

Quenching of the Triplet State of Acetone and Biacetyl by Various Unsaturated Hydrocarbons

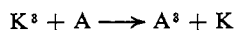
R. E. Rebbert and P. Ausloos

Contribution from the National Bureau of Standards, Washington, D. C. 20234.
Received August 2, 1965

The quenching effect of several unsaturated hydrocarbons on the emission from acetone, excited at 3130 Å., has been determined in the gas phase at 32°. It is noted that addition of an olefin usually results in a pronounced reduction of the phosphorescence emitted by acetone but that the fluorescence yield remains unchanged. It is suggested that acetone transfers its triplet energy to the olefin molecule. The probability that such an energy-transfer process occurs upon collision between the electronically excited acetone and a number of representative olefins is as follows: styrene, 0.5; 1,3-butadiene, 1.45×10^{-2} ; 2,3-dimethyl-2-butene, 1.45×10^{-4} ; 2-pentene, 2.1×10^{-5} ; 1-pentene, 0.65×10^{-5} ; ethylene, 0.26×10^{-5} . It is concluded that when the energy-transfer process is endothermic, the quenching efficiency increases with diminishing ΔH of the reaction. When the energy-transfer process is exothermic, no correlation is seen between the quenching efficiency and the ΔH of the reaction. Because of the low energy of the 0-0 band, corresponding to the S_0-T_1 transition in biacetyl, triplet-state energy transfer from biacetyl to most monoolefins occurs with very low efficiency. The probability that triplet energy will be transferred upon collision is as follows: 1,3-butadiene, 1.6×10^{-4} ; styrene, 2.5×10^{-5} ; 2,3-dimethyl-2-butene, 1.6×10^{-7} .

Introduction

In a number of recent investigations^{1,2} it was demonstrated that, in the gas phase, the phosphorescence emitted by acetone can readily be quenched by aldehydes and azoalkanes, while the fluorescence emission remains unchanged. The experimental observations in these studies were adequately accounted for by the triplet-triplet energy-transfer process



where K^3 represents the acetone molecule excited to the triplet state by an intersystem crossover from the upper singlet, and A^3 represents the aldehyde or azoalkane molecule in the triplet state. It was further demonstrated that biacetyl excited to the triplet state can transfer its electronic excitation energy to the azoalkanes with about the same efficiency as acetone.

In the present study, we report a number of observations related to the efficiency of olefins in quenching the triplet state of acetone and biacetyl in the gas phase. To our knowledge, little is known about the efficiency of olefins in quenching ketone molecules excited to the triplet state. Volman and Graven³ reported a quenching of the decomposition of acetone by 1,3-butadiene which can probably be ascribed to a transfer of electronic excitation energy. Coward and Noyes⁴ noted

that addition of as much as 182 torr of isobutene to 11 torr of biacetyl had little or no effect on the biacetyl phosphorescence, while Cundall and Palmer⁵ pointed out that isomerization of 2-butene sensitized by biacetyl was very inefficient. In the liquid phase, however, experiments carried out by Hammond and co-workers⁶ showed conclusively that various carbonyl compounds do transfer their triplet-state energy to a number of olefins.

Experimental Section

Apparatus. The apparatus used in the present investigation has been described before.⁷ For the acetone-olefin mixtures, the Bausch and Lomb grating monochromator (250-mm. focal length) was set at 3130 Å. (slits were 0.5 mm. wide). The intensity of the incident beam was approximately 10^{14} quanta $\text{cc.}^{-1} \text{sec.}^{-1}$. The light emitted by the mixture passed through a Corning 0-51 filter (transmitting above 3600 Å.) to a 1P28 photomultiplier tube. In the case of the biacetyl-olefin mixtures, the monochromator was set at either 3600 or 4358 Å., and a Corning 3-69 filter (transmitting above 5200 Å.) was inserted between the T-shaped high-quality quartz cell and the photomultiplier tube. The gases were continuously circulated through the quartz cell with a glass-circulating pump in order to ensure efficient mixing and to keep the conversion to a minimum. Although the actual measurements usually took only 5 to 30 sec., no noticeable change in the intensity of the emission could be recorded over a 10-min. period.

In order to prevent prolonged adsorption of the different compounds used in this study on certain parts of the vacuum line, stainless steel valves instead of stopcocks were used, and after each series of measurements the entire apparatus was heated by means of electrical heating tape to about 70°.

Materials. Spectrograde acetone and research grade biacetyl were obtained from the Eastman Organic Chemical Co. 1-cis-3-Pentadiene, 1,4-pentadiene, 1-methylcyclohexene, and cyclohexene were N.B.S. standard samples. Styrene, 2-pentene, 2-methyl-2-butene, 1-pentene, and 2-methyl-1-butene were obtained from the J. T. Baker Chemical Co. Research grade ethylene, propylene, butene-1, isobutene, cis-2-butene, trans-2-butene, and 1,3-butadiene were obtained from the Phillips Petroleum Co. The Chemical Procurement Laboratories, Inc., supplied the 2,3-dimethyl-2-butene. The purity of the compounds was verified by

(4) N. A. Coward and W. A. Noyes, Jr., *J. Chem. Phys.*, **22**, 1207 (1954).

(5) R. B. Cundall and T. F. Palmer, *Trans. Faraday Soc.*, **56**, 1211 (1960).

(6) G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *J. Am. Chem. Soc.*, **86**, 3197 (1964).

(7) R. P. Borkowski and P. Ausloos, *ibid.*, **84**, 4044 (1962).

(1) R. E. Rebbert and P. Ausloos, *J. Am. Chem. Soc.* **86**, 4803 (1964).

(2) R. E. Rebbert and P. Ausloos, *ibid.*, **87**, 1847 (1965).

(3) D. H. Volman and W. M. Graven, *ibid.*, **75**, 3111 (1953).

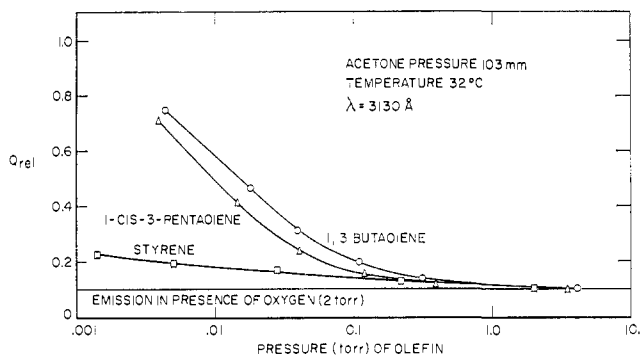


Figure 1. The relative emission from acetone vs. pressure of additive.

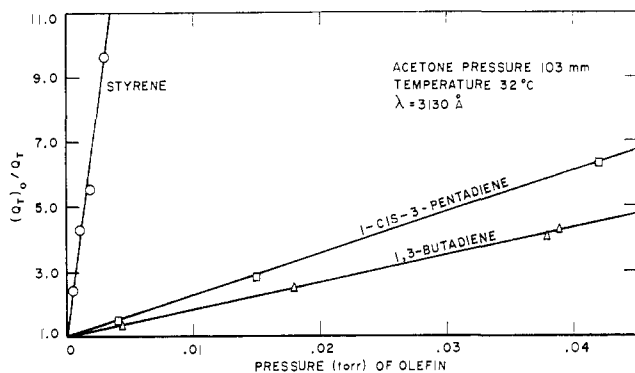


Figure 2. Plots of $(Q_T)_0/Q_T$ for acetone vs. pressure of olefin.

gas chromatography. On the basis of this analysis it was found necessary to purify some of the materials by trapping from the exit of a gas chromatograph. For instance, butene-1 contained a trace of 1,3-butadiene, which, if not removed, would lead to completely erroneous results. 1,2-Pentadiene and 1,4-pentadiene also required extensive purification because of the presence of 1,3-pentadiene.

Results

(a) *Acetone-Olefin Mixtures.* Figure 1 shows how, in the case of the three olefins with the highest quenching efficiencies, the relative yield of the emission from acetone approaches, at sufficiently high concentration of the olefin, a value for the relative emission yield Q_r ($Q_r = 1.0$ for pure acetone), which is about one-tenth that of the emission of pure acetone. Within experimental error the same value for the emission yield is obtained when 2 torr of oxygen is added to acetone or to any acetone-olefin mixture. The horizontal line in Figure 1 represents the values of Q_r observed for numerous acetone-olefin-oxygen mixtures containing any of the olefins listed in Table I. Emission spectra taken by means of a Aminco-Keir spectrophotometer further indicated that the emission spectrum of an acetone (100 torr)-styrene (2 torr) mixture was the same as that of an acetone (100 torr)-oxygen (2 torr) mixture. In accordance with the generally accepted view,⁸ the light emitted by acetone-oxygen or acetone-olefin-oxygen mixtures will be designated as fluorescence, while the emission which is being quenched by oxygen and which apparently originates from the triplet state will be designated as phosphorescence.

(8) W. A. Noyes, Jr., G. B. Porter, and J. E. Jolley, *Chem. Rev.*, **56**, 49 (1956).

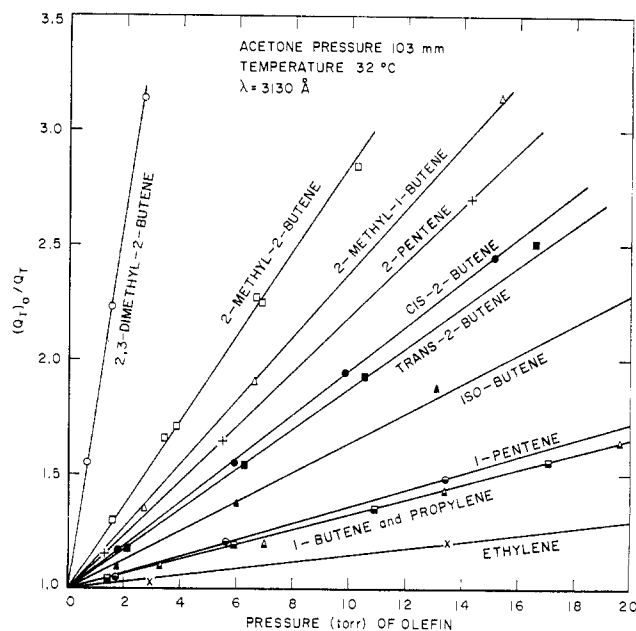


Figure 3. Plots of $(Q_T)_0/Q_T$ for acetone vs. pressure of olefin.

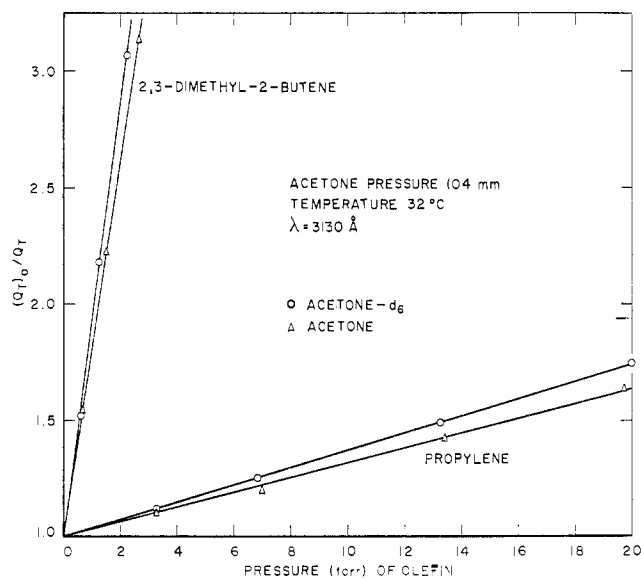


Figure 4. Plots of $(Q_T)_0/Q_T$ for acetone and acetone- d_6 vs. pressure of olefin.

In Figures 2, 3, and 4, $(Q_T)_0/Q_T$ has been plotted against the pressure of the added unsaturate. Q_T is obtained by subtracting the constant emission observed in acetone-olefin-oxygen mixtures from the total emission in the absence of oxygen. $(Q_T)_0$ is the emission for pure acetone minus that of constant emission observed for acetone-olefin-oxygen mixtures.

The effect of propylene and 2,3-dimethyl-2-butene on the emission of CD_3COCD_3 is illustrated in Figure 4. Corresponding experimental values obtained for the CH_3COCH_3 -containing mixtures is shown in the same figure. From these plots it can be derived that the olefins are about 1.14 times more effective in quenching the phosphorescence emitted by CD_3COCD_3 than that emitted by CH_3COCH_3 . It is of interest to note that at 32° and at a pressure of 100 torr the quantum yield of the phosphorescence as well as of the fluorescence

Table I. Relative Efficiencies of Olefins in Quenching Triplet Acetone^a

Styrene	1.0	1,2-Pentadiene	3.1×10^{-5}
1- <i>cis</i> -3-Pentadiene	4.4×10^{-2}	<i>trans</i> -2-Butene	3.1×10^{-5}
1,3-Butadiene	2.9×10^{-2}	Cyclohexane	3.0×10^{-5}
2,3-Dimethyl-2-butene	2.9×10^{-4}	Isobutene	2.2×10^{-5}
1-Methylcyclohexene	6.7×10^{-5}	1-Pentene	1.3×10^{-5}
2-Methyl-2-butene	6.4×10^{-5}	Propylene	1.1×10^{-5}
2-Methyl-1-butene	4.8×10^{-5}	1-Butene	1.1×10^{-5}
2-Pentene	4.2×10^{-5}	Ethylene	0.53×10^{-5}
1,4-Pentadiene	3.8×10^{-5}	Acetylene	$<5 \times 10^{-7}$
<i>cis</i> -2-Butene	3.3×10^{-5}	Benzene	$<5 \times 10^{-7}$

^a Acetone pressure, 103 torr; $\lambda = 3130 \text{ \AA.}$; 32° .

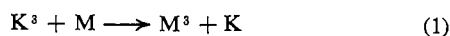
emitted by CD_3COCD_3 is about 30% above that for CH_3COCH_3 .

The relative efficiencies of the olefins in quenching the phosphorescence emitted by acetone are shown in Table I. These values are based on an arbitrary value of unity for styrene which is the most efficient deactivator. It should be noted that addition of up to 20 torr of benzene or acetylene to 100 torr of acetone did not, within experimental error, reduce the emission from acetone. On the basis of our limit of detection it can be estimated that, in order to quench the triplet emission from acetone, these two olefins must undergo at least 2×10^6 more collisions with the excited molecule than does styrene.

(b) *Biacetyl-Olefin Mixtures.* In the case of pure biacetyl (4358 \AA. , 32°) the fraction of the light recorded on the photomultiplier which can be ascribed to emission from the upper singlet, that is, emission which is not quenched by oxygen, is only 1% of the total emission. At 3660 or 4358 \AA. , addition of olefins such as ethylene and 1-pentene did not result in any noticeable reduction of the light emitted from biacetyl. Even the addition of 2,3-dimethyl-2-butene, which is the most efficient monoolefin in the acetone-containing mixtures, quenches the emission from biacetyl to only a very minor extent (Figure 5). Styrene and 1,3-butadiene, on the other hand, were considerably more efficient in quenching the phosphorescent emission from biacetyl than the monoolefins were.

Discussion

(a) *Acetone-Olefin Mixtures.* The results presented in this paper demonstrate that acetone can transfer its triplet-state energy to a large selection of olefins. The fact that only the phosphorescence emission is quenched upon addition of these olefins rules out any participation of the upper singlet state of acetone in the quenching mechanism. Moreover, if it is accepted that the Wigner spin conservation rule applies the energy-transfer reaction can be represented as



where K^3 represents a ketone molecule in a low vibrational level of the triplet state and M^3 a triplet olefin molecule excited to an unspecified vibrational level, probably the lowest level if reaction 1 is endothermic. If one includes reaction 1 in the mechanism generally proposed to account for the fate of the triplet acetone molecule,⁹ the following equation can be derived

(9) (a) J. Hecklen and W. A. Noyes, Jr., *J. Am. Chem. Soc.*, **81**, 3858 (1959); (b) J. Hecklen, *ibid.*, **81**, 3863 (1959).

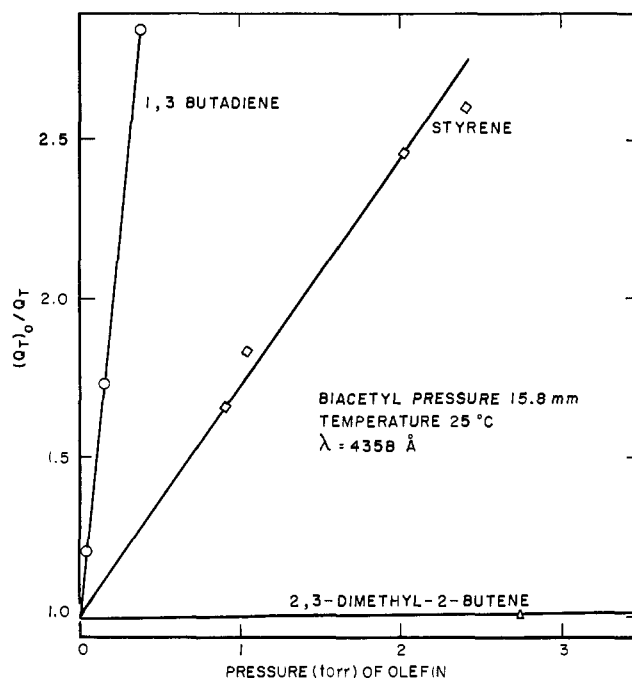


Figure 5. Plots of $(Q_T)_0/Q_T$ for biacetyl vs. pressure of additive.

$$\frac{(Q_T)_0}{Q_T} = 1 + \frac{k_1}{C}[\text{M}]$$

where C represents a summation of the rates of the reactions other than reaction 1 which K^3 can undergo. As seen in Figures 2, 3, and 4, the values of $(Q_T)_0/Q_T$ obtained at various concentrations of any particular added olefin fall on a straight line, the slopes of which provides us with a value of K_1/C . Although C is an unknown constant, it will be the same for all acetone-olefin mixtures so that the slopes of the plots in Figures 2, 3, and 4 provide us with accurate values for the relative quenching efficiencies of the various olefins. The results thus obtained are listed in Table I, taking an arbitrary value of 1 for the quenching efficiency of styrene. The pressure of half-quenching of acetone by styrene is 3.5×10^{-4} torr. If a value of 6 \AA. is assumed for the average of the molecular diameter of acetone and styrene, and a value of 2×10^{-4} sec. is used for the lifetime of triplet-acetone,¹⁰ the probability that acetone will transfer its triplet energy to styrene upon collision is 0.5. Consequently, neglecting differences in the collision cross section, division of the numbers given in Table I by a factor of two provides approximate values for the probability that any particular olefin will undergo a quenching collision with acetone at 32° .

It can be seen (Table I) that the quenching probabilities vary by more than a factor of 10^5 , depending on which olefin is added to acetone. Many of these changes can be qualitatively accounted for by changes in the ΔH of the energy-transfer reaction 1. Unfortunately, accurate information about the energies of the triplet states of the donor and acceptor molecules is not available. According to Hammond, *et al.*,¹¹ the zero vibrational level of the triplet state of acetone lies more

(10) W. E. Kaskan and A. B. F. Duncan, *J. Chem. Phys.*, **16**, 223 (1948).

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

than 70 kcal. above the ground state. On the other hand, because the zero-zero band of the S_0-S_1 transition can be placed around 3600 \AA ,⁸ the zero-zero band of the S_0-T_1 transition must correspond to less than 79 kcal. If one now accepts a value of 82 kcal. for the 0-0 band of the S_0-T_1 transition of ethylene,¹² then reaction 1 will be 3-12 kcal. endothermic. Although the energies of the triplet states of the other monoolefins have not been determined, it can be predicted that they will gradually decrease as more alkyl groups are substituted about the carbon-carbon double bond. Corresponding shifts to lower energies have been reported for the singlet-singlet transition in a series of olefins.¹³ It may thus be anticipated that, in the case of the monoolefins, the endothermicity of the energy transfer will diminish when the substitution about the double bond increases, and that there will be a corresponding increase of the efficiency of the energy-transfer process. The results given in Table I are consistent with this interpretation. It can, for instance, be seen that acetone transfers its triplet energy to propylene, 1-butene, and 1-pentene with about the same probability, indicating that an increase in molecular weight of the olefin does not greatly influence the efficiency of this process. On the other hand, there is a pronounced increase in the efficiency of process 1 for the C_5H_{10} isomers with increased alkyl substitution about the double bond. Similarly, substitution of a methyl group to the double bond of cyclohexene also enhances the probability for energy transfer. On the same basis, the fact that addition of acetylene and benzene to acetone did not result in any observable reduction of the phosphorescence yield is to be expected because the 0-0 band of the S_0-T_1 transition for benzene and acetylene corresponds to 84 and 92 kcal., respectively. The energy transfer from triplet acetone to these two compounds would thus be several kilocalories more endothermic than to ethylene.

Values of 59.5 and 62 kcal. can be assigned¹² to the triplet state of 1,3-butadiene and styrene, respectively. The energy-transfer reaction 1 is thus exothermic by at least 10 kcal./mole for these two conjugated olefins and presumably also for the 1-*cis*-3-pentadiene. The fact that triplet-state energy transfer to the conjugated olefin is exothermic probably accounts for the high probability of this process. It should, however, be noted that the efficiency of the energy-transfer process does not necessarily increase with an increase in the exothermicity of reaction 1. This is demonstrated by the fact that although triplet-state energy transfer to 1,3-butadiene is 2.5 kcal./mole more exothermic than to styrene, 1,3-butadiene is a less efficient quencher than styrene. The positions of the 0-0 band of the S_0-T_1 transition for the nonconjugated diolefins are not known, but on the basis of the results given in Table I they may be

(12) D. F. Evans, *J. Chem. Soc.*, 1351 (1957); 1735 (1960).

(13) E. P. Carr and M. K. Walker, *J. Chem. Phys.*, 4, 751, 756 (1936); E. P. Carr and H. Stücklen, *ibid.*, 4, 760 (1936); 6, 55 (1938).

expected to lie in the vicinity of those corresponding to the monoolefins.

The observation that the phosphorescence emitted by acetone- d_6 is quenched somewhat more readily than that emitted by acetone (Figure 4) can probably be explained on the basis of a difference in lifetime between triplet-state acetone and acetone- d_6 . It has been demonstrated before¹⁴ that in the case of aromatic compounds the triplet state of the deuterated molecule has a longer lifetime than that of the nondeuterated molecule. Also, isotope effects observed in recent studies of the photolysis of $CH_3N_2CH_3-CD_3N_2CD_3$ mixtures^{2,15} indicated that the dissociative lifetime of the deuterated azomethane is longer than that of the perprotonated molecule. It should finally be noted that the higher fluorescence and phosphorescence yield emitted by pure CD_3COCD_3 as compared to that emitted by CH_3COCH_3 (see Results) is also indicative of a longer dissociative lifetime of the deuterated molecule.

(b) *Biacetyl-Olefin Systems*. The fact that the smaller monoolefins have little or no effect on the phosphorescence emitted by biacetyl is consistent with the earlier observations made by Coward and Noyes. The low quenching efficiency is to be expected if one considers that the 0-0 band of the S_0-T_1 transition in biacetyl corresponds¹⁶ to about 56 kcal., so that for the smaller olefins the energy-transfer reaction 1 would be at least 14 kcal. more endothermic when biacetyl instead of acetone is used as the triplet donor. Triplet-state energy transfer does, however, occur to styrene and 1,3-butadiene and with a much smaller efficiency to 2,3-dimethyl-2-butene. Of considerable interest is the fact that, in contrast to the observations reported on the acetone-olefin mixtures, 1,3-butadiene quenches the phosphorescence emitted by biacetyl more effectively than does styrene. This amplifies our remark made earlier in this paper that it is only when the energy-transfer process is endothermic that the ΔH of the reaction plays a determining role. It should be noted that energy transfer from triplet biacetyl to 1,3-butadiene is 2.5 kcal. less endothermic than to styrene.

If we use a value of 6 \AA . for the collision diameter and a value of 1.8×10^{-8} sec. for the lifetime of triplet biacetyl,¹⁷ the following values are obtained for the probabilities that triplet energy transfer will occur upon collision between triplet biacetyl and the olefin: 1,3-butadiene, 1.6×10^{-4} ; styrene, 2.5×10^{-5} ; 2,3-dimethyl-2-butene, 1.6×10^{-7} .

Acknowledgment. This research was supported by a grant from the U. S. Public Health Service, Department of Health, Education and Welfare.

(14) C. A. Hutchinson and B. W. Mangum, *ibid.*, 32, 1261 (1960); M. R. Wright, R. P. Frosch, and G. W. Robinson, *ibid.*, 33, 934 (1960).

(15) P. Ausloos and E. Hatch, to be published.

(16) (a) G. N. Lewis and M. Kasha, *J. Am. Chem. Soc.*, 66, 2100 (1944); (b) W. G. Herbstroeter, A. A. Lamola, and G. S. Hammond, *ibid.*, 86, 4537 (1964).

(17) W. E. Kaskan and A. B. F. Duncan, *J. Chem. Phys.*, 18, 427 (1950).