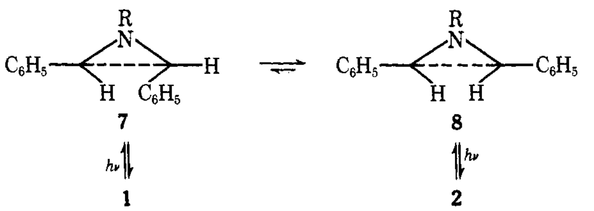
Scheme IV



where dotted lines are employed to indicate strong π interaction. For obvious steric reasons rotational interconversion between **7** and **8** ought to favor the latter and thus ultimately generate a mixture rich in **2**.[19] It is hoped that studies with optically active **1**, currently in progress within our laboratories, will shed further light into the mechanistic picture of the stereoisomerization process.

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(19) Within the frame of the scheme shown in IV, this conclusion is of course only valid if the σ–π interconversions shown occur in the excited state. It is also perhaps interesting to note that the observed interconversion between **1** and **2** may also be rationalized through the initial excited state generation of **7** and **8** depicted in Scheme IV followed by electronic deactivation of these species and subsequent *thermal*, symmetry-controlled, closure to **2** and **1**, respectively. Nonetheless, we tend to favor the mechanistic interpretation of Scheme IV owing to the obvious inability of the "thermal" process to readily accommodate the substantial photostationary predominance of the cis isomer irrespective of N substituent.

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Steric Hindrance in the Transfer of Singlet Electronic Energy

Sir:

Despite the rather large number of studies in recent years on electronic energy transfer, there have been no systematic investigations of the effect of variations of molecular structure, *i.e.*, variations which do not involve changes in the nature of the acceptor chromophore, on the transfer of singlet electronic energy in gas phase interactions. Work on the transfer of triplet energy in the gas phase from acetone to olefins[1] and from benzene to olefins[2] has been reported, but in both cases the transfer process is inefficient and the triplet energy levels of the olefins vary. Also, singlet energy transfer from benzene to a variety of accepters in the gas phase has been reported,[3] but, again, the singlet energy levels of the acceptors vary over a substantial range. In the liquid phase, quenching of fluorescence from a variety of ketones by olefins[4] has been studied as a function of ketone structure, but the process appears to involve a chemical reaction which can lead to new products rather than an electronic energy transfer.

Subtle structural variations which do not significantly alter the electronic energies of the donor and/or acceptor species should, in our opinion, provide a useful probe of the detailed nature of energy transfer mechanisms, particularly those which occur over molecular distances and which are relatively efficient. As a result we have been prompted to investigate the structural parameter in the exothermic transfer of singlet energy from benzene to various aliphatic ketones in the gas phase. The preliminary results reported in this communication confirm that structural dependencies in energy transfer can be measured and, to the best of our knowledge, provide the first quantitative study of steric hindrance in singlet electronic energy transfer in the gas phase.

The bimolecular rate constants and the corresponding hard-sphere effective quenching cross sections for the process singlet benzene + ketone → singlet ketone + benzene are shown in Table I.

Table I. Summary of Fluorescent Quenching Data[a]

Ketone	k_q, M^{-1} sec^{-1} × 10^{-10}	σ^2, Å^2
Acetone	8.27 ± 0.47	10.4 ± 0.6
2-Butanone	8.09 ± 0.23	10.4 ± 0.3
3-Pentanone	9.77 ± 0.52	13.1 ± 0.7
2,4-Dimethyl-3-pentanone	6.24 ± 0.49	8.92 ± 0.7
2,2,4,4-Tetramethyl-3-pentanone	2.03 ± 0.27	3.02 ± 0.4

[a] λ_{ex}, 253.7 nm; [benzene], 15 Torr; temperature, 25°.

The rate constants for bimolecular quenching, k_q, were determined in the standard manner[5] from least mean squares analysis of linear Stern–Volmer plots of $\phi_f{}^0/\phi_f$ *vs.* [ketone]. The singlet lifetime τ_s of benzene was taken to be 75 nsec.[6] Ketone pressures were measured with an MKS Baratron capacitance manometer using a 3-Torr head while the benzene pressure was measured with a mercury manometer. The 253.7-nm line from a Hanovia SH-100 medium-pressure Hg lamp was isolated with a Bausch and Lomb 500-mm grating monochromator using 2-mm slits, and the fluorescence was measured in a standard T-shaped cell. Scattered light corrections were made by totally quenching the benzene fluorescence with O$_2$. The individual values are averages of at least four independent determinations and the uncertainties indicate the average deviation from the mean in each case. The cross sections can be compared with those obtained by Lee and coworkers[7] of ~13–14 Å^2 for cyclobutanone, cyclopentanone, and cyclohexanone at benzene pressures of 2.5 Torr.

Since the benzene singlet lifetime has been independently measured by five laboratories using three different techniques, it seems safe to conclude that the bimolecular rate constants closely approximate absolute values for the conditions of these experiments.

(1) R. E. Rebbert and P. Ausloos, *J. Amer. Chem. Soc.*, **87**, 5569 (1965).

(2) For a summary see E. K. C. Lee in "Excited State Chemistry," J. N. Pitts, Jr., Ed., Gordon and Breach, New York, N. Y., 1970, pp 59–91.

(3) (a) A. Morikawa and R. J. Cvetanović, *J. Chem. Phys.*, **49**, 1214 (1968); (b) E. K. C. Lee, M. W. Schmidt, R. G. Shortridge, Jr., and G. A. Hanniger, Jr., *J. Phys. Chem.*, 73, 1805 (1969).

(4) (a) N. J. Turro, J. C. Dalton, G. Farrington, M. Niemczyk, and D. M. Pond, *J. Amer. Chem. Soc.*, **92**, 6978 (1970); (b) G. D. Renkes and F. S. Wettack, submitted for publication.

(5) J. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966, p 663.

(6) 75 ± 5 nsec appears to encompass the values of τ_s obtained by several laboratories for conditions similar to those used in these experiments. See, for example, (a) T. Chen and E. W. Schlag, in "Molecular Luminescence," E. C. Lim, Ed., W. A. Benjamin, New York, N. Y., 1969, p 381; (b) G. M. Breuer and E. K. C. Lee, *J. Chem. Phys.*, **51**, 3615 (1969); (c) N. Nishikawa and P. K. Ludwig, *ibid.*, **52**, 107 (1970); (d) B. K. Selinger and W. R. Ware, *ibid.*, **53**, 3160 (1970); (e) C. S. Burton and H. E. Hunziker, *ibid.*, **52**, 3302 (1970).

(7) (a) H. A. Denschlag and E. K. C. Lee, *J. Amer. Chem. Soc.*, **90**, 3628 (1968); (b) E. K. C. Lee, *J. Phys. Chem.*, **71**, 2804 (1967); (c) R. G. Shortridge and E. K. C. Lee, *J. Amer. Chem. Soc.*, **92**, 2228 (1970).

The results in Table I clearly indicate that the efficiency of energy transfer is reduced by increased α-methyl substitution around the carbonyl group. Thus it may be concluded that the energy transfer occurs *via* a close interaction of the excited benzene molecule and the carbonyl group. Also, from the magnitude of the cross section it can be concluded that the transfer occurs with a high efficiency in the case of the simple ketones. Viscosity measurements of molecular diameters[8] indicate that a hard-sphere collision cross section of about 25 $Å^2$ is appropriate for the benzene–acetone system. Therefore the energy transfer would appear to have a maximum efficiency of approximately 0.4. If, however, only the π systems of the interacting species determine the effective molecular diameter, a "collision" diameter of 3.5–4 Å is quite reasonable and indicates that the transfer process has a unit efficiency for the simple ketones. The conclusion concerning the efficiency of energy transfer is in line with other work[7,9] but the conclusion regarding transfer distance contrasts with that of Birks, Saltee, and Leite[10] on the system naphthalene–biacetyl in the liquid phase, where they conclude that singlet transfer occurs by an electron transfer mechanism over an 11-Å interaction distance. It is possible, of course, that the mechanism is entirely different in the two phases or in the two systems. We are examining solutions of the benzene–ketone systems in order to ascertain the effect of phase.

Again, we reiterate that the presence of measurable steric effects may provide a useful means of examining electronic energy transfer processes in sufficient detail to obtain basic knowledge about the nature of the interactions. Further work on other systems with this goal in mind is in progress in our laboratory.

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[8] See, *e.g.*, J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids," Wiley, New York, N. Y., 1954.

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Five-Coordinate Rhodium(I) Complexes Containing Small Molecules and a Chelating Triphosphine Ligand[1]

Sir:

Recent extensive studies on tertiary phosphine complexes of the platinum group metal halides have demonstrated many diverse and interesting reactions involving (1) homogeneous catalysis,[2] (2) oxidative addition,[3] (3) coordination of elemental molecules,[4] (4) the Lewis basicity of metal complexes,[5] and (5) stabilization of small molecular fragments.[6] Many of these reactions which utilize the Wilkinson compound,[7] $Rh(Ph_3P)_3Cl$, often yield complexes where one or more of the phosphine ligands is displaced, *e.g.*, in $Rh(Ph_3P)_2COCl$. We became interested in designing a triphosphine ligand that would make the rhodium atom more basic than in $Rh(Ph_3P)_3Cl$ and simultaneously minimize the tendency of one or more phosphine donors to be displaced in chemical reactions. The chelating triphosphine $C_6H_5P[CH_2CH_2P(C_6H_5)_2]_2$ fits these criteria and it was synthesized; however, our initial experiments with this ligand indicated that one of the phosphine donors often bridged to another rhodium atom, thereby producing polynuclear rhodium complexes. In order to relieve the implied chelate-ring strain, the tritertiary phosphine with trimethylene linkages, $C_6H_5P[CH_2CH_2CH_2P(C_6H_5)_2]_2$ (L), was prepared. This ligand should facilitate coordination of all three phosphorus atoms in a monomeric, square-planar complex of the type RhP_3Cl, which would possess a donor set similar to the Wilkinson compound.

Addition of a benzene solution of L to a suspension of $[Rh(C_8H_{12})X]_2$ (X = Cl, Br, I) in refluxing ethanol readily produces the corresponding square-planar complexes, RhLX, in high yields (~80%). The yellow chloride complex, RhLCl, is stable for months in air, whereas the iodide complex, RhLI, changes color in air over a period of several months from orange to brown.

The chloride complex, RhLCl (**1**), reacts with a variety of small molecules to form the five-coordinate, nonionic adducts RhLCl·A where A = BF_3, CO, $HgCl_2$, SO_2, O_2, and S_2.[8] Tensiometric titrations of **1** with BF_3 show sharp breaks at the 1:1 stoichiometry, and the infrared spectrum of the isolated solid shows a strong broad band at *ca.* 1060 cm^{-1}, indicative of a coordinated BF_3 group.[9] The monocarbonyl complex, RhLCl·CO, shows a single CO infrared peak both in solution (CH_2Cl_2, 1956 cm^{-1}) and in the solid state (Nujol, 1957 cm^{-1}); in the more polar solvent, CH_3NO_2, where conductance measurements show some ionization, there is an additional peak of medium intensity. The latter peak at *ca.* 2020 cm^{-1} signifies the presence of the cation $[RhL(CO)]^+$ as discussed below. For comparison, ν(CO) in RhLI·CO occurs at 1937 cm^{-1} (Nujol), indicating greater Rh → CO back bonding when chloride is replaced with iodide.

A microcrystalline light-brown dioxygen complex, $\mathbf{1}\cdot O_2$, is formed rapidly when O_2 is bubbled through a benzene suspension of **1**. This $RhLCl\cdot O_2$ compound is one of the most stable rhodium–dioxygen complexes

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[1] Presented at the 3rd Central Regional Meeting of the American Chemical Society, Cincinnati, Ohio, June 1971, and in the Symposium on Five-Coordinate Complexes, at the 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 1971, Abstracts, No. INORG 96.

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