−59.0°. The latter was used for the determinations of the vapor tensions shown in Table I. These are correlated by the equation $\log_{10}p_{mm} = -(2553/T) + 1.75 \log_{10}T - 0.004911T + 6.3425$, according to which the normal boiling point would be 154.9° and the Trouton constant approximately 20.9 cal./deg. mole.

The Disproportionation Equilibria.—The determination of true equilibrium states in the formation and disproportionation of $CH_3SB(CH_3)_2$ and $(CH_3S)_2BCH_3$, for the purpose of obtaining free energy–temperature relationships, probably would be quite difficult because the catalyst is destroyed too easily. The evidence so far indicates that neither substance is very extensively converted to the adjacent members of the system by long heating. For example a 20.8-cc. sample of $(CH_3S)_2BCH_3$ with 0.3 cc. of B_2H_6 was heated for 34 days at 84°, after which the recovery of $(CH_3S)_2BCH_3$ was 16.7 cc. (80%). The yield of $(CH_3S)_3B$ was 1.6 cc. and of $CH_3SB(CH_3)_2$, 1.96 cc.; and more volatile material representing the catalyst amounted to 1.1 cc. The question of the existence of substances such as $CH_3SBH\text{-}CH_3$ or $(CH_3S)_2BH$, among the catalysts in this system, continues to be interesting.

Acknowledgment.—The generous support of this work by the Office of Naval Research is most gratefully acknowledged. Reproduction of this paper in whole or in part is permitted for any purpose of the United States Government.

LOS ANGELES 7, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MICHIGAN]

The Preparation and Properties of Phosphorus Trifluoride–Borane and Phosphorus Trifluoride–Borane-d_3[1]

BY ROBERT W. PARRY AND THOMAS C. BISSOT

RECEIVED SEPTEMBER 9, 1955

Phosphorus trifluoride and diborane react under pressure in sealed tubes at room temperature to give the new compound F_3PBH_3.[2] Some physical and chemical properties of the new compound are described. Its properties show a striking resemblance to those of carbon monoxide–borane. NF_3 does not add to the BH_3 group, but under appropriate conditions B_2H_6 is oxidized explosively by NF_3.

The compound $Pt(PF_3)_2Cl_2$ prepared by Chatt and Williams[3] bears a striking resemblance to $Pt(CO)_2Cl_2$, and the complex $Ni(PF_3)_4$ prepared by Irvine and Wilkinson[4] is very similar in properties to $Ni(CO)_4$. This experimental resemblance between the coördinating properties of CO and PF_3 suggested the existence of the compound F_3PBH_3, which would be analogous to the $OCBH_3$ of Burg and Schlesinger.[5] On the other hand Chatt[3] pointed out that PF_3 did not add to $AlCl_3$, $AlBr_3$ or BF_3 and he invoked theoretical arguments as the basis for the prediction that a stable bond was unlikely between the boron in boron acids of the Lewis type and the phosphorus of phosphorus trifluoride. If, as suggested by Chatt, the acid–base type of reaction did not occur, the possibility of an oxidation–reduction reaction between B_2H_6 and PF_3 still merited consideration. In view of these interesting possibilities, an experimental study was conducted on the system B_2H_6–PF_3. The formally analogous system B_2H_6–NF_3 also has been examined.

The Preparation and Physical Properties of Phosphorus Trifluoride–Borane, F_3PBH_3.—The high pressure reaction between diborane and excess phosphorus trifluoride (8 atmospheres) proceeds slowly over the period of several days to yield the compound F_3PBH_3 as the primary product. On prolonged standing secondary reactions involving F_3PBH_3 ensue which give as yet undefined liquid products along with appreciable amounts of hydrogen. The primary phosphorus trifluoride–borane adduct also may be obtained by displacing CO from carbon monoxide–borane using a smaller excess of PF_3 (5 atmospheres).

Phosphorus trifluoride–borane is a colorless gas which is spontaneously inflammable in air. The melting point is −116 1 ± 0.2°. The vapor pressure of F_3PBH_3 over the liquid range can be given by the equation

$$\log_{10} P = -1038.9/T + 7.8061$$

Since the pure material resembles carbon monoxide–borane in that it will dissociate into B_2H_6 and PF_3, it was necessary to purify the compound before each reading and to achieve temperature equilibrium rapidly. The vapor pressure data extrapolate to give a boiling point of −61.8°, a heat of vaporization of 4,760 cal. per mole at the boiling point, and a Trouton constant of 22.5.

The molecular weight by vapor density at 25° was 102.7 as compared to a theoretical value of 101.82.

The Dissociation Constant of Gaseous F_3PBH_3 at 25°.—The equilibrium constant for the reaction

$$2F_3PBH_3(g) \rightleftharpoons 2PF_3(g) + B_2H_6(g)$$

was estimated by analyzing equilibrium mixtures according to the procedures described in the Experimental sections. A value for $K_{(atm.)}$ of 1.0 ± 0.3 was obtained at 25°. The uncertainty in the value can be attributed to three factors. First, a number of experimental difficulties were associated with the separation of the large excess of PF_3 from the product and the unreacted diborane.[6] Secondly, since

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[1] Abstracted in part from a dissertation submitted by Thomas C. Bissot to the Horace H. Rackham School of Graduate Studies of the University of Michigan in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] The designation of BH_3 as borane is consistent with the system of nomenclature for boron compounds which was presented by G. W. Schaeffer and T. Wartik at the 125th meeting of the American Chemical Society, Kansas City, Missouri.

[3] J. Chatt and A. A. Williams, *J. Chem. Soc.*, 3061 (1951); J. Chatt, *ibid.*, 3340 (1949).

[4] Irvine and G. Wilkinson, *Science*, **113**, 742 (1951); G. Wilkinson, THIS JOURNAL, **73**, 5501 (1951).

[5] A. B. Burg and H. I. Schlesinger, *ibid.*, **59**, 780 (1937).

[6] The problem is simplified in the case of carbon monoxide–borane since the CO is not condensable with liquid nitrogen whereas the other components are. Since PF_3 boils at −95° and B_2H_6 at −92° chemical procedures had to be employed for analysis.

no effort was made to thermostat the reaction vessel, normal deviation of room temperature from 25° would have some effect. Finally, secondary reactions involving the splitting out of H_2 and the formation of less volatile products complicated the stoichiometry after longer periods of time.

Rate of Decomposition of F_3PBH_3.—In order to compare phosphorus trifluoride–borane with carbon monoxide–borane, their rates of decomposition at room temperature were compared. The decomposition reaction

$$2F_3PBH_3 \longrightarrow B_2H_6 + 2PF_3$$

produces an increase in pressure, and the rate of pressure change with time can be used as a measure of reaction velocity. Rate data are shown in Fig. 1 along with comparable data of Burg and Schlesinger[5] for the $OCBH_3$. The similarity of the rates is striking, particularly in the early phases where side reactions have not complicated the interpretation of pressure measurements.

The mechanism for the decomposition of carbon monoxide–borane has been the subject of some recent controversy.[7] Unfortunately, the current data do not aid in resolving the question; however, they do suggest that the mechanism which explains $OCBH_3$ will also explain F_3PBH_3. It is perhaps significant that both CO and PF_3 might be classed as "secondary bases" as mentioned by Bauer.[7]

Reaction of F_3PBH_3 with Trimethylamine and with Ammonia.—When stoichiometric quantities of F_3PBH_3 and trimethylamine are mixed, the trimethylamine displaces the PF_3 quantitatively to form $(CH_3)_3NBH_3$ and free PF_3. If an excess of trimethylamine is used, the PF_3 which is liberated reacts with the excess trimethylamine in a one to one ratio to give gases and a solid which have not been fully characterized.

When F_3PBH_3 reacts with excess ammonia over the temperature range of −128 to −80°, five molecules of ammonia will be picked up by each molecule of the borane adduct. The reaction product is a white solid which begins to decompose at room temperature with evolution of hydrogen and development of a yellow color. When the solid was heated to about 55°, 1.62 moles of ammonia was evolved per mole F_3PBH_3. It is probable that the original solid product is a mixture. The reaction, which appears to be rather complex, is being studied further. Data suggest rupture of the phosphorus–fluorine bond by the ammonia.

The Properties of Phosphorus Trifluoride–Borane-d_3.—The compound F_3PBD_3 was needed for Raman spectral studies. The deuterated compound had a melting point of −115.1 ± 0.1°. The vapor pressure of the liquid can be given by the equation

$$\log_{10} P = -1010.8/T + 7.6171$$

Extrapolating these vapor pressure data yields a boiling point of −59.8°, a heat of vaporization of 4630 cal. per mole, and a Trouton constant of 22.

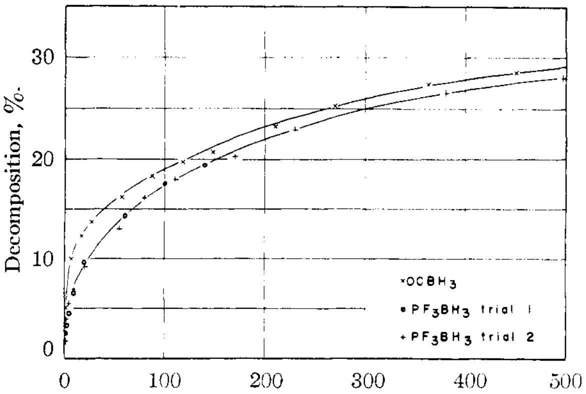

Fig. 1.—Decomposition of $OCBH_3$ and PF_3BH_3 at room temperature.

The Reaction between NF_3 and Diborane.—NF_3 which is formally analogous to PF_3 is known to have essentially no basic properties. It was none the less interesting to compare the behavior of NF_3 and PF_3 in their reaction with diborane. Results can be summarized as follows. (1) Under conditions similar to those used in making F_3PBH_3 and $OCBH_3$ no compound formation between NF_3 and B_2H_6 was observed. (2) In these experiments mixtures of NF_3 and B_2H_6 were stable in the gas phase even under high pressures. (3) Mixtures of NF_3 and B_2H_6 can be violently explosive at temperatures which are low enough to give condensed phases in the system. The conditions necessary to initiate explosive reaction between the two liquids were not clearly defined, but spontaneous explosive reaction was observed only when the contents of the reaction tube were liquefied after the gases had been standing for several days under pressure. This explosion was undoubtedly an oxidation–reduction process with N_2, HF and BF_3 as probable products. The possibility that the reaction was triggered by very small amounts of impurities in the NF_3 such as N_2O, NO or NO_3F or by decomposition products of B_2H_6 remains as a reasonable possibility.

Discussion

The striking similarity between the physical properties of phosphorus trifluoride–borane and carbon monoxide–borane is illustrated by the data in Table I. Even the differences between the deuterated and non-deuterated compounds are comparable. The stability of F_3PBH_3 is somewhat greater than the comparable $OCBH_3$ (see K values in Table I). Its rate of dissociation at room temperature also is somewhat lower than the carbonyl adduct. These facts correlate well with the observation of Chatt and Williams[3] to the effect that

TABLE I

COMPARISON OF THE PROPERTIES OF CARBON MONOXIDE–BORANE AND PHOSPHORUS TRIFLUORIDE–BORANE

	$OCBH_3$	$OCBD_3$[8]	F_3PBH_3	F_3PBD_3
M.p., °C.	−137.0	−134.4	−116.1	−115.1
B.p., °C.	− 64	− 62.2	− 61.8	− 59.8
ΔH vaporization	4750	4760	4760	4630
Trouton constant	23	23	22	22
Dissociation constant $K_{atm.}$ at 25°	2.5[6]	.....	1.0 ± 0.3	.....
Decomposed after 1 hr. at 25°, %	17	.....	14	.....

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[7] A. B. Burg, THIS JOURNAL, **74**, 3482 (1952); S. H. Bauer, Paper presented before the 127th Meeting, American Chemical Society, Cincinnati, Ohio, April 1955.

[8] A. B. Burg, THIS JOURNAL, **74**, 1340 (1952).

PF_3 adducts of the platinum(II) halides are more stable than the corresponding carbonyl compounds.

The initial reaction of F_3PBH_3 with trimethylamine parallels closely the corresponding reaction involving carbon monoxide–borane. Differences are noticed, however, in secondary reactions because the liberated PF_3 reacts directly with trimethylamine whereas CO does not. The reactions of both $OCBH_3$ and F_3PBH_3 with ammonia are more complex and require further study.

The spontaneous inflammability of F_3PBH_3 in air correlates well with the general observation that the reactivity toward oxidizing agents and moisture of the simple borane adducts is inversely related to the strength of the base to which BH_3 is bound. The weak base strength of PF_3 produces a highly inflammable adduct.

The most reasonable model for the molecule would be an ethane-like structure with a σ-bond between the boron and the phosphorus. Double bonding of the type postulated by Chatt[3] for the metal adducts of PF_3 is ruled out by the absence of d electrons on the boron. Other systems involving addition of PF_3 to Lewis acids are under investigation. Further speculation on bonding can best await more complete experimental information.

Experimental

1. **Preparation of Phosphorus Trifluoride.**—The phosphorus trifluoride was prepared by the reaction between phosphorus trichloride and zinc fluoride using a minor modification of the procedure of Chatt and Williams.[3] The crude products were passed through a reflux column at -80° in order to recover unreacted PCl_3, then the impure PF_3 was trapped in a liquid nitrogen trap, and purified by fractionation in the vacuum line.

2. **Diborane.**—Diborane was prepared by the reaction between lithium aluminum hydride and boron trifluoride etherate in ether solution.[9] After purification by low temperature fractionation the vapor pressure at -111.8° was 225 mm. Diborane-d_6 was prepared using lithium aluminum deuteride. The $LiAlD_4$ was prepared *in situ* from lithium deuteride and aluminum chloride.

3. **The Preparation of F_3PBH_3.**—A measured amount of diborane, together with a large excess of PF_3, was condensed in a heavy walled Pyrex bomb tube of 60-ml. capacity. The techniques resemble closely the procedures used by Burg and Schlesinger for the preparation of $OCBH_3$.[5] The bomb tube was allowed to stand several days at room temperature. Maximum yields were usually obtained after four days; longer periods of time frequently resulted in the formation of secondary products, although the factors responsible for the secondary reaction were never completely delineated. After standing, the bomb tube was frozen with liquid nitrogen and the tube opened to the line by means of the vacuum tube opener. Non-condensable gases were removed with a Töpler pump, measured and identified by molecular weight measurements. The condensable portions were distilled through a trap at -155°, at which temperature the F_3PBH_3 is quantitatively retained. The excess B_2H_6 and PF_3 was measured and analyzed by a sealed tube hydrolysis, using the amount of hydrogen generated to determine the portion of B_2H_6 in the mixture. The F_3PBH_3 was freed from less volatile impurities by distilling it through a trap at -128°. The pure F_3PBH_3 showed a vapor pressure of 23.0 mm. at -111.8°.

The less volatile materials formed from secondary reactions were easily separated from the more volatile components by fractional distillation in the vacuum line. Upon hydrolysis of this material only small amounts of hydrogen were liberated. In one case the less volatile materials were separated by fractional condensation and a liquid with a vapor pressure of 5 mm. at -80° was isolated. A measurement of molecular weight by vapor density gave a value of 120. It appeared stable in the vapor phase but polymerized in the liquid phase to give a non-volatile oil. No hydrogen was liberated on addition of water, indicating that it contained no active hydrogens. However, the compound was destroyed by water. These observations plus the fact that the secondary reaction results in the liberation of gaseous hydrogen suggests the tentative formula F_2PBF_2 for the monomeric liquid. The characterization is still incomplete since only very small amounts of material were available and the conditions which favor its formation have not been completely determined. Data for representative runs are summarized in Table II.

TABLE II

DATA ON REACTIONS BETWEEN PHOSPHORUS TRIFLUORIDE AND DIBORANE

	Run number				
	3	4	5	6	8
Conditions					
Vol. of bomb, ml.	62.5	62.9	63.5	61.7	61.7
Initial mmoles B_2H_6	3.28	3.20	3.16	3.22	5.42
Initial mmoles PF_3	19.21	18.18	19.10	17.92	10.71
Initial pressure, atm.	8.72	8.30	8.57	8.36	6.40
Time at 25°, days	2	4	7	22	25
Products					
Mmoles B_2H_6	1.24	0.69	0.27	0.44	2.12
Mmoles PF_3	14.65	13.17	11.37	12.31	4.87
Mmoles PF_3BH_3	4.26	5.01	4.34	4.73	4.50
Mmoles of less volatile by-products	0.01	0.08	1.40	0.38	0.84
Mmoles H_2	0.03	0.55	...	1.29	2.10
Yield PF_3BH_3 based on B_2H_6	65%	78.3%	68.7%	73.5%	41.5%
Apparent equil. constant K_{atm}.	5.73	1.86	0.71	1.18	0.98

TABLE III

VAPOR PRESSURES OF PHOSPHORUS TRIFLUORIDE–BORANE

Temp., °C.	Pressure, mm.		ΔP,
	Obsd.	Calcd.	(calcd. − obsd.)
−127.7	4.1(s)		
−119.7	11.4(s)		
−111.8	23.0	23.4	+0.4
−101.5	56.6	57.0	+0.4
− 98.1	76.4	74.6	−1.8
− 95.7	90.6	89.7	−0.9
− 87.6	162.1	161.6	−0.5
− 79.9	267	270	+3.0

TABLE IV

VAPOR PRESSURE OF PHOSPHORUS TRIFLUORIDE–BORANE-d_3

Temp., °C.	Pressure, mm.		ΔP,
	Obsd.	Calcd.	(calcd. − obsd.)
−119.4	8.0(s)		
−112.0	20.9	22.2	+1.3
−101.5	54.2	53.7	−0.5
− 95.6	85.2	84.2	−1.0
− 84.1	186	187	+1.0
− 79.0	260	259	−1.0

4. **Analysis and Characterization of the F_3PBH_3.**—Hydridic hydrogen in the compound was determined by condensing a weighed sample of gas in the tube and then distilling in an excess of water. The sealed tube was allowed to stand at room temperature for one day, and then the tube was opened to the vacuum line and hydrogen was measured. Observed hydridic hydrogen 2.89%. Theoretical for F_3PBH_3 is 2.97%.

The PF_3 is partially hydrolyzed by the above procedure, and the resulting HF attacks the Pyrex glass enough to make a boron analysis meaningless. Small amounts of PF_3 were always obtained after water hydrolysis; a contaminant which appeared to be SiF_4 was always present as would be expected.

The addition compound was hydrolyzed by 40% NaOH as the first step in obtaining a phosphorus analysis; the P–F bond is cleaved rapidly in alkaline solution.[10] The re-

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(9) I. Shapiro, H. G. Weiss, M. Schmich, S. Skolnik and G. B. L. Smith, THIS JOURNAL, **74**, 901 (1952).

(10) H. S. Booth and A. R. Bozarth, *ibid.*, **61**, 2927 (1939).

sulting solution was acidified and the phosphorous acid was oxidized to phosphoric by evaporating the solution almost to dryness with aqua regia. The precipitation of the ammonium phosphomolybdate was carried out in the usual manner. Considering the precision of the methods for determining phosphorus in compounds of this type, the result, 29.87% P, is in good agreement with the formulation F_3PBH_3 (30.43% P).

5. **Measurement of Physical Properties of H_3BPF_3.**—Conventional techniques were used for vapor density and vapor pressure measurements. Temperatures were measured with ethylene and carbon dioxide vapor pressure thermometers. The melting point was obtained in the vacuum line using the method of Stock.[11]

6. **Reaction of F_3PBH_3 with Trimethylamine.**—One and ninety three hundredths mmoles of F_3PBH_3 was condensed in a 250-ml. bulb with 2.31 mmoles of trimethylamine. When the mixture was warmed to room temperature there was an immediate reaction in which a white solid was produced. The bulb was cooled to −80°, the more volatile products were distilled out, the bulb was weighed, the trimethylamine–borane was sublimed out, and the bulb was reweighed. A 97% yield (0.1362 g.) of $(CH_3)_3NBH_3$ was obtained. Vacuum line distillation of the volatile gases yielded 79.3% of the theoretical PF_3. This was characterized by vapor pressure and molecular weight measurements (obsd. 87.6; theory 87.98). The unrecovered PF_3 (0.4 mmoles) corresponded exactly to the excess of trimethylamine (0.38 mmole), a fact which suggests that a reaction between PF_3 and $N(CH_3)_3$ had taken place to yield the unidentified solid and gaseous products. This postulate was checked by allowing a small amount of trimethylamine to react with an excess of PF_3. An approximately one to one reaction occurred to produce a non-volatile white solid and a mixture of gaseous products which were qualitatively the same as those observed previously.

7. **Reaction of F_3PBH_3 with Ammonia.**—A quantity of dry ammonia, 14.70 mmoles, was condensed on the walls of the reaction tube. Then, 2.20 mmoles of F_3PBH_3 was added and the temperature was raised from −128 to −80° over the period of 2.5 hours. The excess ammonia was then sublimed from the reaction tube at −80°. The amount of ammonia recovered was 3.69 mmoles, meaning that 5.0 moles of ammonia react with one mole of F_3PBH_3.

The reaction product was a white solid which began to decompose at room temperature by turning yellow and giving off small amounts of hydrogen. Upon heating the solid to about 55° an amount of ammonia equivalent to 1.62 moles of the original 5.0 was recovered. During the decomposition a small amount of a white solid of very low vapor pressure was collected in a Dry Ice trap. This white solid burst into flames when the trap was cleaned with concentrated nitric acid.

8. **Preparation of Nitrogen Trifluoride.**—Nitrogen trifluoride was prepared by a modification of the method of Ruff.[12] A closed electrolysis cell was substituted for Ruff's open cell.

The impure NF_3 was bubbled slowly through a warm KI solution. Final purification was achieved by low temperature fractionation in the vacuum line. The gas was passed slowly through a trap cooled to −183° with liquid oxygen. The impurities, principally small amounts of N_2O, condensed, while the NF_3 passed through into a third trap cooled to −208° with low pressure liquid nitrogen (maintained at 100 mm. pressure by pumping through a manostat). Small amounts of dissolved oxygen and nitrogen were pumped from the NF_3 in the third trap to give a product of high purity. The molecular weight of the gas, as determined by vapor density, was 71.2. The theoretical value for NF_3 is 71.01.

9. **The Reaction of Nitrogen Trifluoride with Diboranes.**—The sealed tube high pressure techniques described for the preparation of F_3PBH_3 were employed. In a typical run 2.61 mmoles B_2H_6 and 18.84 mmoles NF_3 were sealed into a bomb tube and allowed to stand for 8 days at room temperature. When the tube was opened to the line, the amount of non-condensable gas was negligible. A mixed pentane bath at −155° was placed around the tube, and the entire contents distilled into the vacuum system. On further fractionation in the vacuum line no fraction could be retained in the −155° trap. Finally, during a transfer distillation a violent explosion occurred. The temperature of the vessel at the time of the explosion was estimated to be about −170°, since a liquid nitrogen Dewar had just been removed and another low temperature bath was to be substituted. The explosion occurred before the second bath was put in place. In a second trial under similar circumstances an explosion occurred while the contents of the reaction tube were being distilled into the vacuum line.

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[11] A. Stock, *Ber.*, **50**, 156 (1917).

[12] O. Ruff, J. Fischer and F. Luft, *Z. anorg. Chem.*, **172**, 417 (1928).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ROCHESTER]

The Ultraviolet Absorption Spectrum of Oxalyl Chloride Vapor; Spectral Evidence for Rotational Isomerism[1]

BY JEROME W. SIDMAN[2]

RECEIVED OCTOBER 27, 1955

The long wave length ultraviolet absorption spectrum of oxalyl chloride has been studied in the vapor phase at temperatures between 25 and 275°. From the temperature dependence of the spectrum, it is concluded that the spectrum is due to two isomeric forms. The *trans*-form shows sharp structure, for which a partial vibrational analysis is presented, whereas the absorption attributed to the *cis*-form appears to be continuous. The results are discussed with reference to the vibrational spectra of oxalyl chloride. The structure of $(ClCO)_2$ is also compared with the structure of the related molecules, $(CHO)_2$ and $(CH_3CO)_2$.

Introduction

Although oxalyl chloride, $(ClCO)_2$, has been the subject of several spectroscopic investigations, a survey of the literature reveals the absence of agreement concerning the existence of rotational isomers of this molecule. Ziomek, Meister, Cleveland and Decker[3] (henceforth called ZMCD) have studied the Raman and infrared spectra of oxalyl chloride, and have performed force constant calculations for both the *cis*- and *trans*-forms. ZMCD conclude that a satisfactory assignment of the Raman and infrared bands can be made by assuming oxalyl chloride to exist in the *trans*-form alone.

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[1] This research was supported by the Office of Ordnance Research under Contract DA-30-115-Ord-620 with the University of Rochester.

[2] Shell Post-Doctoral Fellow, 1955–1956.

[3] J. S. Ziomek, A. G. Meister, F. F. Cleveland and C. E. Decker, *J. Chem. Phys.*, **21**, 90 (1953).