methods. In 1955, a communication by Dresdner on the pyrolysis of CF_3SF_3 with C_3F_6 reported that a mixture of perfluoropentanes had been formed including perfluoroneopentane.[3] The compound was later purified and characterized by melting point[4] and ir[5] and nmr.[6]

Perfluoroneopentane, $C(CF_3)_4$, is also of interest because it possesses high symmetry. It is perhaps the most nearly spherical molecule known and its exterior surface is almost entirely fluorine bound to carbon. Unusual physical properties might be expected from interaction of the projecting nonbonding electrons and from the inert nature of the surface.

The apparatus and technique used to fluorinate neopentane has been described in general by Lagow and Margrave[7] and the new cryogenic reactor developed in our laboratory has been described in detail.[8] This cryogenic fluorination system consists of a 1-in. i.d. nickel reaction tube packed with fluorinated fine copper filings, immersed in a series of four cold baths to carefully control the reaction temperatures and to move a zone of reactants slowly along the length of the reactor, while exposing its surface to fluorination.

Neopentane (2.052 g, 2.82×10^{-2} mol) was condensed into the first two traps of the cold reactor, which had been flushed with helium and cooled to $-78°$. The helium flow was initiated at 20 cc/min and the fluorine flow at 1.5 cc/min and continued for 48 hr. The first trap of the cold reactor was allowed to warm and the third trap was cooled. The helium flow was shut off and 1.5 cc/min of pure fluorine passed through the system. Twenty-four hours later, the last trap was cooled to $-78°$ and the second trap was warmed. A glass trap at the end of the system, filled with NaF, was also cooled to $-78°$. After 24 hr, the third trap was warmed and following another 24 hr, the fluorine was shut off, a helium flow of 20 cc/min was begun, and the last trap of the cold reactor was warmed. Helium was passed through the system for 12 hr after the last trap had reached room temperature. The glass trap was removed from the system, cooled in liquid nitrogen, and evacuated. The trap was then allowed to warm to room temperature and was shaken periodically for 12 hr. The volatile material was pumped off into a liquid nitrogen cooled vial, diluted with CCl_4, and subsequently separated by gas chromatography. A 10 ft × 0.25 in. column of 10% SE-30 on Chromosorb P was held at 0° for the separation. Perfluoroneopentane had a retention time of 3.5 min from injection. Perfluoroneopentane (0.849 g, 0.294×10^{-2} mol) was obtained which corresponds to a 10.4% yield. The melting point was determined in a sealed capillary and found to be 72.5-73° in agreement with the reported value.[4] *Anal.* Calcd for C_5F_{12}: C, 20.84; F, 79.15. Found: C, 20.67; F, 79.23. The gas-phase infrared spectrum contained three strong bands at 1300, 980, and 720 cm^{-1} and a very weak band at 1190 cm^{-1}, in agreement with the reported spectrum. The ^{19}F nmr spectrum consisted of a singlet at -13.92 ppm from an external trifluoroacetic acid reference. A value of -13.8 ppm has been reported for perfluoroneopentane.[6] The mass spectrum of the compound at 70 eV does not contain a parent peak but exhibits a strong P − 19 peak at 269. The CF_3^+ ion is the most intense peak in the spectrum. The known physical properties of this unusual, colorless, and extremely volatile fluorocarbon pose a very interesting problem. The intermolecular forces in fluorocarbons are not well understood; however, one would expect that any attraction would be due primarily to van der Waals interactions. The boiling points of the perfluoropentane isomers, *n*-perfluoropentane and isoperfluoropentane, are known to be 29.3 and 29.9-30.1°, respectively.[1] In contrast, the melting point of perfluoroneopentane is 72.5-73°. Of course, the molecular weights are the same. One might expect that perfluoroneopentane would have a higher melting point that the other two isomers since it should exhibit more regular stacking in its crystalline form. However, one would predict that the normal and iso structures would have stronger van der Waals interactions. Unless the van der Waals interactions have a positive effect on volatility, this disparity in physical properties is striking. It has been observed that highly branched hydrocarbons often have higher melting and boiling points than linear isomers.

Registry No. $C(CF_3)_4$, 374-51-6; neopentane, 463-82-1; fluorine, 7782-41-4.

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Kinetic Study of the Association between Chromium(VI) and[1] Aquopentaamminecobalt(III) in Aqueous Perchlorate Media

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In a previous study of this system[2] a limited amount of data was presented which indicated an observable time-dependent step prior to the establishment of equilibrium concentrations of the species. The present communication presents the results of a more detailed kinetic study for the reaction in which an inner-sphere complex ion is formed presumably by substitution on the chromate ion.

Experimental Section

Reagents. The preparation and standardization of stock solutions of perchloric acid, lithium perchlorate, sodium dichromate, and aquopentaamminecobalt(III) perchlorate have been described in a previous publication.[2] The preparation of the diaquotetraamminecobalt(III) perchlorate has been described by White and Newton.[3]

Procedures. Kinetic measurements were made with a Durrum stopped-flow spectrophotometer thermostated at 25.0 ± 0.1°. The reactions were carried out with large excess of the cobalt salts at 255 and 260 nm for the aquopentaamminecobalt(III) and 290 nm with the diaquotetraamminecobalt(III). Hydrogen ion concentrations of the equilibrium mixtures were determined as previously described.[2] Stock solutions were prepared just prior to use. The reaction system was flushed with these solutions until constant A_e values were obtained and then kinetic traces recorded for the reactions. Triplicate determinations were carried out for each set of concentrations. The kinetic traces (at least 15 A, time data points) were analyzed as a first-order process. The data were adjusted in terms of the expression

(1) A portion of this investigation was carried out under the auspices of the U. S. Atomic Energy Commission.

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Table I. k_f and k_r Calculated as $f([H^+]_0)$ ($I = 0.25\ M$, $T = 25°$, $[Cr(VI)]_0 = 4.49 \times 10^{-4}\ M$)

$10^4[H^+]$, *M*	10^2[complex], *M*	k_f[a]	k_r[a]	No. of expts
	Complex = $Co(NH_3)_5(H_2O)^{3+}$			
1.00[b]	0.167-2.083	2.43 ± 0.07	0.0158 ± 0.0006	27
5.00	0.416-2.083	1.50 ± 0.05	0.0535 ± 0.0006	15
10.0[c]	0.416-2.083	0.85 ± 0.09	0.1009 ± 0.0012	22
50.0	0.408-2.041	0.66 ± 0.34	0.338 ± 0.005	12
	Complex = $Co(NH_3)_4(H_2O)_2{}^{3+}$			
5.0	0.416-2.083	2.27 ± 0.15	0.093 ± 0.001	12
10.0	0.408-2.041	2.35 ± 0.31	0.145 ± 0.003	12

[a] Uncertainty is the standard deviation calculated from the least-squares adjustment of the data in terms of eq 2. [b] Measurements made at both 255 and 260 nm. [c] [Cr(VI)] varied from 0.898 to $4.49 \times 10^{-4}\ M$.

$A = A_e + (A_0 - A_e)e^{-kt}$ with initial estimates of A_0 and k obtained graphically. This expression, with two adjustable parameters A_0 and k, reproduced the data with an average uncertainty of 0.002 arbitrary absorptivity unit. The reproducibility of the rate parameter is demonstrated by the following: at 25°, $[H^+] = 1 \times 10^{-3}\ M$, $I = 0.25$, $[Cr(VI)]_0 = 4.49 \times 10^{-4}\ M$, and $[Co(III)]_0 = 8.33 \times 10^{-3}\ M$, values calculated for the rate parameters (10^2k, sec^{-1}) were 10.62 ± 0.05, 10.77 ± 0.05, 10.80 ± 0.05, and 11.00 ± 0.06 for replicate determinations. For a second independent set of determinations—using freshly prepared reactant solutions under the same concentrations conditions—values calculated were 10.52 ± 0.04, 11.05 ± 0.03, and 10.75 ± 0.04.

Results and Discussion

For the reaction

$$(NH_3)_5CoOH_2{}^{3+} + HCrO_4{}^- = C + H^+ \qquad (1)$$

the kinetic data can be described in terms of a first-order approach to equilibrium due to the concentration conditions under which the reaction was studied. At constant initial hydrogen ion concentration the observed rate as a function of aquopentaamminecobalt(III) concentration is expressed as

$$k_{obsd} = k_r + k_f[Co(NH_3)_5(H_2O)^{3+}] \qquad (2)$$

Table I presents the results obtained when the data were adjusted in terms of eq 2.

Apparent hydrogen ion dependencies, calculated from the usual ln k-ln $[H^+]$ relation are −0.33 ± 0.06 for k_f and 0.79 ± 0.03 for k_r. These nonintegral hydrogen ion dependencies can be interpreted as indicating the existence of parallel paths for both the forward and reverse reaction. The results of such an analysis are

$$k_f = 0.80 \pm 0.20 + (1.68 \pm 0.38) \times 10^{-4}[H^+]^{-1} \qquad (3)$$

$$k_r = (2.18 \pm 0.92) \times 10^{-2} + (63.8 \pm 3.6)[H^+] \qquad (4)$$

In terms of all the reactants the expressions for k_f and k_r are

$$k_f = l[R][HCrO_4{}^-] + m[R][HCrO_4{}^-][H^+]^{-1} \qquad (5)$$

$$k_r = n[C] + p[C][H^+] \qquad (6)$$

where [R] and [C] represent the concentrations of $[Co(NH_3)_5H_2O^{3+}]$ and complex, respectively, and l, m, n, and p are the parameters of (3) and (4).

For each path the velocity of the forward and reverse reactions at equilibrium must be equal (thermodynamic constraint).[4] In addition the transition states must have the same composition for each forward and reverse reaction (microscopic reversibility). Therefore, $l[R][HCrO_4{}^-] = p[C][H^+]$ and $m[R][HCrO_4{}^-][H^+]^{-1} = n[C]$.

$$Q_{l,p} = 1/p = \frac{[C][H^+]}{[R][HCrO_4{}^-]}$$

$$Q_{m,n} = m/n = \frac{[C][H^+]}{[R][HCrO_4{}^-]}$$

$$Q_{kinetic}{}^2 = Q_{l,p}Q_{m,n} = \frac{[C]^2[H^+]^2}{[R]^2[HCrO_4{}^-]^2} = 9.6 \times 10^{-5}$$

The square root of this value, 9.8×10^{-3}, is in surprising agreement with the previously measured value.[2]

The limited data presented for the reaction between Cr(VI) and diaquotetraamminecobalt(III) preclude a detailed analysis such as has been presented for the aquopentaamminecobalt(III)-chromium(VI) system. It is, however, of interest to note that at $1 \times 10^{-3}\ M$ hydrogen ion concentration the value for k_f is *ca.* 2-3 times larger for the tetraammine system while k_r is the same order of magnitude for both systems. This could be meant to imply that the Cr(VI) is a monodentate ligand in both systems although with *cis*-diaquotetraamminecobalt(III) there is no *a priori* constraint for such bonding.

Haight[5] has presented an interesting analysis of these results and demonstrated that they are consistent with the general mechanism for substitution on the tetrahedral hydrogen chromate ion.[6]

Registry No. *cis*-Diaquotetraamminecobalt(III) perchlorate, 39003-79-7; $HCrO_4{}^-$, 15596-54-0.

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