

Alkoxybis(trifluoromethyl)arsines¹

Anton B. Burg and Jaswant Singh

Contribution from the Department of Chemistry, University of Southern California, Los Angeles, California 90007. Received September 25, 1964

The new alkoxyarsines (arsinite esters) $\text{CH}_3\text{OAs}(\text{CF}_3)_2$ (b.p. est. 71°) and $t\text{-C}_4\text{H}_9\text{OAs}(\text{CF}_3)_2$ (b.p. est. 116°) were made by alcoholysis of $(\text{CF}_3)_2\text{AsCl}$, using $(\text{CH}_3)_3\text{N}$ to remove HCl. Unlike the analogous alkoxyphosphines, these do not isomerize in the Arbuzov manner but do form 1:1 BF_3 adducts and react further to produce $(\text{CF}_3)_2\text{AsF}$; cleavage by HCl also occurs. It is understood that arsenic here is both more weakly basic than phosphorus and a less effective π -bond acceptor. Cleavage of $(\text{CF}_3)_2\text{AsOAs}(\text{CF}_3)_2$ by HCl converts both $(\text{CF}_3)_2\text{As}$ groups to $(\text{CF}_3)_2\text{AsCl}$; no $(\text{CF}_3)_2\text{AsOH}$ is observed. Attempts to make the phosphoxyarsine $(\text{CF}_3)_2\text{POAs}(\text{CF}_3)_2$ gave instead $\text{As}_2(\text{CF}_3)_4$ and a higher oxidation state of phosphorus. Similarly, the attempt to make $(\text{CF}_3)_2(\text{O})\text{P}-\text{P}(\text{CF}_3)_2$ by the amine hydrochloride method gave $\text{P}_2(\text{CF}_3)_4$ and the 2:1 amine adduct of $[(\text{CF}_3)_2\text{PO}]_2\text{O}$. Accurate infrared spectra are reported for $(\text{CF}_3)_2\text{AsF}$ and the two alkoxyarsines.

Alkoxybis(trifluoromethyl)phosphines have been made easily by alcoholysis methods^{2,3} which failed for the analogous alkoxyarsines⁴; even attempts to use sodium alkoxides to make $\text{ROAs}(\text{CF}_3)_2$ compounds led at best only to the diarsoxane.⁴ It could be understood that $(\text{CF}_3)_2\text{AsAs}(\text{CF}_3)_2$ and the $(\text{CF}_3)_2\text{AsX}$ compounds are weaker Lewis acids than the analogous phosphines and accordingly are less able to undergo the pertinent $\text{S}_\text{N}2$ alcoholyses; but a vigorously active base might well remove or decompose the CF_3 groups. However, we now have found that high yields of $\text{ROAs}(\text{CF}_3)_2$ compounds can be obtained by alcoholyses of $(\text{CF}_3)_2\text{AsCl}$ when trimethylamine is used to remove HCl.

The formation of 1:1 BF_3 adducts by the new volatile compounds $\text{CH}_3\text{OAs}(\text{CF}_3)_2$ and $t\text{-C}_4\text{H}_9\text{OAs}(\text{CF}_3)_2$ at -78° showed an oxygen-base action not matched by the corresponding alkoxyphosphines,³ and in the present work the failure of $\text{C}_2\text{H}_5\text{OP}(\text{CF}_3)_2$ to react with BF_3 also was demonstrated. It is argued that the BF_3 must be attached through oxygen rather than arsenic since arsines invariably are weaker bases than the analogous phosphines. The base action here seems to be permitted by a poor $\text{O}_{2p}-\text{As}_{4d}$ π -interaction, such that the O atom has a considerably higher electron density than when it engages in the relatively strong $\text{O}_{2p}-\text{P}_{3d}$ π -bonding which may reasonably be assumed for the $\text{ROP}(\text{CF}_3)_2$ compounds.

In further contrast to the alkoxyphosphines, the $\text{ROAs}(\text{CF}_3)_2$ compounds react further with BF_3 in the sense of the fluoride-shift reaction previously ob-

served for boron, silicon, and some carbon compounds,⁵ but not for any of the alkoxyphosphines. Thus both the methoxy- and butoxyarsines give high yields of $(\text{CF}_3)_2\text{AsF}$ and presumably the decomposition products of ROBF_2 .

Related to the poor basic character of arsines is the failure of either alkoxyarsine to undergo an Arbuzov-type isomerization.

Yet another contrast to the CF_3-P chemistry is found in the cleavage of $(\text{CF}_3)_2\text{AsOAs}(\text{CF}_3)_2$ by HCl. Whereas $(\text{CF}_3)_2\text{POP}(\text{CF}_3)_2$ and HCl give $(\text{CF}_3)_2\text{POH}$ and $(\text{CF}_3)_2\text{P}-\text{P}-\text{Cl}$,³ the cacodyl oxide $(\text{CF}_3)_2\text{AsOAs}(\text{CF}_3)_2$ reacts with 2HCl to form H_2O and $2(\text{CF}_3)_2\text{AsCl}$. Apparently any initially formed $(\text{CF}_3)_2\text{AsOH}$ either dehydrates at once to form the cacodyl oxide or reacts directly with more HCl to form H_2O and $(\text{CF}_3)_2\text{AsCl}$ —whereas $(\text{CF}_3)_2\text{POH}$ is quite stable and inert to HCl.³ Again the explanation seems to concern the poor π -bonding action of As_{4d} : whereas $(\text{CF}_3)_2\text{POH}$ is stabilized by $\text{O}_{2p}-\text{P}_{3d}$ π -bonding (and dehydration would lead to a net loss of such π -bonding), the $\text{O}_{2p}-\text{As}_{4d}$ π -interaction is inadequate for such stabilization. Indeed, it appears that the As-Cl bonding here is stronger than the As-O bonding (for the bond energies of H-Cl and H-OH are not very different), whereas the opposite is true for the P-Cl vs. P-O bonding. The situation thus has some similarity to the well-known formation of AsCl_3 from the oxide in concentrated hydrochloric acid solutions—in contrast to the complete hydrolysis of PCl_3 .

Related to the present study were unsuccessful attempts to demonstrate the existence of the phosphinoarsine $(\text{CF}_3)_2\text{PAs}(\text{CF}_3)_2$ and the phosphoxyarsine $(\text{CF}_3)_2\text{POAs}(\text{CF}_3)_2$ by at least two methods. One method sought evidence for a P-P and As-As bond exchange whereby $\text{P}_2(\text{CF}_3)_4$ and $\text{As}_2(\text{CF}_3)_4$ would form $2(\text{CF}_3)_2\text{PAs}(\text{CF}_3)_2$; however, the infrared spectrum of the mixture was not sufficiently different from the sum of the separate spectra, except for some uncertain differences of band intensity. No better result came from the reaction of $(\text{CF}_3)_2\text{AsCl}$ and $(\text{CF}_3)_2\text{PH}$ with $(\text{CH}_3)_3\text{N}$ to remove HCl. The phosphinoarsine may exist in equilibrium with the diphosphine and diarsine, but better evidence is needed. An argument against it would be a considerably smaller delocalization of P_{3p} lone-pair electrons by $\text{P}_{3p}-\text{As}_{4d}$ π -interaction than in the corresponding $\text{P}_{3p}-\text{P}_{3d}$ π -interaction.

When the phosphoxyarsine was sought both by the bond-exchange method (P-O-P with As-O-As) and by the amine hydrochloride method, the chief intelligible product was the diarsine $\text{As}_2(\text{CF}_3)_4$. Hence, phosphorus must have been oxidized, either to the diphosphine dioxide $[(\text{CF}_3)_2\text{PO}]_2$ or to the phosphinic anhydride $[(\text{CF}_3)_2\text{PO}]_2\text{O}$. The latter represents the better hypothesis, for an attempt to make the diphosphine monoxide $(\text{CF}_3)_2(\text{O})\text{P}-\text{P}(\text{CF}_3)_2$ by the amine

(1) It is a pleasure to acknowledge the support of this research through Grant No. GP-199 from the National Science Foundation, which also aided our acquisition of a Beckman IR7 spectrophotometer with NaCl and CsI optics, through Grants No. 14665 and No. GP-199.

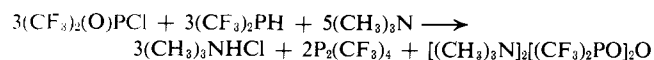
(2) H. J. Emeléus and J. D. Smith, *J. Chem. Soc.*, 380 (1959).

(3) J. E. Griffiths and A. B. Burg, *J. Am. Chem. Soc.*, **84**, 3442 (1962).

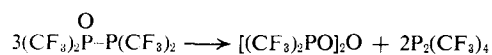
(4) W. R. Cullen, *Can. J. Chem.*, **40**, 575 (1962).

(5) A. B. Burg and J. Banus, *J. Am. Chem. Soc.*, **76**, 3903 (1954).

method led rather to results best interpreted by the equation



Hence it appears that the diphosphine monoxide is unstable relative to a mixture of the diphosphine and the double amine adduct of the phosphinic anhydride; and perhaps even without the amine it would disproportionate according to the equation



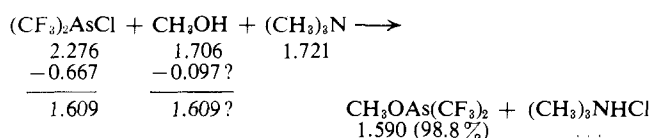
without showing evidence of $[(\text{CF}_3)_2\text{PO}]_2$ as an intermediate.

The experimental work here described was performed by means of a high-vacuum manifold, including series of U-traps and mercury float valves for quantitative high-vacuum fractional condensation. Stopcocks were employed only in such a manner as not to affect quantitative manipulation of the volatile products, or where mercury-sensitive materials were concerned.

Syntheses and Characterizations

Methoxybis(trifluoromethyl)arsine. The iodoarsine $(\text{CF}_3)_2\text{AsI}$ was made by the literature method^{6,7} and converted to $(\text{CF}_3)_2\text{AsCl}$ by necessarily repeated contact with fresh HgCl_2 . For the initial synthesis of $\text{CH}_3\text{OAs}(\text{CF}_3)_2$ the millimole quantities were 3.429 $(\text{CF}_3)_2\text{AsCl}$, 3.553 CH_3OH , and 3.553 $(\text{CH}_3)_3\text{N}$, the last being introduced into the mixture of the others at -30° ; then the mixture stood for 2 hr. at 24° . The final recovery of $\text{CH}_3\text{OAs}(\text{CF}_3)_2$ represented only 85% of the $(\text{CF}_3)_2\text{As}$ groups, and the loss could be attributed to occlusion in the $(\text{CH}_3)_3\text{NHCl}$ and absorption when P_4O_{10} was used to remove the unused methanol.

A more nearly quantitative synthesis is shown by the following stoichiometric equation, with which the quantities employed and recovered are shown in millimoles.



In this experiment the mixture was first allowed to react during 30 min. at 24° and then heated in a sealed tube for 12 hr. at 70° . Then after removal of the volatiles *in vacuo* at 24° the residue was heated further to remove occluded volatiles. The $\text{CH}_3\text{OAs}(\text{CF}_3)_2$ fraction was isolated by high-vacuum fractional condensation in a trap at -78° , through which the excess $(\text{CF}_3)_2\text{AsCl}$ passed slowly. This excess chloroarsine was identified as pure by its molecular weight (249 vs. calcd. 248.5), its 103-mm. volatility at 0° , and its known infrared spectrum.⁸ The yield estimate as 98.8% of the unrecovered $(\text{CF}_3)_2\text{AsCl}$ is based upon the 391.0-mg.

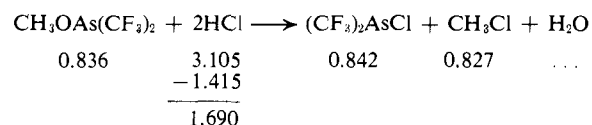
(6) G. R. A. Brandt, H. J. Emel us, and R. N. Haszeldine, *J. Chem. Soc.*, 2552 (1952).

(7) E. G. Walaschewski, *Chem. Ber.*, 86, 273 (1953).

(8) H. J. Emel us, R. N. Haszeldine, and E. G. Walaschewski, *J. Chem. Soc.*, 1552 (1953).

weight of the volatile product, from which we have subtracted 3.1 mg. to account for the possible presence of 0.097 mmole of unused CH_3OH in that fraction. The 0.112-mmole implication of unused $(\text{CH}_3)_3\text{N}$ remains unaccounted for, but this amine could not have been present in the $\text{CH}_3\text{OAs}(\text{CF}_3)_2$ fraction. The final purification of the $\text{CH}_3\text{OAs}(\text{CF}_3)_2$ was by contact with freshly sublimed P_4O_{10} , whereby any remaining CH_3OH would be removed.

The formula $\text{CH}_3\text{OAs}(\text{CF}_3)_2$ was confirmed by determination of the molecular weight in the vapor phase: 244.3 and 244.1 vs. calcd. 244.0. An 80.0-mg. sample (0.3274 mmole), shaken with 15% NaOH solution, gave 0.645 mmole of well-identified HCF_3 (calcd. 0.655 mmole). The HCl cleavage of a 204.1-mg. sample (sealed tube, 12 hr. at 80°) showed the following stoichiometric equation, with quantities in millimoles.



Here again, the $(\text{CF}_3)_2\text{AsCl}$ was identified as pure by its molecular weight, volatility, and infrared spectrum. The CH_3Cl was identified by its molecular weight (50.2 vs. calcd. 50.5), its 39-mm. volatility at -78° , and its well-known infrared spectrum.

t-Butoxybis(trifluoromethyl)arsine. The new compound $t\text{-C}_4\text{H}_9\text{OAs}(\text{CF}_3)_2$ was made primarily in order to test whether it could undergo an Arbuzov-type isomerization, as the analogous $t\text{-C}_4\text{H}_9\text{OP}(\text{CF}_3)_2$ does more easily than $\text{CH}_3\text{OP}(\text{CF}_3)_2$.³ However, there was no change when $t\text{-C}_4\text{H}_9\text{OAs}(\text{CF}_3)_2$ was heated with CH_3I for 144 hr. at 85° . The isomerization could not have occurred during the synthesis, for a BF_3 cleavage gave a major yield of $(\text{CF}_3)_2\text{AsF}$, as described in a later section.

For the synthesis, a vapor-phase mixture of 1.962 mmoles of $(\text{CF}_3)_2\text{AsCl}$ and 1.965 mmoles of $t\text{-C}_4\text{H}_9\text{OH}$ at -20° was treated with $(\text{CH}_3)_3\text{N}$ slightly in excess, introduced from below. After 2 hr. at 24° the volatiles were reflux-fractionated *in vacuo* at -78° , removing a 0.073 most volatile fraction; then unused *t*-butyl alcohol was absorbed by P_4O_{10} . The yield of pure product was 533.8 mg. (1.866 mmoles), representing 95.1% of the initial $(\text{CF}_3)_2\text{AsCl}$. The deficiency is ascribed to occlusion in the $(\text{CH}_3)_3\text{NHCl}$; thus the analogy to the synthesis of $\text{CH}_3\text{OAs}(\text{CF}_3)_2$ seems exact. The molecular formula $t\text{-C}_4\text{H}_9\text{OAs}(\text{CF}_3)_2$ was confirmed by the molecular weight (vapor phase; 285.6 vs. calcd. 286.0) and the 1:1 BF_3 adduct, described later. The infrared spectrum also is confirmatory.

Volatilities. The equilibrium vapor pressure curves of the two alkoxyarsines gave good evidence of purity. For $\text{CH}_3\text{OAs}(\text{CF}_3)_2$ the data and equation of Table I

Table I. Volatility of $\text{CH}_3\text{OAs}(\text{CF}_3)_2$
($\log P = 7.4884 + 1.75 \log T - 0.007168T - 2263/T$)

Temp., $^\circ\text{C}$.	-31.3	-18.7	-15.3	0.00	16.2	19.4	26.3
P_{obsd} , mm.	3.71	9.63	12.15	32.3	80.2	94.0	131.4
P_{calcd} , mm.	3.72	9.59	12.16	32.4	79.8	94.0	131.7

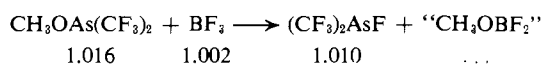
give the normal b.p. as 70.7° and the Trouton constant (T.C.) as 22.3 e.u.; and, for *t*-C₄H₉OAs(CF₃)₂, b.p. 116.1° and T.C. = 21.7 e.u. (Table II). The above-normal Trouton constants would imply some polarity.

Table II. Volatility of *t*-C₄H₉OAs(CF₃)₂
(log *P* = 6.1250 + 1.75 log *T* - 0.004900*T* - 2281/*T*)

Temp., °C.	-5.6	0.00	3.5	21.1	24.8	47.2	51.8
<i>P</i> _{obsd.} , mm.	3.54	5.10	6.38	17.9	21.9	66.1	81.2
<i>P</i> _{calcd.} , mm.	3.51	5.10	6.20	18.1	22.1	66.2	80.9

The Methoxyarsine with Boron Trifluoride. When 0.360 mmole of CH₃OAs(CF₃)₂ and 0.402 mmole of BF₃ were condensed together in a stopcocked reaction tube and left to react at -78°, there was a steady decrease of pressure, reaching a limit after 2 hr. The excess BF₃ was drawn off and measured as 0.044 mmole (absorbed, 0.368), leaving the composition CH₃OAs(CF₃)₂·0.994BF₃. When this product (nonvolatile at -78°) was quickly evaporated and measured as a gas, its average molecular weight was 171, only moderately higher than would be calculated for complete dissociation (156).

In another experiment a mixture of 1.256 mmoles of CH₃OAs(CF₃)₂ and 3.448 mmoles of BF₃ was left for 48 hr. at 24°. The mixture then was subjected to reflux fractionation under high vacuum at -78°, and the effluent was further separated by high-vacuum fractional condensation (-100 to -196°). Recovered were 0.240 mmole of CH₃OAs(CF₃)₂ and 2.446 mmoles of BF₃; the yield of (CF₃)₂AsF was 1.010 mmoles. Thus the stoichiometric equation is written (millimoles)

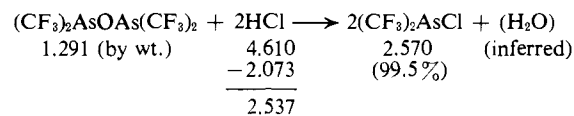


Afterward, the recovery of more BF₃ from the least volatile part suggested the decomposition of "CH₃OBF₂."

The (CF₃)₂AsF was fully identified by its molecular weight (232.8 vs. calcd. 231.9), its volatility (59 mm. at -24° vs. lit.⁸ 62 mm.), and its infrared spectrum.⁸ Our more extensive infrared spectrum is recorded in Table III, along with the spectra of the alkoxyarsines.

The Butoxyarsine with Boron Trifluoride. A mixture of 0.376 mmole of *t*-C₄H₉OAs(CF₃)₂ and 0.416 mmole of BF₃ was kept at -78° for 3 hr., after which 0.046 mmole of BF₃ could be recovered. Thus the formula of the adduct could be written as *t*-C₄H₉OAs(CF₃)₂·0.984BF₃. On warming to 24° a further reaction yielded mainly (CF₃)₂AsF, but a slight trace of (CF₃)₂AsOAs(CF₃)₂ could be identified by its very intense As-O-As stretching band, having peaks at 820 and 800 cm.⁻¹.

The Diarsoxane with HCl. In an attempt to make (CF₃)₂AsOH, the cacodyl oxide, (CF₃)₂AsOAs(CF₃)₂, was heated with dry HCl in a sealed tube for 6 days at 80°—conditions analogous to the synthesis of (CF₃)₂POH.³ However, the main product was (CF₃)₂AsCl, according to the following equation, to which is attached the stoichiometry in mmoles (by gas volume measurement except where weight is specified).



The product (CF₃)₂AsCl here also was identified by its molecular weight (249.4 vs. calcd. 248.4), its volatility (103.5 mm. at 0° vs. lit.⁷ 103.2), and its infrared spectrum.⁸

Table III. Infrared Spectra of Three Arsines^a

Suggested assignments	(CF ₃) ₂ AsF	CH ₃ OAs-(CF ₃) ₂	<i>t</i> -C ₄ H ₉ OAs-(CF ₃) ₂
C-H stretching	...	3006 (1.1)	2993 (8.0)
	...	2966 (1.6)	2976 (5.7)
	...	2946 (2.2)	2948 (2.3)
	...	2844 (2.1)	2918 (1.3)
CH ₃ , δ-a	...	1450 (0.8)	1470 (1.24)
	CH ₃ , δ-e	...	1397 (2.0)
		...	1375 (7.9)
C-F stretching	1213 (47)	1206 (32)	1205 (43)
	1164 (45)	1189 sh (15)	1186 (28)
	1133 (57)	1159 (49)	1158 (87)
	1124 (51)	1121 (58)	1116 (62)
	1119 sh (40)
C-O stretching	...	1034 (19)	926 sh (10)
	912 (15)
<i>t</i> -C ₄ H ₉ effects	891 (2)
	873 (0.3)
	822 (0.45)
	783 (3.0)
CF ₃ , δ-e	739R (2.0)	732 (1.6)	731 (1.7)
	735Q (2.4)
	731P (1.9)
As-F } stretching	692 (11)	634 (3.9)	653 (1.8)
	As-O }
CF ₃ , δ-a	536 (0.36)	535 (0.26)	534 (0.3)
As-CF ₃ stretching	346 (3.4)	357 (1.4)	524 sh (0.16)
	328.5 (3.2)	330.5 (1.5)	338.3 (2.5)
CF ₃ rocking or wagging; CH ₃ torsion?	Not sought	291.5 (0.3)	321 (2.0)
	...	249.5 (0.2)	Not sought
...	...	220 (0.1)	...

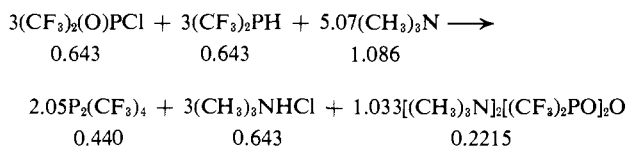
^a Abbreviations: sh = shoulder; δ = deformation; a = asymmetric; e = symmetric.

The Attempt to Make a Diphosphine Monoxide. A mixture of 1.104 mmoles each of (CF₃)₂(O)PCL and (CF₃)₂PH, in vapor form at -50°, was treated with 1.130 mmoles of (CH₃)₃N, entering slowly from below. After slow warming to 24°, the volatiles were separated by high-vacuum fractional condensation, proving to be 0.461 mmole of (CF₃)₂PH, 0.417 mmole of (CF₃)₂(O)PCL, and 0.440 mmole of P₂(CF₃)₄. The purity of the diphosphine was proved by the strict conformity of its infrared C-F stretching pattern to the known frequencies and intensities⁹; no foreign C-F bonds could have been present. Confirmatory was the absence of the intense P=O and P-O-P stretching bands, respectively indicative of a phosphine oxide and a diphosphoxane.³

For a process promoted by amine-removal of HCl, the (CF₃)₂(O)PCL and the (CF₃)₂PH would have been consumed in equimolar proportion. Hence it is reasonable to assume that the 0.044-mmole excess consumption of (CF₃)₂(O)PCL over (CF₃)₂PH was due to occlusion of 0.044 mmole of the expected amine com-

(9) A. B. Burg and J. F. Nixon, *J. Am. Chem. Soc.*, **86**, 357 (1964).

plex $(\text{CF}_3)_2(\text{O})\text{P}(\text{Cl})\cdot(\text{CH}_3)_3\text{N}$ in the solid $(\text{CH}_3)_3\text{NHCl}$. On this basis the main reaction balance would be given in millimoles as



Thus the stoppage when only 60% of the phosphorus reactants had been consumed was due to removal of some 40% of the amine to form the double-amine complex of the phosphinic anhydride.

Infrared Spectra

The infrared spectra of the three compounds shown in Table III were recorded by the Beckman IR7 instrument, using NaCl or CsI optics and windows of KBr or high-density polyethylene, as appropriate. Calibration by well-known bands limited the probable error to 1 cm^{-1} for frequencies below 2000 cm^{-1} . The relative intensity of each feature (peak or shoulder) is shown in parentheses after the frequency (cm^{-1}) and was calculated by the arbitrary definition $k = (100/PL) \log I_0/I$ for pressure P and path L , both in cm. For this purpose the I values were taken quite

literally, so that overlapping bands are overestimated in relation to true intensities.

The assignments are based primarily upon comparisons with phosphorus compounds, assuming that the bonds to arsenic are considerably weaker and vibrate with slightly higher reduced masses. For example, the CF_3 deformation modes generally run about 30 cm^{-1} lower than those for phosphorus compounds, while the As– CF_3 and As–O stretching modes appear about 100 cm^{-1} lower than those for P– CF_3 and P–O.

Not listed in Table III were numerous overtones and combinations for which assignment would be difficult. Very similar for the three compounds were bands at 1266 (1.9), 1263 (1.7), and 1252 (2.6) cm^{-1} , respectively, all probably enhanced by proximity to the very strong C–F stretching bands. The following list of other minor peaks is not necessarily complete: for $(\text{CF}_3)_2\text{AsF}$, 1060 (0.7), 1036 sh (0.4), and 1030 (0.6); for $\text{CH}_3\text{OAs}(\text{CF}_3)_2$, 2237 (0.4), 2050 (0.2), 1890 (0.03), 1850 (0.05), 1666 (0.25), 614 sh (0.7), 475 sh (0.02), and 447 (0.02); for $t\text{-C}_4\text{H}_9\text{OAs}(\text{CF}_3)_2$, 2317 (0.2), 2231 (0.4), 1660 (0.2), and 1563 (0.34)—all in cm^{-1} with relative intensities in parentheses as usual.

The absence of some methyl-group modes is not unusual in compounds having high polarity elsewhere in the molecule; comparison with Table XII of ref. 3 is pertinent.

Halogen Complexes. I. An Investigation by Nuclear Magnetic Resonance of Complexes Formed by Iodine and Some *para*-Substituted Phenyl Methyl Sulfides

David Walter Larsen and A. L. Allred¹

Contribution from the Department of Chemistry and Materials Research Center, Northwestern University, Evanston, Illinois. Received September 23, 1964

According to n.m.r. measurements, the enthalpy of association of iodine and *p*-methoxyphenyl methyl sulfide in carbon tetrachloride is $-6.2 \pm 0.7\text{ kcal./mole}$. The mean lifetime of the complex was measured for several concentrations at -27° . Inductive effects appear to control the association of iodine with various *para*-substituted phenyl methyl sulfides.

Introduction

In the present research, nuclear magnetic resonance spectroscopy provides several types of information about halogen complexes. The mean lifetimes of many halogen complexes in solution have magnitudes in the range where measurement of lifetimes by n.m.r. is feasible. Also, inductive effects and thermodynamic constants may be measured and the results compared with those from other techniques.

Iodine-sulfide systems have²⁻⁸ been investigated previously by cryoscopy, measurements of dipole

moments, and spectrophotometric studies in the visible and ultraviolet regions. For the association of iodine and simple sulfides such as dimethyl, diethyl, and dibenzylsulfides in inert solvents, the equilibrium constants tend to be in the range 30 to 250 l. mole⁻¹ at room temperature and ΔH is usually in the range -6 to -9 kcal./mole .

Experimental

Reagents and Solutions. Methyl phenyl sulfide, *p*-bromophenyl methyl sulfide, *p*-nitrophenyl methyl sulfide, and *p*-methoxyphenyl methyl sulfide were kindly supplied by Dr. W. Brannen of this department. The preparation and purification are described elsewhere.⁹

(3) H. Tsubomura and R. P. Lang, *ibid.*, **83**, 2085 (1961).

(4) M. Good, A. Major, J. Nag-Chaudhuri, and S. P. McGlynn, *ibid.*, **83**, 4329 (1961).

(5) M. Tamres and S. Searles, Jr., *J. Phys. Chem.*, **66**, 1099 (1962).

(6) J. D. McCullough and D. Mulvey, *J. Am. Chem. Soc.*, **81**, 1291 (1959).

(7) J. D. McCullough and I. C. Zimmermann, *J. Phys. Chem.*, **66**, 1198 (1962); *ibid.*, **65**, 888 (1961).

(8) K. A. Jensen, *Z. anorg. allgem. Chem.*, **250**, 245 (1943).

(9) W. Brannen, Thesis, Northwestern University, 1962.

(1) Alfred P. Sloan Research Fellow.

(2) N. W. Tideswell and J. D. McCullough, *J. Am. Chem. Soc.*, **79**, 1031 (1957).