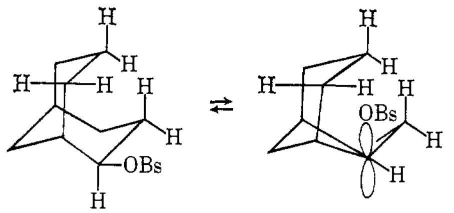
The largest fraction of the driving force ($k_{rel} = 79$) for the reaction of the *exo*-2-brosylate must arise from the relief of eclipsing strain between C_3 and C_7. As the C_3–O bond begins to stretch, C_1, C_3, and the carbinyl hydrogen on C_2 will tend toward coplanarity. This will be accompanied by a movement of C_3 away from C_7 and will reduce the magnitude of the nonbonded interaction between C_3 and C_7 in the transition state relative to the ground state. The product of solvolysis is primarily (>90%) bicyclo[3.3.1]nonene.

The behavior of the *endo*-2-brosylate is interesting since it is of the same order of reactivity as cyclohexyl brosylate. If a model of this compound is constructed,



it will be seen that, as ionization occurs and the C_3 methylene group moves away from the C_7 methylene group, the departing brosylate anion is forced into close proximity to the C_7 position.[16] As a result, any driving force which accrues from the relief of transannular interactions in the starting brosylate is negated by the establishment of an equally serious nonbonded interaction in the transition state. From a comparison of the relative rates of the *exo*-2- and *endo*-2-brosylates, it appears that steric hindrance to ionization brings about a rate decrease of 75-fold.[17]

Acknowledgment. This investigation was initiated with funds from the Petroleum Research Fund (Grant PRF-789), and the authors wish to express their gratitude for the generous support received.

[16] This concept was first suggested for the solvolysis of *endo*-norbornyl derivatives by H. C. Brown. A detailed discussion of this proposal can be found in the paper by H. C. Brown, I. Rothberg, P. von R. Schleyer, M. M. Donaldson, and J. J. Harper, *Proc. Natl. Acad. Sci U. S.*, **56**, 1653 (1966).

[17] For a detailed study of the solvolysis of the *endo*-2-tosylate, see M. Hanack, W. Kraus, W. Rothenwohrer, W. Kaiser, and G. Wentrup, *Ann.*, 703, 44 (1967).

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Received August 14, 1967

Kinetics and Mechanisms of Electron-Transfer Reactions Involving Copper(I) in Perchlorate Solution[1]

Sir:

It is a well-known and often-quoted fact that copper(I) ion is unstable with respect to disproportionation (eq 1)

$$2Cu^+ = Cu^{2+} + Cu(s) \qquad (1)$$

in solutions lacking complexing anions. The equilibrium quotient for reaction 1 is $2 \times 10^6\ M^{-1}$ at 25–35° at ionic strength 1.13 *M* in the presence of perchlorate anions.[2] We have found that appropriate one-electron reductions can be used to generate quantitative yields of Cu^+ in perchlorate solution. Such metastable solutions can, moreover, be used for some time without appreciable disproportionation. Solutions are sensitive to oxygen, however, and all reactions have been studied under nitrogen which had been carefully purified of traces of oxygen. Spectrophotometric measurements, either conventional[3] or stopped-flow,[4] form the basis for all the rate studies reported here.

The reactions of copper(II) with an insufficient amount of the one-equivalent reducing agents Cr(II), V(II), and Eu(II) have been examined. The first of these (eq 2) provides a particularly useful synthetic technique, since the equilibrium lies well toward Cu^+, and since

$$Cr^{2+} + Cu^{2+} = Cr^{3+} + Cu^+ \qquad (2)$$

the other product, $Cr(H_2O)_6{}^{3+}$, is unreactive toward substances whose reactions with copper(I) we have studied. The rate equation is first order with respect to each metal ion concentration; the predominant reaction term has an inverse dependence upon $[H^+]$, but an additional term independent of $[H^+]$ was noted (eq 3). At 25.0° and $C_{ClO_4^-} = 1.00\ M$, $a = 0.22$

$$d[Cu^+]/dt = (a + b/[H^+])[Cr^{2+}][Cu^{2+}] \qquad (3)$$

$M^{-1}\ sec^{-1}$ and $b = 0.56\ sec^{-1}$. The product was verified to be Cu^+ under the conditions of these experiments by two independent methods. The decrease in light absorption of Cu^{2+} at 7500 A ($\epsilon \sim 11\ M^{-1}\ cm^{-1}$) corresponded quite closely to the stoichiometry given in eq 2, rather than to a 1:2 ratio of Cu^{2+}/Cr^{2+} which would be the case were supersaturated metallic copper being generated. Moreover, a number of the rate runs were carried out under conditions where the excess of Cu(II) was slight, so that pseudo-first-order kinetics was not followed. In such cases, appropriate second-order plots were nicely linear and gave the same apparent rate constant at a particular $[H^+]$ as did runs in which pseudo-first-order conditions held. On the other hand, the same experiments when calculated assuming the stoichiometry was such that $0.5Cu^0$, and not Cu^+, was formed gave nonlinear plots. Copper metal was, of course, formed in any experiment where $[Cr^{2+}]_0 > [Cu^{2+}]_0$, and also in runs where $[Cr^{2+}]$ was only slightly less than $[Cu^{2+}]$. The latter observation is consistent with a second step, $Cu^+ + Cr^{2+} = Cu^0 + Cr^{3+}$, that became important under conditions where excess Cu^{2+} was so low that adequate time remained for Cu^+ to react with Cr^{2+} to an appreciable extent. Formation of copper metal in experiments with a bare excess of Cu(II) could be prevented by slow addition of Cr(II) with continuous stirring during the addition.

Reaction of V^{2+} and Cu^{2+} in perchlorate solutions likewise produced Cu^+ although the second-order rate constant was independent of $[H^+]$. Over the range $0.04 < [H^+] < 1.0\ M$, $k_V = 28\ M^{-1}\ sec^{-1}$ at 25.0°. Absence of a term varying as $[H^+]^{-1}$ and the large value of k_V compared to *a* are particularly noteworthy. The former is very likely an indication of an outer-sphere mechanism.[5] The high value of k_V relative to

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[1] Work performed in the Ames Laboratory under the auspices of the U. S. Atomic Energy Commission. Contribution No. 2162.

[2] (a) W. M. Latimer, "Oxidation Potentials," 2d ed, Prentice-Hall Inc., New York, N. Y., 1952, p 185; (b) R. W. Miller, Thesis, University of Illinois, 1961; *Dissertation Abstr.*, 22, 3365 (1962), as cited by L. G. Sillén, "Stability Constants of Metal-Ion Complexes," Section I, Special Publication No. 17, The Chemical Society, London, 1964, p 17.

[3] J. H. Espenson, *J. Am. Chem. Soc.*, **86**, 5101 (1964).

[4] D. W. Carlyle and J. H. Espenson, *Inorg. Chem.*, **6**, 1370 (1967).

[5] B. R. Baker, M. Orhanovic, and N. Sutin, *J. Am. Chem. Soc.*, **89**, 722 (1967), have discussed the role of $[H^+]$ in other reductions of $V(H_2O)_6{}^{2+}$.

a is all the more remarkable in that Cr^{2+} is a much stronger reducing agent than V^{2+}. The inversion of reactivity can be regarded as a point in favor of a substantially different reaction mechanism for each.

An additional point of evidence concerning mechanism is to be found in the observation that in the presence of chloride ion, where the stable complex $CuCl_2^-$ is formed, appreciable concentrations of $(H_2O)_5CrCl^{2+}$ are formed. Whether the chloro complex forms as a consequence of an inner-sphere reaction of $CuCl^+$ with Cr^{2+}, or by reaction of Cu^{2+} and $CrCl^+$, of unspecified mechanism, cannot be stated at the present time.

Europium(II) is not a particularly suitable reducing agent for preparation of Cu^+ since the second-stage reduction is sufficiently fast that some metal is invariably produced. On the basis of initial rates, we estimate the second-order rate constant for the reaction of Eu^{2+} and Cu^{2+} is $\sim 3\ M^{-1}\ sec^{-1}$.

We have studied the reactions of Cu^+ with a variety of oxidizing agents in perchlorate solutions. Among the oxidizing agents of particular interest are VO^{2+}, Hg^{2+}, Fe^{3+} and its complexes, Co(III) complexes, and $HCrO_4^-$. These reactions range from several that were so fast that even at the lowest concentrations no reaction could be detected ($HCrO_4^-$, $Fe(phen)_3^{3+}$), to others that, in the time needed for disproportionation of Cu^+ to set in, had reacted inappreciably ($Co(NH_3)_6^{3+}$), or to only a small extent ($Co(NH_3)_5OH_2^{3+}$).

The reaction of Cu^+ with VO^{2+} (eq 4) is of especial

$$Cu^+ + VO^{2+} + 2H^+ = Cu^{2+} + V^{3+} + H_2O \qquad (4)$$

importance, for Higginson and Sykes[6] studied the catalytic effect of Cu(II) upon the V(III)–Fe(III) reaction in perchlorate solution. They identified the reverse of reaction 4 as the process responsible for catalysis. The predominant term has the form $-d[V^{3+}]/dt = h[Cu^{2+}][V^{3+}][H^+]^{-1}$, with $h \sim 0.3\ sec^{-1}$ at $\mu = 3.0\ M$ and 25.0°. The rate of reaction 4 obeyed the relation in eq 5, with $e = 3.9 \times 10^2\ M^{-2}\ sec^{-1}$

$$d[V^{3+}]/dt = e[Cu^+][VO^{2+}][H^+] \qquad (5)$$

at 25.0° and $\mu = 3.0\ M$. Assuming these are the reverse of one another, we compute that the equilibrium quotient for reaction 4, e/h, is $1.3 \times 10^3\ M^{-2}$, compared to the calculated $(1–2) \times 10^3\ M^{-2}$, based on known standard potentials.

A second and less important term of the form $g[Cu^{2+}] \cdot [V^{3+}]$ was also claimed,[6] but we question whether this is a genuine rate term. The treatment of the catalysis rate data[6] involved an appreciable correction for the uncatalyzed reaction. Certain discrepancies in this contribution were noted;[6] in view of the lack of a corresponding rate term in the forward rate of reaction 4,[7] we are inclined to regard it as a result of the computational procedures employed. Alternatively, catalysis may proceed by a pathway $g[Cu^{2+}][V^{3+}]$ that is *not* the reverse of reaction 4.

A second reaction of Cu^+ to be considered, also invoked in the same Cu(II) catalysis problem, is that with Fe(III). The interpretation offered[6] is the Cu^+ produced in the reverse of reaction 4 is consumed quite rapidly by iron(III). We have carried out a few rate experiments on this reaction (eq 6) and find a second-

$$Fe^{3+} + Cu^+ = Fe^{2+} + Cu^{2+} \qquad (6)$$

order rate constant of $1.2 \times 10^5\ M^{-1}\ sec^{-1}$ at 25 ± 2° (1 *F* perchloric acid).

We are at present carrying out a number of other studies on the generation of Cu^+ in perchlorate solution and in the presence of some anions, and on its reactions with a variety of oxidizing substrates.

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Received August 21, 1967

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(6) W. C. E. Higginson and A. G. Sykes, *J. Chem. Soc.*, 2841 (1962).

(7) The rate constant in the expression $f[Cu^+][VO^{2+}][H^+]^2$ can be estimated: $f = egh^{-1} = 85\ M^{-3}\ sec^{-1}$. Thus an estimated 40% of the reaction should proceed along this path at $[H^+] = 3.0\ M$. Our data indicate an undetectably small contribution of this path, and we set an upper limit $f \leq 8\ M^{-3}\ sec^{-1}$.

The Triplet Energy of a Rigid Azo Compound

Sir:

Although fluorescence has recently been observed for certain azo compounds,[1,2] phosphorescence has never been seen.[3] Thus in contrast to the extensive knowledge of carbonyl triplet energies,[4] no significant experimental evidence is available for determining the triplet level of the azo group.

The several estimates which have been made, however, indicate that an n–π^* singlet–triplet splitting (E_{S-T}) of 15–20 kcal is a reasonable value for both *cis* and *trans* azo compounds.[5] The singlet energy of acyclic aliphatic azo compounds can be estimated as 75 kcal from the broad, structureless ultraviolet absorption,[6] while that for 2,3-diazabicyclooctene-2 is 76 kcal from measurement of the fluorescence spectrum.[7] Thus the azo triplet should not be below 55 kcal. It might be expected that sensitizers of triplet energy below this value would be markedly inefficient in energy transfer to azo compounds.[8]

Attempts to locate the azo triplet experimentally by the use of a series of sensitizers of varying energy have been without success. Hammond[5a] found no readily interpretable pattern in the quantum yield of ethyl azoisobutyrate decomposition using triplet sensitizers ranging in energy from 42.6 to 68.5 kcal. Nelsen[9] found that anthracene and 1,2-benzanthracene (E_T = 42.6 and 47 kcal, respectively) would decompose azocumene with moderate efficiency. We have obtained similar results using pyrene to photosensitize azomethane and azoisobutane decomposition.

This apparent discrepancy between theory and experiment can be rationalized if one says that low-energy sensitizers decompose azo compounds *via* nonvertical energy transfer.[5a] Any attempt, therefore, to locate the triplet using a series of sensitizers must preclude nonvertical transfer. It seemed to us that use of an azo

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(1) C. Steel and T. Thomas, *Chem. Commun.*, 900 (1966).

(2) W. L. Mock, Ph.D. Thesis, Harvard University, 1964.

(3) R. Rebbert and P. Ausloos, *J. Am. Chem. Soc.*, 87, 1847 (1965).

(4) J. Calvert and J. Pitts, "Photochemistry," John Wiley and Sons, Inc., New York, N. Y., 1966, p 298.

(5) (a) J. R. Fox and G. S. Hammond, *J. Am. Chem. Soc.*, **86**, 4031 (1964); (b) D. R. Kearns, *J. Phys. Chem.*, **69**, 1062 (1965); (c) R. Ake, private communication; (d) J. Swenton, private communication.

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(7) T. Thomas and C. Steel, *J. Am. Chem. Soc.*, **87**, 5290 (1965).

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(9) S. F. Nelsen, Ph.D. Thesis, Harvard University, 1965.