

tored by pmr. Appearance of singlets at δ 2.59 and 1.73 is indicative of the formation of acetophenone and cyclopropane, respectively.³⁷

Quantum Yields and Quenching Studies. Degassed benzene solutions of 0.05–0.4 M ketone were irradiated in sealed Pyrex tubes. The tubes were irradiated on a merry-go-round apparatus using a 450-W lamp and a potassium chromate filter solution to isolate the 313-nm irradiation. Variable-temperature runs used a small merry-go-round in an unsilvered quartz dewar containing 95% ethanol using an external light source. Temperature regulation was achieved with a Haake thermoregulator by circulating methanol through a coiled heat exchanger contained within the quartz dewar. Light intensities were calculated using the type II reaction of valerophenone ($\Phi_{\text{cleavage}} = 0.33$) as a secondary actinometer.³⁸ Irradiated solutions were analyzed by flame ioniza-

tion vpc using a 6 ft \times 1/8 in. column of 4% QF-1 and 1% Carbowax 20M on Chromosorb G for ketones 3–6 and a 15 ft \times 1/8 in. column of SE-30 on Chromosorb P at 150° for ketones 6–9. Deuterium isotope effects were determined by simultaneous irradiation of protio and deuterio samples. Stern–Volmer quenching studies were conducted using procedures identical with those used in the quantum yield studies. Solutions of desired 1,3-pentadiene concentrations were prepared by mixing appropriate quantities of a standard benzene stock solution of quencher with benzene solutions of substrate.

Acknowledgment. One of the authors (F. D. L.) wishes to thank Professor Sighart F. Fischer for stimulating discussions of radiationless processes. The authors at Columbia acknowledge the Air Force Office of Scientific Research (Grant No. AFOSR-70-1848D) and the authors at Northwestern acknowledge the Research Corporation for their generous support of this work.

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Single Photon Counting and Magic Multipliers in Direct Measurement of Singlet Excited State Di- π -methane Rearrangement Rates in the Picosecond Range. Mechanistic Organic Photochemistry. LXXXIII^{1a,b}

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Abstract: A single photon counting technique utilizing an on-line PDP-8/I computer was devised and employed to obtain exceedingly rapid rates of singlet excited state decay and rearrangement. In this approach the computer was used both as a multichannel analyzer and also for on-line systematic reiterative convolution, fitting the results to theory. This permitted measurement of rates of decay which were faster than the lamp flash. Additionally, a powerful technique was developed for determination of those rates which were too rapid to measure at room temperature; this utilized a magic multiplier which gives the ratio of room-temperature to low-temperature rates. The rates obtained by this direct procedure were compared with those obtained earlier by an indirect procedure. Singlet excited state decay rates were measured for naphthalene and tetraphenylethylene for evaluation of the method. Both decay and the di- π -methane rearrangement rates were obtained for the excited singlets of 1,1,4-triphenyl-3,3-dimethyl-1,4-pentadiene, 1,1-diphenyl-3,3,5-trimethyl-1,4-hexadiene, 1,1,3,3-tetraphenyl-5-methyl-1,4-hexadiene, and 1,1,5,5-tetraphenyl-3,3-dimethyl-1,4-pentadiene. The rates of rearrangement increased in the preceding sequence with the triphenylpentadiene rearranging at $k_r = 5.8 \times 10^8 \text{ sec}^{-1}$ and the tetraphenylpentadiene at $k_r = 1.4 \times 10^{11} \text{ sec}^{-1}$. Also, there was a nearly perfect ratio between rate of singlet decay and rate of di- π -methane rearrangement. The decay rates increased in the above order with the same two compounds being at the extremes with rates of $k_{\text{dt}} = 7.2 \times 10^{10} \text{ sec}^{-1}$ and $k_{\text{dt}} = 1.8 \times 10^{12} \text{ sec}^{-1}$, respectively. This order of reactivity correlates nicely with expectation based on a rate-limiting bridging step of the π - π^* excited singlet. In the case of decay, evidence was obtained for electronic relaxation at the stage of the bridged biradicaloid species.

In connection with our previous investigations² we were particularly intrigued by the possibility of correlating the reaction rates for rearrangement of the excited singlets of a series of acyclic di- π -methane reactants to structural variations. While there is a tendency in photochemistry, at its present stage of development, to utilize quantum yields as a measure of reactivity, quantum yields really afford only the tendency

of the excited state to form product relative to all other competing processes. Ideally, one should have the absolute rate for unimolecular rearrangement of the excited state of interest.

In our last study on this subject,² we described an indirect method for obtaining such excited state rate constants. Indeed, the method has proven useful for deriving relative rate constants. Nevertheless, it was clear that an absolute method was needed. Additionally with a large number of singlet di- π -methane rearrangements now known,^{2,3} it was of considerable interest to

(1) (a) For a preliminary communication describing some of these results, note H. E. Zimmerman, D. P. Werthemann, and K. S. Kamm, *J. Amer. Chem. Soc.*, **95**, 5094 (1973). (b) For the previous paper of this series, see H. E. Zimmerman, D. W. Kurtz, and L. M. Tolbert, *J. Amer. Chem. Soc.*, **95**, 8210 (1973).

(2) H. E. Zimmerman and A. A. Baum, *J. Amer. Chem. Soc.*, **93**, 3646 (1971).

(3) For a general review of the di- π -methane rearrangement, see S. S. Hixson, P. S. Mariano, and H. E. Zimmerman, *Chem. Rev.*, **73**, 531 (1973).

attempt to correlate the rates of rearrangement with excited state structure and to the mechanistic pathways available.

The problem was certainly not trivial. Thus, for example, single photon counting⁴ has proven to be an excellent method of getting rates of excited singlet disappearance where singlet lifetimes are of the order of 0.5 nsec or more. However, the indication was that the acyclic di- π -methane reactants had lifetimes considerably shorter than this.

Thus, the present study had dual objectives. One was to devise a method capable of obtaining such super-fast rate constants. The other was to apply the technique to the di- π -rearrangement and search for a structure-rate correlation.

The General Approach. Two definitions are basic to the present direct method and the previous indirect approach. These are given in

$$\phi_r = k_r/k_{dt} \quad (a) \quad \text{or} \quad k_r = \phi_r k_{dt} \quad (b) \quad (1)$$

$$\phi_f = k_f/k_{dt} \quad (a) \quad \text{or} \quad k_f = \phi_f k_{dt} \quad (b) \quad (2)$$

where ϕ_r is the singlet reaction quantum yield and ϕ_f is the fluorescence quantum efficiency, k_r is the rate of singlet excited state rearrangement, k_f is the rate of fluorescence, and k_{dt} is the total rate of dissipation of the singlet excited state by all processes. Thus $k_{dt} = k_r + k_f + k_d$, where for convenience, k_d is taken as a decay rate which includes both internal conversion to ground state and also intersystem crossing.

In our previous study,² we combined eq 1b and 2b to give

$$k_r = k_f(\phi_r/\phi_f) \quad (3)$$

This was used in conjunction with fluorescence emission data and reaction quantum yields to give values of k_r for two examples of the di- π -methane rearrangement. The same approach was published independently and simultaneously by Dalton and Turro.⁵

The present approach was predicated instead on direct determination of the k_{dt} 's. It is seen that with the k_{dt} 's available, eq 1b, together with the known quantum yields of reaction, leads directly to the unimolecular rates of singlet excited state rearrangement.

Using single photon counting it is possible to determine the excited state singlet decay curve even where the lifetime is of the same order or shorter than the lifetime of the lamp flash. Knowing the lamp intensity as a function of time and knowing the observed fluorescence decay, one should, in principle, be able to determine the true decay function using several mathematical approaches. In practice, decay times of the order of 1 nsec are routinely available, a number of measurements in the range of 0.5 nsec have been described, and one measurement of a lifetime of 0.4 nsec^{4d} and one at 0.2 nsec^{4e} have been obtained. Shorter lifetimes have not been reported.

The present research used a *ca.* 2 nsec nitrogen flash

(4) (a) For a general review, note J. B. Birks, *Progr. React. Kinet.*, 4, 239 (1967); (b) W. R. Ware, Office of Naval Research Technical Report No. 3, March 1969; (c) L. M. Bollinger and G. E. Thomas, *Rev. Sci. Instrum.*, 32, 1044 (1961); (d) W. R. Ware, "Creation and Detection of the Excited State," Vol. 1, Part A, Marcel Dekker, New York, N. Y., 1971, Chapter 5; (e) R. M. Lambrecht, T. M. Kelly, and J. A. Merrigan, *Chem. Instrum.*, 2, 363 (1970); (f) L. Hundley, T. Coburn, E. Garwin, and L. Stryer, *Rev. Sci. Instrum.*, 38, 488 (1967).

(5) J. C. Dalton and N. J. Turro, *J. Amer. Chem. Soc.*, 93, 3569 (1971).

lamp of special design allowing focussing of the light on the slits of a monochromator preceding the sample chamber. A 1P28 photomultiplier was employed to signal beginning of a light pulse and an RCA 8575 photomultiplier was used to detect the single photons emitted by the sample. This apparatus is described in more detail in the Experimental Section.

In our approach, a PDP-8/I computer was employed to store the number of single photons emitted by the sample at each time delay; thus the computer functioned as a multichannel analyzer. The computer stored both the decay curves of the lamp flash itself and the emission of the sample under study.

A systematic reiterative convolution approach was designed which allowed the computer to determine what values for the excited state decay would lead to the best fit with observed emission when one takes into account the lamp flash. The only assumption was that the singlet excited state decayed either as a single exponential or as a sum of two exponentials. The present version of reiterative convolution proved capable of affording lifetimes of 100 psec, and lower with the sacrifice of accuracy.

Additionally, another device was utilized to obtain still faster rates of decay and reaction. This was predicated on the finding that the lifetime of the singlet excited states presently of interest increased *ca.* 200-fold when measured at 77°K compared with room temperature. Thus, some of the singlet excited states studied decayed too rapidly at room temperature to measure even with use of the reiterative convolution technique but were measurable at 77°K. However, a temperature dependence of the fluorescence quantum efficiency was observed. This must come from a dependence of k_{dt} with temperature if k_f is temperature independent, since the fluorescence quantum yield is just the ratio of these two quantities (note eq 2a). Actually there is evidence that k_f is temperature independent, and this point is discussed later in connection with the interpretation.

If one then takes eq 2a for each of two temperatures, room temperature and 77°K, division gives

$$M = \phi_r^{77}/\phi_r^{rt} = k_{dt}^{rt}/k_{dt}^{77} \quad (4)$$

M then gives the ratio of the decay rates of the singlet at two temperatures. This is a useful ratio. Thus if a low-temperature decay rate is experimentally accessible, one can obtain a much faster room-temperature decay rate by use of this "magic multiplier" M as in eq 5. With such very rapid room-temperature decay

$$k_{dt}^{rt} = M k_{dt}^{77} \quad (5)$$

rates then available, one can proceed to obtain rates of singlet excited state reaction at this temperature from knowledge of the reaction quantum yields using eq 1b. Accordingly, from eq 1b and 5 one obtains

$$k_r^{rt} = M \phi_r^{rt} k_{dt}^{77} \quad (6)$$

Elaboration of the Method. It was observed that the nitrogen flash lamp constructed for this research (note Experimental Section) was unusually steady and reproducible. For example, the half-width of the lamp flash was constant during a series of runs within a few per cent. Such a steady lamp flash proved a requirement for the treatment below. When the sample com-

partment contained one of the di- π -methane systems under study, the emission observed by single photon counting was found to be a peak which was broader than the lamp flash itself, even in the case of the fastest decaying diene. Thus there was needed a means of dissecting the natural singlet decay curve from the emission peak, taking into account the exact shape of the lamp flash exciting the sample.

This problem has been treated by convolution.^{4b,d,e} Thus, the lamp flash is not an instantaneous event; rather, the light pulse can be viewed as composed of a large number of short duration (*i.e.*, δ function) subpulses in juxtaposition. Each of these brief subpulses of light generates a new incremental amount of excited singlets which then begin to decay. Hence, the observed emission in any time interval is the sum of contributions from each batch of singlets produced by the subpulses in the preceding intervals. For example, if I_0 is the intensity of the zero-time subpulse, I_1 is the intensity of subpulse 1, I_2 the next intensity, etc., then the observed emission in interval 2 (*i.e.*, E_2) is the sum of three contributions. These are I_0D_2 (where D_2 is the decay function giving the extent to which the excited state has decayed over two intervals), I_1D_1 (note that the excited states generated by the pulse of intensity I_1 has had only one interval to decay, thence D_1), and similarly I_2D_0 . Hence $E_2 = I_0D_2 + I_1D_1 + I_2D_0$. This is generalized in the equation

$$E_t = \sum_{n=0}^t I_n D_{(t-n)} \quad (7a)$$

The continuous, integral formulation equivalent to this is given in the equation

$$E_t = \int_0^t I(n)D(t-n)dn \quad (7b)$$

This is the well-known convolution integral.

With such convolution expressions, there are techniques for extracting the decay function D (*i.e.*, deconvolution); for negative exponential decay this would afford the rate constants for excited-state decay. However, practically it appears that such direct deconvolution is especially subject to computational difficulties and errors.⁶ The present research therefore sought another approach.

The method developed was a variation of reiterative convolution. We assumed that the general form of the decay function was a single negative exponential or a sum of such exponentials. With a reasonable initial guess for the rate constant and amplitude (note below), it was possible to use eq 7a to determine E_t as a function of time and to compare this with the observed emission curve. Equation 7a, being a summation of discrete terms, is ideally suited for computer methods, since the values of E_t , I_t and D_t could be stored as core arrays.

We could have proceeded to randomly vary the parameters to optimize the fit of the convoluted theoretical decay curve given by eq 7a with the experimental curve. This approach has been used.^{4,6} However, analysis of the problem revealed that it was possible to obtain the variation in E_t as a function of incre-

mental changes in the assumed parameters. Thus, for a sum of negative exponentials

$$D_t = \sum_{j=1}^m a_j e^{-k_j t} \quad (8)$$

Substituting eq 8 into 7a and differentiating with respect to k_j , we obtain

$$\frac{\partial E_t}{\partial k_j} = -a_j \sum_{n=0}^t I_n (t-n) e^{-k_j(t-n)} = K_{tj} \quad (9a)$$

This expression gives the dependence of the calculated emission intensity at time t on the selected magnitude of the decay rate constant k_j . If we assume just a single negative exponential decay, we have only a single k to obtain. If we use the sum of two negative exponentials as the form of the excited singlet decay, then we have such an expression for k_1 and another for k_2 . Here a_j is the coefficient weighting the j th negative exponential. Finally, n is the same time index as in eq 7a and 7b.

Similarly, one can derive the dependence of the emission intensity at time t on each amplitude coefficient a_j by combining eq 7a and 8 and differentiating with respect to a_j .

$$\frac{\partial E_t}{\partial a_j} = \sum_{n=0}^t I_n e^{-k_j(t-n)} = A_{tj} \quad (9b)$$

In any iteration it is seen that the theoretical emission intensity at each time t (*i.e.*, E_t) calculated by the convolution expression of eq 7a will differ by ΔE_t from the experimental emission intensity at this time (*i.e.*, E_t^{exp}). In order to select the best new choices for the rate constants and amplitude coefficients, eq 8 and 9 were used. Thus each of these gives contributions of changes in the k 's and a 's to the total change in the E 's at the different times of observation. Since 512 different times were selected for observation, it is clear that there are 512 equations; each will have two unknowns (one Δk and one Δa if we have assumed a single exponential decay, twice this if a double exponential was used, and etc.). This is most easily formulated in matrix terminology. For the case of a single exponential, for example, eq 10 applies. For

$$\begin{bmatrix} \Delta E_1 \\ \Delta E_2 \\ \Delta E_3 \\ \vdots \\ \Delta E_n \end{bmatrix} = \begin{bmatrix} A_1 K_1 \\ A_2 K_2 \\ A_3 K_3 \\ \vdots \\ A_n K_n \end{bmatrix} \begin{bmatrix} \Delta a \\ \Delta k \end{bmatrix} \text{ or } \overline{\Delta E} = \overline{V} \overline{\Delta} \quad (10)$$

double and higher sums of exponential decays the variation matrix \overline{V} and the $\overline{\Delta}$ vector are expanded (note section on Calculations). The \overline{V} matrix is known for each iteration as is the $\overline{\Delta E}$ vector. One needs to solve for the $\overline{\Delta}$ vector which then gives the incremental changes in a and in k for the next iteration. Since inherent in eq 10 there are only two unknowns and 512 linear equations, the problem is overdetermined. Equation 10 then is solved, as indicated in the section on Mathematical Treatment of Data by a least-squares matrix inversion technique. This is followed by further similar iterations until the values of a and k converge to within limits specified at the start of the calculation.

Results

Test of the Method. In order to test the method, measurements on previously studied compounds were

(6) A. E. W. Knight and B. K. Selinger, *Spectrochim. Acta, Part A*, 27, 1223 (1971); this paper presents an extensive discussion of some of the pitfalls in treatment of single photon counting data.

Table I. Direct Measurement of a Singlet Lifetime and Decay Rates

Compd	Lifetime, ^a nsec	Decay rate, ^a sec ⁻¹	Temp, °K	No. of runs	Std dev, %
Naphthalene	107 ^b 284 ^c	9.35×10^6 3.52×10^6	295 77	4 4	10 3
Tetraphenylethylene	1.13 (1.27) ^{d,e} 4.36 (4.00)	$8.9 (7.9) \times 10^8$ $2.4 (2.5) \times 10^8$	295 77	3 3	5 (28) ^e 1 (2.5)
Triphenyl diene 1	0.025 2.91 (2.83)	4×10^{10} $3.4 (3.5) \times 10^8$	295 77	2 9	~50 ^f 6
Diphenyl diene 2	3.11 (2.63)	$3.2 (3.8) \times 10^8$	77	6	2 (6)
1,1,3,3-Tetraphenyl diene 3	1.90 (1.89)	$5.3 (5.3) \times 10^8$	77	7	14 (17)
1,1,5,5-Tetraphenyl diene 4	0.124	8.1×10^9	77	11	50
1,1,5,5-Bisnortetraphenyl diene 5	0.701 (0.872)	$1.4 (1.15) \times 10^9$	77	5	8 (14)

^a All measurements in methylcyclohexane-isopentane 4:1. ^b Reported as 110 nsec (*n*-hexane) and 120 nsec (cyclohexane).⁷ ^c Lit.⁷ 260–270 nsec at 110°K. ^d Lit.^{8b} 1.1 nsec. ^e In cases where shifting of the lamp flash was needed, the unshifted values are also given (note parentheses). ^f Estimated error.

made; the compounds selected were naphthalene and tetraphenylethylene. In the case of naphthalene the decay rate at room temperature has been reported as $9.10 \times 10^6 \text{ sec}^{-1}$ in *n*-hexane⁷ and as $8.33 \times 10^6 \text{ sec}^{-1}$ in cyclohexane.⁷ For tetraphenylethylene a decay rate of $9.0 \times 10^8 \text{ sec}^{-1}$ was obtained^{8b} at room temperature in benzene.

In the present study a decay rate for naphthalene in methylcyclohexane-isopentane (4:1) was observed as $9.3 \times 10^6 \text{ sec}^{-1}$ (note Table I), in excellent agreement with the literature. However, this case was exceptionally simple as can be seen by reference to Figure 1a which depicts the lamp flash *vs.* time, the observed fluorescence decay, the fitted decay curve derived from the reiterative convolution, and finally the calculated theoretical excited state decay curve. In this instance, the lamp flash is so short relative to the decay time that one almost might have used the observed experimental decay without taking the lamp flash into account. The low-temperature results for naphthalene are equally in agreement with the literature⁷ (note Table I).

A much more stringent test was provided by tetraphenylethylene with its much shorter lifetime. The results proved quite acceptable. However, in performing these experiments it was observed that there was a small but real uncertainty in the position of the lamp flash along the time axis. That this was only a result of time jitter and not variation in the overall observed data was evidenced by the identity in shape of a series of flash or emission curves. Thus the idea was conceived of improving the fit to experiment by shifting the time axis after each reiterative convolution reached an optimum fit; such shifting was utilized for the next reiterative convolution process when the standard deviation improved and was rejected when the standard deviation became larger. In the latter case, shifting in the reverse direction was then implemented. The entire process was continued until an optimum fit resulted. In each case where this approach was employed, the standard deviation among several runs improved considerably (note Table I). However, the actual change in lifetimes and decay rates, resulting from such shift-

ing, differed maximally by 25% in single runs and by 16% in an average of five runs.

The results of measurement for tetraphenylethylene are given in Table I; the unshifted values are given in parentheses when these differ. Figure 1b depicts the lamp flash, the fluorescence emission, the results of reiterative convolution, and the deconvoluted excited state decay curve. Again the agreement with the literature^{8b} was excellent.

Consideration of Potential Complications. There were several potential pitfalls and concerns in measurement of the exceedingly rapid rate constants of interest.

First, it is known that optical density is often temperature dependent;^{9a} optical density changes could lead to variation of fluorescence emission intensity independent of the change in fluorescence quantum yield whose temperature dependence was desired.^{9a} A second source of difficulty is the variation of solvent refractive index with temperature and the possibility^{9a} that this might lead to a variation of light capture by the emission monochromator. A last pitfall^{9b} would prove troublesome if the rate of Brownian rotation of excited singlets in solution were of the same order of magnitude as the rate of fluorescence decay, since then the rate constant could be in error due to depolarization effects. These arise as a result of a preferred directionality of emission from a molecule relative to the directionality of absorption and thus lead to a time dependence of emission relative to cell geometry.

Turning to the first potential problem, optical densities were measured at room temperature and at 77°K. It was indeed found that there were increases in optical density at the lower temperature. Thus an optical density of 0.95 for triphenyl diene 1 became 1.42 at 77°K and an optical density of 1.05 for the 1,1,5,5-tetraphenyl diene 4 became 1.30. However, a study of emission intensity in the spectrofluorometer used revealed only less than 20% dependence on optical density in the optical density ranges used. One interesting aspect is a simple derivation which reveals that maximum light emission, observed at 90° to incident light, and 5 mm from the cell front, occurs at 0.87 optical density. Initially, at low concentration, emitted fluorescence increases linearly with concentration, but eventually the light absorbed at the 5-mm point begins to diminish owing to absorbance in the first half of the cell. The present insensitivity to optical density seems

(7) N. Mataga, M. Tomura, and H. Nishimura, *Mol. Phys.*, **9**, 367 (1967).

(8) (a) J. B. Birks, "Photophysics of Aromatic Molecules," Wiley-Interscience, London, 1970; (b) I. B. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules," Academic Press, New York, N. Y., 1965; (c) E. J. Bowen and J. Sahu, *J. Phys. Chem.*, **63**, 4 (1959); here a unity quantum yield was reported; (d) J. R. Huber, M. A. Mahaney, and W. W. Mantulin, *J. Photochem.*, **2**, 67 (1973).

(9) (a) W. W. Mantulin and J. R. Huber, *Photochem. Photobiol.*, **17**, 139 (1973); (b) M. Shinitzky, *J. Chem. Phys.*, **56**, 5979 (1972).

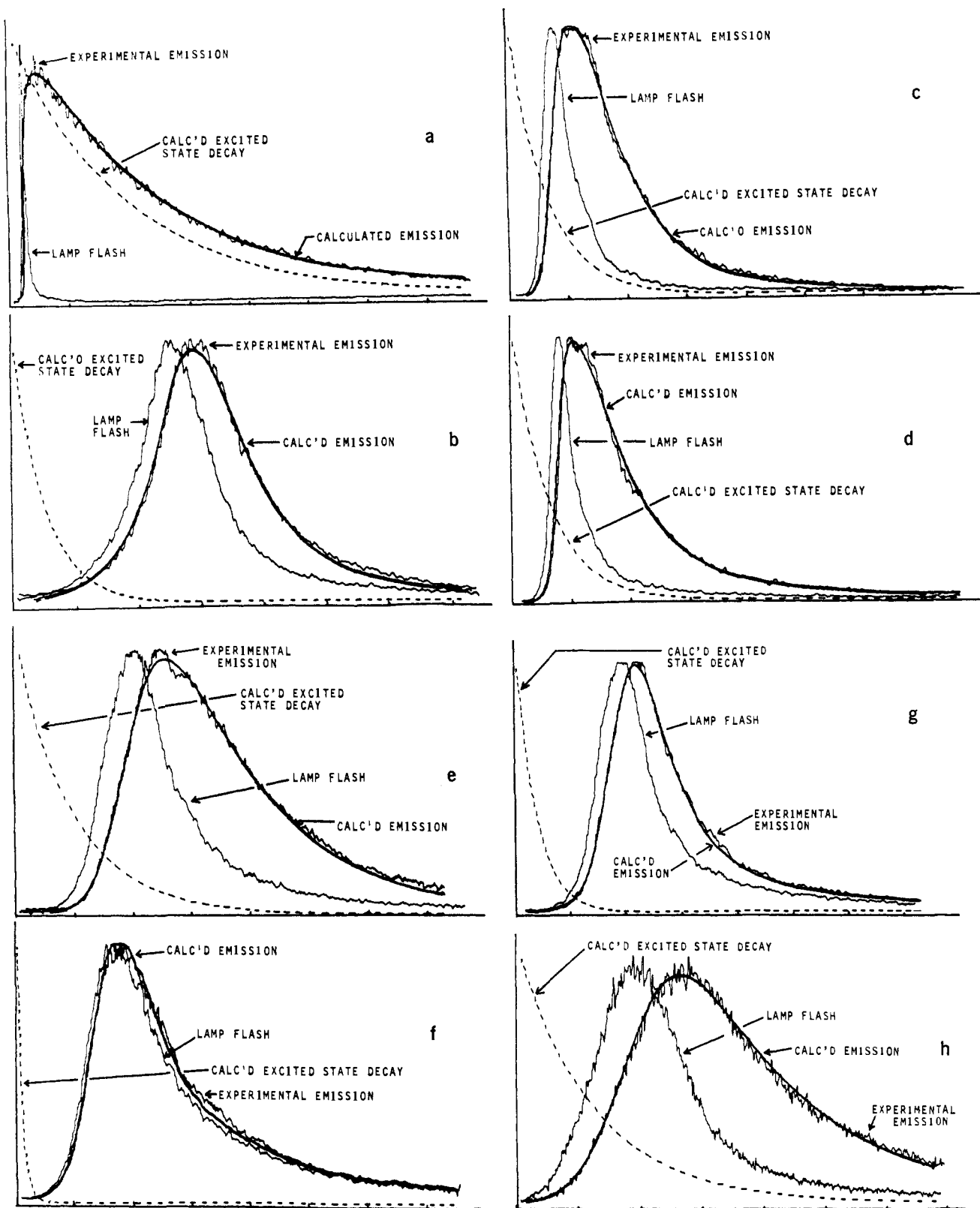


Figure 1. (a) Room temperature naphthalene decay, 50 nsec per division. (b) Room temperature tetraphenylethylene decay, 2 nsec per division. Low temperature decay of: (c) triphenyl diene 1, 5 nsec per division; (d) diphenyl diene 2, 5 nsec per division; (e) 1,1,3,3-tetraphenyl diene 3, 2 nsec per division; (f) 1,1,5,5-tetraphenyl diene 4, 2 nsec per division; (g) bisnortetraphenyl diene 5, 2 nsec per division; (h) 1,1,3,3-tetraphenyl diene 3, 2 nsec per division.

contingent on use of the relatively high optical densities employed near the maximizing value.

The second hazard referred to is the potential dependence on refractive index of light captured from the sample cell by the emission monochromator. This

proved not to be a problem presently as was indicated by two experimental checks. Actually, these two experiments were designed to test both the presence of a refractive index problem and also the optical density problem. In these experiments emission intensity from

Table II. Magic Multipliers and Derived Room Temperature Rates

Compd	Magic mult ^a	$k_{dt},^{296^\circ} \text{sec}^{-1}$	$\tau(295^\circ), \text{nsec}$	ϕ_r^b	$k_r^{296^\circ}, \text{sec}^{-1b}$
Naphthalene	2.2	7.8×10^6	129		
Tetraphenylethylene	4.1	9.4×10^8	1.07		
Diphenyl diene 2	222	7.1×10^{10}	0.014	0.097 ^c	6.9×10^9
Triphenyl diene 1	210	7.2×10^{10}	0.014	0.008 ^d	5.8×10^8
1,1,3,3-Tetraphenyl diene 3	216	1.13×10^{11}	0.009	0.076 ^{e,f}	8.5×10^9 ^f
				0.051 ^{e,g}	5.8×10^9 ^g
1,1,5,5-Tetraphenyl diene 4	225	1.8×10^{12}	0.00055	0.08 ^h	1.4×10^{11}
1,1,5,5-Bisnortetraphenyl diene 5	800	1.1×10^{12}	0.0009	0.0024 ^{i,j}	2.6×10^9 ^{i,j}
				0.0020 ^{i,k}	2.2×10^9 ^k

^a Estimated maximum error for entries 1 and 2, 10%, 20% for the next three, 40% for 4, and 30% for 5. ^b r refers to S_1 unimolecular rearrangement. ^c Reference 10. ^d Reference 2. ^e Reference 11. ^f For the vinyl-vinyl bridging reaction pathway. ^g For the phenyl-vinyl bridging reaction pathway. ^h Reference 12. ⁱ For vinyl-cyclopropane formation. ^j Reference 13. ^k For phenyl-vinyl bridging.

the solvent containing either suspended submicron silicic acid or dissolved 9,10-diphenylanthracene was measured at room temperature and 77°K. Since diphenylanthracene has a room-temperature fluorescence quantum yield of 0.95^{sd} and has been reported to be temperature independent,^{8c,d} both this compound in solution and the silicic acid scatterer should reveal any emission intensity dependence on temperature arising from purely geometric or instrumental (*i.e.*, compound independent) factors. A minor problem arises in the case of diphenylanthracene because of polarization considerations (*vide infra*). However, within a 10% experimental error, emission in the two experiments was temperature independent, indicating the unimportance presently of refractive index and optical density effects.

The last complication derives from polarization effects. Evidence for the absence of difficulties comes from two sources. First, as indicated in the Experimental Section, the polarization of triphenyl diene 1 was found to be the same within experimental error at room temperature and 77°K. This means that the rate of rotation in solution is slow compared with the rate of excited-state decay, and we note that this diene is the slowest decaying di- π -methane system studied. In contrast, naphthalene was completely depolarized at room temperature. Still another case was found in 1,1,3,3-tetraphenyl diene 3 which also was not depolarized at room temperature.

A second source of information on the polarization problem comes from the observation of single negative exponential decays when fits to double exponential were attempted. When rotation in solution is competitive with decay, double exponential decays are observed.^{9b}

This result is not surprising when one considers that the rates of rearrangement of the di- π -methane systems under study are sufficiently rapid that rotation should be slow in contrast.

Application of the Method. Thus, it appeared quite safe to turn to determination of the singlet excited state decay constants of interest. The results obtained for 1,1,4-triphenyl-3,3-dimethyl-1,4-pentadiene (1),² 1,1-diphenyl-3,3,5-trimethyl-1,4-hexadiene (2),¹⁰ 1,1,3,3-tetraphenyl-5-methyl-1,4-hexadiene (3),¹¹ 1,1,5,5-tetraphenyl-3,3-dimethyl-1,4-pentadiene (4),¹² and 1,1,5,5-tetra-

phenyl-1,4-pentadiene (5)¹³ are described in Table I and depicted in Figure 1. Each of these molecules is of interest since the first four undergo the di- π -methane and the last (*i.e.*, 5) has an *a priori* possibility to so rearrange but does not. The decay rate constants were measured at 77°K. With one exception the room-temperature decay rates proved too rapid to measure using this approach alone.

It was the room-temperature decay rates which were needed to obtain the rates of rearrangement, and the magic multiplier method of obtaining these decay rates, described above, was utilized. Thus as noted in a previous section (see eq 5), the much slower low-temperature decay rates could be used in conjunction with the magic multipliers to give the desired room-temperature decay rates. Also, eq 6, when used with the known reaction quantum yields, affords the room-temperature excited state rearrangement rate constants. Table II and eq 11–15 summarize the room-temperature decay rates and the unimolecular rearrangement rates obtained in this fashion.

Comparison of Tables I and II shows that in those cases where a room-temperature decay rate was obtainable directly and by use of the magic multiplier, the results are in excellent agreement. Thus, k_{dt} (direct) for naphthalene was measured as $9.3 \times 10^6 \text{ sec}^{-1}$ (note Table I); the parallel value obtained indirectly (note Table II) is $7.8 \times 10^6 \text{ sec}^{-1}$.

Tetraphenylethylene was a more exacting test in view of its shorter lifetime. The directly measured rate of decay was $8.9 \times 10^8 \text{ sec}^{-1}$ at room temperature which compared well with the indirect value of $9.4 \times 10^8 \text{ sec}^{-1}$. An extreme case was provided by the triphenyl diene 1. Inspection of Tables I and II shows that the directly measured rate of decay was $4 \times 10^{10} \text{ sec}^{-1}$. This does agree within experimental error with the $7.2 \times 10^{10} \text{ sec}^{-1}$ value derived from the magic multiplier. However, the directly measured value, corresponding to a 25 psec lifetime, is at the present limit of capability of the instrumentation and is certainly subject to a large relative error; yet the value obtained is correct as evidenced by the magic multiplier approach.

It should be recognized that the method of magic multipliers, as delineated in eq 4, was derived from eq 2a at two temperatures with the assumption that k_f is temperature independent. The good agreement of the room temperature rates with those obtained by use of the magic multiplier together with the low-tempera-

(10) H. E. Zimmerman and A. C. Pratt, *J. Amer. Chem. Soc.*, **92**, 6259 (1970).

(11) H. E. Zimmerman, R. J. Boettcher, and W. Braig, *J. Amer. Chem. Soc.*, **95**, 2155 (1973).

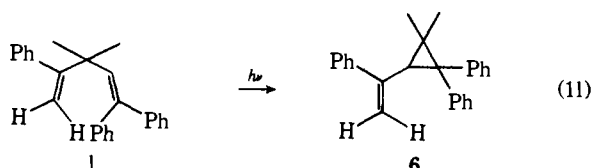
(12) H. E. Zimmerman and P. S. Mariano, *J. Amer. Chem. Soc.*, **91**, 1718 (1969).

(13) H. E. Zimmerman and J. A. Pincock, *J. Amer. Chem. Soc.*, **95**, 2957 (1973).

Table III. Indirectly Measured Decay Rates and Comparison with Direct Measurement

Compd	k_f, sec^{-1a}	ϕ_f^b	k_{dt}, sec^{-1}	$k(\text{indirect})/$ $k(\text{direct})$
Diphenyl diene 2	7.0×10^8	2.8×10^{-4}	2.5×10^{12}	35
Triphenyl diene 1	8.8×10^8	3.2×10^{-4}	2.8×10^{12}	38
1,1,3,3-Tetraphenyl diene 3	8.4×10^8	2.35×10^{-4}	3.6×10^{12}	32
1,1,5,5-Tetraphenyl diene 4	1.5×10^9	1.3×10^{-5}	1.1×10^{14}	63
1,1,5,5-Bisnortetraphenyl diene 5	1.15×10^9	1.8×10^{-5}	6.2×10^{13}	56

^a From the integrated absorption using the modified Einstein relation; these are twice the values from ref 2 and 13 which omitted the refractive index. ^b The triphenyl diene was used as a standard; its value was taken from ref 2.



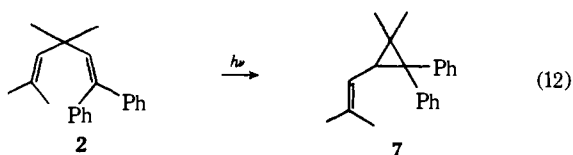
$$k_r = 5.8 \times 10^8 \text{ sec}^{-1}$$

$$k_{dt} = 7.2 \times 10^{10} \text{ sec}^{-1}$$

$$\tau_{RT} = 14 \text{ psec}$$

$$\phi_r = 0.008 \text{ (ref 2)}$$

$$M = 210$$



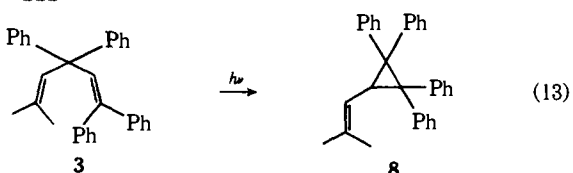
$$k_r = 6.9 \times 10^9 \text{ sec}^{-1}$$

$$k_{dt} = 7.1 \times 10^{10} \text{ sec}^{-1}$$

$$\tau_{RT} = 14 \text{ psec}$$

$$\phi_r = 0.097 \text{ (ref 10)}$$

$$M = 222$$



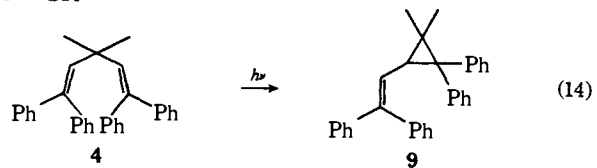
$$k_r = 8.5 \times 10^9 \text{ sec}^{-1}$$

$$k_{dt} = 1.13 \times 10^{11} \text{ sec}^{-1}$$

$$\tau_{RT} = 9 \text{ psec}$$

$$\phi_r = 0.076 \text{ (ref 11)}$$

$$M = 216$$



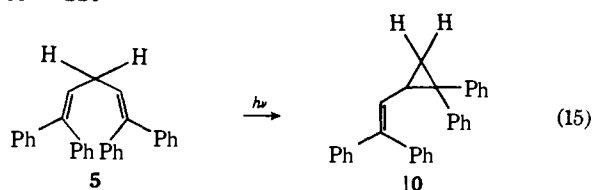
$$k_r = 1.4 \times 10^{11} \text{ sec}^{-1}$$

$$k_{dt} = 1.8 \times 10^{12} \text{ sec}^{-1}$$

$$\tau_{RT} = 0.55 \text{ psec}$$

$$\phi_r = 0.080 \text{ (ref 12)}$$

$$M = 225$$



$$k_r = 2.6 \times 10^9 \text{ sec}^{-1}$$

$$k_{dt} = 1.1 \times 10^{12} \text{ sec}^{-1}$$

$$\tau_{RT} = 0.9 \text{ psec}$$

$$\phi_r = 0.0024 \text{ (ref 13)}$$

$$M = 800$$

ture rates provides support for assumption of the temperature independence of k_f and the validity of the magic multiplier method.¹⁴

Turning attention now to Table II, we find the rates of unimolecular rearrangement of the singlet excited states of the di- π -methane systems **1**, **2**, **3**, **4**, and **5**. These range from $5.8 \times 10^8 \text{ sec}^{-1}$ for triphenyl diene **1** to $1.4 \times 10^{11} \text{ sec}^{-1}$ for tetraphenyl diene **4**. In our previous efforts we have utilized an indirect method described above and summarized in eq 3. The method is predicated on knowledge of k_f which is in principle derivable from the Einstein relationship (note eq 16).

$$k_f = 2.88 \times 10^{-9} \nu_{\text{max}}^2 n^2 \int \epsilon(\nu) d\nu \quad (16)$$

ϵ = extinction coefficient

n = refractive index

ν = absorption frequency

This method was applied to the compounds presently studied and the results are compared with the present direct measurements in Table III. It is seen that the indirect method is in error by a factor in the range of 30–63. Two sources of error seem most likely. The first is simplest; this is that the integrated extinction coefficient needed to obtain k_f is in error due to overlap of S_2 with the S_1 band of interest. This would afford a k_f which is too large, leading to a k_r which would also be too large. Another possibility is failure of the Einstein relationship, as does occur¹⁵ in cases where the excited state geometry is considerably different than that of the ground state. In these cases k_f is indeed observed to be smaller than predicted by the Einstein relationship. Also, considering that the present molecules are styrene-like, it is noted that the absorption maxima corresponding to S_1 and S_2 of styrene occur at 280 nm (ϵ 800) and 238 (10,000). The absorption band at 250 nm (ϵ 13,000–25,500 for **1–5**) used in the indirect method may well then correspond to overlap of S_1 and S_2 , and this affords the simplest rationale of the differences given by the two methods. Finally, despite the problems with the indirect method, it is seen to be quite useful in obtaining relative rates of reaction.

Interpretative Discussion. The first point of interest is that direct measurement of superfast singlet decay rates by the iterative convolution technique has proven possible. Without use of the magic multiplier, decay lifetimes of ca. 100 psec were routinely obtainable; for

(14) (a) Similarly, the literature provides support for temperature independence of k_f ; note ref 8a, p 111; (b) W. R. Dawson and J. L. Kropp, *J. Phys. Chem.*, **73**, 693 (1969); (c) J. L. Kropp, W. R. Dawson, and M. W. Windsor, *ibid.*, **73**, 1747 (1969).

(15) (a) J. B. Birks and D. J. Dyson, *Proc. Roy. Soc., Ser. A*, **275**, 135 (1963); (b) W. R. Ware and B. A. Baldwin, *J. Chem. Phys.*, **46**, 1703 (1964).

example, note the 124 psec 77°K lifetime of 1,1,5,5-tetraphenyl-3,3-dimethyl-1,4-pentadiene (**4**) (Table I). This corresponds to a rate of *ca.* 10^{10} sec⁻¹.

With use of the method of magic multipliers, even faster decaying species can be observed. Thus, even the *ca.* 0.5 psec room-temperature lifetime of the 1,1,5,5-tetraphenyl diene **4**, corresponding to a decay rate of 2×10^{12} sec⁻¹, was measurable (note Table II, entry six)!

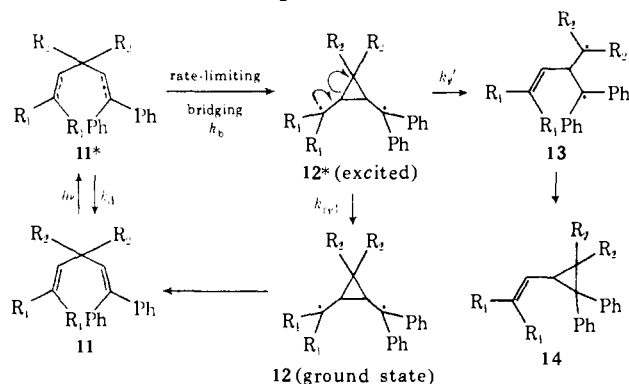
The second conclusion worthy of attention is the test of the indirect method^{2,5} which reveals this to be quite useful for obtaining relative rate constants but subject to problems when used to obtain absolute rates. Indeed, for the method to work at all with certainty, it is best applied to a series of compounds with the same chromophore; otherwise, one should check for deviations from the Einstein relationship and for extraneous absorption maxima.

Next we turn our attention to the actual measured rates themselves. From the photochemical standpoint, we are most interested in the rates at which the excited singlets undergo the di- π -methane rearrangement. Table II and eq 11–15 give these values.

We find that the slowest reacting species is the singlet of the triphenyl diene **1** ($k_r = 5.8 \times 10^8$ sec⁻¹). Next is the diphenyl diene **2** ($k_r = 6.9 \times 10^9$ sec⁻¹). Not much different from this but slightly faster is the 1,1,3,3-tetraphenyl diene **3** ($k_r = 8.5 \times 10^9$ sec⁻¹). Finally, the fastest is the 1,1,5,5-tetraphenyl diene **4** ($k_r = 1.4 \times 10^{11}$ sec⁻¹).

There is a general trend discernible in which the rate increases as terminal phenyl substitution is increased in the diene; methyl substitution also accelerates the rate but to a lesser extent. This effect is in accord with a rate-limiting bridging between vinyl groups of the singlet excited state as had been tentatively assumed in our earlier papers² (note Chart I). Were the ring-

Chart I. Qualitative Valence Bond Mechanism for the Di- π -methane Rearrangement



opening step, following bridging, to be appreciably involved in the rate-limiting process, the 1,1,3,3-tetraphenyl diene **3** would have shown a markedly enhanced rate due to the extra stabilization by these central phenyl groups.¹⁶

Another fascinating point is the near parallelism between the k_r 's, discussed above, and the rates of radiationless decay, that is, the k_d 's. Inspection of Table II reveals that for the most part those com-

(16) In ref 11 evidence was advanced for an enhancement of the triplet process. Thus, for the triplet the second step does seem to participate in controlling the rate.

pounds which have a high k_r also have a large k_d ; here we recognize that k_d is a major portion of k_{at} . This same observation is obvious from comparison of the reaction quantum yields which are very close for three of the four di- π -methane systems under discussion. The one departure from this generalization is an especially high rate of decay relative to its rate of reaction for the triphenyl diene **1**.

This parallelism between decay and reaction rates suggests a connection between the two processes, a point now considered. Thus far the discussion of the di- π -methane rearrangement mechanism has been in terms of the structures of Chart I. These are convenient for descriptive purposes and prediction of the course of such rearrangement. However, the significance of structures such as diradical **12*** needs discussion. For this, let us consider the early stages of the reaction in which the two ethylenic moieties of the excited molecule draw closer (*i.e.*, the bridging step of Chart I in which S_1 (*i.e.*, **11***) gives the bridged species **12***).

It can be shown that terminal bridging of two ethylenic systems in the S_1 manifold is a process involving redistribution of ionic terms of the excited state wave function. Thus the wave function for S_1 for a system such as **11*** \rightarrow **12*** can be shown to be¹⁷

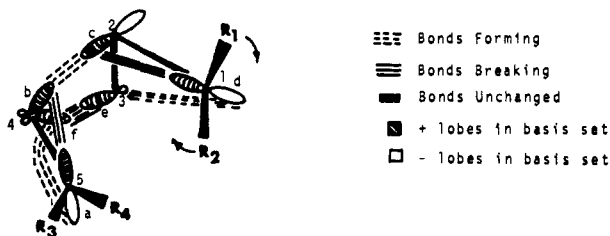
$${}^1\Phi = A^2|\psi_1(1)\bar{\psi}_1(2)\chi_1(3)\bar{\chi}_1(4)| - B^2|\psi_1(1)\bar{\psi}_1(2)\chi_2(3)\bar{\chi}_2(4)| + B^2|\psi_1(1)\bar{\psi}_1(2)\chi_3(3)\bar{\chi}_3(4)| - A^2|\psi_1(1)\bar{\psi}_1(2)\chi_4(3)\bar{\chi}_4(4)| \quad (17)$$

where ψ_1 refers to MO 1 of the four-center system and the χ 's refer to the four orbitals originally comprising the two π bonds. A and B are terms which depend on the extent of bridging with A increasing and B decreasing along the reaction coordinate. This treatment is very similar to that of Slater for the hydrogen molecule dissociation¹⁸ except here we are generating two free valences at atoms 1 and 5 by 2,4 bonding while in the hydrogen molecule case two free valences result from dissociation. The important point to note is that S_1 is an ionic state and that as bridging occurs there is increased weighting due to ionic terms at orbitals 1 and 5.

With increasingly heavy bridging between the π systems a heavy buildup of ionic terms localized at centers 1 and 5 results (*i.e.*, A increases and B decreases). The energy of such a system becomes unfavorable owing to electron–electron repulsion arising from having terms with two electrons in one atomic orbital. It might be lowered by addition of phenyl substitution at the terminal atoms 1 and 5, and this was observed in our earlier work.² Additional delocalization of the ionic weighting results from further overlap with the σ system to give the cyclic array **15** which we have proposed previously. Further, the Möbius, six-electron

(17) (a) This assumes zero differential overlap. (b) The closed shell MO's have not been expanded into single center terms. For the singly occupied MO's we note all the terms are of the form $\chi_1(3)\bar{\chi}_1(4)$ which means a contribution of electron 3 in orbital χ_1 with an α spin at the same time as electron 4 is in this orbital with a β spin. Thus this is an ionic term. (c) The assumption used for simplicity was that the excitation is over the four orbital system comprising atoms 1, 2, 4, and 5. Actually, initially excitation is localized in one of the two π bonds and diffuses over both bonds as bridging begins. (d) Thus the dot-dot formulation of the S_1 configuration of the diradical might be more accurately written as a composite of plus-minus and minus-plus structures.

(18) J. Slater, "Quantum Theory of Molecules and Solids," Vol. 1, McGraw-Hill, New York, N. Y., 1963, p 67.



15

array 15 leads to a closer approach of S_1 and S_0 surfaces, thus accounting for facile conversion to ground state product and ground state reactant. This situation seems more general, and we previously have noted the application of similar reasoning to photochemical processes utilizing cyclic arrays.¹⁹⁻²¹

Hence the biradical formulation is an early gradation of the Möbius array where overlaps a-f and d-e are still weak but b-c is increasing. This corresponds to the rate-limiting stage of the rearrangement as evidenced by stabilization by groups C-1 and C-5 but not at the central methane carbon. The subsequent fully bonded Möbius array is required by the stereochemical evidence.

Returning now to the parallelism between reaction and decay, we suggest that bridging is common to both processes. Further, we suggest that the ground state configuration for the "cyclopropyldicarbonyl diradical" species (*i.e.*, 12) returns to di- π -methane reactant while the excited state species (12*) rearranges.

It is well known²² that thermally generated cyclopropyldicarbonyl diradical systems or their potential precursors undergo central σ -bond fission to give 1,4-dienes. This is not the behavior seen photochemically, and hence there must be *two* cyclopropyldicarbonyl diradical-like species corresponding to the rough resonance descriptions 12 (ground state) and 12* (excited state). With a Möbius six-electron array available one has not only a route for reaction but also one-electron degeneracy of ground and excited states and an approach of S_1 and S_0 surfaces. One then can understand facile decay competitive with rearrangement.

The one case which does not show the expected parallelism between rearrangement and decay is that of 1,1,4-triphenyl-3,3-dimethyl-1,4-pentadiene (1) which has the slowest rate of singlet rearrangement but which has a decay rate quite similar to the diphenyl diene 2. One possibility is that this compound (*i.e.*, 1) has an additional mode of decay not available to the other members of the series. For example, one might envisage reversible 2,5 bridging; this process would be facilitated by the phenyl group at C-4.

The bisnortetraphenyl diene 5 also does not show

(19) Previously²⁰ it has been suggested that at such degenerate points along the reaction coordinate Jahn-Teller effects are to be expected and that enhancement of radiationless decay should result.

(20) (a) H. E. Zimmerman, *J. Amer. Chem. Soc.*, **88**, 1566 (1966); (b) H. E. Zimmerman, *Accounts Chem. Res.*, **5**, 393 (1972); (c) H. E. Zimmerman and G. A. Epling, *J. Amer. Chem. Soc.*, **94**, 8749 (1972).

(21) (a) Note J. Michl, *Mol. Photochem.*, **4**, 243 (1972), for a related discussion of internal conversion of S_1 and S_0 surfaces. (b) L. Salem, W. G. Dauben, and N. J. Turro, *J. Chim. Phys.*, **4**, 694 (1973), have discussed reactions leading to diradical states.

(22) (a) The best model for ground state cyclopropyldicarbonyl diradicals is afforded by the cyclic transition state in which nitrogen elimination would afford such a species if central C-C bond fission did not occur as observed. (b) For leading references, note J. A. Berson and S. S. Olin, *J. Amer. Chem. Soc.*, **92**, 1986 (1970); B. M. Trost and R. M. Cory, *ibid.*, **93**, 5573 (1971).

this parallelism. However, this molecule has been shown¹⁸ to react entirely by a different mechanism not involving the di- π -methane route despite its forming the vinylcyclopropane product expected from a di- π -methane process. The reluctance to undergo the di- π -methane rearrangement has been attributed to lack of central methyl substitution, which inhibits the ring-opening step. The relatively low reaction rate presently encountered (*i.e.*, $k_r = 0.22 \times 10^{10} \text{ sec}^{-1}$; note Table II) supports this view. The actual reaction involves hydrogen migration from the central carbon and no di- π -methane rearrangement is found,¹³ thus any di- π -methane mechanism must be still slower by more than an order of magnitude.

The behavior of bisnortetraphenyl diene 5 also provides evidence on the proposal that bridging is involved in the deactivation process. Hence there is a near identity of k_{dt} for the rearranging tetraphenyl diene 4 and the nonrearranging bisnortetraphenyl diene 5 (see eq 14 and 15); note k_{dt} for 4 is $1.8 \times 10^{12} \text{ sec}^{-1}$ compared with a k_{dt} of $1.1 \times 10^{12} \text{ sec}^{-1}$ for 5. Thus the terminal substitution causes the rates of bridging to be the same while lack of central substitution in 5 precludes completion of the di- π -methane rearrangement.

A final point meriting attention is that the present results clarify a hitherto puzzling result. The quantum efficiencies of the di- π -methane rearrangement of 1,1,5,5-tetraphenyl-3,3-dimethyl-1,4-pentadiene (4) and 1,1-diphenyl-3,3,5-trimethyl-1,4-hexadiene (2) were very similar (*i.e.*, $\phi = 0.080^{12}$ for 4 and $\phi = 0.097^{10}$ for 2). Yet if bridging is rate limiting, the tetraphenyl diene 4 gives rise to a singlet excited state which should react more readily since there are two phenyl groups at *each* end of the diene system to stabilize odd electron density developing during bridging, while triphenyl diene 2 has such stabilization only at one end of the diene species. Thus, with quantum yield data alone, the observed reactivities did not fit any reasonable pattern. However, the rates of rearrangement do differ with the tetraphenyl diene 4 being much more rapid, and it proves to be the nearly parallel rates of decay which obscure the differences in inherent reactivity. This illustrates the danger of using quantum yield information alone in gauging photochemical reactivity.

A comment is needed concerning the significance of the k_r 's and k_{dt} 's measured. Thus, one can inquire how to identify these measured rate constants with constants in the reaction scheme of Chart I. First, it must be emphasized that k_{dt} and k_r are operational constants independent of reaction mechanism. Thus, k_{dt} is measured directly and k_r is defined in terms of measured quantities as in the equation

$$k_r = \phi_r k_{dt} \quad (18)$$

where ϕ_r is the reaction quantum yield. However, in terms of mechanism, we find that the reaction quantum yield is given by

$$\phi_r = \frac{k_b k_r'}{(k_f + k_d + k_b)(k_{rel} + k_r')} = \frac{k_r}{k_f + k_d + k_b} \quad (19)$$

where the rate constants in eq 19 refer to the mechanism

in Chart I. Any intersystem crossing is included in k_d . Rearranging eq 19, we obtain

$$k_r = \frac{k_b k_r'}{k_{rel} + k_r'} = k_b P_r' \quad (20)$$

where P_r' gives the probability of the cyclopropyl-dicarbonyl diradical rearranging to product and k_b is the rate of excited state bridging. Thus eq 20 defines k_r in terms of mechanism while eq 18 does so operationally in terms of observables. We do see that, although k_r cannot be related to a single step, it does give a measure of the rate of forward reaction in terms of rate of bridging multiplied by the probability of successful further reaction.

We conclude with two comments. First, single photon counting is a powerful and most useful technique in photochemistry which is readily applied to the most rapid of reactions. Second, on the chemical side, di- π -methane reactivity now seems to fit a pattern which makes molecular sense.

Experimental Section

Sample Preparation. Methylcyclohexane-isopentane (4:1) was used for emission experiments. Reagent grade solvents were purified by stirring 500 ml with 50 ml of 15% fuming sulfuric acid for 6 hr, washing with water, drying over calcium chloride, and distilling. This was followed by passing through a 2.5×40 cm column of alumina bearing 10% of silver nitrate as described by Murray and Keller.²³ The early and late fractions were discarded. Solvent prepared in this fashion was transparent in the ultraviolet and fluorescence free.

Zone-refined naphthalene (Aldrich) was used. Tetraphenylethylene was recrystallized (mp 223–224°) from chloroform-ethanol, and purity was checked with high-speed liquid chromatography. 1,1,4-Triphenyl-3,3-dimethyl-1,4-pentadiene,² 1,1-diphenyl-3,3,5-trimethyl-1,4-hexadiene,¹⁰ 1,1,3,3-tetraphenyl-5-methyl-1,4-hexadiene,¹¹ 1,1,5,5-tetraphenyl-3,3-dimethyl-1,4-pentadiene,¹² and 1,1,5,5-tetraphenyl-1,4-pentadiene¹³ were synthesized and purified as described previously.

All samples were degassed with five freeze-thaw cycles on a vacuum line using liquid nitrogen for freezing; results so obtained proved reproducible from run to run, and additional agreement with the literature naphthalene results is significant since this fluorescence is especially oxygen sensitive.

Magic Multipliers and Fluorescence Quantum Yields. For each compound the fluorescence spectrum was taken at 295 and 77°K under otherwise identical conditions using an Aminco-Kiers spectrofluorometer with a Hanovia 901C-1 150-W xenon lamp. Concentrations were adjusted to give an optical density in the range of 0.8–1.5, thus minimizing scatter. Self-quenching was shown to be unimportant at this concentration ($<10^{-4}$ M). Excitation wavelengths of 270 nm for naphthalene and the dienes and 310 nm for tetraphenylethylene were used.

The magic multipliers were obtained from a single sample by integrating the emission intensities obtained at two temperatures. Fluorescence quantum yields were obtained by comparison of the integrated emission intensity of the compound of interest with a standard having the same chromophore and peak shape. Presently, 1,1,4-triphenyl-3,3-dimethyl-1,4-pentadiene was used at an optical density of 1.2; a value of $\phi_f = 3.2 \times 10^{-4}$ as derived in ref 2 was used.

Single Photon Counting. Nanosecond Flash Lamp. The lamp was designed as a hermetically sealed, two-piece, demountable aluminum chamber. The chamber consists of a parabolic reflector behind the spark gap and a hemispherical reflector in front. A pair of thoriated tungsten electrodes are mounted coaxially with the light beam which exits through a quartz window in the center of the hemispherical mirror. The lamp was run filled with 2–3 atm of nitrogen and run as a relaxation oscillator using stray capacitance charged through an 8 M Ω resistor chain to 6–10 kV with the cell body being grounded. The lamp provides especially jitter-free and tail-free pulses of ca. 2 nsec at half-maximum and with frequencies between 2 and 20 kHz.

(23) E. C. Murray and R. N. Keller, *J. Org. Chem.*, 34, 2234 (1969).

Optics and Electronics. The lamp is focussed on the slits of a Bausch and Lomb high intensity monochromator but with a beam splitter sending a portion of each flash to a 1P28 photomultiplier which provides the zero time pulse. Following the monochromator is a sample compartment holding 1-cm square quartz cells with long necks terminating in 10/30 joints; provision was made for degassing. A quartz dewar allows cell cooling. Single photon emission is observed at 90° to excitation by an RCA 8575 photomultiplier preceded by interference filters excluding excitation light. Output pulses from the 1P28 and 8575 tubes are processed by amplifier and discriminator (constant fraction for 8575) and led to a time-to-amplitude converter. The analog output, which is linearly proportional to the interval between time zero and the time of single photon emission, is led to a A/D converter and thence to a PDP8/I Digital Equipment Corp. computer which acts as a multichannel analyzer. Photons counted were stored in 512 channels by incrementing core in floating points as each time delay was measured. Differential nonlinearity of the Digital Equipment A/D converter proved to be the main source of scatter in the decay curves and was obviated by use of a Wilkinson type (Northern Scientific) converter (compare Figure 1e with 1h, the latter being obtained with the Wilkinson type converter). Smoothing of the former data improved the standard deviation but did not change the rate constants. Additionally programs were written to store collected intensity vs. time curves on magnetic tape, to punch paper tape copies of emission data, to display the emission curves during and after collection on an x-y scope, to plot individual curves on an x-y recorder, to perform reiterative convolution using a sum of exponentials of up to seven, to reiteratively convolute using a Taylor series model, and to provide a variety of operating routines allowing one to inspect and deal with data obtained. Thus for single photon counting use of a computer rather than a multichannel analyzer has advantages.

Single Photon Counting Procedure. The optical density at the excitation wavelength was maintained between 1.8 and 2.0, thus minimizing scatter. For tetraphenylethylene emission an interference filter at 360 nm was used, and for all other samples a 340-nm interference filter was employed. To avoid counting double photon pulses the monochromator slits were narrowed to the point at which the rate of photon counting was less than $1/20$ th of the lamp frequency,^{4b} which was kept at 2–3 kHz in these runs. Collection was continued until the maximum number of counts per channel was 1100–1200. The lamp flash curve was obtained from a run using pure solvent in the sample cell; this run was made contiguous in time with the sample measurement. It was found that the same lamp flash resulted with use of an empty cell.

Mathematical Treatment of Data. The reiterative convolution program used 9a and 9b to set up the \bar{V} matrix as required for use of eq 10. The $\bar{\Delta E}$ vector of eq 10 was just composed of the differences between experimental emission intensities and the calculated ones (i.e., calculated with the current values of k_j and a_j); that is, $\Delta E_i = E_i - E_i^{\text{exp}}$ for each of the 512 values of time t . To solve eq 10 for the $\bar{\Delta}$ vector, composed of changes in k and a needed for the next iteration, this equation was multiplied on each side by the transpose of the rectangular \bar{V} matrix. Following this, both sides were then premultiplied by the inverse of the $(\bar{V}^T \bar{V})$ matrix to give the least-squares $\bar{\Delta}$ vector;²⁴ i.e.

$$(\bar{V}^T \bar{V})^{-1} \bar{V}^T \bar{\Delta E} = \bar{\Delta} \quad (21)$$

In practice there was an advantage to using a $\bar{\Delta E}$ vector in which each element was weighted proportionally to the reciprocal of the number of counts in that channel, since as has been noted^{4,6} the variance of each channel is proportional to the content of each channel.

The error treatment followed that of ref 6. Here

$$\text{SSQR} = \sum_{t=1}^N (1/E_t^{\text{exp}}) \Delta E_t^2 / \sum_{t=1}^N (1/E_t^{\text{exp}})$$

gives the weighted mean variance of the fit.

$$\text{SSQP} = N / \sum_{t=1}^N (1/E_t^{\text{exp}})$$

(24) This treatment is equivalent to an ordinary least-squares treatment (T denotes transform of the variation matrix); note (e.g.) P. S. Dwyer, *Ann. Math. Statist.*, 15, 82 (1944); J. F. Kenney and E. S. Keeping, "Mathematics of Statistics," Part 2, Van Nostrand, New York, N. Y., 1951, Chapter 10.

affords the theoretically expected mean variance. The ratio of SSQR: SSQP ideally should approach unity but normally will be higher. Presently values of this ratio below 3 were considered acceptable.

Temperature Dependence of Optical Density. The absorption spectra of the triphenyl diene **1** and the 1,1,5,5-tetraphenyl diene **4** were measured at 77°K and at room temperature. The absorbance at low temperature (1.4 for **1** and 1.3 for **4**) is greater than that at room temperature (0.95 for **1** and 1.05 for **4**) presumably due to contraction of the sample, effectively increasing the concentration. The spectra were taken on a Cary 11MS purged with dry nitrogen, first at low temperature and then after allowing the sample to warm to room temperature without moving either the cell or the dewar flask.

Optical Density Dependence of Emission Intensity. The emission spectrum of the triphenyl diene **1** was measured as a function of the optical density in the range 0.9–1.5, under conditions similar to those employed for measuring the magic multipliers (*vide supra*). The emission intensities, expressed in arbitrary units, were: OD = 0.9, 24; OD = 1.2, 16.5; OD = 1.5, 17.

Polarization. A set of Glan prisms was interposed in the excitation and emission beams of the Aminco-Kiers spectrofluorometer. The solutions were made to give an optical density of 1.0 at the wavelength of excitation. The degree of polarization was measured by the method of Azumi and McGlynn.²⁵ For naphthalene (λ_{ex} 312 nm) the degree of polarization increased from zero at room temperature to 0.30 at 77°K. For the triphenyl diene **1** (λ_{ex} 270 nm) the degree of polarization was constant within experi-

mental error: 0.46 at room temperature and 0.31 at 77°K. The degree of polarization at room temperature was 0.28 for the 1,1,3,3-tetraphenyl diene.

Refractive Index Effect on Emission Intensity. A concentrated suspension of fumed silica (Cab-O-Sil Grade M-5, Cabot Corp.) in 4:1 methylcyclohexane–isopentane (45 mg/ml) was prepared as a scatterer. The amount of light scattered at 310 nm was monitored, in arbitrary units, as 6.7 and 6.4, respectively, at room temperature and at low temperature. The magic multiplier of a solution of 9,10-diphenylanthracene (OD = 1.5 at the excitation wavelength, 360 nm) was found to be 1.07 which is not different from unity within experimental error.

The absence of a temperature dependence of emission intensity due to refractive index effects seems to derive from two sources. The usual source of decreased emission intensity assumes perfectly collimated input light reaching the cell while presently the less than perfectly parallel light of the Aminco instrument leads to a counterbalancing increase of light intensity within the cell with increasing glass refractive index. Also, the liquid nitrogen present in the low-temperature runs was found to reduce reflection losses.

Acknowledgment. Support of this research by National Institutes of Health Grant GM07487, the U. S. Army Research Office (Durham), and the National Science Foundation is gratefully acknowledged as is a postdoctoral fellowship from the Schweizerischer Nationalfonds to D. P. W. and a National Science Foundation fellowship to K. S. K. Also thanks are due to Mr. Mark Johnson for assistance with synthetic aspects.

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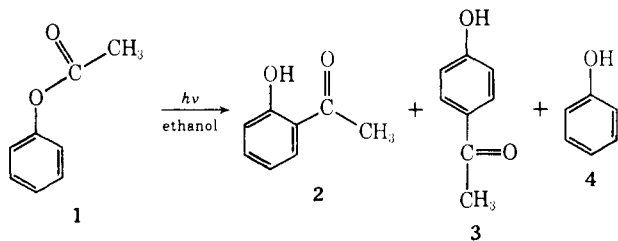
A Mechanistic Study of the Photo-Fries Rearrangement of Phenyl Acetate¹

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Abstract: Evidence is presented for a radical mechanism for the photo-Fries rearrangement of phenyl acetate. Phenoxy radicals were observed in the flash spectra of phenyl acetate in ethanol, hexane, and Freon. An additional transient was identified as a cyclohexadienone, which decayed into *o*-hydroxyacetophenone with a first-order rate constant of $1.25 \pm 0.1 \text{ sec}^{-1}$. An inverse correlation between fluorescence yield of aryl ethers and photochemical yield indicates the photo-Fries reaction proceeds from an excited singlet state. Viscosity effects, coupled with the radicals observed, argue against the "concerted" mechanism. Arguments are presented that the photo-Fries rearrangement is only one example of a general rearrangement of compounds of the type, ArO-X, involving homolytic cleavage to yield radicals ArO· and X· which may recombine or react independently. The role of the solvent cage in these reactions is strongly emphasized.

The photo-Fries rearrangement was first observed by Anderson and Reese in 1960.² A simple example is the rearrangement of phenyl acetate in ethanol to give *o*- and *p*-hydroxyacetophenones and phenol.



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Since the initial discovery, a large body of literature has appeared concerning the scope and mechanism of this reaction. The rearrangement has been found to occur for many derivatives of phenol: phenyl esters,^{3–5} aryl alkyl carbonates,^{6,7} phenoxyacetic acids,⁸ and hydroxyphenyl cinnamates.⁹ A recent review of the photo-Fries rearrangement has been published by Bellus.¹⁰

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