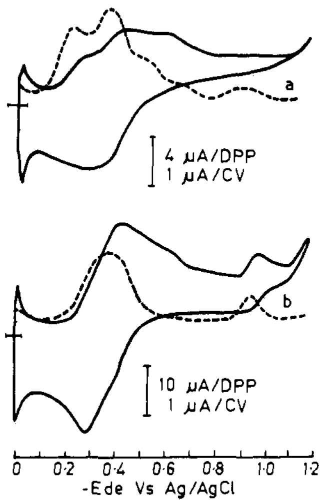

Figure 8. Differential-pulse and cyclic voltammograms of oxygenated $K[Ru(EDTA\text{-}H)H_2O]\cdot 2H_2O$ (1×10^{-3} M) solution of $\mu = 0.1$ M KCl and at *a* ([NaOH]/[ML]) = 1.5: (a) at room temperature; (b) under hot conditions.

chemical studies, the DPP peaks at −0.375 and −0.920 V remained unaffected whereas those at −0.220, −0.520, and −0.660 V decreased in intensity (Figure 8). Similar observations were made for the CV also. The dc polarograms of the solution boiled and cooled under nitrogen were found to be similar to that of solution B1 under nitrogen (Figure 4). When these solutions were exposed to air and oxygen, the original DPP and CV (i.e. before boiling) were reproduced.

The absorption spectrum of solution B2 under oxygen also showed changes on boiling compatible with the results of DPP and CV. Figure 9 compares the spectra before and after boiling. Boiling of solution B2 causes a decrease in the intensity of the peaks at 622 and 390 nm with appearance of peak at 587 (ϵ 31) and 557 nm (ϵ 37) and a change in color of the complex from green to yellow. The peaks at 280 and 224 nm remain unaffected. The original spectrum of **3** was reproduced on exposing the solution to oxygen when the solution turns green.

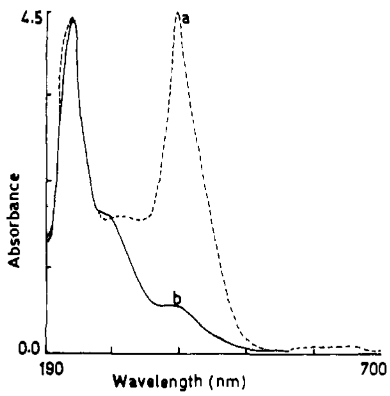

Figure 9. Absorption spectra of oxygenated $K[Ru(EDTA\text{-}H)H_2O]\cdot 2H_2O$ (1×10^{-3} M) solution at $\mu = 0.1$ M KCl and at *a* ([NaOH]/[ML]) = 1.5: (a) at room temperature; (b) under hot conditions.

The electrochemical and spectrophotometric results thus support a reversible binding of dioxygen in complex **3**. Solution C2 does not exhibit this type of reversible behavior with oxygen.

Oxygen Absorption Studies. Solution A2 does not show any oxygen absorption. Thus oxygen does not react with complex **2** in acidic solution. In solution B2, however, absorption of oxygen was observed and the stoichiometry of dioxygen complex was found by the expression

$$N = N_r V / V_r$$

where N_r is the number of moles of oxygen bound per mole of reference complex $[(Ru^{III}EDTA)_2O_2(OH)]$ and V and V_r are volumes of oxygen absorbed by complex **2b** and reference, respectively, at constant temperature and pressure. The value of N was found to be 1. This supports the composition of complex **3** as a μ-peroxo species of Ru(IV). No absorption of oxygen was observed in solution C2.

Registry No. 1, 76095-13-1; **2**, 15282-93-6; **2a**, 68122-22-5; **2b**, 66844-68-6; **2c**, 102682-51-9; **3**, 102682-52-0; **3a**, 102682-53-1; **4**, 102682-54-2; **4a**, 102682-55-3; **4b**, 102682-59-7; **4c**, 102682-58-6; **5**, 102682-56-4; **5a**, 102682-57-5.

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Oxidative-Addition/Addition Reactions of *F-tert*-Butyl Hypochlorite with Perfluoromono- or Perfluorodiiodoalkanes, Pentafluoroiodobenzene, and Hexafluorobenzene

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At 0 °C, $(CF_3)_3COCl$ undergoes oxidative addition reactions with CF_3I, ICF_2CF_2I, $SF_5CF_2CF_2I$, and C_6F_5I to form $CF_3I[OC(CF_3)_3]_2$, $[(CF_3)_3CO]_2ICF_2CF_2I[OC(CF_3)_3]_2$, $SF_5CF_2CF_2I[OC(CF_3)_3]_2$, and $C_6F_5I[OC(CF_3)_3]_2$, respectively. In a further reaction of the latter with $(CF_3)_3COCl$, addition to the ring occurs to form $[(CF_3)_3CO]_2IC_6F_5[(CF_3)_3CO]_2Cl_2$. With C_6F_6, $(CF_3)_3COCl$ gives $C_6F_6[OC(CF_3)_3]_2Cl_2$. The new compounds are stable viscous liquids or low-melting solids.

Introduction

The reactions of hypochlorites continue to attract the attention of chemists who are interested in new materials. Trifluoromethyl hypochlorite and *F-tert*-butyl hypochlorite have been studied most thoroughly, and while they both undergo oxidative addition and/or oxidative displacement reactions in general, $(CF_3)_3COCl$ has the advantage over CF_3OCl as a synthetic reagent because it does not also act indirectly, via its decomposition, as a fluorinating agent. It is interesting to note that with the exception of the reaction of $(CF_3)_3COCl$ with SO_2 to form $(CF_3)_3COSO_2Cl$, there are no examples of its oxidative-addition reactions in which the highest possible oxidation state of the central element is formed, e.g.: S(0) → S(IV), S(II) → S(IV); I(0) → I(III); Te(0) → Te(IV); Pb(O) → Pb(II); Bi(0) → Bi(III).[2-6] In this paper, we

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(1) (a) Portland State University. (b) University of Idaho.

(2) Young, D. E.; Anderson, L. R.; Fox, W. B. *Inorg. Chem.* **1971**, *10*, 2810.

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have utilized the mild oxidizing characteristics of $(CF_3)_3COCl$ to form some new stable (polyfluoroalkyl)iodine(III) and (pentafluorophenyl)iodine(III) derivatives. Although the hypochlorite does undergo addition to the aromatic ring of C_6F_6 or $C_6F_5I[OC(CF_3)_3]_2$, there is no indication for the formation of an I(V) species.

Results and Discussion

Interestingly, $CF_3I[OC(CF_3)_3]_2$ is prepared by condensing $(CF_3)_3COCl$ onto CF_3I. The reaction occurs at 0 °C to give the product in a high yield:

$$CF_3I + 2(CF_3)_3COCl \xrightarrow{0\ ^\circ C} CF_3I[OC(CF_3)_3]_2 + Cl_2 \quad (1)$$

The new (trifluoromethyl)iodine(III) bis(*F-tert*-butoxide) is a light yellow liquid at room temperature. Although no molecular ion was observed in the mass spectrum, the $[M - (CF_3)_3CO]^+$ ion and other appropriate ions such as $[M - (CF_3)_3CO - CF_3]^+$, $[M - 2(CF_3)_3CO]^+$, and I^+ were observed.

When *F-tert*-butyl hypochlorite was reacted with ICF_2CF_2I at 0 °C, the yield of $[(CF_3)_3CO]_2ICF_2CF_2I[(CF_3)_3CO]_2$ was essentially quantitative.

$$ICF_2CF_2I + 4(CF_3)_3COCL \xrightarrow{0\ ^\circ C} [(CF_3)_3CO]_2ICF_2CF_2I[(CF_3)_3CO]_2 + 2Cl_2 \quad (2)$$

Sublimation results in a light yellow solid, which melts rapidly with decomposition at 95 °C.

The mass spectrum did not contain the molecular ion but the following appropriate fragments were found: $[M - (CF_3)_3CO]^+$, $I[(CF_3)_2CO)]_2^+$, $[M - 3(CF_3)_3CO]^+$, and I^+.

If, instead of ICF_2CF_2I, the pentafluorosulfur derivative $SF_5CF_2CF_2I$ was used, the following reaction occurred:

$$SF_5CF_2CF_2I + 2(CF_3)_3COCl \xrightarrow{0\ ^\circ C} SF_5CF_2CF_2I[(CF_3)_3CO]_2 + Cl_2 \quad (3)$$

The light yellow solid melts at 38 ± 0.5 °C.

The reaction of $(CF_3)_3COCl$ with pentafluoroiodobenzene gave two new compounds. This reaction appears to occur in two steps; in the first step the following reaction occurred:

$$C_6F_5I + 2(CF_3)_3COCl \xrightarrow{0\ ^\circ C} C_6F_5I[(CF_3)_3CO]_2 + Cl_2 \quad (4)$$

The new compound, (pentafluorophenyl)iodine(III) bis(*F-tert*-butoxide), is a white solid which melts at 31 ± 1 °C. Although no molecular ion was observed, the mass spectrum did contain the fragments $[M - (CF_3)_3CO]^+$, $[M - 2(CF_3)_3CO]^+$, $(C_6F_5)^+$, and I^+. The second step involved the addition of chlorine and *F-tert*-butoxy groups to the benzene ring:

$$C_6F_5I[(CF_3)_3CO]_2 + 2(CF_3)_3COCl \xrightarrow{0\ ^\circ C} [(CF_3)_3CO]_2IC_6F_5[(CF_3)_3CO]_2Cl_2 \quad (5)$$

The product resulting from reaction 5 was a viscous colorless oil. Although no molecular ion was observed in the mass spectrum, the following ions were observed: $[M - 2(CF_3)_3CO]^+$, $[M - 2(CF_3)_3CO - I]^+$, $[M - 3(CF_3)_3CO]^+$, $[M - 4(CF_3)_3CO]^+$, $(C_6F_5Cl_2)^+$, and $(C_6F_5Cl)^+$.

When hexafluorobenzene was treated with CF_3OF or $(CF_3)_3COF$, it was found that addition occurred more readily with the latter fluoroxy compound.[7] When C_6F_6 and $(CF_3)_3COF$ were equimolar, the products were $C_6F_7[(CF_3)_3CO]$ (60%) and $C_6F_8[(CF_3)_3CO]_2$ (30%) plus dimers and a trace of the tris(*F-tert*-butoxy) adduct $C_6F_9[(CF_3)_3CO]_3$. It was of interest to determine whether $(CF_3)_3COCl$ would add to perfluorobenzene in a manner similar to that found in reaction 5 or in the manner found for $(CF_3)_3COF$.

The reaction occurs at room temperature to give largely a dichloro derivative:

$$C_6F_6 + 2(CF_3)_3COCl \rightarrow C_6F_6[(CF_3)_3CO]_2Cl_2 \quad (6)$$

The mass spectrum did not contain a molecular ion, but other appropriate ions were found: $(M - F)^+$, $(M - Cl)^+$, $[M - (CF_3)_3CO]^+$, $[M - (CF_3)_3CO - Cl]^+$, $[M - (CF_3)_3CO - 2Cl]^+$, and $[M - 2(CF_3)_3CO]^+$. No attempts were made to isolate or determine possible isomers.

The infrared spectra of all new compounds clearly indicate the presence of $t\text{-}C_4F_9O$ groups with absorption bands in the 1146–1309-cm^{-1} region attributable to the C–F stretching frequencies and with bands in the 730–764-cm^{-1} region for the C–F deformation modes. It is likely that the absorption bands around 1000 cm^{-1} are due to the stretching C–O–C vibrations. The absorption bands in the 869–894-cm^{-1} region for $SF_5CF_2CF_2I[(CF_3)_3CO]_2$ are assigned to S–F stretching vibrations; one of the S–F deformation modes was found near 600 cm^{-1}.

The ^{19}F NMR spectrum for $CF_3I[(CF_3)_3CO]_2$ gave two multiplets: the multiplet centered at ϕ −72.6 is attributable to the *F-tert*-butoxide groups; for $I[(CF_3)_3CO]_3$ this resonance was found at ϕ −72.6.[6] The multiplet centered at ϕ −25.5 is due to the presence of the CF_3 group directly attached to I(III). In CF_3IF_2 and $CF_3I(NO_3)_2$ the CF_3 resonance was found at ϕ −28.8 and −25.4, respectively.[8,9] Structural confirmation for $[(CF_3)_3CO]_2ICF_2CF_2I[(CF_3)_3CO]_2$ was obtained from its ^{19}F NMR spectrum: the multiplet centered at ϕ −72.2 is attributable to the *F-tert*-butoxide groups and agrees with the results discussed above. The broad resonance band, centered at ϕ −60.7, is assigned to the CF_2 group on the basis of the relative band area. The ^{19}F NMR spectrum of $SF_5CF_2CF_2I[(CF_3)_3CO]_2$ in $CFCl_3$ solution contains the expected resonances for the SF_5 group (AB_4 pattern): ϕ 60.0 (SF), 47.0 (SF_4). The resonance band at ϕ −72.6 is due to the CF_3 groups while the signals at ϕ −65.1 and −91.6 are assigned to the CF_2I and SF_5CF_2 groups, respectively. In $SF_5CF_2CF_2IF_2(CH_3CN)$ the corresponding peaks were ϕ 57 (SF), 46 (SF_4), −96 (SF_5CF_2) and −87 (CF_2I).[10] In $SF_5CF_2CF_2Br$ the SF_5CF_2 and CF_2Br fluorine resonances were found at ϕ −93.7 and −66.4, respectively.[11] The ^{19}F NMR spectrum for $C_6F_5I[(CF_3)_3CO]_2$ contains resonances at ϕ −72.7, −121.7 (multiplet), −142.9 (multiplet), and −156.9 (multiplet); the relative band areas are 18.1:2.0:1.0:2.0, respectively. The band found at ϕ −72.7 is clearly due to the CF_3 group while for the C_6F_5 group the multiplets centered at ϕ −121.7, −142.9, and −156.9 are due to $F_{2,6}$, F_4 and $F_{3,5}$ nuclei, respectively. In $C_6F_5IF_2$ these values are $\phi(F_{2,6}) = -123.3$, $\phi(F_4) = -144.8$, $\phi(F_{3,5}) = -157.5$.[12]

The oil produced via eq 5 gave a complex NMR spectrum; two types of CF_3 groups were found with one multiplet centered at ϕ −71.9 [$(CF_3)_3CO$ groups bonded to I] and a broad multiplet centered at ϕ −69.8 [$(CF_3)_3CO$ groups on benzene ring]. The relative peak areas are 1.0:1.0. Additional complex and very broad resonances were found for the fluorines of the benzene ring in the region ϕ −115 to −150.

The NMR spectrum of the dichloro-*F-tert*-butoxide derivative of perfluorobenzene contains the very strong multiplet at ϕ −71.6, which is assigned to the CF_3 groups of $(CF_3)_3CO$. Additionally, complex and broad resonances in the region ϕ −115 to −157 were present, and these are attributed to the perfluorocyclic group.

Experimental Section

Materials. The compounds used in this work were obtained from commercial sources: CF_3I, ICF_2CF_2I, C_6F_5I, $(CF_3)_3COH$, C_6F_6, CsF (Peninsular Chem Research); ClF (Pennwalt Chemicals). $(CF_3)_3COH$ was dried and stored over type 5A molecular sieves, C_6F_5I and ICF_2CF_2I

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were treated with mercury prior to use, and the remaining reagents were used without further purification. $(CF_3)_3COCl$ was synthesized by an adaptation of the method used by Young, Anderson, Gould, and Fox[13] suggested to us by Dr. Q. C. Mir. $(CF_3)_3COH$ and a slight excess of ClF were condensed into a pretreated stainless-steel reaction vessel, which was allowed to warm to 0 °C and remain there for approximately 15 h. The contents of the vessel were condensed into a second metal reaction vessel containing an excess amount of CsF. This reaction vessel was shaken frequently white it was warmed slowly to 0 °C. Trap-to-trap distillation was used to separate the $(CF_3)_3COCl$ (−78 °C) from the unreacted ClF (−196 °C). $SF_5CF_2CF_2I$ was prepared by a literature method.[14]

General Procedure. Gases were manipulated in a conventional Pyrex vacuum apparatus equipped with a Heise Bourdon tube gauge and a Televac thermocouple gauge. Infrared spectra were obtained by using a 8.25-cm Monel cell with KBr or KRS-5 windows or as solids between KBr, KRS-5, or NaCl disks on a Perkin-Elmer 476 spectrometer. The spectra were calibrated with a polystyrene film. The NMR spectra were recorded with a Varian Model EM-390 spectrometer operating at 90.0 MHz for proton and 84.67 MHz for fluorine resonances. Me_4Si and F-11 were used as internal standards. The mass spectra were taken on a CEC 21-110B double-focus mass spectrometer equipped with a KV ion accelerator and operated at 70 V or with a VG-7070H5 mass spectrometer. Perfluorokerosene (PFK) was used as an internal standard. Elemental analsyes were determined by Beller Microanalytical Laboratory in Gottingen, West Germany.

CF_3I with $(CF_3)_3COCl$. Into a 75-mL Pyrex-glass vessel equipped with a Kontes Teflon valve and Teflon stirring bar were added 1.019 mmol of CF_3I and 2.916 mmol of $(CF_3)_3COCl$. The reaction mixture was maintained at 0 °C (50 h). Separation and analysis of the volatile material gave $(CF_3)_2CO$, CF_3Cl, CF_3I and Cl_2 (1.010 mmol; theor 1.019 mmol). The light yellow liquid left behind was found to be 0.953 mmol of $CF_3I[OC(CF_3)_3]_2$ and was formed in 94% yield. The infrared spectrum of the liquid had the following bands (cm^{-1}): 1262 (s with sh at 1305), 1244 (s, br with sh at 1215), 1194 (w), 1164 (m), 1115 (s), 1071 (w), 1026 (s), 1007 (ms), 980 (s), 768 (m), 744 (ms), 731 (s), 726 (s), 691 (m).

The ^{19}F NMR spectrum contained two resonance bands at ϕ −25.5 (multiplet) and −72.6 (multiplet) with relative band areas of 1.0:6.2, respectively (theor 1.0:6.0). The mass spectrum for $CF_3I[(CF_3)_3CO]_2$ had the following *m/e* peaks: 431, $[M - (t\text{-}R_fO)]^+$; 362, $[M - (t\text{-}R_fO) - CF_3]^+$; 197, $[(t\text{-}R_fO) - 2F]^+$; 196, $[M - (2t\text{-}R_fO)]^+$; 177, $(CF_2I)^+$; 167, $(IOC_2)^+$; 147, $(C_3F_5O)^+$; 128, $(C_3F_4O)^+$; 127, $(I)^+$; 97, $(C_2F_3O)^+$; 78, $(C_2F_2O)^+$; 69, $(CF_3)^+$; 50, $(CF_2)^+$.

Anal. Calcd for $C_9F_{21}IO_2$: I, 19.1. Found: I, 18.8.

ICF_2CF_2I with $(CF_3)_3COCl$. Into a 75-mL Pyrex-glass vessel equipped with a Kontes Teflon valve and Teflon stirring bar were added 0.5455 mmol of ICF_2CF_2I and a total of 5.63 mmol of $(CF_3)_3COCl$. The reaction mixture was maintained at 0 °C (4 days). Separation and analysis of the volatile material resulted in finding $(CF_3)_2CO$, CF_3Cl, $(CF_3)_3COCl$, and Cl_2. The light yellow solid left behind, $[(CF_3)_3CO]_2ICF_2CF_2I[(CF_3)_3CO]_2$, was obtained in essentially 100% yield. The solid sublimes at 90 °C in a vacuum, with slow decomposition at 85 °C and rapid melting at 95 °C with I_2 evolution. The infrared spectrum of the solid had the following bands (cm^{-1}): 1265 (vs, br with sh at 1309 and 1215), 1190 (ms), 1173 (s), 1150 (s), 1140 (s), 1115 (s), 980 (vs), 970 (vs), 778 (ms), 727 (s), 722 (s), 688 (m), 654 (m with sh at 640), 595 (w), 577 (w), 537 (m), 521 (m), 462 (m).

The ^{19}F NMR spectrum contained two resonance bands at ϕ −60.7 and −72.2 (multiplet) with relative peak areas 1.0:90, respectively (theor 1.0:9.0). The mass spectrum for $[(CF_3)_3CO]_2ICF_2CF_2I[(CF_3)_3CO]_2$ had the following *m/e* peaks: 1059, $(M - t\text{-}R_fO)^+$; 597, $[I(t\text{-}R_fO)_2]^+$; 589, $[M - 3(t\text{-}R_fO)]^+$; 388, $[I(t\text{-}R_fO)_2 - 11F]^+$ or $[IO_2C_8F_7]^+$; 367, $[(OIC_2F_4IO - F)]^+$ or $[(t\text{-}R_fOICF_2CF_2 - 5F)]^+$; 330, $(IO_2C_8F_4)^+$; 324, $(IOC_4F_7)^+$; 305, $(IOC_4F_6)^+$; 300, $(IO_2C_7F_3)^+$; 286, $(IOC_4F_5)^+$; 274, $[I(t\text{-}R_fO - CF_4)]^+$; 267, $(IOC_4F_4)^+$; 266, $[(CF_3)_3COCF]^+$; 248 $(IOC_4F_3)^+$; 233, $(IO_2C_3F_2)^+$; 229, $(IOC_4F_2)^+$; 221, $(IO_2C_2F_2)^+$; 219, $[(CF_3)_3C]^+$; 217, $(IOC_3F_2)^+$; 216, $[(t\text{-}R_fO) - F]^+$; 205, $(IOC_2F_2)^+$; 198, $(IOC_3F)^+$; 128, $(C_3F_4O)^+$; 127, $(I)^+$.

Anal. Calcd for $C_{18}F_{40}I_2O_4$: C, 16.71; F, 58.7; I, 19.61. Found: C, 16.17; F, 57.2; I, 19.76.

$SF_5CF_2CF_2I$ with $(CF_3)_3COCl$. Into a 50 mL Pyrex-glass vessel equipped with a Kontes Teflon valve and Teflon stirring bar were added 1.306 mmol of $SF_5CF_2CF_2I$ and 4.993 mmol of $(CF_3)_3COCl$. The reaction mixture was maintained at 0 °C (3 days). Separation and analysis of the volatile material gave $(CF_3)_2CO$, CF_3CI, and Cl_2 (1.167 mmol; theor 1.306 mmol). The light yellow solid left behind was found to be 1.136 mmol of $SF_5CF_2CF_2I[OC(CF_3)_3]_2$ and was formed in 87% yield; mp 38 ± 0.5 °C. The infrared spectrum of the solid had the following bands (cm^{-1}): 1309 (s), 1270 (vs), 1244 (vs with sh at 1220), 1192 (m), 1155 (s), 1115 (vs), 1023 (wm), 981 (s), 967 (s), 894 (vs), 869 (s), 868 (wm), 770 (wm), 731 (s), 721 (s), 714 (s), 691 (wm), 679 (m), 606 (s), 590 (m), 573 (w), 536 (w), 522 (w), 453 (w).

The ^{19}F NMR spectrum contained the following resonance multiplet bands: ϕ 60.0, 47.0 (doublet of mulitplets), −65.1, −72.6, −91.6 (pentet of multiplets). Respective relative band areas: SF, 1.0; SF_4, 4.0; CF_2I, 2.0; $C(CF_3)_3$, 17.9; SF_5CF_2, 2.0. Coupling constants: $J_{F-SF_4} = 141$ Hz, $J_{SF_4-CF_2} = 15.5$ Hz.

Anal. Calcd for $C_{10}F_{27}ISO_2$: C, 14.58; F, 62.2; S, 3.89; I, 15.40. Found: C, 14.42; F, 62.0; S, 4.00; I, 15.53.

Excess C_6F_5I with $(CF_3)_3COCl$. Into a 200-mL Pyrex-glass vessel equipped with a Kontes Teflon valve and Teflon stirring bar were added 0.8814 mmol of C_6F_5I and 1.28 mmol of $(CF_3)_3COCl$. The reaction mixture was maintained at 0 °C (3.5 days). Analysis of the volatile material showed $(CF_3)_3COCl$ to be present. The white solid left behind, 0.7404 mmol of $C_6F_5I[(CF_3)_3CO]_2$, was obtained in 84% yield; mp 31 ± 1 °C. The infrared spectrum of the solid had the following bands (cm^{-1}): 1635 (wm), 1510 (s), 1406 (w), 1376 (w), 1255 (vs, br with sh at 1303 and 1215), 1188 (m), 1172 (s), 1146 (s), 1115 (s), 1094 (s), 978 (s), 806 (m), 764 (m), 725 (s), 687 (wm), 640 (w), 621 (w), 575 (wm), 537 (m), 521 (wm), 512 (wm), 487 (w), 452 (wm).

The ^{19}F NMR spectrum contained a resonance band at ϕ −72.7 and multiplets at ϕ −121.7, −142.9, and −156.9 (relative band area 18.1:2.0:1.0:2.0, respectively). A molecular ion was not observed but other fragment ions were found. Mass spectrum (*m/e*): 529, $[,m - (t\text{-}R_fO)]^+$; 295, $(IO_2C_5F_4)^+$; 294, $[M - 2(t\text{-}R_fO)]^+$; 237, $(IC_6F_2)^+$; 231, $(IO_2C_6)^+$; 218, $(IC_6F)^+$; 217, $(IOC_3F_2)^+$; 198, $(IOC_3F)^+$; 197, $(C_4F_7O)^+$; 182, $(IC_3F)^+$; 181, $(C_4F_7)^+$; 169, $(C_3F_7)^+$; 168, $(C_5F_4O_2)^+$; 167, $(C_6F_5)^+$ or $(IOC_2)^+$; 163, $(IC_3)^+$; 159, $(IO_2)^+$; 148, $(C_6F_4)^+$; 147, $(C_3F_5O)^+$; 143, $(C_4F_5)^+$ or (IO^+); 129, $(C_6F_3)^+$; 128, $(C_3F_4O)^+$; 117, $(C_5F_3)^+$; 110, $(C_6F_2)^+$; 109, $(C_3F_3O)^+$; 98, $(C_5F_2)^+$; 97, $(CF_3CO)^+$; 95, $(C_5FO)^+$; 93, $(C_3F_3)^+$; 91, $(C_6F)^+$; 83, $(C_4FO)^+$; 78, $(C_2F_2O)^+$; 74, $(C_3F_2)^+$; 72, $(C_6)^+$; 71, $(C_3FO)^+$; 69, $(CF_3)^+$; 60, $(C_5)^+$; 59, $(C_2FO)^+$.

Anal. Calcd for $C_{14}F_{23}IO_2$: I, 16.6. Found: 17.0.

C_6F_5I with Excess $(CF_3)_3COCl$. Into a 200-mL Pyrex-glass vessel equipped with a kontes Teflon valve and Teflon stirring bar were added 0.8515 mmol of C_6F_5I and a total of 1.96 mmol of $(CF_3)_3COCl$. The reaction mixture was maintained at 0 °C (21.5 h). Separation and analysis of the volatile material gave $(CF_3)_2CO$, CF_3Cl, $(CF_3)_3COCl$, and Cl_2 (0.7729 mmol; theor 0.8515 mmol). The white solid left behind was 0.8403 mmol of $C_6F_5I[(CF_3)_3CO]_2$, formed in 99% yield.

To the above white solid product was added 4.0 mmol of $(CF_3)_3COCl$. The reaction mixture was maintained at 0 °C (16 days). Separation and analysis of the volatile material gave $(CF_3)_2CO$, CF_3Cl, and $(CF_3)_3COCl$. A colorless viscous liquid was left behind, which was 0.7835 mmol of $C_6F_5I[(CF_3)_3CO]_4Cl_2$ (yield 93%). The infrared spectrum of the liquid had the following bands (cm^{-1}): 1670 (w), 1507 (w), 1258 (vs, br with sh at 1300 and 1220), 1135 (s with sh at 1165), 1110 (s), 1065 (m), 963 (s, br), 906 (w), 830 (m), 763 (m), 723 (s), 682 (w), 635 (vw), 570 (vw), 534 (m), 511 (wm), 490 (vw), 446 (wm).

The ^{19}F NMR spectrum contained one multiplet at ϕ −71.9 and a broad multiplet at ϕ −69.8 (relative band areas 1.0:1.0). Additional multiplets were found in the region ϕ −115 to −150. The mass spectrum for $C_6F_5I[(CF_3)_3CO]_4Cl_2$ had the following *m/e* peaks: 834, 836, 838, $[M - 2(t\text{-}R_fO)]^+$; 815, 817, $[M - (t\text{-}R_fO) - (t\text{-}R_f) - Cl]^+$; 799, 801, $[M - 2(t\text{-}R_fO) - Cl]^+$; 764, $[M - 2(t\text{-}R_fO) - 2Cl]^+$; 707, 709, 711, $[M - 2(t\text{-}R_fO) - I]^+$; 688, 690, 692, $[C_6F_4(t\text{-}R_fO)_2Cl_2]^+$; 653, 655, $[C_6F_4(t\text{-}R_fO)_2Cl]^+$; 599, 601, 603, $[M - 3(t\text{-}R_fO)]^+$; 578, $[I(t\text{-}R_fO)_2 - F]^+$; 537, 539, $(IO_3C_{13}F_9Cl)^+$; 509, $[I(t\text{-}R_fO)_2 - CF_4]^+$; 459, $(I(t\text{-}R_fO)_2 - CF_3]^+$; 456, $(IO_3C_{11}F_6Cl)^+$; 413, 415, $(IO_3C_9F_5Cl)^+$; 400, 402, 404, $(IO_3C_5F_5Cl_2)^+$; 390, $[I(t\text{-}R_fO)_2 - 3CF_3]^+$; 364, 366, 368, $[M - 4(t\text{-}R_fO)]^+$; 345, 347, $(IOC_6F_5Cl)^+$; 345, 347, 349, $(IC_6F_4Cl_2)^+$; 324, $(IOC_4F_7)^+$; 331, $[(t\text{-}R_fO)CFCFCl]^+$; 329, 331, $(IC_6F_5Cl)^+$; 319, $(IO_2C_7F_4)^+$; 314, $(IO_2C_5F_5)^+$; 310, $(IOC_6F_5)^+$; 305, $(IOC_4F_6)^+$; 300, $(IO_2C_7F_3)^+$; 286, $(IOC_4F_5)^+$; 284, $(IOC_7F_3)^+$; 283, $(IO_2C_4F_4)^+$; 274, $(IOC_3F_5)^+$; 267, $(IOC_4F_4)^+$; 266, $[(CF_3)_3COCF)]^+$, 264, $(IO_2C_4F_3)^+$; 252, $(IO_2C_3F_3)^+$; 248, $(IOC_4F_3)^+$; 237, 239, 241, $(C_6F_5Cl_2)^+$; 235, $[(CF_3)_3CO]^+$; 224, $(IOC_2F_3)^+$; 221, $(IO_2C_2F_2)^+$; 218, 220, 222, $(C_6F_4Cl_2)^+$; 219, $[(CF_3)_3C]^+$; 217, $(IOC_3F_2)^+$; 216, $(t\text{-}R_fO\text{-}F)^+$; 205, $(IOC_2F_2)^+$; 202, 204, $(C_6F_5Cl)^+$; 200, $(C_4F_8)^+$; 199, 201, 203, $(C_6F_3Cl_2)^+$; 198, $(IOC_3F)^+$; 129, $(C_6F_3)^+$; 128, $(C_3F_4O)^+$; 127, $(I)^+$; 124, $(C_4F_4)^+$; 121, $(C_4F_3O)^+$.

Anal. Calcd for $C_{22}Cl_2F_{41}IO_4$: C, 20.25; F, 59.7; Cl, 5.43; I, 9.72. Found: C, 20.49; F, 57.8; Cl, 5.42; I, 10.41.

C_6F_6 with Excess $(CF_3)_3COCl$. Into a 50-mL Pyrex-glass vessel equipped with a Kontes Teflon valve and Teflon stirring bar were added 3.022 mmol of C_6F_6 and a total of 9.926 mmol of $(CF_3)_3COCl$. The

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reaction mixture was maintained at 0 °C (3 days) and room temperature (9 days). Removal of volatile materials at −17 to −23 °C left behind a clear colorless liquid, which was 2.900 mmol of $C_6F_6[(CF_3)_3CO]_2Cl_2$ [yield 96%; bp 79–80 °C (2mm)].

The infrared spectrum of the liquid had the following bands (cm^{-1}): 1740 (w), 1341 (ms), 1264 (s), 1228 (ms), 1204 (ms), 1134 (s), 1093 (m), 1075 (m), 1033 (w), 989 (s), 972 (s), 914 (w), 899 (w), 837 (m), 744 (m), 730 (s), 708 (w), 690 (w), 542 (w).

The ^{19}F NMR spectrum contained a very strong band at ϕ −71.6 and additional multiplets in the ϕ −115 to −157 region. The mass spectrum for $C_6F_6[CF_3)_3CO]_2Cl_2$ had the following *m/e* peaks: 707, 709, 711, $(M - F)^+$; 691, 693, $(M - Cl)^+$; 637, $(M - Cl_2F)^+$; 491, 493, 495, $[M - (t\text{-}R_fO)]^+$; 456, 458, $[M - (t\text{-}R_fO) - Cl]^+$; 437, 439, $[M - (t\text{-}R_fO) - ClF]^+$; 425, 427, $[M - (t\text{-}R_fO)\text{–}CFCl]^+$; 421, $[M - (t\text{-}R_fO) - Cl_2]^+$; 394, 396, $[t\text{-}R_fO(CF)_4Cl]^+$; 285, $(C_{10}F_7O_2)^+$; 237, 239, $(C_6F_6ClO)^+$; 235, $(t\text{-}R_fO)^+$; 225, 227, $(C_5F_5ClO)^+$; 221, 223, $(C_6F_6Cl)^+$; 219, $[(CF_3)_3C]^+$; 211, 213, $(C_7F_4ClO)^+$; 209, 211, $(C_5F_6Cl)^+$; 209, $(C_5F_7O)^+$; 202, $(C_6F_6O)^+$; 197, $(C_4F_7O)^+$; 187, 189, $(C_5F_4ClO)^+$; 186, $(C_6F_6)^+$; 175, 177, $(C_4F_4ClO)^+$; 171, 173, $(C_5F_4Cl)^+$; 159, 161, $(C_4F_4Cl)^+$; 155, $(C_5F_5)^+$; 147, $(C_3F_5O)^+$; 131, $(C_3F_5)^+$; 124, $(C_4F_4)^+$; 117, 119, 121, $(CFCl_2O)^+$; 117, $(C_5F_3)^+$; 113, 115, $(C_2F_2OCl)^+$; 109, $(C_3F_2Cl)^+$; 97, $(CF_3CO)^+$; 93, $(C_3F_3)^+$; 85, 87, $(CF_2Cl)^+$; 78, $(CF_2CO)^+$; 69, $(CF_3)^+$.

Anal. Calcd for $C_{14}Cl_2F_{24}O_2$: C, 23.13; F, 62.72; Cl, 9.75. Found: C, 24.40; F, 63.70; Cl, 10.25.

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Registry No. $(CF_3)_3COCl$, 27579-40-4; CF_3I, 2314-97-8; $I(CF_2)_2I$, 354-65-4; $SF_5(CF_2)_2I$, 51480-07-0; C_6F_5I, 827-15-6; C_6F_6, 392-56-3; $CF_3I[OC(CF_3)_3]_2$, 103067-96-5; $[(CF_3)_3CO]_2ICF_2CF_2I[(CF_3)_3CO]_2$, 103025-27-0; $SF_5(CF_2)_2I[OC(CF_3)_3]_2$, 103025-28-1; $C_6F_5I[(CF_3)_3CO]$, 103025-29-2; $C_6F_5I[(CF_3)_3CO]_4Cl_2$, 103025-31-6; $C_6F_6[(CF_3)_3CO]_2Cl_2$, 103004-24-6.

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Hexaamminecobalt Electron-Self-Exchange Reaction

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The $Co(NH_3)_6{}^{2+/3+}$ electron-transfer reaction is reexamined. Using a semiempirical INDO method, we calculated the ^2E excited state of $Co(NH_3)_6{}^{2+}$ to be lower than previous estimates for the equilibrium geometry. For shorter metal–ligand distances the ^2E state appears to be the ground state. The lowest energy path for electron transfer is via the ^2E state, and this path is spin-allowed contrary to the ground state ($^4T_1$) to ground state ($^1A_1$) path. We also carried out calculations on the binuclear complex $[Co(NH_3)_6]_2{}^{5+}$ and found that the electron transfer is almost adiabatic. Our calculation of the thermal barrier naturally has large error bars, but we may conclude that there is now no apparent discrepancy between theory and experiment for the rate of $Co(NH_3)_6{}^{2+/3+}$ self-exchange.

I. Introduction

The electron-exchange reaction between $Co(NH_3)_6{}^{3+}$ ($^1A_1$) and $Co(NH_3)_6{}^{2+}$ ($^4T_1$) has attracted considerable attention due to the spin transfer that accompanies the electron transfer.[1-4] According to the most recent experimental results[3,4] the rate of the reaction is 10^{-6}–10^{-5} M^{-1} s^{-1}. This low rate can be satisfactorily explained as due to the large difference in Co–N bond length for the two oxidation states,[3,4] without any regard to the spin-forbidden character of the reaction. Buhks, Bixon, Jortner, and Navon examined the latter problem in detail[2] and found that the spin forbiddeness contributes a factor $\Delta_s = 2 \times 10^{-4}$ (dimensionless) to the rate constant. The reaction is thus far from being completely spin forbidden, but since the most recent experimental results apparently do not give room for any electronic nonadiabaticity, there is disagreement between theory and experiment.

A small spin factor Δ_s may be compensated to some extent by a large spatial factor Δ_r (dimension energy). The electronic factor κ is obtained by the Landau–Zener approximation as[5,6]

$$\kappa = \frac{2P_0}{1 + P_0} \tag{1}$$

where

$$P_0 = 1 - \exp[-(\Delta_s\Delta_r)^2/\Delta_0{}^2] \tag{2}$$

Δ_0 may be calculated to be 10^{-3} au for typical metal complexes at room temperature.[7] Buhks et al.[2] did not calculate Δ_r since they compared the ratio of exchange rates between the $Co(NH_3)_6{}^{2+/3+}$ and $Ru(NH_3)_6{}^{2+/3+}$ complexes. Δ_r can be expected to be the same for these two cases, and Δ_r then cancels out in the nonadiabatic theory,[2] where κ is proportional to $(\Delta_r\Delta_s)^2$. However, if eq 2 is used, there would still be the possibility that $(\Delta_r\Delta_s)^2$ is sufficiently large to make P_0 approach unity and thereby offset $\Delta_s{}^2$ partly. The calculation of Δ_r (as described below in section II) showed that Δ_r is close to 10^{-3} au as for other pairs of metal complexes examined earlier.[8,9] Thus the problem with the small spin factor remains.

In several papers preceding the one by Buhks et al.,[2] it was assumed that the normal ground state to ground state reaction path was strictly spin forbidden and that the reaction had to proceed via the ^2E excited state of $Co(NH_3)_6{}^{2+}$ or the $^3T_1$ excited state of $Co(NH_3)_6{}^{3+}$. Buhks et al. showed that the ground state to ground state reaction is allowed by spin–orbit mixing.[2] They also made it appear likely that this path was energetically advantageous compared to the spin-preequilibrium mechanisms via either of the excited states using the argument that the excitation energy to the ^2E was as much as 9000 cm^{-1}. An objection to this

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