CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, STANFORD UNIVERSITY, STANFORD, CALIFORNIA,
AND THE UNIVERSITY OF CALIFORNIA, DAVIS, CALIFORNIA 95616

# Oxidations of Aqueous Chromium(II). I. Hydroxylamine and Some Amine Oxides

BY WILLFRED SCHMIDT, J. H. SWINEHART,[1] AND H. TAUBE

*Received May 23, 1968*

An investigation of the stoichiometry and kinetics of the reduction of hydroxylamine, trimethylamine N-oxide, and dimethylaniline N-oxide by aqueous chromium(II) is described. In each case, 2 mol of chromium(II) is consumed for each mole of oxidant. The rates of the reactions are, however, first-order in each reactant. Evidence is offered in support of the conclusion that the rate-controlling reaction leads to the formation of $NH_3^+$ (from $NH_3OH^+$) or $R_3N^+$ (from amine oxides). These radicals then oxidize chromium(II) without producing nitrogen-containing chromium(III) products. In all cases the chromium(III) product formed is mainly $Cr(H_2O)_6^{3+}$. Oxygen-18 tracer experiments with $NH_3O^{18}H^+$ as oxidant indicate that the attack of chromium(II) on the oxidant takes place at the oxygen.

## Introduction

In aqueous acid solution hydroxylamine can be reduced to ammonium ion and water.[2,3] In the reaction between titanium(III) and hydroxylamine 2 mol of titanium(III) is consumed for each mole of hydroxylamine. The reaction can be used for the quantitative determination of hydroxylamine.[2,4] When the reaction takes place in the presence of vinyl monomers, polymerization occurs, indicating that the reaction takes place in part by a free-radical mechanism.[5] Additive dimerization of the radical intermediate with olefins to yield diamines indicates, at least when the reductant is titanium(III), that the radical formed in the reduction of hydroxylamine is $NH_2$ (or possibly $NH_3^+$ in acid solution).[6,7]

To extend the work, the reduction of hydroxylamine[8] and several N-oxides by aqueous chromium(II) was undertaken. Chromium(II) was chosen as the reductant because the resulting chromium(III) products are not labile to substitution, so that examination of the products provides insight into the mechanism of reaction.

## Experimental Section

**Reagents.**—The following reagent grade chemicals were used without further purification: NaBr, NaF, NaCl, $NH_4F \cdot HF$, $HClO_4$, guanidine hydrochloride, $\alpha,\alpha$-diphenyl-$\beta$-picrylhydrazyl, ethanol, and 1,3-butadiene. $LiClO_4$ was made by the neutralization of $LiOH \cdot H_2O$ (G. F. Smith) with $HClO_4$. The resulting solid was twice recrystallized from water. Solid $(NH_2OH)_2H_2SO_4$ and $(N_2H_4)_2H_2SO_4$ (Matheson Coleman and Bell) were purified by recrystallizing them twice from water. Solid $NH_2OH \cdot HClO_4$ was prepared by the metathesis of $(NH_2OH)_2H_2SO_4$ with $Ba(ClO_4)_2$. Aqueous $TiCl_3$ was obtained from Fisher Scientific Co. as a 20% acidic solution. The water used in all experiments was distilled after having passed through deionization columns. The salt $(NH_2OH)_2H_2SO_4$ with hydroxylamine enriched in $O^{18}$ was prepared by the reduction of nitrite with sulfite[9] in $O^{18}$-enriched water. The chloride salt was converted to the sulfate by heating $NH_2OH \cdot HCl$ in a sulfuric acid solution.

Pyridine N-oxide was prepared by the method of Ochiai[10] and purified by distillation under vacuum. Trimethylamine N-oxide was prepared from an aqueous solution of $H_2O_2$ and trimethylamine.[11] It was recrystallized from water and titrated with standard acid to determine the content of water of hydration. Dimethylaniline N-oxide was prepared by the addition of dimethylaniline to a solution of peracetic acid[11] and was recrystallized from a $CHCl_3$–$CCl_4$ solution.

Chromium(II) perchlorate solutions were prepared by the reduction of the chromium(III) salt with amalgamated zinc under a stream of nitrogen.[12] The solutions were analyzed for chromium(III) by measuring the absorbance at 408 mμ. All hydroxylamine solutions were kept acidic to prevent decomposition into ammonium ion and nitrous oxide.[13] Stock solutions were made up fresh daily. Ionic strength in all experiments was maintained with $LiClO_4$ and $HClO_4$. The acidity was fixed with $HClO_4$.

**Kinetic Measurements and Analysis.**—Kinetic experiments were carried out with a Cary Model 14 spectrophotometer and a Gibson–Durrum stopped-flow apparatus. When the Cary spectrophotometer was used, mixing of the reactants was achieved by injecting through a rubber serum cap one reactant solution, which had been previously thermostated, into a cell containing the other thermostated reactant solution. Temperature control was ±0.5°. The order of mixing the hydroxylamine or amine N-oxide solutions and the chromium(II) solution had no effect on the kinetic behavior of the system. In all experiments reported, the chromium(II) solution was added to the hydroxylamine or amine N-oxide solution. The Gibson–Durrum stopped-flow apparatus has a mixing time of several milliseconds. Temperature control was to ±0.5°. All solutions were deoxygenated by a stream of nitrogen for at least 10 min before using. Chromium(III) products were analyzed by spectrophotometry ($Cr(H_2O)_6^{3+}$, $\epsilon_{408\,m\mu}$ 15.6 and $\epsilon_{574\,m\mu}$ 13.4[14]) and/or by using a cation-exchange column for separation and characterization. On a Dowex 50-X8 column 0.5 *M* $HClO_4$ removes chromium species of charge +2, 1.0 *M* $HClO_4$ removes hexaaquochromium(III), and species of higher charge such as $(CrOH)_2^{4+}$ remain on the column under these conditions.

In the oxygen-18 experiments involving $NH_3^+O^{18}H$ and chro-

---

[1] To whom reprint requests should be directed: Department of Chemistry, University of California, Davis, Calif. 95616.

[2] A. Stahler, *Ber.*, **37**, 4732 (1904).

[3] A. Kurtenack and F. Werner, *Z. Anorg. Allgem. Chem.*, **160**, 333 (1927).

[4] W. C. Bray, M. E. Simpson, and A. A. MacKenzie, *J. Am. Chem. Soc.*, **41**, 1363 (1919).

[5] P. Davis, M. G. Evans, and W. C. E. Higginson, *J. Chem. Soc.*, 2563 (1951).

[6] C. J. Albisetti, D. D. Coffman, F. W. Hoover, E. L. Jenner, and W. E. Mockel, *J. Am. Chem. Soc.*, **81**, 1489 (1959).

[7] The radical $NH_2$ is probably less basic than is $NH_3$, but it seems likely that, in solutions as acidic as those used by us, $NH_3^+$ rather than $NH_2$ is the dominant form.

[8] Since the inception of our studies, a report on reactions of $Cr^{2+}$ with several N-containing compounds, including $NH_2OH$, has appeared: C. F. Wells and M. A. Salam, *Chem. Ind.* (London), 2079 (1967). Their results and conclusions in comparison to ours will be referred to later.

[9] G. K. Rollefson and C. F. Oldenshaw, *J. Am. Chem. Soc.*, **54**, 977 (1932).

[10] E. Ochiai, *J. Org. Chem.*, **18**, 535 (1953).

[11] E. Muller, Ed., "Methoden der Organishen Chemie," Vol. XI, part 2, 4th ed, George Thiene, Stuttgart, 1958, pp 192–195.

[12] H. Taube and H. Myers, *J. Am. Chem. Soc.*, **76**, 2103 (1954).

[13] W. Latimer, "Oxidation Potentials," 2nd ed, Prentice-Hall, Inc., New York, N. Y., 1959, p 97.

[14] L. B. Anderson and R. A. Plane, *Inorg. Chem.*, **3**, 1470 (1964).

mium(II) the resulting hexaquochromium(III) was precipitated as the violet fluoride salt.[15] Water was converted to $CO_2$ for oxygen-18 analysis by heating the sample with guanidine hydrochloride.[16]

Kinetic experiments were performed with both the sulfate and the perchlorate salt of hydroxylamine. While the sulfate salt is nonhydroscopic and easily handled, the perchlorate salt had to be stored and weighed in a drybox owing to its extreme hydroscopicity. The kinetics for each oxidant were checked at three wavelengths between 380 and 450 mμ and found to be independent of wavelength. All experiments reported were carried out at 410 mμ.

For all oxidants, rate constants $k$ are defined by the relation

$$d[Cr(III)]/dt = k[Cr^{2+}][oxidant]$$

The values of $k$ were determined from plots of $\ln(A_\infty - A_t)$ *vs.* time for data obtained under psuedo-first-order conditions. $A_\infty$ and $A_t$ are the absorbances at infinite time and time $t$.

## Results

**Hydroxylamine.**—The ion $Cr(H_2O)_5NH_3^{3+}$ has been shown[17] to be a product of the reaction of chromium(II) with $HN_3$, and it was considered to be a possible product of the reaction of chromium(II) with hydroxylamine. Investigation of the products of the latter reaction using cation-exchange techniques, however, showed that $Cr(H_2O)_6^{3+}$ constitutes more than 95% of the chromium(III) product. A small amount, less than 5%, of the chromium(III) remains on the column even when $2M$ $HClO_4$ is the eluent, and it is therefore concluded that a small part of the reaction produces condensed chromium(III) species. Analysis of the unreacted hydroxylamine issuing from the cation-exchange column with titanium(III) showed that 2 mol of chromium(II) reacts for each mole of $NH_2OH$ consumed. The stoichiometry was also investigated with chromium(II) in excess. The reaction under these conditions was followed spectrophotometrically at 410 mμ and 2 mol of $Cr(H_2O)_6^{3+}$ was produced for every mole of $NH_2OH$ consumed. Excess chromium(II) was oxidized by air and the solution was subjected to analysis by cation exchange. Ammonia analysis confirmed that one $NH_3$ is produced for each $NH_2OH$ originally present. The various observations show that the dominant net change taking place in the reduction of hydroxylamine by chromium(II) is

$$2H^+ + 2Cr(H_2O)_6^{2+} + NH_3OH^+ \longrightarrow NH_4^+ + 2Cr(H_2O)_6^{3+} + H_2O \quad (1)$$

Pseudo-first-order kinetics were obtained whether an excess of chromium(II) or hydroxylamine was used. The first-order plots remained linear over the entire course of the reaction. Table I lists the rate constants $k$ for the reaction of chromium(II) with hydroxylamine. The rate constant $k$ is independent of $[H^+]$; this conclusion is in agreement with that reached by Wells and Salam,[8] who extended their studies to $4 \times 10^{-6}$ $M$ $HClO_4$. Even when allowance is made for ionic strength differences, our value of $k$ at 25° and $\mu = 1.3$ of 0.014 $M^{-1}$ sec$^{-1}$ does not agree with the previously published value of 1.00 $M^{-1}$ sec$^{-1}$ at the same temperature and $\mu = 1.00$.[8]

The data recorded in Table I lead to values for $\Delta H^\ddagger$ and $\Delta S^\ddagger$ of 10.5 ± 0.5 kcal mol$^{-1}$ and −37 ± 2 eu. The small difference in rate constant between experiments with chromium(II) in excess and those with $NH_3OH^+$ in excess is not a matter of concern. The reductant, $Cr(ClO_4)_2$, made a large contribution to the total ionic strength in the experiments with excess chromium(II), and the difference in rate between this group of experiments and the others is undoubtedly a result of the differences in ionic strength.

TABLE I

KINETIC DATA ON THE $Cr(II)$–$NH_3^+OH$ REACTION IN THE PRESENCE OF $ClO_4^-$ [a]

| No. | $[HONH_3^+]$[b] or $[Cr^{2+}]$,[c] $M$ | $[H^+]$, $M$ | $10^3k$, $M^{-1}$ sec$^{-1}$ | Temp, °K |
|---|---|---|---|---|
| 1 | 0.406 | 0.095 | 5.75 | 285.0 |
| 2 | 0.406 | 0.262 | 5.75 | 285.0 |
| 3 | 0.406 | 0.485 | 5.75 | 285.0 |
| 4 | 0.406 | 0.095 | 13.7 | 298.0 |
| 5 | 0.406 | 0.262 | 14.2 | 298.0 |
| 6 | 0.406 | 0.485 | 13.7 | 298.0 |
| 7 | 0.304 | 0.262 | 14.6 | 298.0 |
| 8 | 0.507 | 0.262 | 14.1 | 298.0 |
| 9 | 0.406 | 0.095 | 29.1 | 311.0 |
| 10 | 0.406 | 0.262 | 29.4 | 311.0 |
| 11 | 0.406 | 0.485 | 30.7 | 311.0 |
| 12 | 0.202 | 0.150 | 12.9 | 298.0 |
| 13 | 0.172 | 0.150 | 12.5 | 298.0 |
| 14 | 0.148 | 0.150 | 12.5 | 298.0 |
| 15 | 0.110 | 0.150 | 12.5 | 298.0 |

[a] $\mu = 1.3$. [b] For no. 1–11, $[Cr^{2+}]_{initial} = 5.0 \times 10^{-2}$ $M$. [c] For no. 12–15, $[NH_3OH^+]_{initial} = 2.5 \times 10^{-2}$ $M$.

Table II shows data which were obtained with $SO_4^{2-}$ present in the solution. The results can be represented by the equation

$$k = k_1 + \frac{k_2[HSO_4^-]}{[H^+]}$$

where $10^3k_1$ takes the values 4.0 ± 0.2, 11.5 ± 0.8, and 25.3 ± 0.8 $M^{-1}$ sec$^{-1}$ at 284.0, 296.0, and 308.5°K, respectively, and $10^3k_2$ at the same three temperatures takes the values 10.7 ± 0.8, 17.5 ± 1.4, and 29.0 ± 1.7$M^{-1}$ sec$^{-1}$.

The values of $k_1$ are in reasonable agreement with the values of $k$ determined in the media containing only $ClO_4^-$. When the latter are corrected to the temperatures used for obtaining $k_1$, they become $5.1 \times 10^{-3}$, $12.0 \times 10^{-3}$, and $26.2 \times 10^{-3}$ $M^{-1}$ sec$^{-1}$.

The ion $Cr(H_2O)_5SO_4^+$ is a product when $SO_4^{2-}$ is present in the reaction mixture. At 25° when $[HSO_4^-]/[H^+] = 0.082$, 7.4% of the chromium(II) reacting appears as the sulfate complex, and at $[HSO_4^-]/[H^+] = 0.83$, 22% is present in this form.

Albisetti, *et al.*,[4] noted interference in their reactions of hydroxylamine with titanium(III) if $Br^-$ or $I^-$ was present in the reaction mixture. A series of kinetic experiments was run in the presence of three different halides ($F^-$, $Cl^-$, and $Br^-$) and with hydroxylamine (0.40 $M$) in excess of chromium(II) (0.01 $M$). In these experiments the concentration of halide was

---

[15] A. Laswick and R. A. Plane, *J. Am. Chem. Soc.*, **81**, 3564 (1959).

[16] P. Moore, F. Basolo, and R. G. Pearson, *Inorg. Chem.*, **5**, 223 (1966).

[17] M. Ardon and B. E. Mayer, *J. Chem. Soc.*, 2819 (1962).

TABLE II

KINETIC DATA ON THE $Cr(II)-NH_3^+OH$ REACTION IN THE PRESENCE OF $SO_4^{2-}$ [a]

| $[HSO_4^-]/[H^+]$[b] | $10^3k$, $M^{-1}$ sec$^{-1}$ | Temp, °K |
|---|---|---|
| 0.516 | 9.45 | 284.0 |
| 0.402 | 8.16 | 284.0 |
| 0.279 | 6.90 | 284.0 |
| 0.516 | 20.40 | 296.0 |
| 0.402 | 18.00 | 296.0 |
| 0.279 | 16.15 | 296.0 |
| 0.516 | 40.30 | 308.5 |
| 0.402 | 36.80 | 308.5 |
| 0.279 | 33.40 | 308.5 |

[a] $\lambda$ 410 m$\mu$, $\mu = 1.50$, $[Cr^{2+}]_{initial} = 5.0 \times 10^{-2}$ *M*, and $[NH_3OH^+] = 0.40$ *M*. [b] Calculated using p*K*'s for $HSO_4^-$ of 0.86 in 1 *M* $LiClO_4$ (R. W. Ramette and R. F. Stewart, *J. Phys. Chem.*, **65,** 243 (1961)) and 0.52 in 1 *M* $HClO_4$ (E. Eichler and S. Rabideau, *J. Chem. Soc.*, **77,** 5501 (1955)).

0.007 *M;* $[H^+]$, 0.19 *M;* and $[HSO_4^-]$, 0.11 *M*. The pseudo-first-order rate constants for no halide, $F^-$, $Cl^-$, and $Br^-$ were observed to be 8.8, 9.0, 8.9, and $8.9 \times 10^{-3}$ sec$^{-1}$, respectively. It can be seen that the halide ion at the level used does not affect the rate-determining step. No chromuim compound containing halide was found as product when $F^-$ or $Cl^-$ was present but in the presence of $Br^-$ some $Cr(H_2O)_5Br^{2+}$ was formed.[18] The amount of this ion was not quantitatively determined but was less than 25% of the total chromium(III) product.

The possibility of $N_2H_4$ being an intermediate was investigated by adding 0.1 *M* chromium(II) to 0.4 *M* $(N_2H_4)H_2SO_4$. No detectable reaction took place in 24 hr at 298°K. Because the stoichiometry of the reaction of chromium(II) with $NH_3OH^+$ is 2:1, we can conclude that hydrazine is not an important intermediate in the reaction of chromium(II) with $NH_3^+OH$. We disagree with Wells and Salam,[8] who report that *k* for the chromium(II)–hydrazine reaction at 25° and $\mu = 1.0$ is 1.3 $M^{-1}$ sec.$^{-1}$

Identification of a radical intermediate was undertaken in a manner similar to that of Albisetti, *et al.*[6] Chromium(II) was added to a solution containing hydroxylamine and an excess of 1,3-butadiene. Various amines were isolated in good yield from this reaction mixture.

In a labeling experiment, the sulfate salt of the $O^{18}$-labeled hydroxylamine was treated with a stoichiometric amount of chromium(II). The product, $Cr(H_2O)_6^{3+}$, was precipitated as the fluoride salt by adding the final solution to a concentrated ammonium fluoride solution. The results show that the oxygen in over 0.8 of 6 waters on half of the $Cr(H_2O)_6^{3+}$ come from the oxygen in the hydroxylamine (between $0.4_0$ and $0.4_5$ of the waters on all of the $Cr(H_2O)_6^{3+}$). This experiment combined with the butadiene experiment clearly shows that the initial attack of chromium(II) takes place at the oxygen of hydroxylamine.

Finally, a kinetic experiment with chromium(II) and $NH_3OCH_3^+$ showed that the rate of reaction with this compound was many times slower than the rate of chromium(II) with $NH_3OH^+$ under similar conditions.

**Pyridine N-Oxide.**—No reaction was detectable between 0.4 *M* pyridine N-oxide and 0.1 *M* chromium(II) in an aqueous acidic solution over a 24-hr period. When titanium(III) was used as the reducing agent, the reaction went rapidly to completion. Work on the latter system is still in progress.

**Trimethylamine N-Oxide.**—The rate of reduction of $(CH_3)_3NOH^+$[19] with chromium(II) is considerably faster than the rate of reduction of $NH_3OH^+$. However, it could still be followed kinetically on the Cary spectrophotometer. The stoichiometry is 2 mol of chromium(II) to 1 mol of trimethylamine N-oxide with either reagent in excess. The stoichiometry in excess chromium(II) was determined by observation of the $Cr(H_2O)_6^{3+}$ formed and in excess amine N-oxide by titration of the amine N-oxide with chromium(II). As with the hydroxylamine system, more than 90% of the chromium(III) product is $Cr(H_2O)_6^{3+}$, but a small remainder is in the form of higher charged species. When trimethylamine oxide reacts with chromium(II) in the presence of methyl methacrylate monomer, polymerization of the latter is initiated. The nitrogen-containing product in all cases is trimethylamine. Unlike $NH_3^+$, $(CH_3)_3N^+$ cannot add to olefins without demethylation; therefore direct evidence for the nature of the intermediate radical could not be obtained. Pseudo-first-order kinetics were obtained over the entire course of reaction with either reactant in excess. Table III summarizes the results for a series of concentrations, temperature, and acidities using excess trimethylamine N-oxide. It is noted that over the concentration range of $H^+$ ion studied (0.40–0.90 *M*) the reaction rate is independent of acidity. $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for this reaction were computed to be 7.9 ± 0.3 kcal mol$^{-1}$ and −33 ± 1 eu.

**Dimethylaniline N-Oxide.**—The kinetic experiments on the reduction of dimethylaniline N-oxide by chromium(II) were run in a stopped-flow apparatus. As in the experiments with trimethylamine N-oxide, $HClO_4$ was added to the free base and the acidity of the solution was calculated using the dissociation constant of the conjugate acid.[19] The stoichiometry was again 2 mol of chromium(II) to 1 mol of dimethylaniline N-oxide (either reactant in excess) and more than 90% of the chromium(III) product was $Cr(H_2O)_6^{3+}$ with a small amount of dimeric species. The results of a series of experiments in excess dimethylaniline oxide are summarized in Table IV. In this reaction, as in that of $(CH_3)_3NOH^+$, there is no variation of rate with $[H^+]$ over the range studied (0.11–0.31 *M*). $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for this reaction are 5.7 ± 0.2 kcal mol$^{-1}$ and −32 ± 1 eu.

**$\alpha,\alpha$-Diphenyl-$\beta$-picrylhydrazyl.**—Bawn and Verdin[20] studied the reduction of the stable free radical $\alpha,\alpha$-diphenyl-$\beta$-picrylhydrazyl (DPPH) by iron(II). In

---

[18] F. A. Guthrie and E. L. King, *Inorg. Chem.*, **3,** 916 (1964).

[19] It should be noted that at the acidities of the experiments, the dominant form of the base is $(CH_3)_3NOH^+$: P. A. S. Smith, "Open-Chain Nitrogen Compounds," W. A. Benjamin, Inc., New York, N. Y., 1966, p 22.

[20] C. E. H. Bawn and D. Verdin, *Trans. Faraday Soc.*, **56,** 519 (1960).

TABLE III

KINETIC DATA ON THE REACTION OF CHROMIUM(II) WITH $(CH_3)_3NOH^+$ [a]

| $[(CH_3)_3NOH^+]$, $M$ | $[H^+]$, $M$ | $k$, $M^{-1}$ sec$^{-1}$ | Temp, °K |
|---|---|---|---|
| 0.120 | 0.20 | 0.354 | 284.2 |
| 0.160 | 0.20 | 0.344 | 284.0 |
| 0.200 | 0.20 | 0.364 | 284.4 |
| 0.205 | 0.45 | 0.362 | 285.2 |
| 0.205 | 0.20 | 0.360 | 285.0 |
| 0.205 | 0.45 | 0.396 | 287.8 |
| 0.205 | 0.20 | 0.375 | 287.2 |
| 0.205 | 0.45 | 0.477 | 291.9 |
| 0.205 | 0.20 | 0.494 | 291.9 |
| 0.205 | 0.45 | 0.664 | 297.1 |
| 0.205 | 0.20 | 0.649 | 297.1 |

[a] $\lambda$ 410 m$\mu$, $\mu = 1.0$, and $[Cr^{2+}]_{\text{initial}} = 3.8 \times 10^{-2} M$.

TABLE IV

KINETIC DATA ON THE REACTION OF CHROMIUM(II) WITH $C_6H_5(CH_3)_2NOH^+$ [a]

| $[C_6H_5(CH_3)_2NOH^+]$, $M$ | $[H^+]$, $M$ | $k$, $M^{-1}$ sec$^{-1}$ | Temp, °K |
|---|---|---|---|
| 0.03 | 0.21 | 30.0 | 295.5 |
| 0.04 | 0.21 | 33.2 | 295.5 |
| 0.05 | 0.21 | 31.8 | 295.5 |
| 0.04 | 0.11 | 32.8 | 295.5 |
| 0.04 | 0.31 | 33.0 | 295.5 |
| 0.04 | 0.31 | 20.0 | 282.5 |
| 0.04 | 0.31 | 34.9 | 297.5 |
| 0.04 | 0.31 | 58.5 | 312.5 |

[a] $\lambda$ 410 m$\mu$, $\mu = 1.0$, and $[Cr^{2+}]_{\text{initial}} = 1.2 \times 10^{-2} M$.

additional qualitative experiments they used other reductants and found that the product spectrum for all except chromium(II) agreed with that of $\alpha,\alpha$-diphenyl-$\beta$-picrylhydrazine. Since we were interested in the reaction of N radicals with chromium(II), we repeated the experiment of reducing DPPH with chromium(II) in a 1:1 (v/v) ethanol–water solution. The final solution was passed through a Dowex 50-X8 cation-exchange column. It was found that most, but not all, of the reduced organic product was coordinated to the chromium(III) and that little of the chromium(III) was present as $Cr(H_2O)_6^{3+}$.

## Discussion

The activated complex for the reduction by chromium(II) of hydroxylamine or the amine oxides studied contains 1 mol of chromium(II) and 1 mol of oxidizing agent. The compositions of the activated complexes are hereby specified, but important questions as to their geometry remain to be answered. In view of the great propensity of chromium(II) to capture groups derived from the oxidant, reduction of the present class of oxidants by outer-sphere activated complexes seems unlikely. It moreover seems to be excluded by arguments along the following line.

A one-electron reduction of $NH_3OH^+$ by an outer-sphere mechanism would yield either $NH_3 + OH$ or $NH_3^+ + OH^-$ ($\equiv NH_2 + H_2O$). The former of the possibilities is ruled out by the observation that copious amounts of nitrogen-containing radicals are produced; the latter, by the fact that transfer of oxygen from $NH_3OH^+$ to the chromium is efficient. Thus the evidence requires direct attack on $NH_3OH^+$ by chromium(II) and, to explain the oxygen-tracer results, attack on oxygen rather than on nitrogen

$$H^+ + NH_3O^{18}H^+ + Cr^{2+}(H_2O)_6 \longrightarrow NH_3^+ + (H_2O)_5CrO^{18}H_2^{3+} + H_2O$$

By analogy, and to explain the formation of nitrogen radicals when amine oxides react, we assume a similar reaction for them. Evidence in favor of a one-electron rather than a two-electron reduction is the fact that when butadiene is present, amines are formed in good yield, as well as the fact that $Cr(H_2O)_6^{3+}$ rather than $((H_2O)_4CrOH)_2^{4+}$ is the main product.[21] The fact that, when chromium(II) acts on hydroxylamine, polymerization of methyl methacrylate is initiated also shows that the reducing reaction proceeds at least in part of the formation of radicals.[5] The evidence favoring a one-electron course for the reduction of hydroxylamine by titanium(III) has already been referred to;[6] evidence in support of a one-electron change for the reaction of iron(II) with $(CH_3)_3NOH^+$ has also been adduced.[22]

The radical $NH_2$ is not powerful enough as an oxidizing agent to produce HO from $H_2O$[13] and, on combining the data which are the basis for this conclusion with estimates of the affinity of $NH_2$ for $H^+$, it appears that $NH_3^+$ is also not powerful enough to oxidize water. Thus, $NH_3^+$ must disappear by reaction with chromium(II).

It is interesting that the radicals $NH_3^+$, $N(CH_3)_3^+$, and $N(CH_3)_2C_6H_5^+$ react with chromium(II) without being captured. This has precedent in the behavior of $SO_4^-$ which reacts with chromium(II) without forming $CrSO_4^+$.[23] In principle, $NH_3^+$ can react with chromium(II) by an outer-sphere electron transfer, but it seems more likely that it reacts by abstracting a hydrogen atom from the coordination sphere of the aquated ion

$$Cr(H_2O)_6^{2+} + NH_3^+ \longrightarrow Cr(H_2O)_5OH^{2+} + NH_4^+$$

This kind of reaction path has also been postulated for the reaction of HO (or $SO_4^-$) with $(NH_3)_5CoOH_2^{3+}$ [24] and for the reaction of $SO_4^-$ with $Cr(H_2O)_6^{2+}$.[23]

The fact that the rate of reaction is not affected by $Br^-$ even though the product distribution is affected by $Br^-$ shows that $Br^-$ is not involved in the rate-determining step, and it must therefore react with an intermediate formed in or subsequent to the rate-determining step. The reaction sequence which leads to the formation of $CrBr^{2+}$ undoubtedly is

$$NH_3^+ + Br^- \longrightarrow NH_3 + Br$$

$$Br + Cr^{2+} \longrightarrow CrBr^{2+}$$

Scavenging of Br by chromium(II) is known to be very efficient.[12] Chloride ion and fluoride ion are much more difficult to oxidize than is bromide ion, and this is in accord with the observation that the bromide ion

---

(21) M. Ardon and R. A. Plane, *J. Am. Chem. Soc.*, **81**, 3197 (1959).

(22) J. P. Ferris and R. Gerne, *Tetrahedron Letters*, **24**, 1613 (1964).

(23) D. E. Pennington and A. Haim, to be submitted for publication.

(24) D. D. Thusius and H. Taube, *J. Phys. Chem.*, **71**, 3845 (1967).

(but not the former ions) affects the identity of the products.

According to the rate data, at the lower $[HSO_4^-]/[H^+]$ ratio used for product analysis, 21% of the reaction takes place by the $SO_4^{2-}$-dependent path, while at the higher $[HSO_4^-]/[H^+]$ ratio, 43% takes place by this path. If it is assumed that the sulfate product is formed when $SO_4^{2-}$ is involved in the attack of chromium(II) on $NH_3OH^+$, but not in the reaction of chromium(II) with $NH_3^+$, it would be expected that 10.5 and 22%, respectively, of the chromium(II) would appear as the sulfate complex. The experimental values of 7.4 and 22% of the chromium(III) appearing as the sulfate complex are in reasonable agreement with the supposition advanced.

The rate data for the several oxidants are summarized in Table V. The values of $\Delta S^\ddagger$ are remarkably constant for the series of reactions differing quite markedly in the nature of the substituents on the nitrogen. The increase in rates is in line with the increased stability of the radical generated when OH is abstracted by the reducing agent.

TABLE V

SUMMARY OF KINETIC PARAMETERS

| Oxidant | $k$(298°K), $M^{-1}$ sec$^{-1}$ | $\mu$ | $\Delta H^\ddagger$, kcal mol$^{-1}$ | $\Delta S^\ddagger$, eu |
|---|---|---|---|---|
| $NH_3OH^+$ | 0.0141 | 1.3 | $10.5 \pm 0.5$ | $-37 \pm 2$ |
| $(CH_3)_3NOH^+$ | 0.66 | 1.0 | $7.9 \pm 0.3$ | $-33 \pm 1$ |
| $(CH_3)_2C_6H_5NOH^+$ | 36 | 1.0 | $5.7 \pm 0.2$ | $-33 \pm 1$ |

**Acknowledgments.**—Financial support by the National Institutes of Health, Grants No. 13638-01 and 11767-05, is acknowledged.

---

CONTRIBUTION NO. 2247 FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF CALIFORNIA, LOS ANGELES, CALIFORNIA 90024

# Aquation Kinetics of the Green-Blue Isomer of Dibromodiaquoethylenediaminechromium(III) Cation and of the Magenta Isomer of Bromotriaquoethylenediaminechromium(III) Cation[1]

BY R. GRAHAM HUGHES AND CLIFFORD S. GARNER

*Received May 8, 1968*

The aquation of $Cr(en)(OH_2)_2Br_2^+$ (green-blue isomer) has been investigated by spectrophotometry and by $Br^-$ release in 0.01–2 $F$ $HClO_4$ from 17 to 35°. At 25.01° the aquation rate constant is $k_1 = (3.95 \pm 0.05) \times 10^{-4}$ sec$^{-1}$ in 0.3–2 $F$ $HClO_4$ ($\mu = 2$ $M$, $NaClO_4$); $E_a = 19.8 \pm 0.2$ kcal mol$^{-1}$ and log $PZ$(sec$^{-1}$) = $11.20 \pm 0.01$. The product is magenta $Cr(en)(OH_2)_3Br^{2+}$. Alternatively, but less probably, $k_1$ could be associated with a rate-controlling isomerization to one of the other two possible geometric isomers of $Cr(en)(OH_2)_2Br_2^+$, followed by relatively fast aquation to the observed product. The apparent first-order rate constant $k_2$ for hydrolysis of the latter was determined by spectrophotometry and by $Br^-$ release in 0.01–3 $F$ $HClO_4$ from 25 to 60°; $Cr(en)(OH_2)_4^{3+}$ is the product. In 0.03–3 $F$ $HClO_4$ ($\mu = 3$ $M$, $NaClO_4$) at 40, 50, and 60°, $k_2 = k_{2a} + (k_2'/[H^+])$, where $k_{2a}$ is the first-order rate constant for aquation of magenta $Cr(en)(OH_2)_3Br^{2+}$ and $k_2'$ has been interpreted as $k_{2h}K_a$, $k_{2h}$ being the first-order rate constant for aquation of $Cr(en)(OH_2)_2(OH)Br^+$ and $K_a$ being the first acid dissociation constant of magenta $Cr(en)(OH_2)_3Br^{2+}$. At 25° $k_{2a} = (3 \pm 1) \times 10^{-6}$ sec$^{-1}$ (by extrapolation), $E_a = 22.0 \pm 0.3$ kcal mol$^{-1}$, and log $PZ$(sec$^{-1}$) = $11.62 \pm 0.07$. At 40° and $\mu = 3$ $M$, $k_{2h}$ is estimated as $\sim$0.2 sec$^{-1}$. There is no evidence for Cr–N bond rupture in these aquations. Visible absorption spectra are presented for green-blue $Cr(en)(OH_2)_2Br_2^+$ and magenta $Cr(en)(OH_2)_3Br^{2+}$.

## Introduction

Recently we synthesized the green-blue dibromodiaquoethylenediaminechromium(III) cation, $Cr(en)(OH_2)_2Br_2^+$, in aqueous solution by reaction of diperoxoaquoethylenediaminechromium(IV) monohydrate, $[Cr(en)(OH_2)(O_2)_2] \cdot H_2O$, with hydrobromic acid.[2] We observed that this dibromo complex hydrolyzed in perchloric acid solution to the magenta bromotriaquoethylenediaminechromium(III) cation, $Cr(en)(OH_2)_3Br^{2+}$, which in turn hydrolyzed to the tetraaquoethylenediaminechromium(III) cation, $Cr(en)(OH_2)_4^{3+}$.

We report here a kinetic study of these two reactions, which are of interest for comparison with the corresponding reactions of their chloro analogs[3] and the related dibromo-[4,5] and bromoaquobis(ethylenediamine)chromium(III)[4] cations. This study also provides a further opportunity to examine the possibility of Cr–N bond breakage in competition with Cr–X (X = halogen or pseudohalogen) bond breakage. Such competitive Cr–N breakage has been reported in a variety of chromium(III)–amine complexes.[4,6–11] The

---

[1] (a) Work partly supported by Contract AT(11-1)-34, Project No. 12, between the U. S. Atomic Energy Commission and the university. This paper constitutes Report No. UCLA-34P12-70 to the AEC. (b) Presented at the 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968.

[2] R. G. Hughes and C. S. Garner, *Inorg. Chem.*, **6**, 1519 (1967).

[3] D. M. Tully-Smith, R. K. Kurimoto, D. A. House, and C. S. Garner, *ibid.*, **6**, 1524 (1967).

[4] L. P. Quinn and C. S. Garner, *ibid.*, **3**, 1348 (1964).

[5] A. M. Weiner and J. A. McLean, Jr., *ibid.*, **3**, 1469 (1964).

[6] C. S. Garner and D. J. MacDonald in "Advances in the Chemistry of the Coordination Compounds," S. Kirschner, Ed., The Macmillan Co., New York, N. Y., 1961, pp 266–275.

[7] D. J. MacDonald and C. S. Garner, *J. Am. Chem. Soc.*, **83**, 4152 (1961).

[8] D. J. MacDonald and C. S. Garner, *Inorg. Chem.*, **1**, 20 (1962).

[9] D. C. Olson and C. S. Garner, *ibid.*, **2**, 414 (1963).

[10] J. M. Veigel and C. S. Garner, *ibid.*, **4**, 1569 (1965).

[11] C. Y. Hsu and C. S. Garner, *Inorg. Chim. Acta*, **1**, 17 (1967).