oil mulls. The instrument was calibrated using polystyrene. Mass spectra were obtained using a Hitachi Perkin-Elmer RMU-6E mass spectrometer.

Reagents. The transition-metal oxides were commercially available and Linde commercial grade (98.0%) carbon monoxide was used.

Representative Reactions

Additional experiments are summarized in Table I. In all cases 1–2 mmol of metal oxide was used.

Reaction of Fe_2O_3. Commercial Fe_2O_3 (160 mg, 1.00 mmol) was placed into a borosilicate glass tube (5 mm × 100 mm) which was then packed with borosilicate glass wool. The liner was then inserted into the microreactor which was sealed, pressured to 2000 atm with carbon monoxide, and heated at 300 °C for 24 h. At the end of the reaction period, the bomb was cooled to room temperature, attached to a vacuum line, and carefully opened into a series of two traps cooled to −196 °C. The material which stopped in these traps was combined into one trap and then passed through a trap cooled to −96 °C (toluene slush) into a trap cooled to −196 °C. The −196 °C trap contained carbon dioxide and the −96 °C trap contained $Fe(CO)_5$ (376 mg, 1.92 mmol).

Reaction of MoO_3. Commercial MoO_3 (158 mg, 1.10 mmol) was placed into a glass tube (5 mm × 10 mm) which was then packed with borosilicate glass wool. The liner was then inserted into the microreactor which was sealed, pressured to 2000 atm, and heated at 300 °C for 24 h. At the end of the reaction period, the reactor was cooled to room temperature and then vented into a fume hood. The molybdenum hexacarbonyl (261 mg, 0.989 mmol) was recovered by removing the glass liner, crushing it, and then subliming the product at 40 °C (0.01 Torr).

Additional Reactions. The above procedure was used to prepare $W(CO)_6$ and $Co_2(CO)_8$ except the latter substance was handled in an argon-filled glovebag.

Acknowledgment. The authors are indebted to the National Science Foundation, Grant GP-19873 (The University of Oklahoma), and the Robert A. Welch Foundation, Grants 483 and 505 (Abilene Christian University).

Registry No. $Mo(CO)_6$, 13939-06-5; $W(CO)_6$, 14040-11-0; $Co_2(CO)_8$, 10210-68-1; $Fe(CO)_5$, 13463-40-6; CO, 630-08-0; Fe_2O_3, 1309-37-1; MoO_3, 1313-27-5; WO_3, 1314-35-8; CoO, 1307-96-6.

References and Notes

(1) Part 10: A. P. Hagen and B. W. Callaway, *Inorg. Chem.*, **17**, 554 (1978).
(2) (a) The University of Oklahoma. (b) Abilene Christian University.
(3) F. Calderazzo and F. L'Eplattenier, *Inorg. Chem.*, **6**, 1220 (1967).
(4) J. C. Hileman, D. K. Huggins, and H. D. Kaesz, *J. Am. Chem. Soc.*, **83**, 2953 (1961).
(5) W. Hieber and H. Fuchs, *Z. Anorg. Allg. Chem.*, **248**, 256 (1941).
(6) R. Whyman, *Chem. Commun.*, 1194 (1970); W. Hieber and H. Lagally, *Z. Anorg. Allg. Chem.*, **251**, 96 (1943).
(7) C. B. Cooper III, S. Onaka, D. F. Shriver, L. Daniels, R. L. Hance, B. Hutchinson, and R. Shipley, *Inorg. Chim. Acta*, **24**, L92 (1977).
(8) M. Naumann, German Patent 531 402 (Jan 21, 1930); *Chem. Abstr.*, **25**, 5523 (1931).
(9) M. Naumann, German Patent 547 025 (Jan 13, 1931); *Chem. Abstr.*, **26**, 3632 (1932).
(10) L. Mond, H. Hirtz, and M. D. Cowap, *J. Chem. Soc.*, 798 (1910).
(11) L. Mond, H. Hirtz, and M. D. Cowap, *Z. Anorg. Chem.*, **68**, 207 (1910).
(12) A. P. Hagen and H. W. Beck, *Inorg. Chem.*, **15**, 1512 (1976).
(13) A. P. Hagen, L. L. McAmis, and M. A. Stewart, *J. Organomet. Chem.*, **66**, 127 (1974).

Contribution from the Radiation Laboratory,
University of Notre Dame, Notre Dame, Indiana 46556

Photochemical Primary Processes in Copper(I) Complexes. A Probe for Charge Transfer to Solvent and Charge Transfer to Ligand Excited States

G. Ferraudi

Received September 30, 1977

Photochemical studies of Cu(I) complexes have shown that the reducing tendencies of these systems are enhanced when irradiated with ultraviolet or visible light. A photoinduced reduction of Co(III) complexes by bis(2,9-dimethyl-1,10-phenanthroline)copper(I), $Cu(dmp)_2{}^+$, was reported by McMillin et al.[1] The reduction of Co(III) complexes associated with Cu(I) has been examined by Hurst and co-workers by irradiations of the ligand field bands of the cobalt fragment. They attributed this reaction to an intramolecular electron-transfer process from Cu(I) to Co(III).[2] Also Stevenson and Davis[3] found that evolution of hydrogen and oxidation to cupric ions, as indicated in eq 1, takes place by irradiation of acidic

$$CuX_3{}^{2-} \xrightarrow[+H^+]{h\nu} CuX_3{}^- + {}^1/_2H_2 \qquad (1)$$

$$X^- = Cl^- \text{ or } Br^-$$

solutions of copper(I) halides. Although the role of the intermediates might be very important for any explanation of the photochemical properties of these systems, no efforts have been made to establish their nature. Evidence is provided here for the formation of solvated electrons in the primary process of cuprous halides[4] with subsequent generation of a transient hydride complex. By contrast, the main features of the primary process of $Cu(dmp)_2{}^+$[5] are correlated with radical formation.

Experimental Section

Continuous way irradiations were performed using a 4000 Rayonet photochemical reactor or a 300-W Eimac lamp coupled with a high-intensity Bausch and Lomb monochromator. Ferrioxalate was used as a primary actinometric reference.[6] The light intensity was checked frequently with $Co(NH_3)_5Cl^{2+}$ or $Co(NH_3)_5Br^{2+}$.

Conventional flash photolysis experiments were carried out in an apparatus built in this laboratory. The experimental setup will be described elsewhere.[8] Two flash lamps, FP-8-100 C purchased from Xenon Corp., were fired at energies between 40 and 400 J/flash producing pulses of light with a length of ~30 μs. Tests of the sensitivity, time resolution, and linear responses with flash energy were carried out with $Co(NH_3)_5Br^{2+}$ by already reported procedures.[9]

The preparation of the solutions for photolysis was accomplished as follows. Solid samples of the copper(I) compounds were dissolved in previously deaerated solutions containing the substrates required for the experiment. Solvents were deoxygenated with streams of nitrogen or nitrous oxide in a gastight apparatus. The ionic strength of the reaction medium was adjusted to 1.0 M with $HClO_4$, NaCl, and HCl as indicated elsewhere in the text.

Concentrations of cuprous chloride transformed into cupric species were estimated from spectral changes measured at 280 nm in a cell with 1 mm of optical path. Cu(II) was determined with I^-. Samples of irradiated solutions (1 cm^3) were mixed with 5 cm^3 of 0.2 M I^- and the final volume was adjusted to 10 cm^3 with distilled water. The optical density of $I_3{}^-$ was measured at 400 nm against blanks. Calibration curves were obtained for various concentrations of Cu(II) ($[Cu(II)] \leq 10^{-4}$ M) in the presence of Cu(I) ($[Cu(I)] \leq 10^{-2}$ M).

Yields of H_2 and N_2 are determined by gas chromatography. Hydrogen was also measured by mass spectroscopy. The solutions of cuprous complexes used in these experiments were degassed by three freeze–thaw cycles and saturated with He or N_2O at 1 atm. Gas products, noncondensables at −180 °C, were removed under vacuum from the reaction mixture.

Cuprous chloride, Baker Analyzed, was recrystallized three times from deaerated hydrochloric acid. Solid batches of the compound were manipulated under a nitrogen atmosphere and dried under vacuum. Cuprous bromide, also Baker Analyzed, was purified by a similar method. $[Cu(dmp)_2]ClO_4$ was synthesized and purified by reported procedures.[5] Other chemicals were reagent grade and used without further purification.

Results and Discussion

Photolyses at 280 nm of acid solutions ($[NaCl] + [HCl] = 1.0$ M; $1.0 \geq [HCl] \geq 0.1$ M) containing cuprous chloride ($C \leq 0.01$ M) produced hydrogen and cupric ions ($2\phi_{H_2} = \phi_{Cu^{2+}} = 0.33 \pm 0.04$) in agreement with the stoichiometry reported by Stevenson et al. (eq 1). However, *nitrogen was also found* as a reaction product in solutions saturated with N_2O. The yield of nitrogen increased with decreasing con-

0020-1669/78/1317-1370$01.00/0

Table I. Product Yields for 280-nm Photolyses of $CuCl_3^{2-}$

ϕ^a		
N_2	H_2	Medium conditions^b
0.065 ± 0.004	0.28 ± 0.03	0.1 M HCl, 1 M NaCl
0.16 ± 0.03	0.14 ± 0.02	0.02 M HCl, 1 M NaCl

[a] Average values from three to five determinations. $I_0 = (8.3 \pm 0.3) \times 10^{-4}$ einstein/(L min). [b] Solutions saturated with N_2O at 1 atm.

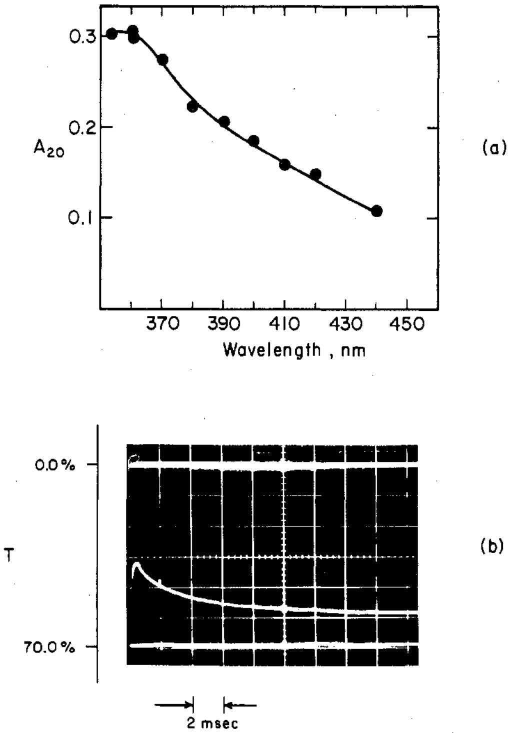

Figure 1. Transient absorbance (A_{20}) observed in flash irradiations of $CuCl_3^{2-}$. (a) Spectrum of the short-lived species obtained 500 μs after the light pulse. $[CuCl_3^{2-}] = 10^{-3}$ M; [HCl] = 1.0M; energy/pulse = 360 J. Optical path is 20 cm. (b) Oscillographic trace of the decay of the transient absorptions followed at 370 nm under conditions stated above.

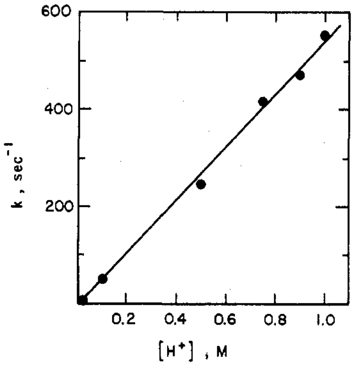

Figure 2. Dependence of the rate constant for decay of the copper hydride transient with acid concentration ($[Cl^-] = 1.0$ M; [HCl] + [NaCl] = 1.0 M; $[CuCl_3^{2-}] = 10^{-3}$ M; energy/pulse = 360 J).

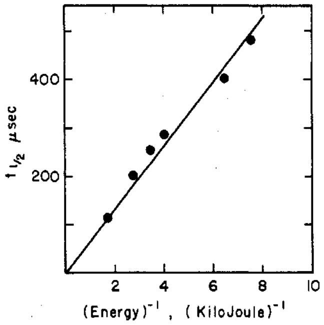

Figure 3. Second-order kinetics of the decay of the radical anion in flash photolyses of $Cu(dmp)_2^+$ ($C = 3 \times 10^{-5}$ M) in acidic ($[CH_3COOH] = 10^{-5}$ M) solutions. Energy/flash = 300 J.

centrations of hydrogen ion (Table I) for 280-nm photolyses of cuprous chloride solutions ([HCl] + [NaCl] = 1.0 M; $[CuCl_3^{2-}] = 2 \times 10^{-2}$ M). Since *hydrogen ions and nitrous oxide* are well-known *scavengers* of the *solvated electron*,[10–12] variations in the composition of the gas mixture with hydrogen ion concentration are expected as a consequence of their competitive reactions.[13]

Some of the reactions that follow the primary process, as indicated in eq 2, are slow enough to be observed by flash photolysis. Transient absorptions with $\lambda_{max} \simeq 360$ nm (Figure 1) were detected in irradiations ($\lambda_{excit} \geq 260$ nm) of $CuCl_3^{2-}$ ($C < 10^{-3}$ M) in acidic solutions ($[HCl] \leq 1.0$ M). Two successive steps (Figure 1b) are apparent in the decay of these absorptions. The shorter lived stage of the reaction obeys a second-order kinetics with a first-order dependence on the concentration of transient and on the concentration of hydrogen ion ([HCl] + [NaCl] = 1.0 M; see Figure 2). Experiments carried out in solutions containing various chloride concentrations ($[HClO_4] + [HCl] = 1.0$ M; $1.0 \geq [Cl^-] \geq 0.5$ M) did not give different values for the rate constant ($k = (5.5 \pm 0.7) \times 10^2\ M^{-1}\ s^{-1}$). The presence of 10^{-2}–10^{-3} M allyl alcohol in the reaction medium produced a faster decay ($k \simeq 3 \times 10^3\ M^{-1}\ s^{-1}$). The generation of solvated electrons as a primary product (see above) suggests that reactions of hydrogen atoms with $CuCl_3^{2-}$ led to the formation of the short-lived transient (reaction 5). The reactivity of this species with hydrogen ions and allyl alcohol provides a good characterization of a metastable hydride complex.[14–16] Similar hydrides of Cu(I) have been postulated as intermediates in redox processes, namely, in the autocatalytic reduction of $Cu^{2+}(aq)$ to $Cu^+(aq)$ by molecular hydrogen.[14] The sequence of reactions 2–6 might be a feasible pathway for the photochemical generation of hydrogen.[18]

$$CuCl_3^{2-} \overset{h\nu}{\rightleftarrows} \{CTTS\} \rightarrow CuCl_3^- + e_{aq}^- \qquad (2)$$

$$e_{aq}^- + H^+ \rightarrow H\cdot \qquad (3)$$

$$H\cdot + H\cdot \rightarrow H_2 \qquad (4)$$

$$H\cdot + CuCl_3^{2-} \rightarrow HCuCl_3^{2-} \qquad (5)$$

$$H^+ + HCuCl_3^{2-} \rightarrow H_2 + CuCl_3^- \qquad (6)$$

The longer lived stage in the observed transient decay also obeyed a second-order kinetics ($k = 0.17 \pm 0.03\ M^{-1}\ s^{-1}$) with zero-order dependence ([HCl] + [NaCl] = 1.0 M; $1.0 \leq [HCl] \leq 0.1$ M) on hydrogen ion concentration and first-order dependence on both transient species and chloride ion concentration ($[HClO_4] + [HCl] = 1.0$ M; $1.0 \geq [HCl] \geq 0.1$ M). This behavior suggests the formation and destruction of polymeric Cu(I)–Cu(II) chloride complexes. Some of the species described in the literature[19] suggest that equilibria like (7)–(9) might be involved in the last stage of the reaction.

$$CuCl_2 + Cl^- \rightleftharpoons CuCl_3^- \qquad (7)$$

$$CuCl_3^- + Cl^- \rightleftharpoons CuCl_4^{2-} \qquad (8)$$

$$CuCl_3^- + CuCl_3^{2-} \rightleftharpoons Cu_2Cl_6^{3-} \qquad (9)$$

The photochemical behavior of cuprous bromide ($CuBr_X^{1-X}$; $X = 2$–4) has most of the features indicated above for cuprous chloride. By contrast, continuous irradiations of acidic solutions ($10^{-7} \leq [H^+] \leq 10^{-5}$ M) of 10^{-3} M $Cu(dmp)_2^+$ saturated with N_2O ($C \simeq 2.5 \times 10^{-2}$ M) at 280 or 500 nm *failed to produce nitrogen and/or hydrogen.* These results *show that* *solvated electrons are formed with a very small yield* ($\phi < 10^{-4}$), if any at all, by this complex. Moreover, transient absorptions (500–600 nm) were observed in flash photolyses of deaerated solutions ($10^{-7} \leq [H^+] \leq 10^{-5}$ M; $[Cu(dmp)_2{}^+] \leq 3 \times 10^{-5}$ M) for excitations at $\lambda > 400$ nm. A second-order dependence in transient concentration (see Figure 3) was obtained for the decay, with a rate constant to extinction coefficient ratio of $k/\epsilon = 8.1 \times 10^5$ cm s^{-1} at 550 nm. Saturation of the solutions with N_2O had no effect on k/ϵ or on the yield of the species produced per flash. Since absorptions of the ligand radical anion (see reaction 12) are placed somewhere in this region,[20] one may assume that the observed species is generated in steps following the primary process as indicated in reactions 10–17. In this sequence the

$$Cu(dmp)_2{}^+ \xrightarrow{h\nu} CTTL \tag{10}$$

$$CTTL \rightsquigarrow Cu(cmp)_2{}^+ \tag{11}$$

$$CTTL \xrightarrow[-OH^-]{+OH_2} Cu(dmp)(dmpH\cdot)^{2+} \tag{12}$$

$$Cu(dmp)(dmpH\cdot)^{2+} \rightleftharpoons Cu(dmp)(dmp^-\cdot)^+ + H^+ \tag{13}$$

$$Cu(dmp)(dmp^-\cdot)^+ \rightarrow Cu(dmp)_2{}^+ \tag{14}$$

$$Cu(dmp)(dmpH\cdot)^{2+} \rightarrow Cu(dmp)^{2+} + dmpH\cdot \tag{15}$$

$$Cu(dmp)^{2+} + dmpH\cdot \rightarrow Cu(dmp)^+ + dmp + H^+ \tag{16}$$

$$dmpH\cdot + dmpH\cdot \rightarrow products \tag{17}$$

steps (10)–(15) are expected to be fast, following the excitation pulse, while (16) and (17) should be the observed reactions in flash photolyses experiments.

The distinct photochemical tendencies of the Cu(I) complexes indicated above show that reactive excited states with a different nature are populated in each case. The *absence of emission at room temperature* seems to be a good indication of the short life of the low-lying excited states. In such a case the direct oxidation–reduction reactions between these states and added substrates seem to be unlikely.[1] However, acid–base reactions of the excited state with solvent molecules (eq 12) are, probably, rapid enough for competition with nonradiative relaxation (eq 11).

The lowest energy absorption band (λ_{max} 450 nm, ϵ_{max} 7×10^3 M^{-1} cm^{-1}) of the $Cu(dmp)_2{}^+$ spectra was previously attributed to a charge transfer to ligand transition (CTTL).[21] Such assignment indicates that a CTTL state might be responsible for the photochemical behavior exhibited by $Cu(dmp)_2{}^+$. By contrast, the dissociation into solvated electrons in the primary process of cuprous halides might be used as an indication of a photoreactive charge transfer to solvent state (CTTS). The possibility of such transitions placed at 350–200 nm in the spectra of cuprous halides seems feasible from photochemical and spectroscopic models.[22] Moreover, the emission observed in glassy solutions (140 K) of cuprous halides[23] suggests that intramolecular excited states might be in the vicinity of the CTTS state. Although ligand to metal charge-transfer excited states are expected to be present, no photochemical evidence for their photoreactivity was obtained with these species.

Acknowledgment. The research described herein was supported by the Office of Basic Energy Sciences of the Department of Energy. This is Document No. NDRL-1785 from the Notre Dame Radiation Laboratory.

Registry No. $CuCl_3{}^{2-}$, 29931-61-1; $Cu(dmp)_2{}^+$, 21710-12-3.

References and Notes

(1) D. McMillin, M. T. Buckner, and B. T. Ahn, *Inorg. Chem.*, **16**, 943 (1977).

(2) J. K. Hurst and R. H. Land, *J. Am. Chem. Soc.*, **95**, 1703 (1973); J. K. Farr, L. G. Hulett, R. Lane, and J. Hurst, *ibid.*, **97**, 2654 (1975).

(3) K. L. Stevenson and D. D. Davis, Abstracts, 172nd National Meeting of the American Chemical Society, San Francisco, Calif., Aug 1976, No. INOR 15.

(4) The species formed by interaction of copper(I) with chloride ions have been recently studied by K. Sugasaka and A. Fujii, *Bull. Chem. Soc. Jpn.*, **49**, 82 (1976). According to these authors the absorption band at 275 nm corresponds only to $CuCl_3{}^{2-}$. Such species should be regarded as the main substrate under the experimental conditions of this work.

(5) For $Cu(dmp)_2{}^+$ synthesis see J. R. Hall, N. I. Marchant, and R. A. Plowman, *Aust. J. Chem.*, **15**, 480 (1962). For properties of $Cu(dmp)_2{}^+$ and $Cu(dmp)^+$ see S. Sundarajan and E. L. Wehry, *J. Phys. Chem.*, **76**, 1528 (1972).

(6) C. A. Parker and G. E. Hatchard, *Proc. R. Soc. London, Ser. A*, **235**, 518 (1956).

(7) J. F. Endicott, G. J. Ferraudi, and J. R. Barber, *J. Phys. Chem.*, **79**, 630 (1975).

(8) E. V. Srisankar and G. Ferraudi, work in progress.

(9) For descriptions of flash photlysis techniques see G. Ferraudi and J. F. Endicott, *Inorg. Chem.*, **12**, 2389 (1973).

(10) L. M. Dorfman and I. A. Taub, *J. Am. Chem. Soc.*, **85**, 2370 (1963).

(11) S. Gordon, E. J. Hart, M. S. Matheson, J. Rabani, and J. K. Thomas, *Discuss. Faraday Soc.*, **36**, 214 (1963).

(12) J. A. Dilts and D. F. Shriver, *J. Am. Chem. Soc.*, **90**, 5769 (1968); **91**, 4088 (1969).

(13) Since $k_3 \sim 2.3 \times 10^{10}$ M^{-1} s^{-1}, $k_{N_2O} \sim 8.7 \times 10^9$ M^{-1} s^{-1}, and $[N_2O] \sim 2.5 \times 10^{-2}$ M for 1 atm, a ratio $\phi_{H_2}/\phi_{N_2} \simeq 46[H^+]$ is expected under a steady-state approximation.

(14) G. M. Whitesides, J. San Filippo, Jr., E. R. Stredonski, and Ch. P. Cassey, *J. Am. Chem. Soc.*, **91**, 6542 (1969).

(15) G. M. Whitesides and J. San Filippo, Jr., *J. Am. Chem. Soc.*, **92**, 6611 (1970).

(16) R. K. Boeckman, Jr., and R. Michalak, *J. Am. Chem. Soc.*, **96**, 1623 (1974).

(17) E. A. von Hahn and E. Peters, *J. Phys. Chem.*, **69**, 547 (1965).

(18) A limit of $k_5(H^{\cdot} + Cu(I)) \geq 10^8$ M^{-1} s^{-1} is required for a good competition between steps (4) and (5) in the experimental conditions of this work.

(19) R. D. Willet and R. E. Rundle, *J. Chem. Phys.*, **48**, 838 (1964); R. D. Willet, *ibid.*, **41**, 2243 (1964); B. Morosin and E. C. Lingafelter, *Acta Crystallogr.*, **13**, 807 (1960); M. Kato, H. Jonassen, and J. Fanning, *Chem. Rev.*, **64**, 99 (1964).

(20) Formation of a transient species with those features already described was observed by reaction of $e_{aq}{}^-$ and dmp: G. Ferraudi, unpublished observations.

(21) P. Day and N. Sanders, *J. Chem. Soc. A*, 1530 (1967).

(22) M. F. Fox, "Concepts of Inorganic Photochemistry", A. W. Adamson and P. D. Fleishauer, Ed., Wiley, New York, N.Y., 1975.

(23) Emission at ~20000 cm^{-1} was observed (ref 24) in ultraviolet excitations of glassy solutions of cuprous halides. This emission was attributed to a $3d^94p \rightarrow 3d^{10}$ transition.

(24) M. V. Belyi and P. Krivenko, *Chem. Abstr.*, **63**, 6945*g* (1965); N. E. Luschik and S. G. Zazubovich, *ibid.*, **16**, 12423*g* (1962).

Contribution from the Department of Chemistry,
Arizona State University, Tempe, Arizona 85281

Kinetics of the Hexachloroiridate(III) Reduction of Iodate Ion

James P. Birk

Received October 6, 1977

As part of a study of the reactions of transition-metal complexes with oxyhalogen species, we have reported the reduction of $BrO_3{}^-$ by $IrCl_6{}^{3-}$.[1] The kinetics were quite straightforward, with the principal term in the rate law being of the form $k[BrO_3{}^-][IrCl_6{}^{3-}][H^+]^2$. This rate law is in accord with the behavior expected for reactions of oxyanions.[2] The $IrCl_6{}^{3-}$ reduction of $ClO_3{}^-$ has also been studied.[3] This reaction is first order in both $[IrCl_6{}^{3-}]$ and $[ClO_3{}^-]$ and exhibits a complex $[H^+]$ dependence, which appears minimally to require parallel reaction paths zero, first, and second order in $[H^+]$. We report here on the $IrCl_6{}^{3-}$ reduction of the third halate, iodate.

Experimental Section

The preparation of all reagents, procedures for measuring reaction rates, and data handling procedures have been described previously.[1,4] Ionic strength was maintained at 0.500 M by addition of $LiClO_4$, and pseudo-first-order conditions were maintained throughout. First-order plots were linear for >90% reaction.