[CONTRIBUTION FROM THE CHEMISTRY LABORATORIES OF THE OHIO STATE UNIVERSITY]

Phase Studies on the Binary Systems of Diethyl Ether with the Methyl Chlorosilanes

BY HARRY H. SISLER AND ROBERT MATTAIR

Recent publications from this Laboratory[1,2] have reported studies of various binary systems of aliphatic and aromatic ethers with tetrachlorides of carbon, silicon, germanium and tin. The results of studies of the silicon tetrachloride systems indicate that this compound does not readily form solid addition compounds with ethers. In order to extend our knowledge of this field, and perhaps to obtain some suggestion as to the reasons for the failure of such compounds to be formed with silicon tetrachloride, it was decided to determine the effect of substituting a methyl group for a chlorine atom by studying the systems methyl trichlorosilane–diethyl ether, dimethyl dichlorosilane–diethyl ether and trimethyl chlorosilane–diethyl ether. The methyl chlorosilanes are sterically similar to silicon tetrachloride but differ in the electrical charge characteristics of the molecule.

Experimental

Preparation of Materials and Experimental Method.—The diethyl ether was obtained from Merck and Co. and the silane derivatives from the Anderson Chemical Laboratories. These compounds were purified by distillation at atmospheric pressure through a five-foot column packed with glass helices. In each case a middle fraction was collected over a twelve to twenty-four-hour period at a reflux ratio of 30:1. The boiling range was, in no case, larger than 0.5°. The freezing points of the purified products were as follows: diethyl ether, −123.5° and −116.0°, methyl trichlorosilane, −77.5°, dimethyl dichlorosilane, −75.5°, and trimethyl chlorosilane, −56.0°. All these values are in good agreement with values found in the literature[3] except in the case of trimethylchlorosilane, in which case a freezing point of −56°, slightly more than a degree higher than that reported by Booth and Suttle[4] was obtained.

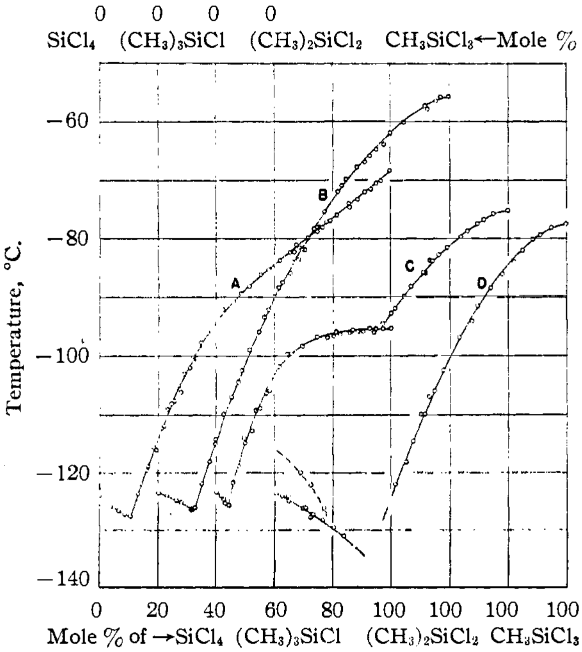

Fig. 1.

The experimental method consisted in taking cooling curves of synthetic mixtures of the two components of the various systems studied. The temperatures were indicated and recorded by a Micromax self-recording potentiometer using a copper–constantan thermocouple. The freezing point cell and the experimental technique are described in previous publications from this Laboratory.[1] An accuracy of ±1.5° has been claimed for this method, but, because of the very low temperatures at which freezing takes place in these systems, and of the difficulty with supercooling, the range of experimental error should be increased to ±2.0°.

Because of the low temperatures involved and the necessity for working in a closed system, it seemed unfeasible, in those systems in which only the lower melting form of diethyl ether was obtained, to attempt to obtain the freezing point curve for the higher melting form by such means as seeding. Varying the rate of cooling, and cooling to temperatures far below the freezing point were tried in the monomethyl trichlorosilane and dimethyldichlorosilane systems without success, and the freezing point curves for only the lower melting form of diethyl ether were obtained in these systems. The authors can suggest no reason why the higher melting form should be obtainable in some systems but not in others.

Considerable variation of the rate of cooling did not change the indicated freezing point for various mixtures, so it is believed that equilibrium was attained. No system was completed from a single batch of material, and, in most of the systems, the data were obtained using materials from several different batches.

Discussion and Conclusions

The data obtained for the systems are represented graphically in Fig. 1. The data for the methyltrichlorosilane system are given in curve D; for the dimethyldichlorosilane system, in curve C; and for trimethylchlorosilane, in curve B. The curve for the silicon tetrachloride–diethyl ether system[2] is included for purposes of comparison (curve A).

As is shown by curve D, points on the freezing point curve of both high and low-melting forms of diethyl ether were obtained in the methyl trichlorosilane system. Though it was not possible to complete the system because of excessive supercooling in the region of twenty to forty mole per cent. of methyltrichlorosilane, it appears from the data obtained that methyltrichlorosilane does not form a compound with diethyl ether under the conditions of the experiment.

Curve C show that dimethyldichlorosilane and diethyl ether form an addition compound. The maximum in the curve is so exceedingly flat, how-

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[1] Sisler, Wilson, Gibbins, Bater and Mattair, THIS JOURNAL, **70**, 3818 (1948).

[2] Sisler, Batey, Pfahler and Mattair, *ibid.*, **70**, 3821 (1948).

[3] Burkhard, Rochow, Booth and Hartt, *Chem. Rev.*, **41**, 97–149 (1947).

[4] Booth and Suttle, THIS JOURNAL, **68**, 2658 (1946).

ever, as to make it impossible to establish with any certainty the composition of the compound. The very flat nature of the curve in this region indicates that whatever compound is formed, it is not very stable. An eutectic was obtained at four to five mole per cent. of dimethyl dichlorosilane and about −125.5°.

The data in curve B give no indication whatever of compound formation between trimethyl chlorosilane and diethyl ether. An eutectic was obtained at twelve to thirteen mole per cent. trimethyl chlorosilane and about −126.0°.

We may thus conclude that the methyl chlorosilanes, like silicon tetrachloride, do not form very stable compounds with diethyl ether. The results of these studies are not in conflict, therefore, with the very tentative suggestion in a previous publication[2] that there isn't room about the silicon atom in silicon tetrachloride or, since the steric requirements of the methyl group are not less than those of the chlorine atom, in the methyl chlorosilanes, for the approach of the oxygen atom from the ether.

In connection with the very weak compound formed by the dimethyl dichlorosilane with diethyl ether, it is interesting to note that work with the ethyl chlorosilanes[5] indicates that dimethyl dichlorosilane would have the highest dipole moment of the three chlorosilanes studied in this work, and suggests the possibility that the weak crystalline compound between dimethyl dichlorosilane and diethyl ether may depend upon dipole interaction for its existence.

Summary

Phase studies of the systems methyl trichlorosilane–diethyl ether, dimethyl dichlorosilane–diethyl ether, and trimethyl chlorosilane–diethyl ether were carried out by the freezing point method. Weak compound formation was observed in the case of dimethyl dichlorosilane.

(5) McCusker, Witucki and Curran, Paper presented to Phys. and Inorganic Section, American Chemical Society Meeting, Sept., 1947.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE OHIO STATE UNIVERSITY]

Addition Compounds of Chromic Anhydride with Some Heterocyclic Nitrogen Bases

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The ability of pyridine to act as a base by sharing the pair of electrons on its nitrogen atom with various molecules capable of acting as Lewis acids is well known. The interest in this Laboratory in molecular addition compounds, as well as previous work on the pyridine–sulfur trioxide compound by one of the authors,[1] caused the authors to undertake a study of the reactions of pyridine and related nitrogen bases with chromic anhydride. The results of studies with pyridine, α-picoline, β-picoline, γ-picoline, quinoline and isoquinoline are reported in this paper. Reactions of this type in the case of chromic anhydride are complicated by the fact that, in addition to its acidic properties, chromic anhydride is a strong oxidizing agent. Conditions of the various reactions must, therefore, be subjected to rather more stringent requirements than in the case of such compounds as sulfur trioxide.

Experimental

Preparation of Materials.—The chromic anhydride used in this study was Mallinckrodt C.P. grade. It was dried in an electrically heated furnace under vacuum at a temperature of 140° in the presence of phosphorus pentoxide. It was then ground to a fine powder with a mortar and pestle and placed in the drier for another two-day drying period. It was stored over phosphorus pentoxide.

J. T. Baker C.P. grade pyridine was used, but all the other bases were obtained from the Eastman Kodak Company. All were fractionally distilled using a four-foot column packed with glass helices at atmospheric pressure, except quinoline and isoquinoline, which were distilled under reduced pressure. The amines were dried over barium oxide and, where necessary, were treated with activated charcoal before distillation. A middle fraction having a very narrow boiling range (<1°) and a very narrow range of refractive index (agreeing with values recorded in the literature) was collected in each case.

Preparation of the Addition Compounds.—The general method for carrying out the reactions was to add an excess of the nitrogen base to a weighed quantity of the chromic anhydride at room temperature or below, and, after solution had been effected, to evaporate the excess amine, and to weigh the crystalline residue. The apparatus in which this operation was carried out is shown in Fig. 1. After the system was evacuated, stopcocks A and B were closed, the reaction flask disconnected from the system at J and K, and weighed. A sample of chromic anhydride was then introduced into the flask, the system again evacuated and weighed. An excess of nitrogen base was drawn into the system through stopcock B, and, in most runs, the system was shaken until solution or reaction appeared to be complete. The reaction flask was then re-attached to the system, the traps I, II and III cooled with liquid air, and the excess of nitrogen base allowed to distil off under vacuum. The reaction flask was protected against the light throughout the process of evaporation. The removal of the excess of nitrogen base was detected in three ways: (a) visually, from the physical appearance of the reaction mixture, (b) gravimetrically, by the sharp decrease in the rate of weight loss of the reaction system which was weighed from time to time as the point of complete evaporation of excess amine was approached, and (c) manometrically, by the decrease in vapor pressure in the system as measured by the thermocouple gage. It was found that conclusions based upon (a), (b) or (c) are consistent and in the latter runs (c) was used as the chief indication of solvent removal. At the end of the period of evaporation the stopcocks A and B were closed and the reaction flask again removed and weighed. Thus the weights of both the initial chromic anhydride and the solid reaction product were obtained.

Analytical Methods.—The various reaction products were analyzed for hexavalent chromium by dissolving the product in a dilute solution of phosphoric and perchloric

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[1] Sisler and Audrieth, THIS JOURNAL, 61, 3392 (1939).