Racemization of Sulfoxides. A portion of sulfoxide sufficient to give approximately 2° rotation in a 1.6-dm cell was weighed out and dissolved in 10 ml of solvent. The allyl *p*-tolyl sulfoxide, however, received special treatment because of its optical instability. The substance was prepared in the form of an ether solution which was rapidly fanned almost to dryness under a powerful air stream and then taken up in alcohol or toluene. Sufficient solution for ten measurements was prepared at once and preserved in a freezer at $-15°$. The phenyl, naphthyl, and benzyl sulfoxides require such a high temperature that the high-pressure cell could not be preheated. Reaction times of about 10 hr were used in order to reduce the effect of the 4-min characteristic time in thermal equilibration.

Hydrolysis of *t*-Butylethylmethylsulfonium Ion. Solutions were made up as for racemization, but the excess acid was exactly neutralized before heating. Progress of the reaction was determined by titration with standard alkali.

Rearrangement of Allyl Thiocyanate. Allyl thiocyanate was prepared from allyl chloride and ammonium thiocyanate.[19] Reaction mixtures were prepared by dissolving 0.30 g in 10 ml of carbon tetrachloride, and rearranged to the isothiocyanate by heating for several hours at 54.2°. The progress of the reaction was followed by ir analysis. The spectra were scanned very slowly by hand in the 2000–2200- and 1200–1500-cm^{-1} regions using a Perkin-Elmer Model 421 spectrometer, and the composition was determined by comparison with the spectra of known synthetic mixtures covering the range of 23–31% reaction, where the method was most sensitive.

High-Pressure Apparatus. The apparatus has been described previously,[20] but the oil-filled thermostat has been replaced by a 200-lb aluminum ingot which has been bored to receive the high-pressure vessel. An oil film is used to improve the thermal contact.

Calculation of Activation Volumes. The logarithm of the ratio of the rate constant at pressure to the rate constant at 1 atm (k_p/k_1) was plotted against pressure, and the best straight line was drawn through the origin and the other points. The slope was used to evaluate the activation volume according to the equation

$$RT(\partial \ln k/\partial P)_T = -\Delta V^*$$

In all cases where comparison was possible, either directly or by calculation using activation parameters, our values of k_1 agreed satisfactory with those previously reported.

Acknowledgement. The authors are indebted to the National Science Foundation which supported this work by Grant No. GP-1718.

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[19] W. Young, I. Webb, and H. Goering, *J. Amer. Chem. Soc.*, **73**, 1076 (1951).

[20] K. R. Brower, *ibid.*, **80**, 2105 (1958).

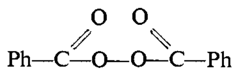
Photolysis of Dibenzoyl Peroxide[1]

Harold C. Box, Edwin E. Budzinski, and Harold G. Freund

Contribution from the Biophysics Department, Roswell Park Memorial Institute, Buffalo, New York 14203. *Received September 20, 1969*

Abstract: The dissociation of dibenzoyl peroxide by radiation from a high-pressure mercury lamp was observed by electron spin resonance spectroscopy. Measurements were made on single crystals of dibenzoyl peroxide irradiated at 4.2°K. From the magnitude of the dipole–dipole interaction between the pairs of radicals formed by each dissociation it is concluded that phenyl radicals are produced, *i.e.*, Ph—C(=O)—O—O—C(=O)—Ph → 2CO$_2$ + 2Ph.

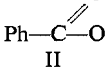
Perhaps the most familiar of organic peroxides is dibenzoyl peroxide (I), which is used extensively



$$\mathrm{Ph{-}C({=}O){-}O{-}O{-}C({=}O){-}Ph}$$

I

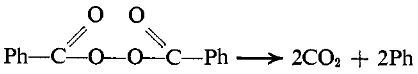
in the plastics industry to initiate polymerization. Thermal dissociation of the weak peroxide bond yields benzoyloxy radicals (II) which initiate the polymerization process.



$$\mathrm{Ph{-}C({=}O){-}O}$$

II

The process can be accelerated by using ultraviolet light to promote dissociation. Phenyl radicals, which also initiate polymerization, and CO$_2$ can also be formed in the decomposition of peroxide, *i.e.*



$$\mathrm{Ph{-}C({=}O){-}O{-}O{-}C({=}O){-}Ph} \longrightarrow 2CO_2 + 2Ph$$

Using electron spin resonance (esr) spectroscopy, Symons and Townsend[2] attempted to detect the formation of radicals in ultraviolet-irradiated glasses containing dibenzoyl peroxide. However, they were unable to detect any esr absorption. In this report, we give an account of the dissociation of dibenzoyl peroxide in single crystals of dibenzoyl peroxide exposed to ultraviolet irradiation at 4.2°K, as observed by esr spectroscopy.

Experimental Section

Single crystals of dibenzoyl peroxide were grown by slow evaporation from benzene solutions. The crystals are orthorhombic, belonging to the space group $P2_12_12_1$, with four molecules per unit cell. The crystal structure of dibenzoyl peroxide has been determined from X-ray diffraction measurements by Sax and McMullan.[3]

The esr measurements were made using a K-band spectrometer (24.0 Gc/sec) utilizing superheterodyne detection. A crystal was mounted on a copper wire and suspended at the center of the cylindrical sample cavity which resonated in the TE011 mode. The cavity was immersed in liquid helium (4.2°K) in a dewar provided with sapphire windows. The crystal was exposed to light from an Osram high-pressure Hg lamp (HBO, 100 W). The light was focused on the crystal by quartz lenses.

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[1] Supported by Public Health Grant No. RH 00450 and AEC Contract No. AT(30-1)3558.

[2] M. C. R. Symons and M. G. Townsend, *J. Chem. Soc.*, 263 (1959).

[3] M. Sax and R. K. McMullan, *Acta Crystallogr.*, **22**, 281 (1967).

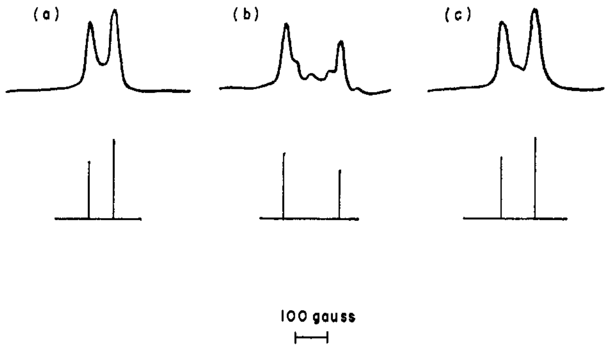


Figure 1. Esr absorption spectra obtained with magnetic field applied parallel to the *a*, *b*, and *c* axes. The spectra were obtained from an oscillographic display of the absorption at 4.2°K. Magnetic field strength increases to the right. Stick diagrams show calculated intensities of transitions.

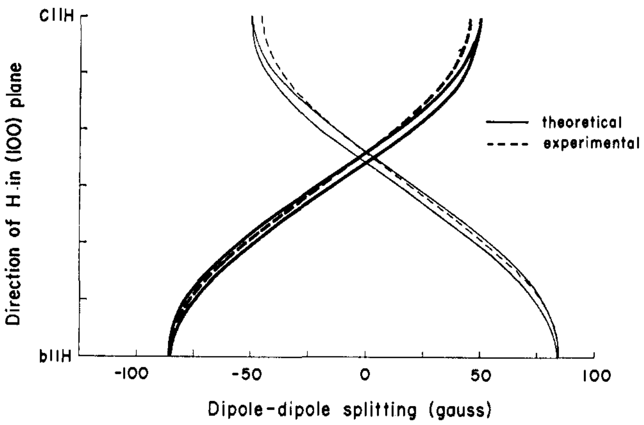


Figure 2. Calculated (—) and observed (- - -) dipole–dipole splitting with the magnetic field parallel to the (100) plane. Heavier lines represent the stronger transition.

Theoretical Considerations

Irradiation of dibenzoyl peroxide results in the formation of pairs of radicals. The spin Hamiltonian which is used to describe a pair of interacting spins in the presence of an external magnetic field is

$$\mathcal{H} = \beta\mathbf{H}\cdot\mathbf{g}\cdot(\mathbf{S}_1 + \mathbf{S}_2) + \mathbf{S}_1\cdot\mathbf{A}\cdot\mathbf{S}_2 \qquad (1)$$

where β is the Bohr magneton, **H** is the magnetic field intensity, $\mathbf{S}_1$ and $\mathbf{S}_2$ represent the electron spins, **g** is the *g* tensor, and **A** is the tensor which describes the magnetic dipole–dipole interaction between electron spins.[4] The components of the **A** tensor are expectation values

$$A_{ij} = \beta^2 g_{\mathrm{fs}}^2 \left\langle \frac{\mathrm{r}^2\delta_{ij} - 3\mathrm{r}_i\mathrm{r}_j}{\mathrm{r}^5} \right\rangle \qquad (2)$$

where $g_{\mathrm{fs}} = 2.0023$ and $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$, where $\mathbf{r}_1$ and $\mathbf{r}_2$ define the spatial positions of the spins. In our example, the *g* value is nearly isotropic and can be treated as a constant. Taking the direction of the applied field as parallel to the *z* axis the eigenvalues of (1) corresponding to the triplet state are given by

$$\begin{aligned} E_1 &= A_{zz}/4 + \left[(g\beta\mathrm{H})^2 + \left(\frac{A_{xx} - A_{yy}}{4}\right)^2 + \left(\frac{A_{xy}}{2}\right)^2\right]^{1/2} \\ E_0 &= -A_{zz}/2 \qquad (3) \\ E_{-1} &= A_{zz}/4 - \left[(g\beta\mathrm{H})^2 + \left(\frac{A_{xx} - A_{yy}}{4}\right)^2 + \left(\frac{A_{xy}}{2}\right)^2\right]^{1/2} \end{aligned}$$

This solution is exact if the applied field is parallel to a principal axis of the **A** tensor. By esr spectroscopy we observe the allowed transition between levels $\mathrm{E}_0 \rightarrow \mathrm{E}_1$ and $\mathrm{E}_{-1} \rightarrow \mathrm{E}_0$. At the high magnetic field intensity used in our experiments (8550 G) the field intensities at which resonance occurs are given by

$$\mathrm{H}_{\pm} = \mathrm{H}_0 \mp 3\mathrm{A}_{zz}/4g\beta \qquad (4)$$

H_+ refers to the transition $\mathrm{E}_0 \rightarrow \mathrm{E}_1$, H_- to the transition $\mathrm{E}_{-1} \rightarrow \mathrm{E}_0$, and $\mathrm{H}_0 = h\nu/g\beta$, where ν is the microwave frequency of the energy used to stimulate the transitions. Of interest are the relative intensities of the two transitions. Let F be the intensity of $\mathrm{E}_0 \rightarrow \mathrm{E}_1$ transitions relative to $\mathrm{E}_{-1} \rightarrow \mathrm{E}_0$ transitions. From the differences in population between levels, calculated from a Boltzmann distribution in which the small effect due to the dipole–dipole interaction energy is ignored, we obtain

$$F = \frac{1 - \exp(-g\beta\mathrm{H}/kT)}{\exp(g\beta\mathrm{H}/kT) - 1} \qquad (5)$$

Analysis of Results

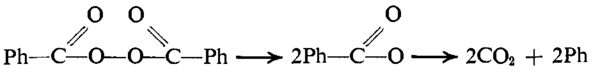
The esr absorption of a single crystal of dibenzoyl peroxide at 4.2°K following exposure to light is shown in Figure 1. The three spectra shown are for orientations in which the magnetic field was parallel to one of the crystal axes, so that the four molecules in the unit cell are equivalently oriented with respect to the field. For other orientations, the absorption is generally more complicated. The *g* value of the absorption did not deviate significantly from that of the diphenylpicrylhydrazyl reference (2.0036). The two largest peaks in each of the spectra of Figure 1 are attributed to radical pairs; the weaker peaks apparent in Figure 1b were not analyzed. The dipole–dipole coupling between radicals is very anisotropic. The components of the dipole–dipole coupling tensor were determined experimentally using eq 4. The principal values of this tensor and the direction cosines of the principal axes, measured with respect to the crystal axes, are given in Table I.

Table I. Principal Values (G) and Direction Cosines of the Principal Axes of the Dipole–Dipole Coupling Tensor[a]

	a	*b*	*c*
197	±0.30	±0.95	0.00
−92	0.00	0.00	+1.00
−98	±0.95	∓0.30	0.00

[a] Within the accuracy of the experimental measurements, one principal axis lies parallel to the *c* axis. Consequently, only two sets of direction cosines are required to specify the symmetrically related **A** tensors rather than four, as would be anticipated for the $P2_12_12_1$ space group.

The magnitude of the dipole–dipole coupling suggests that the esr absorption is due to a pair of phenyl radicals formed by the dissociation of dibenzoyl peroxide. The dissociation may be visualized as a two-step process. Assuming phenyl radicals are



$$\mathrm{Ph{-}\overset{\overset{O}{\Vert}}{C}{-}O{-}O{-}\overset{\overset{O}{\Vert}}{C}{-}Ph \longrightarrow 2Ph{-}\overset{\overset{O}{\Vert}}{C}{-}O \longrightarrow 2CO_2 + 2Ph}$$

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[4] A. Carrington and A. D. McLaughlan, "Introduction to Magnetic Resonance," Harper and Row, New York, N. Y., 1967, p 115.

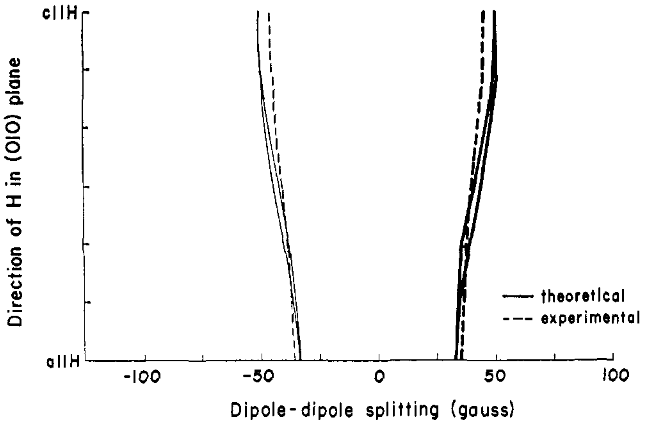

Figure 3. Calculated (—) and observed (- - -) dipole–dipole splitting with the magnetic field parallel to the (010) plane. Heavier lines represent the stronger transition.

formed, the dipole–dipole coupling can be calculated theoretically. Since the separation between phenyl radicals would be large compared to atomic dimensions we can calculate the quantity A_{zz} from the expression

$$A_{zz} = \frac{\beta^2 g_{fs}^2}{R^3}(1 - 3\cos^2\theta) \qquad (6)$$

where **R** is a vector drawn between the mean positions of interacting electrons on adjacent phenyl radicals and θ is the angle between **R** and **H**. Let

$$\mathbf{R} = R\boldsymbol{\mu} \qquad (7)$$

The obvious choice for **R** is a vector drawn between nuclei of the pair of phenyl carbon atoms whose connection has been severed. Assuming that the position of the phenyl group has not been affected by the dissociation, we deduce from the crystal structure of dibenzoyl peroxide that there are four possible symmetry-related directions for $\boldsymbol{\mu}$, one of which is

$$\boldsymbol{\mu} = 0.334\mathbf{i} + 0.942\mathbf{j} + 0.022\mathbf{k} \qquad (8)$$

where **i**, **j**, and **k** are unit vectors along the *a*, *b*, and *c* crystal axes and $|\mathbf{R}| = 5.66$ Å. It was found, however, that a value of $|\mathbf{R}| = 6.48$ Å is more compatible with the experimental results. The larger value of $|\mathbf{R}|$ is consistent with some delocalization of the unpaired electrons on the phenyl radical. Using eq 4, 6, 7, and 8, the resonance fields were calculated for crystal orientations in which the magnetic field is parallel to the (100), (010), and (001) planes. The results are shown in Figures 2–4 by the solid lines. The resonance fields as derived from the experimentally determined **A** tensor (Table I) are shown by the dashed lines.

The low-field absorption in Figure 1b is more intense than the high-field absorption. This result is consistent with the prediction of eq 5, taking H = 8550 and $T = 4.2$°K. The calculated intensity ratio is indicated in Figure 1 by the stick diagrams. Note that in Figures 1a and 1c the situation is reversed; the high-field absorption is more intense than the low-field absorption. The reversal results from the change in sign of the dipole–dipole interaction, as shown by eq 4 and 6. In Figures 2–4, the more intense absorption is indicated by the heavier lines. After warming an irradiated dibenzoyl peroxide crystal to room temperature the esr signal disappears.

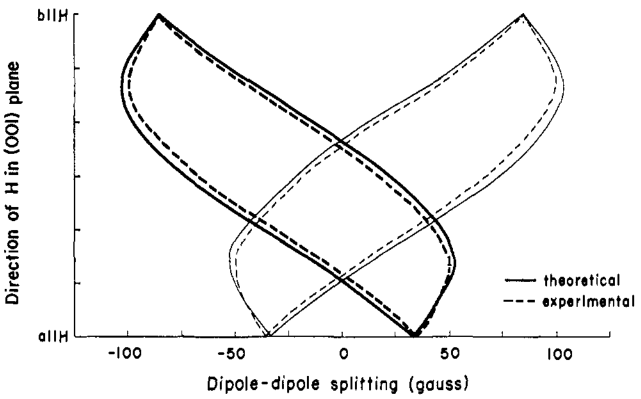

Figure 4. Calculated (—) and observed (- - -) dipole–dipole splitting with the magnetic field parallel to the (001) plane. Heavier lines represent the stronger transition.

Discussion

It is found that phenyl radicals, but not benzoyloxy radicals, are produced by dissociation of dibenzoyl peroxide in single crystals irradiated with ultraviolet light. Two reasons can be given for the absence of benzoyloxy radicals. (1) Benzoyloxy radicals formed in pairs might be expected to recombine. (2) Ultraviolet excitation may force the degradation of the benzoyloxy radicals, producing phenyl radicals and CO_2. Phenyl–benzoyloxy radical pairs are not observed either, and it would seem that only the latter reason can explain this absence. A phenyl–benzoyloxy pair of radicals should be stable because of the large separation between them. It is interesting that stable pairs of benzoyloxy radicals can be produced by ionizing radiation in single-crystal solid solutions of dibenzoyl disulfide containing dibenzoyl peroxide.[5] Benzoyloxy radical pairs are indicated by dipole–dipole couplings which are larger by a factor of approximately 6 than the couplings described in this paper. Recombination of benzoyloxy radicals occurs if the temperature of the solid solution is allowed to rise a few degrees above 4.2°K. Benzoyloxy radical pairs are *not* observed in solid solutions subjected to ultraviolet irradiation, again indicating that mechanism 2 operates. Bevington and Lewis[6] used ^{14}C-labeled dibenzoyl peroxide to demonstrate the incorporation of phenyl and benzoyloxy radicals in polystyrene subjected to ultraviolet irradiation during polymerization. In their experiment the monomer acts as a scavenger for radicals so that capture of benzoyloxy radicals and photodissociation of benzoyloxy radicals are competitive processes.

There is no well-defined hyperfine structure associated with the esr absorption of the phenyl radicals observed in our study. Consequently, nothing has been inferred concerning the distribution of the unpaired electron in this most interesting radical. However, endor measurements of the hyperfine coupling in phenyl radicals will be attempted in the near future.

Recently Weiner and Hammond[7] used esr spectroscopy to observe free-radical formation in polycrystal-

(5) Unpublished results obtained in this laboratory.

(6) J. C. Bevington and T. D. Lewis, *Trans. Faraday Soc.*, **54**, 1340 (1958).

(7) S. Weiner and G. S. Hammond, *J. Amer. Chem. Soc.*, **91**, 2182 (1969).

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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Contribution from the Department of Chemistry,
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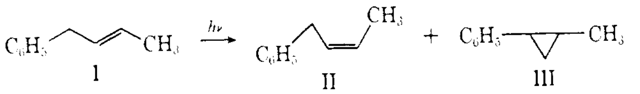
Received March 16, 1970

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).