[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

The Action of Carbon Disulfide on Trimethylamine and Trimethylphosphine

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In the course of a study of the factors influencing the stability of the addition compounds formed by the alkyl derivatives of the Group V elements, it appeared of interest to examine the carbon disulfide derivatives. Although trimethylphosphine–carbon disulfide has been established as a definite compound for nearly ninety years,[2,3] the literature relating to the existence of a similar compound of trimethylamine and carbon disulfide is in a highly confused state. Thus Davies and Walters[4] state: " . . . (tertiary) amines and arsines do not combine with carbon disulfide," while Jensen[5] writes: "Trimethylamine forms a compound with carbon disulfide which can be formulated . . . as the betaine of dithioformic acid, Me_3NCS_2."

Neither source presents either experimental evidence or references for these contradictory statements.

Bleunard[6] reported that trimethylamine reacted "violently" with carbon disulfide to give a crystalline product, $Me_3N \cdot CS_2$. Unfortunately, he did not report any analytical data and his amine, isolated from sugar-beet liquors, was of doubtful purity. Schmidt[7] attempted to prepare pure trimethylamine by recrystallizing the product reported by Bleunard from alcohol. However, the amine he obtained in this way formed a chloroplatinate whose analysis (for platinum) corresponds to a mixture of roughly 60% trimethylamine and 40% dimethylamine.

In view of these conflicting data, the behavior of trimethylamine toward carbon disulfide was carefully investigated using highly purified reagents and high vacuum techniques. No evidence of reaction was observed. With all components of the mixture in the gas phase at room temperature (23°), the pressure exerted by the mixture was equal to the sum of the pressures of the two pure components. In the liquid phase at temperatures from −80 to 25°, no reaction occurred as indicated by the fact that the vapor pressure of the resulting liquid mixture was never less than that calculated for a simple solution of the components.

Addition of water had no effect beyond that of solution of part of the trimethylamine. Therefore the discrepancy between the present study and those of Bleunard[6] and Schmidt[7] cannot be attributed to this factor.

Treatment of carbon disulfide with dimethylamine led to immediate reaction with the formation of a white solid of very low volatility. Two volumes of dimethylamine reacted per volume of carbon disulfide. There can be little doubt that the reaction proceeded in accordance with the equation

$$2Me_2NH + CS_2 \longrightarrow (Me_2NH_2)^+(Me_2NCS_2)^- \quad (I)$$

In the presence of dimethylamine, trimethylamine reacted with carbon disulfide to the extent of approximately half of the dimethylamine that was utilized. Presumably, the reaction is

$$Me_3N + Me_2NH + CS_2 \longrightarrow (Me_3NH)^+(Me_2NCS_2)^- \quad (II)$$

but is complicated by the concurrent reaction I.

In view of these results, it must be concluded that trimethylamine and carbon disulfide do not form a stable addition compound and that the products obtained by both Bleunard and Schmidt were the result of impurities in their trimethylamine.

In sharp contrast to the behavior of trimethylamine, liquid trimethylphosphine under similar conditions readily combines with carbon disulfide in a 1:1 ratio. The product, a red solid, is highly stable, exhibits no appreciable volatility in the high vacuum apparatus and undergoes no apparent change in contact with air or water. It melts with decomposition at 114 ± 3° (sealed tube).

The gas phase reaction of trimethylphosphine and carbon disulfide differs from all other addition reactions previously studied in this Laboratory in that it is not virtually instantaneous. Although the product of the reaction is identical with that of the liquid phase reaction, its formation at low pressures (50 mm.) may take more than a week. The rate of reaction is dependent on the surface area, and does not follow a simple rate law. The reaction between trimethylphosphine and trimethylboron, on the other hand, is at least 99.5% complete within three minutes.

These unexpected complications in the formally simple reaction, $Me_3P + CS_2 \rightarrow Me_3P{:}CS_2$, make it appear likely that carbon disulfide, in its mode of reaction with basic substances, differs fundamentally from such typical acids as trimethylboron, boron trifluoride and hydrogen chloride. These latter substances have been termed "primary acids" by Lewis and Seaborg[8]; carbon disulfide apparently belongs with the "secondary acids," acids which require an appreciable energy of activation in their reactions with bases.

Trimethylamine and trimethylphosphine were treated similarly with carbon dioxide, but no evidence of reaction was observed, contrary to a recent inference in THIS JOURNAL.[9]

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[1] Atomic Energy Commission Predoctoral Fellow in the Physical Sciences, 1948–1949.

[2] Hofmann, *Ann. Suppl.*, **1**, 1 (1861).

[3] Hantzsch and Hibbert, *Ber.*, **40**, 1508 (1907).

[4] Davies and Walters, *J. Chem. Soc.*, 1786 (1935).

[5] Jensen, *J. prakt. Chem.*, [2] **148**, 101 (1937).

[6] Bleunard, *Compt. rend.*, **87**, 1040 (1878).

[7] Schmidt, *Ann.*, **267**, 261 (1892).

[8] Lewis and Seaborg, THIS JOURNAL, **61**, 1886 (1939).

[9] Wright and Moore, *ibid.*, **70**, 3865 (1948).

Experimental Part

Apparatus and Methods.—High vacuum apparatus and techniques were utilized throughout. The methods and equipment are described in a recent publication by Sanderson.[10] Temperatures between 0 and −80° were measured with vapor tension thermometers.[10]

Materials.—The compounds used were first purified by standard techniques and then purified in the high vacuum apparatus by fractional distillation until they were tensiometrically homogeneous. Trimethylamine and trimethylphosphine were freed of water and primary and secondary amines by allowing the substance to remain in a sealed tube over freshly sublimed phosphorus(V) oxide for several days.

Trimethylamine and Carbon Disulfide.—Trimethylamine (0.336 millimole) and carbon disulfide (0.316 mmole.) were condensed in a reaction flask of known volume, fitted with a manometer. The pressure, at 23°, with all components in the gas phase, corresponded to 0.652 mmole. The flask was then cooled until condensation occurred, and the pressure exerted by the liquid measured at three temperatures between −60 and −80°:

Temp., °C.	−61	−66.1	−78
Press., obs., mm.	17.7	12.5	4.6
Press., calcd. for ideal soln.	15.6	10.7	4.1

The observed values are slightly higher than those calculated. The discrepancy is probably due to positive deviations of carbon disulfide–trimethylamine solutions from Raoult's law.

Water vapor (0.31 mmole.) was added to the mixture. The pressure at 23° dropped to 223 mm. Allowing for the solubility of trimethylamine in water, the calculated pressure is 216 mm.

Dimethylamine and Carbon Disulfide.—Dimethylamine (0.437 mmole.) and carbon disulfide (0.438 mmole.) were condensed in the reaction flask. As soon as the materials melted, there was a rapid reaction to give a white solid. Residual gas in the flask (0.220 mmole.) was removed and its purity and identity established as carbon disulfide by its vapor pressure of 29.4 mm. at −28.5°. The product was of exceedingly low volatility and could not be distilled in the high vacuum equipment.

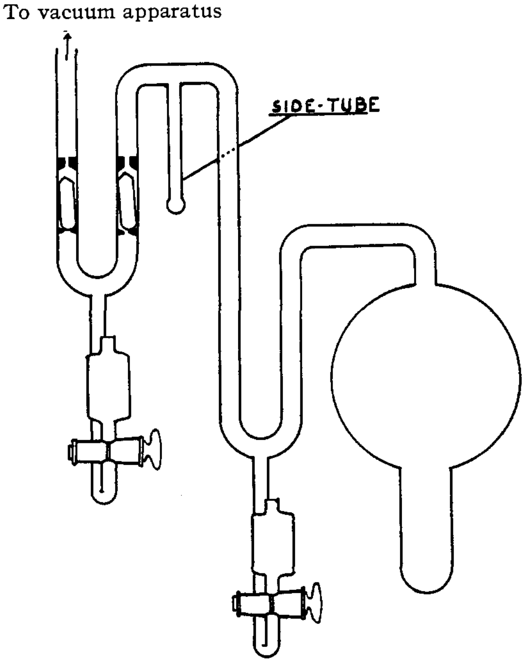

Fig. 1.—Reaction flask for study of gas phase reaction.

In a similar experiment, trimethylamine (0.446 mmole.), dimethylamine (0.437 mmole.) and carbon disulfide (0.437 mmole.) were placed in the reaction flask. A white non-volatile product was again obtained and 0.116 mmole. of carbon disulfide and 0.214 mmole. of trimethylamine were recovered. The product therefore contained (in mmoles.) 0.232 Me_3N:0.437 Me_2NH:0.321 CS_2, which is the ratio 2.17 Me_3N:4.09 Me_2NH:3.00 CS_2. Other experiments indicate that this ratio is not fixed but will vary with the ratio of trimethylamine and dimethylamine present in the reactants.

Trimethylamine and Carbon Dioxide.—Trimethylamine (0.366 mmole.) and carbon dioxide (0.367 mmole.) were condensed in the reaction flask. No evidence of reaction was observed. The pressure of the gas mixture at 25° corresponded to 0.732 mmole., and the pressure above the liquid at −78° was 103 mm., approximately the value expected for the quantity of carbon dioxide present, if no reaction had occurred.

Trimethylphosphine and Carbon Disulfide.—Carbon disulfide (0.376 mmole.) was condensed in the lower tip of the reaction flask. Trimethylphosphine (0.373 mmole.) was condensed on the wall in a ring above the carbon disulfide. As the flask warmed, no reaction occurred until the pressure rose to one mm.; then a pink color appeared in the liquid. Almost immediately, the region where the trimethylphosphine had been condensed turned bright red, and the liquid evaporated completely. The pressure reached a maximum when the flask came to room temperature, then fell slowly almost to zero. A trace of residual gas was identified as carbon disulfide, vapor pressure 11.5 mm. at −43.8°.

The product was not volatile at room temperature. At elevated temperatures (100°), gas was evolved. This gas was not reabsorbed at room temperature; it could be condensed at low temperatures (vapor pressure 0.9 mm. at −78°), but it was not further identified. Another sample of the solid was sealed in a small tube under vacuum and heated in a melting-point bath. No visible change occurred until at 114 ± 3° the solid melted to a black liquid which bubbled rapidly, and which remained black after cooling. The opacity of the solid prevented a more exact determination of the melting point.

For the gas phase reaction, a flask of about 600-ml. volume was used, fitted with a manometer through which gas could be admitted by lowering the mercury level (Fig. 1). Carbon disulfide (0.873 mmole.) was condensed in the flask. Mercury was raised in the manometer and the carbon disulfide was allowed to fill the flask as vapor at room temperature (22°). A measured amount of trimethylphosphine was condensed in the side-tube and closed off from the rest of the vacuum apparatus. As it vaporized, the trimethylphosphine was allowed to bubble through about five mm. of mercury in the manometer into the flask containing the gaseous carbon disulfide. When bubbling ceased, the mercury level was raised and the unused trimethylphosphine was measured elsewhere in the apparatus; by difference, the amount introduced was 0.871 mmole.

The pressure in the reaction flask decreased at such a rate that a plot of the reciprocal of the pressure against the time was linear after the first two to six hours, as is characteristic of a second-order reaction. After one hundred hours, the reaction was 88% complete. Typical data are reported below.

Time, hr.	0	2	6	24	50	74	100
Press., mm.	54.4	50.6	42.4	20.8	11.9	8.6	6.8

A similar experiment in which the surface area of the reaction zone was increased by a factor of 3.20 increased the second-order rate constant by a factor of 1.40. The product appeared to have been deposited uniformly over the entire available surface. These facts, together with the initial deviations from second-order kinetics, show that the reaction is largely heterogeneous.

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[10] Sanderson, "Vacuum Manipulation of Volatile Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948.

Trimethylphosphine and Trimethylboron.—Following the above procedure, gaseous trimethylphosphine (1.02 mmoles.) was bubbled through mercury into gaseous trimethylboron (0.94 mmole.). From the first reading (three minutes after the first trimethylphosphine was admitted) until over an hour had elapsed, the pressure in the reaction flask corresponded to 0.09 mmole. of unreacted gas. Since complete reaction would have left 0.08 mmole., the reaction was at least 99.5% complete within the first three minutes.

Summary

1. Contrary to reports in the literature, pure trimethylamine and carbon disulfide do not combine to form an addition compound at temperatures from −80 to 25° and pressures up to 2.5 atm. Under the same conditions, trimethylphosphine and carbon disulfide readily react to form a 1:1 molecular addition compound.

2. Dimethylamine and carbon disulfide readily react in the ratio 2 Me_2NH : 1 CS_2 to form a white solid of low volatility, probably $(Me_2NH_2)^+$-$(Me_2NCS_2)^-$. It is concluded that earlier reports claiming the formation of addition compounds between carbon disulfide and trimethylamine resulted from the presence of dimethylamine in the trimethylamine used.

3. The gas phase reaction of trimethylphosphine with carbon disulfide proceeds at a rate several orders of magnitude slower than the reaction of trimethylphosphine with a typical Lewis "primary" acid, such as trimethylboron.

4. Neither trimethylamine nor trimethylphosphine reacts with carbon dioxide at temperatures down to −80°.

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The Infrared Spectrum of Thiophosphoryl Chloride

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Several investigations of the Raman spectrum of liquid thiophosphoryl chloride have been reported in the literature[3-6] but no measurements of its infrared spectrum have hitherto been published. The appearance of three depolarized lines in the Raman spectrum indicates a pyramidal structure for the molecule with symmetry C_{3v}, and this is consistent with the results of electron diffraction investigations.[7] The molecule is therefore a symmetric top and should possess six distinct fundamental frequencies, three totally symmetric (Type A_1) and three doubly degenerate (Type E). These frequencies should be active both in the infrared and in the Raman spectrum.

Six Raman frequencies were reported by Thatte[3] and by Simon and Schulze[4] but Gerding and Westrik[5] reported only five and considered that the sixth Raman shift reported by the former authors at 382 cm.$^{-1}$ corresponded to the strong 435 cm.$^{-1}$ shift excited by the 4347.5 Å. mercury line. These conclusions were confirmed by Delwaulle and François.[6] By comparing the Raman spectra of phosphorus trichloride, phosphoryl chloride and thiophosphoryl chloride, Gerding and Westrik deduced that the sixth frequency for thiophosphoryl chloride should lie in the region of 240 cm.$^{-1}$ and probably be masked by the intense band at 250 cm.$^{-1}$. Similar conclusions were reached by Delwaulle and François by comparing the Raman spectra of thiophosphoryl trichloride, thiophosphoryl bromodichloride thiophosphoryl chlorodibromide and thiophosphoryltribromide. The latter authors pointed out that since the masses of the chlorine and sulfur atoms are approximately the same it is not surprising that the missing P–Cl bending frequency should almost coincide with the P–S bending frequency. A similar coincidence is observed in the Raman spectrum of phosphorus oxyfluoride.

Though it was not possible to observe infrared absorption bands in the region of 250 cm.$^{-1}$ with the facilities at our disposal,[8] an investigation of the infrared spectrum of thiophosphoryl chloride was carried out over the regions accessible with sodium chloride and potassium bromide prisms. This provides a check on the assignment based on the Raman data and it was also anticipated that some evidence concerning the location of the missing frequency might be obtained from an analysis of the combination tones observed at higher frequencies.

Experimental

Thiophosphoryl chloride was prepared by heating phosphorus trichloride and sulfur in stoichiometric proportions in a closed tube at 130° for several hours.[9] The resultant product was distilled several times and the fraction distilling at 114–115° under 700 mm. was used in subsequent

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(1) Published as Contribution 1969 from the Laboratories of the National Research Council of Canada.

(2) Guest Worker of the Division of Chemistry, National Research Council of Canada.

(3) Thatte, *Nature*, **138**, 468 (1936).

(4) Simon and Schulze, *Naturwissenschaften*, **25**, 669 (1937).

(5) Gerding and Westrik, *Rec. trav. chim.*, **61**, 842 (1942).

(6) Delwaulle and François, *Compt. rend.*, **224**, 1422 (1947).

(7) Beach and Stevenson, *J. Chem. Phys.*, **6**, 75 (1938).

(8) This frequency is close to the lower limit attainable with a thallium bromide/thallium iodide (KRS-5) prism. See Plyler, *J. Research Natl. Bur. of Standards*, **41**, 125 (1948).

(9) Henry, *Ber.*, **2**, 638 (1869).