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Proton Magnetic Resonance in Stannane, the Methylstannanes and Related Compounds[1]

BY N. FLITCROFT AND H. D. KAESZ

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Proton magnetic resonances in SnH_4, the methylstannanes $[(CH_3)_nSnH_{4-n}]$, $(CH_3)_3Sn^-$, Li^+ and $(CH_3)_3PbH$ have been obtained. Chemical shift of the protons as well as spin–spin coupling between the various magnetically active nuclei in these molecules has been determined. The protons bonded to tin or lead are less shielded than those bonded to carbon in these derivatives. The trends observed in tin–proton spin–spin coupling constants are discussed in the light of possible structural changes occurring in the stannanes.

Introduction

We have studied proton magnetic resonance in SnH_4, the series of methylstannanes and $(CH_3)_3PbH$ to determine the chemical shift of protons bonded directly to a heavy atom of the main group metals, and to compare this with the unusually high chemical shift of protons bonded to transition metals.[2] The only reports of the chemical shift of tin-bonded protons in the literature are incomplete references to unpublished work, such as footnote 12 in the review by Green[2b] or the paper by Duffy, Feeney and Holliday.[3] For $(CH_3)_3PbH$, our results and interpretations are not entirely in keeping with the results nor with the interpretation of the spectrum previously reported for this compound.[3]

We have also determined the constants for the spin–spin interaction between the metal-bonded hydrogen with magnetically active isotopes of the metal, and with other protons in the molecule, which serve to indicate that no appreciable exchange of metal-bonded protons was occurring. The tin–proton spin–spin coupling constants in SnH_4, the methylstannanes and $(CH_3)_4Sn$ were compared to see whether any systematic trend was occurring in that series of compounds, similar to trends observed in the methyltin halides.[4]

Experimental

Sample Preparation.—The volatile and air-sensitive compounds were handled and sealed into sample tubes on a chemical high-vacuum line.[5] SnH_4 was prepared and purified by the method of Emeléus and Kettle.[6] $(CH_3)_2SnH_2$ and $(CH_3)_3SnH$ were prepared by the reduction of the corresponding chlorides with $LiAlH_4$,[7] $(CH_3)_2SnCl_2$ was purchased from the Metal & Thermit Co., and $(CH_3)_3SnCl$ prepared in 93% yield from $(CH_3)_4Sn$ and $SnCl_2$ by an adaptation of the method reported by Anderson.[8] $(CH_3)_3PbH$ was prepared from $(CH_3)_3PbCl$, after Becker and Cook.[9]

The reduction of CH_3SnCl_3 by $LiAlH_4$ was found to give extremely poor yields of CH_3SnH_3. A milder reducing medium, the aqueous borohydride method of Schaeffer and Emilius,[10] was used to obtain that hydride from $K(CH_3SnO_2)$; $NaBH_4$ (1.5 g.) was added to a solution of $K(CH_3SnO_2)$ (prepared according to Pfeiffer and Lehnardt[11] from $SnCl_2 \cdot 2H_2O$ (15 g.), excess KOH (30 g.) and CH_3I) which was then added over 0.5 hour to a well-stirred solution of 6 *M* HCl (150 ml.) in a three-necked flask. The resulting evolved gas was collected at −78° under reduced pressure, and subsequently fractionated on the vacuum line giving approximately 3 g. of CH_3SnH_3; v.p. found 268 mm., required[7] 273.5 mm., at −23°.

Solutions of the alkyltin anions were prepared in CH_3NH_2 by reduction of $(CH_3)_3SnCl$ or $(CH_3)_2SnCl_2$, with the calculated amount of Li. N.m.r. tubes containing samples were stored at reduced temperature. At room temperature irreversible decomposition occurs; hence such tubes should be handled carefully as the pressures developed (due to solvent and, perhaps, some H_2) can lead to explosions.

Apparatus and Procedures.—Proton magnetic resonances were measured on a Varian A-60 spectrometer both for neat liquids and solutions in neopentane and cyclopentane. Neat samples of SnH_4 and of $(CH_3)_3PbH$ and its cyclopentane solution were not stable at room temperature, and were scanned at −50° on a Varian 4300B spectrometer (at fixed frequency, 40.000 Mc. at 9,396 gauss) equipped with a temperature-regulating probe. Only the low field satellites of the tin-bonded proton resonances fell within the normal operating range of the A-60 spectrometer, but the high-field satellites could be brought within range and the tin–proton spin–spin coupling measured by the side-band technique, using a calibrated Hewlett-Packard model 200 D audiofrequency oscillator. The spectra obtained on the 4300B spectrometer were measured and also calibrated by this audiofrequency oscillator. A complete set of spectra will be sent to the Chemical and Petroleum Research Laboratory (Carnegie Institute of Technology, Pittsburgh 13, Pa.) for publication in the catalog of nuclear magnetic resonance spectral data of the A.P.I. Research Project 44.

Results and Discussion

The results of our measurements are summarized in Table I. Data for the tetramethyl derivatives were repeated for purposes of comparison; these were in good agreement with previous reports. The values reported here are believed to be accurate to within 1%, or better, especially when obtained on the A-60 spectrometer. The solutions of the hydrides in hydrocarbons contained traces (*ca.* 0.5 to 1%) of dimethyl ether or dioxane from the reaction mixtures from which the hydrides were obtained. Separate experiments on solutions of these hydrides at concentrations up to 50% ether by volume showed that the chemical shift between the methyl protons and the metal-bonded protons varied only up to 0.14 p.p.m., with no change in the spin–spin coupling.

The data for $(CH_3)_3PbH$ are only partially in agreement with previously reported work.[3] The absolute τ-values for the chemical shifts of Pb–*H* and Pb–C*H*$_3$ appear to be in poor agreement with our values, but this is only because of differences in the standards being used in the two experiments. In fact, the difference between the resonance of the methyl protons and one of the resonances at τ = 2.98 (Table I) taken as the Pb*H* proton in the previous work is in good agreement with the difference between these two resonances

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[1] This work was supported by Grant no. 1073-Al from the Petroleum Research Fund.

[2] (a) G. Wilkinson and J. M. Birmingham, *J. Am. Chem. Soc.*, **77**, 3421 (1955); (b) see also the recent review by M. L. H. Green, *Angew. Chem.*, **72**, 719 (1960).

[3] R. Duffy, J. Feeney and A. K. Holliday, *J. Chem. Soc.*, 1144 (1962).

[4] (a) J. R. Holmes and H. D. Kaesz, *J. Am. Chem. Soc.*, **83**, 3903 (1961); (b) G. P. Van der Kelen, *Nature*, **193**, 1069 (1962).

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

[6] H. J. Emeléus and S. F. A. Kettle, *J. Chem. Soc.*, 2444 (1958).

[7] A. E. Finholt, A. C. Bond, K. E. Wilzbach and H. I. Schlesinger, *J. Am. Chem. Soc.*, **69**, 2692 (1947).

[8] H. H. Anderson, *Inorg. Chem.*, **1**, 648 (1962).

[9] W. E. Becker and S. E. Cook, *J. Am. Chem. Soc.*, **82**, 6264 (1960).

[10] (a) G. W. Schaeffer and Sr. M. Emilius, *ibid.*, **76**, 1203 (1954); (b) see also, W. L. Jolly, *ibid.*, **83**, 335 (1961).

[11] P. Pfeiffer and R. Lehnardt, *Ber.*, **36**, 1057 (1903).

TABLE I

CHEMICAL SHIFTS AND SPIN–SPIN COUPLING CONSTANTS IN STANNANE, THE METHYLSTANNANES, TRIMETHYLSTANNYLLITHIUM AND TRIMETHYLPLUMBANE

	Main resonance(s) and H–H spin coupling constant			Satellite doublets of main resonance[g] Coupling constants, c.p.s.				
Tin compounds	τ_{Sn-H} [mult.][a]	τ_{SnCH_3} [mult.][a]	J_{HCSnH}, c.p.s.	$^{119}Sn–H$	$^{117}Sn–H$	$^{13}C–H$	$^{119}SnCH_3$	$^{117}SnCH_3$
SnH_4[b]	6.15 [1]	..	..	1931	1846	...	..	..
CH_3SnH_3[c]	5.86 [4]	9.73 [4]	2.7	1852	1770	130	62[h]	
$(CH_3)_2SnH_2$[c]	5.24 [7]	9.83 [3]	2.55	1758	1682	126.5	58.0	55.5
$(CH_3)_3SnH$[c]	5.27 [10][d]	9.82 [2]	2.37	1744	1664	128.5	56.5	54.5
$(CH_3)_4Sn$[e]	..	9.86 [1]	..	..	..	128	54	51.5
$(CH_3)Sn^-$, Li^+[f]	..	10.4 [1]	..	..	..		14[h]	
Lead compounds	τ_{PbH} [mult.][a]	τ_{PbCH_3} [mult.][a]	J_{HCPbH}	$^{207}Pb–H$	..	$^{13}C–H$	$^{207}PbCH_3$	
$(CH_3)_3PbH$								
This work[i]	2.32 [10][j]	9.15 [2]	1.47	2379	..	136	66.7	..
Others[k]	2.98 [?] 5.8 [?]	9.7 [?]		?			(68)	
$(CH_3)_4Pb$								
This work	..	9.13 [1]	..	..	..	132.5	60.5	..
Others[l]	..	9.3	..	..	..	133		

[a] Resonances were observed at the multiplicity given in brackets. Center of resonance given in τ-value, *i.e.*, p.p.m. with respect to $(CH_3)_4Si$, $\tau = 10.00$; *cf.* G. V. D. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958). [b] Neat liquid at −50°; chemical shift measured for 9% solution in cyclopentane containing 9% toluene internal standard whose methyl resonance was taken at $\tau = 7.68$ under these conditions. [c] Neat liquid and solution at 40°; chemical shift measured for 9% solution in neopentane with 9% toluene as internal standard, whose methyl resonance was taken at $\tau = 7.68$ under these conditions. [d] Multiplet of which only eight peaks were separately resolved. [e] See also N. Muller and D. E. Pritchard, *J. Chem. Phys.*, **31**, 1471 (1959), or H. D. Kaesz, *J. Am. Chem. Soc.*, **83**, 1514 (1961). [f] Approximately 0.1 *M* solution in CH_3NH_2; methyl protons of solvent taken at $\tau = 7.77$. [g] Satellites due to splitting of proton resonance by isotopes ^{119}Sn, ^{117}Sn, ^{13}C and ^{207}Pb (natural abundance: 8.6, 7.6, 1.1 and 21.1%, respectively), best observed for neat liquids; satellite peaks contain same multiplicity as listed for main resonance. [h] Satellite resonances due to the two magnetically active tin isotopes were not resolved; this value represents an average value of both coupling constants. [i] Neat liquid and solution at −50°; chemical shift measured for 9% solution in cyclopentane containing 9% toluene as internal standard, whose methyl resonance is taken at $\tau = 7.68$ under these conditions. [j] Multiplet of which only six peaks were separately resolved due to lesser resolution of spectrometer with temperature variation insert, and cold atmosphere around sample near magnet. [k] Data taken from Duffy, Feeney and Holliday[3] converted to τ-values by taking the resonance of their external standard CH_2Cl_2 to be at $\tau = 4.7$. [l] H. Spiesecke and W. G. Schneider, *J. Chem. Phys.*, **35**, 726 (1961), measured in the gas phase.

measured in this work. Also, the two resonances reported previously, which would be the ^{207}Pb-satellites of the main methyl peak, show a separation (68 c.p.s.) in satisfactory agreement with that found by us (see Table I). On the other hand, we did not see any resonance at $\tau = 5.8$, and there were other features of the spectrum of this compound as previously reported which did not agree with ours, but this is discussed below (see spin–spin coupling).

Chemical Shift of Metal-bonded Hydrogen in SnH_4, the Methylstannanes and $(CH_3)_3PbH$.—The most striking feature of the proton magnetic resonance in SnH_4, the methylstannanes and $(CH_3)_3PbH$ is the low chemical shift of the metal-bonded hydrogen atom(s) which appears to be less shielded than protons in the methyl group. That this chemical shift is not due to some exchange phenomenon of a labile proton is demonstrated by the spin–spin coupling of the metal-bonded hydrogen with the methyl hydrogens as well as by the appearance of sharp spin–spin coupling satellites due to interaction of the proton with the magnetically active isotopes of the metal (^{117}Sn, ^{119}Sn and ^{207}Pb; see below). The low shielding of protons bonded to tin or lead (τ = 6 and 2, respectively) is in marked contrast to the high shielding found for protons bonded to transition metals (whose chemical shifts are reported to be in the region τ = 15 to 40[2]). Application of the localized diatomic approximations of Kern and Lipscomb[12] to the Sn–H or Pb–H bond might prove an interesting test of that theory, which was considered valid for a light atom bonded to a heavy atom. The anomalous high-field chemical shift for H bonded to Co in $HCo(CO)_4$ was attributed[12] mainly to the electron populations in the large and diffuse 4s- and 4p-orbitals of that metal. For most of the elements following a transition series, the same or analogous orbitals are much less diffuse, in keeping with the general contraction in radii that is observed in moving across a long row in the periodic table. This would qualitatively predict some differences in the shielding of protons in main group metal hydrides as compared to transition metal hydrides.

On the other hand, it might be necessary to take into account factors arising from the nature of the entire molecule containing the M–H bond system, as for instance in the treatment by Fixman.[13] The importance of the other bonds formed by the metal should not be overlooked, as is illustrated by the work of Pitcher, Buckingham and Stone.[14] The anomalous shift to low field of the ^{19}F-resonance of CF_2 groups bonded directly to certain transition metals was attributed[14] in the main to paramagnetic contributions from low-lying excited states in the bonds between the metal and carbon atom of the CF_2 group bonded directly to it. Perhaps some factor inherent in the weakness of the Pb–C bonds compared to the Sn–C bonds accounts for observed differences in the chemical shift in the two series of derivatives.

Chemical Shifts for Methyltin Anions.—Solutions of $(CH_3)_3Sn^-$, Li^+ and $(CH_3)_2Sn^{-2}$, $2Li^+$ in CH_3NH_2 contained a number of small peaks in addition to the peaks attributable to solvent. Knowledge of the chemical shifts (and coupling constants, discussed below) for the methyltin hydrides enabled us to identify the resonances due to the methyltin anions.

The resonance of the methyl protons in $(CH_3)_3Sn:^-$ is assigned at $\tau = 10.4$, and confirmed by the presence of *Sn*CH_3 spin-coupling satellites surrounding the major peak at approximately the expected relative intensity. An attempt was made to observe the resonance in the dianion $(CH_3)_2Sn^{-2}$, formed from the corresponding dihalide and the calculated amount of Li in CH_3NH_2. The resulting solution gave a strong resonance at approximately the same position as that found for solu-

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(12) R. M. Stevens, C. W. Kern and W. N. Lipscomb, *J. Chem. Phys.*, **37**, 279 (1962).

(13) M. Fixman, *ibid.*, **35**, 679 (1961).

(14) E. Pitcher, A. D. Buckingham and F. G. A. Stone, *ibid.*, **36**, 124 (1962).

tions of $(CH_3)_3Sn^-$, near $\tau = 10.4$, so it is unlikely that we were observing the resonance of the free dimethylstannyl dianion in this solution (see also discussion of coupling constants in methyltin anions, below).

Spin–Spin Coupling in SnH_4, the Methylstannanes and $(CH_3)_3PbH$.—Certain interesting trends may be observed in the spin–spin coupling constants presented in Table I. Starting at a maximum value for the Sn–H coupling constant in SnH_4, this parameter decreases progressively upon substitution of methyl groups on tin up to $(CH_3)_3SnH$. For the coupling constant *Sn–CH*$_3$, the value for $(CH_3)_4Sn$ is at a *minimum*, and increases progressively as protons are substituted for methyl groups, up to CH_3SnH_3. These trends may be explained by a combination of the theory of spin–spin coupling and the effects of the electronegativity of a substituent on the hybridization of a central atom.

The Fermi contact contribution[15] to the spin–spin coupling constant between two nuclei is directly proportional to the product of the electron densities of the two bonding orbitals, through which they interact, at their respective nuclei. For atoms with hybridized bonding orbitals, the contact contribution is proportional to the percentage s-character in the hybridized atomic orbital used in forming the bond. In the coupling *Sn–H*, the variation in percentage s-character of the orbital on tin makes the major contribution to the variation in the contact term in the valence bond connecting the two atoms. This is also believed to be true for the *Sn–C*H_3 system since components other than the hybridization of the Sn atomic orbital do not change appreciably (as supported by the observation that the ^{13}C*–H* coupling constants stay practically the same in the series of compounds containing methyl groups bonded to tin; see Table I). The hybridization of the orbitals on tin, however, will depend upon the relative electronegativities of the substituents. We can expect, on the basis of concepts recently expressed and summarized by Bent,[16] that the s-character of an atom tends to concentrate in orbitals that are directed toward the less electronegative groups. In this case, the hydrogen atom, as expected, appears more electronegative than the methyl group.[17] The trends observed, then, are entirely reasonable. Progressive substitution of methyl groups for hydrogen in SnH_4 should cause a *reduction* from 25% in s-character in the Sn-orbitals of the Sn–H bond(s), and also, therefore, a *reduction* in Sn–H coupling, in agreement with observation. Similarly, substitution of H for methyl group in $(CH_3)_4Sn$ should cause progressively an *increase* from 25% in the s-character of the Sn-orbital in the Sn–CH_3 bond(s), and an *increase* in the *Sn-C*H_3 coupling.

In $(CH_3)_3PbH$, the coupling ^{207}Pb*–C*H_3 is seen to increase over that observed in $(CH_3)_4Pb$, in accordance with the trend observed for the analogous tin compounds. It is likely that the same considerations apply in both series of derivatives. In contrast with the previous work,[3] we were able to observe *H*Pb*C*H_3 coupling in $(CH_3)_3PbH$. The methyl protons appeared as a doublet, and the lead-bonded hydrogen atom as a resonance approximating a decet, both containing the same separation, namely 1.4_7 c.p.s. In addition, we observed ^{207}Pb satellites of the Pb*H* resonance. Neither of these was observed by the previous workers. Because of our spectral data (resulting either from increased resolution or improved sample purity) we must conclude that negligible exchange of lead-bonded hydrogen is occurring in the neat (and ammonia-free) liquid during the lifetime of the magnetic resonance experiment.

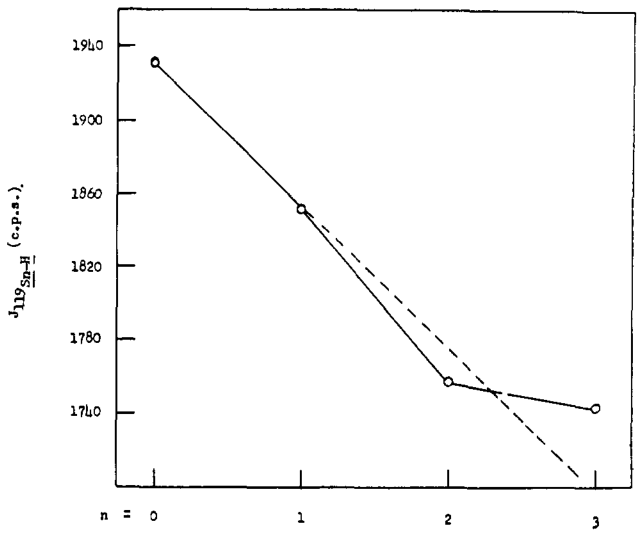

Fig. 1.—$J_{^{119}Sn-H}$ as a function of n for the series $(CH_3)_n$-SnH_{4-n}. If the substituent effects were additive, the points for $n = 2$ and $n = 3$ would have fallen on the extrapolated (dotted) line.

Spin–Spin Coupling in the Methyltin Anions.—The value of the *Sn–C*H_3 coupling constant in $(CH_3)_3Sn\!:^-$, Li^+ is very low (Table I). This is further in qualitative agreement with the concepts reviewed by Bent.[16] An unshared pair may generally be regarded as electrons bound to an atom of essentially zero electronegativity. If so, this would place a great deal of s-character in the lone pair, and decrease that in the tin orbitals in the bonds to the methyl groups.[18] The relationship of the Sn–CH_3 coupling in $(CH_3)_3Sn\!:^-$ to that in $(CH_3)_4Sn$ is approximately comparable to the relationship of ^{31}P*C*H_3 coupling in $(CH_3)_3P\!:$ to that in $(CH_3)_4P^+$. In $(CH_3)_3P\!:$, the coupling is 2.7 c.p.s.[19a] while in the quaternary salt it is 14.6 c.p.s.[19b] The presence of a lone pair on the central atom seems to decrease the coupling of this atom to protons on the groups bonded to it.

The free dianion $(CH_3)_2\ddot{Sn}\!:^{-2}$ would contain two lone pairs and by similar arguments might be expected to show even less *Sn*C*H*$_3$ coupling than in $(CH_3)_3Sn\!:^-$. However, the resonance observed for the reduction product of $(CH_3)_2SnCl_2$ with Li in CH_3NH_2 was a singlet with satellites not markedly shifted from that observed for $(CH_3)_3Sn\!:^-$ (see above) with the important difference that the *Sn*C*H*$_3$ coupling constant was larger, *i.e.*, 19.5 c.p.s. On the basis of the data, we believe that the dimethylstannyl dianion is mostly solvolyzed in CH_3NH_2 solution to give the species $(CH_3)_2HSn\!:^-$. Such a species would not be expected to have any markedly different chemical shift with respect to the

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[15] (a) N. F. Ramsey, *Phys. Rev.*, **91**, 303 (1953); (b) M. Karplus and D. H. Anderson, *J. Chem. Phys.*, **30**, 6 (1959).

[16] H. A. Bent, *Chem. Rev.*, **60**, 275 (1960), and *Can. J. Chem.*, **38**, 1235 (1960).

[17] The electron-attracting abilities of various substituents are estimated by the Taft σ^* function, for which hydrogen has a value of −0.49 compared to the methyl group, 0.00; *cf.* R. W. Taft, in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956.

[18] It has been pointed out that, in particular, for atoms containing non-bonding electrons, a configuration interaction of low-lying triplet states with bonding M.O.'s joining the coupled atoms can lead to a contribution to the coupling of *opposite* sign to the σ-contribution, and result in a lowered net observed coupling constant; *cf.* J. R. Holmes, D. Kivelson and W. C. Drinkard, *J. Chem. Phys.*, **37**, 150 (1962). It is not possible at this time to make any quantitative estimate of this contribution in the systems discussed in this work.

[19] (a) See problem t, p. 21 in J. D. Roberts, "An Introduction to the Analysis of Spin–Spin Splitting . . . .," W. A. Benjamin, Inc., New York, N. Y., 1961, and also verified in these laboratories; (b) G. Martin and G. Mavel, *Compt. rend.*, **253**, 644 (1961).

$(CH_3)_3Sn:^-$ ion, and, by the trends in coupling constants observed in the neutral stannanes, substitution of a hydrogen for a methyl group in the trimethyltin anion would be expected to increase the *SnCH*$_3$ coupling, as observed. Due to rapid solvolytic proton exchange, the tin-bonded hydrogen atom would not be expected to split the tin-methyl resonance into a doublet, nor would it be possible to observe a resonance for this proton as distinct from the solvent protons in such dilute solutions.

Substituent Effects on *Sn–H* and *Sn–CH*$_3$ Coupling.—The effect of substituting CH_3 for H on the coupling *Sn–H* in SnH_4 and the methylstannanes is not strictly additive, as illustrated in Fig. 1. The coupling for $(CH_3)_3SnH$ strongly deviates from the extrapolated straight line, and is larger than might have been expected if the effects were additive. The first three points are nearly linear, except for a slight alternation in positions which, though small, we nevertheless feel is real. A similar pattern of behavior, including a slight alternation, is observed for the effects of substitution of H for CH_3 in the coupling *Sn–CH*$_3$ (starting with $(CH_3)_4Sn$ and extrapolating to the methylstannanes). There have been other observations of non-additivity of substituent effects, such as the increasing positive deviations obtained for *C–H* or *Si–H* coupling, by substitution of halogens (particularly F) in CH_4 or SiH_4,[20] or for the coupling *Sn–CH*$_3$ upon substitution of Cl for CH_3 in $(CH_3)_4Sn$.[4] A discussion of possible explanations for these deviations is given by Juan and Gutowsky.[20b]

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[20] (a) N. Muller and P. I. Rose, *J. Am. Chem. Soc.*, **84**, 3973 (1962); (b) *cf.* discussion and references in C. Juan and H. S. Gutowsky, *J. Chem. Phys.*, **37**, 2198 (1962).

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The Chemical Properties of Dioxygen Difluoride[1]

BY A. G. STRENG

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Dioxygen difluoride has a remarkably high oxidizing power, even at very low temperatures. The reactivity of O_2F_2 with Cl_2, Br_2, I_2, P, S, and their lower fluorides, as well as with the fluorides of nitrogen, with HCl, HBr, H_2S and with some other compounds was studied. Formation of intermediate addition products was observed in the reactions with ClF, BrF_3, SF_4, HCl and HBr. Most intermediates have only a transitory existence.

Introduction

Dioxygen difluoride, O_2F_2, is the second member of the oxygen–fluoride family, consisting of OF_2,[2a] O_2F_2,[2b] O_3F_2[3] and O_4F_2.[4] It is an orange-yellow solid which melts at 109.7°K. to an orange-red liquid. Dioxygen difluoride is sufficiently stable at temperatures below its melting point but decomposes rapidly into O_2 and F_2 at temperatures close to its normal boiling point, 216°K.

Dioxygen difluoride has been known since 1933, when Ruff and Menzel achieved its preparation.[2b] Since then a number of investigations have been devoted to the methods of preparation of O_2F_2 and to its thermodynamic and physical properties[5–8]; but very little has been published about its chemical properties. Only recently, when this paper was ready for typing, there appeared a very interesting article, by R. T. Holzmann and M. S. Cohen [*Inorg. Chem.*, **1**, 972 (1962)], describing the reaction of O_2F_2 with tetrafluoroethylene.

Since dioxygen difluoride is stable only at low temperatures, its chemistry was studied in a temperature region which is substantially below the usual range of chemical studies.

An exploratory study of the behavior and reactivity of dioxygen difluoride with various substances was made in order to obtain information on the basic chemistry of O_2F_2 and its ability to form addition products.

Reagents Used

Dioxygen difluoride was prepared directly from the elements by the method described elsewhere.[9] It was stored in a Pyrex glass cylinder, frozen at 90°K. Chlorine monofluoride, ClF, nitryl fluoride, NO_2F, phosphorus trifluoride, PF_3, and silicon tetrafluoride, SiF_4, were also prepared by the well known methods.[10–13]

All other reagents were the commercial products of the highest available purity, supplied by Stauffer Chemical Co., General Chemical Division of Allied Chemical Co., Pennsalt Chemicals Corp., E. I. du Pont de Nemours and Co., Matheson Co., Air Reduction Co. and others. Most of these reagents were further purified by fractional distillation.

Experimental Technique

The experiments were carried out either in a closed vacuum system made of Pyrex glass or in one made of Kel-F, fitted with stainless-steel valves and T-pieces. Mercury manometers with a protective layer of Kel-F oil were used for measuring the gas pressure.

The experimental conditions were varied according to the requirements of each combination of reagents. In most cases, O_2F_2 was first frozen on the walls or on the Raschig-ring packing of the reaction vessel. The second reagent was then added in small portions by vacuum distillation and condensed above the O_2F_2. The vessel was then slowly warmed to the temperature of reaction. The solid and liquid products remained in the reaction vessel, and the gaseous products were removed for analysis. The reaction vessel was then cooled again to the original

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[1] This paper describes a part of the work sponsored by the Office of Naval Research, under Contract Nonr-3085(01).

[2] (a) P. Lebeau and A. Damiens, *Compt. rend.*, **185**, 652 (1927); (b) O. Ruff and W. Menzel, *Z. anorg. u. allgem. Chem.*, **211**, 204 (1933).

[3] S. Aoyama and S. Sakuraba, *J. Chem. Soc. Japan*, **59**, 1321 (1938).

[4] A. V. Grosse, A. G. Streng and A. D. Kirshenbaum, *J. Am. Chem. Soc.*, **83**, 1004 (1961).

[5] O. Ruff and W. Menzel, *Z. anorg. u. allgem. Chem.*, **217**, 85 (1934).

[6] H. J. Schumacher and P. Frisch, *Z. physik. Chem.*, **B37**, 1 (1937).

[7] A. D. Kirshenbaum and A. V. Grosse, *J. Am. Chem. Soc.*, **81**, 1277 (1959).

[8] A. D. Kirshenbaum and A. G. Streng, *J. Chem. Phys.*, **35**, 1440 (1961).

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