Table II. Effect of Complex Concentration on the Rate Constant of the Aquation of *cis*-$[CrI(H_2O)(en)_2]^{2+}$ in 0.001 M $HClO_4$ ($\mu = 1.0$, $NaClO_4$)

C_0, M	10^3k, s^{-1} [a]	C_0, M	10^3k, s^{-1} [a]
0.021 5	2.42 ± 0.02	0.005 00	2.71 ± 0.03
0.011 4	2.46 ± 0.01	0.001 36	3.52 ± 0.04
0.005 20	2.74 ± 0.03	0.001 33	3.57 ± 0.03

[a] Obtained from least-squares analyses; errors given are statistical standard deviations.

Table III. Activation Parameters for the Aquation of the *cis*-$[CrI(H_2O)(en)_2]^{2+}$ Cation

$[H^+]$, M	μ, M	$\Delta H^\ddagger$, kJ mol^{-1}	$\Delta S^\ddagger$, J K^{-1} mol^{-1}
0.01	1.0	83.0 ± 1.2[a]	−21.5 ± 2.1[a]
0.10	0.10	87.1 ± 2.3	−6.8 ± 7.8
0.10	1.0	85.6 ± 1.7	−12.2 ± 5.7
1.0	1.0	87.7 ± 2.3	−5.5 ± 7.8

[a] The error is the standard deviation evaluated from the least-squares analysis.

the aquation of the bromo complex, the rate constants in 0.1 M $HClO_4$ were 7–9% higher than those in 1 M $HClO_4$. Aquation of the iodo complex, on the other hand, gave rate constants in 0.1 M $HClO_4$ 9–12% higher than those in 1 M $HClO_4$.

Plots of k_{obsd} vs. $[H^+]$ are parabolic in nature with an essentially limiting value reached for k_{obsd} above a $[H^+]$ of 0.4 M. The nature of this plot suggests that the acid hydrolysis is accompanied by another competing side reaction. The higher rate constants in lower acid concentrations may be attributed to two competing side reactions: (1) the direct base hydrolysis of the *cis*-$[CrX(H_2O)(en)_2]^{2+}$ cation (X = Br^- or I^-)

$$cis\text{-}[CrX(H_2O)(en)_2]^{2+} + OH^- \rightarrow cis\text{-}[Cr(OH)(H_2O)(en)_2]^{2+} + X^- \quad (1)$$

(2) the aquation of the hydroxo complex in equilibrium with the aqua complex

$$cis\text{-}[CrX(H_2O)(en)_2]^{2+} + H_2O \rightleftharpoons cis\text{-}[CrX(OH)(en)_2]^{+} + H_3O^+ \quad (2)$$

$$cis\text{-}[CrX(OH)(en)_2]^{+} + H_2O \rightarrow cis\text{-}[Cr(OH)(H_2O)(en)_2]^{2+} + X^- \quad (3)$$

$$cis\text{-}[Cr(OH)(H_2O)(en)_2]^{2+} + H_2O \rightarrow cis\text{-}[Cr(H_2O)_2(en)_2]^{3+} + OH^- \quad (4)$$

or some combination of these schemes. Of the two possible sequences, base catalysis would appear to be more plausible for the following reasons.

Base hydrolysis (eq 1) of Co(III) complexes can occur even in weakly acidic solutions; but for Cr(III) complexes direct base hydrolysis is normally important only in basic solutions.[17] However, base catalysis may occur for Cr(III) complexes if the substrate has at least one aqua ligand whose acidity is greater than the amine ligand. In the case of *cis*-$[Cr(H_2O)(en)_2]^{3+}$ the pK_a values for the loss of the protons from the coordinated water molecules are 4.8 and 7.2,[15] respectively, while the corresponding trans complex has pK_a values of 4.1 and 7.5.[15] The pK_a values for the loss of a proton from the amine ligand is not known; but, since the acidities of Co(III) and Cr(III) complexes are similar,[18] it is not unreasonable to expect the pK_a values for the Cr(III) complex to be >14. Thus the relative acidities of the ligands are such that base catalysis could easily occur.

The decrease in the rate constant with increasing ionic strength is similar to that observed by Rogers and Staples[19] in their study of the hydrolysis of $[CrCl(RNH_2)_5]^{2+}$ complexes over the $[H^+]$ range 0.005–1 M $HClO_4$ and is consistent with base catalysis.

In 0.001 M $HClO_4$ ($\mu = 1.0$), the rate constants were observed to increase with decreasing complex concentration as shown by the data in Table II. Thus in 0.001 M $HClO_4$ and perhaps even at acid concentrations less than 0.1 M, the rate law is given as eq 5, which yields $k_1 \approx 1.65 \times 10^{-6}$ mol L^{-1} s^{-1} and $k_2 \approx 2.35 \times 10^{-3}$ s^{-1}. It would appear that k_2 represents the direct aquation of the complex and that k_1 is related to the base-catalyzed side reaction at low acid concentrations. Thus at acid concentrations which do not favor base catalysis, k_1 decreases rapidly and direct aquation is the observed reaction. The value of 2.35×10^{-3} s^{-1} for k_2 in 0.001 M $HClO_4$ is larger than the limiting value of k_2; thus it would appear that there is a slight contribution to k_2 via a yet undetermined pathway at low acid concentrations.

$$-\frac{d[\text{complex}]}{dt} = k_{obsd}[\text{complex}] = \left(\frac{k_1}{[\text{complex}]} + k_2\right)[\text{complex}] \quad (5)$$

The activation parameters for the aquation of the *cis*-$[CrI(H_2O)(en)_2]^{2+}$ cation were calculated from rate constants at four different temperatures, and the values are listed in Table III. Within experimental error, the enthalpies of activation in 0.10 and 1.0 M $HClO_4$ are the same. The lower value of the enthalpy of activation in 0.01 M $HClO_4$ may be attributed to contributions by base catalysis.

Acknowledgment. J.C.C. wishes to thank the Committee on Research of the University of Northern Iowa for the partial support of this work and Miss Kimberly Henkle for her assistance. J.W.V. wishes to thank Mr. Thomas Zupancic for his assistance.

Registry No. *cis*-$[CrI(H_2O)(en)_2]^{2+}$, 81097-63-4.

---

(17) Garner, C. S.; House, D. A. in "Transition Metal Chemistry"; Carlin, R. L., Ed.; Marcel Dekker: New York, 1970; Vol. 6, p 211.

(18) Garner, C. S.; House, D. A. *Ibid.*, p 177.

(19) Rogers, G. A.; Staples, P. J. *J. Chem. Soc.* **1965**, 6834.

Contribution from the Department of Chemistry,
Indiana-Purdue University at Fort Wayne,
Fort Wayne, Indiana 46805

The Trichlorocuprate(I) Ion in Aqueous Solution. Dependence of CTTS Absorption Band and Formation Constant on Temperature

C. R. Davis and K. L. Stevenson*[1]

Received October 20, 1981

In our studies of the photooxidation of chloro complexes of copper(I) in aqueous solution,[2-5] we concluded that the initial step in such a reaction is the absorption of a photon in a charge-transfer-to-solvent (CTTS) transition in the tri-

---

(1) To whom correspondence should be addressed.

(2) K. L. Stevenson and D. D. Davis, *Inorg. Nucl. Chem. Lett.*, **12**, 905 (1976).

(3) D. D. Davis, G. K. King, K. L. Stevenson, E. R. Birnbaum, and J. H. Hageman, *J. Solid State Chem.*, **22**, 63 (1977).

(4) D. D. Davis, K. L. Stevenson, and C. R. Davis, *J. Am. Chem. Soc.*, **100**, 5344 (1978).

(5) K. L. Stevenson, D. M. Kaehr, D. D. Davis, and C. R. Davis, *Inorg. Chem.*, **19**, 781 (1980).

0020-1669/82/1321-2514$01.25/0

Table I. Spectral Properties of $CuCl_3^{2-}$ at the CTTS Band

temp, °C	λ_{max}, nm	ϵ_{max}, M^{-1} cm^{-1}	β
10	273.6	4341	1.18
15	273.7	4237	1.16
20	274.1	4298	1.02
25	273.4	4183 (4)	0.985
30	274.8	4237	0.853
35	275.0	4162	0.833

chlorocuprate(I) species and the concomitant formation of a hydrated electron. We cited spectral evidence[4] for the CTTS transition that was very similar to that observed in other anionic species[6] with known CTTS behavior. We were able to resolve the spectra of the two stable complexes present in aqueous solutions of CuCl in Cl^- medium, namely, $CuCl_2^-$ and $CuCl_3^{2-}$, and to calculate the formation constant, β, for the reaction

$$CuCl_2^- + Cl^- \rightleftharpoons CuCl_3^{2-} \qquad (1)$$

at 25 °C.[4] We measured the net quantum yield for the reaction

$$CuCl_3^{2-} + H^+ \xrightarrow{h\nu} CuCl_3^- + {}^1/_2H_2(g) \qquad (2)$$

at a variety of ionic strengths, wavelengths, chloride ion concentrations, and temperatures.[4] The temperature studies indicated that the quantum yield decreases from about 0.8 at 280 K to a constant value of about 0.5 at temperatures greater than 310 K, from which we deduced an electron-scavenging mechanism consistent with Noyes[7,8] germinate-pair and JOS theory.[9,10] Our interpretation of the temperature dependence of quantum yield was predicated on the assumption that temperature had little or no effect on the equilibrium of eq 1, and hence the photochemically active species, $CuCl_3^{2-}$, was present at about the same concentration at all temperatures studied. However, it has seemed worthwhile since then to measure the formation constant at several other temperatures, with use of the same spectral deconvolution techniques originally employed. We now report the results of these measurements, yielding not only the fact that β is relatively constant over the temperature range studied but also the value of $\Delta H°$ for eq 1, as well as more evidence for the assignment of the 275-nm band in $CuCl_3^{2-}$ to a CTTS transition.

Experimental Section

Spectra were taken on thermostated 0.01 M solutions of CuCl in 1 M acid, 3 M ionic strength, and $0.25\ M \leq [Cl^-] \leq 1.7$ M, prepared as described previously,[4] in a 0.05-cm cell in the wavelength range 220–300 nm with a Beckman ACTA M-VI spectrophotometer at five temperatures from 10 to 35 °C. The solutions were prepared at 20 °C, and because we observed that the volume of 3 M $NaClO_4$ solutions changes less than 1% from this at the two temperature extremes, no concentration corrections were deemed necessary.

The spectral deconvolution procedure previously used[4] was refined somewhat in that four wavelengths in the vicinity of the absorption band from 270 to 280 nm rather than one were used to calculate the optimum value of β and the results averaged for each temperature.

Results and Discussion

The spectra of the two complexes are virtually identical with those reported earlier[4] with some very subtle changes with temperature. Table I summarizes the spectral properties of the CTTS band of $CuCl_3^{2-}$, the primary spectral feature at wavelengths longer than 250 nm.

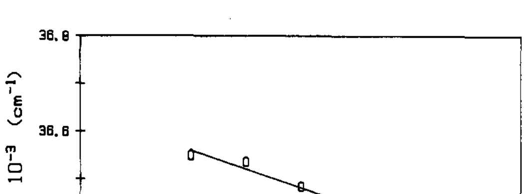

Figure 1. Plot of $\bar{\nu}$ of λ_{max} for $CuCl_3^{2-}$ vs. Celsius temperature.

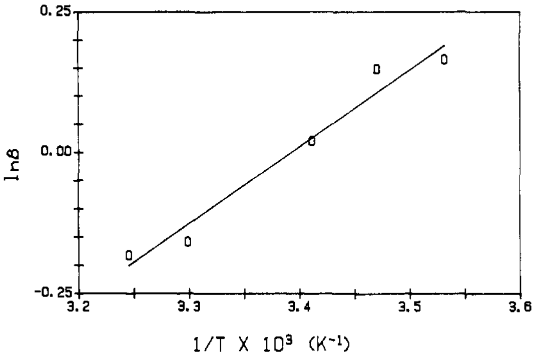

Figure 2. Plot of ln ($[CuCl_3^{2-}]/[CuCl_2^-][Cl^-]$) vs. $1/T$, for solutions with μ = 3 M.

The datum at 25 °C is a more precise recalculation for the spectra measured and reported[4] 2 years earlier than the rest of the spectra. It was decided that changes in the instrument parameters over the 2-year period were probably sufficient to justify excluding the 25 °C datum from comparisons requiring very high precision such as the ones that follow. Nevertheless, the values of λ_{max}, ϵ_{max}, and β at 25 °C are in general agreement with the values obtained at the other temperatures in Table I.

The temperature dependence of λ_{max} is illustrated in Figure 1 in which $\bar{\nu}$ (cm^{-1}) is plotted vs. Celsius temperature. The least-squares slope of -8.03 cm^{-1} deg^{-1} or -23.0 cal mol^{-1} deg^{-1} is consistent with the generally observed[6] negative value of $d\bar{\nu}/dT$ for CTTS transitions. This value compares to -35.7 cal mol^{-1} deg^{-1} for aqueous I^-[11] and -33.0 cal mol^{-1} deg^{-1} for aqueous Br^-,[12] two ions whose CTTS transitions have been extensively studied.[6]

Figure 2 is a plot of ln β vs. $1/T$, which yields $\Delta H° = 2660$ cal mol^{-1} for the association reaction (1). The only other known measurement of this quantity is by Sukhova et al.[13], who reported a value of -4600 cal mol^{-1} measured at only three temperatures at an ionic strength of about twice that used in these studies under the assumption that a large number of mono- and polynuclear complexes of the type $Cu_xCl_y^{x-y}$ exist in solution, an assumption that more recent evidence[4,14,15] tends to contradict for at least the conditions studied here.

These results confirm our assumption that the concentrations of $CuCl_3^{2-}$ do not change enough in the temperature range 10–35 °C to account for the large drop in quantum yield for reaction 2. Also, there is not enough of a shift in wavelength

---

[6] M. J. Blandamer and M. J. Fox, *Chem. Rev.*, **70**, 59 (1970).

[7] R. M. Noyes, *J. Am. Chem. Soc.*, **77**, 2042 (1955).

[8] R. M. Noyes, *J. Am. Chem. Soc.*, **78**, 5486 (1956).

[9] J. Jortner, M. Ottolenghi, and G. Stein, *J. Phys. Chem.*, **66**, 2029 (1962).

[10] J. Jortner, M. Ottolenghi, and G. Stein, *J. Phys. Chem.*, **68**, 247 (1964).

[11] S. D. Hamann and N. K. King, *Nature (London)*, **215**, 1263 (1967).

[12] M. J. Blandamer, T. R. Griffiths, L. Shields, and M. C. R. Symons, *Trans. Faraday Soc.*, **60**, 1524 (1964).

[13] T. G. Sukhova, O. N. Temkin, and R. M. Flid, *Russ. J. Inorg. Chem. (Engl. Transl.)*, **14**, 483 (1969).

[14] K. Sugasaka and A. Fujii, *Bull. Chem. Soc. Jpn.*, **49**, 82 (1976).

[15] S. Ahrland and B. Targeson, *Acta Chem. Scand., Ser. A*, **A31**, 615 (1977).

of either the $CuCl_2^-$ or $CuCl_3^{2-}$ species to change the fact that at the irradiating wavelength of 274 nm the only absorbing species is $CuCl_3^{2-}$, and thus our original observation of the drop in quantum yield with increasing temperature is still valid.

Acknowledgment. The authors gratefully acknowledge the financial support of the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Registry No. $CuCl_2^-$, 15697-16-2; $CuCl_3^{2-}$, 29931-61-1; Cl^-, 16887-00-6.

Contribution from the Department of Chemistry,
Cornell University, Ithaca, New York 14853

Disproportionation of Dimethoxyborane

Peter M. Jeffers* and S. H. Bauer

Received October 5, 1981

Recently we reported[1] on the partial reduction, in the gas phase, of trimethoxyborane by hydrogen, effected by flowing mixtures of the gases through a low-power microwave discharge. Here we describe tests conducted to confirm the occurrence of the disproportionation reaction

$$6HB(OCH_3)_2 \rightleftarrows B_2H_6 + 4B(OCH_3)_3 \qquad (1)$$

This route for the production of diborane was discovered by Burg and Schlesinger in 1933;[2] the gas-phase kinetics were studied by Uchida et al.[3] That it takes place in the liquid phase was reported by the latter authors in 1956.[4] From thermochemical data summarized by Dewar and McKee,[5] it follows that in the gas phase, for reaction 1, $\Delta H°_{300} \approx -22$ kcal/mol. We estimated $\Delta S°_{300} \approx -30$ eu. Hence K_{eq}^{300} (atm^{-1}) $\approx 3 \times 10^9$. The disproportionation would go almost to completion were it not rate limited.

Concurrently we extended our previous investigations to determine the magnitude of the experimental parameters for our small generator so as to optimize the yield of the dimethoxy compound and to minimize the loss of boron bearing species.

Brief Test on the Liquid Phase. A continuous-flow system with three parallel microwave discharge paths was constructed. The three streams were combined, and the flow was directed through a trap at −78 °C (to remove the methanol); the volatile products were condensed in a liquid-nitrogen (LN) trap. The accumulated material from a 2-h run was then brought up to −120 °C, degassed at that temperature, and then raised to −78 °C, from which it was distilled into a freshly cleaned Pyrex bulb (chromic acid, distilled water–acetone) at LN temperature. When the sample was warmed to 20 °C not all of the liquid had vaporized. The presence of some liquid proved essential. After 20 h of remaining at room temperature, B_2H_6 was demonstrated to be present, by both IR and mass spectral analysis. The conversion was incomplete; the material in the gas phase had the ratio $HB(OCH_3)_2/B(OCH_3)_3 > 1$. We consider this to be essentially a confirmation of the 1956 reports,[4] in contrast to our attempts to reproduce the gas-phase kinetics data published in 1959.

Disproportionation (?) in the Gas Phase. (i) All our attempts to establish reaction 1 in reactors which duplicated *as closely as possible* the experimental configuration described by Uchida[3] were negative. These are detailed below. The combined streams from the three microwave tubes entered a 20 cm long tube (2-cm diameter), packed either with glass wool or with 2–4-mm chuncks of graphite. The reactor was wrapped with heating tape for temperature control, and the catalysts were degassed. The outflow was directed into two traps fitted with cold fingers and sampling ports. No B_2H_6 could be detected in the traps or effluents for reactor temperatures 20–120 °C.

The $HB(OCH_3)_2$ from the microwave tubes was trapped at −120 °C after being passed through a −78 °C trap to remove most of the CH_3OH. Various portions of the dimethoxy compound were fed through the reactor, which had either glass wool or graphite chuncks, for periods from 5 min to 15 h at temperatures ranging from 20 to 95 °C; no B_2H_6 was generated. The products always were $B(OCH_3)_3$ and H_2, in addition to white deposits (B_2O_3?) which appeared in the traps and on the glass wool.

(ii) We tested the "uncatalyzed" reaction as follows. A 250-mL Pyrex flask was thoroughly cleaned with chromic acid, distilled water, and acetone, attached to a mercury manometer, and wound with a heating tape. The bulb was thoroughly evacuated under extended heating, filled with a mixture which consisted of 70% $HB(OCH_3)_2$ and 30% $B(OCH_3)_3$ to a total pressure of 14.5 torr, and allowed to remain at 20 °C for 23 h. No change in pressure was noted. To this flask was added an additional sample of approximately 40% $HB(OCH_3)_2$ to a total pressure of 136 torr and warmed to 60 °C for 20 h and then to 80 °C for an additional 20 h. No significant change in pressure was noted. Were equilibrium attained, we would have observed a pressure decrement of 9.3 torr. We concluded that in a *clean* vessel the rate for reaction 1 in the gas phase was so slow as to be insignificant at 80 °C.

(iii) Concurrently a portion of the 70% material was kept in an infrared cell (40-cm^3 volume) at a pressure of 12 torr. After 23 h at room temperature, the infrared spectrum showed that almost all the dimethoxy compound had decomposed. Only trimethoxyborane and hydrogen were present in the gas phase, as demonstrated by mass spectral analysis. We concluded that decomposition of the dimethoxyborane occurred heterogeneously on silica (and possibly NaCl) surfaces which had not been thoroughly cleaned. However, the reaction products did not produce B_2H_6.

Careful reading of the two papers in which reaction 1 was presumed to have occurred in the gas phase showed that no direct demonstration of the presence of diborane was made by either group of investigators. All the analytical conclusions were based on the magnitudes of the residual pressure of gas left after removal of the di- and trimethoxyboranes. Our experiments indicate that this gas was hydrogen, which may have resulted from the reaction of the dimethoxy compound with moisture adsorbed on the glass walls or possibly with OH from hydrated silica or with methyl alcohol which evaded the −78 °C trap. Uchida et al.[3] reported reaction 1 to be second order and heterogeneous, efficiently catalyzed by charcoal. They presented rate data for 40, 60, and 80 °C. Although our experiments were conducted at pressures $^1/_3$ and $^1/_{30}$ those of Uchida's, the sensitivity of the analysis for B_2H_6 should have yielded a detectable absorption band if in fact reaction 1 had occurred at the rates reported by these authors.

Optimized Conditions for Dimethoxyborane Production. In the three-stream microwave generator, the flows of hydrogen

---

*To whom correspondence should be addressed at the Department of Chemistry, SUNY—Cortland, Cortland, NY 13045.

(1) Jeffers, P. M.; Bauer, S. H. *Inorg. Chem.* **1981**, *20*, 1698.
(2) Burg, A. B.; Schlesinger, H. I. *J. Am. Chem. Soc.* **1933**, *55*, 4020.
(3) Uchida, H. S.; Kreider, H. B.; Murchison, A.; Masi, J. F. *J. Phys. Chem.* **1959**, *63*, 1414.
(4) (a) From the chemical abstracts only: Uchida, H. S.; Murchinson, A.; Kreider, H. B.; Masi, J. F. Technical Report CCC-1024-TR-153; Callery Chemical Co.: Callery, PA, 1955. (b) Murchinson, A.; Mulik, J. D.; Uchida, H. S.; Masi, J. F. Technical Report CCC-1024-TR-208; Callery Chemical Co.: Callery, PA, 1956.
(5) Dewar, M. J. S.; McKee, M. L. *J. Am. Chem. Soc.* **1977**, *99*, 5231.

0020-1669/82/1321-2516$01.25/0