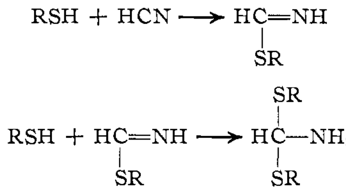
intensity to about half and after the addition of 2 equiv of the thiol, no 2086-cm^{-1} band could be found. It is clear that the thiol added to the cyanide ion (or hydrogen cyanide) in a fashion such as



$$\mathrm{RSH + HCN \longrightarrow \underset{SR}{HC{=}NH}}$$

$$\mathrm{RSH + \underset{SR}{HC{=}NH} \longrightarrow \overset{SR}{\underset{SR}{HC{-}NH_2}}}$$

Attempts were made to isolate and characterize the product of the reaction which precipitates when the reaction is carried out in aqueous solution. However, it is quite unstable and we were not successful in characterizing it.

It is interesting to note that Kolthoff found a maximum rate depression when the thiol:cyanide ratio was about 2:1 in agreement with the stoichiometry observed above. The slower oxidation at higher cyanide ion concentrations is probably due to oxidation of the thiol–cyanide complex. The simplest interpretation for the course of the thiol oxidation is then

$$\mathrm{RSH + HO^- \rightleftharpoons RS^- + H_2O} \quad \text{(fast)}$$

$$\mathrm{RS^- + Fe(CN)_6{}^{3-} \longrightarrow RS\cdot + Fe(CN)_6{}^{4-}} \quad \text{(slow)}$$

$$\mathrm{2RS\cdot \longrightarrow RSSR} \quad \text{(fast)}$$

Thus this reaction also appears to fall in the pattern suggested at the beginning of this paper.

Ligand displacement on ferricyanide has also been proposed as a step in the ferricyanide oxidation of sulfite ion.[7] More recently, Swinehart has prepared the supposed intermediate and has found that it does not behave in the required fashion.[8] We also have examined the reaction by adding excess labeled cyanide ion to the ferricyanide solution before the addition of sulfite ion. The ferrocyanide isolated at the end of the reaction had an activity corresponding to 0.01 ± 0.01% exchange. Thus, ligand displacement does not occur, and the reaction probably involves electron abstraction from sulfite.[8]

The ferricyanide oxidation of iodide ion has an unusual rate law,[9] which might suggest ligand displacement. Again, the addition of labeled cyanide prior to the initiation of the reaction led to an insignificant amount of exchange, 0.014 ± 0.01%.

Since none of the typical good nucleophiles, CN^-, RS^-, $S_2O_3{}^{2-}$, and I^-, is able to effect reasonably rapid ligand displacement on ferricyanide, it appears unlikely that any ferricyanide oxidation will involve such a step. Ferricyanide appears to react uniquely *via* electron transfer.

Experimental Section

Reaction of 2-Mercaptoethanol with Cyanide Ion.—A 2 *M* aqueous potassium cyanide solution was found to have its $C{\equiv}N$ Raman line at 2086 cm^{-1}. A 0.5 *M* solution of potassium cyanide in 60% acetone had a peak at the same position. The addition of enough 2-mercaptoethanol to make a 0.5 *M* solution led to a decrease in the 2086-cm^{-1} band to approximately half of its original intensity. When the amount of mercaptoethanol corresponded to a 1 *M* solution, the 2086-cm^{-1} band disappeared.

When 2-mercaptoethanol was added to 1 *M* aqueous potassium cyanide, a pale yellow precipitate was formed which rapidly darkened on exposure to air.

Ferricyanide Oxidation of *n*-Octanethiol.—To a 250-ml flask was added 60 ml of acetone and a solution of potassium ferricyanide (0.24 g, 7.2×10^{-4} mole) in 40 ml of 2.5×10^{-3} *M* potassium carbonate–2.5×10^{-3} *M* potassium bicarbonate buffer. To this solution was added 7 ml (5.4×10^{-3} mole, 6.56×10^{5} dpm/ml) of potassium cyanide-C^{14} solution and 0.1 g (7.2×10^{-4} mole) of *n*-octanethiol. The mixture was cooled in an ice bath, and yellow crystals of potassium ferrocyanide precipitated over a period of 3 hr, giving 0.04 g (13%) after washing with 60% acetone. The ferrocyanide was dissolved in 1 ml of water and counted in a liquid scintillation counter using Cab-O-Sil and a toluene solution of PPO and POPOP.[10] After correcting for the acivity due to potassium an activity of 31 dpm was found. Thus, the maximum extent of exchange was 0.04%.

Oxidation of Sulfite Ion.—To a solution of 0.316 g (0.96 mmole) of potassium ferricyanide in 35 ml of water was added 5 ml of potassium cyanide-C^{14} solution (3.85 mmole, 5.16×10^{5} dpm/ml) and 0.114 g (0.72 mmole) of potassium sulfite. After 0.5 hr at room temperature, 60 ml of acetone was added and the mixture was cooled in an ice bath for 1 hr. The precipitate of potassium ferrocyanide was washed with 300 ml of cold 60% aqueous acetone in small portions and then with 50 ml of dry acetone. After drying under reduced pressure, titration with permanganate indicated it to be 99+% potassium ferrocyanide. A solution of 0.05 g of the latter in 1 ml of water was counted in a liquid scintillation counter using Cab-O-Sil and a toluene solution of PPO and POPOP. After correcting for the activity due to potassium, the solution gave 5 dpm/0.1 mmole. Thus, the extent of exchange is no greater than 0.01%.

Oxidation of Iodide Ion.—To a solution of 0.593 g (1.8 mmoles) of potassium ferricyanide in 33 ml of water was added 7 ml (5.4 mmoles, 5.16×10^{5} dpm/ml) of potassium cyanide-C^{14} and 0.896 g (5.4 mmoles) of potassium iodide. After 1 hr, the potassium ferrocyanide was isolated as described above and counted giving 7 dpm/0.1 mmole. This corresponds to 0.014% exchange.

---

(7) J. Veprěk-Šiška and D. M. Wagnerová, *Collection Czech. Chem. Commun.*, **10**, 1390 (1965).

(8) J. H. Swinehart, *J. Inorg. Nucl. Chem.*, **27**, 2313 (1967).

(9) A. Indelli and G. C. Guaraldi, *J. Chem. Soc.*, 36 (1964).

(10) C. F. Gordon and A. L. Wolfe, *Anal. Chem.*, **32**, 574 (1960).

CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY,
UNIVERSITY OF MANCHESTER, MANCHESTER, ENGLAND,
AND THE OHIO STATE UNIVERSITY, COLUMBUS, OHIO 43210

The Aggregation of Alkylthiotricarbonylmanganese. Trimeric *vs.* Tetrameric Formulations

BY BRIAN F. G. JOHNSON,[1] PHILIP J. POLLICK,[2]
I. G. WILLIAMS,[1] AND ANDREW WOJCICKI[2]

Received December 13, 1967

Our interest in developing new synthetic routes to thiocyanatocarbonyl complexes of the transition elements has led to an investigation of reactions of the metal carbonyls with the organic thiocyanates. Re-

---

(1) University of Manchester.

(2) The Ohio State University.

ported here are the observations on the behavior of dimanganese decacarbonyl toward methyl and ethyl thiocyanates.

The main products of these reactions are the complexes $[Mn(CO)_3SR]_n$, which we found to be identical with the alkylthiotricarbonyls prepared elsewhere[3] and formulated as trimers on the basis of osmometric molecular weight measurements in benzene. Nevertheless, two early observations were inconsistent with the original trimeric assignments. First, our initial molecular weight determinations, carried out in chloroform, were in much better agreement with the tetrameric rather than the trimeric formulations. Second, a mass spectral study of the dimeric compounds $[M(CO)_4SR]_2$ (M = Mn, R = C_2H_5, n-C_4H_9; M = Re, R = C_6H_5)[4] provided evidence for higher molecular weight species arising from thermal decomposition of the dimers. With manganese, tetramers, $[Mn(CO)_3SR]_4$, were observed whereas with rhenium, both tetramers, $[Re(CO)_3SR]_4$, and trimers, $[Re(CO)_3SR]_3$, were detected.

The foregoing evidence prompted us to reexamine the extent of aggregation, n, of the complexes $[Mn(CO)_3SR]_n$. We now report the results of this study.

Experimental Section

Materials.—Dimanganese decacarbonyl was obtained from Pressure Chemical Co.; it was purified by sublimation at 50° ($\sim$0.1 mm). Methyl and ethyl thiocyanates were purchased from Eastman Organic Chemicals and used without further purification. All solvents, except hexane and low-boiling (30–60°) petroleum ether, were reagent grade. Woelm alumina (acid, grade I) was used in chromatography.

Reaction of Alkyl Thiocyanates with Dimanganese Decacarbonyl.—Dimanganese decacarbonyl (6.0 g, 15 mmoles) was added to methyl thiocyanate (3.0 g, 38 mmoles) in 125 ml of toluene. The reaction mixture was refluxed under nitrogen at an oil bath temperature of 130 ± 10° until the initial yellow color had changed to red-orange and a brown precipitate had begun to appear (*ca.* 1 hr). The solution was evaporated to dryness at 100° ($\sim$20 mm) and the yellow-orange residue was extracted with 300 ml of hexane. The extracts were passed through an alumina column (5 × 4 cm), thus removing the unreacted $Mn_2(CO)_{10}$ (4.3 g), characterized by infrared spectroscopy. Elution with benzene of the first band remaining in the column, followed by the removal of the solvent in a stream of nitrogen, afforded 0.21 g (5.1% based on total dimanganese decacarbonyl) of yellow-orange crystals which decomposed at 210° (uncorrected).

Anal. Calcd for $(C_4H_3O_3SMn)_n$: C, 25.82; H, 1.62. Found: C, 25.52; H, 1.66. Molecular weight data are summarized in Table I.

The infrared spectrum shows CO stretching frequencies (cm^{-1}) at 2048 vw, 2024 vs, 2016 m, 2006 sh, 1986 vw, 1952 vs, and 1910 vw (cyclohexane solution); other prominent peaks (cm^{-1}) are at 2934 w, 1430 m, 1088 vw, 969 m, 669 s, 627 s, 523 m, and 470 vw (KBr pellet). The proton magnetic resonance spectrum consists of a sharp signal at τ 7.69.

Another band was removed from the column with chloroform; however, the material was present in insufficient quantities for characterization.

The analogous ethyl compound was prepared by a similar procedure. It was purified by dissolution in a minimum quantity of chloroform and precipitation with low boiling (30–60°) petroleum ether. The crystals, which were collected on a filter and dried at 25° ($\sim$0.1 mm), melted at *ca.* 200° (uncorrected).

TABLE I

MOLECULAR WEIGHT DATA FOR $[Mn(CO)_3SR]_n$ COMPLEXES

		Mol wt		
		Calcd		Found
R	Solvent	Trimer	Tetramer	
CH_3	Chloroform	558	744	750, 710, 693, 719, 725, 803[a]
C_2H_5	Chloroform	600	800	812
	Cyclohexane			827[b]
	Benzene			637[b]
	Ethyl acetate			815[b]

[a] Measured osmometrically by Galbraith Laboratories, Inc., Knoxville, Tenn. [b] Measured osmometrically by E. W. Abel.

Anal. Calcd for $(C_5H_5O_3SMn)_n$: C, 30.00; H, 2.52. Found: C, 29.82; H, 2.64. Molecular weight data are given in Table I.

The infrared spectrum shows CO stretching absorptions (cm^{-1}) at 2020 vs, 2014 sh, 1992 w, 1965 sh, 1947 vs, 1932 sh, and 1908 w (cyclohexane solution); other prominent bands (cm^{-1}) are at 3000 w, 2984 w, 2943 w, 2885 vw, 2840 vw, 1460 s, 1432 m, 1384 m, 1267 m, 1086 w, 1053 m, 1038 m, 981 m, 771 m, 670 s, 627 s, 523 s, and 470 w (KBr pellet). The proton magnetic resonance spectrum consists of a quartet at τ 7.27 and a triplet at τ 8.84 ($J \sim 8$ cps). A second band was again observed on the column, but the amount of the compound was too small for characterization.

Mass Spectra.—Spectra were measured on an AEI MS-9 mass spectrometer at 70 ev. The most abundant peaks are listed in Tables II and III.

TABLE II

MASS SPECTRUM OF $[Mn(CO)_3SCH_3]_4$[a]

Relative abundances of ions, A			
Ion[b]	A	Ion[b]	A
$Mn_4S_4(CH_3)_4(CO)_{12}^+$	12.0	$Mn_4S_4(CH_3)_4^+$	44.0
$Mn_4S_4(CH_3)_4(CH_3)_4(CO)_9^+$	80.0	$Mn_4S_4(CH_3)_3^+$	40.0
$Mn_4S_4(CH_3)_4(CO)_6^+$	15.4	$Mn_4S_4(CH_3)^+$	56.0
$Mn_4S_4(CH_3)_4(CO)_4^+$	65.0	$Mn_4S_4^+$	52.0
$Mn_4S_4(CH_3)_4(CO)_3^+$	100.0	$Mn_4S_4(CH_3)_4^{2+}$ [c]	39.0
$Mn_4S_4(CH_3)_4(CO)_2^+$	26.0	$Mn_2S_2(CH_3)_2^+$	
		$Mn_4S_4(CH_3)_2^{2+}$ [c]	13.4
$Mn_4S_4(CH_3)_4(CO)^+$	42.0	$Mn_2S_2(CH_3)^+$	

[a] Only ions with relative abundance ⩾12 are included. [b] Additional unassigned peaks: *m/e* 380, A 20.0; *m/e* 353, A 12.0; *m/e* 261, A 16.0. [c] Exact values of abundances were difficult to determine because of extensive overlap of peaks.

TABLE III

MASS SPECTRUM OF $[Mn(CO)_3SC_2H_5]_4$[a]

Relative abundances of ions, A			
Ion	A	Ion	A
$Mn_4S_4(C_2H_5)_3H(CO)_{10}^+$ [b]	52.0	$Mn_4S_4(C_2H_5)^+$	40.0
$Mn_4S_4(C_2H_5)_4(CO)_9^+$		$Mn_4S_4H_2^+$	16.2
$Mn_4S_4(C_2H_5)_3H(CO)_2^+$ [b]	41.0	$Mn_4S_4H^+$	37.0
$Mn_4S_4(C_2H_5)_4(CO)^+$		$Mn_4S_4^+$	83.0
$Mn_4S_4(C_2H_5)_3H(CO)^+$ [b]	34.0	$Mn_4S_4(C_2H_5)_4^{2+}$ [b]	52.0
$Mn_4S_4(C_2H_5)_4^+$		$Mn_2S_2(C_2H_5)_2^+$	
$Mn_4S_4(C_2H_5)_2H(CO)^+$ [b]	27.0	$Mn_4S_4(C_2H_5)_3H^{2+}$	16.2
$Mn_4S_4(C_2H_5)_3^+$		$Mn_4S_4(C_2H_5)_2^{2+}$ [b]	16.2
$Mn_4S_4(C_2H_5)_2H^+$	23.0	$Mn_2S_2(C_2H_5)^+$	
$Mn_4S_4(C_2H_5)H_3^+$	100.0		

[a] Only ions with relative abundance ⩾12 are included. [b] Exact values of abundances were difficult to determine because of extensive overlap of peaks.

Infrared Spectra.—Infrared spectra were recorded on a Beckman Model IR-9 spectrophotometer. Matched 0.05-mm KBr cells were used for measurements on solutions.

X-Ray Diffraction Patterns.—The X-ray powder patterns of

---

[3] E. W. Abel and B. C. Crosse, *J. Chem. Soc., Sect. A*, 1141 (1966).

[4] K. Edgar, B. F. G. Johnson, J. Lewis, I. G. Williams, and J. M. Wilson, *ibid.*, 379 (1967).

the methyl complex were observed with a Debye-Scherrer camera using Cu Kα radiation with a nickel filter.

Proton Magnetic Resonance Spectra.—Nmr spectra were recorded on a Varian Associates A-60 spectrometer using $CDCl_3$ solutions. Tetramethylsilane was employed as an internal standard.

Molecular Weights.—Measurements were made on *ca.* 1 × 10^{-2} *M* solutions with a Mechrolab Model 301-A osmometer.

Analyses.—Microanalyses were performed by A. Bernhardt, Mikroanalytisches Laboratorium im Max-Planck-Institut für Kohlenforschung, Mülheim (Ruhr), Germany.

Results and Discussion

Dimanganese decacarbonyl reacts with methyl and ethyl thiocyanates to yield the alkylthiotricarbonyls, $[Mn(CO)_3SR]_n$, as the main products. These reactions are similar to those reported previously for triiron dodecacarbonyl and several organic thiocyanates.[5,6] There, in addition to metal carbonyl alkyl sulfides, mixed carbonyl alkyl sulfide–sulfide complexes were also isolated. However, no evidence for manganese analogs of the latter compounds was obtained in this study. Because of the relatively low yields of the alkyl sulfides prepared, this method of synthesis offers little advantage over the other procedures reported in the literature.[3,7]

The infrared and proton magnetic resonance spectra of the complexes synthesized in our laboratories are essentially identical with those reported for the $[Mn(CO)_3SR]_3$ derivatives. Furthermore, the X-ray diffraction patterns of the methylthiotricarbonyls prepared here and in Bristol are exactly the same.[8] The combined evidence establishes unequivocally the identity of our derivatives with those previously reported.

In the mass spectra of the methyl and ethyl complexes the most important feature is the appearance of parent molecular ions corresponding to the tetrameric formulations $[Mn(CO)_3SR]_4$. It is significant that peaks corresponding to trimeric species, $[Mn(CO)_3SR]_3$, are not detectable. As has been observed with other polymeric carbonyl compounds,[4,9,10] the fragmentation schemes involve a stepwise loss of carbon monoxide groups to give the ions $Mn_4(SR)_4(CO)_{12-n}^+$ (n = 1–12) and, finally, $Mn_4(SR)_4^+$.

$$Mn_4(SR)_4(CO)_{12}^+ \longrightarrow Mn_4(SR)_4(CO)_{12-n}^+ + nCO \quad (1)$$

This pattern is supported in some measure by the appearance of metastable ions corresponding to the loss of one or more carbonyl groups. With the ethyl derivative, loss of ethylene fragments also occurs, and ions such as $Mn_4S_4(C_2H_5)_3H(CO)_{10}^+$ are observed in significant amounts. In the case of the methyl compound, complete elimination of carbon monoxide is followed by successive loss of CH_3 radicals eventually to give $Mn_4S_4^+$

$$Mn_4S_4(CH_3)_4^+ \longrightarrow Mn_4S_4(CH_3)_{4-m}^+ + mCH_3 \; (m = 0\text{–}4) \quad (2)$$

The pattern is more complicated with the ethyl compound, where loss of ethylene fragments is again observed, *e.g.*

$$Mn_4S_4(C_2H_5)_4^+ \longrightarrow Mn_4S_4(C_2H_5)_3H^+ + C_2H_4 \quad (3)$$

Such removal of olefinic groups from other alkyl sulfide complexes was reported previously.[4]

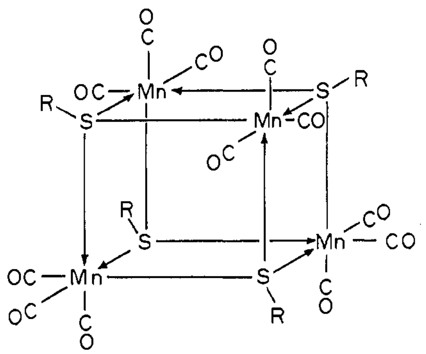


Figure 1.—A possible structure of $[Mn(CO)_3SR]_4$ in which each alkyl sulfide group functions as a five-electron donor.

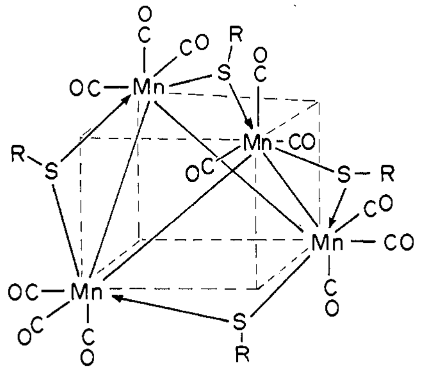


Figure 2.—One of the tautomeric forms describing another possible structure of $[Mn(CO)_3SR]_4$.

Although the above mass spectral data demonstrate the tetrameric nature of the isolated $[Mn(CO)_3SR]_n$ (R = CH_3, C_2H_5) species,[11] osmometric molecular weight measurements, summarized in Table I, seemingly cast some doubt on the integrity of these units in solution. It may be seen that the extent of aggregation, n, is apparently sensitive to the nature of the solvent employed. Accordingly, for the ethyl derivative, n is approximately 4 in cyclohexane, chloroform, and ethyl acetate, but *ca.* 3 in benzene. A parallel behavior is manifested by the *p*-tolyl complex, $[Mn(CO)_3(p\text{-}SC_6H_4CH_3)]_n$; there the values of n range from 3 to 4 depending on the solvent employed.[12]

In order to shed some light on the possible prevalence of trimer–tetramer equilibria in solution, we have carried out the following experiment. Both

---

[5] R. L. Downs, A. Wojcicki, and P. J. Pollick, Abstracts, 148th National Meeting of the American Chemical Society, Chicago, Ill., Aug 30–Sept 4, 1964, p 31-O.

[6] J. M. Coleman, A. Wojcicki, P. J. Pollick, and L. F. Dahl, *Inorg. Chem.*, **6**, 1236 (1967).

[7] A. G. Osborne and F. G. A. Stone, *J. Chem. Soc., Sect. A*, 1143 (1966).

[8] *d* spacings (Å): 8.12 vs, 7.08 m, 3.53 w, 3.23 vw, 3.00 vw, 2.87 vw, 2.72 w, 2.49 vw, 1.96 vw. We thank Dr. E. W. Abel for a sample of the methylthiotricarbonyl from his laboratory.

[9] J. Lewis, A. R. Manning, J. R. Miller, and J. M. Wilson, *J. Chem. Soc., Sect. A*, 1663 (1966).

[10] B. F. G. Johnson, J. Lewis, I. G. Williams, and J. M. Wilson, *ibid.*, 341 (1967).

[11] In the course of preparation of this paper M. Ahmad, G. R. Knox, F. J. Preston, and R. I. Reed, *Chem. Commun.*, 138 (1967), reported preliminary mass spectral results on the methylthiotricarbonyl derivative, their conclusion being in agreement with ours.

[12] E. W. Abel, private communication.

benzene and chloroform solutions containing equimolar mixtures (*ca.* 4.4 mmoles/l. each) of the methyl and the ethyl derivative were stored for 1 hr at 25° in a closed system under nitrogen. Solvent was then removed from each solution in a stream of nitrogen and the residual solids were dried for 1 hr at 25° (~0.01 mm). Mass spectra of these samples showed only ions attributable to the parent methyl and ethyl complexes, and none due to mixed derivatives of the type $Mn_4(CO)_{12}(SCH_3)_n(SC_2H_5)_{4-n}$ (n = 1–3). The latter would be expected to form if equilibrium between the trimeric and the tetrameric species were indeed established in solution. Hence these results support retention of integrity of the tetramers in solution; the apparently contradictory evidence derived from the molecular weight data is not understood.

The exclusively tetrameric nature of $[Mn(CO)_3SR]_n$ species when contrasted with the prevalence of both $[Re(CO)_3SR]_3$ and $[Re(CO)_3SR]_4$[4] further emphasizes structural differences between compounds of the same apparent chemical composition formed by the first and third members of a transition metal triad.[13] Although the structures of $[Mn(CO)_3SR]_4$ cannot be elucidated from the data on hand, one possible molecular arrangement, which bears resemblance to that found in $[(CH_3)_3PtCl]_4$,[14] is depicted in Figure 1. Here each sulfur atom functions as a five-electron donor and no metal–metal bonding need be invoked. Alternatively, the SR groups could lie along four of the edges of a manganese tetrahedron. Such a structure, shown in Figure 2, would require metal–metal interactions; moreover, the possibility of valence tautomerism involving other, similar forms also must be considered.

Acknowledgments.—P. J. P. and A. W. wish to acknowledge support of this study by the National Science Foundation. We are also grateful to Dr. E. W. Abel for the information concerning the molecular weights discussed herein.

(13) See. for example, C. H. Wei and L. F. Dahl, *J. Am. Chem. Soc.*, **88**, 1821 (1966). and references therein.

(14) R. E. Rundle and J. H. Sturdivant, *ibid.*, **69**, 1561 (1947).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
NORTH CAROLINA STATE UNIVERSITY,
RALEIGH, NORTH CAROLINA 27607

Nuclear Magnetic Resonance Studies on Redistribution Reactions of Some Pentavalent Organoantimony and Organoarsenic Dihalides[1]

BY C. G. MORELAND, M. H. O'BRIEN, C. E. DOUTHIT,
AND G. G. LONG

Received May 8, 1967

As previously reported,[2] solutions of two different trimethylantimony dihalides, $(CH_3)_3SbX_2$ and $(CH_3)_3SbY_2$, disproportionate when mixed and form a mixed halide, $(CH_3)_3SbXY$. Similar redistribution reactions have now been observed with compounds in each of the following additional dihalide series: (a) trimethylarsenic, $(CH_3)_3AsX_2$; (b) triphenylarsenic, $(C_6H_5)_3AsX_2$; (c) tribenzylarsenic, $(C_6H_5CH_2)_3AsX_2$; (d) triphenylantimony, $(C_6H_5)_3SbX_2$; and (e) tribenzylantimony, $(C_6H_5CH_2)_3SbX_2$. Reported in this paper are pmr and ^{19}F chemical shifts for the various species in solution and equilibrium constants for redistribution reactions for each series.

Experimental Section

The ^1H and ^{19}F nmr studies were carried out using a Varian HA-100 high-resolution spectrometer equipped with a variable-temperature probe. The temperature of the sample was regulated to ±1° by a Varian variable-temperature controller (V4343) which had been previously calibrated with a thermocouple in place of the sample. The pmr spectra were run on precalibrated chart paper at either 500- or 250-cps sweep width with tetramethylsilane as the internal reference. The ^{19}F chemical shifts were obtained by the side-band technique with $CFCl_3$ as the internal reference. The concentrations of the samples studied ranged from 0.025 to 0.300 M in $CDCl_3$ or $CHCl_3$. The concentration chosen for a given series depended upon the solubility of the compounds. In Table I are reported the pmr and ^{19}F nmr spectral parameters for the various parent dihalides and mixed halides in $CHCl_3$ solution. The chemical shifts for the methyl and methylene protons given in Table I are essentially temperature independent from −20 to 70°.

TABLE I

METHYL AND METHYLENE PROTON AND ^{19}F CHEMICAL SHIFTS FOR R_3MX_2 AND R_3MXY SPECIES IN SOLUTION[a,b]

Species in $CHCl_3$ soln	δ,[c] ppm downfield from TMS at −60°	ϕ^*,[c] ppm upfield from $CFCl_3$ at −60°
$(CH_3)_3AsF_2$	2.17 (t)	53.2 (m)
$(CH_3)_3AsCl_2$	3.00 (s)	...
$(CH_3)_3AsFCl$	2.66 (d)	77.4 (m)
$(CH_3)_3AsBr_2$	3.23 (s)	...
$(C_6H_5CH_2)_3AsF_2$	3.25 (t)	76.0 (m)
$(C_6H_5CH_2)_3AsCl_2$	3.92 (s)	...
$(C_6H_5CH_2)_3AsFCl$	3.66 (d)	99.7 (m)
$(C_6H_5)_3AsF_2$	...	87.3
$(C_6H_5)_3AsFCl$	...	68.8
$(C_6H_5CH_2)_3SbF_2$	3.26 (t)	126.6 (m)
$(C_6H_5CH_2)_3SbCl_2$	3.72 (s)	...
$(C_6H_5CH_2)_3SbFCl$	3.46 (d)	131.7 (m)

[a] Chemical shift values for species in solution where R = CH_3 or C_6H_5, M = Sb, and X = F, Cl, Br, or I are given in ref 2. [b] Chemical shift values reported for the mixed halide species are for separate signals, *i.e.*, no exchange averaging. [c] t = triplet, d = doublet, s = singlet, m = multiplet.

At least ten independent measurements on each of a series of solutions over a range of relative concentrations of the reactants of 1:2 to 2:1 were made in arriving at the values of K reported in Table II. The ranges of values obtained are given in Table II.

The majority of the compounds studied were prepared by following known procedures.[3-7] Triphenylantimony dichloride was

---

(1) Presented in part before the Division of Inorganic Chemistry, 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967.

(2) G. G. Long, C. G. Moreland, G. O. Doak, and M. Miller, *Inorg. Chem.*, **5**, 1358 (1966).

(3) G. G. Long, G. O. Doak. and L. D. Freedman. *J. Am. Chem. Soc.*, **86**, 209 (1964).

(4) G. O. Doak. G. G. Long, and L. D. Freedman, *J. Organometal. Chem.* (Amsterdam), **4**, 82 (1965).

(5) M. H. O'Brien, G. O. Doak, and G. G. Long, *Inorg. Chim. Acta*, **1**, 34 (1967).

(6) I. P. Tsukervanik and D. Smirnov, *Zh. Obshch. Khim.*, **7**, 1527 (1937); *Chem. Abstr.*, **31**, 8518 (1937).

(7) G. T. Morgan and F. M. G. Micklethwait, *Proc. Chem. Soc.*, **28**, 68 (1912).