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Oxidation of Elemental Mercury with Trifluoromethyl Radicals. Synthesis for Bis(trifluoromethyl)mercury

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We have recently developed in our laboratory a general synthesis for trifluoromethyl organometallic compounds.[2] Trifluoromethyl radicals generated from C_2F_6 in a glow discharge were shown to react with metal halides to produce completely substituted trifluoromethyl organometallic compounds in high yields. The preparation of $Hg(CF_3)_2$ by this method[2] is a facile synthesis which is now operable in our laboratory on a scale of 8 g/4 hr. Haszeldine and Emeleus, in the first preparation of trifluoromethylmercury compounds, established that CF_3I reacts on heating and/or irradiation with mercury metal to yield only CF_3HgI[3] and that the use of amalgams was necessary to produce $(CF_3)_2Hg$.[4] We have found trifluoromethyl radicals generated from C_2F_6 in radiofrequency discharge are capable of oxidizing mercury metal directly to bis(trifluoromethyl)mercury.

A glow discharge is a convenient source of reactive radicals which are likely to be formed in excited electronic vibrational states and rotational states but have little translational energy. The reaction of trifluoromethyl radicals with Hg appears to take place in the gas phase. The elemental mercury is placed on the bottom surface of the plasma reactor and vaporized through the plasma zone. The presence of electronically excited mercury atoms, established by the characteristic lines in the visible spectrum, definitely increases the reaction rate and is probably essential for this reaction. If metallic mercury is placed in a boat or container slightly ahead of the recombination zone of the plasma, no reaction occurs. Gentle heating of the mercury to 45°C increases the concentration of excited mercury atoms in the plasma and markedly increases the overall yield. The use of cadmium amalgam does not influence the reaction.

If a mixture of C_2F_6 (95%) and CF_3I (5%) is used, CF_3HgI and $(CF_3)_2Hg$ are formed in a ratio of about 2:1. With pure CF_3I, nearly quantitative conversion to C_2F_6 and HgI_2 with the formation of only traces of $(CF_3)_2Hg$ is observed. The reaction sequence of eq 1–9 is probable.

$$C_2F_6 \overset{rf}{\rightleftarrows} 2CF_3\cdot \tag{1}$$

$$CF_3I \overset{rf}{\rightleftarrows} CF_3\cdot + I\cdot \tag{2}$$

$$Hg + I\cdot \rightarrow \cdot HgI \tag{3}$$

$$Hg^* + CF_3\cdot \rightarrow \cdot HgCF_3 \tag{4}$$

$$\cdot HgCF_3 + I\cdot \rightleftarrows \cdot HgI + CF_3\cdot \tag{5}$$

$$\cdot HgI + CF_3\cdot \rightleftarrows CF_3HgI \tag{6}$$

$$\cdot HgI + I\cdot \rightleftarrows HgI_2 \tag{7}$$

$$\cdot HgCF_3 + I\cdot \rightarrow IHgCF_3 \tag{8}$$

$$\cdot HgCF_3 + CF_3\cdot \rightarrow Hg(CF_3)_2 \tag{9}$$

The results indicate that the high CF_3 radical recombination rate k_{-1} and the abstraction of iodine atoms by mercury and/or $Hg-CF_3$ compounds are limiting factors for the yields of $(CF_3)_2Hg$ or CF_3HgI. The absence or nearly negligible formation of CF_3HgI in the plasma reactions of CF_3I with Hg or C_2F_6 with HgI_2[2] may be due to its low volatility and therefore long exposure time to the reactive plasma. Pure CF_3Br in a radiofrequency discharge over mercury does not yield trifluoromethylmercury compounds.

These results raise the possibility of the synthesis of other trifluoromethyl organometallic compounds via reactions of trifluoromethyl radicals with metallic substrates.

Experimental Section

In a typical experiment about 30 ml of Hg was placed in a reactor similar to that described previously.[2] The C_2F_6 flow rate was adjusted to 8 mmol/hr; the radiofrequency power level (13.6 MHz, inductive coupling) was adjusted to about 25 W allowing the mercury to warm up to 35–40°C. The operating pressure was approximately 2 mm. Bis(trifluoromethyl)mercury was collected downstream at −78°, dissolved in ether, separated from elementary mercury by filtration, and purified by sublimation. The average yield was 0.25 mmol/hr (80 mg/hr). The products were identified by their characteristic ^{19}F NMR spectra: for $Hg(CF_3)_2$, δ −40.5 ppm, $J_{^{199}HgF}$ = 1287 Hz; for $HgCF_3I$; δ −43.5 ppm, $J_{^{199}HgF}$ = 1760 Hz (in ether, vs. external TFA). Parent ions in the mass spectrum were at m/e 336–342 and 394–400, respectively.

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Registry No. Hg, 7439-97-6; C_2F_6, 76-16-4; $Hg(CF_3)_2$, 371-76-6.

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Crystal Structure of β-Zirconium Tribromide

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The structures of zirconium trichloride, tribromide, and triiodide were first deduced from powder data and shown to consist of linear chains of face-sharing ZrX_6 octahedra.[1–3] There was disagreement, however, on the space group assignment and therefore disagreement on whether the metal ions are paired[1] or equally spaced along the chain.[2,3] Sub-

Table I. Thermal Parameters for $ZrBr_3$ and Root-Mean-Square Thermal Displacements (in Å) of the Atoms along Their Principal Ellipsoid Axes

	B_{11}	B_{22}	B_{33}	B_{12}	$\mu(r_1)$	$\mu(r_2)$	$\mu(r_3)$
Zr	0.0161 (4)	0.0161 (4)	0.0177 (5)	0.0082	0.167 (6)	0.167 (6)	0.189 (3)
Br	0.0167 (4)	0.0256 (5)	0.0116 (4)	0.0128	0.153 (3)	0.153 (3)	0.210 (2)

sequent data[4] on a single crystal of zirconium tribromide substantiated the powder work of Dahl[2] et al. but could not be refined to differentiate between an ordered structure in which the metal ions are evenly spaced and a disordered structure in which the metal ions are unevenly spaced but for which only an "averaged" unit cell of evenly spaced metal ions could be determined by X-rays. The resolution of this order–disorder problem is important because the interpretation of the electrical and magnetic properties of these one-dimensional systems depends on the relative spacings of the metal ion sites. The availability of well-developed crystals allowed us to pursue and resolve this problem.

Experimental Section

Crystals of $ZrBr_3$ were grown from a eutectic melt of Al_2Br_6–$ZrBr_4$ as previously described.[4] The crystal chosen was a needle with a hexagonal cross section symmetrically bounded by the (100, 010, $\bar{1}$10, and 001) faces. The crystal was sealed in a Lindemann glass capillary under dry N_2 and placed on a Syntex $P\bar{1}$ autodiffractometer equipped with a graphite-monochromated Mo Kα radiation source. The preliminary Syntex routines indicated a hexagonal cell of Laue symmetry D_{6h}-$6/mmm$ with $a = b = 6.7275$ (20) Å, $c = 6.2992$ (14) Å, and $V = 246.91$ (13) Å^3 in agreement with data previously reported.[1–4] The lattice lengths and associated symmetry were verified by partial rotation photographs along each of three reciprocal axes and by conventional oscillation and Weissenberg techniques. A careful examination of these photographs gave no indication for the existence of a higher lattice as reported in the case of HfI_3.[5] Data were collected for one-fourth of the sphere $(hkl, \bar{h}kl)$ for $3° \leq 2\theta \leq 50°$ using a variable-scan rate of 2–24°/min with a background to scan time ratio of 0.67. The intensities of two standard reflections monitored periodically throughout the data collection indicated stability of the intensities. The data were corrected for Lorentz–polarization and absorption ($\mu = 277.10$) and merged under the D_{6h} Laue symmetry to yield 92 independent reflections, 7 of which had $I < 2\sigma(I)$. These data represent 100% of the total possible unique and symmetry-allowed reflections, all of which were used in the least-squares refinement. An examination of the intensities for all equivalent reflections showed experimentally that no violations of the systematic absences $\{h\bar{h}0l\}$ for l odd occur. These systematic extinctions are consistent with $P6_3/mcm$ (D_{6h}^3), $P6_3cm$ (C_{6v}^3), or $P\bar{6}c2$ (D_{3h}^2) as the probable space groups. Any of these three space groups require the two zirconium and six bromine atoms per unit cell to be in special positions and that the metal atom layer and the halogen atom layer be equally spaced along the c lattice direction. The centrosymmetric choice, $P6_3/mcm$ in accordance with the previously reported results, was substantiated by the successful least-squares refinement of the model. For this space group the two metal atoms are fixed in the special set 2b (0, 0, 0; 0, 0, $^1/_2$) while the six halogen atoms were set to occupy the special set 6g (x, 0, $^1/_4$; 0, x, $^1/_4$; $\bar{x}$, $\bar{x}$, $^1/_4$; $\bar{x}$, 0, $^3/_4$; 0, $\bar{x}$, $^3/_4$; x, x, $^3/_4$). With the crystallographic asymmetric unit comprised of one zirconium and one bromine atom the structure is based only on one variable positional parameter and five independent anisotropic thermal parameters. Full-matrix anisotropic refinement of this model including terms for anomalous dispersion of Zr and Br led to a final unweighted agreement index R_1 of 0.023 and a weighted R_2 of 0.036. The final value of x for the bromine positional parameter is 0.3212 (2). The anisotropic thermal parameters together with their associated root-mean-square displacements are given in Table I.

Discussion

The space group and final refined parameters for $ZrBr_3$ are in agreement with previous work done on this system[2–4] but are of higher precision. The zirconium to bromide ion distance is 2.6738 ± 0.0009 Å, the intrachain zirconium ion separation is 3.1496 ± 0.0007 Å, half of the c axis length, and the interchain zirconium ion separation is 6.7275 ± 0.0020 Å, the a axis length. The space group chosen, $P6_3/mcm$, requires the metal and halogen layers of atoms to be evenly spaced, and the data presented in Figure 1 and Table I show that this equal-spacing model is correct. If metal ion pairing were present, the zirconium ion thermal ellipsoid would be expected to be significantly longer in the metal-to-metal direction (i.e., the c axis), while the bromide ion thermal ellipsoid would be expected to be elongated in the direction normal to the c axis. The latter would arise due to a puckering effect of nonequivalent bromides of a Zr_2Br_9 unit. As can be seen from the root-mean-square displacement values, the elongation of the zirconium ion thermal ellipsoid in the c direction, $\mu(r_3)$, is only a statistically borderline value (i.e., 3σ) from the root-mean-square displacement values in the ab plane and is well within 3σ of the average root-mean-square displacement for this ion. This value of $\mu(r_3)$ for the zirconium ion is in fact smaller than $\mu(r_3)$ for the bromide ion, which represents the thermal motion of the bromide *around* the c axis. There is no elongation of the bromide ellipsoid in the direction normal to the c axis. The lack of significant distortion of the thermal ellipsoids, the small values for all of the root-mean-square displacements, and the small values for the isotropic thermal parameters (3.01 Å^2 for Zr, 2.23 Å^2 for Br) support the conclusion that the zirconium ions are evenly spaced and not paired along the chain.

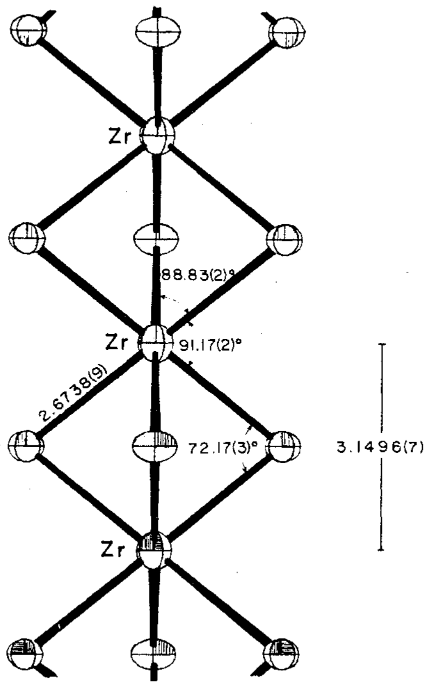

Figure 1. A section of the linear chain of $ZrBr_3$ viewed normal to the c axis. The thermal ellipsoids represent 50% probability.

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Registry No. $ZrBr_3$, 24621-18-9.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Business Offices, Books and Journals Division, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for \$4.00 for photocopy or \$2.50 for microfiche, referring to code number AIC504279-12-75.

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The Aquation of Nitritopentaamminechromium(III) Catalyzed by Hydrogen, Chloride, and Bromide Ions[1]

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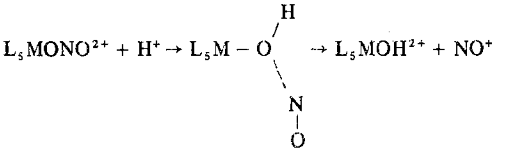
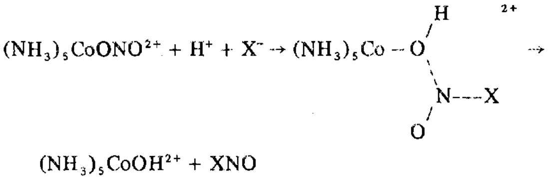
Kinetic and mechanistic studies of diazotization and deamination reactions[2] have established that nitrosation can proceed via the species N_2O_3, NO^+ (or H_2ONO^+), and XNO ($X^- = Cl^-, Br^-, I^-, SCN^-$). In the coordination chemistry of nitrite ion, the N_2O_3 pathway has been uncovered in the formation reactions of nitritopentaammine complexes of cobalt(III), chromium(III), rhodium(III), iridium(III), and platinum(IV).[3-5] The NO^+ pathway is featured in the acid-catalyzed aquations of nitrite complexes of chromium(III), cobalt(III), rhodium(III), and iridium(II).[6-9] We



$$L_5MONO^{2+} + H^+ \rightarrow L_5M-O\begin{matrix}H\\N{=}O\end{matrix} \rightarrow L_5MOH^{2+} + NO^+ \qquad (1)$$

previously[10] reported the operation of the XNO pathway in the halide-catalyzed aquation of $Co(NH_3)_5ONO^{2+}$.



$$(NH_3)_5CoONO^{2+} + H^+ + X^- \rightarrow \left[(NH_3)_5Co-O\begin{matrix}H\\N{\cdots}X\\O\end{matrix}\right]^{2+} \rightarrow (NH_3)_5CoOH^{2+} + XNO \qquad (2)$$

In the present note, we report that chloride and bromide ions catalyze the aquation of $Cr(NH_3)_5ONO^{2+}$, and thus we provide evidence for the generality of the XNO pathway in the coordination chemistry of nitrite ion.

Experimental Section

Nitritopentaamminechromium(III) nitrate was prepared by reaction of aquopentaamminechromium(III) with nitrite ion.[11] This salt was transformed into the corresponding perchlorate by dissolution in the minimum amount of water followed by precipitation with a saturated solution of sodium perchlorate.[12] Anal. Calcd for $[Cr(NH_3)_5ONO](ClO_4)_2$: Cr, 13.61. Found: Cr, 13.50, 13.75.

Table I. Kinetics of the Acid-Catalyzed Aquation of $Cr(NH_3)_5ONO^{2+}$ [a]

$10^2[H^+]$, M	10^3k_{obsd}, sec^{-1}	10^2k_H, M^{-1} sec^{-1} [e]
2.50	1.66 ± 0.14[b]	6.64
5.02	3.49 ± 0.10[c]	6.95
9.99	6.96 ± 0.21[d]	6.97
20.0	14.0 ± 0.7[d]	7.00

[a] At 10°, $\mu = 1.00$ M, $[Cr(III)] \sim 3 \times 10^{-4}$ M. [b] Average of seven measurements. [c] Average of three measurements. [d] Average of four measurements.. [e] $k_H \equiv k_{obsd}/[H^+]$.

Lithium perchlorate was obtained as a solid from solutions prepared by dissolution of lithium carbonate in perchloric acid. The solid was recrystallized twice from water. The water used was purified as described previously.[10] Lithium chloride and sodium bromide were reagent grade and were used as received.

The lithium perchlorate solutions were standardized acidimetrically by an ion-exchange procedure. Chromium analyses were carried out spectrophotometrically following oxidation of chromium to CrO_4^{2-} in alkaline solution.

All kinetic measurements were carried out spectrophotometrically in a Cary 118 recording spectrophotometer equipped with a thermostated cell compartment and a modified thermostated cell holder. The cell holder ends were sealed with Suprasil windows (Amersil Inc., Hillside, N.J.) and the holder was filled with water. The temperature of the water was monitored continuously by means of a Digitec Model 581C digital thermistor thermometer. A solution containing all the desired components (lithium perchlorate, perchloric acid, and the halide salt when necessary) except the chromium(III) complex was prepared and 3.00 ml was placed in a square 1-cm cell. The cell was placed in the cell compartment. The precautions given by Matts and Moore[6] in handling $Cr(NH_3)_5ONO^{2+}$ were followed. The solutions of the chromium(III) complex were prepared at 0° and were used within 1–2 hr. Just before the start of a kinetic run, the chromium(III) solution was allowed to reach temperature equilibrium and approximately 0.1 ml was added to the 1-cm cell by means of a Cuvette Add-A-Mixer (Precision Cells, Inc., Hicksville, N.Y.). All measurements were carried out at 10° and ionic strength 1.00 M, and were followed at 240 nm. Pseudo-first-order rate constants were obtained from ln $(A_t - A_\infty)$ vs. time plots. A_t and A_∞ are the absorbances at time t and at the completion of the reaction, usually 8–10 half-lives.

Results and Discussion

The earlier studies[6] of the acid-catalyzed aquation of $Cr(NH_3)_5ONO^{2+}$ were carried out using sodium perchlorate to adjust the ionic strength. Since lithium perchlorate appears to be a better background electrolyte when acid-dependent pathways are operative,[10] we repeated the measurements at ionic strength 1.00 M using lithium perchlorate, and the results are summarized in Table I. It is seen that k_{obsd} is proportional to $[H^+]$ in the range 0.0250–0.200 M and, therefore, in agreement with the earlier work, the rate law is $k_H[Cr(NH_3)_5ONO^{2+}][H^+]$. Taking into account the difference in ionic media, our value of k_H, $6.89 \pm 0.12 \times 10^{-2}$ M^{-1} sec^{-1}, in $LiClO_4$ compares favorably with the value reported previously,[6] $5.34 \pm 0.1 \times 10^{-2}$ M^{-1} sec^{-1} in $NaClO_4$.

Addition of chloride or bromide strongly accelerates the rate of aquation, and the results of the kinetic measurements are presented in Tables II and III, respectively. It is seen that when k_{obsd} is corrected for the contribution of the acid-catalyzed path, the corrected values increase linearly with $[H^+]$ and with the concentration of halide ion. Therefore, the halide-catalyzed paths obey a rate law of the form $k_X \cdot [H^+][X^-][Cr(III)]$, with $k_X = 3.12 \pm 0.10$ and 27.9 ± 1.3 M^{-2} sec^{-1} for chloride and bromide ions, respectively.

The results obtained in the present work parallel exactly those obtained previously[10] for the acid- and halide-catalyzed aquations of $Co(NH_3)_5ONO^{2+}$. Indeed, a plot of log k for $Co(NH_3)_5ONO^{2+}$ vs. log k for $Cr(NH_3)_5ONO^{2+}$ is a straight line of slope 1.09 (see Figure 1). Consequently, we infer that