JOURNAL
OF THE AMERICAN CHEMICAL SOCIETY

Registered in U.S. Patent Office.

VOLUME 97, NUMBER 15 JULY 23, 1975

The Triplet Energies of Azulene, β-Carotene, and Ferrocene

William G. Herkstroeter

Contribution from the Research Laboratories, Eastman Kodak Company, Rochester, New York 14650. *Received September 27, 1974*

Abstract: Employing a graded series of sensitizers whose triplet energies span the range from 23 to 43 kcal/mol, we measured by flash kinetic spectrophotometry the rates of energy transfer to each of the three quenchers, azulene, β-carotene, and ferrocene. Our results show that azulene has a triplet energy very near 39 kcal/mol and the triplet energies of β-carotene and ferrocene can be bounded within the limits of 21 to 25 and 38 to 41 kcal/mol, respectively. The fact that energy transfer to ferrocene remains moderately efficient with sensitizers having energies much less than 38 kcal/mol suggests a change in the geometry of the ferrocene triplet concomitant with energy transfer.

Azulene, β-carotene, and ferrocene are three substances frequently employed as triplet-state quenchers and are particularly useful in this role in kinetic studies of photochemical reactions. Since estimates of quenching efficiencies are often required, knowledge of the triplet energy levels in quenchers can be important. At present, however, the locations of the triplet energy levels in azulene, β-carotene, and ferrocene are each the subject of some controversy.

Ware in 1963 placed an upper limit on the triplet energy of azulene when he demonstrated that azulene quenches anthracene triplets at the diffusion-controlled rate.[1] This result was expanded by Lamola et al. in 1965, who confirmed Ware's result, but also observed that azulene was ineffective as a quencher of tetracene triplets.[2] On the basis of these results, Lamola et al. confined the triplet energy of azulene between 31 and 39 kcal/mol. In 1969 Rentzepis reported the detection of azulene phosphorescence with a 0-0 band at 30 kcal/mol, which he assigned to the $T_1 \rightarrow S_0$ transition.[3] One year later, however, Glandien and Kroening observed that the triplet energy of azulene is higher than that of perylene.[4] They measured the activation energy for the quenching of the perylene triplet by azulene and this value added to the perylene triplet energy, known experimentally, yields Glandien and Kroening's reported azulene triplet energy of 40 kcal/mol. A redetermination by Kroening of the azulene triplet energy based on azulene's quenching effect on the delayed fluorescence of perylene and 3,4-benzopyrene yielded a value of 38.6 kcal/mol.[5] Rentzepis' value for the azulene triplet energy has been widely cited and Glandien and Kroening's work has been largely ignored, but we can see no basis for making such a distinction. Molecular orbital calculations do not settle the issue. Pariser's calculations have placed the azulene triplet at 34 kcal/mol,[6] those of Fratev et al. at 35 kcal/mol,[7] and those of Hofer and Hedges at 37 kcal/mol,[8] whereas Pancir and Zahradnik predict an azulene triplet energy of 41 kcal/mol.[9]

As a quencher of singlet oxygen, β-carotene has become well known. Efficient quenching by energy transfer is interpreted to mean that the excited state to which the quencher is excited is lower in energy than the state being quenched in the energy donor. Because β-carotene had been found to quench singlet oxygen more efficiently than other known quenchers, it had been assumed that this quenching occurs at the diffusion-controlled rate.[10] Merkel and Kearns report a confirmation of this assumption following their direct measurement of a rate constant close to that of a diffusion-controlled rate constant for this reaction in benzene.[11] A somewhat smaller value for this rate constant was reported by Farmilo and Wilkinson.[12] These results indicate that β-carotene's triplet state, the excited state responsible for the quenching, must be less than or equal in energy to the lowest singlet state of oxygen, known to lie 22.5 kcal/mol above the ground state.[13-15] In contrast to the above summary, Matheson and Lee measured the rate constant for the quenching of singlet oxygen by β-carotene in Freon 113 and report a value of $1.4 \times 10^9\ M^{-1}\ \text{sec}^{-1}$, a value only one-twentieth that of a diffusion-controlled reaction in this solvent.[16] We find it difficult to reconcile these different experimental results; it seems unlikely that the change of solvent would shift energy levels enough to observe these differences. Other investigators also have made estimates of the triplet state energy of β-carotene. Mathis, on the basis of theoretical considerations, proposed that β-carotene's triplet state lies only 17 kcal/mol above its ground state,[17] whereas Land *et al.*, who measured the rate at which oxygen quenches triplet β-carotene, set upper and lower bounds of 28.5 and 22.5 kcal/mol, respectively, for the energy content of triplet β-carotene.[18]

Ferrocene was first reported to phosphoresce by Scott and Becker in 1961.[19] This phosphorescence consisted of a broad band with a maximum near 500 nm (57 kcal/mol). Since it was necessary to excite ferrocene to the S_2 or S_3 state in order to observe this phosphorescence, Scott and

Becker proposed that this phosphorescence may proceed from an upper excited triplet rather than the lowest excited triplet state. The authenticity of this luminescence was questioned six years later by McGlynn et al., who were unable to detect it.[20] But, Smith and Meyer in 1968 succeeded in recording this same phosphorescence assigned to ferrocene.[21] Mueller-Goldegg and Voitlaender in the same year, however, attributed this phosphorescence to one or more of ferrocene's photolysis products.[22] Three years later, Schandry and Voitlaender detected no ferrocene phosphorescence when, employing laser excitation, they attempted to excite ferrocene directly to its phosphorescent state,[23] although Krieger and Voitlaender later suggested that the wavelength selected for excitation in this experiment may have been incorrect.[24] Scott and Becker[25] in 1964 and later McGlynn et al.[20] reported weak, long-wavelength absorption in ferrocene with the 0-0 band near 710 nm (40 kcal/mol); this transition, believed to be ligand field in character, was assigned to $T_1 \leftarrow S_0$ absorption. This assignment was questioned by Gray et al., in 1971, on the basis that a corresponding transition was not observed in ruthenocene; these workers believed that the absorption band at 530 nm (54 kcal/mol) is the longest wavelength singlet-triplet absorption band that can be observed experimentally.[26] Calculations by Scott and Becker place the lowest ferrocene triplet 41 kcal/mol above the ground state,[25] whereas calculations by Gray et al.[26] and also by Krieger and Voitlaender[24] place this excited state significantly higher in energy at 53 and 52 kcal/mol, respectively. Dannenberg and Richards proposed a mechanism for the ferrocene photosensitized isomerization of piperylene that would require that the $T_1 \leftarrow S_0$ energy gap in ferrocene be about 32 kcal/mol.[27,28] Not to be overlooked is a 1966 paper by Fry, Liu, and Hammond reporting that ferrocene quenches anthracene triplets in benzene solution at the diffusion-controlled rate.[29] Provided this quenching occurs exclusively by energy transfer, this result should be interpreted to mean that the ferrocene triplet lies below the anthracene triplet (43 kcal/mol) in energy. Although others have suggested alternative quenching mechanisms for ferrocene, Fry, Liu, and Hammond found no evidence that they apply. Koerner von Gustorf et al. now have good evidence that ferrocene quenches the triplet of 9-fluorenone (53 kcal/mol) efficiently and exclusively by energy transfer.[30] More recent studies of energy transfer to ferrocene by Kikuchi et al. have led to an estimated ferrocene triplet energy of 43 ± 3 kcal/mol.[31]

It was our purpose to try to resolve experimentally the controversies surrounding the assignments of the lowest triplet energies in azulene, β-carotene, and ferrocene in order to facilitate more rational utilization of these substances as quenchers in photochemical reactions.

Results and Discussion

Flash Kinetic Spectrophotometry. None of the experimental techniques for direct observation of triplet states could be applied here to solve the controversies about azulene, β-carotene, and ferrocene. Neither azulene nor β-carotene phosphoresces, even at liquid nitrogen temperature, and although ferrocene has been reported to phosphoresce, the source of this phosphorescence is controversial. Absorption spectra of azulene and β-carotene in a heavy-atom solvent such as ethyl iodide did not reveal any new absorption bands that could be assigned to singlet-triplet absorption. Detection of the $T_1 \leftarrow S_0$ band in ferrocene has been claimed, but its position is controversial. We also tried to view triplet-triplet absorption following direct flash excitation of solutions containing azulene, β-carotene, and ferrocene, but without success. The failure of these flash experiments can most likely be attributed either to triplet lifetimes shorter than 10 μsec, the time-resolution limit of our flash photolysis apparatus, or totally inefficient intersystem crossing to the triplet manifold. With β-carotene, it has been reported that both of these reasons apply.[32]

Our approach to the determination of the triplet energies of azulene, β-carotene, and ferrocene was to apply an indirect experimental technique and to measure by flash kinetic spectrophotometry the rates of energy transfer to each of these compounds from a series of sensitizers spanning a broad energy range.[33,34] It is, after all, quenching ability that is of primary concern to the photochemist employing quenchers. This experimental technique had already been applied to acceptors of triplet energy such as biacetyl,[35] some aliphatic and aromatic azides,[36,37] and the individual geometric isomers of stilbene,[33] α-methylstilbene,[33] and some azastilbenes.[38] Lamola reports the utility of this method in determining triplet energies of compounds after other methods had either failed or yielded erroneous or equivocal results.[39] The rule is that energy transfer from triplet sensitizer (S^{*3}) to the quencher (Q), as given in eq 1, remains

$$S^{*3} + Q \rightleftharpoons S + Q^{*3} \qquad (1)$$

diffusion controlled until the sensitizer has less than 3 kcal/mol of energy in excess of that required to excite the quencher from the ground state to its lowest triplet state.[35,40] With lower energy sensitizers, the rate of drop in the efficiency of energy transfer to the quencher depends upon the nature of the quencher. For biacetyl and *trans*-stilbene, this change fits the Arrhenius equation,[33,35] whereas for the other previously investigated quenchers listed above, the rates drop much less than predicted by this equation. "Nonvertical energy transfer" is the explanation offered for this deviation in behavior from the Arrhenius equation by these quenchers and it requires that they undergo substantial geometrical changes concomitant with the energy transfer process;[44] the geometrical changes lower the energy of the quencher triplet states and thus reduce the energy requirements for their excitation.[33,45-47] Triplet energy determinations, unless otherwise specified, are for molecules in their ground state geometries. For all types of quenchers (in their ground state configurations), triplet energy levels can be estimated to be 2 or 3 kcal/mol below the point where energy transfer from sensitizer to quencher drops below the diffusion-controlled level.[33,35,48] A requirement of this experimental method is that the quenching of the sensitizer triplet occurs by exchange energy transfer involving excitation of the quencher to its lowest triplet state and that there be no significant contributions from other quenching mechanisms such as dipole-dipole energy transfer exciting the quencher to its lowest excited singlet state,[48] electron transfer, charge transfer, hydrogen abstraction, radical or radical ion formation, and the Schenck "relay" mechanism.[49]

To carry out these experiments, it was necessary to have a series of triplet sensitizers which spanned a broad energy range and whose triplet-triplet absorption could be monitored following flash excitation. A series of sensitizers with triplet energies above 41 kcal/mol had been reported upon previously.[33] However, below 41 kcal/mol in energy only a limited number of sensitizers had been applied in this manner. Porter et al., for example, measured the rates at which oxygen quenches some sensitizers with energies as low as 23 kcal/mol.[50] The literature lists additional compounds with triplet energies in the range between 23 and 41 kcal/mol. We have investigated many of these substances and find them satisfactory as sensitizers in flash kinetic spectrophotometry experiments. Table I lists the sensitizers employed in this study. No appropriate sensitizer was found whose triplet energy lies below 23 kcal/mol.

Table I. Low-Energy Sensitizers with Readily Observed Triplet–Triplet Absorption Bands

Sensitizer	Triplet energy E_T, kcal/mol[a]	Wavelength for monitoring triplet–triplet absorption, nm
3,4:9,10-Dibenzopyrene[b]	40.2[c]	728
5-Methyl-3,4:9,10-dibenzopyrene	38.5[c]	735
5,8-Dimethyl-3,4:9,10-dibenzopyrene	37.3[c]	730
3,4:8,9-Dibenzopyrene	34.4[c]	525
Anthanthrene	33.8[c]	585
Tetracene[b]	29.3[d]	487
Pyranthrene	26.9[e]	595
Zinc phthalocyanine	26.1[f]	490
Violanthrene[g]	25[h]	640
Isoviolanthrene[i]	24[h]	590
Pentacene[b]	23[j]	498

[a] These values are experimental values unless noted otherwise. [b] Used previously as a sensitizer in flash kinetic spectrophotometry as reported in ref 50. [c] Reference 51. [d] S. P. McGlynn, M. R. Padhye, and M. Kasha, *J. Chem. Phys.*, **23**, 593 (1955). [e] Calculated value reported by G. G. Hall, *Trans. Faraday Soc.*, **53**, 573 (1957). [f] P. S. Vincett, E. M. Voight, and K. E. Rieckhoff, *J. Chem. Phys.*, **55**, 4130 (1971). [g] According to *Chem. Abstr.*, the preferred name for this compound is dinaphtho[1,2,3-*cd*:1',2',3'-*lm*] perylene. [h] This value based on calculations by W. F. Smith, Jr., W. G. Herkstroeter, and K. L. Eddy, *J. Am. Chem. Soc.*, 97, 2764 (1975). [i] According to *Chem. Abstr.*, the perferred name for this compound is dinaphtho-[1,2,3-*cd*:3',2',1'-*lm*]perylene. [j] Calculated value reported in ref 52.

The technique of flash kinetic spectrophotometry can be applied to measure rate constants for energy transfer by the influence of added quenchers on the rates of decay of sensitizer triplet states. Any increase in the first-order depopulation rate of the sensitizer will be proportional to the quencher concentration; the rate constant for energy transfer can be determined on the basis of eq 2.[53,54] Here k_q is the rate

$$\frac{d[S^{*3}]}{dt} = k_d[S^{*3}] + k_q[S^{*3}][Q] + k_s[S^{*3}]^2 \tag{2}$$

constant for energy transfer (or quenching), k_d is the rate constant for decay of sensitizer triplets in the absence of quencher, and k_s is the second-order rate constant for triplet-triplet annihilation of the sensitizer. Added quencher should have no influence on the second-order term involving k_s. Because low concentrations of sensitizer were employed in the experiments described here, self-quenching of sensitizer triplets is unimportant and is not included.

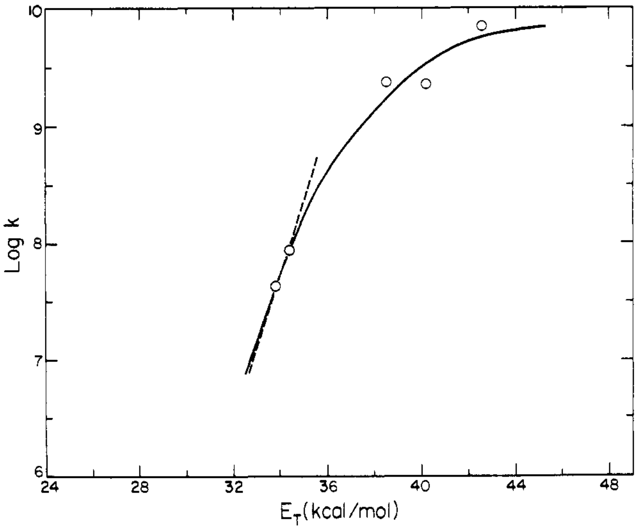

Figure 1. Plot of the logarithms of the rate constants for energy transfer to azulene vs. the triplet energies of the sensitizers. The dotted line represents the slope expected on the basis of the Arrhenius equation.[44]

Rates of energy transfer from the various triplet sensitizers to the three quenchers in question were measured by flash kinetic spectrophotometry. Table II lists the measured rate constants for azulene, β-carotene, and ferrocene and Figures 1–3 show the respective plots of the logarithms of these rate constants vs. the triplet energies of the sensitizers.

As noted earlier, no transients were observed upon direct flash excitation of solutions containing azulene, β-carotene, or ferrocene. In the presence of added sensitizer, no transients other than sensitizer triplets were observed and the only effect of the three quenchers in question was to increase the term for first-order sensitizer triplet decay (k_s + k_q[Q]), but to leave unchanged the term for second-order sensitizer triplet decay involving k_s. We believe that the experiments described here measure exchange energy transfer free from any contributions assignable to the alternative quenching mechanisms noted above. Perhaps the strongest argument in favor of electronic, exchange energy transfer is the fact that the plots of Figures 1–3 are relatively smooth,

Table II. Measured Rate Constants[a] for Energy Transfer to Azulene, β-Carotene, and Ferrocene in Benzene Solution at 22°

Sensitizer	E_T, kcal/mol	Sensitizer concn, *M*	Azulene	β-Carotene	Ferrocene
Triphenylene	(66.6)[b]	4.0×10^{-5}			5.9×10^{9}[c]
2-Acetonaphthone	(59.3)[b]	4.0×10^{-5}			5.4×10^{9}[c]
9-Fluorenone	(53)[d]	4.0×10^{-5}			5.1×10^{9}[c]
Benzanthrone	(47.0)[e]	4.0×10^{-5}			5.7×10^{9}[c]
Anthracene	(42.6)[f]	4.0×10^{-5}	7.4×10^{9} (7.2×10^{9})[g]	6.6×10^{9}	4.4×10^{9}[c]
3,4:9,10-Dibenzopyrene	(40.2)[h]	4.0×10^{-5}	2.3×10^{9}	6.1×10^{9}	3.0×10^{9}
5-Methyl-3,4:9,10-dibenzopyrene	(38.5)[h]	1.2×10^{-5}	2.4×10^{9}		1.8×10^{9}
5,8-Dimethyl-3,4:9,10-dibenzopyrene	(37.3)[h]	1.2×10^{-5}			1.1×10^{9}
3,4:8,9-Dibenzopyrene	(34.4)[h]	2.5×10^{-5}	9.0×10^{7}	4.6×10^{9}	6.8×10^{8}
Anthanthrene	(33.8)[h]	2.0×10^{-5}	5.6×10^{7}	5.5×10^{9}	4.8×10^{8}
Tetracene	(29.3)[h]	2.5×10^{-5}		3.2×10^{9}	1.0×10^{8}
Pyranthrene	(26.9)[h]	5.0×10^{-7}		3.8×10^{9}	1.7×10^{8}
Zinc phthalocyanine	(26.1)[h]	4.0×10^{-6}		1.7×10^{9}	2.6×10^{7}
Violanthrene	(25)[h]	5.0×10^{-7}		2.4×10^{9}	1.4×10^{7}
Isoviolanthrene	(24)[h]	5.0×10^{-7}		1.5×10^{9}	1.3×10^{7}
Pentacene	(23)[h]	5.0×10^{-6}		2.7×10^{9}	4.0×10^{7}
Singlet oxygen	(22.5)[i]	$\sim 1 \times 10^{-3}$			9.0×10^{6}[j]

[a] Units of the rate constants are M^{-1} sec^{-1}. [b] W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *J. Am. Chem. Soc.*, 86, 4537 (1964). [c] This value taken from ref 24. [d] K. Yoshihara and D. R. Kearns, *J. Chem. Phys.*, 45, 1991 (1966). [e] Reference 33. [f] Reference 55. [g] This value taken from ref 2. [h] See Table I. [i] References 13–15. [j] This value taken from ref 12.

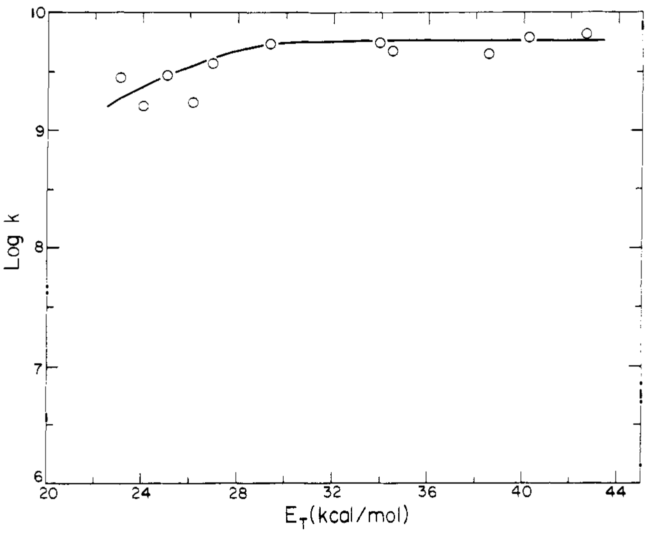

Figure 2. Plot of the logarithms of the rate constants for energy transfer to β-carotene vs. the triplet energies of the sensitizers.

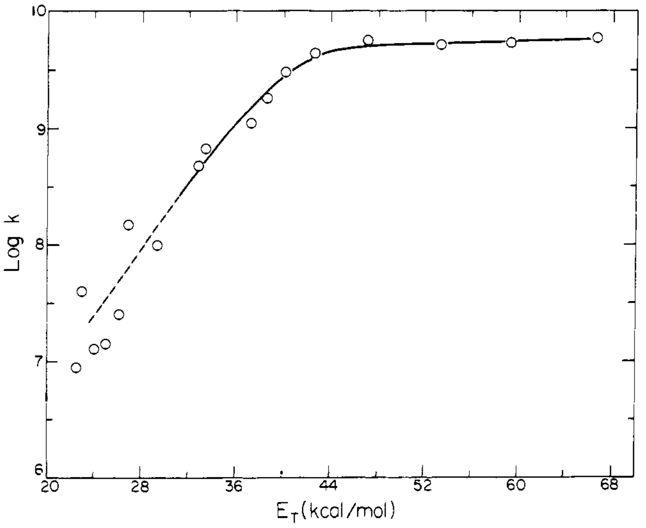

Figure 3. Plot of the logarithm of the rate constants for energy transfer to ferrocene vs. the triplet energies of the sensitizers.

monotonic functions of the triplet energies of the sensitizers. Special considerations for ferrocene are discussed below.

Energy transfer in the reverse direction, indicated by the dotted arrow in eq 1, can be observed whenever the triplet quencher Q^{*3} has both sufficient energy and a sufficiently long lifetime to be intercepted by the sensitizer.[35] In measuring rates of energy transfer for the purposes described here, it is preferable that reversible energy transfer not occur, because of the complications it introduces into the analysis of rate data. We believe that, under our experimental conditions, eq 1 and 2 apply to our kinetic measurements with no corrections necessary for reverse energy transfer from quencher triplet back to sensitizer. Included in Table II are the experimental concentrations of the sensitizers. The combination of these low sensitizer concentrations and short quencher triplet lifetimes, cited below, is sufficient to ensure that only the forward energy-transfer step occurs to a measurable extent.

Azulene. Concerning the controversy about the azulene triplet, our results support the assignment of 39 kcal/mol to the energy of this excited electronic state. The lowest energy sensitizer for which diffusion-controlled energy transfer to azulene was measured was anthracene, whose triplet energy is 42.6 kcal/mol;[55] the drop in the efficiency of energy transfer to azulene is observed with sensitizers immediately below anthracene in triplet energy.

Table III. Thermal Effects on the Quenching of Anthanthrene Triplets by Azulene[a]

Temp, °C	k_q, M^{-1} sec^{-1}
12.0	4.1×10^7
22.5	5.6×10^7
33.0	8.1×10^7

[a] These measurements were carried out in degassed benzene solution with an anthanthrene concentration of 2×10^{-5} and an azulene concentration of 8×10^{-6} *M*.

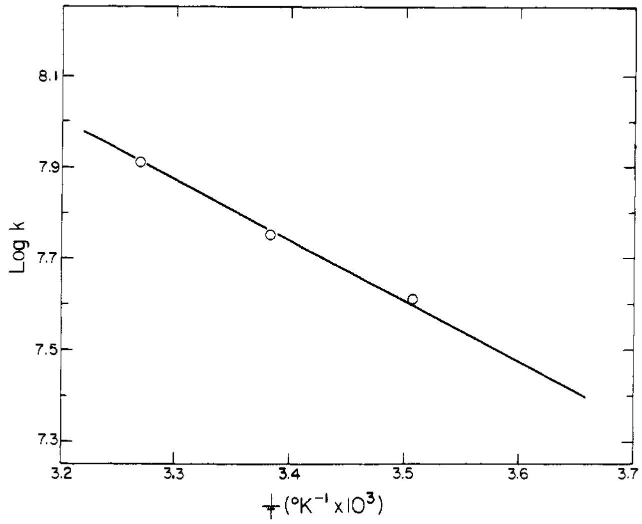

Figure 4. Plot of the logarithms of the rate constants for energy transfer from the triplet state of anthanthrene to azulene vs. the reciprocal of the absolute temperature.

With lower energy sensitizers, one must consider the possibility of reverse energy transfer from azulene triplet back to the sensitizer. In the case of azulene, Glandien and Kroening have previously demonstrated that the triplet lifetime is less than 1.5 μsec, a value sufficiently small to rule out such a process.[4]

With lower energy sensitizers, azulene behaves in the manner previously observed for biacetyl and *trans*-stilbene in that the efficiency of energy transfer drops in accord with the Arrhenius equation. When plotting the logarithm of the measured rate constant vs. the sensitizer triplet energy E_T, a slope of $+1/(2.3RT)$ (0.74 mol kcal^{-1} at 22°) is predicted by the Arrhenius equation;[44] a straight line with this slope has been drawn in Figure 1. As is evident, the final slope of the azulene plot closely matches the slope of the straight line. Although there are only two azulene data points on this part of the plot, the experimental slope is entirely compatible with the predicted slope. It did not prove feasible to expand the experimental plot in this region owing to a scarcity of satisfactory sensitizers with appropriate triplet energies.

A second method was employed to verify the 39 kcal/mol assignment for the triplet energy of azulene. With the sensitizer anthanthrene, whose triplet energy is 33.8 kcal/mol,[51] the activation energy for energy transfer from sensitizer to azulene was 5.9 kcal/mol. The data and plot relevant to this determination are given in Table III and Figure 4, respectively. Enthalpy is the thermodynamic function that best approximates electronic energy.[56] At room temperature the activation enthalpy for energy transfer from triplet anthanthrene to azulene is found to be 5.2 kcal/mol and this number added to the known value for the triplet energy of anthanthrene yields 39.1 kcal/mol for the azulene triplet energy, a number in good agreement with that previously reported by Glandien and Kroening[4] and also by Kroening.[5]

Hochstrasser and Li have located the 0-0 band of the $S_1 \leftarrow S_0$ transition in azulene at 14,652 cm^{-1} or 41.8 kcal/mol.[57] The energy assignment of 39 kcal/mol for the lowest triplet of azulene means that, as previously noted by Kroening,[5] azulene has a small splitting of less than 3 kcal/mol between the S_1 and T_1 states.

The question remains as to the origin of the phosphorescence that Rentzepis observed with an estimated 0-0 band at 30 kcal/mol.[3] If this phosphorescence does indeed emanate from azulene's lowest triplet as Rentzepis claims, then this lowest triplet is ineffective in accepting energy from triplet sensitizers with sufficient energy; such a situation is without precedent. Alternatively, the observed phosphorescence may be from a transition other than $T_1 \rightarrow S_0$. Phosphorescence from the S_2 to the T_2 states would have the correct energy gap according to the calculations of Pancir and Zahradnik,[9] but such a phenomenon also would be without precedent.

β-Carotene. From Figure 2 it is evident that energy transfer to β-carotene has become somewhat less efficient than diffusion controlled for the lowest energy sensitizers employed. Truscott et al. have shown that triplet β-carotene has a lifetime of 9 μsec in benzene.[32] Since the sensitizers are present only at concentrations near 1×10^{-5} *M*, this lifetime should be sufficiently short to rule out complications from back energy transfer involving triplet β-carotene and ground state sensitizer. There appears to be some scatter for the last four points in the figure, but, nevertheless, each of these rate constants has a value slightly less than half as large as the measured rate constants for energy transfer for the higher energy sensitizers and indicates an efficiency about half as large as that of a diffusion-controlled reaction.

One of the best-known quenchers of singlet oxygen is β-carotene. Foote and Denny estimated this reaction to proceed at the diffusion-controlled rate.[10] Recent direct measurements of the rate constant for this reaction in benzene have yielded values of $2 \times 10^{10}\ M^{-1}\ sec^{-1}$ by Merkel and Kearns[11] and $1.3 \pm 0.2 \times 10^{10}\ M^{-1}\ sec^{-1}$ by Farmilo and Wilkinson.[12] Ware has shown that, because of the high diffusibility of oxygen, diffusion-controlled reactions involving molecular oxygen in benzene at room temperature occur with a rate constant of $3.0 \times 10^{10}\ M^{-1}\ sec^{-1}$.[58] Merkel and Kearns's measured rate constant for quenching of singlet oxygen by β-carotene is two-thirds that of a diffusion-controlled reaction and Farmilo and Wilkinson's[12] rate constant is slightly less than half as large.

Pentacene, our lowest energy triplet sensitizer, has a triplet energy at 23 kcal/mol[52] that is only 0.5 kcal/mol greater than the energy of singlet oxygen.[13-15] With pentacene, our measured rate constant for energy transfer to β-carotene is $2.7 \times 10^9\ M^{-1}\ sec^{-1}$. A value comparable to this has been reported for this same reaction by Sykes and Truscott.[59] Although the measured rate constants for energy transfer from both pentacene and singlet oxygen to β-carotene differ substantially in magnitude, β-carotene quenches both species at close to one-half the diffusion-controlled rate. This difference in magnitude is the result of the diffusion of oxygen through solvents at a higher rate than is possible for larger organic molecules.[58] In the case of β-carotene and our triplet sensitizers, the limiting diffusion-controlled rate constant is close to $6 \times 10^9\ M^{-1}\ sec^{-1}$ and this value agrees reasonably well with the diffusion-controlled rate constants reported previously for energy transfer to the cis and trans isomers of both stilbene and α-methylstilbene.[33]

Table IV. The Rate Constants for Quenching by Ferrocene with Various Sensitizers in Solvents of Different Dielectric Constants

Sensitizer	E_T, kcal/mol	k_q, $M^{-1}\ sec^{-1} \times 10^{-10}$		
		Cyclohexane	Benzene	Acetonitrile
Anthracene	(42.6)		0.44[a]	1.12
Anthanthrene	(33.8)	0.076	0.048	0.094
Violanthrene	(25)		0.0014	0.0058

[a] This value is from ref 29.

When energy transfer occurs at exactly one-half the diffusion-controlled rate, the sensitizer and the quencher are isoenergetic.[35] On this basis the triplet state of β-carotene must be close in energy to triplet pentacene and singlet oxygen. That triplet β-carotene may be nearly degenerate in energy with singlet oxygen had been suggested by Land et al.[18] as well as Merkel and Kearns.[11] Because of a certain amount of experimental error in the measured rate constants, we propose bounding the triplet energy level of β-carotene between 21 and 25 kcal/mol.

We can offer no explanation for the apparent inefficiency of energy transfer between singlet oxygen and β-carotene in Freon 113 as reported by Matheson and Lee[16] and can only say that their result appears to be inconsistent with the two other independent measurements of the rate constant for this reaction. It seems unlikely that the change of solvent from benzene to Freon 113 would shift the energy levels of the molecules involved to the extent necessary to account for the differences in the measured rate constants.

Ferrocene. The plot in Figure 3 for ferrocene shows that ferrocene quenches all sensitizers with triplet energies greater than 41 kcal/mol at the diffusion-controlled rate. It appears that the ferrocene triplet is close to 40 kcal/mol in energy, because for lower energy sensitizers the quenching efficiency drops. It was unexpected to discover that this drop occurs at a substantially smaller rate than predicted by the Arrhenius equation.

In order to interpret these results, one must give special consideration to a variety of possible quenching mechanisms. Mechanisms other than exchange energy transfer that merit consideration include electron transfer, charge-transfer formation, and heavy-atom enhancement of the rate of depopulation of sensitizer triplet. Also, energy transfer in the reverse direction could, in the absence of the necessary corrections in the kinetic analysis, bring about the appearance of quenching rate constants that are too small in magnitude. These eventualities were investigated experimentally. Dipole-dipole energy transfer from the sensitizer triplet to the lowest excited singlet state in the quencher, an inefficient process under ideal conditions,[48,60] can be ruled out on the basis of the large energy gap between the low-energy sensitizer triplet states and ferrocene's lowest excited singlet state.

Possible quenching by electron transfer was checked by comparing the rates at which ferrocene quenches the triplets of anthracene, anthanthrene, and violanthrene in benzene and acetonitrile. This quenching mechanism would be expected to be facilitated in more polar solvents, as has been demonstrated previously.[61-63] Results summarized in Table IV show that ferrocene quenches more efficiently in acetonitrile than in benzene. In cyclohexane solvent, however, where only anthanthrene sensitizer was tried, quenching by ferrocene is more efficient than in benzene. Electron-transfer quenching would seem to be unimportant for ferrocene.

Heavy-atom quenching can be discounted on the basis that the rate constants for quenching by ferrocene correlate with the triplet energies of the sensitizers. One would expect the heavy-atom quenching mechanism to make a constant contribution to the quenching of each sensitizer. Farmilo and Wilkinson[12] report a rate constant of $9.0 \pm 2.0 \times 10^6$ M^{-1} sec^{-1} for the quenching of singlet oxygen by ferrocene and have proposed heavy-atom catalysis of intersystem crossing as the mechanism. This data point has also been included in Figure 3 and Table II, where singlet oxygen can be regarded as a sensitizer with an energy of 22.5 kcal/mol. If Farmilo and Wilkinson's proposal is correct,[12] all of the measured rate constants for quenching by ferrocene contain a maximum contribution of approximately 1×10^7 M^{-1} sec^{-1} assignable to heavy-atom quenching.

With regard to charge-transfer quenching, it is known that rate constants for quenching by this mechanism do not necessarily correlate with the dielectric constant of the solvent,[64,65] so that the data of Table IV do not eliminate this reaction from consideration. Kikuchi et al. have, in fact, proposed that ferrocene quenches low energy triplet sensitizers with the intermediacy of a short-lived charge-transfer complex.[31] We have, however, measured rate constants for quenching by ferrocene of many more low energy sensitizers than Kikuchi et al. used. With our current data, we believe that the charge-transfer quenching mechanism can be discounted because of the correlation between the measured rate constants and the sensitizer triplet energies as illustrated in Figure 3. It is difficult to see why such a correlation would obtain, if charge-transfer quenching were the principal mechanism. There is, granted, some scatter involving the data points for pyranthrene and pentacene and charge-transfer quenching may make a measurable contribution with these sensitizers.

Reverse energy transfer from ferrocene triplet to sensitizer (the reverse of eq 1) can be eliminated on the basis that variation of the concentration of anthanthrene sensitizer by a factor of 10 (from 5×10^{-6} to 5×10^{-5} M) had no effect upon the measured rate constants. This most likely means that the lifetime of the ferrocene triplet in fluid benzene solution is substantially less than 10 μsec and would account for our inability to detect any transients following flash excitation of ferrocene solutions.

After considering other quenching mechanisms, we are still left with a series of rate constants for quenching by ferrocene that, according to Figure 3, give a correlation with the sensitizer triplet energy. Although heavy-atom-catalyzed intersystem crossing and charge-transfer quenching may make contributions to the measured rate constants for quenching by ferrocene, they can tell only a small fraction of the whole story. For example, if one subtracts ferrocene's maximum possible heavy-atom quenching constant from each of the measured quenching constants, the plot of the data will, except for the three smallest values, still appear nearly indentical with that shown in Figure 3. Charge-transfer quenching seems unlikely except for two low-energy sensitizers. Koerner von Gustorf has good evidence that ferrocene quenches the triplet of 9-fluorenone exclusively by exchange energy transfer[30] and we believe that with all sensitizers having triplets greater than 28 kcal/mol, exchange energy transfer makes the major contribution to ferrocene's quenching capabilities.

With ferrocene, as with azulene, anthracene is the lowest energy sensitizer for which the rate of energy transfer is diffusion controlled. Our quenching experiments, along with those of Fry, Liu, and Hammond,[29] argue against ferrocene's lowest triplet being much above 40 kcal/mol in energy. Considering the break point in the plot of Figure 3, we estimate that ferrocene's triplet energy is bounded between 38 and 41 kcal/mol. These limits are completely consistent with the previous assignment of 40 kcal/mol by Scott and Becker[25] and also McGlynn et al.[20] on the basis of their $T_1 \leftarrow S_0$ absorption measurements. Also, Scott et al.[66] have shown that the mechanism for the ferrocene photosensitization of piperylene isomerization does not require that ferrocene's triplet be 32 kcal/mol above the ground state as proposed by Dannenberg and Richards,[27,28] but is consistent with the triplet energy assignment of 40 kcal/mol.

With lower energy sensitizers, the slope of ferrocene's plot in Figure 3 is much shallower than azulene's plot in Figure 1. This behavior obtains even if one eliminates from consideration all data points for sensitizer triplets less than 28 kcal/mol in energy. The activation energy for energy transfer from anthanthrene to ferrocene and from tetracene to ferrocene was on the order of only 1 and 3 kcal/mol, respectively. In contrast to azulene, ferrocene's behavior with the lower energy sensitizers is typical of quenchers that can undergo a change in geometry concomitant with their acceptance of energy. This new geometry must lead to a lowering of the triplet state energy in order to bring about an increase in the rate of energy transfer over that predicted by the Arrhenius equation. This type of quencher also yields small measured activation energies as shown by Whitten et al. for several isomerizable azastilbenes.[38] It is tempting to make an analogy with ferrocene and to propose that this molecule undergoes a change in geometry that meets these requirements. Krieger and Voitlaender have, in fact, speculated about the possibility of a large Stokes shift in ferrocene.[24] It is not obvious to us, however, just what the precise nature of such a geometrical change should be.

Experimental Section

Materials. All reagents were purified until impurities could no longer be detected by thin-layer chromatography. Azulene was purchased from the Aldrich Chemical Co. and was used as received. β-Carotene was an Eastman reagent chemical and was chromatographed on Woelm silica gel (activity 1) with a 1:1 mixture of cyclohexane and benzene and then recrystallized from a 1:1 mixture of benzene and methanol. Ferrocene was an Eastman practical chemical and was recrystallized twice from ethanol.

The sensitizers 3,4:8,9-dibenzopyrene and 3,4:9,10-dibenzopyrene were purchased from Koch-Light Laboratories, Ltd. and were each recrystallized from benzene. Anthanthrene was purchased from K & K Laboratories, Inc. and was recrystallized twice from benzene. Tetracene was an Eastman reagent chemical and was recrystallized three times from benzene. Pentacene was obtained from Aldrich Chemical Co. and was recrystallized from 1,2,3-trimethylbenzene. Zinc phthalocyanine was an Eastman reagent chemical and was used as received. Pyranthrone, violanthrone, and isoviolanthrone all were purchased from K & K Laboratories, Inc. and were reduced to pyranthrene, violanthrene, and isoviolanthrene, respectively, by distillation with zinc powder.[67] Both 5-methyl-3,4:9,10-dibenzopyrene and 5,8-dimethyl-3,4:9,10-dibenzopyrene were prepared and purified according to the method of Buu-Hoi and Lavit.[68]

Benzene, acetonitrile, and cyclohexane were Mallinckrodt Nanograde solvents. The first two were used as received and the last was purified by passage down a chromatography column packed in two separate layers with Woelm basic activated alumina and silica gel, respectively.

Procedures. Kinetic measurements were carried out on a conventional flash photoelectric apparatus. Two xenon flash lamps (Kemlite Z8H20) were positioned on opposite sides of a sample cell holder inside a cylindrical housing whose inner walls were coated with highly reflective paint (Eastman white reflectance coating). The energy of the flash discharge was 400 J (2-μF capacitor charged to 20 kV). The flash output returned to one-third peak intensity within 15 μsec. The monitoring source was a quartz-halide 100-W lamp (Osram 64625) powered by a regulated dc power supply (Sorensen QSB12-8). The lamp was mounted in a housing on an optical bench in series with a collimating lens, the flash chamber, a focusing lens, and a 0.25-m monochromator (Jarrell-

Ash). The monitoring beam, after passing through the sample cell, was focused on the entrance slit of the monochromator. Light intensity as a function of time was measured by means of a photomultiplier tube (RCA 4463) located at the exit slit of the monochromator. The output from the photomultiplier was fed into a cathode-follower amplifier and then into a wide-band oscilloscope (Tektronix 555). Oscillographs were photographed with an oscillograph-record camera.

The cylindrical Pyrex glass sample cells were 25 cm long and 15 mm o.d. with flat windows fused to the ends. The cells were connected by side arms to bulbs where solutions were contained during the degassing procedure. Solutions were degassed by subjecting them to several freeze–pump–thaw cycles on a high-vacuum manifold prior to sealing the sample containers.

The oscillographs were enlarged to facilitate more precise measurement of the transient phenomena. The lifetimes of sensitizer triplets were measured by the recovery rate of the monitoring beam after the excitation flash. Kinetic analysis was by the method of Linschitz and Sarkanen.[53,54]

Acknowledgment. The author wishes to acknowledge helpful discussions with Dr. W. F. Smith, Jr., and the technical assistance of Mr. K. L. Eddy and Mr. J. E. Sconiers.

References and Notes

(1) W. R. Ware, *J. Chem. Phys.*, **37**, 923 (1963).
(2) A. A. Lamola, W. G. Herkstroeter, J. C. Dalton, and G. S. Hammond, *J. Chem. Phys.*, **42**, 1715 (1965).
(3) P. M. Rentzepis, *Chem. Phys. Lett.*, **3**, 717 (1969).
(4) M. Glandien and P. Kroening, *Z. Phys. Chem. (Frankfurt am Main)*, **71**, 149 (1970).
(5) P. Kroening, *Z. Phys. Chem. (Frankfurt am Main)*, **86**, 225 (1973).
(6) R. Pariser, *J. Chem. Phys.*, **25**, 1112 (1956).
(7) F. Fratev, G. Hiebaum, and A. Gochev, *Chem. Phys. Lett.*, **16**, 349 (1972).
(8) O. C. Hofer and R. M. Hedges, *Chem. Phys. Lett.*, **6**, 67 (1970).
(9) J. Pancir and R. Zahradnik, *J. Phys. Chem.*, **77**, 114 (1973).
(10) (a) C. S. Foote and R. W. Denny, *J. Am. Chem. Soc.*, **90**, 6233 (1968); (b) C. S. Foote, R. W. Denny, L. Weaver, Y. Chang, and J. Peters, *Ann. N.Y. Acad. Sci.*, **171**, 139 (1970).
(11) P. B. Merkel and D. R. Kearns, *J. Am. Chem. Soc.*, **94**, 7244 (1972).
(12) A. Farmilo and F. Wilkinson, *Photochem. Photobiol.*, **18**, 447 (1973).
(13) L. Herzberg and G. Herzberg, *Astrophys. J.*, **105**, 353 (1947).
(14) L. Wallace, *Astrophys. J., Suppl. Ser.*, **7**, 165 (1962).
(15) R. P. Wayne, *Adv. Photochem.*, **7**, 314 (1969).
(16) I. B. C. Matheson and J. Lee, *Chem. Phys. Lett.*, **14**, 350 (1972).
(17) P. Mathis, Thesis, University of Orsay, France, 1970, as cited by P. Mathis and J. Kleo, *Photochem. Photobiol.*, **18**, 343 (1973).
(18) E. J. Land, A. Sykes, and T. G. Truscott, *Chem. Commun.*, 332 (1970).
(19) D. R. Scott and R. S. Becker, *J. Chem. Phys.*, **35**, 516, 2246 (1961).
(20) A. T. Armstrong, F. Smith, E. Elder, and S. P. McGlynn, *J. Chem. Phys.*, **46**, 4321 (1967).
(21) J. J. Smith and B. Meyer, *J. Chem. Phys.*, **48**, 5436 (1968).
(22) A. Mueller-Goldegg and J. Voitlaender, *Z. Naturforsch., Teil A*, **23**, 1236 (1968).
(23) R. Schandry and J. Voitlaender, *Z. Naturforsch., Teil A*, **26**, 1772 (1971).
(24) R. Krieger and J. Voitlaender, *Z. Naturforsch., Teil A*, **27**, 1444 (1972).
(25) D. R. Scott and R. S. Becker, *J. Organometal. Chem.*, **4**, 409 (1965).
(26) Y. S. Sohn, D. N. Hendrickson, and H. B. Gray, *J. Am. Chem. Soc.*, **93**, 3603 (1971).
(27) J. J. Dannenberg and J. H. Richards, *J. Am. Chem. Soc.*, **87**, 1626 (1965).
(28) J. J. Dannenberg, Ph.D. Thesis, California Institute of Technology, 1967.
(29) A. J. Fry, R. S. H. Liu, and G. S. Hammond, *J. Am. Chem. Soc.*, **88**, 4781 (1966).
(30) A. Gilbert, J. M. Kelly, and E. Koerner von Gustorf, *Mol. Photochem.*, **6**, 225 (1974).
(31) M. Kikuchi, K. Kikuchi, and H. Kokobun, *Bull. Chem. Soc. Jpn.*, **47**, 1331 (1974).
(32) T. G. Truscott, E. J. Land, and A. Sykes, *Photochem. Photobiol.*, **17**, 43 (1973).
(33) W. G. Herkstroeter and G. S. Hammond, *J. Am. Chem. Soc.*, **88**, 4769 (1966).
(34) W. G. Herkstroeter in "Physical Methods of Chemistry", Vol. 1, Part 3B, A. Weissberger and B. W. Rossiter, Ed., Wiley-Interscience, New York, N.Y., 1969, pp 534 and 535.
(35) K. Sandros, *Acta Chem. Scand.*, **18**, 2355 (1964).
(36) F. D. Lewis and W. H. Saunders, Jr., *J. Am. Chem. Soc.*, **90**, 7033 (1968).
(37) L. J. Leyshon and A. Reiser, *J. Chem. Soc., Faraday Trans. 2*, 1981 (1972).
(38) D. G. Whitten, P. D. Wildes, and C. A. DeRosier, *J. Am. Chem. Soc.*, **94**, 7811 (1972).
(39) A. A. Lamola in "Energy Transfer and Organic Photochemistry", Vol. XIV, P. A. Leermakers and A. Weissberger, Ed., Wiley-Interscience, New York, N.Y., 1969, p 115.
(40) Throughout the text, the term "diffusion controlled" is employed to signify a reaction involving triplet energy transfer that is exothermic by 3 kcal/mol or more. It is recognized that, as reported recently, when solvent viscosities are low, this process frequently shows less than unit efficiency owing to the escape of either the triplet sensitizer or the quencher from the solvent cage prior to reaction.[41–43]
(41) P. J. Wagner and I. Kochevar, *J. Am. Chem. Soc.*, **90**, 2232 (1968).
(42) A. Fenster and H. E. Johns, *J. Phys. Chem.*, **77**, 2246 (1973).
(43) N. J. Turro, N. E. Schore, H. C. Steinmetzer, and A. Yekta, *J. Am. Chem. Soc.*, **96**, 1936 (1974).
(44) The Arrhenius equation in logarithmic form is $\log k = (-E_a/2.3RT) + \log A$, where k is the measured rate constant, E_a the activation energy, and A the preexponential factor. In the usual application of this equation, one plots $\log k$ vs. $1/T$ and obtains a slope equal to $-E_a/2.3R$. We apply the Arrhenius equation in an alternative manner here. If one takes the difference between two values of the above equation, one obtains $\Delta \log k = -\Delta E_a/2.3RT$. If the deficiency in the energy of the sensitizer triplet to excite the quencher is made up by thermal activation energy, then one can substitute ΔE_T for ΔE_a, where ΔE_T is the difference in triplet energies between sensitizer and quencher. A plot of $\Delta \log k$ vs. $-\Delta D_T$ would be expected to have a slope of $1/2.3RT$. A shallower slope is taken to mean that the system does not fit the Arrhenius equation. In practice in the figures, the abscissas and the ordinates are labeled E_T and $\log k$, respectively, because these values are measured directly and have the same units as $-\Delta E_T$ and $\Delta \log k$, respectively.
(45) Reference 39, pp 60–70.
(46) (a) G. S. Hammond and J. Saltiel, *J. Am. Chem. Soc.*, **85**, 2516 (1963); (b) J. Saltiel and G. S. Hammond, *ibid.*, **85**, 2515 (1963).
(47) J. Saltiel, J. D'Agostino, E. D. Megarity, L. Metts, K. R. Neuberger, M. Wrighton, and O. C. Zafiriou, "Organic Photochemistry", Vol. 3, O. L. Chapman, Ed., Marcel Dekker, New York, N.Y., 1973, pp 14–17.
(48) Reference 39, pp 40–50.
(49) G. O. Schenck and R. Steinmetz, *Bull. Soc. Chim. Belg.*, **71**, 781 (1962).
(50) O. L. J. Gijzeman, F. Kaufman, and G. Porter, *J. Chem. Soc., Faraday Trans. 2*, 708 (1973).
(51) B. Muel and M. Hubert-Habart, *Adv. Mol. Spectrosc., Proc. Int. Meet., 4th*, **2**, 647 (1962).
(52) G. G. Hall, *Proc. R. Soc. London, Ser. A*, **213**, 113 (1952).
(53) H. Linschitz and K. Sarkanen, *J. Am. Chem. Soc.*, **80**, 4826 (1958).
(54) Reference 34, pp 570–572.
(55) M. R. Padhye, S. P. McGlynn, and M. Kasha, *J. Chem. Phys.*, **24**, 588 (1956).
(56) We thank a referee for his suggestion to use the activation enthalpy rather than the activation energy in determining the triplet energy of azulene.
(57) R. M. Hochstrasser and T. Y. Li, *J. Mol. Spectrosc.*, **41**, 297 (1972).
(58) W. R. Ware, *J. Phys. Chem.*, **66**, 455 (1962).
(59) A. Sykes and T. G. Truscott, unpublished results cited in ref 18.
(60) R. G. Bennett, R. P. Schwenker, and R. E. Kellogg, *J. Chem. Phys.*, **41**, 3040 (1964).
(61) H. Leonhardt and A. Weller, *Ber. Bunsenges. Phys. Chem.*, **76**, 791 (1963).
(62) W. R. Ware and H. P. Richter, *J. Chem. Phys.*, **48**, 1595 (1968).
(63) K. Kaneta and M. Koizumi, *Bull. Chem. Soc. Jpn.*, **40**, 2254 (1967).
(64) P. J. Wagner and A. E. Kemppainen, *J. Am. Chem. Soc.*, **91**, 3085 (1969).
(65) R. W. Yip, R. O. Loutfy, Y. L. Chow, and L. K. Magdzinski, *Can. J. Chem.*, **50**, 3426 (1972).
(66) J. P. Guillory, C. F. Cook, and D. R. Scott, *J. Am. Chem. Soc.*, **89**, 6776 (1967).
(67) A. I. Vogel, "Practical Organic Chemistry", 3rd ed, Longmans, Green and Co., London, 1956, p 748.
(68) N. P. Buu-Hoi and D. Lavit, *Recl. Trav. Chim. Pays-Bas*, **75**, 1194 (1956).