

Acknowledgment. This study was supported by the National Science Foundation.

(17) National Science Foundation Postdoctoral Fellow, 1964–1965.

Peter J. Wagner,¹⁷ George S. Hammond

Contribution No. 3270

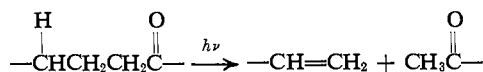
The Gates and Crellin Laboratories of Chemistry
California Institute of Technology, Pasadena, California

Received June 28, 1965

Type II Photolysis of 2-Octanone

Sir:

Considerable controversy exists as to the nature of the excited state responsible for photoelimination in ketones having γ -hydrogen atoms (type II photolysis). Michael and Noyes concluded that excited singlet



states were involved, based upon vapor-phase studies of 2-pentanone and 2-hexanone in the presence of biacetyl.¹ Ausloos and Rebbert² concluded that excited triplets were involved in 2-pentanone photolysis since biacetyl quenched the type II reaction without affecting the fluorescence yield.

Table I. Effect of Quencher Concentration on Rate of 1-Pentene Formation

Quencher, M	$R(1\text{-pentene})$ $\times 10^6,$ $M \text{ min.}^{-1}$	$R(\text{trans-DCE})$ $\times 10^5,$ $M \text{ min.}^{-1}$
0	11.8	...
<i>cis</i> -DCE, 0.81	8.5	6.25
<i>cis</i> -DCE, 0.83	8.03	5.68
<i>cis</i> -DCE, 1.80	5.80	7.66
<i>cis</i> -DCE, 3.05	4.46	11.35
<i>cis</i> -DCE, 3.99	3.57	11.55
<i>cis</i> -DCE, 5.53	2.81	14.55
<i>cis</i> -DCE, 11.20	2.12	...
<i>cis</i> -DCE, 12.49	2.12	...
Piperylene, 0.0109	8.54	
Piperylene, 0.0195	7.10	
Piperylene, 0.0417	5.45	
Piperylene, 0.0813	4.50	
Piperylene, 0.162	3.55	
Piperylene, 0.311	3.23	
Piperylene, 0.618	2.60	
Piperylene, 0.914	2.36	
Piperylene, 7.2	2.36	

The accompanying communication by Wagner and Hammond utilizing piperylene as triple state quencher for 2-pentanone and 2-hexanone provides convincing evidence that both excited singlets and triplets can be involved in these reactions.³ Since our study closely parallels and confirms that of Wagner and Hammond we wish to communicate the results at this time.

We have studied the effect of both *cis*-dichloroethylene and piperylene (1,3-pentadiene) on the rate of 1-pentene formation from liquid 2-octanone under conditions of constant illumination. Both olefins are expected to

(1) J. L. Michael and W. A. Noyes, Jr., *J. Am. Chem. Soc.*, **85**, 1027 (1963).

(2) P. Ausloos and R. E. Rebbert, *ibid.*, **87**, 4512 (1964).

(3) P. J. Wagner and G. S. Hammond, *ibid.*, **87**, 4009 (1965).

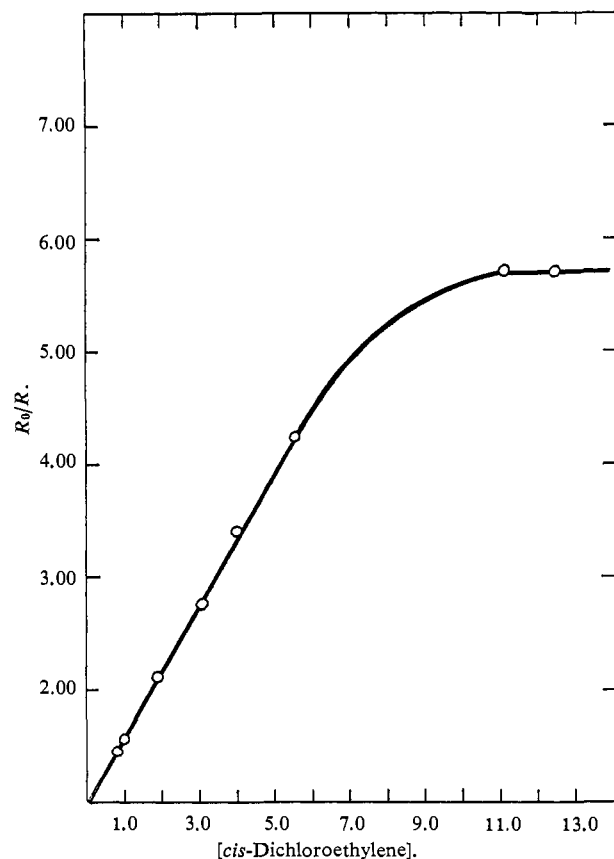


Figure 1. Ratio of rate of 1-pentene formation (neat) to rate in the presence of *cis*-dichloroethylene vs. concentration of *cis*-dichloroethylene.

act as triplet-state quenchers in this system, the latter being particularly efficient.⁴

Measured amounts of 2-octanone and quencher were sealed in quartz cells of approximately 1.8-ml. capacity, deoxygenated, and inserted in a quartz water bath at 1.5–3.5°. Photolysis was effected with a General Electric H100-A4/T lamp.⁵ Analyses were carried out by gas chromatography. Concentrations of acetone, 1-pentene, and *trans*-dichloroethylene were followed with time.⁶ The rates of acetone and 1-pentene formation were essentially the same, although the latter was most reliable. Table I summarizes the results.

Figures 1 and 2 show plots of R_0/R for 1-pentene against *cis*-dichloroethylene and piperylene concentrations, respectively (Stern–Volmer Plot). It is apparent that piperylene is a much more efficient quencher for this reaction than is *cis*-dichloroethylene by a factor of about 60, but significantly in both cases the maximum extent of quenching is approximately 80%. The amount of nonquenchable reaction (~20%) may reasonably be attributed to reaction through the excited singlet state with the remainder of the photoelimination occurring through the excited triplet state. This compares with Wagner and Hammond's results of

(4) G. S. Hammond, N. J. Turro, and P. A. Leermakers, *J. Phys. Chem.*, **66**, 1144 (1962).

(5) The effective absorption occurs between 300 and 315 m μ . In all cases 2-octanone absorbs essentially 100% of the incident light.

(6) Energy transfer from 2-octanone to *cis*-dichloroethylene results in isomerization to the *trans* olefin.³ Although a similar isomerization occurs with piperylene, it could not be followed under the analytical conditions employed here.

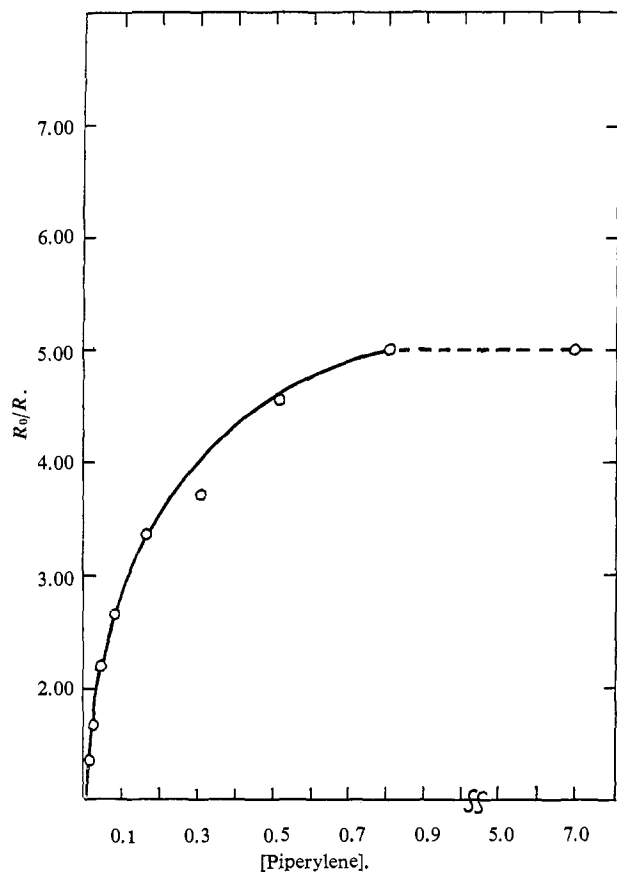


Figure 2. Ratio of rate of 1-pentene formation (neat) to rate in the presence of piperylene vs. concentration of piperylene.

95 and 60% triplet reaction for 2-pentanone and 2-hexanone photolyses, respectively.

The initial slope in Figure 2 can be equated to k_q/k_r (k_q = rate constant for quenching, k_r = sum of rate constants for reactions quenched) as pointed out by Wagner and Hammond. Our value of ~ 34 is greater than that expected based on Wagner and Hammond's values of 5 and 40 for 2-hexanone and 2-pentanone, respectively which have been correlated by those authors with the relative ease of abstraction of secondary vs. primary hydrogen by alkoxy radicals. It appears that other factors also may be operative.

Acknowledgment. The author thanks Messrs. K. R. Weishaupt and P. M. Sieczka for invaluable technical assistance.

Thomas J. Dougherty

Yerkes Research and Development Laboratory
Film Department
E. I. du Pont de Nemours and Company, Inc.
Buffalo, New York 14207

Received July 28, 1965

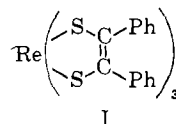
Six-Coordinate Trigonal-Prismatic Complexes¹

Sir:

The octahedral six-coordinate transition metal ion was one of the great stereochemical triumphs of the nineteenth century.² It is often emphasized in basic textbooks that for six-coordinate metal complexes,

- (1) This research was supported by the National Science Foundation.
(2) A. Werner, *Z. anorg. Chem.*, **3**, 267 (1893).

the trigonal-prismatic or hexagonal-planar structure "...cannot be correct."³ Thus, it is of considerable interest that the six-coordinate complex $\text{Re}(\text{S}_2\text{C}_2\text{Ph}_2)_3$ ⁴⁻⁶ (I) has recently been shown to have a near perfect



trigonal-prismatic array of donor atoms in a crystalline sample.⁷ The maxim "six-coordination equals octahedral complex" has seemingly been violated for the first time. Since the requirements of crystal packing may be responsible for the unusual structure of I, it is urgent to determine whether the trigonal-prismatic structure will remain faithful in liquid solutions. Furthermore, we must ask if this exceptional geometry is limited to rhenium⁸ or to this particular ligand (or to both), for it is to be noted that I is a member of a large class of six-coordinate transition metal complexes containing structurally similar sulfur-donor ligands.^{9,10} This class of complexes includes at least nine different central metals and at least five different bidentate sulfur ligands.^{5,6,10-14}

In this communication, we report some of the important physical properties of I, in solution and in the solid, and compare these properties with those of other members of the class. We also report some new six-coordinate complexes which almost certainly have trigonal-prismatic structures.

An analytically pure sample of compound I was prepared by treating an ethanol solution of ReCl_5 with P_4S_{10} -benzoin reaction product in xylene solution.⁴ Green crystals of I are soluble in most organic solvents and can be recovered unchanged. The solid sample has a magnetic moment of 1.79 B.M. and in CHCl_3 and THF gives a single broad e.s.r. line (width, 75 gauss) at $g = 2.015 \pm 0.003$ (in good agreement with the observed magnetic moment). Furthermore, a polycrystalline sample shows but one broad line (width, 60 gauss), also at $g = 2.015 \pm 0.003$. This line appears to be symmetrical, indicating little if any anisotropy in the g tensor. A frozen glass e.s.r. spectrum of I at 77°K. in DMF-CHCl_3 shows a complex hyperfine pattern but little anisotropy in the g

(3) F. Basolo and R. C. Johnson, "Coordination Chemistry," W. A. Benjamin, Inc., New York, N. Y., 1964, p. 12.

(4) G. N. Schrauzer, V. Mayweg, H. W. Finck, U. Müller-Westerhoff, and W. Heinrich, *Angew. Chem.*, **76**, 345 (1964).

(5) G. N. Schrauzer, H. W. Finck, and V. Mayweg, *ibid.*, **76**, 715 (1964).

(6) J. H. Waters, R. Williams, H. B. Gray, G. N. Schrauzer, and H. W. Finck, *J. Am. Chem. Soc.*, **86**, 4198 (1964).

(7) R. Eisenberg and J. A. Ibers, *ibid.*, **87**, 3776 (1965).

(8) Rhenium forms complexes with unusual structures, e.g., ReH_3^{2-} (S. C. Abrahams, A. P. Ginsberg, and K. Knox, *Inorg. Chem.*, **3**, 558 (1964)), and $\text{Re}_2\text{Cl}_8^{2-}$ (F. A. Cotton and C. B. Harris, *ibid.*, **4**, 330 (1965)).

(9) The possibility of a trigonal-prismatic structure was first suggested for Co complexes containing bidentate sulfur-donor ligands, based on the dissimilarity of their electronic spectra with those of typical octahedral Co(III) systems.¹⁰

(10) C. H. Langford, E. Billig, S. I. Shupack, and H. B. Gray, *J. Am. Chem. Soc.*, **86**, 2958 (1964).

(11) R. B. King, *Inorg. Chem.*, **2**, 641 (1963).

(12) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *J. Am. Chem. Soc.*, **86**, 2799 (1964).

(13) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *Inorg. Chem.*, **4**, 55 (1965).

(14) The metals included to date are Co, Fe, Ru, Os, Re, Cr, Mo, W, and V. The ligands are $[\text{S}_2\text{C}_2\text{Ph}_2]$, $[\text{S}_2\text{C}_2(\text{CF}_3)_2]$, tdt (toluene-3,4-dithiolate), bdt (benzene-1,2-dithiolate), and mnt (maleonitriledithiolate).