of the polymer occur. This may be a negative factor in situations where there is the need to rapidly cycle the polymer from one redox state to another, as in electrochromism. Such may not be important in constant current applications, since the overall polymer structure would be fixed.

Since the variation in C is too small to account for the changes in $D_{CT}C^2$, the value of D_{CT} must also be larger for the +/0 state of the polymer than for the 2+/+ state. The fundamental reason for the larger value of D_{CT} for the more reduced system is not clear. With the view that charge transport occurs via a self-exchange process, the change in the fundamental rate constant can be attributed to the change in the structure of the polymer. Changes in the structure of the polymer are likely the significant factor in changes in the cyclic voltammetry waves for the first and second reduction illustrated in Figure 1. Whatever the explanation, the changes in the charge-transport rate in the various redox levels may have practical consequence. Note that >20 mA/cm^2 can be sustained for $[(PQ^{2+})_n]_{surf}$ or $[(BPQ^{2+})_n]_{surf}$ film thicknesses exceeding 1 μm. This establishes that thick films of redox polymer derived from a viologen can yield significant steady-state current that might be required in energy conversion and storage or synthetic applications. Additionally, the greater value of D_{CT} for the +/0 form of the polymers compared to the 2+/+ form suggests that the purple/yellow colors associated with the +/0 forms might prove more valuable in electrochromism applications where speed is an important concern. The lack of long-term durability of the doubly reduced polymers derived from I and II in aqueous electrolytes,[2] however, remains a practical limitation in any application despite the improved rate of charge transport.

The results for the polymers derived from I or II accord well with results[6] from polymers having M(2,2′-bipyridine)$_3^{2+}$ redox centers in that the value of D_{CT} is larger for the more reduced redox state. It may be that the similar increase in D_{CT} for the more reduced state of the polymes is due to the fact that all of the systems studied give lower electrostatic repulsions between the redox centers for the more reduced state. Studies of polymers that can increase electrostatic repulsions between redox centers by reduction will be undertaken in this laboratory to establish factors influencing charge transport in redox polymers.

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A Pulse Radiolysis Study of the Azulene Triplet State

A. A. Gorman,* I. Hamblett, and R. J. Harrison

Contribution from the Chemistry Department, The University of Manchester, Manchester M13 9PL, UK. *Received March 13, 1984*

Abstract: The triplet state of azulene has been produced in benzene by pulse radiolysis and a lifetime of 11 ± 1 μs determined. This is longer than previously reported values. The identity of this species has been confirmed by witnessing its formation and quenching via essentially diffusion-controlled triplet energy-transfer processes involving respectively 1,3-cyclohexadiene as donor and perylene as acceptor. A triplet energy of 40.1 ± 0.2 kcal mol^{-1} has been determined by establishment of an equilibrium for triplet energy transfer between anthracene and azulene.

I. Introduction

Over the last 2 decades the non-alternant hydrocarbon azulene (Az) has played an important role in mechanistic organic photochemistry as a triplet quencher.[1] In spite of this diagnostic use the two key characteristics of $^3Az^*$, its triplet energy and its lifetime, have been subjects of considerable discussion. Experimental values for the triplet energy of <43,[2] 31-39,[3] 30,[4] 40,[5] 38.6,[6] and close to 39[7] kcal mol^{-1} have been quoted, and, perhaps more understandably, molecular orbital calculations have also yielded a wide range of values, 34,[8] 35,[9] 37,[10] and 41[11] kcal mol^{-1}. Although a triplet lifetime of less than 1.5 μs has been reported,[5,6] the most reliable lifetime data appear to be those published recently by Görner and Schulte-Frohlinde as a result of a pulsed laser study.[12] In this work $^3Az^*$ was produced by triplet energy transfer from various sensitizer molecules and an absorption spectrum with λ_{max} 360 nm and a lifetime of 4 ± 2 μs in benzene reported. However, according to these authors the transient appeared within the rise time of the laser pulse (10 ns) and was formed in the same yields in deaerated and aerated benzene. Neither of these facts appears consonant with quoted concentrations and rate constants for electronic energy transfer from sensitizer triplets to azulene and oxygen. In this work we have addressed ourselves to the

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Table I. Rate Constants (L mol^{-1} s^{-1})[a] for Triplet Energy Transfer in Benzene between Azulene and Sensitizers (S) of Known Triplet Energy

sensitizer	E_T/kcal mol^{-1}	S → Az	Az → S
benzophenone	68.6[b]	1.2×10^{10}	
1,3-cyclohexadiene	~51.0[c]	1.0×10^{10}	
anthracene	42.7[d]	6.3×10^{9}[e]	7.5×10^{7}[f]
perylene	35.1[b]		9.5×10^{9}

[a] Determined by pulse radiolysis unless otherwise stated. [b] Reference 18. [c] Reference 19. [d] Reference 20. [e] Determined by pulsed nitrogen laser excitation at 337 nm. [f] Calculated from the equilibrium constant for triplet energy transfer.

problem of characterizing this important triplet state by means of the pulse radiolysis technique. Ideally we wished to (a) identify the triplet–triplet absorption of ^{3}Az* as reported by Görner and Schulte-Frohlinde,[12] (b) witness triplet energy transfer to an acceptor molecule and confirm that the triplet energy donating species has a lifetime identical with that of the transient suspected to be ^{3}Az*, (c) demonstrate the production of the latter as a result of triplet energy transfer by witnessing its time-resolved formation, and (d) establish an equilibrium for triplet energy transfer between Az and a suitable donor/acceptor of known triplet energy, thus allowing accurate determination of the Az triplet energy. These aims have been achieved. Although our approach to the examination of triplet state reactivity using the pulse radiolysis technique has been detailed elsewhere,[13] a brief summary is given here for the sake of clarity.

Energy absorption of a 20–50-ns pulse of high-energy electrons (several MeV) by an aromatic liquid such as benzene (B) produces significant yields of short-lived bound excited states of the matrix molecules[14] according to eq 1. After the pulse these species decay

$$B \rightsquigarrow {}^1B^*,\ {}^3B^* \qquad (1)$$

via the normal photophysical channels or, in the presence of suitable additive molecules, pass on their electronic excitation energy. Since the rate of transfer is purely concentration dependent for exothermic processes, a solute of concentration 100-fold higher than other additives will be essentially exclusively excited. The short lifetimes of ^{1}B*[15] and ^{3}B* in liquid benzene, 12 and 3 ns, respectively,[16] and the short lifetime of the singlet state of the acceptor molecule mean that the formation of the triplet state of the latter will, in general, be complete within 50 ns of the electron pulse. Its subsequent lifetime will be governed by the composition of the solution with respect to further low-concentration additives.

II. Experimental Section

Pulse radiolysis experiments were performed at the Christie Hospital and Holt Radium Institute, Manchester, using the Vickers 10-MeV linear accelerator with pulse widths of 20–50 ns. Kinetic absorption measurements were made with the apparatus described by Keene and Hodgson.[17] Voltage wave forms at the anode of either an EMI 9783R photomultiplier or a silicon SH 100 diode coupled to a 56-Ω load resistance, rise time <5 ns, were transferred to the memory of a modified Commodore 2001-32 PET via a Tektronix 7912 AD Transient Digitizer. Irradiations were carried out at ambient temperature, and solutions were deaerated by prolonged bubbling with argon. In this work ground-state absorption by azulene was a problem. In those instances where relatively high concentrations of this material ($>5 \times 10^{-4}$ mol L^{-1}) were used it was necessary to restrict the optical path length of the cell to 5 mm in order to maintain sufficient analyzing light intensity below 365 nm.

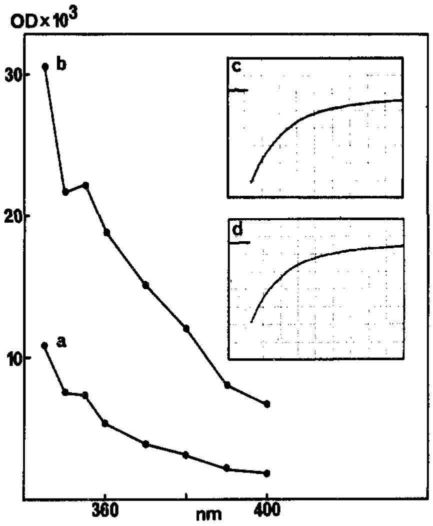

Figure 1. Transient absorption spectra measured 1 μs after the absorption of a 50-ns electron pulse (5-mm cell) by deaerated benzene containing (a) azulene (10^{-3} mol L^{-1}) and (b) 1,3-cyclohexadiene (10^{-1} mol L^{-1}) and azulene (10^{-3} mol L^{-1}). Insets: time dependence of azulene triplet decay monitored at 370 nm after absorption of a 50-ns electron pulse (2.5-cm cell) by deaerated benzene containing (c) azulene (10^{-2} mol L^{-1}), 1.6% absorption/division, 5 μs/division, and (d) 1,3-cyclohexadiene (10^{-1} mol L^{-1}) and azulene (2×10^{-3} mol L^{-1}), 2.6% absorption/division, 5 μs/division.

Pulsed laser experiments were performed as previously described.[13a] Benzene (AnalaR) was distilled from phosphorus pentoxide after sulfuric acid–water–bicarbonate–water treatment. Azulene (Aldrich) was sublimed. Benzophenone (EtOH), anthracene (EtOH), and perylene (toluene) were recrystallized. 1,3-Cyclohexadiene (Fluka) was distilled from lithium aluminum hydride under nitrogen before use.

III. Results and Discussion

In the light of the considerations outlined in the introduction we have used the pulse radiolysis technique to witness triplet energy transfer both to and from Az and to determine the corresponding rate constants which are summarized in Table I.

1. Triplet Energy Transfer from Benzene to Azulene. Pulse radiolysis of a deaerated solution of Az (10^{-3} mol L^{-1}) in benzene resulted in "immediate" formation of a species apparently exhibiting an absorption maximum at ~355 nm. By monitoring the bleaching of Az at 620 nm it was possible to correct the transient absorption in the 340–400-nm region for changes in the Az ground-state absorption. This yielded the spectrum shown in Figure 1a which shows no significant maximum down to 345 nm, the shortest wavelength at which sufficient analyzing light was transmitted through a 5-mm cell. If this transient is indeed ^{3}Az* its formation must take place by triplet energy transfer from benzene (eq 2) since direct laser excitation of Az in benzene yields no such species.[12,19] Its subsequent lifetime will be governed in

$${}^3B^* + Az \rightarrow B + {}^3Az^* \qquad (2)$$

principle by eq 3 and 4, but no dependence of this property on Az concentration was observed. Although the λ_{max} value before

$${}^3Az^* + Az \xrightarrow{k_{sq}} Az + Az \qquad (3)$$

$${}^3Az^* \xrightarrow{k_d} Az \qquad (4)$$

correction (~355 nm) was similar to that reported by Görner and Schulte-Frohlinde (360 nm),[12] the exponential decay (Figure 1c) corresponded to a lifetime of 11.7 μs which is to be compared with the reported value of 4 ± 2 μs.[12] Confirmation of the identity of this species as ^{3}Az* was obtained as follows.

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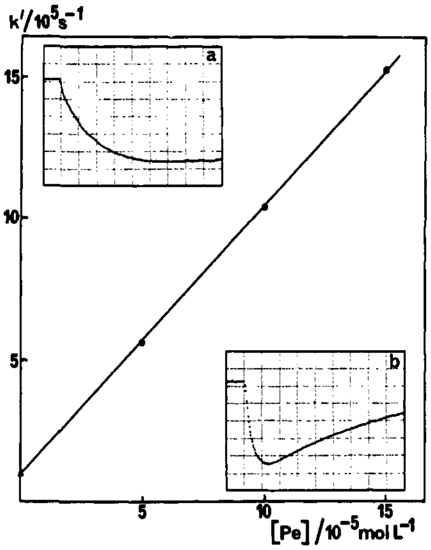

Figure 2. First-order constants for perylene triplet formation vs. perylene concentration. Insets: (a) time dependence of perylene triplet formation monitored at 490 nm after absorption of a 50-ns electron pulse by deaerated benzene (2.5-cm cell) containing azulene (5×10^{-3} mol L^{-1}) and perylene (5×10^{-5} mol L^{-1}), 4.0% absorption/division, 1 μs/division; (b) repeat of (a) with time scale of 5 μs/division.

2. Triplet Energy Transfer from Azulene to Perylene. Pulse radiolysis of deaerated benzene solutions of Az (5×10^{-3} mol L^{-1}) containing various concentrations of perylene (Pe; 5–20 $\times 10^{-5}$ mol L^{-1}) resulted in "slow" exponential grow-in of ^{3}Pe* (Figure 2) as a result of the operation of eq 5. The first-order rate constant

$$^3\mathrm{Az}^* + \mathrm{Pe} \xrightarrow{k_{\mathrm{et}}} \mathrm{Az} + {}^3\mathrm{Pe}^* \qquad (5)$$

for ^{3}Pe* formation, k', is given by eq 6 (cf. eq 3, 4, and 5), and

$$k' = k_{\mathrm{d}} + k_{\mathrm{sq}}[\mathrm{Az}] + k_{\mathrm{et}}[\mathrm{Pe}] \qquad (6)$$

a plot of k' vs. [Pe] (Figure 2) gave a value for k_{et} of 9.5×10^9 L mol^{-1} s^{-1} and an intercept, 9.1×10^4 s^{-1}, which was insensitive to [Az] over the range 1-5 $\times 10^{-3}$ mol L^{-1}. This places a limit of $<2 \times 10^6$ L mol^{-1} s^{-1} on the self-quenching rate constant and gives a lifetime of 11.0 μs for ^{3}Az*. This is in excellent agreement with that of 11.7 μs for the transient observed on pulse radiolysis of benzene containing only Az (section III.1). The rate constant for triplet energy transfer from Az to Pe of 9.5×10^9 L mol^{-1} s^{-1} clearly corresponds to a substantially exothermic process (cf. ref 1a, 13a, 21). Az thus possesses a triplet state which is significantly higher in energy than that of Pe (35.1 kcal mol^{-1} [18]). The exponential decay of ^{3}Pe* in the presence of Az (5×10^{-3} mol L^{-1}; Figure 2b) corresponds to a lifetime of 40 μs, exactly the same as that obtained when ^{3}Pe* formation was sensitized by naphthalene. There is therefore no kinetic evidence for a lower lying triplet state of Az than the one sensitizing ^{3}Pe* formation. This result simply supports conclusions already reached by Herkstroeter.[7]

3. Triplet Energy Transfer from Benzophenone and 1,3-Cyclohexadiene to Azulene. Görner and Schulte-Frohlinde have reported that on laser excitation of triplet donors in the presence of Az the "360-nm transient" appeared "within the rise time of the laser pulse (10 ns)". This is not easy to understand since at the employed values of [Az] the grow-in of ^{3}Az* should exhibit a lifetime of 100–600 ns depending on individual experimental conditions, assuming it is produced via a bimolecular triplet energy-transfer process. It was thus important to be able to demonstrate the grow-in of this species as a result of triplet energy transfer. Two sets of experiments have been performed with this aim in view.

(a) Triplet Energy Transfer from Benzophenone to Azulene. Pulse radiolysis of deaerated benzene solutions of benzophenone (BP; 10^{-2} mol L^{-1}) containing various concentrations of Az (0–10^{-4} mol L^{-1}) resulted in "immediate" formation of ^{3}BP* (Figure 3), the absorption of which was monitored at 525 nm. The strictly exponential decay of this species was dependent on Az concentration, thus allowing straightforward determination of the rate constant for triplet energy transfer (eq 7), $k_{\mathrm{et}} = 1.2 \times 10^{10}$ L mol^{-1} s^{-1}.[22] It was not possible to witness the corresponding grow-in

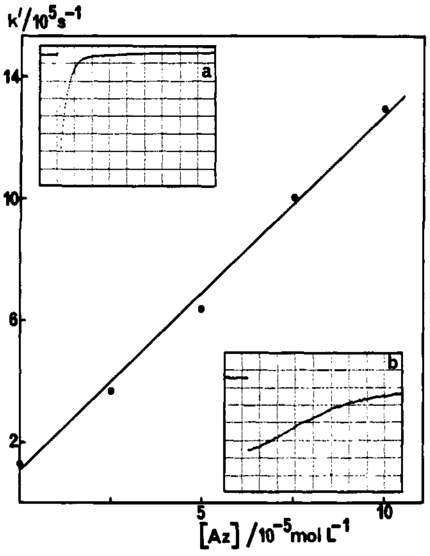

Figure 3. First-order constants for benzophenone triplet decay vs. azulene concentration. Insets: (a) time dependence of transient absorption monitored at 525 nm after absorption of a 20-ns electron pulse by deaerated benzene (2.5-cm cell) containing benzophenone (10^{-2} mol L^{-1}) and azulene (10^{-4} mol L^{-1}), 2.0% absorption/division, 2 μs/division; (b) time dependence of transient absorption monitored at 380 nm for an experiment identical with (a), 0.6% absorption/division, 2 μs/division.

$$^3\mathrm{BP}^* + \mathrm{Az} \xrightarrow{k_{\mathrm{et}}} \mathrm{BP} + {}^3\mathrm{Az}^* \qquad (7)$$

of ^{3}Az* in the 350–400-nm region. This is simply a consequence of the fact that ^{3}BP* also absorbs in this region.[23] A hint of grow-in was observable at 380 nm (Figure 3b), and the decay at this wavelength, analyzed after complete decay of ^{3}BP* (cf. Figure 3a,b), corresponded to a lifetime of 10.2 μs, close to values already determined for ^{3}Az* (sections III.1 and III.2). That the failure to observe the grow-in of ^{3}Az* is a consequence of donor triplet absorption in the critical spectral region was confirmed as follows.

(b) Triplet Energy Transfer from 1,3-Cyclohexadiene to Azulene. We have recently characterized the triplet state of 1,3-cyclohexadiene (CHD) which is readily produced by pulse radiolysis of benzene solutions of CHD.[13b] It exhibits a $\lambda_{\max}$ of 310 nm, does not absorb significantly in the 360–400-nm range, and has a relaxed triplet energy of ~51 kcal mol^{-1}.[19] This value was clearly likely to be sufficient to sensitize the formation of ^{3}Az*, and this turned out to be the case. Pulse radiolysis of deaerated benzene solutions of CHD (10^{-1} mol L^{-1}) containing various concentrations of Az resulted in "slow" grow-in of ^{3}Az* (Figure 4). The rate constant for triplet energy transfer (eq 8) was determined in the usual manner by plotting first-order constants for grow-in, k', against Az concentration (Figure 4). The k_{et} value

$$^3\mathrm{CHD}^* + \mathrm{Az} \xrightarrow{k_{\mathrm{et}}} \mathrm{CHD} + {}^3\mathrm{Az}^* \qquad (8)$$

of 1.0×10^{10} L mol^{-1} s^{-1} clearly corresponds to a substantially exothermic reaction. The intercept corresponds to the decay constant of ^{3}CHD* produced under identical conditions of dose and concentration in the absence of Az and monitored at 310 nm (Figure 4b). This clearly identifies ^{3}CHD* as the triplet energy donor in these experiments. The spectrum and lifetime, 11.0 μs, of ^{3}Az* produced in this manner, were essentially identical with

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(22) Görner and Schulte-Frohlinde quote a value of 8×10^9 L mol^{-1} s^{-1}.[12]

(23) For instance the extinction coefficients of ^{3}BP* at 360 and 525 nm are 2660 and 7120, respectively.[19]

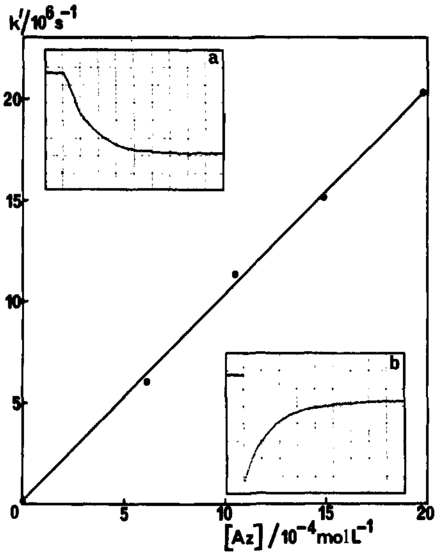

Figure 4. First-order constant for azulene triplet formation vs. azulene concentration. The data point at zero concentration is the first-order constant for 1,3-cyclohexadiene triplet decay, cf. inset (b). Insets: (a) time dependence of azulene triplet formation monitored at 370 nm after absorption of a 50-ns electron pulse by deaerated benzene (2.5-cm cell) containing 1,3-cyclohexadiene (10^{-1} mol L^{-1}) and azulene (1.5×10^{-3} mol L^{-1}), 2.4% absorption/division, 50 ns/division; (b) time dependence of 1,3-cyclohexadiene triplet decay monitored at 310 nm after absorption of a 50-ns electron pulse by deaerated benzene (2.5-cm cell) containing 1,3-cyclohexadiene (10^{-1} mol L^{-1}), 2.0% absorption/division, 2 µs/division.

those determined by pulse radiolysis of deaerated benzene containing Az only. This is demonstrated in Figure 1. The four separate determinations of the $^3Az^*$ triplet lifetime have thus yielded values of 11.7, 11.0, 10.2, and 11.0 µs. We therefore place its lifetime at 11 ± 1 µs. At this stage the only remaining problem was an accurate determination of the triplet energy of this species.

4. Triplet Energy Equilibration between Anthracene and Azulene. When the energy difference between a triplet donor and acceptor decreases to about 4 kcal mol⁻¹, back transfer of triplet energy may become important,[24] assuming that significant relaxation of the acceptor triplet does not occur following the energy-transfer process. For appropriate concentrations of donor and acceptor it is possible to observe the establishment of an equilibrium between the two triplet states if their natural decays are slow relative to the energy-transfer processes. Such equilibria have been described previously,[13a,25] and by suitable manipulation of concentrations we have been able to demonstrate the establishment of an equilibrium between Az and anthracene (An), eq 9. For a true equilibrium the free energy change, ΔG_T, may be

$$^3An^* + Az \underset{k_{et}^{b}}{\overset{k_{et}^{f}}{\rightleftharpoons}} An + {^3Az^*} \tag{9}$$

assumed to equal the difference in electronic excitation energies of the two triplet states, ΔE_T. Thus, eq 10 should hold where $K = [An][^3Az^*][^3An^*]^{-1}[Az]^{-1}$.

$$-\Delta E_T = 2.303RT \log K \tag{10}$$

Pulse radiolysis of deaerated benzene solutions of An ($6-8 \times 10^{-2}$ mol L^{-1}) containing Az ($4-10 \times 10^{-4}$ mol L^{-1}) resulted in "immediate" formation of $^3An^*$ followed by rapid exponential decay to an equilibrium position, dependent on ground-state concentrations, and subsequent bleeding of this equilibrium (Figure 5a). This interpretation was confirmed by the fact that the spectrum of the absorbing species was identical with that of $^3An^*$ for both the fast and slow components of the decay as shown in Figure 5. In this figure is also shown a semilogarithmic plot of log OD vs. time for the $^3An^*$ decay monitored at 425 nm. By assuming, as is reasonable in this case, that a negligible number of triplet states are lost via natural decay before equilbrium is established, i.e., $^3An^*$ lost equals $^3Az^*$ gained, a ratio $[^3An^*]/[^3Az^*]$ could be determined from optical densities at the end of the electron pulse and at the arrowed time shown in Figure 5. Averaging over four separate experiments, using different concentrations and assuming a generous error of ±25%, an equilibrium constant of 84 ± 21 and a ΔE_T value of −2.6 ± 0.2 kcal mol⁻¹ were determined. The triplet energy of Az is therefore placed at 40.1 ± 0.2 kcal mol⁻¹. In order to avoid problems associated with back transfer we have determined the rate constant for triplet energy transfer from An to Az in benzene, k_{et}^{f} in eq 9, by means of pulsed nitrogen laser excitation of An at 337 nm with [An] = 1.85×10^{-4} mol L^{-1} and [Az] = $0-4.6 \times 10^{-5}$ mol L^{-1}. The thus determined k_{et}^{f} value of 6.3×10^9 L mol⁻¹ s⁻¹[26] and an equilibrium constant of 84 yield a value for k_{et}^{b} (eq 9) of 7.5×10^7 L mol⁻¹ s⁻¹.

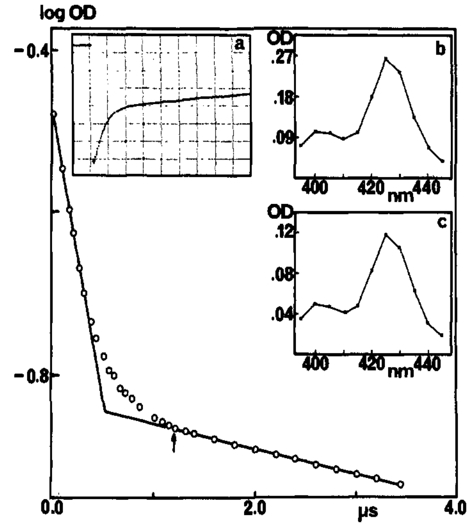

Figure 5. Semilogarithmic plot for transient absorption monitored at 425 nm after absorption of a 20-ns electron pulse by deaerated benzene (2.5-cm cell) containing anthracene (8.1×10^{-2} mol L^{-1}) and azulene (7.2×10^{-4} mol L^{-1}). Insets: (a) corresponding time dependence of transient absorption monitored at 425 nm, 8.1% absorption/division, 500 ns/division; (b and c) corresponding transient absorption spectra measured 150 ns and 3 µs, respectively, after the electron pulse.

IV. Conclusions

In agreement with others[7,12] we can find spectroscopic and kinetic evidence for only one low-lying triplet state of azulene in benzene solution. This species exhibits triplet–triplet absorption between 400 and 345 nm, increasing in intensity toward the ultraviolet, and a lifetime of 11 ± 1 µs. Although this lifetime is appreciably longer than previously reported values, it is supported by kinetic absorption measurements and triplet energy-transfer experiments. The identity as azulene triplet has been rigorously established as a consequence of witnessing both (a) its time-resolved formation as a result of the quenching of 1,3-cyclohexadiene triplet at an essentially diffusion-controlled rate and (b) its time-resolved sensitization of perylene triplet formation, again at a close to diffusion-controlled rate. The electronic excitation energy of this species is now firmly placed at 40.1 ± 0.2 kcal mol⁻¹.

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Registry No. Az, 275-51-4; CHD, 592-57-4; Pe, 198-55-0; An, 120-12-7; BP, 119-61-9.

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(26) Previously quoted values are 7.2×10^9,[3] 7.4×10^9,[7] and 5×10^9 [12] L mol⁻¹ s⁻¹.