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Triplet-State Energy Transfer in Liquid Solutions. Acetone-Photosensitized cis–trans Isomerization of Pentene-2

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Abstract: The acetone photosensitization of pentene-2 cis–trans isomerization and of biacetyl phosphorescence have been investigated in liquid solution. Spectroscopic evidence is presented which proves that the sensitization of pentene-2 proceeds from the triplet state of acetone and not from the singlet state. The quantum yields for the acetone-sensitized cis-to-trans and trans-to-cis processes in solution at 25° were found to be $\Phi_{CT} = 0.63$ and $\Phi_{TC} = 0.40$, respectively, for pentene-2 concentrations greater than about 1.0 M. Since $\Phi_{CT} + \Phi_{TC} = 1.0 \pm 0.1$, under these conditions, energy transfer from triplet acetone to pentene-2 is virtually 100% efficient. The sensitization constant K_S^P (product of the bimolecular energy-transfer rate constant k_t^P and the sensitizer lifetime τ_T) for energy transfer from triplet acetone to pentene-2 at 25° was found to be $K_S^P \simeq 10\ M^{-1}$, in a variety of solvents. This leads to a value for the energy-transfer rate constant of $k_t^P \approx 10^7\ M^{-1}\ sec^{-1}$, which is some three orders of magnitude smaller than the theoretical diffusion-controlled value. It is concluded that the bimolecular energy-transfer rate constant for the acetone–pentene-2 energy-transfer process actually involves three competing processes, with a triplet acetone and ground pentene-2 collision complex as an intermediate. In neat acetone solutions, the rates of triplet–acetone sensitization of pentene-2 isomerization and of biacetyl phosphorescence were found to be about five times larger than the corresponding sensitization rates in mixed solvent systems. The larger K_S values in neat acetone are interpreted in terms of triplet–triplet energy transfer between acetone molecules. The effect of dissolved oxygen on the energy-transfer process was investigated, and from these and other data it is concluded that the lifetime of the acetone triplet state in solution is quite short ($\sim 10^{-6}$ sec) as a result of some intrinsic deactivation process, rather than the result of oxygen or other impurity quenching. The acetone triplet-state lifetime was found to be temperature dependent, with $\tau_T(-78)/\tau_T(25) \simeq 20$ in methanol solution. We observed no deuterium effect on the acetone triplet-state lifetime in solution at room temperature.

I. Introduction

In the past few years there have been numerous investigations of photosensitized molecular rearrangements. One of the simplest and most widely investigated of these is the photosensitized cis–trans isomerization of olefins.[3–5] In order to fully char-

acterize a photosensitized reaction, it is necessary to determine: (1) the nature of the excited state of the sensitizer from which the energy is transferred; (2) the nature of the energy-transfer process, i.e., quantum efficiency, rate constant, temperature dependence, etc.; (3) the nature of the excited state of the reacting molecule which is sensitized, and the molecular rearrangement which results. In the present study, we have been primarily concerned with aspects 1 and 2 of the acetone sensitized isomerization of pentene-2.

In the ketone-photosensitized isomerization of mono-olefins and dienes, it is generally believed that the triplet state of the ketone sensitizes the triplet state of the

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(4) S. Sato, K. Kikuchi, and M. Tanaka, J. Chem. Phys., 39, 293 (1963).
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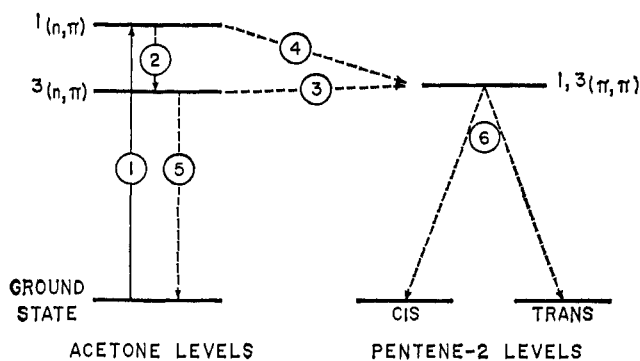
Figure 1. Rates of competing radiationless processes in energy transfer from excited acetone to pentene-2: (1) light absorption by acetone, (2) acetone intersystem crossing, (3) triplet-to-triplet energy transfer, (4) singlet-to-triplet energy transfer, (5) relaxation of acetone triplet state, without energy transfer, (6) relaxation of triplet-state pentene-2 to give cis- and trans-pentene-2.

olefin.[6-10] While the evidence on this point is reasonably convincing, theoretical considerations suggest that it is also possible for the *singlet* excited state of a ketone to sensitize the *triplet* state of an olefin (reaction 4, Figure 1).[11,12] For this and other reasons, a direct determination of the nature of the excited states involved in the acetone-sensitized pentene-2 isomerization seemed desirable.

The mechanism of the energy-transfer process in the ketone-sensitized isomerization of olefins is interesting in other respects. In the first place, Hammond[9] has suggested that this process may involve a non-Franck–Condon energy transfer. If this were the case, then one might expect the energy-transfer rate constant to depend on temperature, but there is little experimental information on this aspect of ketone–olefin energy transfer. Secondly, although triplet energy transfer between identical molecules is well known in crystalline systems,[13] there have been essentially no studies of triplet–triplet energy transfer between identical molecules in a liquid system. Since ketones are believed to function as triplet-state sensitizers of the olefin isomerization, these systems also appeared to provide a convenient means for investigating triplet–triplet energy transfer between ketone molecules in a liquid system.

In the present work we have examined in some detail the acetone-photosensitized isomerization of pentene-2 in a variety of solvent systems including neat acetone. To obtain additional information about the excited-state properties of acetone, we have also investigated the acetone-sensitized phosphorescence of biacetyl.

II. Experimental Details

Materials. The acetone was Baker and Adamson reagent, Matheson Coleman and Bell Spectroquality, or Volk 99.5% acetone-d_6. Methanol and hexane were MCB Spectroquality, heptane

was MCB Chromatoquality, and 3-methylpentane was Phillips technical grade. Ultraviolet analysis of the solvents showed no measurable absorption at wavelengths longer than acetone absorption. Vpc analysis showed that the main impurity in distilled Phillips technical grade cis-pentene-2 was trans-pentene-2; the only other peak in the vpc amounted to less than 0.1% of the pentene-2. trans-Pentene-2 was obtained by preparative vpc, starting with Phillips 99% mixed pentene-2. All solutions were degassed by repeated freezing, pumping, thawing, and shaking cycles. cis/trans ratios were determined by vpc, using a Wilkins QF-1 column.

Illumination. The light source was a 200-w superpressure mercury arc. Quantum yields were measured using a Jena 3130 A interference filter in the exciting beam, and an Eppley calibrated thermopile to measure the absorbed and transmitted light. (The manufacturer's calibration of the thermopile was checked by ferrioxalate actinometry.) For the concentration studies, a series of degassed samples were sealed in Pyrex tubes and irradiated simultaneously, with a superpressure mercury arc. The light intensity was monitored during the period of irradiation with an RCA 935 phototube. Since the Pyrex tubes did not transmit wavelengths shorter than about 3000 A, and since acetone only absorbs appreciably below 3300 A, only light in the region 3000–3300 A was effective. Most of the light was centered around the 3130-A Hg line.

In all experiments, irradiation times were sufficiently short so that the per cent conversion of cis-to-trans or trans-to-cis pentene-2 was small.

Emission spectra and lifetimes were obtained with the apparatus described previously.[14]

III. Results

A. Quantum Yields and Photostationary States. The results of a number of measurements of the quantum yields Φ_{CT} and Φ_{TC} for the acetone-photosensitized processes cis-pentene-2 → trans-pentene-2 and trans-pentene-2 → cis-pentene-2, in degassed solutions at 25°, are presented in Table I. The excitation wavelength was 3130 A in each case, and the quantum yield is defined by

$$\Phi = \frac{\text{net molecules of pentene-2 isomerized}}{\text{quanta absorbed by acetone}}$$

The Φ_{CT} and Φ_{TC} values were found to be constant for pentene-2 concentrations greater than about 1.0 M (limiting quantum yield), but fell off at lower concentrations. The sum of the limiting quantum yields Φ_{CT} + Φ_{TC} is seen to be on the order of 1.0 ± 0.1.

Table I. Quantum Yields for Acetone-Photosensitized Isomerization of Pentene-2 in Degassed Solution at 25°

Starting isomer	Solvent	Acetone concn, vol %	Quantum yield (±0.05)	Average
trans	Acetone	100	0.42	
trans	Methanol	50	0.38	Φ_{TC} = 0.40
cis	Acetone	100	0.64	
cis	Methanol	50	0.65	
cis	Heptane	20	0.61	Φ_{CT} = 0.63

The acetone-sensitized photostationary trans/cis ratio of pentene-2 was measured in several solvents at 300, 200, and 77°K, and the results are presented in Table II. Note that the 77°K measurements were carried out under conditions such that statistically every acetone molecule had at least one pentene-2 neighbor. The photostationary state was determined by approaching from both the trans-rich and cis-rich directions. Fi-

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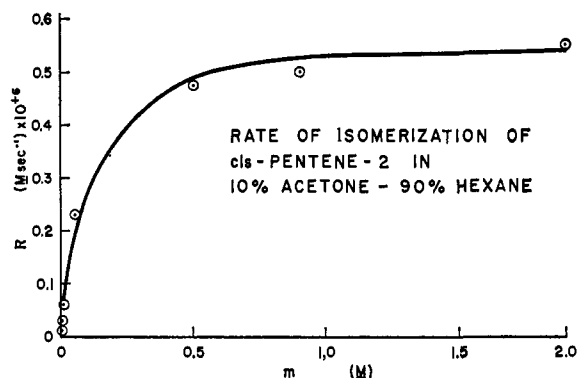(14) R. F. Borkman and D. R. Kearns, *ibid.*, 44, 945 (1966).

Figure 2. Rate of acetone-photosensitized isomerization of cis-pentene-2 vs. pentene concentration in 10% acetone–90% hexane solution.

nally, a solution with this photostationary composition was prepared and illuminated for a period of time to verify that the composition remained unchanged. The ratio of quantum yields, $\Phi_{CT}/\Phi_{TC} = 1.6 \pm 0.2$ at $25°$, was equal within experimental error to the photostationary ratio $[trans]_S/[cis]_S = 1.7$ at $25°$. This provides a check of the internal consistency of our results. In addition, our measured photostationary ratio at $25°$ is in agreement with the value obtained by Hammond, et al.,[15] at $25°$.

Table II. Acetone-Photosensitized Pentene-2 Photostationary Ratio

Solvent	Pentene-2 concn, M	Acetone concn, vol %	Temp, °K	$[trans]_S/[cis]_S$
Heptane	0.01	10	300	1.8 ± 0.1
Methanol	0.01	10	300	1.7
Acetone	0.5	100	300	1.7
Ether–IPA	0.5	10	300	1.7
Ether–IPA	0.5	10	200	2.5
Acetone	1.0	100	200	2.5
Ether–IPA	1.0	30	77	1.1

The rates of competing side reactions appeared to be negligible relative to the isomerization reaction. A vpc analysis of the volatile products from an irradiated solution of acetone and pentene-2 showed, for example, that the quantum yield for the production of methane (the major product of acetone photolysis in solution)[16] was on the order of $\Phi(CH_4) = 0.005$, compared to the isomerization quantum yield of $\Phi_{CT} + \Phi_{TC} = 1.0$.

B. Sensitization Rate Constants. (i) **Solvent Dependence.** The initial rates of the acetone-photosensitized isomerization of cis- and trans-pentene-2 were measured as a function of pentene-2 concentration in various degassed solvents at room temperature. Typical plots of the initial rate of isomerization, R, as a function of the pentene-2 concentration, m, and of R^{-1} vs. m^{-1} are shown in Figures 2 and 3. It may be noticed from Figure 2 that R approaches a constant limiting value, R_{max}, at pentene-2 concentrations greater than about 1 M. From these rate data, we have calculated (see Appendix) the quenching or sensitization
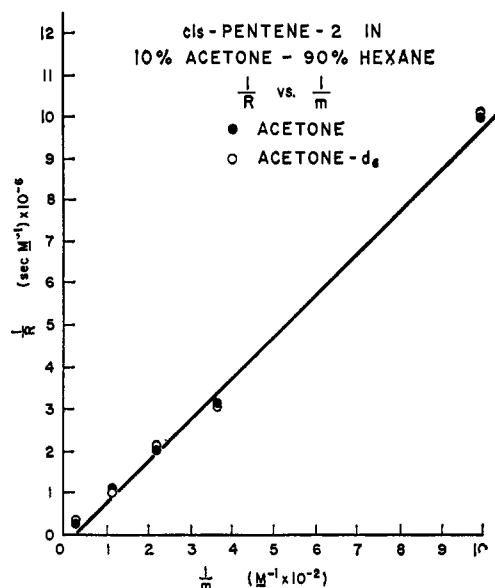
(15) G. S. Hammond, N. J. Turro, and P. A. Leermakers, J. Phys. Chem., 66, 1144 (1962).

(16) R. Pieck and E. W. R. Steacie, Can. J. Chem., 33, 1304 (1955).

Figure 3. Reciprocal rate vs. reciprocal pentene concentration for cis-pentene-2 in 10% acetone–90% hexane solution.

constant, K_S^P, defined by $K_S^P = \tau_T k_t^P$ for energy transfer from triplet acetone to pentene-2, where τ_T is the acetone triplet-state lifetime in solution, and k_t^P is the rate constant for energy transfer. The K_S^P values obtained in this way are shown in Table III. It may be noted from these data that, with the exception of the neat acetone solutions, K_S^P was within experimental error the same in all solvent systems used. In neat acetone solution, K_S^P was about five times larger.

Table III. Sensitization Constants for Energy Transfer from Triplet Acetone to Pentene-2 in Degassed Solution at $25°$

Starting isomer	Solvent	Acetone concn, vol %	Sensitization constant, K_S^P, M^{-1} $\pm 30\%$
cis	Methanol	10	8
cis	3-Methylpentane	13	6
cis	Hexane	10	10
cis	Methanol	10	10
cis	Heptane	10 (acetone-d_6)	10
cis	Hexane	10 (acetone-d_6)	10
cis	Methanol	10 (acetone-d_6)	10
trans	Hexane	10	6
cis	Acetone	100	44
cis	Acetone	100	40
trans	Acetone	100	60

In conjunction with the photosensitized isomerization studies, we investigated the acetone-sensitized phosphorescence of biacetyl in liquid solutions. By a method analogous to that employed for the isomerization results, we obtained values for the acetone–biacetyl sensitization constant, defined by $K_S^B = k_t^B \tau_T$. In a degassed 0.05 M acetone solution in hexane at $25°$, we obtained $K_S^B = 3 \times 10^3$ M^{-1}, while in neat acetone, we found $K_S^B = 18 \times 10^3$ M^{-1}. Although there is considerable uncertainty in these values, the sensitization constant in neat acetone is clearly greater than that in hexane solution, $K_S^B(\text{neat})/K_S^B(\text{hexane}) =$

6 ± 3. It should be noted that this ratio of sensitization constants is comparable to the ratios $K_S{}^P(\text{neat})/K_S{}^P(\text{mixed solvents})$ obtained from the acetone-pentene-2 data in Table III.

(ii) Deuterium Effect. The sensitization constant for the acetone-d_6-photosensitized isomerization of pentene-2 was measured and found to be identical with that obtained with acetone-h_6. These results are also presented in Table III.

(iii) Oxygen Effect. In nondegassed (aerated) hexane solution the sensitization constant $K_S{}^P$ for energy transfer from acetone to cis-pentene-2 was found to be on the order of 1.0 M^{-1}, or about a factor of 10 less than the values shown in Table III for degassed solutions. It was observed, however, that a mild degassing treatment sufficed to restore the sensitization rate to 10 M^{-1}, the value observed in well-degassed solutions. That is, insofar as the photosensitized isomerization was concerned, a single degassing to a pressure of about 0.1 mm above the frozen solution was as effective as four or five freeze–pump–thaw cycles at 10^{-3} mm, including a bulb-to-bulb vacuum distillation in each cycle. (Qualitatively similar results were obtained in neat acetone.) The oxygen concentration in the aerated solutions was assumed to be on the order of 10^{-3} M, the published oxygen solubility at $25°$.[17] The oxygen concentration in the well-degassed soutions was estimated by measuring the phosphorescence lifetime of biacetyl, in a sample of solvent subjected to the same degassing procedure as used in the isomerization studies. The oxygen concentration in degassed solution, calculated from our biacetyl emission data, assuming diffusion-controlled oxygen quenching of the triplet state,[18] was on the order of 10^{-6} M.

(iv) Temperature–Viscosity Effects. The rate of isomerization of a 2 M solution of cis-pentene-2 in a solvent consisting of acetone, 2-propanol, and ether, in a ratio of 1:1:2, was investigated at room temperature, $200°K$, and $77°K$. Under these high-concentration conditions, the rate, $R = R_{\max}$, is directly proportional to Φ_{CT} (see Appendix). Thus, the relative $R_{\max}$ values, in conjunction with the value $\Phi_{CT} = 0.63$ at $300°K$, reported in section IIIA, permitted calculation of Φ_{CT} at 200 and $77°K$. The results were: $\Phi_{CT} = 0.75$ at $200°K$ and 0.47 at $77°K$, with an uncertainty of about 10% in each case. These values, together with the photostationary ratios in Table II, and the relation $\Phi_{CT}/\Phi_{TC} = [trans]_S/[cis]_S$, permit calculation of Φ_{TC} at 200 and $77°K$, with the results: $\Phi_{TC} = 0.30$ at $200°K$ and 0.43 at $77°K$. From these data we see that within experimental error $\Phi_{CT} + \Phi_{TC} = 1.0$ at all three temperatures.

The effect of temperature on the rate of acetone-photosensitized cis-pentene-2 isomerization was also investigated at low pentene-2 concentrations. Under these conditions, the rate, $R = R_{\text{low}}$ can be used to calculate $K_S{}^P$ (see Appendix). R_{low} was measured at 25 and $-78°$, and the quantity $K_S{}^P(25)/K_S{}^P(-78)$ was calculated from the measured ratio $R_{\text{low}}(25)/R_{\text{low}}(-78)$. The results obtained for 10^{-2} M cis-pentene-2 are shown in Table IV.

(17) J. H. Hildebrand and R. L. Scott, "Solubility of Non-Electrolytes," 3rd ed, Reinhold Publishing Corp., New York, N. Y., 1950, p 243.

(18) H. L. J. Backstrom and K. Sandros, *Acta Chem. Scand.*, **12**, 823 (1958).

Table IV. Temperature Dependence of Acetone Sensitization of Pentene-2 Isomerization or Biacetyl Phosphorescence in Liquid Solution

Acceptor	Concn, M	Solvent	$K_S(25)/K_S(-78)$
cis-Pentene-2	1×10^{-2}	Methanol	1[a]
cis-Pentene-2	1×10^{-2}	Neat acetone	2[a]
Biacetyl	1×10^{-4}	Methanol	0.5[b]
Biacetyl	1×10^{-4}	Ethanol–toluene	0.5[b]
Biacetyl	3×10^{-5}	Neat acetone	3[b]

[a] $K_S{}^P(25)/K_S{}^P(-78) = [R_{\text{low}}(25)/R_{\text{low}}(-78)][\Phi_{CT}(-78)/\Phi_{CT}(25)]$; see Appendix. [b] $K_S{}^B(25)/K_S{}^B(-78) = [I_P(25)/I_P(-78)][\tau_P{}^B(-78)/\tau_P{}^B(25)]$; see text, section IVB.

The temperature dependence of acetone-photosensitized biacetyl phosphorescence was also investigated in liquid solution. The ratio of biacetyl phosphorescence intensities, $I_P(25)/I_P(-78)$, was measured, and the quantity $K_S{}^B(25)/K_S{}^B(-78)$ was calculated (see section IVB). These results are also presented in Table IV.

IV. Discussion

A. Nature of the Excited State of Acetone Which Sensitizes Pentene-2 Isomerization. If we assume that the cis–trans isomerization reaction proceeds through a common intermediate,[19,20] then the fact that $\Phi_{CT} + \Phi_{TC} = 1.0 \pm 0.1$, for [pentene-2] > 1.0 M, implies that $\Phi_{ET} = 1.0 \pm 0.1$, where the energy-transfer quantum yield is defined by

$$\Phi_{ET} = \frac{\text{number of pentene-2 molecules sensitized}}{\text{number of quanta absorbed by acetone}}$$

That is, under these conditions, every excited acetone molecule eventually transfers its excitation energy to a pentene-2 molecule. Note that this says nothing about the efficiency of energy transfer during a single acetone–pentene-2 collision.

We previously reported that the fluorescence of acetone in solution at room temperature was totally unaffected by pentene-2, even when pentene-2 was used as the solvent, but that the phosphorescence of acetone at $77°K$ was completely quenched by pentene-2.[14] We conclude that energy transfer to pentene-2 proceeds only from the phosphorescent triplet state of acetone, and not from the singlet state. Because the over-all efficiency of the sensitization process is near unity, the intersystem crossing yield from the excited singlet to the excited triplet state of acetone must also be near unity, $\Phi_{IC} = 1.0 \pm 0.1$.

Although these results establish that the photosensitization process proceeds from the triplet state of acetone, they do not prove that the triplet state of the olefin is involved. Assuming that the Wigner spin rules are not violated, triplet-state pentene-2 molecules should be produced by energy transfer from triplet acetone.

(19) The assumption of a common intermediate is based on theoretical predictions,[6] and on the fact that $\Phi_{CT} + \Phi_{TC}$ is found to be unity for several other photosensitized cis–trans isomerizations.[10] In a common intermediate process, we have $0 \leq \Phi_{CT} + \Phi_{TC} \leq 1$, whereas in a two-intermediate process, $0 \leq \Phi_{CT} + \Phi_{TC} \leq 2$; see ref 20. The fact that $\Phi_{CT} + \Phi_{TC}$ has never been found to exceed unity provides strong evidence that the cis–trans isomerization reaction is a one-intermediate process.

(20) Z. R. Grabowski and A. Bylina, *Trans. Faraday Soc.*, **60**, 1131 (1964).

Because we have been unable to detect, by electron spin resonance, the production of pentene-2 in its triplet state,[21] we do not have direct proof for the involvement of the pentene-2 triplet state in the photosensitization reaction. If an excited singlet state of pentene-2 were being sensitized by energy transfer from the triplet state of acetone, it is indeed remarkable that no energy transfer from the higher lying singlet state of acetone could be observed, even in neat pentene-2 solutions of acetone.

B. Lifetime of Acetone Triplet State in Solution.
(i) Evidence That the Acetone Triplet-State Lifetime in Degassed Solution Is Intrinsic.
Triplet–triplet absorption[22] and phosphorescence emission studies[14] have established $\tau_T \leq 3 \times 10^{-5}$ sec for the lifetime of triplet acetone in room temperature liquid solution. From a quenching study, Wilkinson and Dubois[23] found a value of $\tau_T = 4 \times 10^{-7}$ sec. As this value was based on the assumption of diffusion-controlled energy transfer from acetone to biacetyl, it must be taken as a lower limit on the true lifetime. Any of the following processes could be responsible for this short triplet-state lifetime in solution: (i) diffusion-controlled quenching by molecular oxygen, (ii) diffusion-controlled quenching by other impurities in solution, or (iii) a rapid intrinsic relaxation process (including perhaps a reversible excited-state decomposition or reaction, direct conversion of electronic excitation energy into vibrational energy, etc.).

The following experimental results indicate that the short triplet-state lifetime of acetone, in degassed solution at room temperature, is not due to quenching by oxygen.

(1) We were able to observe phosphorescence from biacetyl, in degassed solutions identical with those used in the isomerization studies, and the observed biacetyl lifetime (8×10^{-5} sec) indicates that the concentration of oxygen was less than 10^{-6} M. This should have been low enough to permit observation of acetone phosphorescence under the same conditions, if the acetone lifetime were determined primarily by oxygen quenching, but no phosphorescence was observed.

(2) It was found that the sensitization constant, K_S^P, was lower in aerated than in degassed solutions, but that a mild degassing restored the rate to that observed in the well-degassed solutions. If the acetone triplet-state lifetime were determined by oxygen, the ratio of K_S^P in the degassed solution ($[O_2] \simeq 10^{-6}M$) to that in the aerated solution ($[O_2] \simeq 10^{-3}$ M) would be 10^3, whereas, experimentally, we find K_S^P(degassed)/K_S^P(aerated) $\simeq 10$. It should be noted that the ratio of aerated and degassed K_S^P values, 10, together with the assumption that the aerated lifetime is determined by

diffusional oxygen quenching according to $\tau_T = (k_D \cdot [O_2])^{-1} = 1 \times 10^{-7}$ sec, implies a lifetime in degassed solution of 1×10^{-6} sec, in reasonable agreement with the value of Wilkinson and Dubois.

The following observations suggest that the triplet-state lifetime is not a result of quenching by other impurities in our solutions.

(3) We found that the sensitization constant $K_S^P = k_t^P \tau_T$ for triplet-energy transfer from acetone to pentene-2 was independent of solvent (except for the special case of neat acetone which is discussed below). Since k_t^P should be a constant for all solvents of the same viscosity,[24] we conclude that the lifetime τ_T is the same in the various solvents. For these studies we purposely used a variety of solvents, ranging from nonpolar (hexane and 3-methylpentane) to very polar solvents like methanol. In particular, the 3-methylpentane was a technical grade material and no effort was made to purify it.

Thus, our solvents undoubtedly contained very different kinds and amounts of impurities, and it is unlikely that the same quenched lifetime would be obtained in every case.

Since acetone was a common ingredient in all of the solutions, one might suppose that some impurity in acetone itself was responsible for the short triplet-state lifetime of acetone. In our experiments, we used several kinds of acetone: reagent, Spectroquality, and acetone-d_6 from an entirely different source, and the apparent acetone lifetime was the same in every case. Furthermore, the apparent acetone triplet-state lifetime was found to increase, not decrease, when neat acetone was used as the solvent. These results suggest that the lifetime of the acetone triplet state is not due to quenching by impurities in the acetone or to self-quenching.

Pentene-2 was also a common ingredient in the solutions studied. The cis-pentene-2 was obtained commercially, and was purified by a simple distillation. trans-Pentene-2 was prepared and purified by preparative vpc, starting with commercial mixed pentene-2, and hence should have been considerably purer than the cis material. In spite of the different origins of the pentene-2 samples, the same apparent lifetime for acetone was obtained.

(4) While carrying out preliminary isomerization studies to determine the initial rate behavior, we observed that the rate of acetone-sensitized pentene-2 isomerization was constant for irradiation times corresponding to pentene-2 conversions (e.g., for cis → trans) from 0 to 15%. For longer irradiation times the measured rate of isomerization began to decrease, owing to the trans → cis back reaction, as predicted by integration of our rate equations (Appendix). The initial constancy of the rate indicates that the acetone lifetime was not changing appreciably as the irradiation proceeded. This result suggests that the acetone triplet-state lifetime was not determined by any photochemically generated impurity, which might accumulate as the irradiation proceeded.

(5) Although both acetone and 1-bromonaphthalene phosphoresce in rigid media at 77°K, only the latter compound exhibited any detectable phosphorescence emission in a rigid glycerine solution at Dry Ice temperature. The fact that we were able to observe

(21) We were unable to observe electron spin resonance from triplet-state pentene-2, in an acetone–ether–2-propanol glass at 77°K, under conditions where pentene-2 was known to be undergoing isomerization. Using the same experimental setup, we were easily able to observe the $\Delta m = 2$ transition for naphthalene in ether–IPA glass at 77°K. These results suggest that the concentration of triplet pentene-2 was on the order of 10^2- to 10^3-fold smaller than the concentration of triplet-state naphthalene, or that the lifetime of pentene-2 triplet state was less than 10^{-3} sec under these conditions. It is also possible that the failure to observe an epr signal is due to the large zero-field splitting expected in monoolefins. An attempt to observe spin resonance in the same system at 4°K was also unsuccessful.

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(23) F. Wilkinson and J. T. Dubois, *J. Chem. Phys.*, 39, 377 (1963).

(24) S. Siegel and H. Judeikis, *ibid.*, 41, 648 (1964).

1-bromonaphthalene phosphorescence indicates that quenching impurities including oxygen were not mobile in the frozen glycerine lattice at 200°K. Although the impurities which might quench the triplet state of acetone are not necessarily the same as those responsible for 1-bromonaphthalene quenching, it seems reasonable to assume that the impurities responsible for acetone quenching would also be immobile in the frozen glycerine lattice. Yet, we could observe no acetone phosphorescence in the frozen glycerine solutions at 200°K. This result indicates that the acetone triplet-state lifetime is intrinsically short ($<3 \times 10^{-5}$ sec) even at 200°K in rigid glycerine solution.

From these various observations, we conclude that the triplet-state lifetime of acetone in solution at room temperature is determined by some intrinsic decay process, rather than by a diffusion-controlled impurity quenching mechanism.

(ii) Temperature Dependence of Acetone Triplet State. Lifetime in Liquid Solution. The Acetone–Biacetyl System. If the concentration of biacetyl in solution is sufficiently low ([biacetyl] $<10^{-3}$ M), direct light absorption by biacetyl and singlet-state energy transfer from acetone to biacetyl are of negligible importance,[23] and the intensity of triplet-state acetone-sensitized phosphorescence of biacetyl is given by

$$I_P = \frac{\Phi_P{}^B k_t{}^B \Phi_{IC} L[B]}{\tau_T{}^{-1} + k_t{}^B[B]}$$

where $\Phi_P{}^B$ = quantum yield for biacetyl phosphorescence, L = light absorbed by acetone, Φ_{IC} = intersystem-crossing yield of acetone, τ_T = acetone triplet-state lifetime, and $k_t{}^B$ = bimolecular rate constant for acetone-to-biacetyl triplet energy transfer. For [B] $\leq$ 10^{-4} M, I_P is approximately of the form

$$I_P = K_S{}^B \Phi_P{}^B L[B]$$

where $K_S{}^B = k_t{}^B \tau_T$ and $\Phi_{IC} = 1.0$. The ratio $I_P(-78)/I_P(25)$ is thus given by

$$\frac{I_P(-78)}{I_P(25)} = \frac{K_S{}^B(-78)\Phi_P{}^B(-78)}{K_S{}^B(25)\Phi_P{}^B(25)}$$

If we assume that the *radiative* triplet $\rightarrow$ ground transition probability in biacetyl is independent of temperature, we have $\tau_P{}^B(25)/\tau_P{}^B(-78) = \Phi_P{}^B(25)/\Phi_P{}^B(-78)$, and

$$\frac{K_S{}^B(-78)}{K_S{}^B(25)} = \frac{I_P(-78)}{I_P(25)} \frac{\tau_P{}^B(25)}{\tau_P{}^B(-78)}$$

where $\tau_P{}^B$ is the phosphorescence lifetime of biacetyl. For 10^{-4} M biacetyl in methanol–acetone solution, we have (Table IV)

$$\frac{K_S{}^B(-78)}{K_S{}^B(25)} = \frac{\tau_T(-78)}{\tau_T(25)} \frac{k_t{}^B(-78)}{k_t{}^B(25)} = 2$$

Since the difference in triplet-state energies of biacetyl and acetone is quite large, about 8000 cm^{-1}, it is likely that triplet energy transfer from acetone to biacetyl will be nearly diffusion controlled.[25] If we assume that $k_t{}^B = k_D$, where k_D is the bimolecular rate constant for

a diffusion-controlled process, and is inversely proportional to the viscosity η, then

$$\frac{\tau_T(-78)}{\tau_T(25)} \frac{\eta(25)}{\eta(-78)} = 2$$

In methanol $\eta(25)/\eta(-78) = 0.1$, so that $\tau_T(-78)/\tau_T(25)$ = 20. This indicates that the triplet-state lifetime of acetone in methanol solution increases by a factor of about 20 upon cooling to $-78°$. Since $\tau_T(25) \simeq 10^{-6}$ sec, we conclude that $\tau_T(-78) \simeq 10^{-5}$ sec.

C. Nature of the Acetone–Pentene Triplet Energy-Transfer Process. **(i) Magnitude of the Energy-Transfer Rate Constant.** Wilkinson and Dubois[23] studied triplet-state energy transfer from acetone to biacetyl and obtained a sensitization constant of $K_S{}^B = 8 \times 10^3$ M^{-1} in degassed hexane solution at 25°. Comparing this value with our value of $K_S{}^P$ for the acetone–pentene-2 system, in degassed hexane at 25°, we find
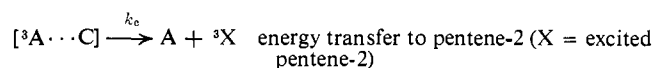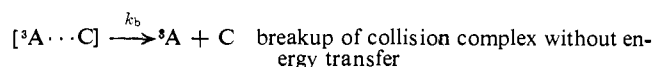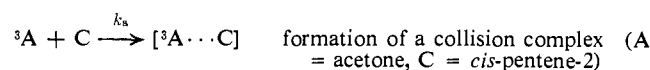
$$\frac{K_S{}^P}{K_S{}^B} = \frac{k_t{}^P \tau_T}{k_t{}^B \tau_T} = 10^{-3}$$

or, since the lifetime factor should cancel out

$$k_t{}^P/k_t{}^B = 10^{-3}$$

Consequently, in hexane solutions, and presumably in our other solvents, triplet energy transfer from acetone to pentene-2 at room temperature is about *1000-fold slower* than transfer from acetone to biacetyl. Triplet energy transfer from acetone to biacetyl is presumably diffusion controlled[25] and therefore $k_t{}^P \simeq 2 \times 10^7$ M^{-1} sec^{-1}.

The fact that $k_t{}^P$ is less than diffusion controlled implies that the energy-transfer step, which was originally taken to be a single step (see Appendix, reactions 3 and 3'), must actually involve the following three distinct steps. The symbol [^{3}A $\cdots$ C] denotes a

^{3}A + C $\xrightarrow{k_a}$ [^{3}A$\cdots$C]   formation of a collision complex (A = acetone, C = *cis*-pentene-2)

[^{3}A$\cdots$C] $\xrightarrow{k_b}$ ^{3}A + C   breakup of collision complex without energy transfer

[^{3}A$\cdots$C] $\xrightarrow{k_c}$ A + ^{3}X   energy transfer to pentene-2 (X = excited pentene-2)

collision complex, in which pentene-2 is adjacent to an excited acetone molecule, but in which the excitation energy still resides on the acetone. Transfer of energy from an excited pentene-2 molecule back to acetone[3,26] has not been included for several reasons. In the first place, energy transfer is *more* efficient, not less efficient, when neat acetone is used as the solvent (Table III). Secondly, relaxation of the vibrationally and electronically excited pentene-2 is expected to be too rapid to allow back transfer to occur. If we invoke the steady-state approximation, and set d[^{3}A $\cdots$ C]/dt = 0, we find that the over-all bimolecular energy-transfer rate constant $k_t{}^P$ can be reexpressed as

$$k_t{}^P = (k_a k_c)/(k_b + k_c) = k_a \chi$$

where the "collision efficiency," $\chi = k_c/(k_b + k_c)$, is the fraction of collisions between excited acetone and

(25) G. Porter and F. Wilkinson, *Proc. Roy. Soc.* (London), **A264**, 1 (1961).

(26) H. L. J. Backstrom and K. Sandros, *Acta Chem. Scand.*, **16**, 958 (1962).

ground-state pentene-2 molecules resulting in energy transfer to pentene-2. If the nearest-neighbor energy-transfer rate, k_c, is fast compared to the rate of "break-up" of the complex, k_b, then $\chi \rightarrow 1$, $k_t{}^P = k_a$, and the process will be diffusion controlled. If, however, $k_c \ll k_b$, then $k_t{}^P = k_c(k_a/k_b)$, and $k_t{}^P$ should then be less than diffusion controlled and independent of viscosity, since k_a and k_b should have the same viscosity dependence.[27] If we assume that the $[^3A\cdots C]$ complex has negligible stability (i.e., a collision complex) then k_a and k_b will have the same temperature dependence, and $k_t{}^P$ will depend on temperature only if k_c is temperature dependent. In the mixed solvent systems, we found $k_t{}^P \simeq 10^{-3}k_D$, indicating that $\chi = 10^{-3}$ and $k_c = 10^{-3}k_b$. (Theoretically, $k_b = 4.4 \times 10^9$ sec^{-1}, and thus $k_c = 4.4 \times 10^6$ sec^{-1}.[27]) We, therefore, predict that energy transfer from acetone to pentene-2 will be independent of viscosity and that any temperature dependence in $k_t{}^P$ will arise from k_c.

(ii) **Temperature Dependence of the Sensitization Rates.** For low pentene-2 concentrations, the limiting rate is given by (see Appendix)

$$R_{\text{low}} = \Phi_{\text{CT}}LK_S{}^P m$$

where m is the cis-pentene-2 concentration. Thus, for a fixed light intensity and fixed m, R_{low} is proportional to $K_S{}^P$. From Table IV we have

$$K_S{}^P(25)/K_S{}^P(-78) = 1$$

or

$$\frac{k_t{}^P(25)}{k_t{}^P(-78)} \frac{\tau_T(25)}{\tau_T(-78)} =$$

$$\frac{k_c(25)}{k_c(-78)} \frac{\tau_T(25)}{\tau_T(-78)} \frac{k_a(25)/k_b(25)}{k_a(-78)/k_b(-78)} = 1$$

To the extent that the collision complex has negligible stability, the ratio k_a/k_b should be independent of temperature and viscosity, and, therefore

$$\frac{k_c(25)}{k_c(-78)} \frac{\tau_T(25)}{\tau_T(-78)} = 1$$

Since $\tau_T(25)/\tau_T(-78) = {}^1/_{20}$ (section B), we have $k_c(25)/k_c(-78) = 20$; i.e., the nearest-neighbor energy-transfer rate constant, k_c, for triplet energy transfer from acetone to pentene-2, is temperature dependent with an activation energy on the order of 1500 cm^{-1}.

The question arises as to why energy transfer from acetone to pentene-2 should be three orders of magnitude slower than the theoretical diffusion-controlled limit, and why k_c is temperature dependent. In this regard we note that the triplet-state energy of acetone has been estimated to be 28,000 cm^{-1},[14] and the triplet-state energy of pentene-2, while unknown, will presumably be similar to that of ethylene, about 29,000 cm^{-1}.[28] These triplet-state energies imply that triplet–triplet energy transfer from acetone to pentene-2 is endothermic and, therefore, might require an activation energy on the order of 1000 cm^{-1}. This is consistent with the observed temperature dependence of k_c, but only in the range 25 to $-78°$. The fact that energy transfer from acetone to pentene-2 competes

with acetone phosphorescence at 77°K indicates that energy transfer does not proceed exclusively by a thermally activated mechanism with an activation energy of 1500 cm. (If it did, the rate at 77°K would have been only 0.4, instead of the observed $k_c \geq 10\tau_P{}^{-1} = 10^4$ sec^{-1}.) The discrepancy between the observed and calculated k_c values at 77°K may be due to the large uncertainty in the activation energy for k_c. Alternatively, it is possible that there are two energy-transfer mechanisms: a thermally activated process which predominates near room temperature, and a quantum-tunneling process which becomes important at lower temperatures. The possibility of more than one energy-transfer mechanism is suggested by our studies of the photostationary trans/cis ratio as a function of temperature. The fact that photostationary ratio first increases to a maximum and then begins to decrease with decreasing temperature can only be interpreted in terms of a mechanism involving competing processes.

D. Photosensitized Isomerization in Neat Acetone. We observed that the sensitization constants, $K_S = k_t\tau_T$, for the acetone-photosensitized isomerization of pentene-2 or the acetone-sensitized phosphorescence of biacetyl were approximately five times larger when acetone was used as the solvent than when other solvent systems were used. Any or all of the following factors could be responsible for this increase in K_S.

(i) The collision efficiency, χ, for energy transfer between an excited acetone molecule and a pentene-2 or biacetyl molecule is larger in neat acetone than in all other solvents.

(ii) The acetone triplet-state lifetime, τ_T, is longer in neat acetone than in all other solvent systems.

(iii) The rate of triplet energy migration is greater in neat acetone than in mixed solvent systems.

It is difficult to believe that acetone exhibits some special enhancement of the collision efficiency, since no such effects were noted with any of the other solvent systems, which ranged from nonpolar to quite polar. Furthermore, since χ must be near unity for the acetone-sensitized biacetyl phosphorescence in mixed solvents, there is little possibility in this case that χ could increase in neat acetone.

In section IVB we presented evidence which indicated that the lifetime of the acetone triplet state in degassed solutions is intrinsic and independent of the nature of the solvent. It is difficult, therefore, to believe that the acetone triplet-state lifetime could be longer in neat acetone; if anything we, would expect it to be shorter as a result of self-quenching[3,18] or triplet-triplet annihilation.[29] A comparison of the temperature dependence of $K_S{}^B$ in neat acetone and in mixed solvents further supports this notion. If the increase in $K_S{}^B$ in neat acetone is due to a change in τ_T, then the observed temperature dependence of $K_S{}^B$ in neat acetone (Table IV), and the assumption that $k_t{}^P$ is a diffusion constant with $k_t{}^P(25)/k_t{}^P(-78) = \eta(78)/\eta(25) = 5$ lead to the surprising conclusion that τ_T increases by only a factor of 1.7 in going from 25 to $-78°$. In contrast to this, we demonstrated that in methanol solution τ_T increased by a factor of 20, in going from 25 to $-78°$. It would indeed be sur-

(27) N. Edelstein, A. Kwok, and A. H. Maki, J. Chem. Phys., 41, 179 (1964).

(28) D. F. Evans, J. Chem. Soc., 1735 (1960).

(29) H. Sternlicht, G. C. Nieman, and G. W. Robinson, J. Chem. Phys., 38, 1326 (1963).

prising if the temperature dependence of τ_T in neat acetone were so completely different from that observed in methanol.

Let us now consider the possibility that the increase in K_S in neat acetone is due to an increase in k_t, rather than to an increase in τ_T. If we adopt this assumption, then $K_S(\text{neat})/K_S(\text{methanol}) = k_t(\text{neat})/k_t(\text{methanol}) = 5$. This result implies that in neat acetone, triplet-state excitation energy is transported at a rate which is some five times greater than that predicted by ordinary molecular diffusion. While one might postulate that diffusion of triplet-state acetone molecules in acetone is anomalously fast, the observed temperature dependence of K_S^B in neat acetone appears to be inconsistent with an energy-transfer mechanism involving only diffusion of excited molecules. From Table IV we have

$$\frac{K_S^B(25)}{K_S^B(-78)} = \frac{k_t^B(25)}{k_t^B(-78)} \frac{\tau_T(25)}{\tau_T(-78)} = 3$$

in neat acetone. Now, $\tau_T(-78)/\tau_T(25) = 20$ in methanol solution, and if we assume that the same is true in neat acetone, we obtain $k_t^B(25)/k_t^B(-78) \simeq 60$. Over this same temperature range, the viscosity of acetone increased by only a factor of 5. The 60-fold change in k_t^B in neat acetone clearly cannot be explained on the basis of a molecular diffusion mechanism alone.

A consistent and reasonable explanation for our data can be obtained by postulating that in neat acetone there are two mechanisms for transporting triplet-state excitation energy: first, by the usual molecular diffusion of excited triplet-state acetone molecules, and second, by triplet–triplet energy transfer between acetone molecules. According to our present knowledge of energy-transfer rates (derived from crystal studies),[13] triplet–triplet energy transfer between acetone molecules in solution is expected to result in an energy-transfer rate constant which is as large, if not larger, than that predicted on the basis of a molecular diffusion mechanism alone, $k_D \simeq 10^{10} M^{-1} \text{sec}^{-1}$. If the rate of triplet energy transfer between acetone molecules is on the order of or slightly larger than k_D, the rate of energy transfer in acetone solution could easily be on the order of five times larger than predicted by molecular diffusion alone.

Under the assumption that the temperature dependence of the triplet-state lifetime of acetone is the same in neat acetone as in methanol solution, we found that $k_t^B(25)/k_t^B(-78) \simeq 60$. This result implies that the acetone triplet–triplet energy-transfer process is very temperature dependent, much more so than the molecular diffusion process. Studies of the emission properties of biacetyl-doped acetone crystals provide further evidence that triplet–triplet energy transfer between acetone molecules is temperature dependent. As we have previously discussed, the phosphorescence of biacetyl in neat acetone is sensitized by triplet energy transfer from acetone, at room temperatures down to at least $-78°$. However, at $77°K$, in crystalline acetone doped with biacetyl ([B] = 1.0 to $10^{-4} M$), we were unable to observe acetone-sensitized phosphorescence of biacetyl. In addition, there was no change in the lifetime of the acetone phosphorescence over the same concentration range. Although it is possible that the biacetyl was not soluble in the acetone

crystal, even to the extent of $10^{-4} M$, we observed no evidence for precipitation of biacetyl in any of the mixed crystals. Subject to unequivocal proof that biacetyl is actually dissolved in crystalline acetone, we may conclude that triplet–triplet energy-transfer in crystalline acetone at $77°K$ is slower than the acetone phosphorescence process ($\simeq 10^4 \text{sec}^{-1}$). This supports our contention that triplet energy transfer between acetone molecules is strongly temperature dependent.

That energy transfer between acetone molecules should be temperature dependent may be connected with the fact that the excited states of acetone, like formaldehyde, may be nonplanar.[30] The fact that there is such a large difference in energy (12,000 cm^{-1}) between the Franck–Condon maxima for absorption and emission in acetone[14] suggests that there is indeed a significant difference between the geometry of the ground and excited state. If this is so, there would most probably be a very small Franck–Condon factor associated with energy transfer from a vibrationally relaxed triplet-state acetone molecule to a neighboring acetone molecule in its ground electronic state. Transfer from or to vibrationally excited acetone molecules, on the other hand, might have a much larger Franck–Condon factor, with the result that triplet–triplet energy transfer between acetone molecules would be temperature dependent.

E. Comparison of the Quenching of the Triplet State of Acetone in Solution and in the Vapor Phase. After our work was completed, the investigations of Rebbert and Ausloos[31] came to our attention. These authors investigated the vapor-phase quenching of the excited states of acetone by various unsaturated hydrocarbons, including pentene-2. In agreement with our conclusion regarding the nature of the excited states involved in the energy-transfer process, they too conclude that energy transfer from acetone to the olefins proceeds from the triplet state of acetone.

From their data, Rebbert and Ausloos[31] calculated a collision efficiency of $\chi = 2.1 \times 10^{-5}$ for the triplet energy transfer from acetone to pentene-2 in the vapor phase at $32°$. As the following argument indicates, this value is consistent with the value of $\chi = 10^{-3}$ which we obtain in solution. Other things being equal, the ratio of the collision efficiencies in solution and in the vapor phase should be equal to the ratio of the lifetimes of the collision complex in the two different phases. In solution, the lifetime of the collision complex will be approximately equal to the reciprocal of the rate constant for breakup of the collision complex, or $1/k_b = 2.3 \times 10^{-10}$ sec. In the vapor phase the "lifetime of the collision complex" may be approximated as the time during which two colliding molecules are within an interaction distance of each other. Since triplet–triplet energy transfer is believed to involve an exchange mechanism,[29] the interaction radius will be on the order of magnitude of the van der Waal's radius, or about 10 A. Using this value we calculate a collision lifetime of approximately 3.3×10^{-12} sec in the vapor phase. The ratio of the collision lifetime is, therefore, on the order of 0.7×10^2, in good agreement with the observed ratio of the collision efficiencies, $\chi(\text{soln})/\chi(\text{vapor}) = 10^{-3}/(2 \times 10^{-5}) = 0.5 \times 10^2$.
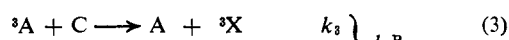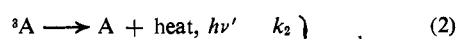
(30) J. C. D. Brand, *J. Chem. Soc.*, 858 (1956).
(31) R. E. Rebbert and P. Ausloos, *J. Am. Chem. Soc.*, 87, 5569 (1965).

From an investigation of the relative quenching efficiencies of various unsaturated hydrocarbons, Rebbert and Ausloos[31] concluded that the transfer of triplet-state energy from acetone to pentene-2 and other monoolefins is endothermic. Based on this conclusion, one would expect the nearest-neighbor transfer rate to be temperature dependent. Our studies of the temperature dependence of the acetone-photosensitized isomerization of pentene-2 provide the first experimental evidence that k_c, the nearest-neighbor energy-transfer rate constant, does depend upon temperature.

Appendix

The kinetic analysis is based on reactions 1–5

$$A + h\nu \longrightarrow {}^3A \qquad\qquad \Phi_{IC}L \qquad (1)$$

$$\left.\begin{array}{l} {}^3A \longrightarrow A + \text{heat}, h\nu' \quad k_2 \\ {}^3A + Q \longrightarrow A + Q \quad\quad k_2' \end{array}\right\} \tau_T^{-1} \qquad (2)\ (2')$$

$$\left.\begin{array}{l} {}^3A + C \longrightarrow A + {}^3X \quad k_3 \\ {}^3A + T \longrightarrow A + {}^3X \quad k_3' \end{array}\right\} k_t^P \qquad (3)\ (3')$$

$${}^3X \longrightarrow C \qquad\qquad k_4 \qquad\qquad (4)$$

$${}^3X \longrightarrow T \qquad\qquad k_5 \qquad\qquad (5)$$

where A and ${}^3A$ = ground state and triplet state of acetone, L = light absorbed by acetone, Φ_{IC} = acetone intersystem-crossing yield, Q = quenchers, e.g., oxygen, impurities, ${}^3X$ = triplet-state intermediate in pentene-2 isomerization. Since energy transfer is demonstrated to originate from the triplet state of acetone, all reactions involving excited singlet states have been omitted, and the rate of generation of triplet acetone is given by $\Phi_{IC}L$, where Φ_{IC} = 1.0 ± 0.1.[14] The sum of reactions 2 and 2' can be identified with the lifetime of acetone triplet state in solution, $\tau_T = (k_2 + k_2'[Q])^{-1}$.

Imposing the steady-state condition on $[{}^3A]$ and $[{}^3X]$ we find for the cis → trans reaction, for example

$$\frac{d[T]}{dt} = -k_3'[{}^3A][T] + k_5[{}^3X]$$

where

$$[{}^3X] = \frac{k_3[{}^3A][C] + k_3'[{}^3A][T]}{k_4 + k_5}$$

and

$$[{}^3A] = \frac{\Phi_{IC}L}{\tau_T^{-1} + k_3[C] + k_3'[T]}$$

For short irradiation times, $[T] \ll [C] \equiv m$, and the initial rate, R, becomes

$$R = \frac{d[T]}{dt} = \frac{k_3\alpha\Phi_{IC}Lm}{\tau_T^{-1} + k_3m} \qquad (A)$$

where $\alpha = k_5/(k_4 + k_5)$. A plot of $1/R$ vs. $1/m$ yields a straight line with slope $(\alpha\Phi_{IC}LK_S^P)^{-1}$, where $K_S^P = k_3\tau_T$. At high pentene-2 concentrations, $k_3m \gg \tau_T^{-1}$, and eq A becomes: $R_{max} = \alpha\Phi_{IC}L$. Thus, the K_S^P values were calculated from $K_S^P = S/R_{max}$, where $S = (\alpha\Phi_{IC}LK_S^P)^{-1}$ is the slope of the R^{-1} vs. m^{-1} plot. Since the K_S^P values obtained using cis-pentene-2 starting material ($K_S^P = k_3\tau_T$) were essentially the same as those obtained with trans starting material ($K_S^P = k_3'\tau_T$), we conclude that $k_3 \simeq k_3' \equiv k_t^P$ at 25°.

From eq A, the limiting isomerization rate at low pentene-2 concentration ($k_3m \ll \tau_T^{-1}$) is $R_{low} = \alpha\Phi_{IC}K_S^P \cdot Lm$. From the relation $R_{max} = \alpha\Phi_{IC}L$, and the empirical equation $R_{max} = \Phi_{CT}L$, we can equate $\alpha\Phi_{IC}$ to Φ_{CT}, the limiting quantum yield at high pentene-2 concentration. The low-concentration rate is thus given by

$$R_{low} = \Phi_{CT}K_S^PLm \qquad (B)$$

Equation B was used to obtain the ratio of K_S^P values at two temperatures, from measurement of $R_{low}(T)/R_{low}(T')$ and $\Phi_{CT}(T)/\Phi_{CT}(T')$.