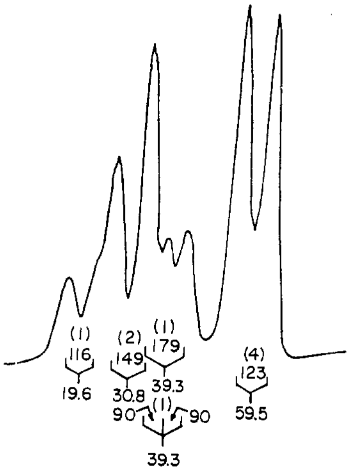

Figure 9.—B^{11} nmr spectrum of $(CH_3)_4NB_9H_{12}NH$ in CH_3CN at 19.3 Mc.

$CH_3CNB_9H_{11}NH$.—To a solution of 600 mg of $(CH_3)_4NB_9H_{12}NH$ in a small volume of acetonitrile cooled in an ice bath was added dropwise a cold, concentrated solution of bromine in acetonitrile until the bromine color was no longer discharged. The mixture was poured into a cold aqueous solution of sodium acetate and sodium bisulfite. The resulting precipitate was collected and dried first at 0° (0.1 mm) and then at 25° (0.1 mm). The product was then sublimed onto a −80° cold finger at 80° (0.1 mm) to give 300 mg of $CH_3CN \cdot B_9H_{11}NH$, mp 85–88°.

Anal. Calcd for $CH_3CN \cdot B_9H_{11}NH$: B, 59.1; H, 9.2; C, 14.6; N, 17.0; hydrolytic H_2, 2450 cc/g. Found: B, 61.1; H, 9.5; C, 15.2; N, 16.0; hydrolytic H_2, 2288 cc/g.

The product must be stored in an inert atmosphere as it decomposes in air. A pentane solution of $CH_3CN \cdot B_9H_{11}NH$ in air rapidly deposits a flocculent solid which contains OH groups (by infrared analysis).

The mass spectrum of $CH_3CNB_9H_{11}NH$ (solid injection) shows no parent peak, but an intense peak occurs at m/e 41 corresponding to CH_3CN^+, and the spectrum cuts off at m/e 125 corresponding to $^{11}B_9H_{11}NH^+$. Thus, complete fragmentation occurs to CH_3CN and $B_9H_{11}NH$.

The H^1 nmr spectrum in CD_3CN shows a single peak at τ 6.98 (CH_3CN). The infrared spectrum shows peaks at 3400 (N–H str), 2550 (B–H str), and 2340 cm^{-1} (C≡N str). The ultraviolet spectrum in acetonitrile solution has λ_{max} 2410 A (ϵ 10,400).

$CH_3CN \cdot B_9H_{11}NH$ can also be prepared by treatment of an acetonitrile solution of $B_9H_{12}NH^-$ with iodine, N-chlorosuccinimide, N-bromosuccinimide, or N-iodosuccinimide.

Treatment of a solution of $CH_3CN \cdot B_9H_{11}NH$ in benzene with triethylamine gave $(C_2H_5)_3NB_9H_{11}NH$ as a colorless solid identified by the presence of resonance peaks characteristic of ethyl groups in its H^1 nmr spectrum and by the absence of infrared absorption characteristic of C≡N.

Reaction of $CH_3CNB_9H_{11}NH$ with lithium aluminum hydride or lithium borohydride in THF gave $B_9H_{12}NH^-$, isolated as the tetramethylammonium salt and identified by comparison with an authentic sample.

Acknowledgment.—We wish to thank Drs. P. A. Wegner and W. H. Knoth for their critical reading of the manuscript.

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The Interaction of Phosgene with Lewis Acids

By KARL O. CHRISTE

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Vapor pressure–composition isotherms indicate the following relative order of Lewis acidity toward phosgene: $AlCl_3 > SbCl_5 > BCl_3$. Whereas $AlCl_3$ forms a well-defined 1:1 adduct with $COCl_2$, the BCl_3–$COCl_2$ system shows a positive deviation from Raoult's law. Contrary to earlier literature reports $COCl_2$ forms only a 1:1 adduct with $AlCl_3$. The adduct is a white solid melting at 25° and has a dissociation pressure of 36 and 440 mm at 0 and 25°, respectively. Its infrared spectrum agrees only with an oxygen-bridged coordination complex and not with any ionic structure postulated earlier.

Introduction

Complex formation between $COCl_2$ and the Lewis acid $AlCl_3$ was first described by Baud.[1] The existence and characterization of the following complexes were reported: (i) $Al_2Cl_6 \cdot 5COCl_2$, liquid, mp −2°, vapor pressure 760 mm at 30°; (ii) $Al_2Cl_6 \cdot 3COCl_2$, liquid, mp 9°, and (iii) $2Al_2Cl_6 \cdot COCl_2$, solid, decomposing at 150°. Later, the properties of solutions of $AlCl_3$ in liquid $COCl_2$ were extensively studied by Germann and coworkers.[2–8] Based on their work these solutions were considered as a solvent system of acids and bases,[9,10] assuming for the solvent a self-ionization comparable to that of H_2O. Consequently, the $AlCl_3$–$COCl_2$ adducts were generally believed to be ionic, containing $COCl^+$ or CO^{2+} cations and $AlCl_4^-$ anions. More recently, Huston[11] has shown in a tracer study of the $COCl_2$–$AlCl_3$ system that the exchange rate of radioactive chlorine between $AlCl_3$ and $COCl_2$ is slow. It was therefore suggested that the active agent in solutions of $AlCl_3$ in liquid $COCl_2$ is $AlCl_3$ itself and not CO^{2+} or $COCl^+$. However, interaction between $COCl_2$ and $AlCl_3$ through a chlorine atom, without actually break-

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(1) E. Baud, *Compt. Rend.*, **140**, 1688 (1905).
(2) A. F. O. Germann, *Science*, **61**, 71 (1925).
(3) A. F. O. Germann, *J. Phys. Chem.*, **28**, 885 (1924).
(4) A. F. O. Germann, *ibid.*, **29**, 138 (1925).
(5) A. F. O. Germann, *ibid.*, **29**, 1148 (1925).
(6) A. F. O. Germann and C. R. Timpany, *ibid.*, **29**, 2275 (1925).
(7) A. F. O. Germann and G. H. McIntyre, *ibid.*, **29**, 102 (1925).
(8) A. F. O. Germann and D. M. Birosel, *ibid.*, **29**, 1469 (1925).
(9) L. F. Audrieth and J. Kleinberg, "Non-Aqueous Solvents," John Wiley and Sons, Inc., New York, N. Y., 1953.
(10) T. Moeller, "Inorganic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1953.
(11) J. L. Huston, *J. Inorg. Nucl. Chem.*, **2**, 128 (1956).

ing the strong C–Cl bond, was not ruled out. In addition, the latter author[11] reported the existence of a new adduct having the composition $AlCl_3 \cdot COCl_2$ and was not able to prepare compound iii claimed by Baud.[1]

Besides the above-mentioned $AlCl_3$ adducts only one additional complex of $COCl_2$ with a Lewis acid, having the composition $SbO_2Cl \cdot 0.5COCl_2$, has been reported.[12] Its infrared spectrum was recorded; however, no conclusions about the nature of the adduct could be reached, since both the carbonyl and CCl_2 stretching vibrations were shifted to lower frequencies.

Summarizing, there is presently very little known about the interaction of $COCl_2$ with Lewis acids. Only the $AlCl_3$–$COCl_2$ system has been studied to some extent. However, even in this case the reports contain contradictions concerning the existence and stoichiometry of certain adducts and nothing is known about their exact nature. Therefore, the purpose of this investigation was to study the interaction of $COCl_2$ with various Lewis acids and to characterize any resulting adducts.

Experimental Section

Materials and Apparatus.—The materials used in this work were manipulated in a standard Pyrex glass high-vacuum system which had stopcocks and joints lubricated with Halocarbon grease (high-temperature grade). Hygroscopic nonvolatile compounds were handled in the dry nitrogen atmosphere of a glove box. Phosgene and BCl_3 (both from The Matheson Co., Inc.) were purified by several low-temperature vacuum distillations. The purity of the volatile starting materials was determined by measurement of their vapor pressures and infrared spectra. Antimony pentachloride (Hooker Chemical Corp.) was purified by vacuum distillation (10 mm) in the dry nitrogen atmosphere of a standard vacuum distillation apparatus. Aluminum trichloride (A.R., Mallinckrodt), $MoCl_5$ (Climax Molybdenum Co.), and WCl_6 (Alfa Inorganics, Inc.) were subjected to a vacuum sublimation before use.

Infrared Spectra.—Infrared spectra were recorded on a Beckman Model IR-9 prism-grating spectrophotometer in the range 4000–400 cm^{-1}. Screw-cap metal cells equipped with neoprene O rings and AgCl windows were used for solid samples. The solids were used directly as dry powders since Nujol mulls resulted in inferior quality spectra.

Vapor Pressure–Composition Isotherms.—All vapor pressure–composition isotherms were measured at 0 or 25° using standard vacuum techniques. In the case of Lewis acids having negligible vapor pressures at 0°, about 0.05 mole was transferred in the glove box into a 100-ml round-bottom flask equipped with a magnetic Teflon-coated stirring bar. After connecting to the vacuum line, the whole system was repeatedly purged with dry helium. A known quantity of freshly purified $COCl_2$ (usually about 0.9 mole) was condensed into the flask and stirred several hours at 0°. Phosgene was removed in small steps by allowing the $COCl_2$ to expand into a known volume. Each time, the corresponding vapor pressure was measured using a mercury manometer. Corrections were made for the change in volume due to the displacement of the mercury. These measurements were continued, until the pressure above the Lewis acid had decreased to zero. From the known quantity of $COCl_2$ and the total and incremental volume of $COCl_2$ gas removed, the per cent molar compositions corresponding to the measured vapor pressures could be easily calculated. In every case, all the $COCl_2$ used had been completely removed, leaving the exact amount of Lewis acid used. The composition of the residue was confirmed by elemental analyses. For a volatile Lewis acid, such as BCl_3, tensimetric titrations were done in both directions, *i.e.*, titrating BCl_3 with $COCl_2$ and $COCl_2$ with BCl_3.

Results

Vapor Pressure–Composition Isotherms.—Boron trichloride and $SbCl_5$ are both liquid at 0° and miscible with $COCl_2$ over the entire composition range. The vapor pressure of the binary mixtures at 0° as a function of the molar composition is shown in Figure 1. The broken lines represent the vapor pressures of a mixture of two ideal liquids according to Raoult's law. For BCl_3, only a positive deviation from Raoult's law was observed over the entire composition range. For $SbCl_5$, a small negative deviation from Raoult's law was found between 50 and 100 mole % $SbCl_5$.

Figure 2 shows the vapor pressure at 0° above a solution of $AlCl_3$, $MoCl_5$, and WCl_6 in $COCl_2$ plotted as a function of the molar composition. Whereas $AlCl_3$ readily dissolves in $COCl_2$, the solubility of $MoCl_5$ is considerably lower and WCl_6 is only sparingly soluble in liquid $COCl_2$ at 0°. A sharp "break" in the vapor pressure curve was found for the $AlCl_3$–$COCl_2$ system at a 1:1 molar composition. In the $MoCl_5$–$COCl_2$ and the WCl_6–$COCl_2$ systems the mole per cent $COCl_2$ given in Figure 2 is not necessarily that of the actual solution but represents the over-all mole per cent $COCl_2$ present in the heterogeneous mixture (owing to the unknown solubility of the solid in $COCl_2$). Therefore, the vapor pressures above the $MoCl_5$ and WCl_6 solutions should not be compared since the mole fractions of the actual homogeneous solutions are unknown. However, it should be pointed out that in the $MoCl_5$–$COCl_2$ and the WCl_6–$COCl_2$ systems the vapor pressure curve shows no "break" indicating no relatively stable adduct between $COCl_2$ and either WCl_6 or $MoCl_5$. Figure 3 shows the vapor pressure of the $AlCl_3$–$COCl_2$ system at 25°. At this temperature the 1:1 $AlCl_3$–$COCl_2$ adduct is liquid. The vapor pressure curve was measured over the entire composition range. No indications were obtained for the existence of any $COCl_2$–$AlCl_3$ adducts having compositions other than 1:1.

Physical Properties of the $AlCl_3 \cdot COCl_2$ Adduct.—The 1:1 $AlCl_3$–$COCl_2$ adduct is a white crystalline solid at 0°. It is very soluble in excess $COCl_2$ and melts at 25°. It is relatively unstable and dissociates readily into $COCl_2$ and $AlCl_3$. The dissociation pressures above the complex at 0 and 25° are 36 and 440 mm, respectively. Under vacuum, $COCl_2$ can be easily removed at ambient temperature, $AlCl_3$ remaining.

Infrared Spectrum of the $AlCl_3$–$COCl_2$ Adduct.—Figure 4 shows the infrared spectrum of the 1:1 $AlCl_3$–$COCl_2$ adduct recorded at ambient temperature. The bands marked by an asterisk correspond to free $COCl_2$ being present due to dissociation of the complex. The exact frequencies and their assignments are listed in Table I. The infrared spectrum of solid $AlCl_3$ was also recorded and shows absorptions at 599, 497, 465, and 418 cm^{-1}, corresponding somewhat to the 625, 484, and 420 cm^{-1} bands observed for gaseous Al_2Cl_6.[13]

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[12] K. Dehnicke, *Z. Anorg. Allgem. Chem.*, **312**, 237 (1961).

[13] W. Klemperer, *J. Chem. Phys.*, **24**, 353 (1956).

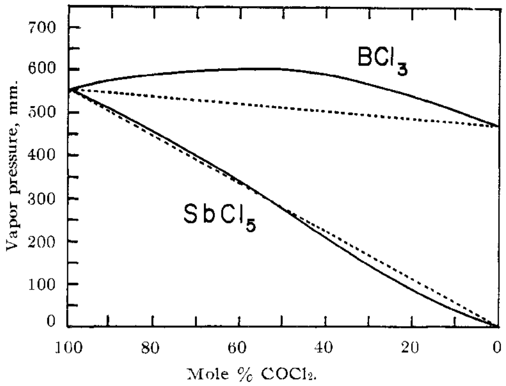

Figure 1.—The vapor pressure–composition isotherms of the binary systems $COCl_2$ with BCl_3 and $SbCl_5$ at 0°. The broken lines represent the curves expected according to Raoult's law.

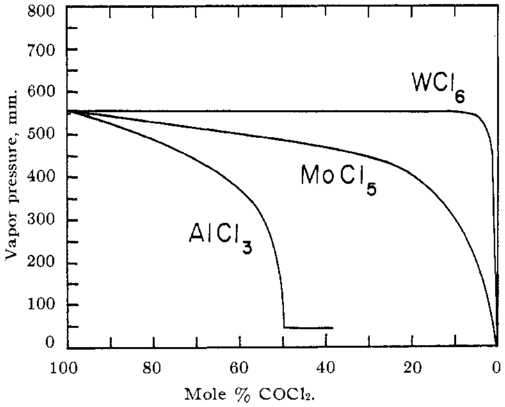

Figure 2.—The vapor pressure–composition isotherms of the binary systems $COCl_2$ with $AlCl_3$, $MoCl_5$, and WCl_6 at 0°.

Table I

Infrared Spectrum of the 1:1 $AlCl_3$–$CoCl_2$ Adduct and Its Assignment

Frequency obsd, cm^{-1}	Assignment	
	$AlCl_3 \cdot COCl_2$	Free $COCl_2$[a] and $AlCl_3$ (solid)
1960 w, br	$2\nu_{as}(CCl_2)$	
1808 s		$\nu(C{=}O)$
1695 w, sh		$2\nu_{as}(CCl_2)$
1670 vw, sh	$(\nu_{as}(CCl_2) + \nu_s(CCl_2))$	
1635 vs	$\nu(C{=}O)$	
1495 w		
1416 vw	$2\nu_s(CCl_2)$	$(\nu_{as}(CCl_2) + \nu_s(CCl_2))$
1202 w		
1164 vw		$2\nu_s(CCl_2)$ and $2\pi(OCCl_2)$
1118 w		
1020 vw, sh		$(\nu_s(CCl_2) + \delta_{as}(OCCl))$
981 vs	$\nu_{as}(CCl_2)$	
950 vw, sh		
851 s		$\nu_{as}(CCl_2)$
817 w, sh		$(\nu_s(CCl_2) + \delta_s(OCCl))$
690 ms	$\nu_s(CCl_2)$	
599 w		$AlCl_3$
565 s, br		$\nu_s(CCl_2)$, $\pi(OCCl_2)$, and $2\delta_s(OCCl)$
498 vs	$\nu_{as}(AlCl_3)$	$AlCl_3$
468 m, sh		$AlCl_3$
412 mw		$AlCl_3$

[a] E. Catalano and K. S. Pitzer, *J. Am. Chem. Soc.*, **80,** 1054 (1958).

Discussion

Vapor Pressure–Composition Isotherms.—In a binary system containing at least one volatile component vapor pressure–composition isotherms are a useful tool in determining the possible existence and stoichiometry of adducts. If both components are liquid and completely miscible, such as $COCl_2$ and BCl_3 or $SbCl_5$, the vapor pressure–composition isotherm would result in a straight line (Raoult's law) for an ideal mixture. A positive deviation from Raoult's law indicates less interaction between two different molecules than between two molecules of the same kind. Correspondingly, a negative deviation from Raoult's law is indicative of a positive interaction between the two components. Figure 1, depicting the vapor pressure–composition isotherms of the BCl_3–$COCl_2$ and the $SbCl_5$–$COCl_2$ systems at 0°, shows a negative interaction between $COCl_2$ and BCl_3, *i.e.*, either no complex formation or if a very weak complex is formed it is masked by positive deviations from Raoult's law owing to other causes. For $SbCl_5$, a slightly negative deviation from Raoult's law is observed in the range 50–0 mole % $COCl_2$, indicating the possible formation of an extremely weak adduct between $COCl_2$ and $SbCl_5$.

If the species in contact with $COCl_2$ is a solid and if effects caused by its solubility in $COCl_2$ can be neglected, the vapor pressure isotherm should have a constant value over the entire composition range. Its asymptotic approach to zero at low $COCl_2$ content is due to the measuring technique. Tungsten hexachloride, sparingly soluble in $COCl_2$, fits this description quite well (see Figure 2). For $MoCl_5$, the $COCl_2$ vapor pressure decreases more rapidly due to the greater solubility of $MoCl_5$ in $COCl_2$, but again, no adduct formation can be observed. For $AlCl_3$, the existence of adducts having an $AlCl_3$:$COCl_2$ mole ratio other than 1.0, claimed previously,[1] could not be confirmed. The vapor pressure–composition isotherm of the $AlCl_3$–$COCl_2$ system at 25°, depicted in Figure 3, clearly shows that only a 1:1 adduct is formed in this system. Therefore, the previous reports of $Al_2Cl_6 \cdot 5COCl_2$, $Al_2Cl_6 \cdot 3COCl_2$, and $2Al_2Cl_6 \cdot COCl_2$[1] should be considered erroneous. The vapor pressure–composition isotherms of the $AlCl_3$–$COCl_2$ system, measured at 0 and 25°, agree well with those reported previously for the composition range 100–55 mole % $COCl_2$.[7]

From the vapor pressure–composition isotherm it can be concluded that the complexing tendency of the Lewis acids with $COCl_2$ has the following order: $AlCl_3 > SbCl_5 > BCl_3$. Whereas $AlCl_3$ forms a well-defined adduct of moderate stability, BCl_3 shows only a positive deviation from Raoult's law. This finding is quite unexpected, when we compare the order observed for similar oxygen-bridged donor–acceptor complexes (proof for this structure will be given later) of $POCl_3$[14] and ethyl acetate[15] with the trichlorides of the third main group of the periodic system. In the case of the

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(14) E. W. Wartenberg and J. Goubeau, *Z. Anorg. Allgem. Chem.*, **329,** 269 (1964).

(15) M. F. Lappert, *J. Chem. Soc.*, 542 (1962).

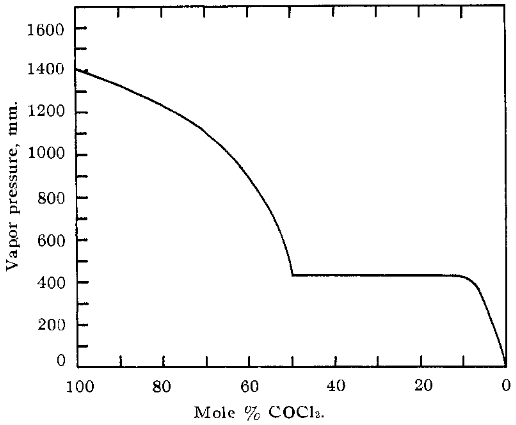
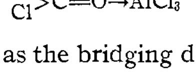


Figure 3.—The vapor pressure–composition isotherm of the binary system $COCl_2$–$AlCl_3$ at 25°.

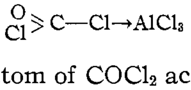
latter adducts, BCl_3 always acted as a stronger acceptor molecule than $AlCl_3$. The fact that $AlCl_3$ forms a relatively stable adduct with $COCl_2$ but BCl_3 does not may be due to a basic difference between BCl_3 and $AlCl_3$. Boron trichloride is monomeric and is best described by an sp^2 hybridization model involving an additional one-third double bond for each B–Cl bond. Thus BCl_3 must rehybridize from sp^2 to sp^3, if its coordination number changes from three in BCl_3 to four in forming a donor–acceptor complex. The energy change associated with this rehybridization has been estimated from the relative overlap integrals for the σ bonds and found to be very small.[16] However, the loss of π-bond energy is considerable and has to be compensated by the formation of the new B–O–C bond. Therefore, no adduct is expected to form, if the boron–donor bond energy is lower than the π-bond energy loss in BCl_3. Aluminum trichloride does not exist under the given conditions in the monomeric form. It is a chlorine-bridged dimer. Therefore, the coordination around aluminum is already tetrahedral and adduct formation is possible if the aluminum–donor bond energy is higher than that of the Al–Cl bridge. Since the donor strength of the oxygen atom in $COCl_2$ is higher than that of the chlorine atom (as discussed later), $AlCl_3$ can still form an adduct with $COCl_2$, but BCl_3 cannot.

Structure of the $AlCl_3$–$COCl_2$ Adduct.—A 1:1 adduct between $AlCl_3$ and $COCl_2$ could have any of the following structures: (i) ionic complex, $[CoCl]^+[AlCl_4]^-$, (ii) coordination complex



$$\begin{matrix}Cl\\Cl\end{matrix}\!>C{=}O\rightarrow AlCl_3$$

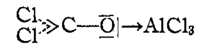
with oxygen acting as the bridging donor atom, and (iii) coordination complex



$$\begin{matrix}O\\Cl\end{matrix}\!\geqslant C{-}Cl\rightarrow AlCl_3$$

with one chlorine atom of $COCl_2$ acting as the bridging donor atom. Coordination complexes based upon an Al_2Cl_6 unit, requiring a coordination number of five and an electron decet for the aluminum atom, are unlikely and, therefore, will not be considered.

The infrared spectrum of this adduct should allow a clear-cut decision between the three models given above. Model i requires a tetrahedral anion (symmetry T_d) and either a bent (symmetry C_s) or linear (symmetry $C_{\infty v}$) cation. The anion would show two infrared-active vibrations; however, only the antisymmetric stretching vibration would occur within the observed frequency range (400–4000 cm^{-1}).[17,18] The cation would show, for either the linear or the bent structure, three infrared-active vibrations. By comparison with the known spectra of OCCl radical[19] and ONCl,[20] it seems probable that only the two stretching vibrations would occur within the observed range. Therefore, we expect to observe in this range a total of three stretching vibrations for model i, one of which should have a frequency of about 490 cm^{-1}, characteristic of $AlCl_4^-$.[18,21] For either model ii or iii, symmetry C_s is required assuming that the C–Z–Al bond angle is not 180°. This assumption is supported by the known structure of the benzoyl chloride–$AlCl_3$ adduct[22] and a number of other oxygen-bridged donor–acceptor complexes,[16] all of which show bond angles of the bridging atoms considerably smaller than 180°. Thus, models ii and iii are expected to show the same number of fundamental vibrations (18) out of which seven are stretching vibrations, all infrared active. However, the frequency difference between the two antisymmetric $AlCl_3$ stretching vibrations may not be large enough to observe a splitting into two separate bands, particularly if free rotation of the $AlCl_3$ group or if a C–Z–Al bond angle not too different from 180° is assumed. This effect would decrease the number of stretching vibrations actually observed to six. Consequently, no distinction between models ii and iii can be made on the basis of the number of observed bands. However, models ii and iii can be easily distinguished by their characteristic frequency shifts. For model ii, the carbonyl band should be shifted noticeably to lower frequency, whereas both the antisymmetric and the symmetric CCl_2 stretching vibrations should be shifted to higher frequencies. This effect can be easily understood by considering the significant contribution of the resonance structure



$$\begin{matrix}Cl\\Cl\end{matrix}\!\gg C{-}\underline{\overline{O}}|\rightarrow AlCl_3$$

to the over-all potential energy of model ii. Thus, a decrease of the C═O and an increase of C—Cl bond orders is expected in comparison to free $COCl_2$. For model iii, the reverse effect is expected based on similar considerations.

Examination of the observed spectrum of the 1:1 $COCl_2$–$AlCl_3$ adduct (see Figure 4 and Table I) shows that model i must be ruled out, since (after subtracting the bands due to free $COCl_2$[23] and solid $AlCl_3$)

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[16] I. Lindquist, "Inorganic Adduct Molecules of Oxo-Compounds," "Anorganische und Allgemeine Chemie in Einzeldarstellungen," Vol. 4, M. Becke-Goehring, Ed., Academic Press Inc., New York, N. Y., 1963.

[17] H. Gerding and H. Houtgraaf, *Rec. Trav. Chim.*, **72**, 21 (1953).

[18] G. L. Carlson, *Spectrochim. Acta*, **19**, 1291 (1963).

[19] M. E. Jacox and D. E. Milligan, *J. Chem. Phys.*, **43**, 866 (1965).

[20] L. Landau, *J. Mol. Spectry.*, **4**, 276 (1960).

[21] R. West and P. T. Kwitowski, *J. Am. Chem. Soc.*, **88**, 5280 (1966).

[22] S. E. Rasmussen and N. C. Broch, *Acta Chem. Scand.*, **20**, 1351 (1966).

[23] E. Catalano and K. S. Pitzer, *J. Am. Chem. Soc.*, **80**, 1054 (1958).

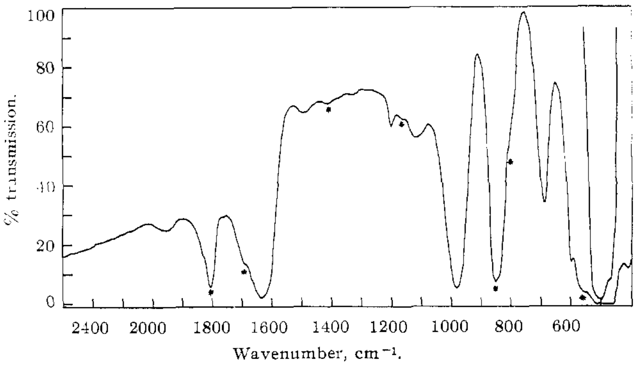
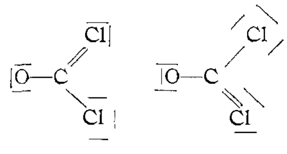


Figure 4.—The infrared spectrum of 1:1 $COCl_2$–$AlCl_3$ adduct. The bands marked by an asterisk are due to free $COCl_2$.

at least four stretching vibrations are observed and three of these occur at frequencies higher than 650 cm^{-1}. Only model ii can explain the observed shift of the carbonyl band to a lower frequency and that of the two CCl_2 stretching vibrations to a higher frequency. Therefore, the observed spectrum was assigned on the basis of model ii. The assignment of the C=O and CCl_2 vibrations does not present any difficulty. The antisymmetric stretching vibration of $AlCl_3$ is assigned to the very strong band at 498 cm^{-1}, in good agreement with the band observed at 495 cm^{-1} in the spectrum of solid $Cl_3PO \cdot AlCl_3$.[14] Recently,[24] a slightly higher frequency of about 535 cm^{-1} was reported for this vibration in similar oxygen-bridged adducts between $AlCl_3$ and dialkyl ethers. This frequency shift, however, may be due to the different nature of the oxygen atom in a carbonyl group compared with that in an ether and to the different state of the sample (solid and solution). The same authors[24] suggest frequencies of about 550 and 320 cm^{-1} for the symmetric stretching vibration of $AlCl_3$ and the "Al–O stretching" vibration, respectively (the C–O and Al–O stretching vibrations are better described as antisymmetric and symmetric Al–O–C stretching vibrations, respectively). Although it is difficult to identify these frequencies with group frequencies owing to mixing,[24] these values differ considerably from the assignments proposed by Wartenberg and Goubeau[14] for these modes in adducts between $AlCl_3$ and phosphorus oxyhalides ($\nu_s(AlCl_3)$ $\sim$350 cm^{-1} and "ν(Al–O)" $\sim$440 cm^{-1}). Susz and coworkers[25] have assigned a frequency of about 650 cm^{-1} to the "Al–O stretching" frequency in oxygen-bridged nitrobenzene–$AlCl_3$; however, this assignment appears unlikely.[24] Based on these discrepancies and the presence of additional bands due to solid $AlCl_3$ and free $COCl_2$, no attempts are made to assign $\nu_{sym}(AlCl_3)$, the "Al–O stretching," and $\pi(OCCl_2)$ of $COCl_2 \cdot AlCl_3$. The bands of free $COCl_2$ and solid $AlCl_3$ are due to the considerable dissociation pressure of $COCl_2 \cdot AlCl_3$ at ambient temperature at which the spectra were recorded. Considering the facts that the symmetric $AlCl_3$ stretching vibration may occur below 400 cm^{-1},[14] that the splitting of the antisymmetric stretching vibration of $AlCl_3$ into two bands is unlikely to be observed, and that the assignment of the low-intensity "Al–O stretching vibration" is uncertain, the observed number of stretching vibrations showing predicted frequency shifts and band intensities agrees well with model ii.

Comparison of the infrared spectrum of $COCl_2 \cdot AlCl_3$ with that reported for $SbO_2Cl \cdot 0.5COCl_2$[12] shows that for either adduct, the C=O stretching vibration occurs at considerably lower frequency (1635 and 1633 cm^{-1}, respectively) than in the spectrum of free $COCl_2$. The infrared spectrum of $SbO_2Cl \cdot 0.5COCl_2$ was recorded[12] as a Nujol mull and its quality is somewhat poor. Since it was shown[14,21] that Nujol mulls generally do not result in reliable spectra for this kind of complex, the failure to observe the expected frequency shifts for the CCl_2 stretching vibrations may be entirely due to the recording technique. Therefore, the possibility that the $AlCl_3 \cdot COCl_2$ and $SbO_2Cl \cdot 0.5COCl_2$ adducts are similar in nature cannot presently be excluded.

The fact that $AlCl_3 \cdot COCl_2$ adduct contains an oxygen and not a chlorine bridging atom agrees well with the known structure of similar complexes of $AlCl_3$ with donors such as $POCl_3$,[14] benzophenone,[26] acetophenone,[26] benzoyl chloride,[22,27] and acetyl chloride.[28] However, for some of the acyl chlorides, both oxygen bridging and $RCO^+AlCl_4^-$ formation were observed.[27,28] Comparison of the infrared spectra of 1:1 adducts of $AlCl_3$ with $COCl_2$, acetyl chloride,[28] benzophenone,[26] and acetophenone[26] shows that the greatest shift of the C=O frequency (relative to the free donor molecule) is obtained for the $COCl_2$ adduct ($\Delta\nu$(C=O), 173 cm^{-1}) and the smallest shift for acetophenone ($\Delta\nu$(C=O), 120 cm^{-1}). This clearly indicates that the infrared shifts of the carbonyl frequency are not a direct measure of the electronegativity of the substituents attached to the carbonyl group. Thus, the statement "acyl halides are very poor donors and almost no donor properties remain in phosgene"[16] is obviously not applicable to the $AlCl_3$ adducts. The surprising relatively high donor strength of $COCl_2$ toward $AlCl_3$ may be due to considerable contribution of the resonance structures



to the over-all potential energy in $COCl_2$,[29,30] thus increasing the electron density about the oxygen atom. This may also be one of the reasons why oxygen acts as a stronger donor than chlorine in $COCl_2$.

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