secured by twists of copper wire. In other cases (see Table I and Figure 2), the aliquots were individually subjected to an additional freeze-thaw cycle before the tubes were fused shut under an atmosphere of nitrogen. The sealed tubes were then placed in an 80° bath for known periods of time. Upon removal from the 80° bath, the tubes were stored at −78°. Infrared spectra over the region 2100–1800 cm^{-1} were recorded for all of the samples of a given run at the same time.

For reasons set forth in the discussion, the kinetic data collected cannot be said to be of high quality. However, plots of $\ln (A - A_\infty)$ *vs.* time were approximately linear for 2–3 half-lives. (In all cases, the 1855-cm^{-1} band of $Ni_2(CO)_2(C_5H_5)_2$ was used to monitor the extent of substrate consumption. It should be noted that diphenylacetylene absorbs weakly at this frequency so that A_∞ was not zero for the kinetic runs reported here.)

The reported pseudo-first-order rate constants and the fit to eq 9 were obtained from standard least-squares analyses.

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Stereochemistry of the Mercury-Catalyzed Aquation of *cis*-$[Ru(en)_2Cl_2]^+$

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There has been considerable interest recently in the mechanism of the Hg^{2+}-catalyzed aquation reactions of chloro(amine)cobalt(III) complexes. Posey and Taube[2] have shown these reactions to be SN1(lim) in character, while stereochemical studies[3-5] have indicated that they generally involve intermediates different in geometry from those encountered in the uncatalyzed aquations. Thus, the Hg^{2+}-induced aquation of D-$[Co(en)_2Cl_2]^+$ yielded a mixture of 70% D-$[Co(en)_2(H_2O)Cl]^{2+}$ and 30% *trans*-$[Co(en)_2(H_2O)Cl]^{2+}$, compared with the complete retention observed in the spontaneous reaction.[3] Both square-pyramidal[5] and trigonal-bipyramidal[3] geometries have been inferred for the five-coordinate intermediates. However, except for a kinetic study of the Hg^{2+}-catalyzed aquation of $[Rh(NH_3)_5Cl]^{2+}$ in mixed solvents,[6] no studies have been made of the corresponding reactions of the complexes of the second- and third-row transition elements. This paper reports the stereochemical results of the Hg^{2+}-catalyzed aquation of *cis*-$[Ru(en)_2Cl_2]^+$ and compares these with previous data[7] for the spontaneous aquation.

Experimental Section

Materials.—*cis*-$[Ru(en)_2Cl_2]Cl \cdot H_2O$ and D(−)-$[Ru(en)_2Cl_2]I$ were prepared by published methods.[8] All other reagents were analytical grade.

Geometrical Retention Experiment.—Fresh solutions of *cis*-$[Ru(en)_2Cl_2]Cl \cdot H_2O$ and $Hg(NO_3)_2$ in 0.2 *M* H_2SO_4 were mixed to give the final concentrations $[Ru^{3+}] = 7.5 \times 10^{-4}$ *M* and $[Hg^{2+}] = 1.5 \times 10^{-3}$ *M*. The uv–vis spectrum of the solution was measured periodically on a Cary 14 spectrophotometer. After 30 min, concentrated HCl was added to give a final [HCl] = 2.5 *M*. The uv–vis spectrum was then recorded periodically for 24 hr to observe the regeneration of $[Ru(en)_2Cl_2]^+$.

Optical Retention Experiment.—The ord spectrum of D(−)-$[Ru(en)_2Cl_2]I$ (8.2×10^{-4} *M*) in 0.2 *M* H_2SO_4 was recorded using a Cary ORD/CD instrument. A fresh solution of $Hg(NO_3)_2$ in 0.2 *M* H_2SO_4 was added to give the final concentration $[Ru^{3+}] = 6.6 \times 10^{-4}$ *M* and $[Hg^{2+}] = 1.3 \times 10^{-3}$ *M*. After 30 min concentrated HCl was added (2 *M*) and the ord spectrum was recorded after a further 4 hr (Table I).

TABLE I
COMPARISON OF THEORETICAL AND REGENERATED SPECIFIC ROTATIONS AT ROTATIONAL MAXIMA

Wavelength, nm	[α] of pure D(−)-$[Ru(en)_2Cl_2]^+$	[α] regenerated by addition of HCl to aquated soln
368	−1590 ± 50	−1640 ± 50
333	+250	+150
307	+1350	+1280
280	−1620	−1530

Results and Discussion

Addition of Hg^{2+} to an acidic solution of *cis*-$[Ru(en)_2Cl_2]^+$ caused the uv–vis spectrum to change rapidly over 10 min to that of *cis*-$[Ru(en)_2(H_2O)Cl]^{2+}$ (ϵ_{329} 1650). This peak at 329 nm then slowly decreased, probably due to conversion to *cis*-$[Ru(en)_2(H_2O)_2]^{3+}$. The addition of excess HCl at this stage regenerated the calculated uv–vis spectrum of *cis*-$[Ru(en)_2Cl_2]^+$ within 24 hr. No evidence was found for the presence of the trans isomer.

The rapid production of *cis*-$[Ru(en)_2(H_2O)Cl]^{2+}$ *via* the Hg^{2+}-induced aquation of *cis*-$[Ru(en)_2Cl_2]^+$ was also evident from the ord studies. Thus, the ord spectrum had changed after 15 min to a curve with rotational maxima at 340, 303, and 260 nm ([α] = −550, +670, −970, respectively). The optical retention experiment (Table I) therefore shows that, within experimental error, the reaction sequence

$$cis\text{-}[Ru(en)_2Cl_2]^+ + Hg^{2+} + H_2O \longrightarrow [Ru(en)_2(H_2O)Cl]^{2+} + HgCl^+$$

$$[Ru(en)_2(H_2O)Cl]^{2+} + HCl \longrightarrow [Ru(en)_2Cl_2]^+$$

occurs with overall retention of geometric and optical configuration. This is most readily interpreted in terms of complete retention in each step.

A previous study[7] has shown that the spontaneous aquation of *cis*-$[Ru(en)_2Cl_2]^+$ also occurs with retention of geometric and optical configuration. The similar stereochemical course of the aquation in the presence and absence of Hg^{2+} is further confirmed by the observation of the same isosbestic points (341 and 317 nm) in both cases. However, identical mechanisms are unlikely since the earlier kinetic studies[7] suggest an SN2 mechanism for the spontaneous aquation of *cis*-$[Ru(en)_2Cl_2]^+$. This seems very improbable in the presence of Hg^{2+}, and the retention of configuration observed here is best explained in terms of an SN1 mechanism involving a square-pyramidal intermediate. It is inconsistent with a trigonal-bipyramidal interme-

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diate, which would be expected to lead to rearrangement. It is interesting that this proposal of a square-pyramidal geometry for the intermediate $[Ru(en)_2Cl]^{2+}$ is in accord with Pearson's theoretical prediction[9] that this is the most stable geometry for a five-coordinate low-spin d^5 complex.

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Association of Group V Pentafluorides in the Gas Phase

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In a recent mass spectrometric study, Lawless[1] reported evidence for dimers of SbF_5 and BiF_5 in the gas phase but found no evidence for $(BiF_5)_n$, $n = 3$ or 4, nor presumably for $(SbF_5)_n$, $n > 2$. From these observations Lawless suggested that the dimers have a double fluorine bridge structure and that the preferred interpretation[2] of the ^{19}F nmr spectrum of liquid SbF_5 should be in terms of dimeric units. Müller, *et al.*,[3] have also shown that the mass spectrum of gaseous SbF_5 contains small amounts of dimeric ions. However, a number of recent studies suggest higher concentrations of SbF_5 dimer than were found in either of these mass spectrometric studies;[4-7] some also find evidence for higher agglomerates.[5,7]

The concentration of associated species will be greatest in the saturated vapor which is in equilibrium with either the solid or liquid phase. In the work of Lawless,[1] this condition will be more nearly approached for BiF_5 than for SbF_5. Using a molecular beam source mass spectrometer,[7] we were able to find substantially more dimer in SbF_5 vapor than either Lawless[1] or Müller, *et al.*,[3] as well as higher agglomerates up to the pentamer. Therefore we have studied the saturated vapors of PF_5, AsF_5, and BiF_5 to gain insight into the vapor-phase structure of the group V pentafluorides.

The molecular beam sources and collimating orifices were fabricated from Monel and heavily prefluorinated. Effusion took place from either a 0.025- or a 0.038-cm diameter orifice. The temperature of the gas inlet was maintained by melting slush baths, and the solid sources were heated with resistive windings. Source temperatures were monitored continuously with thermocouples. The mass spectrometer was a modified EAI quadrupole with an Extranuclear Laboratories power supply. The electron energy in the ion source was 70 eV. The molecular beam, electron beam, and resultant ions were on mutually perpendicular axes.

PF_5 was obtained from Matheson, AsF_5 and BiF_5 were supplied by Ozark-Mahoning, and SbF_5 was from Allied Chemicals. All were used without further purification. PF_5 and AsF_5 were handled on a Monel vacuum line; BiF_5 was loaded into the solid effusion source in a dry, oxygen-free helium atmosphere ($O_2 + H_2O$ concentration below 1 part in 10^6).

PF_5 vapor was sampled effusively from a gas–solid equilibrium at 162°K; AsF_5 was similarly studied at 191°K. In neither case could any association be detected, which means an upper limit of dimeric ions of less than 1 part in 10^4.

For BiF_5 a satisfactory molecular beam was obtained between 341 and 361°K, corresponding to vapor pressures between 1.2 and 2.1 Torr. The fragmentation pattern for BiF_5 at an effusion source temperature of 360°K obtained in this study and that due to Lawless are given in Table I. Similar data, for SbF_5, including a comparison with the work of Müller, *et al.*, are given in Table II. The data obtained in this study for SbF_5 were for an effusion source at room temperature (~298°K, vapor pressure of $SbF_5 \cong 2$ Torr). Abundances of associated ions were independent of the effu-

Table I

Relative Intensities of Fragment Ions from BiF_5

Mass	Ion	Rel intensity	
		Ref 1	This work[a]
209	Bi^+	13	24
228	BiF^+	10	26
247	BiF_2^+	38	62
266	BiF_3^+	10	2
285	BiF_4^+	100	100
418	Bi_2^+	0.3	0.3
437	Bi_2F^+	0.3	0.3
456	$Bi_2F_2^+$	0.2	0.2
475	$Bi_2F_3^+$	0.5	0.1
494	$Bi_2F_4^+$	0.3	0.2
513	$Bi_2F_5^+$	3.4	4.0
551	$Bi_2F_7^+$	3.5	2.6
589	$Bi_2F_9^+$	18.0	13.5
857	$Bi_3F_{12}^+$	ND[b]	0.05
895	$Bi_3F_{14}^+$	ND	0.07

[a] Not corrected for transmission. Oven temperature 360°K. [b] ND, not detected.

Table II

Relative Intensities of Fragment Ions from SbF_5

Mass	Ion	Rel intensity		
		Ref 3[a]	Ref 1[b]	This work[c]
121	Sb^+	10.8	8.0	4
140	SbF^+	10.0	7.0	23
159	SbF_2^+	18.8	25	47
178	SbF_3^+	10.8	20	26
197	SbF_4^+	100	100	100
216	SbF_5^+	0.72	NR[d]	ND[e]
413	$Sb_2F_9^+$	0.24	0.2	8.9
415	$Sb_2F_9^+$	0.40	NR	13.7
417	$Sb_2F_9^+$	0.13	NR	4.7
629	$Sb_3F_{14}^+$	NR	ND	0.06
631	$Sb_3F_{14}^+$	NR	ND	0.10
633	$Sb_3F_{14}^+$	NR	ND	0.07
635	$Sb_3F_{14}^+$	NR	ND	0.02

[a] Conventional inlet and ion source (source temperature not quoted). [b] Conventional inlet, temperature 363–383°K. [c] Beam inlet at room temperature—not corrected for transmission. [d] NR, not reported. [e] ND, not detected.

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