symmetry. Although molecular orbital calculations are helpful in the semiquantitative description of these transitions, the validity of attempting to represent them as a difference between one-electron energy levels for ground-state equilibrium bond lengths is probably dubious.[15]

Comparison of the spectrum of *trans*-$PtCl_4(OH)_2^{2-}$ with that of *trans*-$PtCl_4(H_2O)_2$ is helpful in attaining a qualitative understanding of the bonding situation. The striking shift to higher energy of the band at 274 mμ for the dihydroxo complex which results from protonation of the hydroxide ligands suggests participation of oxygen π (e_u) orbitals in the originative molecular orbital. For the diaquo species the transition is probably best represented by $b_{2u} \rightarrow b_{1g}$. This assignment is substantiated by the fact that the diammine complex exhibits an absorption band at nearly the same energy. Platinum–chlorine bonding in these complexes is undoubtedly quite similar, although the energy of the a_{1g} antibonding orbital (Figure 2) is presumably somewhat higher in the *trans*-$Pt(NH_3)_2Cl_4$ species because of the greater σ-bonding ability of ammonia. Finally, the high-energy transition for each of the three complexes is much less sensitive to changes in the axial bonding and probably arises from an orbital comprised mainly of chlorine σ-type atomic orbitals; a reasonable assignment is $2e_u \rightarrow b_{1g}$.

As noted earlier, molecular orbital calculations have been performed in order to corroborate the conclusion reached about the relative ligand-field strengths of hydroxide and chloride in *trans*-$PtCl_4(OH)_2^{2-}$. Except for several modifications, the LCAO–MO theory which was employed closely followed that described by Ballhausen and Gray.[16] Numerical radial wave functions were calculated in the usual fashion.[17-19] For the platinum–chlorine and platinum–oxygen bond lengths in *trans*-$PtCl_4(OH)_2^{2-}$, values of 2.310 and 2.026 Å, respectively, were used.[12] Since appreciable ionicity exists for *trans*-$PtCl_4(OH)_2^{2-}$, a Madelung correction[20] was included to improve the results of the simple Wolfsberg–Helmholz calculations. Further information, including one-electron energy levels, linear combinations of ligand orbitals, group overlap integrals, and a complete set of eigenvectors, is on file with the American Society for Information Science;[21] other details about the computations are available upon request.

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Reactions of Trifluoromethyl Hypofluorite with Sulfur and with Other Substances Containing Divalent Sulfur[1]

BY ROBERT E. BAILEY AND GEORGE H. CADY

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Trifluoromethyl hypofluorite, CF_3OF,[2] is known to react in either of two ways: (1) as a fluorinating agent somewhat less active than elemental fluorine or (2) by addition of the O–F group across an unsaturated configuration.[3-6] The reactions of hypofluorites with substances containing divalent sulfur have not been previously examined, with the exception of Porter and Cady's exploratory work with elemental sulfur.[3] In the present work, the reactions of CF_3OF with thiophosgene, CCl_2S, carbonyl sulfide, O=C=S, and elemental sulfur have been studied.

Experimental Section

Trifluoromethyl hypofluorite was prepared by the usual method[7] and stored in glass tubes at 90°K. All manipulations were performed in a glass vacuum line equipped with a diffusion pump using Kel-F-3 oil (Minnesota Mining and Manufacturing Co.) and stopcocks lubricated with Kel-F-90 grease. Mixtures of products were separated by fractional codistillation.[8] Infrared spectra were obtained with a Beckman IR-10 spectrometer using a 10-cm cell with silver chloride windows. A Varian HR-60 spectrometer was used for the determination of nmr spectra with $CFCl_3$ as internal standard.

Reaction of CF_3OF with Thiophosgene.—A solution of 4 mmol of CCl_2S in 10 mmol of CF_2Cl_2 at −78° was exposed to 4 mmol of CF_3OF initially at a pressure of 100 Torr while stirring with a Teflon-covered magnet. Reaction was complete in about 10 min as shown by the disappearance of the yellow color of CCl_2S. The most volatile products, COF_2, SOF_2, CF_2Cl_2, and SF_4 were then removed by distillation from the reactor, while held at −78°, into a trap at −183°. The remaining materials were then separated by fractional codistillation giving 0.8 mmol of CF_3OCFCl_2, 1 mmol of $CF_3OSCFCl_2$, and 0.1 mmol each of two unidentified products of about equal volatility.

$CF_3OSCFCl_2$.—The ^{19}F nmr spectrum consisted of two resonances with relative intensities 3:1. One was a doublet, ϕ^* +61.4 ppm, and the other a quartet, ϕ^* +28.0 ppm, with $J = 9.2$

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Hz. Infrared absorptions were found at 1271 (vs), 1223 (vs), 1188 (vs), 1070 (m), 939 (m), 868 (s), 820 (s), 787 (w), and 544 cm^{-1} (w). The mass spectrum obtained using 70-eV electrons contained "parent peaks" at 218, 220, and 222. Fragments consistent with the proposed structure also were found. *Anal.* Calcd for $CF_3OSCFCl_2$: C, 11.0; Cl, 32.5; F, 34.9; mol wt 219. Found: C, 12.6, 10.7; Cl, 32.6; F, 34.8; mol wt (by vapor density) 215.

CF_3OCFCl_2.—The ^{19}F nmr spectrum consisted of two resonances with relative intensities 3:1; a doublet ϕ^* +55.9 ppm, and a quartet ϕ^* +14.3 ppm with J = 10.7 Hz. Infrared absorptions occurred at 1520 (vw), 1287 (vs), 1238 (vs), 1212 (vs), 1147 (s), 1115 (vs), 915 (s), 870 (s), and 670 cm^{-1} (w). The heaviest ion in the mass spectrum was CF_3OCFCl^+. Other ions were consistent with the proposed structure. *Anal.* Calcd for CF_3OCFCl_2: C, 12.9; S, 0.0; mol wt 187. Found: C, 13.0; S, 0.5; mol wt (by vapor density) 184.

Reaction of Trifluoromethyl Hypofluorite with Carbonyl Sulfide.—Carbonyl sulfide (5 mmol) and CF_3OF (5 mmol) were condensed into a 500-ml glass bulb. No reaction was observed in 2 weeks at room temperature but in 3 hr at 100° 75% of the reactants was consumed. After pumping away materials volatile at −78°, the remaining substances were separated by fractional codistillation. The previously known compounds, $(CF_3O)_2CO$,[9] 0.5 mmol, and $CF_3OC(O)F$,[10] 1.2 mmol, were identified by their infrared spectra and vapor densities. Besides traces of unidentified additional products, still another substance was found in moderate yield, 0.2 mmol. This substance almost surely was $CF_3OSC(O)OCF_3$.

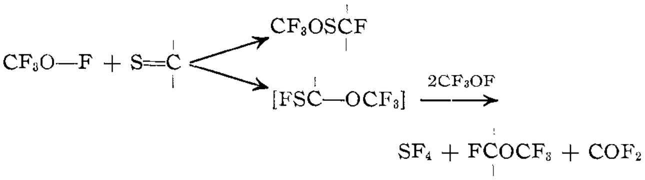
Evidence for $CF_3OSC(O)OCF_3$.—The ^{19}F nmr spectrum consisted of two resonances with equal intensities, ϕ^* +58.5 ppm and ϕ^* 62.2 ppm with $J < 1$ Hz. Infrared absorptions occurred at 1824 (m), 1774 (vw), 1281 (s), 1254 (s), 1222 (s), 1201 (s), 1177 (s), 1081 (s), 942 (w), 877 (w), 793 (w), and 607 cm^{-1} (w). Molecular weight: calcd, 230; obsd (vapor density), 230.

Reaction of CF_3OF with Sulfur.—At 75 Torr, 2 mmol of CF_3OF was slowly added to an excess of carefully dried sulfur in a bulb at 0°. After 10 min all of the CF_3OF was consumed. As reported by Porter and Cady,[3] this reaction mixture had a tendency to decompose depositing elemental sulfur. In the present study, the volume of gas obtained after decomposition of the first product was 1.4 times the original volume of CF_3OF. The decomposition appeared to be catalyzed by Kel-F grease. Nearly complete decomposition of the mixture took place in the gas phase in 2 days at 23° yielding COF_2, SSF_2, SF_4, and elemental sulfur with some SOF_2 and SiF_4. The gaseous decomposition products were identified after fractional codistillation by their infrared spectra. For SSF_2, SF_4, and SOF_2, the spectra corresponded in every detail to those reported by Seel and Budenz.[11] Porter and Cady[3] had identified sulfur, COF_2, and SF_4 as products.

Fractional codistillation of a reaction mixture immediately after completion of reaction revealed five compounds in approximately equal amounts: COF_2, SSF_2, and three addition compounds of CF_3OF and sulfur, A, B, and C. Compound A decomposed very readily into equal amounts of COF_2 and SSF_2, and had infrared absorption bands at 1276 (s), 1234 (s), 1154 (s), and 680–715 cm^{-1} (s). With a boiling point of about 0°, its molecular formula probably was CF_3OS_2F. Compound B, with a boiling point of about 25°, decomposed into COF_2 and SSF_2 in the ratio 2:1. Infrared absorptions were found at 1261 (s), 1199 (s), 1173 (s), 920 (m), 740 (s), 715 (s), and 535 cm^{-1} (w). The molecular formula probably was $(CF_3O)_2S_2$. Compound C appeared to decompose into COF_2 and SF_4. Nmr spectra for compounds A, B, and C were not obtained due to their rapid decomposition, even at −50°, in CF_3Cl or SF_6 solution.

Discussion

An opportunity exists for the addition of CF_3OF to a thiocarbonyl to go in two ways. The trifluoromethoxyl group may become attached either to the sulfur or to the carbon atom. If on the sulfur, a thioperoxide compound is formed as observed in our experiments. On the other hand, if the trifluoromethoxyl group is attached to the carbon of the thiocarbonyl, the product should be a sulfenyl fluoride. Only traces of compounds that appeared to be sulfenyl fluorides were observed. By contrast, substantial yields of compounds having the trifluoromethoxyl group attached to the carbon atom of the thiocarbonyl were found. It is proposed that under the conditions of these reactions, in the presence of CF_3OF, the sulfenyl fluoride is fluorinated with the formation of a C–F bond and an S(IV) compound. This reaction subsequent to the initial addition is not unreasonable in the light of the previously observed reactivity of sulfenyl fluorides.[12,13] Thus, one can say that the ratio of thioperoxide to ether in the final reaction mixture reflects the proportion of addition of the trifluoromethoxyl to the sulfur or to the carbon of the thiocarbonyl, respectively. In the reaction of CF_3OF with thiophosgene, nearly equal amounts of the two addition products $CF_3OSCFCl_2$ and CF_3OCFCl_2 were found. In contrast, carbonyl sulfide gave a preponderance of the carbon methoxyl product, $CF_3OC(O)F$, with only small amounts of a thioperoxide product, $CF_3OSC(O)OCF_3$. (The latter product may arise from the addition of COF_2 to $CF_3OSC(O)F$.) Apparently the direction of addition is controlled by the polarity of the carbon–sulfur bond, with little polarity in thiophosgene and somewhat more in carbonyl sulfide as a result of resonance involving oxygen. Consistent direction in the addition of pentafluorosulfur hypofluorite to unsymmetrical olefins has been previously observed[14–16] and can be rationalized either on the basis of polar direction with the oxygen positive with respect to the fluorine or on the basis of initial free radical attack by the fluorine in a chain as suggested by Place and Williamson.[16] The mixture of products in our CF_3OF addition reactions shows an unexpected ambivalence in the direction of addition.



The properties of the new compounds prepared in these addition reactions, $CF_3OSCFCl_2$, CF_3OCFCl_2, and $CF_3OSC(O)OCF_3$, are much as one expects. They are somewhat sensitive to moisture but stable at room temperature. The nmr coupling of $CF_3OSCFCl_2$ is somewhat larger than usual for fluorine atoms separated by five bonds, perhaps due to the more bulky chlorines

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forcing a preference for some configurations of the chain. Perfluoroalkyl peroxides and disulfides are well known, in general being more stable than the corresponding hydrocarbon-based compounds. The fluorinated thioperoxides reported here are among the first of this class of compound to be reported.

The gentle reaction of CF_3OF with elemental sulfur is very interesting in that several compounds related to the recently characterized S_2F_2 isomers apparently were formed.

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The Preparation of Sodium Cobalt Tetracarbonyl[1]

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In the course of spectroscopic studies, numerous preparations of $NaCo(CO)_4$ were made in this laboratory. Many of these were carried out by the reaction of Na amalgam and $Co_2(CO)_8$ in THF.[2] This is a standard preparation of a salt widely used in synthetic work.[3] At first, the reaction proceeded smoothly and in reasonable time, as indicated in the literature. In time, however, we were unable to make the reaction proceed. The difficulties are indicated here, some of their implications are discussed, and a better method of preparation is given.

Results

At the beginning of the work, a portion of a sample of solid Na amalgam, prepared several years earlier in the usual manner,[4] was added to $Co_2(CO)_8$ dissolved in THF which had been dried over CaH_2–$LiAlH_4$ and the mixture was shaken. The reaction proceeded smoothly from the original very dark brown solution of $Co_2(CO)_8$ to the light yellow solution of $NaCo(CO)_4$ in THF in about 1 hr. In an "improvement" of our technique, we prepared the amalgam *in situ*, added a more concentrated THF solution of $Co_2(CO)_8$ to it, and then shook the mixture. When the solution did not turn yellow after shaking for about 2 hr, it was transferred to another tube with its freshly prepared amalgam and subjected to another period of shaking. The desired yellow color was usually obtained after one to three transfers.

In time, the development of the spectroscopic work led to a need to ensure the absence of traces of H_2O (and O_2) in the $NaCo(CO)_4$ solutions. Consequently, the THF was dried and deoxygenated in a rigorous manner (see Experimental Section) and the method of preparing the amalgam and handling the materials were improved. As a result of these precautions, there was no visual evidence for a reaction even after long standing. However, after several weeks of stirring a mixture of amalgam and $Co_2(CO)_8$ solution prepared under these conditions, an infrared spectrum of the still dark brown solution showed that the $Co_2(CO)_8$ had been consumed and that $Co(CO)_4^-$ ion had been formed. The same reaction was found to take place in a THF solution of $Co_2(CO)_8$ to which *no* sodium amalgam had been added.

As these difficulties were becoming serious, we began to investigate other methods of preparing $NaCo(CO)_4$ which would be suitable for the present purposes. The use of Na in place of Na amalgam seems to lead to the same reaction difficulties. It was found, however, that powdered NaOH reacts with $Co_2(CO)_8$ in THF to yield the desired yellow solution of $NaCo(CO)_4$ in 1–2 hr. The reaction gives a clean solution of the salt. In particular, no NaOH is present in solution in significant amount although there are some traces of water. A white, solid salt may be isolated by vacuum removal of the solvent. A dry solution of $NaCo(CO)_4$ in THF may be prepared by dissolving the solid salt, prepared as above, in dry THF.

Discussion

The reaction between Na amalgam and $Co_2(CO)_8$ in THF is viewed as taking place by eq 1.[2] The results

$$2Na + Co_2(CO)_8 \longrightarrow 2Na^+ + 2Co(CO)_4^- \qquad (1)$$

cited here show that the reaction is more complicated than indicated by this equation. The reaction to form $NaCo(CO)_4$ is slow or does not proceed when the THF is effectively dried and the Na amalgam is formed under conditions which discourage the formation of NaOH. In fact, it is difficult to escape the conclusion that our success with the amalgam reaction in the early phases of our work was due to the presence of NaOH either brought in with the amalgam and/or formed from water in the solvent.

THF is a Lewis base and hence it is capable of undergoing the reaction with $Co_2(CO)_8$ reported for a number of such bases[5–7] and shown in eq 2. Our results, ob-

$$3Co_2(CO)_8 + 12THF \longrightarrow 2Co(THF)_6[Co(CO)_4]_2 + 8CO \qquad (2)$$

tained by stirring a THF solution of $Co_2(CO)_8$ for several days, show that this reaction takes place slowly at room temperature. This reaction forms an explanation for the slow consumption of the $Co_2(CO)_8$ with the formation of $Co(CO)_4^-$ under the more stringent conditions of preparing and stirring a mixture of Na amalgam and $Co_2(CO)_8$ in THF.

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