the emission to be classified as a fluorescence.[6] On the basis of the half-width and lifetime, the emission is classified as a phosphorescence, $^2E \rightarrow {}^4A_2$. The Stokes shift is attributed to a significant perturbation of the ^2E state by the close-lying $^4T_2$ state. The observation of only one emission maximum for the dithiocarbamates contrasts the two maxima reported by Cancellieri and coworkers.[4] Measurements on $Cr(dmtc)_3$, described below, suggest that the 11.0-kK maximum ($\bar{\nu}_{1/2}$ = 2.0 kK) observed by these workers is due to an impurity. An undiluted powder purified only by recrystallization gave a broad emission ($\bar{\nu}_{1/2}$ = 2.0 kK) in the solid state centered at 10.5 kK but only the narrower emission ($\bar{\nu}_{1/2}$ = 0.80 kK) in the EPA–$CHCl_3$ glass. After this powder was vacuum sublimed, only the narrower emission was obtained from the solid. A brown residue that was insoluble in organic and inorganic solvents remained in the apparatus. Infrared scans of this powder before and after sublimation were identical as were the melting points and thin layer plates (silica gel). The C, H, and N analyses did indicate that the presublimed powder was higher in per cent C and H but lower in per cent N than the theoretical values.

The 83°K absorption spectrum of $Cr(dtp)_3$ shows weak bands at 13.1, 13.7, and 17.4 kK in polymer and crystal. In addition two peaks are observed at 19.2 and 18.6 kK. Jørgensen[1] has assigned the 18.6-kK peak as a spin-forbidden transition, while others have suggested that both peaks are components of the $^4T_1$ state.[7] The bands at 13.1 and 13.7 kK are assigned as the $^2E \leftarrow {}^4A_2$ and $^2T_1 \leftarrow {}^4A_2$ transitions, respectively. Cancellieri[4] observed weak absorption bands for this complex in hydrocarbon solvents at 11.1 and 11.8 kK and assigned them to the $^2E \leftarrow {}^4A_2$ transition. We also observed these bands in hydrocarbon solvents but only when no solvent reference was used. These bands, which are not observed in CCl_4, can be assigned as fourth-order C–H stretch vibrations in the solvent. The weak band at 17.4 kK is, by analogy to the xanthate and dithiocarbamate complexes, one of the two transitions to the trigonally split $^2T_2$ state. The other component may be the band at 18.6 kK on the peak of the $^4T_1 \leftarrow {}^4A_2$ absorption band.

Emission at 83°K from $Cr(dtp)_3$ could not be detected using photomultiplier detection or photographic detection with a Spex 1800 spectrograph.

Glassy solution emission intensities observed for these chelates at 77°K are generally weak, suggesting very low quantum yields. No chemical evidence for any irreversible photolysis in glassy solution was detected under these excitation conditions, although some decomposition was observed for solid material allowed to stand for periods of weeks. Steady irradiation of the $Cr(exan)_3$ and $Cr(mxan)_3$ complexes in EPA and polymer glasses at any temperature greater than 77°K produced an exponential decrease in the emission intensity with time. After 6–8 min of irradiation an equilibrium intensity was reached. This decrease in intensity was independent of excitation wavelength from 250 to 620 nm. The initial intensity could be recovered by allowing the sample to remain in the dark. The decrease in intensity was not observed when the sample was in direct contact with liquid nitrogen (77°K). Since the emission intensity and lifetime of these two complexes is temperature dependent,[8] experiments were performed to eliminate the possibility that excitation radiation warmed the sample. First, a copper–constantan thermocouple was placed directly into the irradiated portion of the sample. No temperature change was detected during irradiation. Finally, a sample of $Cr(aca)_3$ in EPA was irradiated under the same conditions and the emission monitored. The emission intensity of this complex is temperature dependent.[9] No decrease in intensity with exposure time was observed for $Cr(aca)_3$. The fact that the emission intensity decrease is observed in polymer as well as EPA eliminates a solvent–complex interaction. This phenomenon cannot be explained at present.

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Antimony-121 and Iron-57 Mössbauer Effect in Substituted Iron Pentacarbonyls

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Although the ^{57}Fe Mössbauer effect in $Fe(CO)_5$ and its derivatives has been the subject of many investigations over the past 8 years[1-7] and although the mono- and disubstituted $(C_6H_5)_3P$ compounds have been studied,[1-3] Mössbauer spectra of the analogous $(C_6H_5)_3As$ and $(C_6H_5)_3Sb$ derivatives have not been reported. As the Mössbauer effect can be observed with ^{121}Sb,[8,9] the latter compounds can be studied by a double Mössbauer experiment, a technique which has given interesting results for compounds containing Fe–Sn bonds.[10,11] We report here the ^{57}Fe Mössbauer spectra of the series $(C_6H_5)_3MFe(CO)_4$ and $((C_6H_5)_3M)_2Fe(CO)_3$, where M is P, As, or Sb, and the ^{121}Sb spectra of the two antimony derivatives.

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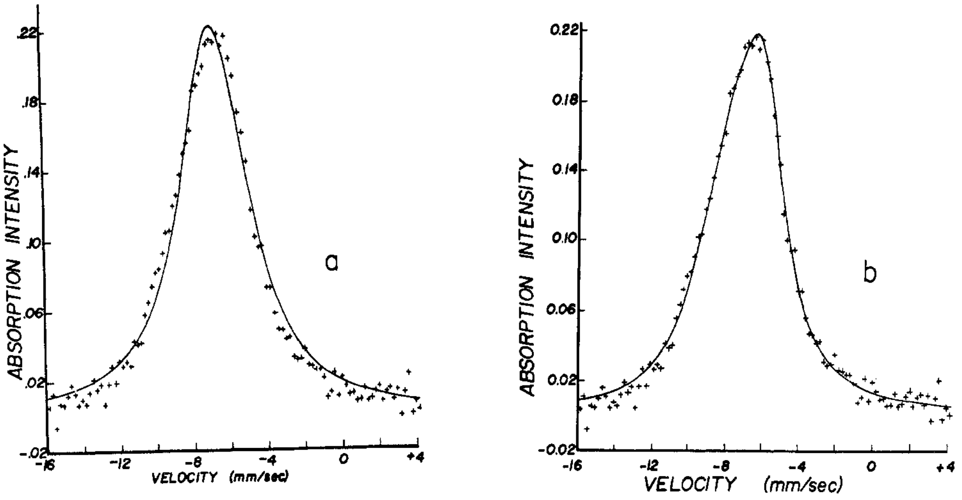

Figure 1.—Example of ^{121}Sb Mössbauer spectra at 4.2°K: (a) fit with negative e^2qQ to $((C_6H_5)_3Sb)_2Fe(CO)_3$ data; (b) fit with positive e^2qQ, showing improvement in χ^2.

TABLE I

^{121}Sb MÖSSBAUER PARAMETERS[a]

Compound	Temp, °K	Width, mm/sec	δ_{Sb},[b] mm/sec	e^2qQ, mm/sec	χ^2
$(C_6H_5)_3Sb$[c]	80	3.2 ± 0.4	−0.9 ± 0.2	+17 ± 2	
$((C_6H_5)_3Sb)_2Fe(CO)_3$[d]	80	3.0	+1.5 ± 0.1	+18 ± 1	262
		[3.0]	[+2.2 ± 0.1]	[−13 ± 1]	[280]
$(C_6H_5)_3SbFe(CO)_4$[d]	80	3.0	+2.8 ± 0.2	+16 ± 2	330
		[3.0]	[+3.6 ± 0.2]	[−19 ± 2]	[310]
$(C_6H_5)_3Sb$[c]	4.2	2.82 ± 0.02	−1.29 ± 0.01	+17.5 ± 0.1	
$((C_6H_5)_3Sb)_2Fe(CO)_3$[e]	4.2	2.68 ± 0.06	+1.58 ± 0.02	+10.9 ± 0.3	218
		[3.74 ± 0.11]	[+1.75 ± 0.02]	[−4.9 ± 0.9]	[440]
$(C_6H_5)_3SbFe(CO)_4$[e]	4.2	3.26 ± 0.06	+1.68 ± 0.02	+9.0 ± 0.3	302
		[3.92 ± 0.07]	[+1.78 ± 0.02]	[−4.9 ± 0.6]	[500]

[a] Our samples contained about 20 mg of Sb/cm² and gave intensities of 2–3% at 80°K; about 10 mg of Sb/cm² with intensities of ~30% at 4.2°K. [b] Isomer shifts are quoted relative to InSb. The measured shifts were 1.70 mm/sec more negative with the $Ni_{21}Sn_2B_6$ source and 8.40 mm/sec more negative with the $CaSnO_3$ source. [c] Values reported in ref 9 and converted to InSb as isomer shift standard. [d] In order to calculate e^2qQ, the width had to be constrained, and a typical value of 3.0 mm/sec was picked. From the χ^2 value it is seen that the fit with e^2qQ negative (in brackets) was not appreciably better or worse than the one with e^2qQ positive. [e] The fit with e^2qQ negative (in brackets) gave considerably larger values of χ^2 and abnormally large widths, thus showing clearly that the sign of e^2qQ is positive (see also Figure 1).

Experimental Section

The compounds were prepared by treating $Fe_3(CO)_{12}$ with $(C_6H_5)_3P$, $(C_6H_5)_3As$, or $(C_6H_5)_3Sb$ in tetrahydrofuran, according to the procedure of Clifford and Mukherjee.[12] These reactions produce a mixture of $(C_6H_5)_3MFe(CO)_4$ and $((C_6H_5)_3M)_2Fe(CO)_3$, which must then be separated by recrystallization, the phosphorus derivatives from petroleum ether (bp 60–90°) and the others from acetonitrile. Purity was established by elemental analyses, melting points, and infrared spectra, the last being in agreement with reported spectra.[12-14]

The procedures for the Mössbauer experiments have been described.[9] The ^{121}Sb spectra at 80°K were taken with a source of $Ni_{21}{}^{121}Sn_2B_6$;[15] those at 4°K, with a $Ca^{121}SnO_3$ source, using the facilities at Argonne National Laboratory.[8,9] Both source and absorber were cooled for low-temperature runs. All the derivatives gave ^{57}Fe spectra typical of a single iron site with quadrupole splitting $\Delta = |e^2qQ/2|$. The ^{121}Sb spectra were fit to the eight-line theoretical quadrupole pattern for the $^7/_2$–$^5/_2$ transition,[8,9] using a quadrupole moment ratio of 1.34[16] and asymmetry parameter $\eta = 0$. Although the intensity was too low at 80°K to distinguish between signs of the quadrupole coupling constant, at 4°K the sign of e^2qQ was easily determined to be positive for both mono- and disubstituted derivatives (Figure 1).

Results and Discussion

In interpreting the results reported in Table I, the isomer shift calibration of Ruby, *et al.*,[17] can be used for determining approximate values of electron density at the Sb nucleus. At the configuration $5s^1p^3$ (assumed for InSb, $\delta_{Sb} = 0$) the change in δ_{Sb} is about −11 mm/sec per 5s electron and +1.7 mm/sec per 5p electron. A large increase in δ_{Sb} occurs when $(C_6H_5)_3Sb$ is complexed in the carbonyl compounds. Using the measurements at 4°K (Table I), together with the above calibration, the increase in δ_{Sb} corresponds to a removal of about 0.26 5s electron from Sb or, less likely, an addition of 1.7 5p electrons. The shift upon complexing is large enough formally to correspond to a change from Sb(III) to Sb(V).[8,9] A σ donation from the Sb lone pair to Fe could account for the change in δ_{Sb} if the lone pair has some 5s character, which is quite reasonable, as the bond angles in $(C_6H_5)_3Sb$ will surely be less than 120°.[18] It is difficult to imagine π back-bonding being strong enough to add almost 2 5p electrons to Sb.

Further support for a σ-bonding scheme comes from

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the data on quadrupole coupling. A positive e^2qQ corresponds to an excess of 5p electrons along the threefold symmetry axis (z axis) in $(C_6H_5)_3Sb$.[9] The fact that the sign of e^2qQ remains positive upon complexing indicates no large increase in 5p population along the x and y axes. A π back-donation from Fe would primarily increase p_x and p_y densities. If this were a major interaction, the sign of e^2qQ should become negative. However, the reduction in magnitude (from +17 to about +10 mm/sec) *is* consistent with a σ donation along the z axis from a hybrid orbital with some p character.

The parameters δ_{Sb} and e^2qQ change somewhat more upon complexing for $(C_6H_5)_3SbFe(CO)_4$ than for $((C_6H_5)_3Sb)_2Fe(CO)_3$. The infrared spectrum of the latter indicates both $(C_6H_5)_3Sb$ groups are in axial positions.[14] It is expected that a σ interaction along the Sb–Fe–Sb axis would be weakened at either Sb nucleus due to the presence of the other. The monosubstituted compound should have a stronger effect at Sb since no other important σ interaction occurs along the Sb–Fe bond axis. Again, these differences are not easily explained by a π interaction.

The ^{57}Fe results are reported in Table II. Two obvious effects are the second-order Doppler shift in δ_{Fe} of ~0.06 mm/sec and the reduced intensities upon raising the temperature. The features of particular interest involve trends in δ_{Fe} and Δ_{Fe} at a given temperature. First, there is a large increase in Δ_{Fe} on changing from a monosubstituted to a disubstituted compound, and for $(C_6H_5)_3As$ and $(C_6H_5)_3Sb$, an increase in δ_{Fe} as well. In the monosubstituted series both δ_{Fe} and Δ_{Fe} are about equal for $(C_6H_5)_3As$ and $(C_6H_5)_3Sb$ and somewhat smaller for $(C_6H_5)_3P$. In the disubstituted case the trend in Δ_{Fe} is the same: $(C_6H_5)_3Sb \approx (C_6H_5)_3As > (C_6H_5)_3P$, while δ_{Fe} varies through the series $(C_6H_5)_3Sb > (C_6H_5)_3As > (C_6H_5)_3P$. The splittings for $((C_6H_5)_3Sb)_2Fe(CO)_3$ and $((C_6H_5)_3As)_2Fe(CO)_3$ are among the largest observed for low-spin iron complexes. Since the geometry of these compounds is similar, D_{3h} for the disubstituted[12-14] and probably C_{3v} for the monosubstituted,[14] the above trends should reflect the relative changes in the Fe–M bond as M is varied. It is not feasible to isolate all the possible effects from the limited data. However, if the Fe–M bond is primarily σ, as the ^{121}Sb results indicate for those compounds, and since increasing δ_{Fe} corresponds to decreasing the 4s electron density at Fe, the trend in δ_{Fe} would indicate $(C_6H_5)_3Sb$ is the weakest σ donor and $(C_6H_5)_3P$ the strongest in the series[19] (the latter donating more electron density to the 4s orbitals of Fe). The increase in δ_{Fe} upon disubstitution of a weak σ donor ($(C_6H_5)_3Sb$ or $(C_6H_5)_3As$) for a strong π acceptor (CO) could then be explained simply by increased d shielding at Fe.

TABLE II

^{57}Fe MÖSSBAUER PARAMETERS[a]

Compound	Temp, °K	δ_{Fe},[b] mm/sec	Δ_{Fe}, mm/sec
$(C_6H_5)_3PFe(CO)_4$[c]	80	0.07	2.40
	295	0.12	2.47
$(C_6H_5)_3AsFe(CO)_4$[d]	80	0.10	2.71
	295	0.15	2.68
$(C_6H_5)_3SbFe(CO)_4$[d]	80	0.10	2.67
	295	0.15	2.63
$((C_6H_5)_3P)_2Fe(CO)_3$[e]	80	0.06	2.62
	295	0.12	2.68
$((C_6H_5)_3As)_2Fe(CO)_3$	80	0.16	3.24
	295	0.20	3.17
$((C_6H_5)_3Sb)_2Fe(CO)_3$	80	0.19	3.16
	295	0.27	3.16

[a] Samples contained 5–10 mg of Fe/cm^2 and gave intensities of 5–12% at 80°K and 1–3% at 295°K. Errors are estimated as ±0.01 mm/sec at 80°K and ±0.03 at 295°. [b] Relative to $Na_2Fe(CN)_5NO \cdot 2H_2O$ at 295°K. [c] Values reported in the literature, on the same scale (δ, Δ): 0.14, 2.42;[3,5] 0.17, 2.54;[1] 0.08, 2.53 mm/sec.[19] [d] These samples upon standing developed an impurity with $\delta_{Fe} \cong 0.6$ and $\Delta_{Fe} \cong 0.9$ mm/sec. [e] Values reported in the literature (δ, Δ): 0.16, 2.76;[2] 0.13, 2.71 mm/sec.[19]

The large variations in Δ_{Fe} reflect variations in V_{zz}, the component of the field gradient tensor along the axial symmetry axis, since $\eta = 0$ for either D_{3h} or C_{3v} symmetry. For Fe(0), V_{zz} will depend primarily on the population distribution in the 3d orbitals. It appears reasonable that V_{zz} should change markedly as $(C_6H_5)_3Sb$ or $(C_6H_5)_3As$ is substituted for CO due to the change in overall 3d population, as indicated above. The fact that in a series the $(C_6H_5)_3P$ compounds have the smallest Δ_{Fe} (and $|V_{zz}|$) cannot be as readily explained. However, the similarity of δ_{Fe} and Δ_{Fe} for $(C_6H_5)_3PFe(CO)_4$ and $Fe(CO)_5$[20] indicates either similar bonding for the two ligands or, more likely, compensating effects on these parameters by distinctly different types of bonding, such a case corresponding to $(C_6H_5)_3P$ as a strong σ donor.

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The Deuterolysis of Monofluorophosphate

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The kinetics and equilibria of the hydrolysis of the difluoro- and monofluorophosphates have been studied[1,2] as a function of pH. Herein we report the kinetics observed for the deuterolysis of PO_3F^{2-} as a function of pD and temperature. A kinetic isotope effect of 2.1 is observed.

Experimental Section

Materials.—Sodium monofluorophosphate was obtained from the Ozark-Mahoning Co., Tulsa, Okla. Ionic fluoride was present to the extent of less than 0.18% by weight. Deuterium oxide (99.7% D_2O) and deuterium chloride solution (99% DCl) in D_2O were purchased from Merck & Co., Inc., St. Louis, Mo. Other chemicals used in this study were of reagent quality and were used without further purification.

Rate Measurements.—A solution of Na_2PO_3F in D_2O was made just prior to use for each kinetic study. Na_2PO_3F was deter-

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