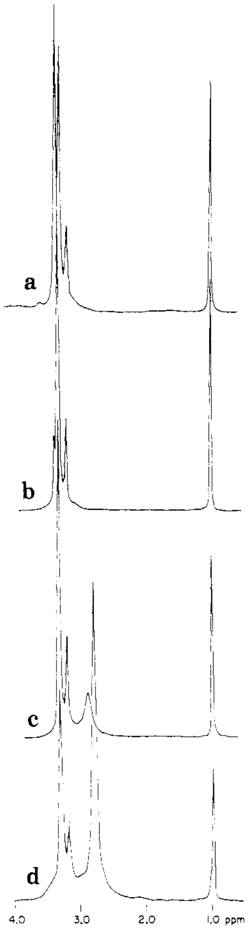

Figure 1. Proton resonance spectra of acetophenone–$AlCl_3$ solutions in SO_2 at −74 °C with neopentane as internal reference: (A) 1.19 equiv of acetophenone; (B) 1.56 equiv of acetophenone; (C) 1.99 equiv of acetophenone; (D) 3.7 equiv of acetophenone.

Table II. Concentrations and Equilibrium Constants for Solutions of Acetophenone and $AlCl_3$

sample	T, °C	[2:1]	[1:1]	$[PhCOCH_3]$	$K_{(2:1)}$
D	−74	0.0188	0.00153	0.00252	4890
D	−64	0.0180	0.00300	0.00259	2320
D	−54	0.0166	0.00299	0.00336	1650
E	−74	0.0227	0.00188	0.00540	2240
E	−64	0.0201	0.00344	0.00644	908
E	−54	0.0218	0.00316	0.00512	1340
F	−74	0.0187	0.00212	0.0179	494
F	−64	0.0168	0.00266	0.0193	327
F	−54	0.0127	0.00423	0.0219	137

Table III. Chemical Shifts for Ketone-$AlCl_3$ Complexes in SO_2 Solution at −64 °C

	^1H: δ_{CH_3}	^{13}C δ_{CH_3}	$\delta_{C=O}$	δ_{C_1}
acetophenone				
1:1 complex	3.32	27.2	217.6	141.4
trans 2:1 complex	3.25	26.0	214.3	139.7
cis 2:1 complex	3.14	26.4	215.1, 216.4	139.0
acetone				
1:1 complex	2.94	30.5	232.5	
trans 2:1 complex	2.80	31.7	232.2	
cis 2:1 complex	2.66	30.6	230.3	

0.27 ± 0.08. The relative concentrations of free acetophenone and the 1:1 complex may be calculated from the chemical shift of their averaged signal. This, in conjunction with the relative areas of the three separate peaks, yields the concentrations of acetophenone and the 1:1 complex. From these concentrations the equilibrium constant for formation of the 2:1 complex from free acetophenone and the 1:1 complex may be calculated. The results are listed in Table II for those samples containing appreciable concentrations of free acetophenone. The equilibrium constant for formation of the 1:1 complex is too large to be determined by NMR methods. Average values for K_2 at −74, −64, and −54 °C are 2500 ± 1500, 1200 ± 800, and 1000 ± 600. The large errors reflect the fact that the values are based upon, and very sensitive to, the chemical shift of a rather broad line. The decrease of the equilibrium constant with increasing temperature agrees with theory.

Aluminum trichloride normally complexes with one molecule of Lewis base to yield an adduct with tetrahedral coordination about aluminum. With tetrahydrofuran as base, a 2:1 complex has been isolated with a trigonal bipyramid structure having the ether moieties in the axial positions.[3] We propose that the two different 2:1 complexes with acetophenone have trans and cis (one axial and one equatorial) stereochemistry about aluminum. Although the two ligands are equivalent in the trans isomer, they need not be in the cis isomer.

A single signal is seen in the proton resonance spectrum for each 2:1 isomer. Only one signal is observed at Ξ = 26 059 533 in the ^{27}Al spectrum for all three complexes at −64 °C. Since exchange is slow at that temperature, it is

Table IV. Concentrations of the 2:1 Adducts in Solutions of Acetone and $AlCl_3$

sample	T, °C	$[AlCl_3]$ [a]	$[(CH_3)_2CO]$ [a]	[cis 2:1]	[trans 2:1]	[cis]/[trans]
G	−74	0.0145	0.0145	0.00033	0.00159	0.20
G	−64	0.0145	0.0145	0.00036	0.00162	0.22
G	−54	0.0145	0.0145	0.00037	0.00160	0.23
H	−74	0.0188	0.0250	0.00101	0.00541	0.19
H	−64	0.0188	0.0250	0.00108	0.00529	0.20
H	−54	0.0188	0.0250	0.00124	0.00534	0.23
I	−74	0.0111	0.0223	0.00225	0.00619	0.36
I	−64	0.0111	0.0223	0.00218	0.00674	0.32
J	−74	0.0088	0.0231	0.00184	0.00559	0.33
J	−64	0.0088	0.0231	0.00151	0.00531	0.28
K	−74	0.0083	0.0248	0.00136	0.00506	0.27
K	−64	0.0083	0.0248	0.00163	0.00657	0.25

[a] Mole fraction of reagent originally added.

reasonable to assume that the ^{27}Al chemical shift is approximately the same for all species where aluminum is coordinated to carbonyl oxygens. The ^{13}C NMR spectrum of a sample containing some free acetophenone has three signals in the methyl region and five in the carbonyl region, two of which are of equal intensity and line width. From this spectrum and that of a sample that is primarily the 1:1 complex, it is possible to assign all the signals except those of the ortho, meta, and para carbons, where there is severe overlap. The pair of weak carbonyl signals must be from the cis isomer. The relative intensity of the trans carbonyl signal is more than twice that of the cis signals; therefore, the stronger signal in the proton spectrum is also assigned to the trans isomer. Chemical shifts are listed in Table III.

Since solvated cationic and anionic aluminum-containing species are obtained when $AlCl_3$ is dissolved in acetonitrile,[10] it is necessary to consider the assignment of the signals in the proton and carbon resonance spectra to such species. This assignment may be rejected on the basis of the ^{27}Al spectra. Neutral oxygen coordinated $AlCl_3$ species have chemical shifts from 26 058 956 ($AlCl_3$) to 26 059 489 ($[CH_3]_2O\cdot AlCl_3$), whereas cationic species are found in the region 26 056 131 ($[CH_3CN]mAlCl_2^+$) to 26 056 780 ($Al[H_2O]_6^{3+}$).[4] No lines corresponding to cationic species were found in this study.

To ascertain if 2:1 complex formation of ketones with $AlCl_3$ is a general phenomenon, acetone and diethyl ketone were also studied. The overall conclusions are similar to those with acetophenone, but there is some difference in detail. From solutions with an excess of $AlCl_3$ to those with somewhat less than 2 equiv of acetone, a strong and a weak signal can be assigned to a 1:1 complex in both the proton and ^{13}C spectra. The ratio of the intensities varies with sample composition and temperature, but the weak signal is always present. The ^{27}Al resonance spectrum of an acetone-containing sample has a strong sharp line at Ξ = 26 059 534, which is assigned to the neutral complexes, and a weak broad line at 26 056 798, which is assigned to cationic species.[11] Therefore, the weak line in the proton resonance spectra is also assigned to such species by analogy with acetonitrile.[10] Two proton signals are also seen for the 2:1 complex, but their relative intensities are constant. They are assigned to cis and trans structures by analogy with acetophenone. The chemical shifts are listed in Table III, and the concentrations of the 2:1 complexes are listed in Table IV.

The 2:1 complex with acetone is more stable relative to the 1:1 complex than it is for acetophenone. It is not possible to calculate K_2, since no free acetone is observed until 2 equiv of ketone is included for each $AlCl_3$. At that point no 1:1 complex is observed. Since 2:1 complex is observed with equivalent amounts of reactants, the system can be treated according to eq 6 and 7. The concentration

$$2(CH_3)_2CO\cdot AlCl_3 \rightleftharpoons [(CH_3)_2CO]_2AlCl_3 + AlCl_3 \quad (6)$$

$$K_3 = \frac{[[(CH_3)_2CO]_2AlCl_3][AlCl_3]}{[(CH_3)_2CO\cdot AlCl_3]^2} \quad (7)$$

of $AlCl_3$ may be approximated as equal to the 1:1 complex that has disproportionated. The results of these calculations are presented in Table V.

Table V. Concentrations and Equilibrium Constants for Solutions of Acetone and $AlCl_3$

sample	T, °C	[2:1]	[1:1]	$[AlCl_3]$	K_3
G	−74	0.00192	0.0107	0.00192	0.032
G	−64	0.00198	0.0106	0.00198	0.035
G	−54	0.00197	0.0106	0.00197	0.035
H	−74	0.00642	0.0121	0.00780	0.034
H	−64	0.00637	0.0122	0.00073	0.031
H	−54	0.00656	0.0118	0.00092	0.043

There is severe overlap of the proton resonance signals from the various species in the system diethyl ketone–$AlCl_3$, at least in part due to their multiplicity because of proton spin–spin coupling. This overlap does not occur in the proton-decoupled carbon resonance spectra, but relative intensities are not sufficiently accurate to warrant quantitative calculations. The qualitative behavior is similar to that of acetone.

It is interesting to note that the rapid exchange of free acetophenone with that in the 1:1 complex does not proceed via the 2:1 complex, at least at low temperature. At temperatures above −54 °C a generalized averaging occurs to yield by 25 °C a single averaged line for all ketone species. This suggests that at low temperature the mechanism of exchange is via dissociation of the 1:1 complex.

Our studies show that formation of ketone–$AlCl_3$ complexes is facile and that these could therefore compete for the aluminum chloride used as catalyst in the Friedel–Crafts reaction. Measurements of reaction kinetics and studies of intermediates should, therefore, be done only during the first few percent of these reactions.

Registry No. *trans*-$[PhCOCH_3]_2AlCl_3$, 83174-79-2; *cis*-$[PhCOCH_3]_2AlCl_3$, 83213-32-5; *trans*-$[(CH_3)_2CO]_2AlCl_3$, 83174-80-5; *cis*-$[(CH_3)_2CO]_2AlCl_3$, 83213-33-6; $AlCl_3$, 7446-70-0; Al, 7429-90-5; $PhCOCH_3AlCl_3$, 23444-00-0; $(CH_3)_2COAlCl_3$, 34430-84-7.

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(11) The authors thank a referee for suggesting this measurement.