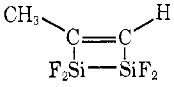
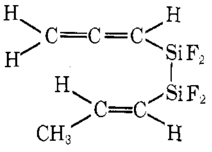
let (in ^{19}F nmr) were the same (1.0 Hz). The mass spectrum of this compound showed the highest mass peak at *m/e* 250. These data suggest that the compound may be III and support the postulated ring structure of compound II.

Discussion

The two compounds from this reaction may be compared with the products identified in other related reactions. In the reaction between SiF_2 and propyne,[4] IV and V were obtained. In the reaction between SiF_2 and acetylene,[4] VI and VII were obtained. In all the three reactions, four-membered ring compounds were obtained. In the reaction of 3,3,3-trifluoropropyne, no open-chain products were observed. Both V and VII were formed by the addition of $\cdot SiF_2SiF_2\cdot$ biradicals on two acetylene molecules. The formation of V involved a hydrogen atom migration from one methyl group, whereas the formation of VII presumably involved the migration of an acetylenic hydrogen. From the facts that there are no methyl hydrogens available for rearrangement in $CF_3C{\equiv}CH$ and that the presence of CF_3 groups may facilitate the ring-closure process,[7] the formation of the six-membered ring product II is reasonable in this case.


IV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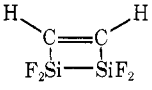
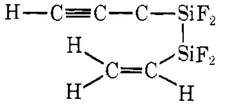

VI


VII

Acknowledgment.—We are grateful to the National Research Council of Canada and the Ontario Department of University Affairs for financial support. C. S. L. thanks the Ontario Department of University Affairs for an Ontario Graduate Fellowship.

[7] N. L. Allinger and V. Zalkow, *J. Org. Chem.*, **25**, 701 (1960).

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Kinetic Study of the Chromium(II) Reduction of Azidopentaamminechromium(III)

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Received September 24, 1970

Studies on the rates of reduction of pentaaminechromium(III) complexes by chromium(II) provide an interesting and possibly mechanistically useful comparison to the more widely studied pentaaminecobalt(III) complexes. The reaction of chromium(II) with the fluoro, chloro, bromo, and iodo complexes of $(NH_3)_5$-Cr^{3+} has been studied by Ogard and Taube.[2] The rate trends with the various bridging ligands follow those found in the $(NH_3)_5Co^{3+}$ series;[3,4] however the rate constants are ~10^8 times greater in the cobalt series. It seems worthwhile to extend this study to the rather different azide bridging ligand and to determine if the trends observed previously can be extended more generally.

Experimental Section

All solutions used in the kinetic study were prepared in water which had been distilled from alkaline permanganate solution in an all-glass apparatus. Lithium perchlorate solutions were prepared by dissolving reagent grade lithium perchlorate (G. F. Smith Chemical Co.) in water and were filtered through a 5-μ Millipore filter (Millipore Filter Corp.). The lithium perchlorate solutions were standardized by titration, with standard sodium hydroxide, of the hydrogen ion eluted from a cation ion exchange column initially in the hydrogen ion form.

Chromous perchlorate solutions were prepared by dissolving electrolytic grade chromium (99.999% purity, United Mineral and Chemical Corp.) in dilute perchloric acid–lithium perchlorate solutions. The solution was standardized periodically by reaction of an aliquot with a known excess of ferric ammonium sulfate and then determining the excess ferric ion iodometrically.

All solutions used to study the chromium(II) reduction were degassed with high-purity argon and handled using standard syringe techniques.

A sample of $(NH_3)_5CrN_3(ClO_4)_2$ was prepared as described by Linhard and Berthold[5] and purified by ion-exchange chromatography[6] on Rexyn 102 (H) weak-acid cation-exchange resin (Fisher Scientific Co.) in the sodium ion form. The ion-exchange procedure was carried out at ~2° by immersing the ion-exchange column in a cold bath. The eluent was aqueous sodium chloride in increasing concentration up to 0.50 *M*. The band of ion-exchange resin containing the required complex was separated physically from the remainder of the resin, collected, and washed with water and then treated with sufficient dilute (~0.1 *M*) perchloric acid to free the complex from the resin. The resin was filtered off and sufficient 70% perchloric acid was added to the filtrate to make it ~1 *M* in perchloric acid. The mixture was cooled for 4 hr in a refrigerator and then the product was collected and washed with ethanol and ether and dried under vacuum. The sample was stored in a refrigerator. *Anal.* Calcd for $(NH_3)_5CrN_3(ClO_4)_2$: Cr, 13.76; H, 3.97; N, 29.63. Found: Cr,[7] 13.80; H, 3.76; N, 29.71.

The absorption spectrum of $(NH_3)_5CrN_3(ClO_4)_2$ dissolved in water shows maxima at 382 nm (ϵ 93.4 M^{-1} cm^{-1}) and 500 nm (ϵ 154 M^{-1} cm^{-1}). These values are in reasonable agreement with those previously reported,[8] 382 nm (ϵ 93.4 M^{-1} cm^{-1}) 498 nm (ϵ 145 M^{-1} cm^{-1}).

The kinetics of the chromium(II) reduction of $(NH_3)_5CrN_3^{2+}$ was followed spectrophotometrically at 500 nm on a Bausch and Lomb precision spectrophotometer. The reaction was initiated by adding the required amount of a solution of chromium(II) from a syringe to a solution of the azido complex plus $HClO_4$ and $LiClO_4$ to give a final ionic strength (I) of 1.0 *M* in a 5-cm path length spectrophotometer cell. The temperature of the reaction solution was controlled as described previously.[9]

In all cases the reactions were carried out with at least a 25-fold excess of reducing agent over oxidizing agent. Rate constants were determined from the usual plot of log $(A_t - A_\infty)$ *vs.* time, where A_t and A_∞ are the absorbances at time *t* and after the reaction is complete, respectively.

The chromium(III) product of the reduction was characterized spectrophotometrically after ion-exchange separation. A reaction solution containing 5.35×10^{-3} *M* $(NH_3)_5CrN_3^{2+}$,

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[1] Author to whom correspondence should be addressed.

[2] A. E. Ogard and H. Taube, *J. Amer. Chem. Soc.*, **80**, 1084 (1958).

[3] J. P. Candlin, J. Halpern, and D. L. Trimm, *ibid.*, **86**, 1019 (1964).

[4] J. P. Candlin and J. Halpern, *Inorg. Chem.*, **4**, 766 (1965).

[5] M. Linhard and W. Berthold, *Z. Anorg. Allg. Chem.*, **279**, 173 (1955).

[6] This purification step was found to be necessary in order to remove a significant fraction of lower (<2+) charged species from the sample, as well as some higher (>2+) charged species.

[7] Chromium was determined spectrophotometrically as chromate after oxidation with alkaline hydrogen peroxide.

[8] M. Linhard, H. Siebert, and W. Weigel, *Z. Anorg. Allg. Chem.*, **278**, 287 (1955).

[9] R. J. Balahura and R. B. Jordan, *J. Amer. Chem. Soc.*, **92**, 1533 (1970).

4×10^{-2} *M* Cr^{2+}, and 0.35 *M* $HClO_4$ was allowed to react for ~3 hr and then exposed to air to oxidize the excess chromium(II). The solution was then placed on a column (50 mm long and 10 mm in diameter) of Dowex 50W-X8 cation-exchange resin immersed in a cold bath at ~5°. The resin had been pretreated with dilute perchloric acid, water, 50% acetone, ethanol, and distilled water. The elution of chromium(III) product was carried out with decreasingly dilute solutions of a stock solution of 0.5 *M* $NaClO_4$ and 0.1 *M* $HClO_4$. A band with ion-exchange properties typical of a 2+ chromium(III) complex was eluted from the column with an eluent solution of about 50% dilution of the stock solution. The absorption spectrum of this product was recorded on a Cary Model 14 spectrophotometer. The total amount of chromium in this product was determined spectrophotometrically as chromate after oxidation with alkaline hydrogen peroxide.

Results

The total amount of chromium in the 2+ charged product from the ion-exchange experiment was equal to 96.5% of the initial $(NH_3)_5CrN_3^{2+}$. The maxima in the visible spectrum of this product are in good agreement with the values of 434 nm (ε 66.4 M^{-1} cm^{-1}) and 585 nm (ε 67.5 nm) reported by Swaddle and King[10] for $(H_2O)_5CrN_3^{2+}$. These results show that the reaction proceeds virtually completely by an inner-sphere mechanism with transfer of the azide ion ligand.

The kinetic results, which are summarized in Table I, are consistent with the rate law

$$-\frac{d[(NH_3)_5CrN_3^{2+}]}{dt} = k_1[Cr^{2+}][(NH_3)_5CrN_3^{2+}] \qquad (1)$$

TABLE I

KINETIC DATA FOR THE REDUCTION OF AZIDOPENTAAMMINECHROMIUM(III) BY CHROMIUM(II)

Temp, °C	$[H^+]$, *M*	$10^2[Cr^{2+}]$, *M*	$10^3[(NH_3)_5CrN_3^{2+}]$, *M*	10^2k_1,[a] M^{-1} sec^{-1}
15.0	0.20	6.06	1.172	0.842
24.8	0.20	6.36	0.614	1.82
	0.20	6.36	1.210	1.77
	0.20	3.18	1.266	1.78
	0.74	3.18	1.300	1.76
35.0	0.20	6.20	1.124	3.56
	0.20	6.06	1.085	3.55
	0.20	3.10	1.044	3.54
	0.74	3.10	1.196	3.47
44.0	0.20	3.03	1.134	6.60
	0.20	3.03	0.589	6.47
	0.74	3.03	1.124	6.47

[a] The temperature dependence of k_1 gives values for $\Delta H_1^{\ddagger}$ and $\Delta S_1^{\ddagger}$ of 12.4 ± 0.4 kcal mol^{-1} and −24.9 ± 1.3 cal mol^{-1} deg^{-1}, respectively. Errors are estimated standard errors, calculated from a least-squares best fit as described by P. D. Lark, *et al.*, "The Handling of Chemical Data," Pergamon Press, Oxford, 1968, p 148.

The activation enthalpy and entropy $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are given in Table II along with values for the chromium(II) reductions of other chromium(III) systems for comparison.

The data in Table II for $(NH_3)_5CrX^{2+}$ systems show that the reactivity order for varying X^- is $I^- > Br^- > Cl^- > N_3^- > F^-$. This is the same reactivity order observed for the analogous reaction of $(NH_3)_5CoX^{2+}$ complexes;[3,4] however the overall changes in reactivity are much greater in the chromium(III) system. This may simply be due to a greater spread in thermodynamic stability of the $(NH_3)_5CrX^{2+}$ systems, as is found in the $(H_2O)_5CrX^{2+}$ system. Unfortunately very few data on thermodynamic stability are available for the chromium(III)–ammine complexes. It may also be noted that the rate trends in the $(NH_3)_5CrX^{2+}$ system are largely due to changes in $\Delta H^{\ddagger}$. Values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are not available for the reduction of the cobalt(III) complexes.

TABLE II

KINETIC RESULTS FOR THE CHROMIUM(II) REDUCTION OF SOME CHROMIUM(III) COMPLEXES

Oxidant	k_1,[a] M^{-1} sec^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal mol^{-1} deg^{-1}
$(NH_3)_5CrF^{2+}$ [b]	2.7×10^{-4}	13.4	−30
$(NH_3)_5CrN_3^{2+}$ [c]	1.8×10^{-2}	12.4	−24.9
$(NH_3)_5CrCl^{2+}$ [b]	5.1×10^{-2}	11.1	−27[d]
$(NH_3)_5CrBr^{2+}$ [b]	0.32	8.5	−33
$(NH_3)_5CrI^{2+}$ [b]	5.5	. . .	. . .
$(H_2O)_5CrF^{2+}$ [e]	2.3×10^{-2}	13.7	−20
$(H_2O)_5CrCl^{2+}$ [f]	29	8.0	−25
$(H_2O)_5CrN_3^{2+}$ [g]	6.9	9.6	−22.8

[a] Values calculated at 25° and $I = 1.0$ unless otherwise stated. [b] Reference 2. [c] This work. [d] This value is incorrectly given as −23 in ref 2. [e] D. L. Ball and E. L. King, *J. Amer. Chem. Soc.*, **80,** 1091 (1958). [f] Values obtained by interpolation from results at $I = 0.2$ and 5.0 *M:* R. V. James and E. L. King, *Inorg. Chem.*, **9,** 1301 (1970). [g] R. Snellgrove and E. L. King, *ibid.*, **3,** 288 (1964).

Comparison of the $(NH_3)_5CrX^{2+}$ and $(H_2O)_5CrX$ complexes for $X^- = Cl^-$ and N_3^- indicates the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are more favorable by ~3 kcal mol^{-1} and 2 cal mol^{-1} deg^{-1} for the pentaaquo systems. However, this trend is not borne out for $X^- = F^-$, but the correlation is too limited as yet to know whether there is something unusual about the reduction of $(H_2O)_5CrF^{2+}$.[11] It may be noted that if the changes recorded above did hold for $(H_2O)_5CrF^{2+}$, then the calculated rate constant at 25° would be ~0.11 or five times greater than the observed value. Therefore the activation parameters cannot be explained by the intervention of some more favorable mechanism for $(H_2O)_5CrF^{2+}$. Qualitatively the differences in reactivity between the pentaaquo and pentaammine systems might be due to the lower ligand rearrangement energies in the aquo system as has been suggested by Pennington and Haim[12] and discussed with reference to chromium(III) by DeChant and Hunt.[13]

Acknowledgment.—The authors wish to acknowledge the financial support for this work by the National Research Council of Canada, under contract NRC A2950.

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[10] T. W. Swaddle and E. L. King, *Inorg. Chem.*, **3,** 234 (1964).

[11] If this correlation holds approximately for $(H_2O)_5CrBr^{2+}$ and $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are estimated to be 5.5 kcal mol^{-1} and −30 cal mol^{-1} deg^{-1}, then the calculated rate constant at 0° is 63 M^{-1} sec^{-1}. The latter value is consistent with the lower limit of 60 M^{-1} sec^{-1} given by D. L. Ball and E. L. King, *J. Amer. Chem. Soc.*, **80,** 1091 (1958).

[12] D. E. Pennington and A. Haim, *Inorg. Chem.*, **5,** 1887 (1966).

[13] M. J. DeChant and J. B. Hunt, *J. Amer. Chem. Soc.*, **90,** 3695 (1968).

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Reactions of 1,6-Dicarba-*closo*-hexaborane(6)

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Received September 28, 1970

As an extension of our recent studies[2] of the carborane 2,4-$C_2B_5H_7$, we have examined a few character-

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[2] R. R. Olsen and R. N. Grimes, *J. Amer. Chem. Soc.*, **92,** 5072 (1970).