line di-*t*-butyl peroxide at −70°. The esr absorption is attributed to *t*-butoxy radicals. Apparently there was no evidence for radical pair formation. However, this result is not surprising, since we find that in order to stabilize radical pairs produced in dibenzoyl peroxide crystals and in dibenzoyl disulfide–dibenzoyl peroxide mixed crystals, it is necessary to maintain the temperature well below 77°K.

Photochemistry of *trans*-1-Phenyl-2-butene

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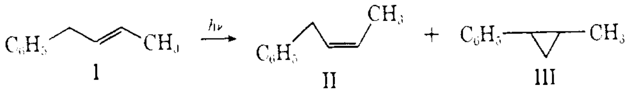
Received March 16, 1970

Abstract: The spectroscopy and photochemistry of *trans*-1-phenyl-2-butene have been investigated in the gas phase. On excitation in the 0–0 band, the following quantum yields were obtained: fluorescence, 0.25; formation of 1-phenyl-2-methylcyclopropane, 0.135; and formation of *cis*-1-phenyl-2-butene, 0.18. All processes were found to decrease at shorter wavelengths. The cyclization process has been shown to occur from a vibrationally excited upper triplet state (T_2), while *cis*-*trans* isomerization occurs *via* the lowest triplet (T_1) of the molecule. From the experimental data, the quantum yield for intersystem crossing from the triplet state T_2 to the ground state was calculated equal to 0.27 ± 0.05.

We recently reported[2] that in contrast to the liquid-phase photolysis,[3] irradiation of *trans*-1-phenyl-2-butene (I) in the vapor phase leads to the formation of two products: *cis*-1-phenyl-2-butene (II) (also found in the liquid-phase photolysis) and 1-phenyl-2-methylcyclopropane (III) (probably the *trans* isomer).



The effects of exciting wavelength and of foreign gas (*n*-butane) indicate that III is formed from a vibrationally excited intermediate.

The present work was undertaken to study in detail the spectroscopy and the photochemistry of I in the vapor phase and to elucidate the mode of formation of the cyclopropane derivative.

Experimental Section

(a) Materials. *trans*-1-Phenyl-2-butene (95% pure), obtained from Aldrich Chemical Co., was purified by preparative gas chromatography (6-m × 0.94-cm FFAP column). Analysis by capillary gas chromatography showed that the main impurity remaining was the *cis* isomer at a concentration always smaller than 0.05%. *n*-Butane (Phillips Pure grade), acetone (Matheson Spectroquality), acetophenone (Baker Analyzed reagent), fluorobenzene (Eastman Spectrograde), and toluene (Phillips Research grade) were used after bulb-to-bulb distillations, while oxygen (AirCo), carbon monoxide (Matheson Research grade), and neon (Matheson Prepurified were used directly from their containers.

All compounds were thoroughly degassed at −196° before use.

(b) Apparatus. A grease-free vacuum line was fitted with mercury cutoffs and Hoke valves, Types 417 and 413.

Absorption and emission spectra were determined as described by Mettee (Figure 1 of ref 4).

The optical system for most photolysis experiments is shown in Figure 1. S is a Hanovia 1000-W Hg–Xe high-pressure lamp operated at 32 V dc and 32 A; L_1, L_2, and L_3 are quartz lenses; P_1 and P_2 are RCA 935 phototubes; P_m is a IP28 photomultiplier, operated at 400 V; R_1 is a Hewlett-Packard 680 recorder and R_2 is a Hewlett-Packard 7100B double-pen recorder; M is a Bausch and Lomb 0.5-m grating monochromator with a linear reciprocal dispersion of 1.6 nm mm^{-1}. Entrance and exit slits were 2 mm. F is a mercury vapor filter to eliminate any possible mercury resonance radiation and Q is a quartz plate at 45° to the incident beam, acting as a beam splitter. The cell C (318-ml total volume including access tubing) was 20 cm in length and all three windows were 4.5 cm in diameter. The side window was 6 cm from the front window.

The cell, the storage reservoir, the analytical section, and the corresponding valves were housed in an oven which was normally used as a black box, but which could be heated to 100°.

Pressure was measured by either a mechanical dial manometer (Wallace-Tiernan FA 141) in the range 0.1–20 Torr or by a mercury manometer for higher pressures.

Correction for variation of phototube sensitivity with wavelength was made from the manufacturer's curve and never exceeded 5% in the range 240–270 nm.

For Hg-sensitized experiments, a Hanovia low-pressure mercury lamp (cold-cathode SC-2537) operated at about 35 W was used, and the light emitted was filtered through a Corning C-S 7-54 filter to provide only the 254-nm resonance line.

(c) Procedure. In order to avoid condensation of I on cold points inside the cell (metallic surfaces of the valves), the reservoir of *trans*-1-phenyl-2-butene was kept at 23° (room temperature, 26–27°) during the time the compound was allowed to fill the cell (1 hr). The pressure in the cell was then about 0.8 Torr (saturated vapor of I at 23°). The light intensity absorbed was about 20%. Known pressures and volumes of added gases were expanded and condensed into the cell while I was kept at liquid nitrogen temperature in the cold finger of the cell. After several flash vaporizations, gases were allowed to mix overnight.

Actinometry was performed by photolysis of acetone at 130°. The quantum yield of carbon monoxide was taken as unity and was

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[1] The material in this article is included in a dissertation submitted to the Department of Chemistry at the University of Texas at Austin in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1970. The author wishes to thank the National Science Foundation and the Camille and Henry Dreyfus Foundation for support of this work through grants to Professor W. Albert Noyes, Jr. Also he wishes to thank the Mobil Foundation for a fellowship during 1969–1970 and the Robert A. Welch Foundation for a special grant which made possible the purchase of the grating spectrograph used in this work. The author is greatly indebted to Dr. W. Albert Noyes, Jr., for his continued interest throughout the course of this work, and he wishes also to thank the many colleagues at The University of Texas at Austin with whom the work was discussed.

[2] M. Comtet, *J. Amer. Chem. Soc.*, **91**, 7761 (1969).

[3] H. Morrison and R. Peiffer, *ibid.*, **90**, 3428 (1968).

[4] H. D. Mettee, *J. Chem. Phys.*, **49**, 1784 (1968).

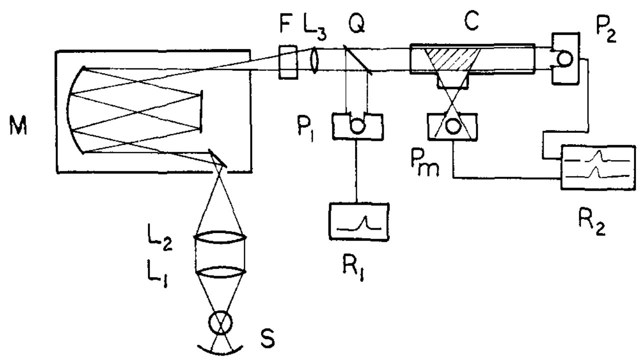

Figure 1. Schematic of the optical arrangement.

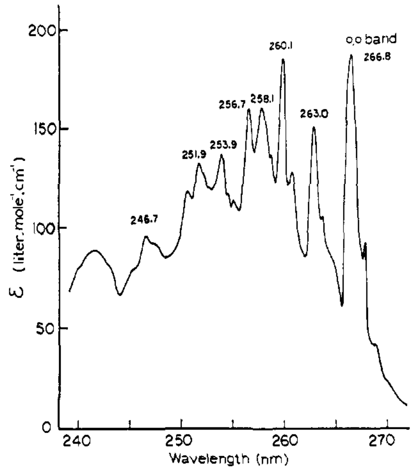

Figure 2. Vapor-phase absorption spectrum of *trans*-1-phenyl-2-butene: Jarrell-Ash spectrometer; spectral resolution, 0.04 nm; pressure, 0.8 Torr; temperature, 26°.

determined by mass spectrographic analysis of the fraction noncondensable at −196°, using neon as a standard.

Photolysis products were condensed in a small Pyrex tube attached to the vacuum line through a 6-mm Cajon coupling and kept at liquid nitrogen temperature for 2 hr. The products were then diluted with a known amount of *n*-hexane containing *t*-butylbenzene as an internal standard for gas chromatography. All analyses were carried out on the capillary MBMA[5] column of a Perkin-Elmer gas chromatograph, and the peak areas were recorded with a Disc integrator. Correction was made for the difference of sensitivity of the flame ionization detector toward the different molecules analyzed. Under typical experimental conditions, the total conversion of I did not exceed 2% and corrections were not necessary for the back-reaction.

Results

Absorption Spectrum. The vapor-phase absorption spectrum of *trans*-1-phenyl-2-butene is shown in Figure 2. The absolute pressure at 23° was 0.8 Torr, as determined by gas chromatography, and calculation of extinction coefficients is based on this determination. The strong absorption at λ 266.8 nm corresponds to the 0–0 band. This spectrum is almost identical with the absorption spectrum of toluene in the gas phase as determined by Burton.[6]

Fluorescence Spectrum. The fluorescence spectrum of I excited at 266.8 nm and 58° ($P \simeq 7$ Torr) is shown in Figure 3. The shortest wavelength peak in the emission spectrum corresponds to 0–0 band. The spectrum has not been corrected for variation of photomultiplier sensitivity with wavelength.

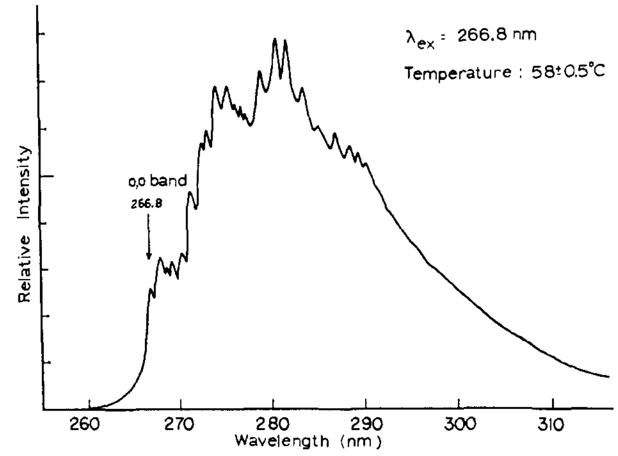

Figure 3. Fluorescent spectrum of *trans*-1-phenyl-2-butene: spectral resolution, 0.24 nm.

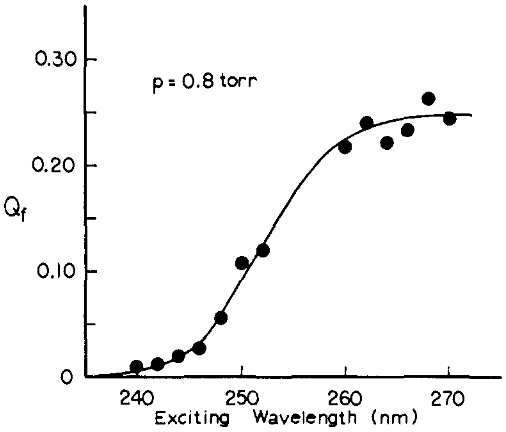

Figure 4. Effect of exciting wavelength on the absolute fluorescent yield of *trans*-1-phenyl-2-butene: Bausch and Lomb monochromator slits, 1 mm; temperature, 26°.

Absolute Fluorescent Yield. The absolute quantum yield of fluorescence of I has been determined at room temperature. Absolute values were obtained by comparison with toluene. Burton[6] determined the quantum yield of fluorescence of toluene to be 0.30 ± 0.07 by excitation at 266.8 nm and for pressures in the range 15–20 Torr. However, it has been shown that the quantum yield of fluorescence of benzene[7] increases sharply at low pressure, and it is possible that the same phenomenon could occur with toluene. To avoid any low-pressure effects, a mixture of 0.8 Torr of toluene + 100 Torr of *n*-hexane was excited at 266.8 nm (1-mm slit) and the yield of fluorescence was taken equal to 0.30 ± 0.07. By this method, the absolute fluorescent quantum yield $Q_f^{266.8}$ for *trans*-1-phenyl-2-butene was found equal to 0.25 ± 0.07 at 0.8 Torr pressure.

The effect of exciting wavelength on the absolute fluorescent yield at a pressure of 0.8 Torr is shown in Figure 4. Oxygen quenches the fluorescence of *trans*-1-phenyl-2-butene in a typical Stern–Volmer fashion, as shown in Figure 5.

Formation of Products. (a) Direct Photolysis. Excitation of I in the range 240–270 nm leads to the forma-

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(5) *m*-Bis(*m*-phenoxyphenoxy)benzene + Apiezon L.

(6) C. S. Burton and W. A. Noyes, Jr., *J. Chem. Phys.*, **49**, 1705 (1968).

(7) G. B. Kistiakowsky and C. S. Parmenter, *ibid.*, **42**, 2942 (1965).

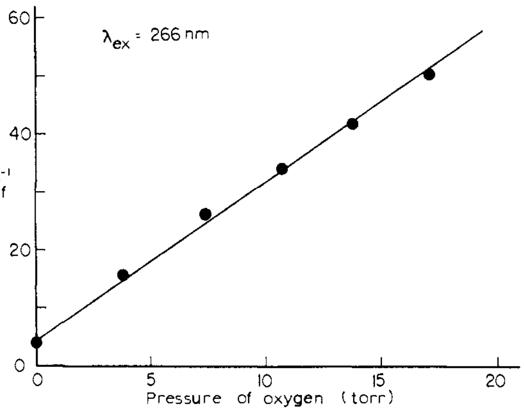

Figure 5. Stern–Volmer quenching plot for the fluorescent yield of *trans*-1-phenyl-2-butene *vs.* oxygen pressure: equation, Q_f^{-1} = 4 + [5.76 × 10^4(O$_2$)].

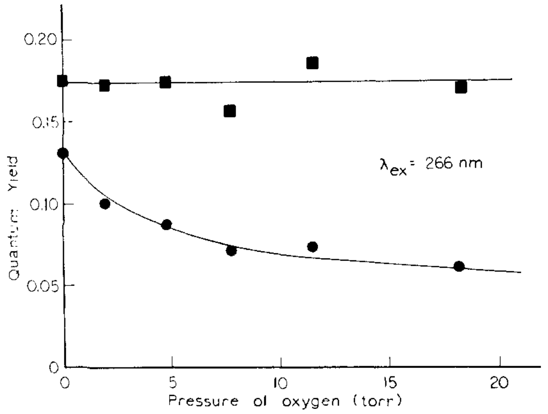

Figure 6. Quenching of the formation of products by oxygen: ■, *cis*-1-phenyl-2-butene; ●, 1-phenyl-2-methycyclopropane; pressure of *trans*-1-phenyl-2-butene, 0.8 Torr; temperature, 26°.

tion of two main products, II and III. The effect of exciting wavelength upon the quantum yield of formation of the products is presented in Table I, while the effect of added *n*-butane has been reported previously.[2] Figure 6 shows the effect of oxygen on the quantum yield of formation of II and III.

Table I. Effect of Exciting Wavelength on the Photolysis of *trans*-1-Phenyl-2-butene

Wave-length, nm	Φ_{II}	Φ_{III}	Φ_{III}/Φ_{II}
266	0.18	0.13_2	0.73_5 ± 0.02
261	0.15_7	0.12_6	0.82 ± 0.02
252	0.075	0.066_5	0.88_5 ± 0.02
247	0.024_6	0.024_2	0.98 ± 0.02

(b) Photosensitized Reactions. Acetophenone, E_T = 73 kcal, and fluorobenzene, E_T = 84 kcal (E_T is the excitation energy of the triplet state), used successively as triplet sensitizers, led to the formation of II only and cyclization was not observed with these sensitizers.[8]

On the other hand, Hg($^3P_1$) photosensitization (E_T = 112 kcal) leads to the formation of both II and

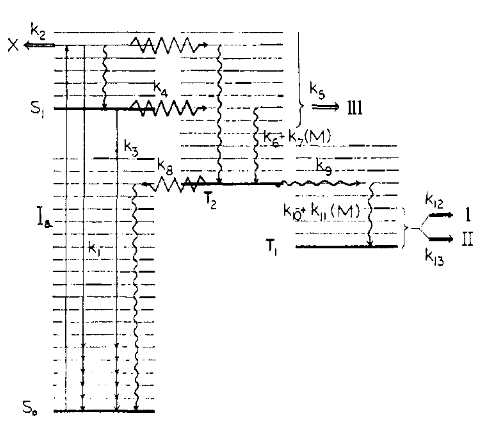

Figure 7. Schematic energy level diagram. Radiative transitions between states are given by solid lines, wavy lines are vibrational relaxation processes, and broken lines are intersystem crossing between states of different multiplicity. Double lines represent the formation of products.

III in almost the same ratio (III/II = 0.83) as that for direct photolysis at 254 nm. The possibility of direct photolysis of I at 254 nm was ruled out by study of the quenching of Hg($^3P_1$) atoms by CO molecules (σ^2 = 4.07).[9] High pressures of CO dramatically decreased the formation of both products because of the quenching of the sensitizer. In the direct photolysis, high pressure of CO would not affect the quantum yield of II, apart from a slight increase as in the case of *n*-butane.

Discussion

In the following discussion, we will assume that *trans*-1-phenyl-2-butene can be considered to consist of two different noninteracting chromophores. Consequently, we will consider a singlet and a triplet state (S_1, T_2) associated with the aromatic ring and a singlet and triplet state (S_2, T_1) associated with the olefinic group. Owing to the lack of information concerning the spatial geometry of the molecule in the gas phase, it is difficult to estimate the degree of interaction between these two chromophores. However, comparison of the absorption spectrum of I with that of toluene indicates that there is no interaction between the S_1 and S_2 singlets in the molecule (the 0–0 bands of I and of toluene appear at identical wavelength). The triplet energy levels are not observed by spectroscopy (no phosphorescence), but the energy difference $T_2 - T_1$ can be tentatively evaluated to be about 10 kcal in the noninteracting molecule (assuming the olefin triplet energy to be 75 kcal[10]). Similarly, the singlet energy difference $S_2 - S_1$ is about equal to 30 kcal. A slight interaction would decrease the energy of T_1 and increase by the same amount the energy of T_2, but both triplets could still be considered to be associated with the respective chromophores.

The most probable processes following absorption of a quantum by I to form the first excited singlet state are represented in Figure 7.

The decrease of the quantum yield of fluorescence for molecules such as benzene,[11] toluene,[6] and the xylenes[12]

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[8] (a) W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *J. Amer. Chem. Soc.*, **86**, 4537 (1964); (b) D. F. Evans, *J. Chem. Soc.*, 2753 (1959).

[9] J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966, p 81.

[10] M. A. Golub and C. L. Stephens, *J. Phys. Chem.*, **70**, 3576 (1966).

[11] W. A. Noyes, Jr., W. A. Mulac, and D. A. Harter, *J. Chem. Phys.*, **44**, 2100 (1966).

at a wavelength shorter than the 0–0 absorption band seems to be a general feature of benzene derivatives. This decrease may be due to a valence isomerization of I to a benzvalene type of intermediate (step 2),[13] which rapidly reverts to the starting material and thereby results in a decrease of other photochemical processes.

By absorption into the zeroth vibrational level of the first excited state

$$\mathrm{TPB} + h\nu\ (266.8\ \mathrm{nm}) = {}^1\mathrm{TPB}^0$$

the molecule can either fluoresce or cross over to a high vibrational level of the triplet manifold

$$ {}^1\mathrm{TPB}^0 = \mathrm{TPB} + h\nu \qquad (3)$$

$$ = {}^3\mathrm{TPB}^\mathrm{V} \qquad (4)$$

The steady-state assumption shows the fluorescent yield to be

$$Q_\mathrm{f} = k_3/(k_3 + k_4)$$

Because of the identity of the absorption and fluorescence spectra of I and toluene, we can assume the singlet lifetimes for both molecules to be very close, and consequently we will take $k_3 = 5.8 \times 10^6\ \mathrm{sec}^{-1}$.[14] This gives $k_4 = 1.7 \times 10^7\ \mathrm{sec}^{-1}$ for the rate constant of intersystem crossing.

The quenching of fluorescence by oxygen seems also to be a characteristic of aromatic molecules.[15] Lee and coworkers[16] have shown that $\mathrm{O_2}(^3\Sigma_g^-)$ molecules can quench the singlet state of benzene by either energy transfer or collision-induced intersystem crossing. In view of the results of Parmenter,[15] this last process seems to be predominant, and accordingly we may write the quenching step as

$$ {}^1\mathrm{TPB} + \mathrm{O_2}(^3\Sigma_g^-) = {}^3\mathrm{TPB}^\mathrm{V} + \mathrm{O_2}(^3\Sigma_g^-)$$

with a rate constant k_q. The steady-state assumption leads to

$$Q_\mathrm{f}^{-1} = 1 + \frac{k_4}{k_3} + \frac{k_\mathrm{q}}{k_3}[\mathrm{O_2}] \qquad \text{(a)}$$

The slope from Figure 5 is $5.76 \times 10^4\ \mathrm{mol}^{-1}$, which, when multiplied by k_3, gives $k_\mathrm{q} = 3.3 \times 10^{11}\ \mathrm{l.\ mol^{-1}\ sec^{-1}}$. Thus, the effective cross section for quenching by oxygen is about $35 \times 10^{-16}\ \mathrm{cm}^2$.

Oxygen molecules also quench the formation of III but have no detectable effect on the quantum yield of II in the pressure range 0–20 Torr. Thus, the quenching efficiency of oxygen toward the fluorescence yield is larger by a factor of 10 than toward the cyclization process (step 5). If the cyclopropane derivative were formed from the singlet state (or from a state directly derived from it, such as the vibrationally excited ground state) we would expect the quenching by $\mathrm{O_2}$ to be the same for both processes 3 and 5, which is obviously not the case. This shows that III is formed from a vibrationally excited triplet (or the vibrationally excited ground state derived from it). The difference in the quenching effects for products II and III may be entirely due to the vibrational relaxation efficiency of $\mathrm{O_2}$. As already observed by addition of *n*-butane, the formation of III largely depends on the vibrational level from which this process occurs. Therefore, in addition to an electronic quenching of $\mathrm{T_1}$, increasing pressure of $\mathrm{O_2}$ will decrease the formation of III and will correspondingly increase the number of molecules reaching $\mathrm{T_1}$.

Moreover, a significant consumption of the starting material has been observed (~15% at the highest pressure of oxygen used), and though no photooxidation products could be isolated, chemical quenching may be an important process in this system. The results of the triplet photosensitization reactions support this mechanism. Excitation by a low-energy triplet donor ($E_\mathrm{T} \leqslant$ 84 kcal) leads only to the formation of the expected geometrical isomer II formed from a "cold" triplet state, while III is definitely not formed. On the other hand, III is efficiently produced by $\mathrm{Hg}(^3\mathrm{P}_1)$ photosensitization. The cyclization process may come from the second vibrationally excited triplet, $\mathrm{T_2}$, of the molecule, which probably lies around 84 kcal and which corresponds to the triplet of the benzene chromophore. Applying the steady-state approximation to the processes depicted in Figure 7, the following expressions may be derived for excitation in the 0–0 band.

$$\Phi_\mathrm{II} = \frac{k_4k_9k_{13}[k_6 + k_7(\mathrm{M})]}{(k_3 + k_4)(k_8 + k_9)(k_{12} + k_{13})[k_5 + k_6 + k_7(\mathrm{M})]} \qquad \text{(b)}$$

and

$$\Phi_\mathrm{III}^{-1} = \frac{(k_3 + k_4)(k_5 + k_6)}{k_4k_5} + \frac{k_7(k_3 + k_4)}{k_4k_5}(\mathrm{M}) \qquad \text{(c)}$$

The one-step processes 6 and 7 used to derive eq b and c are indeed an oversimplification of what must be a very complicated process, *i.e.*, a multiquantum cascade mechanism. Such a process would lead to a general expression of the type

$$\Phi_\mathrm{III}^{-1} = \frac{\sum_0^n a_j(\mathrm{M})^j}{\sum_0^n b_{j-1}(\mathrm{M})^{j-1}} \qquad \text{(d)}$$

where n is the number of vibronic levels and a_j and b_j are coefficients containing the individual rate constants. Such a treatment is far more sophisticated than the data warrant.

Figure 8 shows that relation c is only correct at low pressures of *n*-butane. At high pressures a deviation from linearity is observed, probably due to the cascade mechanism (higher terms in (d) became important). From the slope and the intercept of the curve in Figure 8, we can derive the following rate constant ratios at 26°

$$\frac{k_6}{k_5} = 4.7 \qquad \frac{k_7}{k_5} = 5.2 \times 10^3\ \mathrm{l.\ mol^{-1}}$$

For pressures of *n*-butane smaller than 5 Torr, vibrational deactivation of the excited triplet state is mainly due to a unimolecular process, while for pressures larger than 50 Torr bimolecular relaxation predominates.

According to the proposed mechanism, the formation of the triplet is independent of pressure when I

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(12) W. A. Noyes, Jr., and D. A. Harter, *J. Amer. Chem. Soc.*, **91**, 7585 (1969).

(13) K. E. Wilzbach and L. Kaplan, *ibid.*, **90**, 1116 (1968).

(14) I. B. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules," Academic Press, New York, N. Y., p 47.

(15) C. S. Parmenter and J. R. Rau, *J. Chem. Phys.*, **51**, 2242 (1969).

(16) E. K. C. Lee, M. W. Schmidt, R. G. Shortridge, and G. A. Haninger, Jr., *J. Phys. Chem.*, **73**, 1805 (1969).

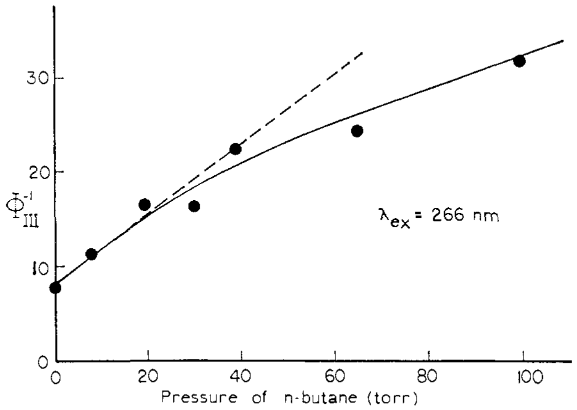

Figure 8. Reciprocal of the quantum yield of formation of 1-phenyl-2-methylcyclopropane *vs.* *n*-butane pressure: pressure of 1, 0.8 Torr; temperature, 26°.

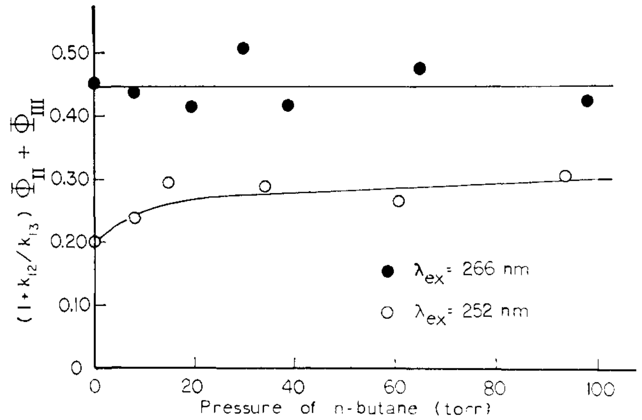

Figure 9. Φ_s *vs.* *n*-butane pressure.

is excited in the 0–0 band. But, in the triplet manifold, increasing pressure of inert gas will decrease the formation of III, while the formation of I and II will increase by the corresponding amount. Consequently, the sum $\Phi_s = \Phi_I + \Phi_{II} + \Phi_{III}$ (where Φ_I is the quantum yield of re-formation of the original molecule from the triplet state) will remain constant. Φ_I cannot be measured directly but is related to Φ_{II} by the relation

$$\frac{\Phi_I}{\Phi_{II}} = \frac{k_{12}}{k_{13}}$$

where the branching ratio k_{12}/k_{13} is equal to 0.8, as determined by Morrison in the liquid phase.[3] Figure 9 shows the plot of $(1 + k_{12}/k_{13})\Phi_{II} + \Phi_{III}$ *vs.* *n*-butane pressure: Φ_s indeed remains constant and is equal to 0.445 within experimental error. From (b) and (c) we can derive the theoretical expression

$$\Phi_s = k_4\frac{k_9[k_6 + k_7(\mathrm{M})] + k_5(k_8 + k_9)}{(k_3 + k_4)(k_8 + k_9)[k_5 + k_6 + k_7(\mathrm{M})]}$$

For Φ_s to remain constant, each coefficient of the *n*-butane concentration in the polynomial must be set equal to zero. This leads to the following set of equations

$$1 + \frac{k_5}{k_6}\left(1 + \frac{k_8}{k_9}\right) - 0.445\left(1 + \frac{k_3}{k_4}\right) \times \left(1 + \frac{k_8}{k_9}\right)\left(1 + \frac{k_5}{k_6}\right) = 0 \quad \text{(e)}$$

$$1 - 0.455\left(1 + \frac{k_3}{k_4}\right)\left(1 + \frac{k_8}{k_9}\right) = 0 \quad \text{(f)}$$

The only unknown ratio in eq e and f is k_8/k_9. The values obtained are 0.97 from (e) and 0.685 from (f). Considering the complexity of the mechanism and the assumptions made, the agreement is good and $k_8/k_9 = 0.83 \pm 0.14$ will be taken as an average value.

This important result is somewhat surprising. One would expect the intramolecular triplet–triplet energy transfer (process 9) to be much faster than the spin-forbidden intersystem crossing to the ground state. Recently, Sigal[17] studied the effect of concentration on the *cis–trans* isomerization of 1-phenyl-2-butene in the liquid phase and reported the value of k_8 to be 1.0×10^7 sec^{-1}. If this value is adopted, the rate constant k_9 for intramolecular triplet–triplet energy transfer is calculated to be 1.2×10^7 sec^{-1}. This value can be compared with 2×10^8 sec^{-1} determined by Morrison[3] and 2×10^6 sec^{-1} from Sigal.[17] Because $k_8/k_9 = \Phi_{isc}/(1 + k_{12}/k_{13})\Phi_{II} = 0.83 \pm 0.14$, the quantum yield for intersystem crossing Φ_{isc} can be estimated equal to 0.27 ± 0.05.

In conclusion, it is found that the sum of all the processes identified after absorption of 1 quantum by I, *i.e.*, fluorescence, cyclization, *cis–trans* isomerization, and intersystem crossing from the triplet state to the ground state, is equal to 0.98 despite a fairly large experimental error (±0.15).

One question to be resolved is the mechanism of formation of III. It is possible that a 1–2 H shift occurs, but the mechanism suggested by Zimmerman[18] is also feasible. The problem is currently under investigation by a tracer technique.

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(17) C. S. Nakagawa and P. Sigal, *J. Chem. Phys.*, **52**, 3277 (1970).

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