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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[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.

[6] See, for example, the spectrum of azomethane in hexane: G. Kortüm and H. Rau, *Ber. Bunsenges. Physik. Chem.*, **68**, 973 (1964).

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

[8] G. Porter and F. Wilkenson, *Proc. Roy. Soc.* (London), **A264**, 1 (1961).

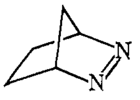
[9] S. F. Nelsen, Ph.D. Thesis, Harvard University, 1965.

Table I. Photolysis at 366 mμ of 0.02 M 2,3-Diazabicycloheptene-2 at 20°

Sensitizer (concn, M)	E_T, kcal[4]	Solvent	k_1,[a] 10^{-3} sec^{-1}	Φ
Anthracene (0.053)	42.6[b]	Toluene	2.7	<0.00017
Pyrene (0.050)	48.7	Hexane	0.65	0.00029
β-Acetonaphthone (0.10)	59.3	Hexane	3.3	0.0079
Phenanthrene (0.10)	62.2	Hexane	9.0	0.0077
Phenanthrene (0.050)	62.2	Toluene	9.0	0.0054
Thioxanthone (0.052)	65.5	Toluene	13	1.0
Triphenylene (0.108)	66.6	Toluene	1.6	0.77[c]
Benzophenone (0.10)	68.5	Hexane	530[d]	0.97

[a] Experimental rate constant for decay of sensitizer triplet; see footnote *b*. [b] W. G. Herkstroeter and G. S. Hammond, *J. Am. Chem. Soc.*, **88**, 4769 (1966). [c] Photolyzed at 313 mμ. [d] H. L. J. Backstrom and K. Sandros, *Acta Chem. Scand.*, **14**, 48 (1960).

compound of rigid structure would accomplish this end since changes in geometry concomitant with energy transfer would be highly unfavorable.[10] It was hoped that an azo group incorporated into a bicyclooctyl system would meet this requirement. Unfortunately, such a compound proved to be rather photostable, so the bicycloheptyl analog[12] I was used instead. We have obtained the quantum yields of nitrogen formation shown in Table I.



I

Although we cannot presently explain the difference within the two groups of sensitizers, the distinction between those of high and low energy is clear. A high quantum yield of nitrogen formation implies efficient triplet energy transfer since benzophenone and triphenylene are known to have high intersystem-crossing ratios,[13] and virtually all the light is absorbed by the sensitizer.

Since energy transfer is efficient only when the sensitizer is of higher energy than the acceptor,[8] the data indicate that the triplet compound I lies between 62.2 and 65.5 kcal. The singlet of I is at 84.4 kcal[1] so that the singlet–triplet splitting becomes 18.9–22.2 kcal. Although there is likely to be some influence of structure on E_{S-T}, our value is roughly in agreement with the estimated value.[5] The sensitizer decay constants listed in Table I show clearly that the observed break in quantum yield is not a function of sensitizer lifetime.

Results qualitatively similar to ours have been noted by Andrews and Day,[14] who used various sensitizers and an alkylidenepyrazoline. Their cutoff was apparently less well defined than ours but occurred in the region 55–65 kcal.

It would be interesting to measure energy transfer rates to rigid and nonrigid azo compounds using kinetic spectroscopy as has been elegantly done by Hammond and co-workers[15] for stilbenes. Such experiments could lend a great deal of support to the arguments given above.

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(10) Two types of geometrical changes which might occur in an acyclic azo compound but not in a rigid system are twisting about the N=N bond[5b] and straightening of one or two C–N bonds in the molecular plane.[11] In support of the idea that one of these processes does occur, we mention that we have observed efficient photosensitized *trans-cis* isomerization of azomethane.

(11) J. Alster and L. Burnelle, *J. Am. Chem. Soc.*, **89**, 1261 (1967).

(12) S. Cohen, R. Zand, and C. Steel, *ibid.*, **83**, 2895 (1961).

(13) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin Inc., New York, N. Y., p 131.

(14) S. D. Andrews and A. C. Day, *Chem. Commun.*, 667 (1966).

(15) See footnote *b*, Table I.

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Heterocyclic Metallo-Indene Systems

Sir:

The preparation of five-membered unsaturated organometallic heterocycles and spirocycles through the reaction of a 1,4-dilithium system and a metallic or pseudo-metallic halide has received extensive attention in the literature. This type of reaction has produced a host of novel metallocyclopentadienes[1–4] when 1,4-dilithio-1,2,3,4-tetraphenylbutadiene, originally described by Smith and Hoehn,[5] was the reactive organometallic intermediate employed. Similarly, metallofluorenes[6,7] and perfluorinated analogs[8] have been prepared by the reactions of the respective 2,2′-dilithiobiphenyl systems. Thus far this particular type of reaction has not been exploited for the synthesis of metallo-indenyl counterparts of the above heterocycles, although three such compounds are known. These have been prepared by specific reactions of diphenylacetylene with $Fe_3(CO)_{12}$ to give a ferraindene complex,[9] with triphenylaluminum to give an aluminole,[10] and with selenium tetrachloride to give a selenium heterocycle.[11]

The reaction of diphenylacetylene with *n*-butyllithium produces a dilithium intermediate (I) which has been previously characterized by the carbonation studies of Mulvaney, *et al.*[12] This reagent appeared to offer a facile entry into such metallo-indenyl derivatives. We have developed improved techniques for the generation of I and herein report our initial successful results on the subsequent reactions of I to afford a variety of heterocyclic and spirocyclic metallo-indenyl systems.

The reaction of diphenylacetylene with *n*-butyllithium in 1:1 diethyl ether–tetrahydrofuran (THF)

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(4) E. H. Braye, W. Hübel, and I. Caplier, *ibid.*, **83**, 4406 (1961).

(5) L. I. Smith and H. H. Hoehn, *ibid.*, **63**, 1184 (1941).

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