Table II. Significant Infrared Peaks

	P-H str	C-O str	N-O str	P-H bend
CF_3PH_2	2348 2337			841 sh 830 821 sh
$(CF_3)_2PH$	2353			856 810
$CF_3PH_2Ni(CO)_3$	2352	2103 2058		856 c
$(CF_3PH_2)_2Ni(CO)_2$	2350	2102 2052		852 c
$(CF_3)_2PHNi(CO)_3$	2360	2105 2060		852
$[(CF_3)_2PH]_2Ni(CO)_2$	2359	2102 2058		850
$CF_3PH_2CoNO(CO)_2$	2350	2073 2027	1820	863 c
$(CF_3)_2PHCoNO(CO)_2$	2355	2083 2040	1820	865

coming from reaction 4: CuO-combustion analysis gave water in appropriate yield. Reaction 10 was proved by finding in the ^{19}F nmr spectrum a pattern exactly matching that of an authentic sample of "NiPPNi"—a second-order spectrum centered at 52.2 ppm upfield of Cl_3CF and with main outer peaks 99 cps apart. The central complex of peaks is somewhat more cleanly resolved than in the very similar spectrum of $P_2(CF_3)_4$ (δ 46.9 ppm; outer-peak separation, 85 cps). The infrared spectrum also identified "NiPPNi": C-O stretching at 2092 and 2075 cm^{-1}; C-F stretching at 1174, 1148, 1132, and 1119 cm^{-1}. It is estimated that reactions 9 and 10 accounted for no more than a 10% loss of yield in reaction 4.

It is interesting that the pure product $(CF_3)_2PHNi(CO)_3$ from the dark reaction 4 failed to develop the "NiPPNi" color in sunlight. Reaction 9 probably requires free $(CF_3)_2PH$ as well as catalysts not easily specified.

A separate experiment showed that "NiPPNi" is destroyed, with liberation of $P_2(CF_3)_4$, by action of $(CF_3)_2PH$ in great excess. This result explains why the color, appearing early in reaction 4 in sunlight, fades out when the tube is kept for some hours in the dark. Thus the very early formation of "NiPPNi" suggests a nonequilibrium steady state. However, when the photochemical process has gone so far as to give 3-4 mole % concentrations of "NiPPNi," the color will not fade out in the dark because the available $(CF_3)_2PH$ is not enough to destroy much of the "NiPPNi."

No such photochemical process was found in relation to processes other than 4 (or incipient 5) nor in the action of PH_3 on $Ni(CO)_4$.[1] Most probably the diphosphines P_2H_4 and $(CF_3PH)_2$ were not formed in appreciable proportions and would not have competed with the monophosphines as ligands.

Registry No. $Ni(CO)_4$, 13463-39-3; CF_3PH_2, 420-52-0; $NOCo(CO)_3$, 14096-82-3; $(CF_3)_2PH$, 460-96-8; $CF_3PH_2Ni(CO)_3$, 37478-09-4; $(CF_3PH_2)_2Ni(CO)_2$, 37478-10-7; $CF_3PH_2CoNO(CO)_2$, 37478-11-8; $(CF_3)_2PHNi(CO)_3$, 37478-12-9; $[(CF_3)_2PH]_2Ni(CO)_2$, 37478-13-0; $(CF_3)_2PHCoNO(CO)_2$, 37534-36-4.

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Fluorine-19 Nuclear Magnetic Resonance Studies on Fluoroborate Species in Aqueous Solution[1]

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The behavior of fluoroborates in water has been recently studied potentiometrically[3] to determine the composition of species which are present in metastable amounts with respect to equilibrium with BF_4^-. Because the BF_4^- ion is kinetically slow to form except in highly acidic media, only the species BF_3OH^-, $BF_2(OH)_2^-$, and $BF(OH)_3^-$ are present after short times. The dissociation quotient for $HBF_3(OH)$ is estimated at >0.2 and the quotient for $HBF_2(OH)_2$ is estimated to be $>10^{-4}$.

The properties of BF_4^- in water have been known for some time and the physical evidence for the tetrahedral structure was reviewed previously.[1] The kinetics of the equilibrium reaction

$$H_2O + BF_4^- = BF_3OH^- + HF \tag{1}$$

has been studied by Wamser[4] and by Anbar and Gutman.[5] The latter authors studied the kinetics and the rate law in detail for both the forward reaction above and the exchange reaction for BF_4^- with fluoride ion. The reaction parameters for the hydrolysis and exchange reaction show that these two processes occur through the same rate-determining step. From the potentiometric measurements it is apparent that the fluoroborate species, other than BF_4^-, exchange or equilibrate with boric acid much more rapidly although the exchange mechanisms are not known.

Kuhlmann and Grant[6] have shown that the ^{19}F resonance of BF_4^- produces a quartet of equivalent lines with a coupling constant for the B-F interactions of 1-4 Hz depending on the concentration and nature of the cations. Also, the ^{11}B spectra for 7 *M* $NaBF_4$ solutions exhibit the sharp 1:4:6:4:1 quintet expected for the ^{11}B coupled to four equivalent F nuclei with a coupling constant of 4.6 Hz. By boiling solutions containing $NaBF_4$ in the presence of calcium carbonate a small amount of hydrolysis was effected and the ^{19}F and ^{11}B spectra were observed for what was believed to be BF_3OH^-. A weak ^{19}F quartet was observed 6.2 ppm downfield from the BF_4^- quartet. The ^{11}B resonance spectrum consisted of a partially resolved quartet with a coupling constant of 12.7 Hz. The wider resonance lines of BF_3OH^- compared with BF_4^- are attributed to the quadrupolar broadening in the unsymmetrical BF_3OH^-.

We have examined the ^{19}F spectra of solutions expected to contain BF_3OH^-, $BF_2(OH)_2^-$, and $BF(OH)_3^-$ in different amounts. Estimates of equilibrium quotients were made from these data along with potentiometric measurements of hydrogen ion and fluoride ion concentrations.

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(1) Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corp.

(2) (a) Reactor Chemistry Division, Oak Ridge National Laboratory. (b) Product Certification Division, Oak Ridge National Laboratory.

(3) R. E. Mesmer, K. M. Palen, and C. F. Baes, Jr., *Inorg. Chem.*, to be submitted for publication.

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(6) K. Kuhlmann and D. M. Grant, *J. Phys. Chem.*, 68, 3208 (1964).

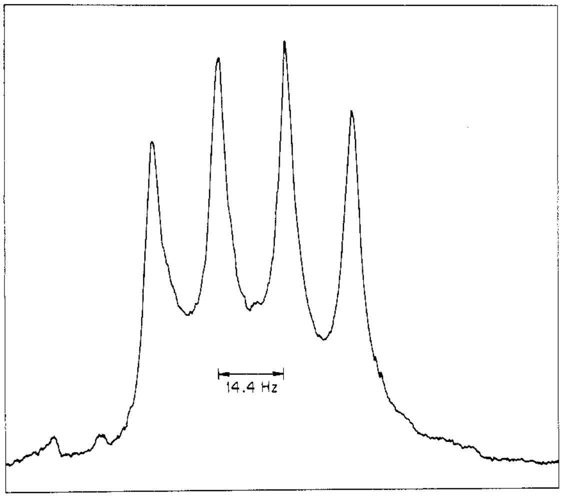

Figure 1. ^{19}F quartet due to the ^{19}F–^{11}B coupling in a 1 *m* solution of $NaBF_3OH$ at pH of 4.3 at 27° (chemical shift from C_6F_6 −22.95 ppm).

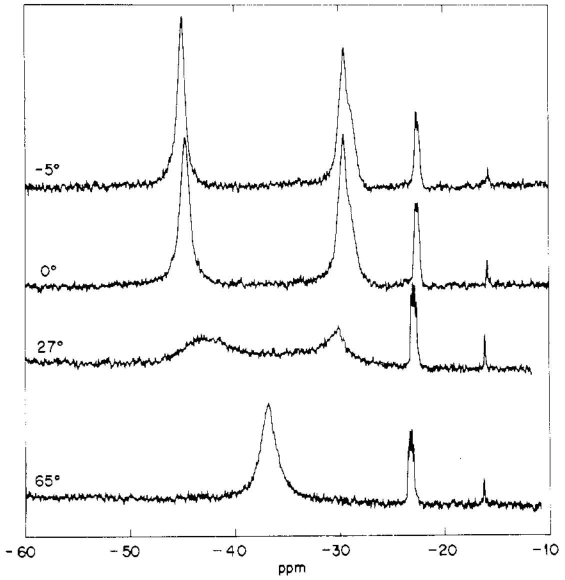

Figure 2. ^{19}F spectra of a solution with the composition 1 *m* $NaBF_3OH$ and 1 *m* $NaB(OH)_4$ (F:B ratio of 1.5) as a function of temperature (C_6F_6 reference).

Experimental Section

^{19}F spectra were observed using a Bruker high-resolution nmr spectrometer system with a transmitter frequency of 84.67 MHz and field strength of 21,140 G. The system is equipped with an internal-lock field-frequency control for long-term stability. The probe was thermostated for temperature control to ±1°. The Pyrex sample tube (10-mm o.d.) and reference capillary (3-mm o.d.) containing C_6F_6 were mounted concentrically in the probe for spinning. Samples were run immediately after addition of solutions to the Pyrex tubes to avoid attack of the glass. Experimental conditions (*e.g.*, pH) were chosen essentially to eliminate contamination by SiF_6^{2-}. At the acidities studied, the expected sharp SiF_6^{2-} line was not observed in any of the spectra reported here; however, if solutions were made strongly acidic, the presence of a small amount of SiF_6^{2-} was observed within 1 hr. Peak areas were obtained by integration to obtain estimates of the species present.

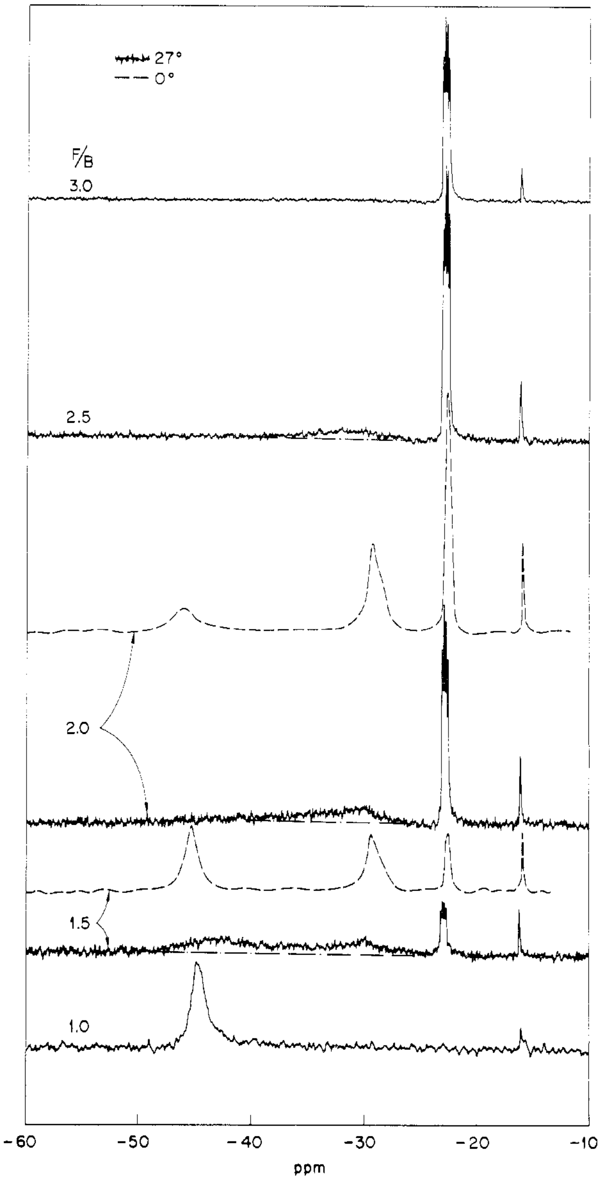

Figure 3. ^{19}F spectra at 27° of solutions prepared from mixtures of $NaBF_3OH$ and $NaB(OH)_4$ having F:B ratios from 1.0 to 3.0 and boron content of 1 *m* (C_6F_6 reference).

$NaBF_3OH$ was prepared by a considerably modified procedure based on the method of Ryss and Slutskaya.[7] The stoichiometric amount of HF solution was added to a slurry of NaF and H_3BO_3 at about −5°. $NaBF_3OH$ crystals were obtained by adding alcohol slowly to the resulting solution at −10°. The product was characterized by X-ray diffraction and petrographic analysis. Analysis of the product gave 10.1% B (10.03% theoretical) and 52.3% F (52.87% theoretical). A stock solution of this material was used as a source for boron and fluorine for the solution preparations in this study. Solutions of $NaB(OH)_4$ were also prepared from boric acid and sodium hydroxide. Mixtures of these two solutions were then prepared with F:B ratios between 3.0 and 1.0 and total boron concentrations of 1 and 2 *m*. The free fluoride concentration was determined with a lanthanum fluoride electrode standardized against a dilute solution of NaF in 1 or 2 *m* NaCl. The pH was determined by means of a glass electrode standardized against a dilute HCl solution in 1 or 2 *m* NaCl. All measurements were made over a pH range where HF concentrations were low and gave no interference with the response of the glass electrode. Data for equilibrium quotients were obtained in the pH range 5-7.

Results

The ^{19}F spectrum of a 1 *m* solution of $NaBF_3OH$ at pH of about 4 and free fluoride concentration of 0.06 *m* is shown in Figure 1. The intensities of the quartet due to coupling with ^{11}B are slightly nonequivalent because of the superposition of the septet resulting from the ^{10}B coupling. The ^{11}B–^{19}F coupling constant is 14.4 Hz and the chemical shift from C_6F_6 is −22.95 ppm.

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[7] I. G. Ryss and M. M. Slutskaya, *J. Gen. Chem. USSR*, 22, 451 (1952).

Table I. Summary of Equilibrium Quotients[a] Calculated from the ^{19}F Spectra

[B], *m*	F:B	Temp, °C	Log $Q_{3,2}$	Log $Q_{2,1}$	Log $Q_{1,0}$
1.0	2.0	27	13.4 ± 0.2	6.9 ± 0.3	−0.4 ± 0.4
			(13.689 ± 0.003)[b]	(7.06 ± 0.02)	(−0.4 ± 0.2)
1.0	2.0	0	13.9 ± 0.1	7.2 ± 0.1	−0.1 ± 0.2
1.0	1.5	27	13.6 ± 0.2	6.95 ± 0.2	−0.4 ± 0.2
1.0	1.5	0	13.6 ± 0.1	7.1 ± 0.1	−0.2 ± 0.1
2.0	1.5	27	13.4 ± 0.1	7.05 ± 0.1	−0.24 ± 0.1
2.0	1.5	0	13.77 ± 0.1	7.36 ± 0.1	−0.35 ± 0.2

[a] Where $Q_{x,y} = [BF_x(OH)_{3-y}^-]/[B(OH)_3][F^-]^x[H^+]^y$. [b] Potentiometric data from ref 3.

Table II. ^{19}F Nmr Data on Fluoroborate Solutions; Chemical Shifts (ppm)[a]

Soln compn					Chem shifts, ppm			
Temp, °C	[B], *m*	F:B	−log [H$^+$][b]	[F$^-$],[b] *m*	$F^- + BF(OH)_3^-$	$BF_2(OH)_2^-$	BF_3OH^-	BF_4^-
27	1.0	3.0	4.31	0.06			−22.95 (*J* = 14.4 Hz)	−16.10
27	1.0	2.5	5.45	0.19		−30.7	−22.94	−16.09
27	1.0	2.0	6.03	0.35		−30.1	−22.91	−16.13
27	1.0	1.5	6.67	0.57	−43.1	−30.1	−23.01	−16.20
27	1.0	1.0	7.55	0.74	−44.9			16.09
0	1.0	2.0	6.25	0.35	−46.3	−29.3	−22.68	−15.98
0	1.0	1.5	6.83	0.57	−43.1	−30.1	−23.01	−16.20
65	2.0	1.5			−37.0[c]		−23.29	−16.30
27	2.0	1.5	7.05	1.05	−43.1	−30.2	−23.10	−16.20
0	2.0	1.5	7.37	1.11	−44.94	−29.63	−22.68	−15.94
−5	2.0	1.5			−45.23	−29.64	−22.68	−15.88
27	2.0	4.0						−15.18 (*J* = 2.49 Hz)
27	2.0	3.0					−22.42 (*J* = 14.3 Hz)	

[a] C_6F_6 external reference (no susceptibility corrections were made). [b] Potentiometric data. [c] Single peak resulting from exchange among F^-, $BF(OH)_3^-$, and $BF_2(OH)_2^-$.

The spectra of 1 *m* solutions of borates with F:B (total fluoride to total boron) ratios from 3.0 to 1.0 are shown in Figure 2. The peaks at about −16, −23, −30, and −44 ppm are assigned, respectively, to BF_4^-, BF_3OH^-, $BF_2(OH)_2^-$, and the fourth to a combination of free fluoride and $BF(OH)_3^-$. The assignments of the BF_4^-, $BF_3(OH)^-$, and F^- peaks were made by addition of these ions under conditions where they persist at equilibrium and by comparison with the spectra reported in the literature.[7,8] The source of $NaBF_3OH$ contained about 3% $NaBF_4$ which under the conditions of these experiments is kinetically stable toward hydrolysis and inert toward exchange of fluorides.

The resonances occurring at −44 and −30 ppm involve species participating in a chemical-exchange process such as

$$H_2O + BF_2{}^*(OH)_2^- = BF(OH)_3^- + HF^* \qquad (2)$$

i.e., the $BF_2(OH)_2^-$ exchanges F^- ions with the $BF(OH)_3^-$ species. The $BF(OH)_3^-$ ion presumably exchanges even more rapidly with F^- and is not observed as a separate resonance peak in any of our experiments. This exchange is evidenced by the width of the peak and the fact that the integrated area of the fluoride peak is always greater than that of the free fluoride concentration measured potentiometrically. This latter observation is, however, not conclusive since there are medium changes between the reference solutions used in the potentiometric measurements and the fluoroborate solutions.

Rates of Exchange. Figure 3 shows spectra of a solution containing 1 *m* $NaBF_3OH$ and 1 *m* $NaB(OH)_4$, *i.e.*, a F:B ratio of 1.5 and a boron concentration of 2 *m*. At 0° the resonance peaks for the free fluoride and the $BF_2(OH)_2^-$ are well resolved but devoid of fine structure. At 27° these two peaks are partially overlapping and are completely coalesced at 65° at the mean position as expected for exchange between equally populated sites. The lifetime for fluorine on $BF_2(OH)_2^-$ was estimated at 27° to be 0.6 msec, but a detailed analysis of this reaction in terms of the rate law was not attempted. This lifetime is shorter than that reported by Connick and Poulson[9] for AlF_2^+ (16 msec). The activation energy estimated from the peak separation at 27° and the peak width at 65° is 14 kcal/mol. This quantity does not correspond to the exchange process alone, however, since the equilibrium is also expected to shift with temperature.

It is clear from all the available information on the fluoroborate species that the lifetimes of BF_4^- and BF_3OH^- are much greater than for either $BF_2(OH)_2^-$ or $BF(OH)_3^-$. For example, the study by Anbar and Gutman has shown that the exchange and hydrolysis reactions of BF_4^- proceed through the same rate-determining step and that both reactions are very slow under the conditions of our nmr studies. The potentiometric studies have shown that $BF_3(OH)^-$ is formed in solution from $B(OH)_3$, $BF_2(OH)_2^-$, $BF(OH)_3^-$, and F^- in a few minutes and likewise it is known[3,4] that BF_3OH^- is rapidly converted to the less fluorinated borates in water. Even at 0° $BF(OH)_3^-$ is not observed as a separate resonance peak while the other fluoroborates are resolved. Therefore, the order of increasing rates of exchange for the fluoroborate species is $BF_4^- < BF_3(OH)^- < BF_2(OH)_2^- < BF(OH)_3^-$.

Fluoroborate Equilibria. These direct observations of the fluoroborate species along with potentiometric data for the H^+ and F^- concentrations enable us to obtain estimates of the equilibrium quotients for the reactions

$$B(OH)_3 + xF^- + (x-1)H^+ = BF_x(OH)_{4-x}^- + (x-1)H_2O \qquad (3)$$

The integration of the nmr peaks (see Figure 3) cannot be done with great accuracy especially for the species with broad signals resulting from exchange. However, semiquantitative estimates have been made from these data which are summarized in Table I. The previously reported potentiometric data for 1 *m* NaCl are also shown for comparison. Calculations were made from measurements at 27 and 0° where signals for the composite of $F^- + BF(OH)_3^-$ were observed. The agreement with the previous data[3] is satisfactory and gives semiquantitative evidence for the validity of the assignments made here.

(8) M. Noshiro and Y. Jitsugiri, *Bunseki Kagaku*, **18**, 1200 (1969).

(9) R. E. Connick and R. E. Poulson, *J. Amer. Chem. Soc.*, **79**, 5153 (1957).

Appreciable concentrations of polyborates occur in concentrated solutions of boric acid above a pH of 6.5. The previously reported results[10] on the stabilities of the polyborates were used to take this factor into account in the calculation of the quotients in Table I.

We make the following observation about the possible occurrence of fluoropolyborates in these concentrated solutions. It is unlikely that fluoride would occur in bridging positions in polyborate structures since the complexes of fluorides with metal ions are monomeric in aqueous solutions. Also, one might expect the substitution of a fluoride for hydroxide in a terminal position of a polyborate species to occur with a stability similar to that of $BF(OH)_3^-$, *e.g.*

$$B_3(OH)_{10}^- + F^- = B_3(OH)_9F^- + OH^- \qquad \log Q \approx -0.4$$

If species do indeed exist with such stabilities, they would appear in only very minor amounts under these experimental conditions.

Chemical Shifts. The chemical shifts observed for the various compositions are given in Table II. It is interesting to compare this system with the similar fluoroberyllate species. Hogben, *et al.*,[11] observed the ^{19}F nmr spectra of the four fluoroberyllate species $BeF_x(H_2O)_{4-x}{}^{2-x}$ where x is 1-4. Each of these species gives a quartet with the chemical shifts regularly spaced at 84.8, 87.4, 89.8, and 92.4 ppm (mean positions) upfield from trifluoroacetic acid in going from BeF_4^{2-} to $BeF(H_2O)_3^+$.

Interestingly this is the reverse of the order observed for the hydroxylfluoroborates. These resonances are downfield from C_6F_6 by amounts increasing in the order (see Table II) $BF_4^- < BF_3(OH)^- < BF_2(OH)_2^- < BF(OH)_3^-$. This reversal of the shifts for the hydroxyfluoroborates from the corresponding fluoroberyllates may be due to the difference in the OH^- and H_2O as ligands, since the OH^- is expected to be more tightly bound than the H_2O. Also, the trends observed by Coyle and Stone[12] for the species BF_xY_{3-x} are similar to that observed for the fluoroborates. BF_2Cl and $BFCl_2$ are downfield from BF_3 51.5 and 99.0 ppm, respectively. Likewise, BF_2BR and $BFBr_2$ are downfield from BF_3 at 60.4 and 130.4 ppm, respectively.

Registry No. $B(OH)_3$, 10043-35-3; F_2, 7782-41-4; $BF(OH)_3^-$, 32554-53-3; $BF_2(OH)_2^-$, 32554-52-2; $BF_3(OH)^-$, 18953-00-9; BF_4^-, 14874-70-5.

Acknowledgment. We gratefully acknowledge the assistance of L. O. Gilpatrick, who provided the sample of $NaBF_3OH$ used in this work.

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Photoelectron Spectra and Electronic Structure of Pentacarbonylmanganese Halides

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The photoelectron spectra of the pentacarbonylmanganese halides have previously been studied by Orchard and coworkers.[1] A parameter-free approximate molecular orbital study of this series has also been reported by Fenske and DeKock.[2] It was immediately recognized that these two independent studies agreed very closely in their interpretation of the electronic structure of these complexes. Particularly gratifying was the agreement that, within the limits of Koopmans' theorem, the sequence of the uppermost occupied orbitals in all three molecules is 8e > 7e > $2b_2$ and that 8e is primarily halogen in character. Despite this success, the molecular orbital treatment contained one feature which could not be adequately explained at the time. The treatment predicted that the $9a_1$ orbital, which is greater than 70% p_σ halogen, should lie between the primarily halogen 8e and the primarily metal 7e. In the original spectra of Orchard and coworkers, the $9a_1$ orbital was not observed or assigned.

Recently Brown and Chambers[3] have published another theoretical study of the electronic structures of the pentacarbonylmanganese–halogen molecules using the SCCC method. This method does not place the $9a_1$ orbital in the region of the 8e, 7e, and $2b_2$ ionizations. Furthermore, it reverses the order of the 7e and $2b_2$ levels and offers a completely new assignment for the ionizations in pentacarbonylmanganese iodide. The interpretation of this latter compound has played a key role in the assignment of the levels and in the assessment of their orbital per cent character (*vide infra*).

Much of the difficulty in the original ionization assignments and in the detection of the ionization from the $9a_1$ energy level was undoubtedly due to the instrumentation available. It permitted only a single slow scan across the energy region and the signal to noise ratio was such that low-intensity bands could not be readily distinguished from erratic base line characteristics. As a consequence of the molecular orbital studies of Fenske and DeKock, Orchard and coworkers initiated further studies of the photoelectron spectra of the pentacarbonylmanganese halides and identified the existence and energy placement of the $9a_1$ orbital in $Mn(CO)_5Cl$ and $Mn(CO)_5Br$.[4] Their results are in accord with the calculational predictions. With the improved instrumentation now available, we have obtained a set of well-resolved photoelectron spectra of the series $Mn(CO)_5X$, where X = Cl, Br, I, plus the spectrum of one additional compound, $Mn(CO)_4(CNCH_3)Br$, which is shown to aid greatly in a definitive assignment of the ionizations and in the interpretation of the electronic structure.

Experimental Section

Spectra were measured using a Varian IEE-15 electron spectrometer in the uv configuration. The helium source was pure to 0.0001%. Blank spectra showed no observable system contamination, and spectra of argon at high counting rate indicated no significant secondary source ionizations. Argon was used as a single internal standard. No inconsistencies have been observed when double standards were used. Sample purity was established by infrared analysis. Spectra of the halides were measured at 20–25°. The spectrum of $Mn(CO)_4(CNCH_3)Br$ was obtained at 50°. In all cases, separate spectra were measured at different time intervals until the supply of sample introduced to the spectrometer was depleted. No changes in any of the spectra were observed. Although the maximum counting rate was high (10,000–20,000 counts/sec), the technique of time

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