

theoretical yield) after 3 hr at room temperature, the product isolated gave no spectroscopic evidence compatible with **7**, but it contained a number of degradation products. In order to gain insight into the stability of **7**, the following synthesis was conducted. The product from the reaction of 3,4-di-*O*-acetyl-D-xylal<sup>19</sup> with EtOH-BF<sub>3</sub>-PhH<sup>10</sup> was deacetylated, and the resulting anomers of ethyl D-glycero-pent-2-enopyranoside were separated<sup>20</sup> (plc). One of these<sup>21a,c</sup> was strangely inert to MnO<sub>2</sub> oxidation, a phenomenon currently under investigation; however, the other<sup>21b,c</sup> afforded an oily ketone<sup>22</sup> with ir, uv, and nmr characteristics consistent with those of **7** (or its anomer!). When the latter ketone was treated as above with water-methanol-triethylamine, the absorption at 214 m $\mu$  disappeared immediately, but formaldehyde was not liberated. The residue obtained upon isolation indicated drastic decomposition; however, comparison (tlc) with the material derived from **2c** showed several common components. Furthermore, its principal infrared absorptions were present also in the material from **2c**. *Significantly, the saturated ketone resulting from partial hydrogenation of 2c does not produce formaldehyde when treated with triethylamine.* The dienolate ion of **7** initially formed in the retroaldol reaction of **2c** evidently provides the impetus for formaldehyde liberation.

**Acknowledgment.** We are grateful to the National Research Council of Canada for financial support and to Mr. Brian Sayer of McMaster University for the 100-MHz nmr determinations.

(19) F. Weygand, "Methods of Carbohydrate Chemistry," Vol. 1, Academic Press, New York, N. Y., 1962.

(20) Each isomer was characterized as its 3,5-dinitrobenzoate.<sup>8</sup>

(21) (a)  $[\alpha]^{20}_D + 44.3^\circ$  (c, 5.8, chloroform); (b)  $[\alpha]^{20}_D + 22.2^\circ$  (c, 2.33; chloroform); (c) rigid assignment of these as  $\alpha$  or  $\beta$  anomers awaits current X-ray crystallographic examination.

(22) Characterized as its semicarbazone.

(23) Undergraduate research participant.

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### The Chromium(II) Reduction of *cis*-Dichlorotetraammineruthenium(III). A Reversible Electron Transfer Prior to the Rate-Limiting Step

Sir:

The details of inner-sphere electron-transfer reactions have usually been represented as a combination of three steps:<sup>1-3</sup> an association step in which the bridge between the two metal ions is formed, the nuclear rearrangement that leads to the change in oxidation state, and the decomposition of the resultant binuclear product. Direct information about these binuclear intermediates has been obtained in only a few systems. Newton and Baker have reviewed the evidence concerning those intermediates composed partly or wholly of actinide ions.<sup>4</sup> In most of these and other systems studied to date,<sup>5,6</sup> the decomposition of the product

(1) H. Taube, *Advan. Inorg. Chem. Radiochem.*, **1**, 1 (1959).

(2) H. Taube, "The Robert A. Welch Foundation Conferences on Chemical Research, VI," Houston, Texas, Nov 1962.

(3) R. D. Cannon and J. E. Earley, *J. Am. Chem. Soc.*, **88**, 1872 (1966).

(4) T. W. Newton and F. B. Baker, *Advances in Chemistry Series*, No. 71, American Chemical Society, Washington, D. C., 1967, p 268.

binuclear intermediate is an important kinetic step. Occasionally, H<sup>+</sup> dependencies have given some information concerning the reactivity of the intermediate.<sup>4,7</sup> However, systems in which formation of the product binuclear intermediate is reversible are unusual.<sup>8</sup> It is the observation of such a reversible system in which chloride ion serves as the bridge that prompts this communication.

[Ru(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>]Cl · 2/3H<sub>2</sub>O was prepared by the procedure of Gleu.<sup>9</sup> The compound was pure as evidenced by analysis for ruthenium (by persulfate ion oxidation to a mixture of RuO<sub>4</sub><sup>2-</sup> and RuO<sub>4</sub><sup>-</sup>, and spectrophotometric analysis at 4150 Å, an isobestic point,  $\epsilon$  1075)<sup>10</sup> (*Anal. Calcd*: Ru, 35.2. *Found*: Ru, 35.2) and by spectrophotometric analysis ( $\lambda$  ( $\epsilon$ ): 3530 (1580), 3100 (1350), 2620 Å (500); *lit.*<sup>11</sup> 3520 (1640), 3100 (1380), 2620 Å (510)). All kinetic experiments were run in 0.10 *N* *p*-toluenesulfonic acid in order to avoid ClO<sub>4</sub><sup>-</sup> reduction by Ru(II).<sup>12</sup> Transmittance *vs.* time curves were obtained on a Durrum-Gibson stopped-flow spectrometer.

To establish the stoichiometry of the reaction, excess *cis*-Ru(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub><sup>+</sup> was allowed to react with Cr(II), and the spectrum of the resultant solution was obtained. The maximum at 6030 Å ( $\epsilon$  15  $\pm$  2 *M*<sup>-1</sup> cm<sup>-1</sup>) is in good agreement with literature values for CrCl<sup>2+</sup><sup>13,14</sup> and indicates this product results from the electron-transfer process. Blank experiments in which some *cis*-Ru(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub><sup>+</sup> was reduced by Cr(II) and then mixed with *cis*- and *trans*-CrCl<sub>2</sub><sup>+</sup>, prepared by the method of King, *et al.*,<sup>14</sup> established the absence of Ru(II) catalysis of CrCl<sub>2</sub><sup>+</sup> aquation. The absence of a product derived from a dibridged transition state is consistent with the reduction by Cr(II) of another *cis*-dichloro system.<sup>15</sup>

The pseudo-first-order rate constants for the reduction of *cis*-Ru(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub><sup>+</sup> by Cr(II),  $k_{\text{obsd}}$ , are listed in Table I. It is apparent that the data do not fit the normal second-order rate law found for most electron-transfer reactions. Note, for instance, that run 6 has 20 times the [Cr<sup>2+</sup>] of run 8, whereas the first-order rate constant changes by less than a factor of 4. However, a plot of  $k_{\text{obsd}}^{-1}$  *vs.* [Cr<sup>2+</sup>]<sup>-1</sup> gives a straight line with slope of 1.4  $\times$  10<sup>-5</sup> *M* sec and an intercept of 6.5  $\times$  10<sup>-3</sup> sec. The fit of the data to this plot is illustrated

(5) See, for instance, (a) J. H. Espenson, *Inorg. Chem.*, **4**, 1533 (1965); (b) R. K. Murmann and J. C. Sullivan, *ibid.*, **6**, 892 (1967), and references therein; (c) see also, H. Taube, *J. Chem. Educ.*, **45**, 452 (1968); (d) J. Stritar and H. Taube, private communication from Professor J. Stritar.

(6) R. N. F. Thorneley and A. G. Sykes, *Chem. Commun.*, 331 (1969); (b) D. Seewald and N. Sutin, Paper M005, 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968.

(7) J. H. Espenson, *Inorg. Chem.*, **4**, 1025 (1965); M. P. Liteplo and J. F. Endicott, *J. Am. Chem. Soc.*, **91**, 3982 (1969).

(8) A. W. Adamson and E. Gonicik, *Inorg. Chem.*, **2**, 129 (1963); D. H. Huchital and R. G. Wilkins, *ibid.*, **6**, 1022 (1967).

(9) (a) K. Gleu and W. Breuel, *Z. Anorg. Allgem. Chem.*, **237**, 335 (1938); (b) K. Gleu and W. Cuntze, *ibid.*, **237**, 187 (1938).

(10) (a) S. L. Woodhead and J. M. Fletcher, *J. Chem. Soc.*, 5039 (1961); (b) E. V. Luoma and C. H. Brubaker, Jr., *Inorg. Chem.*, **5**, 1637 (1966).

(11) W. Hartman and C. Buschbeck, *Z. Physik. Chem.* (Frankfurt), **11**, 120 (1957).

(12) J. F. Endicott and H. Taube, *J. Am. Chem. Soc.*, **84**, 4984 (1962); *Inorg. Chem.*, **4**, 437 (1965).

(13) J. H. Espenson and J. P. Birk, *ibid.*, **4**, 527 (1965), report  $\lambda_{\text{max}}$  6070 Å ( $\epsilon$  16.4 *M*<sup>-1</sup> cm<sup>-1</sup>); *cis*-CrCl<sub>2</sub><sup>+</sup> has  $\lambda_{\text{max}}$  6400 Å ( $\epsilon$  19.6).<sup>14</sup>

(14) E. L. King, M. J. M. Woods, and H. S. Gates, *J. Am. Chem. Soc.*, **80**, 5015 (1958).

(15) D. E. Pennington and A. Haim, *Inorg. Chem.*, **5**, 1887 (1966); see also ref 2.

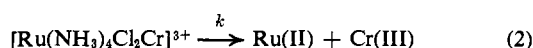
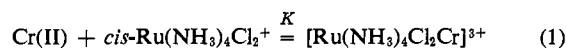
**Table I.** The Rate of Reduction of *cis*-Ru(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub><sup>+</sup> by Cr(II)<sup>a</sup>

Run	λ <sup>b</sup>	[Cr(II)], M × 10 <sup>3</sup>	[Ru(III)] <sub>0</sub> , M × 10 <sup>4</sup>	k <sub>obsd</sub> , sec <sup>-1</sup>	k <sub>calcd</sub> , <sup>c</sup> sec <sup>-1</sup>
1	3530	2.75	1.66	77.6	86.2
2	3530	1.66	1.66	73.4	66.7
3	3530	1.04	0.62	48.5	49.8
4	3530	6.28	0.50	116	115
5	4300	6.50	1.32	120	115
6	4500	14.80	2.71	132	135
7	4500	4.86	2.71	106	106
8	4500	0.66	0.64	36.0	35.8

<sup>a</sup> At 25°; [H<sup>+</sup>] = μ = 0.10 N *p*-toluenesulfonic acid. <sup>b</sup> Wavelength of observation. <sup>c</sup> See text.

by values of *k*<sub>calcd</sub>, listed in the last column of Table I; these *k*<sub>calcd</sub>'s are obtained from the above-mentioned parameters and [Cr(II)].

Such a reciprocal plot is compatible with the mechanism<sup>16</sup>



which yields

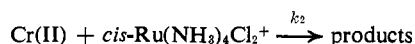
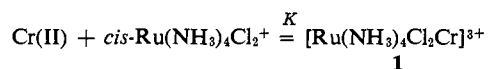
$$k_{\text{obsd}} = \frac{kK[\text{Cr(II)}]}{1 + K[\text{Cr(II)}]}$$

in which *K* = 460 M<sup>-1</sup> and *k* = 150 sec<sup>-1</sup> (at 25°, 0.1 N *p*-toluenesulfonic acid).

Evidence for the existence of **1** other than the saturation of the observed pseudo-first-order rate by excess Cr(II) includes new absorption bands not caused by either reactants or products. These bands occur at 4200 ± 200 Å with a shoulder at about 5200 Å. One observes under all conditions a smooth first-order decrease in absorptivity at these wavelengths. Runs 4 and 5 serve to establish that the same phenomenon is being observed at both the maximum for *cis*-Ru(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub><sup>+</sup> and at the wavelength where only the intermediate absorbs. These observations eliminate the possibility that consecutive reactions, the first Cr(II) dependent and the second Cr(II) independent, account for the absorptivity changes. If this were the case, one predicts from the Cr(II) concentration necessary to give a pseudo-first-order rate constant independent of [Cr(II)] that the lowest [Cr(II)] used should exhibit a maximum in the absorptivity-time curve. In addition, by extrapolation of the absorptivity-time curves to zero time, one can obtain a value for the extinction coefficient of **1** assuming the value of *K* found from the kinetic plots. Such calculations of the extinction coefficient of **1** yield a value of ε<sub>4500</sub> = 900 ± 100 M<sup>-1</sup> cm<sup>-1</sup> over a range of [Cr(II)] that changes [I]<sub>t=0</sub> from 24 to 84% of the total Ru.

This evidence compels us to conclude that a bridged intermediate exists in the reaction between Cr(II) and

(16) Another mechanism compatible with the data is

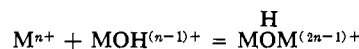


with *k*<sub>2</sub> = 7.1 × 10<sup>4</sup> M<sup>-1</sup> sec<sup>-1</sup>. We find this mechanism less satisfying because it requires Cr(II) and Ru(III) to interact by two separate and distinct pathways. See also ref 17.

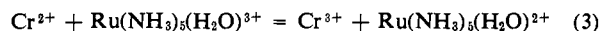
*cis*-Ru(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub><sup>+</sup>,<sup>17</sup> and that this intermediate is in equilibrium with reactants. The question of interest then becomes: What is the correct assignment of valence states in the intermediate, **2** or **3**? The difficulty



in accepting **2** as the intermediate is the magnitude of *K*: Cannon and Earley<sup>8</sup> estimated equilibrium constants for reactions of the type

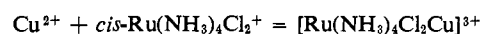


In their summary these values usually lie between 10<sup>-1</sup> and 10 for *n* = 2 or 3. With a Cl<sup>-</sup> bridge, a smaller value would be expected. Hence the observed value of 460 M<sup>-1</sup> is too large to be consistent with **2**. The apparent difficulty in accepting **3** as the intermediate is reversibility of formation of the intermediate: the change in free energy for the reaction



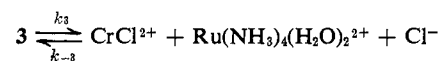
is about -13 kcal mole<sup>-1</sup>.<sup>18</sup>

We have attempted to distinguish between **2** and **3** on the basis of the chemical similarity between Cr(II) and Cu(II). If Cr(II) forms a strong complex with *cis*-Ru(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub><sup>+</sup>, one would expect Cu(II) to do so also. Spectra of mixtures of *cis*-Ru(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub><sup>+</sup> with Cu(II) were reproduced by addition of the spectra of the separated components. From this observation, we place an upper limit on the equilibrium constant



of 2 M<sup>-1</sup>.<sup>19</sup> On the basis of this experiment we propose the oxidation state assignment of the binuclear complex is Cr(III)-Ru(II), as given by **3**.

Using estimates of the affinity of Ru(III) and Cr(III) for Cl<sup>-</sup> from available data,<sup>20</sup> and assuming the affinity of Ru(II) for Cl<sup>-</sup> is small, we estimate from eq 3 that the over-all reaction of Cr(II) with *cis*-Ru(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub><sup>+</sup> has an equilibrium constant of 10<sup>7</sup>. Our data can then be used to calculate rate and equilibrium constants for the process



We measure *k*<sub>3</sub> = 150 sec<sup>-1</sup> and calculate *k*<sub>-3</sub> = 7.5 × 10<sup>-3</sup> M<sup>-2</sup> sec<sup>-1</sup> and *k*<sub>3</sub> = 2 × 10<sup>4</sup> M<sup>2</sup>. This last value gives a measure of the instability of a binuclear metal ion complex with Cl<sup>-</sup> serving as the bridging ligand.

A pertinent question to be asked is why the formation of **3** from reactants is so readily reversible while conversion to products is slow. If consideration is given to the lability of the metal ion centers, the answer becomes apparent. Both Cr(III) and Ru(III) are very inert, Ru(II) is somewhat more labile, and Cr(II) is

(17) Other investigations in this laboratory indicate that kinetic schemes similar to that outlined in eq 1 and 2 are observed for *cis*-Ru(NH<sub>3</sub>)<sub>4</sub>H<sub>2</sub>OCl<sup>2+</sup> and Ru(NH<sub>3</sub>)<sub>5</sub>Cl<sup>2+</sup>. Our conclusion concerning this latter complex is consistent with data obtained by Stritar and Taube.<sup>5d</sup>

(18) (a) T. J. Meyer and H. Taube, *Inorg. Chem.*, **7**, 2369 (1968); (b) W. M. Latimer, "Oxidation Potentials," Prentice-Hall Inc., New York, N. Y., 1952.

(19) This assumes the extinction coefficient of the binuclear complex would have a value greater than 500 M<sup>-1</sup> cm<sup>-1</sup> at some wavelength between 7000 and 3000 Å. (Note the value for [Ru(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>Cr]<sup>3+</sup> of 900 M<sup>-1</sup> cm<sup>-1</sup> at 4500 Å.)

(20) See ref 12 and C. F. Hale and E. L. King, *J. Phys. Chem.*, **71**, 1779 (1967).

very labile. Hence the system takes advantage of a (presumably) relatively rapid electron-transfer reaction,  $2 \rightleftharpoons 3$ , and the lability of Cr(II) to gain a rapid path to reactants, whereas conversion to products requires slow substitution on Ru(II). The much greater rate of substitution on Cr(II) compared to that on Ru(II) more than compensates for the unfavorable  $3 \rightleftharpoons 2$  equilibrium. We believe this is an excellent example of substitution reactions dominating an electron-transfer process.<sup>5c</sup>

**Acknowledgment.** We thank Professor H. Taube for helpful discussions and the Public Health Service for financial support (Grant GM-14830). Funds for purchase of the stopped-flow spectrometer were provided by the National Science Foundation (Grant GP-8318).

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### Oxidized Radon in Halogen Fluoride Solutions<sup>1</sup>

Sir:

It has been shown in previous tracer experiments that radon forms a fluoride of very low volatility.<sup>2,3</sup> Solutions of oxidized radon have now been prepared by reaction of microgram amounts of the element with bromine trifluoride, bromine pentafluoride, and chlorine trifluoride. The halogen fluorides can be vacuum distilled from the solutions at room temperature without volatilization of radon. This behavior suggests that radon is present in the solutions as an ionic species, possibly  $\text{Rn}^{2+}$ . Solids obtained by evaporation of the solutions to dryness have not been identified but appear to be identical with the simple fluoride formed in the reaction of radon and fluorine.<sup>2</sup> The solids liberate elemental radon on hydrolysis, leaving very little activity in the aqueous phase. Since krypton difluoride and xenon difluoride also hydrolyze in this manner, it is probable that the product is radon difluoride in each instance.

Hazeltine and Moser<sup>4</sup> recently reported that non-volatile, nonextractable radon species could be produced in aqueous solutions through the use of oxidants, such as hydrogen peroxide, potassium permanganate, and potassium persulfate. However, they observed the species only in solutions containing radon and its parent, radium-226, and not in solutions containing radon alone. Flohr and Appelman<sup>5</sup> repeated the experiments and found that the nonvolatile species could be removed from solution by centrifugation. They concluded that no radon compound was present but that radium coprecipitated with suspended matter in the solutions and then produced radon which was mechanically trapped in the solid.

(1) Work performed under the auspices of the U. S. Atomic Energy Commission.

(2) P. R. Fields, L. Stein, and M. H. Zirin, *J. Am. Chem. Soc.*, **84**, 4164 (1962).

(3) P. R. Fields, L. Stein, and M. H. Zirin, "Noble Gas Compounds," H. H. Hyman, Ed., University of Chicago Press, Chicago, Ill., 1963, pp 113-119.

(4) M. W. Hazeltine and H. C. Moser, *J. Am. Chem. Soc.*, **89**, 2497 (1967).

(5) K. Flohr and E. H. Appelman, *ibid.*, **90**, 3584 (1968).

The present experiments were carried out in a shielded cell with gaseous  $^{222}\text{Rn}$ , which was collected from a 5-Ci radium chloride solution, passed through a drying tube containing calcium sulfate, and condensed in a trap on a metal vacuum line at  $-195^\circ$ . The gas was partially purified by distillation at  $-78^\circ$  after radiolytic hydrogen and oxygen were pumped off. In the first experiment, approximately 0.25 Ci of radon (1.5  $\mu\text{g}$ ) was condensed in a Kel-F tube containing 8 ml of frozen bromine pentafluoride at  $-195^\circ$ . The mixture was allowed to thaw and warm to room temperature for 1.5 hr, during which time it was shaken several times. At the end of this period, the radon was found to be concentrated in the liquid phase at the bottom of the tube. The position of radon was determined by measuring the  $\beta$ - $\gamma$  emission of its daughters with a Jordan meter, using a technique similar to that previously described.<sup>2</sup> The solution was then vacuum distilled at room temperature. The bromine pentafluoride distillate was found to be inactive, and the radon was found to be concentrated in the dry residue remaining in the Kel-F tube.

Solutions of approximately 0.12 Ci of radon in 6 ml of bromine trifluoride and 0.32 Ci of radon in 4 ml of chlorine trifluoride were prepared in a similar manner. The reaction of radon with bromine trifluoride was incomplete, probably because of partial condensation of the gas on the test tube walls above the frozen trifluoride. Five per cent of the activity appeared in the first distillate fraction, whereas none appeared in later fractions. All distillate fractions from the chlorine trifluoride solution were found to be inactive.

Aliquots of a solution which contained 15 mCi of radon per ml of bromine trifluoride were removed with Kel-F pipets in a glove box and progressively diluted with inactive bromine trifluoride. The solutions then showed  $\beta$ - $\gamma$  activities corresponding to the dilution factors. The solutions were centrifuged and decanted from test tube to test tube without loss of activity. To verify that radon was present in the diluted samples as well as the short-lived  $\beta$ - $\gamma$  emitting daughters,  $^{214}\text{Pb}$  and  $^{214}\text{Bi}$ , the activity was checked over a period of 22 days and was found to decay with the half-life of  $^{222}\text{Rn}$  (3.8 days). Some radiation decomposition of bromine trifluoride was noted in the undiluted stock solution, which changed from a yellow color to a deep orange color within 3 days. The reduction products ( $\text{Br}_2$  and  $\text{BrF}$ ) were distilled from the solution without volatilization of radon.

In a comparison of the electronic structures of group VIII elements, it can be noted that 18 electrons are added in completed shells between argon and krypton and 18 between krypton and xenon, whereas 32 electrons are added between xenon and radon. The longer interval between xenon and radon (filling of 4f orbitals as well as 5d, 6s, and 6p orbitals) undoubtedly produces a greater change in the properties of these two elements than that between preceding pairs of elements in the series. It is not surprising, therefore, to find that radon is much more "metallic" than xenon. The first ionization potential of radon is only 10.75 V, comparable to that of iodine (10.45 V) and much lower than ionization potentials of other halogens or hydrogen. The low volatility of radon fluoride has led Weinstock<sup>6</sup> to pro-

(6) B. Weinstock, ref 3, p 119.