very similar to the textbook example.[12] Resonances for the two sets of multiplets of the B_4 fluorine atoms are located at ϕ −92.9 and −96.9. The nine absorptions[13] for the A fluorine atom are centered at ϕ −130.7, −134.5, −135.3, −138.3, −138.8, −139.6, −142.6, −143.3, −146.9. The average $J \cong 160$ cps for the A fluorine nucleus and $J = 162$ for the B_4 nuclei.

Stability of $CsPF_2S_2$ toward Hydrolysis.—A saturated DMSO solution of $CsPF_2S_2$ was prepared. The solution was combined with an equal volume of water, and the ^{19}F nmr spectrum of the resulting mixture showed no reaction after 7 hr. Also, there was no reaction within the same length of time when *ca.* 0.1 *N* HCl solution was substituted for the water.

Acknowledgment.—This work was carried out under the sponsorship of the U. S. Army Missile Command, Redstone Arsenal, Ala., under Contract No. DAAH01-67-C-0655.

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[13] H. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p 340.

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New Preparation of Difluorocarbamyl Chloride, $ClC(O)NF_2$

BY RONALD L. CAUBLE AND GEORGE H. CADY

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While $ClC(O)NF_2$ has been prepared by the reaction of Al_2Cl_6 with $FC(O)NF_2$,[1] it may also be obtained by irradiating N_2F_4 and $(ClCO)_2$ with Pyrex-filtered ultraviolet light.

In a typical run, 12 mmoles of $(ClCO)_2$ and 18 mmoles of N_2F_4 were held in a 2-l. glass bulb with a finger containing a medium-pressure, 350-w, water-cooled mercury lamp, and irradiated for 2 days. The flask then contained in decreasing amounts $COCl_2$, $ClC(O)NF_2$, CO_2, *cis*-N_2F_2, COClF, N_2F_4, SiF_4, HNF_2, COF_2, and N_2O. All known compounds were identified by their characteristic infrared spectra. About 20% of the $(ClCO)_2$ was converted into $ClC(O)NF_2$, which was purified by fractional codistillation.[2]

The average molecular weight of the pure compound obtained from vapor density measurements was 115.3 g/mole (calcd for $ClC(O)NF_2$, 115.5).

The F^{19} nmr spectrum was taken on a Varian Associates high-resolution, 40-Mc nuclear magnetic resonance spectrometer with a Model No. V-4311 fixed-frequency radiofrequency transmitter using 65 mole % CCl_3F as an internal standard. The spectrum showed a single, broad band at −41.8 ppm. This is close to Shreeve and Fraser's[1] value of −40.4 ppm which employed an external standard.

The infrared spectrum was taken at gas pressures ranging from 1 to 100 mm using a Beckman IR10 spectrometer and a Monel cell equipped with silver chloride windows, having a length of 10 cm. The infrared spectrum (in cm^{-1}) is: 3629 (vw), 1975 (vw), 1845 (vs), 1800 (s), 1117 (vw), 1071 (m), 947 (s), 910 (vvs), 770 (w, doublet), 645 (m, doublet), 521 (w), 474 (vvw). These values agree to within 5 cm^{-1} with those reported by Shreeve and Fraser.[1]

When water vapor was placed in an infrared cell along with difluorocarbamyl chloride the following reaction occurred

$$ClC(O)NF_2 + H_2O \longrightarrow HCl + HNF_2 + CO_2$$

All products were identified by their characteristic infrared spectra.

Acknowledgment.—This work was performed in part under contract with the Office of Naval Research. The nmr spectrum was acquired by B. J. Nist.

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[2] G. H. Cady and D. P. Siegwarth, *Anal. Chem.*, **31**, 618 (1959).

CONTRIBUTION FROM THE RICHARD BENBRIDGE
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A Photochemical Preparation of 1,1,2,2-Tetrachloro-1,2-dimethyldisilane

BY DALE REEDY AND GRANT URRY

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While 1,1,2,2-tetrachloro-1,2-dimethyldisilane long has been recognized as a major constituent of the "disilane fraction" produced in the course of the direct synthesis of methylchlorosilanes,[1-3] it so far has not been obtained in a pure state. This apparently is the consequence of the extreme difficulties encountered in attempts to separate the 1,1,2,2-tetrachloro-1,2-dimethyldisilane from 1,1,2-trichloro-1,2,2-trimethyldisilane also present in the "disilane fraction."[4] A procedure involving photochemical chlorination has been suggested as a means of obtaining 1,1,2,2-tetrachloro-1,2-dimethyldisilane in a "reasonably pure" state since 1,1,2-trichloro-1,2,2-trimethyldisilane chlorinates at a faster rate than the other disilane.[5]

We wish to report a simple and convenient means of obtaining this and other symmetrically substituted disilanes in a high degree of purity with no difficult separation problems.

The recent study by Gunning and his associates[6] of

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[4] K. Tarama, A. Taketa, M. Kumada, and M. Kuriyagawa (Tokyo Shibaura Electric Co.), Japanese Patent 13,010 (1960); *Chem. Abstr.*, **55**, 10319*d* (1960).

[5] M. Kumada, M. Ishikawa, and S. Maeda, *J. Organometal. Chem.* (Amsterdam), **2**, 478 (1964).

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TABLE I

VAPOR TENSION OF 1,1,2,2-TETRACHLORO-1,2-DIMETHYLDISILANE

	Temp, °C									
	27.3	36.5	48.1	54.8	65.5	71.7	83.1	91.1	98.6	102.8
p (obsd), mm	5.00	8.35	14.8	20.9	33.9	45.3	71.5	99.1	131.1	149.1
p (calcd), mm	5.02	8.31	15.1	20.8	34.0	44.6	71.6	98.0	130.0	151.6

the mercury-sensitized photolysis of methylsilanes has demonstrated the fact that photolysis of monosilanes produces hydrogen and disilanes. Thus it was shown that the photolysis of methylsilane resulted mainly in 1,2-dimethyldisilane and hydrogen, while in the photolysis of dimethylsilane, 1,1,2,2-tetramethyldisilane was the chief product along with hydrogen. In our work we have extended this study to chlorosilanes and found the reaction to be a convenient means of obtaining symmetrically substituted chlorodisilanes.

In a typical reaction, 901.6 cc at STP of methyldichlorosilane (40.22 mmoles), purified by repeated fractional condensation,[7] was irradiated for a period of 6 hr. The irradiation was effected in the vapor phase in the presence of mercury. The irradiation chamber consisted of a 1-l. bulb fitted internally with a spiral quartz, low-pressure mercury vapor lamp. The measured sample of methyldichlorosilane was distilled slowly through the irradiation chamber from a bulb maintained at ambient temperature to one maintained at −10°. The noncondensable gas, presumably hydrogen, formed during the irradiation, was continually removed through a long diffusion capillary located between the −10° bulb and an automatic Toepler pump. This arrangement promoted an even flow of reactant through the irradiation chamber in addition to maintaining a low steady-state concentration of hydrogen. The latter is essential in minimizing the "quenching effect."[8]

The distillation of the measured methyldichlorosilane in this fashion generally required 0.5 hr. After the distillation was complete, all of the unchanged silane was returned to the original bulb and the distillation repeated several times in this manner until the total irradiation time was 6 hr.

At the end of this irradiation the noncondensable material was measured and burned over copper oxide at 300°. By this means it was shown to be hydrogen (8.21 mmoles) with a small amount of methane (0.025 mmole) admixed.

The volatile, condensable products of the photolysis were separated by fractional condensation methods. Distillation through a series of U-tube traps, maintained at −45, −95, −126, and −195°, respectively, afforded a reasonable separation into the following fractions. A crude disilane fraction, which condensed in the −45° trap, was shown to consist of 88% 1,1,2,2-tetrachloro-1,2-dimethyldisilane and 12% 1,1,2-trichloro-1,2-dimethyldisilane by gas chromatography, by nuclear magnetic resonance, and by the average apparent molecular weight of the mixture. A second fraction, condensed in the −95° trap, consisted of the starting material, methyldichlorosilane (22.3 mmoles), and methyltrichlorosilane (3.58 mmoles). Both constituents of the second fraction were identified by their respective retention times in a gas chromatographic column and the amounts were verified by alkaline hydrolysis of the mixture. A small unmeasurable amount of methyldichlorosilane was condensed in the −196° trap.

An oily liquid, formed in small amounts, remained in the irradiation chamber. This material probably contains higher polysilanes of limited volatility.

The crude disilane fraction, described earlier, was simply converted to pure 1,1,2,2-tetrachloro-1,2-dimethyldisilane by chlorination at 70° for a period of 8 hr. During this treatment the 1,1,2-trichloro-1,2-dimethyldisilane is chlorinated to 1,1,2,2-tetrachloro-1,2-dimethyldisilane with virtually no chlorination of the silicon–silicon bond. The irradiation and chlorination reaction produced 1.125 g of pure 1,1,2,2-tetrachloro-1,2-dimethyldisilane (4.94 mmoles).

The product of this synthesis gave the following analytical result. *Anal.* Calcd for $C_2H_6Cl_4Si_2$: C, 10.53; H, 2.50; Cl, 62.5; Si, 24.45. Found: C, 10.52; H, 2.63; Cl, 62.3; Si, 24.55.

Alkaline hydrolysis of the product yielded 100.8% of the amount of the hydrogen calculated for 1,1,2,2-tetrachloro-1,2-dimethyldisilane. This gives an estimated purity of 99.2%, assuming an impurity of 1,1,2-trichloro-1,2-dimethyldisilane.

No such impurity is indicated by the molecular weight, determined by two vapor density measurements as 229.0 and 228.0 (calculated value is 228.0).

The vapor tensions observed and calculated for the product are given in Table I. The calculated values were obtained using the equation $\log p_{\mathrm{mm}} = 8.0709 - (2214.7/T)$, from which an extrapolated boiling point of 153.8° also can be calculated.

The melting point of 1,1,2,2-tetrachloro-1,2-dimethyldisilane is 2.4° and the nuclear magnetic resonance spectrum consists of a single line centered at $\delta = 1.03$ (relative to external TMS).

In summary, a typical 6-hr irradiation converts 45% of the monosilane to higher silanes. The monosilane consumed produces a 56% yield of 1,1,2,2-tetrachloro-1,2-dimethyldisilane. Higher homologous polysilanes of limited volatility account for essentially all of the additional consumed monosilane.

This photochemical coupling reaction converts trichlorosilane to hexachlorodisilane and hydrogen. 1,2-Dichloro-1,1,2,2-tetramethyldisilane also can be formed by photochemical coupling of dimethylchlorosilane. Since the irradiations of both of these silanes are ef-

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(7) The purity of the dimethylchlorosilane was determined to be 97.5%, the only contaminant being 2.5% of methyltrichlorosilane.

(8) S. Bywater and E. W. R. Steacie, *J. Chem. Phys.*, **19**, 319 (1951).

fected in a fashion identical with the case described, there is little point in repeating these descriptions here. The only differences among these photochemical preparations lie in the conditions of chlorination of the mixed disilane to produce the pure disilane. In the preparation of hexachlorodisilane this chlorination requires a temperature of 105° while in the preparation of 1,2-dichloro-1,1,2,2-tetramethyldisilane the chlorination proceeds smoothly at room temperature.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND
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A Calorimetric Study of Molten Na_2MoO_4–MoO_3 Mixtures at 970°K

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Liquid oxide mixtures which contain metal cations and complex oxygen-containing anions (such as borate, phosphate, or silicate species) form an interesting and important class of ionic melts. In this general area we have recently reported the results of calorimetric studies of the liquid systems PbO–V_2O_5 at 685°[1] and PbO–B_2O_3 at 800°.[2]

In this note, we wish to report a related study of the liquid mixtures formed by Na_2MoO_4 and MoO_3 at 970°K. More specifically, we have measured the enthalpies of solution of $MoO_3(s)$ and $Na_2MoO_4(l)$ in molten Na_2MoO_4–MoO_3 mixtures at this temperature. The present study was motivated by our interest in finding new solvents for high-temperature calorimetry of mixed solid oxides such as spinels and silicates. However, these new results have certain interesting features which have implications outside the immediate domain of calorimetry.

Experimental Section

The materials used in the present work were Baker Analyzed reagent $Na_2MoO_4 \cdot 2H_2O$ and MoO_3. Prior to each experiment, a mixture of these compounds of the desired composition was melted down in the gold crucible used for calorimetry. The calorimeter, sample container, and general experimental procedures have been described elsewhere.[3] In each calorimetric experiment, a small sample of known weight of either MoO_3 or Na_2MoO_4 (0.5–1.0 mmole) was dissolved in about 15 g of molten oxide mixture. Both solutes dissolved rapidly in the nonviscous melts. As in our earlier work, calibration was by the gold drop method, based on the heat content equation for gold given by Kelley.[4]

Results and Discussion

We present in Figures 1 and 2 graphs of the molar enthalpies of solution of $MoO_3(s)$ and $Na_2MoO_4(l)$ in molten Na_2MoO_4–MoO_3 mixtures as functions of melt composition. The composition variable adopted is the mole fraction of MoO_3 in the binary system Na_2O–MoO_3: $X_{MoO_3} = n_{MoO_3}/(n_{MoO_3} + n_{Na_2O})$. The composition range covered in the present study was from $X_{MoO_3} = 0.50$ (pure molten Na_2MoO_4) to $X_{MoO_3} = 0.9$, which is close to the liquidus at 700°.[5] Because of the expected experimental difficulties associated with calorimetry in very basic melts (*e.g.*, attack on platinum), no attempt was made to extend this study to the Na_2O-rich side of the system.

Each addition of solute changed the melt composition by 0.5 to 1.0 mole %. For those composition regions in which the partial enthalpy of solution changes rapidly with concentration (notably near $X_{MoO_3} = 0.5$), the precision of the calorimetric data does not permit a reliable extrapolation to zero moles of added solute. Therefore, all calorimetric data have been plotted against the average mole fraction of MoO_3

$$\bar{X}_{MoO_3} = \frac{X_{MoO_3}(\text{initial}) + X_{MoO_3}(\text{final})}{2}$$

Even so, our results will, to a good approximation, represent the partial molal enthalpies of MoO_3 and of Na_2MoO_4.

In discussing the experimental results we shall, as in our earlier work, adopt the Lux–Flood approach to the acid–base properties of oxide melts.[6,7] In this approach, the basicity of the melt is measured by the oxygen ion activity, governed by the equilibrium

$$\text{acid} + O^{2-} = \text{base} \qquad (1)$$

Among the considered oxides, Na_2O is a very strong base, while MoO_3 is a strong acid. We may write a series of possible consecutive acid–base steps that may occur when MoO_3 is added to an initially Na_2O-rich melt

$$O^{2-}\text{ (in melt)} + MoO_3(s) = MoO_4^{2-}\text{ (in melt)} \qquad (2)$$

$$MoO_4^{2-}\text{ (in melt)} + MoO_3(s) = Mo_2O_7^{2-}\text{ (in melt)} \qquad (3)$$

$$Mo_2O_7^{2-}\text{ (in melt)} + MoO_3(s) = MoO_3\text{ (in melt)} \qquad (4)$$

Note that when the melt contains a mixture of several molybdate species such as those above or their polymers, it constitutes a buffered acid–base system.

The calorimetric results are in accord with an interpretation along these lines. Since Na_2O is a very strong base, it is reasonable to assume that the MoO_4^{2-} anion, which is present in high concentration at the Na_2MoO_4 composition, has a relatively small dissociation constant. Presumably the composition $X_{MoO_3} = 0.50$ corresponds to the first equivalence point in the "titration" of Na_2O by MoO_3. The very pronounced composition dependence observed in the heat of solution of

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