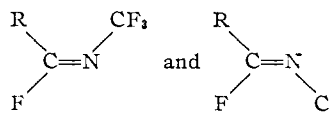
terest because one would expect its spectrum to correspond to a mixture of the two isomeric forms



The N–CF_3 resonance proved to be a doublet, with separations of the components, in cycles/sec., approximately the same at 17 mc. (about 4,200 gauss) as at 40 mc. The doublet splitting must therefore be due to spin–spin coupling, leading to the inference that either the two forms have the same resonance spectrum or, as seems more probable, the preparation and purification[6] yielded an essentially isomerically pure product. If the latter is true, the data still do not suffice to show which of the two forms was present.

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The Infrared Spectrum of Cuprous Chloride Vapor

BY WILLIAM KLEMPERER, STUART A. RICE AND R. STEPHEN BERRY

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The infrared spectrum of cuprous chloride vapor in equilibrium with the liquid has been measured from 500 to 220 cm.$^{-1}$. One strong absorption with maximum at 350 cm.$^{-1}$ was observed. The observed spectrum is in agreement with the existence of a cyclic polymer as the principal species in the vapor. The bonds of the polymer are considerably weaker than those in the diatomic monomer.

Diverse experiments indicate that cuprous chloride vapor in equilibrium with the liquid phase consists primarily of polymeric species. Vapor density measurements of Brewer and Lofgren[1] are consistent with the existence of a single polymer-monomer equilibrium, namely, trimer–monomer. If it is assumed that the trimer has a cyclic structure then the thermal data of the above authors indicate the trimer to have an average bond energy of 2.8 e.v. as compared to 3.8 e.v. in the monomer. Since there is in general a rough correlation between bond energy and bond stretching force constant it appears that information concerning the type of bonding present in the trimer can be obtained from a study of the infrared spectrum of the trimeric molecule.

The experimental technique is similar to that used in previous studies.[2,3] The temperature at which cuprous chloride has appreciable vapor pressure is low enough (approximately 1000°) to permit the use of a relatively simple furnace and cell. The furnace used is an aluminum oxide tube wound with Kanthal A-1 resistance wire. The cell is a 1.5 meter Vycor tube 45 mm. in diameter. The cell windows are polyethylene and nitrogen is used as inert gas to prevent condensation of the hot vapors on the windows which are at room temperature.

Although it is possible to study either the absorption or emission spectrum of a substance with the above apparatus, as previously discussed,[3] emission studies suffer from much self-absorption and from the presence of radiation from the hot cell walls. This latter radiation can be removed only by reducing the aperture of the optical system, with the concurrent loss in spectral resolution. Since absorption studies do not suffer from these shortcomings they were used principally. For absorption studies it is necessary to modulate the light before is passes through the sample since the sample is at about the same temperature as the light source.

The spectrum was observed with a Perkin–Elmer Model 12 monochromator using cesium bromide and cesium iodide optics in the spectral region 500 to 200 cm.$^{-1}$. Only one intense absorption was observed with a maximum at 350 cm.$^{-1}$. There was no noticeable absorption around the region of 420 cm.$^{-1}$.

In cuprous chloride a well developed spectrum was observed when the sample was at approximately 900°, while for cuprous bromide no definite absorption or emission was detected at temperatures up to 1400°. In the course of the studies on cuprous bromide the Vycor tube melted and in view of the reactivity of cuprous bromide with steel no other easily available cell could be used. Therefore it was not possible to measure the spectrum of cuprous bromide with the present apparatus.

Results and Discussion

The observed spectrum of cuprous chloride is in full agreement with previous work on the presence of a polymeric molecule in the gas in equilibrium with the liquid. There is no evidence of any absorption by the monomer CuCl, whose vibration frequency is 416.9 cm.$^{-1,4}$ at pressures where the previously mentioned 350 cm.$^{-1}$ absorption is well developed. It is impossible to make arguments for this large displacement of the absorption maximum from the vibration frequency due to hot transitions since the anharmonicity is only 1.6 cm.$^{-1}$. Furthermore, in a diatomic molecule in a $^1\Sigma$ electronic state the effects of rotational structure and anharmonicity approximately cancel so that the resulting absorption maximum lies near the true vibration frequency.[3] The absorption with maximum at 350 cm.$^{-1}$ is thus attributed to the polymer of cuprous chloride.

The observed spectrum, namely, a single bond stretching motion, is consistent with a cyclic structure for the polymer. In the case of an open chain one would expect two types of stretching motions of widely different frequencies corresponding, re-

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[1] L. Brewer and N. L. Lofgren, THIS JOURNAL, **72**, 3038 (1950).

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

[3] W. Klemperer and S. A. Rice, *ibid.*, in press.

[4] G. Herzberg, "The Spectra of Diatomic Molecules," 2nd edition, D. Van Nostrand, New York, N. Y., 1950.

spectively, to the stretching of terminal groups and to the stretching of interior bonds. The arguments concerning the number of stretching motions depend of course on the structure of the molecule. It must be borne in mind, however, that the spectrum was observed at moderately high temperature. Under these conditions an absorption band due merely to a single vibrational mode will be much broader than the same band at 0°K.[3,5] Consequently, absorptions due to two or more active modes of approximately equal frequencies cannot be separated readily. Thus the appearance of a single absorption at a frequency far removed from that of the diatomic monomer is evidence for the existence of a cyclic polymer.

It is impossible on the basis of the infrared spectrum described above to determine the structure of the cyclic polymer. In view of the studies of Brewer and Lofgren[1] the evidence is that the polymer is trimeric. For the purpose of estimating bond stretching force constants it will be assumed that the molecule has symmetry D_{3h}. For this structure there will be two infrared active bond stretching motions both of symmetry E'. Using the structure proposed by Schomaker and Wong[6] on the basis of electron diffraction studies, namely, a hexagon with equal bond lengths and a 90° Cu–Cl–Cu angle, and neglecting the angle bending forces and all interaction force constants, one obtains a bond stretching force constant of 1.1×10^5 dynes/cm. in the cuprous chloride trimer. This force constant is considerably smaller than 2.30×10^5 dynes/cm. which obtains for the diatomic monomer.

While the above consideration can only give a very rough picture of the forces in the trimer, qualitatively there is agreement between the force constants and bond energies, namely, weaker bonds in the trimer than in the monomer. This behavior is encountered in other systems where chlorine is bonded to two metal atoms. In the aluminum chloride dimer it is observed[2] that the bond stretching force constant for Al–Cl bonds involved in bridging the aluminum atoms is one-half the magnitude of the force constant for stretching the outer or normal Al–Cl bonds. There is, however, considerable difference between the geometry of the bridges of the two systems. In Al_2Cl_6 the Cl–Al–Cl bridge angle is small,[7] while in Cu_3Cl_3 the angle with metal atom at the vertex is open.[6] In both systems, however, the M–Cl–M bridge angle is quite similar being 90° in Cu_3Cl_3 and 100° in Al_2Cl_6. It is uncertain whether the geometry of a bridged system is determined primarily by the directional properties of the metal atom, or the constancy of the M–Cl–M angle is indicative of strong directional properties of both the metal and halogen atoms. It is probable that the $AlCl_4^-$ ion is tetrahedral and that $CuCl_2$ is linear and that the geometry of these structures is reflected in the bridge-bonded polymers. There are unfortunately, insufficient low frequency spectral data to permit evaluation of the angle bending force constants which would allow more conclusive statements concerning the directional forces present in bridged systems to be made.

Acknowledgment.—The authors wish to express their indebtedness to Professor Verner Schomaker for several important suggestions. The Research Corporation has generously aided this work. One of us (W.K.) gratefully acknowledges an Arthur B. Lamb Fellowship.

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(5) W. Klemperer and L. Lindemann, *J. Chem. Phys.*, **25**, 397 (1957).

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(7) K. J. Palmer and N. Elliott, THIS JOURNAL, **60**, 1852 (1938).

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[JOINT CONTRIBUTION FROM THE MCPHERSON CHEMISTRY LABORATORIES OF THE OHIO STATE UNIVERSITY AND THE W. A. NOYES LABORATORY OF CHEMISTRY OF THE UNIVERSITY OF ILLINOIS]

Powder X-Ray Diffraction and Infrared Investigation of the Product of the Chromium(VI) Oxide–Liquid Ammonia Reaction

BY RUSSELL S. DRAGO AND HARRY H. SISLER[1]

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The infrared spectra and the X-ray powder diffraction patterns of the products of the reaction between chromium trioxide and liquid ammonia were studied and were compared with results obtained from similar investigations of several known compounds. It was concluded that the reaction product consists of ammonium chromate, an ammine chromium(III) chromate polymer of indefinite composition, a nitroammine chromium(III) chromate polymer and probably a small amount of hexammine chromium(III) chromate. Equations are suggested to account for the formation of these products and for the reported characteristics of the reaction.

It has been shown[2] that when chromium(VI) oxide reacts with liquid ammonia approximately one-fourth of the chromium is reduced to the +3 state. It was postulated that the formation of a precipitate accounted for the fact that all of the chromium is not reduced. The analytical data obtained did not permit positive identification of the product but two possibilities were considered: $Cr(NH_4)_3(CrO_4)_3 \cdot xNH_3$ and $Cr(CrO_3NH_2)_3 \cdot xNH_3$. It was also shown that the amount of nitrogen produced was only approximately one-half of the stoichiometric amount based on the amount of chromium reduced and assuming the reaction

$$2CrO_3 + 2NH_3 \longrightarrow 2Cr^{+++} + 6OH^- + N_2 \quad (1)$$

Most of the "missing" nitrogen was released when the reaction product was heated.

Further studies[3] revealed that the product gives

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