example is provided by the reaction of H_2 with I, a six-coordinate Re^{I} complex, to form the seven-coordinate Re^{III} complex II. This reaction is not reversed under 60 psi of N_2 pressure; in this respect it is unlike the addition of H_2 to $CoH(N_2)L_3$ to form CoH_3L_3, a readily reversible reaction.

A hydrido–ethylene complex, $ReH(C_2H_4)(dppe)_2$[7] (VII), is formed on shaking a benzene solution of I under 60 psi of ethylene pressure. No evidence was found for insertion of C_2H_4 into the Re–H bond; retention of the latter in VII is demonstrated by the τ 16.92 quintet in the ^1H nmr spectrum. The bound ethylene proton resonance occurs at τ 7.64 (CS_2 solution),[14] considerably shifted from the value for free ethylene (τ 4.67 in CCl_4) or ethylene in Zeise's salt (τ 5.27),[15] but not excessively different from the shift for π-bonded ethylene (ν(C=C), 1541 cm^{-1}) in $[Re(CO)_4(C_2H_4)_2]PF_6$ (τ 6.6 in D_2O).[16] It appears reasonable to formulate VII as a six-coordinate π-ethylene complex of Re^{I}, and to view its formation as a simple substitution reaction. The only other stable hydrido–ethylene complexes of which we are aware are $NbH(C_5H_5)_2(C_2H_4)$[17a] and *trans*-$[PtH(C_2H_4)(PEt_3)_2]BPh_4$;[17b] the latter has been formulated as a four-coordinate π-ethylene complex.

Carbon monoxide slowly displaces N_2 from I in benzene solution to form the carbonyl analog, *trans*-$ReH(CO)(dppe)_2$[7] (VIII), in quantitative yield. That VIII has retained trans geometry is confirmed by the presence of a high field quintet and its value of J(P–H) (Table I). The low value of ν(CO) is consistent with the suggestion of Chatt, *et al.*,[1] that terminal carbonyl complexes with low ν(CO) will have dinitrogen analogs. Finally, we note that the higher value of τ(Re–H) for the N_2 complex I, as compared to the CO complex VIII, suggests that N_2 has a somewhat smaller trans influence than CO.[9] A similar conclusion has been reached on other grounds.[18]

Acknowledgment. We thank Mr. C. R. Sprinkle for the preparation of starting materials and the molecular weight determinations.

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[14] A peak with intensity corresponding to ~0.5 proton is found at τ 4.58 (CS_2 solution). We attribute this to free ethylene from slight dissociation or decomposition of the complex.

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[17] (a) F. N. Tebbe and G. W. Parshall, *J. Amer. Chem. Soc.*, **93**, 3793 (1971); (b) A. J. Deeming, B. F. G. Johnson, and J. Lewis, *Chem. Commun.*, 598 (1970).

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Steric Hindrance in Triplet Electronic Energy Transfer[1]

Sir:

Systematic studies of the rates of triplet electronic energy transfer processes have mainly focused upon the effects of energetics on the efficiency of energy transfer.[2–4] These studies have led to the following conclusions: (1) when the triplet energy of the donor exceeds the triplet energy of the acceptor by more than 3 kcal/mol, the energy transfer rate is at the diffusion-controlled limit; (2) as the triplet energy of the donor decreases below this level, energy transfer rates drop very sharply. Several exceptions to these general rules have been noted and explained as steric hindrance to triplet energy transfer.[5–8] Since the accepted electron-exchange formulation for triplet energy transfer requires an effective collision between the donor and acceptor molecules,[9] the possibility of steric hindrance might be expected. However, there have been no systematic studies of the magnitude of steric effects upon the rates of triplet electronic energy transfer.[10]

We have measured the rates of quenching of triplet triphenylene in benzene solution by a series of azo compounds with a variety of steric properties. The triplet energy of triphenylene has been established to be 66.6 kcal/mol in a nonpolar solvent.[11] The determination of triplet energies for aliphatic acyclic azo compounds has been more difficult, but the best estimates are about 53–56 kcal/mol.[12,13] Thus, triplet energy transfer from triphenylene to an azo compound is sufficiently exothermic to allow a prediction of a diffusion-controlled rate constant. Small substituent effects upon the triplet energies of individual azo compounds should not affect this prediction. We have found, however, that the rate of triplet energy transfer from triphenylene to azo compounds can be substantially less than the diffusion-controlled limit, depending upon the steric bulk of the substituents surrounding the azo functional group.

All of the azo compounds were synthesized by the method of Stowell[14] and were determined to be >95% pure by gas chromatographic analysis. Samples were prepared in purified[4] benzene and degassed by five freeze–pump–thaw cycles to an ultimate pressure of at least 10^{-5} Torr. Quenching rates were determined by standard flash photolytic kinetic techniques,[4] using a modified Xenon Model 710 apparatus.[15] Rate constants were obtained as the slopes of linear Stern–Volmer plots of observed first-order decay rate constants,

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[1] Presented in part at the 8th Western Regional Meeting of the American Chemical Society, San Francisco, Calif., Oct 1972.

[2] (a) H. L. J. Bäckström and K. Sandros, *Acta Chem. Scand.*, **12**, 823 (1958); (b) *ibid.*, 14, 48 (1960); (c) K. Sandros, *ibid.*, **18**, 2355 (1964).

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[5] W. G. Herkstroeter, L. B. Jones, and G. S. Hammond, *ibid.*, **88**, 4777 (1966).

[6] G. S. Hammond and R. S. Cole, *ibid.*, **87**, 3256 (1965).

[7] P. J. Wagner and I. Kochevar, *ibid.*, **90**, 2232 (1968).

[8] R. R. Sauers, P. Valenti, and E. Tavss, 7th Middle Atlantic Regional Meeting of the American Chemical Society, Philadelphia, Pa., Feb 1972, Abstract N7.

[9] A. A. Lamola in "Energy Transfer and Organic Photochemistry," P. A. Leermakers, A. Weissberger, A. A. Lamola, and N. J. Turro, Ed., Interscience, New York, N. Y., 1969, pp 44–50.

[10] Recently, a study of the quenching of the photoreactions of α,α-dimethylvalerophenone and β,β-dimethyl-α-ketobutyrophenone has led to the conclusion that steric hindrance is unimportant in triplet energy transfer from these hindered ketones: P. J. Wagner, J. M. McGrath, and R. G. Zepp, *J. Amer. Chem. Soc.*, **94**, 6883 (1972).

[11] W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *ibid.*, **86**, 4537 (1964).

[12] S. Collier, D. Slater, and J. Calvert, *Photochem. Photobiol.*, **7**, 737 (1968).

[13] P. S. Engel and P. D. Bartlett, *J. Amer. Chem. Soc.*, **92**, 5883 (1970).

[14] J. Stowell, *J. Org. Chem.*, 32, 2360 (1967).

[15] A full description of the flash photolysis apparatus will be published in a full paper.

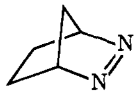
using at least five different quencher concentrations.[16] The measured quenching rate constants are listed in Table I.

Table I. Rate Constants for Quenching of Triplet Triphenylene[a]

Quencher	Rate constant, M^{-1} sec^{-1} [b]
trans-Stilbene[c]	6×10^9
Azo-*n*-butane	6×10^9
Azoisobutane	3×10^9
Azo-*sec*-butane	6×10^8
Azo-1-adamantane	6×10^8
Azo-*tert*-butane	3×10^8

[a] In benzene solution at room temperature; measured triphenylene triplet lifetime 1×10^{-4} sec. [b] Estimated error limits ±20%. [c] This case represents the diffusion-controlled rate previously measured to be 7×10^9 M^{-1} sec^{-1}; see ref 4.

The quenching rates clearly drop sharply as substitution is increased about the azo functional group. A completely diffusion-controlled rate is observed only with azo-*n*-butane, and the quenching rates steadily decrease as the alkyl substituents proceed from primary to secondary to tertiary. Except perhaps for azo-1-adamantane, the observed rate constants correlate extremely well with what would be expected purely on the basis of steric effects. The rate of quenching of triplet triphenylene by a cis azo compound, 2,3-diazabicyclo[2.2.1]heptene-2 (**1**) (E_T = 60 kcal/mol), has been determined to be 3×10^9 M^{-1} sec^{-1} in benzene solution.[18] Although the azo functional group in **1** is attached to secondary substituents, the cis stereochemistry almost certainly renders the chromophore more accessible than the trans stereochemistry of the corresponding azo-*sec*-butane.



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Based upon Dexter's theoretical formulation of electron-exchange energy transfer,[19] it has been calculated that triplet energy transfer rates should fall off one order of magnitude for each 1.2 Å increase in separation between the donor and acceptor chromophores.[10,20] Molecular models and calculations indicate that a tertiary substituent, such as *tert*-butyl or 1-adamantyl, possesses a van der Waals radius which would extend about 1 Å beyond that of a π system.[10] Thus, triplet energy transfer from triphenylene to azo-*n*-butane proceeds at a diffusion-controlled rate because the donor and acceptor chromophores may come into direct contact, but triplet energy transfer from triphenylene to azo-*tert*-butane occurs at a rate one order of magnitude less than diffusion-controlled because the tertiary substituents keep the donor and acceptor chromophores (van der Waals radii) separated by about 1 Å. The specific orientation which leads to this prediction involves the azo compound lying flat over the plane of the triphenylene molecule.

The rate of singlet energy transfer from triphenylene to azo-*tert*-butane has been determined both by fluorescence lifetime quenching and by fluorescence intensity quenching to be 5.6×10^9 and 6.2×10^9 M^{-1} sec^{-1}, respectively.[13] Since this rate constant is at the diffusion-controlled limit, it would appear that steric hindrance is substantially less important in the transfer of singlet electronic excitation in solution.[21,22]

We are currently determining the rates of quenching of lower energy sensitizer triplet states by the same series of azo compounds, in order to ascertain the effect of energetics upon the magnitude of these steric effects.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the Research Corporation for generous support of this work.

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[16] Although the subject of energy transfer to azo compounds has been the source of substantial confusion,[13,17] the method of monitoring triplet decay rates assures that we are observing only triplet quenching.

[17] P. D. Bartlett and P. S. Engel, *J. Amer. Chem. Soc.*, **90**, 2960 (1968).

[18] These experiments were performed by C. C. W. under conditions identical with those reported herein; cited by P. S. Engel, *ibid.*, **91**, 6903 (1969).

[19] D. L. Dexter, *J. Chem. Phys.*, **21**, 836 (1953).

[20] B. Smaller, E. C. Avery, and J. R. Remko, *ibid.*, 43, 922 (1965).

(21) A. Yekta and N. J. Turro, 164th National Meeting of the American Chemical Society, New York, N. Y., Aug 1972, Abstract PHYS-53.

(22) Steric hindrance is important in vapor-phase singlet energy transfer, however: K. Janda and F. S. Wettack, *J. Amer. Chem. Soc.*, **94**, 305 (1972).

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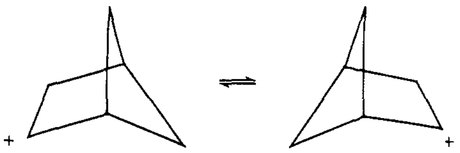
Nature of the 2-Bicyclo[2.1.1]hexyl Cation[1]

Sir:

It is commonly observed that cyclobutylcarbinyl derivatives rearrange on solvolysis to cyclopentyl compounds.[2] A particularly interesting example of this type of rearrangement is found with bicyclo[2.1.1]hexyl-2 derivatives for here the rearranged ion is degenerate with the unrearranged ion (eq 1). This case has been studied by Meinwald and Gassman[3] and by Meinwald and Crandall.[4] They have presented evidence showing a rearrangement of the type shown above and found the rate of solvolysis to be greater than might be expected for simple open ions. This led to the suggestion that the species formed on ionization might be a bridged ion (eq 2).



(1)

This appeared to be a case in which a stable ion or equilibrating group of ions might be found. Thus, the reaction of 2-chlorobicyclo[2.1.1]hexane[5] with antimony

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(1) This investigation was supported by grants from the National Institutes of Health and the National Science Foundation.

(2) *Cf.* R. Breslow in "Molecular Rearrangements," P. de Mayo, Ed., Interscience, New York, N. Y., 1963, p 278.

(3) J. Meinwald and P. G. Gassman, *J. Amer. Chem. Soc.*, **85**, 57 (1963).

(4) J. Meinwald and J. K. Crandall, *ibid.*, **88**, 1292 (1966).

(5) The chloride was prepared from bicyclo[2.1.1]hexan-2-ol[6] by the reaction with thionyl chloride. Its properties were identical with those of material prepared by a different method.[7]

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(7) R. Srinivasan and F. I. Sonntag, *J. Amer. Chem. Soc.*, **89**, 407 (1967).