# Photochemistry of the Gas–Solid Interface. The System 1,3-Pentadiene–Pyrex

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**Abstract:** Irradiation of *cis*- or *trans*-1,3-pentadiene in Pyrex or quartz vessels with the emission from a medium pressure mercury arc transmitted by Pyrex (λ >280 nm) results in geometrical isomerization of the diene. It is found using filtered light that the group of lines at 366 nm is most effective in promoting the reaction. Impurity effects and thermal reactions are probably unimportant. Results of experiments in which the path length of light through cells was varied, together with results of internal reflection photolysis experiments, show that light is initially absorbed by a surface chromophore described as strongly adsorbed diene. By internal reflection spectroscopy, the surface species is found to have an absorption maximum at ~360 nm and an onset of ~570 nm. The proposed mechanism involves triplet–triplet energy transfer from the surface state to gaseous 1,3-pentadiene.

The earliest study of electronic energy transfer at the gas–solid interface seems to have been by Kautsky and de Bruijn.[2] More recent reports are concerned with transfer from polymeric[3,4] or crystalline[5] triplet photosensitizers to gaseous 1,3-pentadiene. Studies of solution-phase photosensitized cis–trans isomerization of 1,3-pentadiene served as a basis for interpretation of results in these systems.[6]

Further information about cross phase energy transfer and other heterogeneous photochemical processes may be obtained by using internal reflection spectroscopy (IRS) to study the surface states and internal reflection photolysis (IRP) to excite selectively the surface states in the presence of a vapor phase.[7]

In the course of earlier work,[5] we found that illumination of *cis*-1,3-pentadiene vapor contained in a Pyrex vessel (λ >280 nm) resulted in an appreciable rate of formation of the trans isomer, even though the diene is sensibly transparent in this wavelength region.[8] This observation of a photochemical reaction in the apparent absence of light absorption led us to investigate the influence of the vessel surface in this system.

## Experimental Section

**Reagents.** Both *cis*- and *trans*-1,3-pentadiene were purchased from Chemical Samples Co. The stated purity of 99% was verified by gas chromatography In each case the main impurity was the other 1,3-pentadiene isomer; two unidentified components having retention times shorter than trans were also detected. Liquid samples of cis and trans having a minimum purity of 99.9% were obtained through preparative gas chromatography, but in vapor samples of cis taken from the liquid at temperatures below −30° the trans impurity increased considerably. There was a slow conversion of cis to trans under storage conditions, presumably due to a small amount of room light which entered the sample bulb. The purified samples of 1,3-pentadienes were used except in the cases noted. As a test for impurity effects, the rate of photoisomerization was measured under identical conditions using purified cis in one set of experiments and cis as obtained from the supplier in another set. The "unpurified" sample was purchased more than a year after the first sample was obtained. "Unpurified" cis was also used for photolysis following various wall treatment procedures, for internal reflection photolysis, and in determining the intensity dependence of the isomerization rate. Chemical Samples Co. was also the supplier of *n*-pentane (99.9%), *cis*-2-pentene (98%), and *cis,trans*-2,4-hexadiene (99%). The 1,3-butadiene was J. T. Baker instrument grade. Spectroquality carbon tetrachloride and carbon disulfide and reagent grade ethyl iodide were obtained from Matheson, Coleman and Bell. Cyclohexane (99.94%) was Phillips research grade. These liquid reagents and 1,3-butadiene were used without further purification. Oxygen, Baker extra dry, was passed over silica gel at −78°. All liquid samples from which vapor fractions were taken for photolysis or spectroscopy were stored at −78° behind stopcocks on the vacuum line in bulbs covered with aluminum foil. Liquid samples and 1,3-butadiene were outgassed immediately after introduction into the vacuum line by several trap to trap distillations; vapor fractions were again outgassed by two trap to trap distillations before experimental use.

**Photolysis Apparatus and Procedure.** The Pyrex vacuum line was of conventional design. All cells were of Pyrex except where noted. Apiezon N grease was used in stopcocks and standard tapers. Except where indicated otherwise, photolyses were carried out with a cylindrical reaction cell (32-mm o.d., 35-mm optical path length, 61.7-cm$^3$ volume including dead space) mounted in a stationary position with its central axis vertical. This cell was irradiated with a lamp mounted above it. A Masonite light shield with an aperture of 38-mm diameter was placed between the cell and lamp; it supported the shutter and, where used, filters. No lenses or mirrors were used to focus light from this lamp.

In addition to this stationary cell, several portable cells were employed. Eight nearly identical cylindrical cells with outside diameter of 32 mm and optical path length of 30.2 mm (volume including dead space, 31.1 cm$^3$) were used. Visible uv spectra were taken of windows prior to fusing them to the bodies of these cells; transmission characteristics were also checked after construction. The windows were identical (within 2%) in transmission characteristics for λ >340 nm, showed small differences in the 280–340 nm region, and were typically opaque (transmission <1%) for λ ≤280 nm. These "matched" cells were irradiated using a carousel, and with the lamp used for irradiating the stationary cell. In the latter case, positioning was made reproducible by means of a wooden jig.

The effect of various wall treatments on the rate of photoisomerization was determined using one of these eight cells. The following treatments were used: (1) methanol saturated with

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[1] National Aeronautics and Space Agency Trainee, 1966–1968; National Science Foundation Predoctoral Fellow, 1968–1970.

[2] H. Kautsky and H. de Bruijn, *Naturwissenschaften*, **19**, 1043 (1931); *Chem. Abstr.*, **26**, 1517 (1932).

[3] R. E. Moser and H. G. Cassidy, *J. Polym. Sci., Part B*, **2**, 545 (1964).

[4] G. R. Demare, M. C. Fontaine, and P. Goldfinger, *J. Org. Chem.*, **33**, 2528 (1968); G. R. Demare, M. C. Fontaine, P. Goldfinger, G. Huybrechts, and M. Sapir, *Bull. Soc. Chim. Belg.*, **80**, 259 (1971).

[5] R. L. Daubendiek, H. Magid, and G. R. McMillan, *Chem. Commun.*, 218 (1968).

[6] G. S. Hammond, P. A. Leermakers, and N. J. Turro, *J. Amer. Chem. Soc.*, **83**, 2396 (1961); *J. Phys. Chem.*, **66**, 1144 (1962); G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *J. Amer. Chem. Soc.*, **86**, 4537 (1964).

[7] IRP was probably first employed by K. Kuschnir and T. Kuwana, Case Western Reserve University, personal communication, 1969.

[8] American Petroleum Institute Project 44 Serial No. 46 and 48.

KOH for 1 hr at 75–80°; (2) a mixture of concentrated $H_2SO_4$ (4 parts) and concentrated $HNO_3$ (1 part) for 1 hr at 100–110°; (3) concentrated $HNO_3$ for 1 hr at 95–105° (after cooling to ambient, the cell was, in each of the above cases, rinsed 15 times with tap water and 15 times with distilled water); (4) oxygen at high temperature. The cell was placed in an oven and oxygen was led directly to the lowermost part of the cell through a section of 6-mm Pyrex tubing which was coiled several turns inside the oven. The temperature was raised from ambient to 500° during the first hour, then raised from 500 to 600° during the second hour. Oxygen flow was maintained while cooling. The treatments were carried out in the order listed. Following each of the four treatments, the cell was outgassed overnight before initiating photolysis.

For variable path length experiments, two Pyrex cylindrical cells (25-mm o.d.) were used, one with windows designated set A, one with set B. One cell was shortened by removing a section of 25-mm tubing; the other was lengthened by adding a section of 25-mm tubing. The specifications of these cells are listed in Table I.

Table I. Photoisomerization Rate for Different Optical Path Lengths[a]

| Path length, mm | Cell volume, $cm^3$ | $10^{-10} \times \text{rate}_{c \rightarrow t}$, molecules $sec^{-1}$ |
|---|---|---|
| | Windows: set A | |
| 8.0 | 5.4 | 5.21 |
| | | 3.72 |
| | | 5.31 |
| | | 0.16[b] |
| 38.8 | 16.6 | 5.90 |
| | | 5.10 |
| | | −0.30[b] |
| | Windows: set B | |
| 45.5 | 19.4 | 4.45 |
| | | 5.14 |
| | | 4.34 |
| 12.4 | 7.0 | 2.79 |
| | | 2.01 |
| | | 0.38[b] |
| | | −0.03[b] |

[a] Incident intensity at 366 nm = 7.1 × $10^{15}$ quanta $sec^{-1}$; initial pressure of *cis*-1,3-pentadiene = 0.6 ± 0.02 Torr. [b] Blank.

Table II. Percentage Transmission of Mercury Lines by Glass Filters[a]

| Filter | Wavelength, nm | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 289.4 | 296.7 | 302.5 | 313.0 | 334.1 | 366.0 | 404.5 | 435.8 |
| CS# 0–51[b] | <1 | <1 | <1 | <1 | <1 | 3.6 | 69.2 | 81.3 |
| CS# 7–37[b] | <1 | <1 | <1 | <1 | 6.2 | 29.5 | <1 | <1 |
| Pyrex 1 | ~1 | 6.6 | 16.6 | 44.2 | 79.8 | 90.0 | 90.0 | 90.0 |
| Pyrex 2 | <1 | 2.0 | 6.5 | 29.5 | 69.2 | 81.5 | 83.0 | 83.0 |
| Glass 3 | <1 | <1 | <1 | <1 | <1 | 63.8 | 91.2 | 91.2 |

[a] Determined with Cary 15 spectrophotometer. [b] Corning Glass Co. designation.

Light from the mercury arc was collimated using a Pyrex lens system, and positioning of the cells was such that irradiation of the side walls was avoided. These experiments were extended using a much longer cell (305 × 41 mm o.d.). This cell was used in conjunction with light from a General Electric BH6 high pressure mercury arc transmitted by a Corning CS No. 7-37 filter (incident intensity ~1.3 × $10^{16}$ quanta $sec^{-1}$); this radiation was sufficiently well collimated so that none impinged upon the side walls of the cell.

A few photolyses were carried out in a quartz cell (100 × 25-mm o.d.). Incident radiation was filtered through a Pyrex plate.

The internal reflection photolysis cell is illustrated in Figure 1. The planar end seals joined the 4-mm rod at an angle of ~70°. The vapor being photolyzed occupied the volume (5.03 $cm^3$) between the 4-mm rod and the 9-mm tubing, and the side arm behind the stopcock. During experiments in which the intensity of radiation scattered by the light pipe was estimated, the volume between the 9-mm tubing and 32-mm tubing was occupied by actinometric solution. For IRP, light from the collimator on the lamp housing was focused onto a 2.4-mm aperture by a Pyrex lens system. The IRP cell was aligned so that all light leaving the aperture struck the entrance to the light pipe. The minimum angle of incidence in the light pipe was 50°. The IRP cell was positioned by inserting its standard taper into a matching outer cone whose position was fixed, then rotating about this axis to a wooden stop where the cell was fastened. In all cases but the one already noted, the light source for photolyses was a 673A Hanovia 550-W medium pressure mercury arc. The characteristics of filters which were used are listed in Table II. To test the dependence of rate on light intensity, three brass screens (16 wires per cm) were used as neutral density filters. Their transmission characteristics individually and in series were determined with a Cary 15 spectrophotometer and with a medium pressure mercury arc and photocell circuit. When placed in the photolysis light path (no lens or collimating mirrors were used), no shadows were noticeable for distances ≥2 cm from the screen. Photolyses were carried out with one screen placed at several different positions to test for possible shadowing effects. None were evident. In use, screens were >4 cm from the cell and from each other.

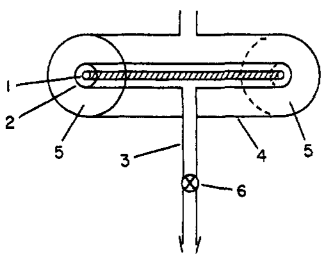

Figure 1. Internal reflection photolysis cell: (1) light pipe, 4-mm rod; (2) cell wall, 9-mm o.d. tube; (3) side arm, 8-mm o.d. tube; (4) outer wall of actinometer chamber, 32-mm o.d.; (5) end seals; (6) Teflon high vacuum stopcock.

Photolyses were not initiated unless the pressure of noncondensables in the vacuum line was $<10^{-6}$ Torr. The material to be photolyzed was outgassed by two trap-to-trap distillations, transferred to the appropriate cell, and mixed by raising and lowering the mercury level in a 300-$cm^3$ bulb 20 times. The vapor was then divided between the cell and connecting tubing. Cell contents were photolyzed; vapor in the connecting tubing was taken for gas chromatographic analysis of the starting material. For analyses of starting material and products, complete transfer of all components condensable at −196° was effected. Cell pressure readings greater than 5 Torr were taken with a mercury manometer. Pressures less than this were estimated from the response of the chromatograph to vapor which occupied the known volume of connecting tubing. Cell temperatures, measured with a copper–constantan thermocouple fixed to the cell wall, were typically 35° during photolysis. In kinetic studies, conversions were ≤7%. Separation of components of the reaction mixture was accomplished on a 30-ft 0.25-in. column of 15% β,β′-oxydipropionitrile on Chromosorb W 60–80 mesh. The chromatograph, an F & M Model 700, was equipped with a flame detector. Peak areas for *cis*- and *trans*-1,3-pentadiene were calibrated for the entire range of concentrations used in analyses.

Potassium ferrioxalate actinometry was used to estimate light intensities.[9] Incident intensity of 366-nm radiation in light transmitted by the Pyrex lens was estimated by photolysis of potassium ferrioxalate solution with a Corning CS No. 7-37 filter in the optical

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(9) C. A. Parker, *Proc. Roy. Soc., Ser. A*, 220, 104 (1953); C. G. Hatchard and C. A. Parker, *ibid.*, **235**, 518 (1956); J. H. Baxendale and N. K. Bridge, *J. Phys. Chem.*, **59**, 783 (1955).

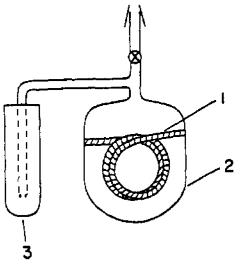

Figure 2. Cell for internal reflection spectroscopy: (1) light pipe, 4-mm rod, 23 cm long; (2) cell body, 50-mm o.d.; (3) coldfinger equipped with heater and asbestos insulation.

train; intensity of 366-nm radiation without this filter could be calculated from the intensity measured with it and its transmission characteristics. The intensity of radiation scattered by the light pipe in IRP was estimated with and without a CS No. 7-37 filter in the optical train. Results obtained without the filter could be predicted to within 10% on the basis of the following information: (1) actinometric results obtained using the filter; (2) transmission properties of the filter; (3) relative intensities of pertinent mercury emission lines;[10] (4) absorbed intensities of these lines by the actinometry solution;[11] (5) quantum efficiencies of the actinometer at the wavelengths of interest.[9,12]

**Internal Reflection Spectroscopy Apparatus and Procedure.** Light pipe cells were used for IRS. Cells designated 1 and 2 were of the design illustrated in Figure 2. Cells designated 3 and 4 utilized straight rods as in the IRP cell (Figure 1), but did not have the 32-mm jacket. Cell 1 was used for *cis*-1,3-pentadiene. Cell 2 was used for *cis*-1,3-pentadiene, 1,3-butadiene, *cis,trans*-2,4-hexadiene, and *n*-pentane. Cell 3 was used for *n*-pentane and carbon disulfide. Cell 4 was used for carbon tetrachloride. Each IRS cell had a coldfinger which was insulated with asbestos; a coil of heating wire was imbedded in the insulation. Before taking spectra with these cells, the rate of condensation when liquid nitrogen was placed about the coldfinger and the rate of vaporization after removal of the coolant for various heater voltages were measured with a mercury manometer; these rates were measured for samples of *n*-pentane and *cis*-1,3-pentadiene. A reading of 0.0 Torr was noted 120 sec after placing liquid nitrogen around the coldfinger, and after removing the $N_2$ with the heater current off the sample showed no measurable pressure for 270 sec. The exteriors of the IRS and IRP cells were completely blackened except for small openings on either end which permitted radiation to enter and leave the light pipe. The cells used for IRS and IRP experiments represent modifications of a cell described in the literature.[13] All photolysis cells and IRS cells 1 and 2 were annealed in a Wilt oven before using them in experiments. In the annealing process the temperature was raised from ambient to 550° over a period of 2 hr, then lowered to ambient over the next 2 hr.

A single beam spectrophotometer[14] was used in all IRS experiments. The light source was a 55-W quartz-iodide tungsten lamp driven by an IBM 219980 direct current 12-V power supply. The lamp was operated at a black body temperature of 2800–3000°K. The lamp in combination with a Schoeffel prism monochromator and an EMI 9592B photomultiplier in a Pacific housing were mounted on opposing vertical ends of the sample compartment which was a light-tight, cubic black box approximately 20 in. on an edge. The black box and components were positioned on a Barry Controls vibrationless table damped to 3 Hz. A Fluke Model 412B served as the high voltage supply for the photomultiplier tube. Philbrick P85 operational amplifiers in the current follower mode were situated in a Philbrick RP operational amplifier manifold. A Helipot 7035B was connected across the 15-V direct current power supply in the Philbrick manifold. The signal was monitored with a Hewlett-Packard X–Y recorder with the *x* axis in the time mode, and with a United Systems digital voltmeter.

The cells were outgassed and filled on the vacuum line. Samples were outgassed by trap to trap distillation with pumping before introduction into the cell. Manometer readings were taken with the vapor occupying the cell and adjoining section of the line; then the material was completely transferred to the cell. Cell pressures were calculated from known volume relationships assuming ideality. The cells were clamped securely inside the sample compartment (minimum angle of incidence, 50°), and light entering and leaving the light pipe was focused using lenses and, where needed, front surface mirrors. The sample was kept frozen until the proper settings had been made and a recorder base line had been established. With the high voltage to the photomultiplier tube turned off, the Helipot was adjusted to raise the output 10.00 V off ground. The photomultiplier voltage was then increased until a reading of 0.000 V was observed. The recorder was then switched on for approximately 500 sec in order to estimate the base line drift and noise level. Room lights were then extinguished, the sample compartment was opened, and the dewar of liquid nitrogen was removed from around the coldfinger. The base line was again recorded for 100–150 sec before applying current to the heater. The decreased intensity of light falling on the photomultiplier which occurred on vaporization of samples was recorded as a positive voltage change. The sample was then condensed with liquid nitrogen and, after setting the monochromator for a different wavelength, the process was repeated. Monochromator slit widths were chosen to give a half band width of 10 nm except where noted otherwise.

The liquid-phase spectrum of *cis*-1,3-pentadiene was taken *vs.* air with a 1-cm fused silica cuvette. The sample was taken from three sealed 1-cm$^3$ ampoules as supplied by Chemical Samples Co. The ampoules were opened and their contents were transferred inside a glove bag which was flushed with nitrogen. The cuvette was closed with a plastic cover before removal from the glove bag and left unopened until after the spectrum had been recorded. The 10-cm cells were used for taking spectra employing ethyl iodide as solvent. The cell in the reference beam was filled with a cyclohexane–ethyl iodide solution. The *cis*- and *trans*-1,3-pentadiene and cyclohexane solutions were all approximately 3 *M*.

An attempt was made to detect the spectrum of adsorbed pentadiene by transmission spectroscopy. Two of the eight matched photolysis cells were connected in a configuration such that the spectrophotometer light beam passed through both cells end on. Special precautions were taken to avoid contamination with diene before taking the blank spectrum of the cells. Both cells were treated with oxygen at high temperature following the procedure outlined above. A new vacuum line section was constructed for evacuating them. The entire new section including cells was annealed before making final connections, and it was isolated from the rest of the line by a trap kept at −196°. Liquid *cis*-1,3-pentadiene (outgassed) in quantity sufficient to give a cell pressure of 296 Torr was placed in a bulb that was joined to the connecting tubing but separated from the cells by a break-seal. After scanning the spectrum of the empty cells over the wavelength range 750 to 340 nm several times, the break-seal was opened and the spectrum was again scanned several times.

## Results and Discussion

**Photochemical Reaction.** Illumination of *cis*- or *trans*-1,3-pentadiene vapor in Pyrex or quartz vessels with the emission from the medium pressure mercury arc transmitted by Pyrex (λ >280 nm) results in isomerization of the diene. The isomerization rate is directly proportional to incident intensity over a tenfold range. Accordingly, the data in Tables II and III show that

**Table III.** Relative Photoisomerization Rates with Various Filters[a]

| Filter | Rate with filter/rate without filter |
|---|---|
| CS #0-51 | 0.088 |
| CS #7-37 | 0.191 |
| Pyrex 1 | 0.733 |
| Pyrex 2 | 0.683 |
| Glass 3 | 0.440 |

[a] Illuminations in stationary cell; pressure of *cis*-1,3-pentadiene = 3.9 Torr; temperature 35°.

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(10) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966, p 696.

(11) Reference 10, p 784.

(12) J. Lee and H. H. Seliger, *J. Chem. Phys.*, 40, 519 (1964).

(13) W. N. Hansen, *Anal. Chem.*, **35**, 765 (1963).

(14) N. Winograd, Ph.D. Thesis, Case Western Reserve University, Cleveland, Ohio, 1970.

the line at 366 nm promotes ~65% of the reaction. Wavelengths longer and shorter than 366 nm are responsible for ~5 and 30% of the reaction, respectively. The extinction coefficient for gaseous *cis*-1,3-pentadiene which can be calculated from the spectrum of liquid *cis*-1,3-pentadiene for λ 366 nm, assuming Beer's law, is too small by a factor of >100 to account for the rate of isomerization, assuming $\phi_{c\rightarrow t} = 0.5$. An estimate of the actual quantum yield is deferred.

The cis–trans photoisomerization appears uncomplicated by side reactions; the only products detected by gas chromatography were the two isomers of 1,3-pentadiene. No products were noncondensable at −196°. Products of intramolecular cyclization should have been detectable by gas chromatography but none were evident. Not more than small losses of diene were observed for long illumination times. In one experiment a mixture of *cis*-1,3-pentadiene (18.3 Torr) and *n*-pentane (13.1 Torr) was photolyzed for 62.3 hr, resulting in an 8.2% conversion to the trans isomer. The ratio of gas chromatographic peak areas *n*-pentane/1,3-pentadiene was 0.732 and 0.785 in the starting material and product analyses, respectively. In another case, *cis*-1,3-pentadiene (3.9 Torr) was photolyzed for 18 days;[15] after photolysis the 1,3-pentadiene was 59.5% trans. The total amount of 1,3-pentadiene decreased by at most 11% in this experiment. The recovery of 1,3-pentadiene from 1,3-pentadiene–1,3-butadiene mixtures was unaffected by the added gas. The slight decrease in 1,3-pentadiene noted in long photolyses may be indicative of some dimerization of polymerization; however, the rates of these reactions cannot be more than one-tenth the rate of isomerization. Since cis–trans isomerization is the dominant process, it is the only reaction that will be discussed.

The possible importance of thermal isomerization was tested in two experiments. A Pyrex cell containing *cis*-1,3-pentadiene (9.8 Torr) was kept in the dark at 85–95° for 68 hr in one case and at 110–116° for 65 hr in the other. No reaction product was detected in either experiment.

Photoisomerization may occur at different rates in different cells. In eight cells matched for dimensions and transmittance (at 366 nm), the percentage conversions of *cis*-1,3-pentadiene at 1 Torr upon illumination at constant intensity for 17.25 hr were 3.67, 3.67, 3.71, 3.42, 4.73, 6.14, 4.73, and 5.74. The vessel dependence shown by the rate of photoisomerization is evidence of a surface process; it does not, however, indicate whether the rate is enhanced or diminished at the wall. Variable path length experiments were performed to distinguish between the two possibilities. Results with cells having different sets of windows are given in Table I. For cells with window set A, the rate of photoisomerization was nearly independent of path length of light through the cell; rates measured in cells with window set B showed a somewhat stronger dependence on path length. The different behavior may reflect changes in the window due to the necessarily strong heating when the cells were shortened and lengthened. The large amount of scatter in the data illustrates a difficulty in handling small samples (total 1,3-pentadiene, ~$10^{-7}$ mol; amount of product, ~$10^{-9}$ mol). A small quantity of residual cis or trans in the vacuum line from earlier experiments can easily bias the results. For cells with either set of windows, the rates observed with the shortened vessels are faster than can be accounted for by homogeneous excitation. In photolyses which were attempted with a 305-mm cell and a more intense source than used with the shorter cells, the extent of isomerization (cis to trans) for a pressure of 0.7 Torr and 48-hr irradiation was too low (<0.1%) to permit accurate estimates of the rate. Using the cells described in Table I, conversions of 2 to 4% were typical. The variable path length experiments suggest that photoexcitation occurs at the illuminated surface of the cell windows. The IRP results in Table IV provide the clearest answer to the question of activation or deactivation at the wall. The intensity of scattered 366 nm radiation noted must be considered an upper limit. Due to back reflection at the exit of the light pipe and conduction of light by the end seal, it is probable that much of the radiation detected by the actinometer did not pass through the layer of 1,3-pentadiene vapor. The upper limit to the intensity of scattered light in IRP was 7% that used for variable path length experiments. The rates are comparable in the two types of photolyses; therefore, the IRP results are better understood in terms of excitation of some light absorber at the surface of the Pyrex rod by coupling to the evanescent wave of the totally reflected radiation.

**Table IV.** Isomerization of *cis*-1,3-Pentadiene by Internal Reflection Photolysis[a]

| $P_{\text{diene}}$ | $10^{-10}$ × rate$_{c\rightarrow t}$, molecules sec$^{-1}$ | (rate$_p$)/(rate$_{1.26}$)[b] IRP | (rate$_p$)/(rate$_{1.26}$)[b] Conventional[c] |
|---|---|---|---|
| 1.26 | 2.41 | 1.00 | 1.00 |
| 1.41 | −0.18[d] | | |
| 4.59 | 3.76 | 1.56 | 1.57 |
| 0.66 | 1.28 | 0.53 | 0.75 |

[a] Incident intensity of 366 nm radiation = 3.9 × $10^{15}$ quanta sec$^{-1}$; scattered intensity ≤4.9 × $10^{14}$ quanta sec$^{-1}$. [b] Ratio of rate of isomerization at given diene pressure to rate at 1.26 Torr. [c] Conventional illumination method. [d] Blank.

**Internal Reflection Spectroscopy.** Internal reflection spectroscopic experiments were undertaken to investigate the chromophore on a Pyrex surface in contact with 1,3-pentadiene vapor. The IRS involved a point by point analysis. The decrease in light intensity transmitted through the Pyrex light pipe noted on vaporization of the sample was recorded at wavelengths of interest. The intensity changes were reversed when samples were condensed by placing liquid nitrogen about the coldfinger. The intensity changes occurred in times which were no longer than those required for sample vaporization and condensation.

The internal reflection spectrum obtained for *cis*-1,3-pentadiene is shown in Figure 3. The spectrum shown for cell no. 2 is a summary of four sets of data; three sets were normalized to the fourth set, then an average was taken at each wavelength. The data shown in Figure 3 are presented in absorbance units in Figure 4. In calculating the absorbance, a base line

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[15] Based on initial rates, if there were no back reactions, this is more than sufficient time for *cis*-1,3-pentadiene at this pressure to be completely converted to *trans*-1,3-pentadiene.

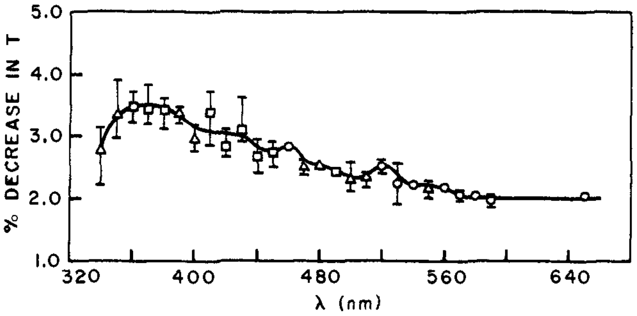

Figure 3. Internal reflection spectrum of *cis*-1,3-pentadiene on Pyrex. Percentage decrease in transmitted light intensity upon vaporization. Cell 2: ○, △, □, average with standard deviation, respectively of two, three, or four observations. Pressure of diene, 336 Torr. Room temperature, 26°. Vapor pressure of diene at 26°, 363 Torr.

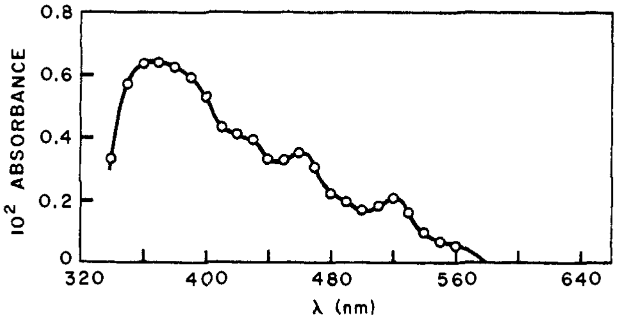

Figure 4. Internal reflection spectrum of *cis*-1,3-pentadiene adsorbed on Pyrex.

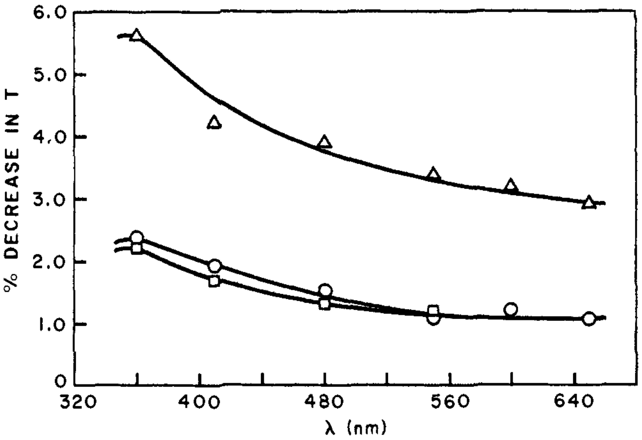

Figure 5. Effect of cell pressure on the internal reflection spectrum of *cis*-1,3-pentadiene. Decrease in transmitted intensity upon vaporization. Cell 2. Pressure of diene: □, 239 Torr; ○, 273 Torr; △, 311 Torr. Room temperature 23°. Vapor pressure of diene at 23°, ~347 Torr.

of 2.0 was assumed. This value was chosen because of the near constancy of the change in transmitted intensity upon vaporizing the sample for wavelengths extending from 570 to 650 nm.

An appreciable decrease in intensity on vaporizing the sample is seen only at high pressures, with large decreases being observed only at pressures approaching saturation (Figure 5). Spectra of 1,3-butadiene and *cis, trans*-2,4-hexadiene are similar to the spectrum of 1,3-pentadiene. Figure 6 shows that the less volatile hexadiene causes a larger decrease in reflectivity than does butadiene even though the spectrum of the latter was taken with a cell pressure more than 10 times that of the former. For 1,3-pentadiene at constant concentration, the decrease in intensity is markedly greater at 19 than at 23° (Figure 7). The reversibility of the intensity change, the development of the change in times no longer than those elapsed during the volatilization and condensation, and the fact that, in order to observe intensity changes of >1%, pressures high relative to saturation are required suggest that these observations result from multilayer adsorption.

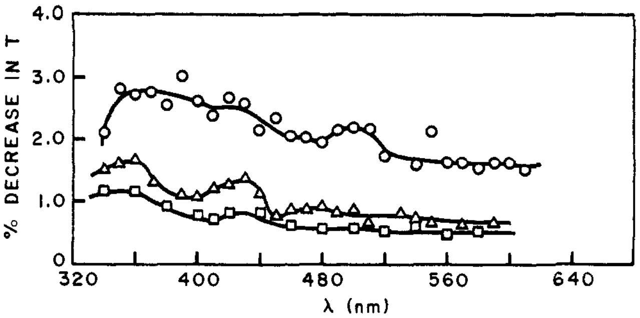

Figure 6. Internal reflection spectra of *cis,trans*-2,4-hexadiene and 1,3-butadiene. Decrease in transmitted intensity upon vaporization. Cell 2. ○, *cis,trans*-2,4-Hexadiene at 70 Torr; room temperature, 27.5°; △, 1,3-butadiene at 962 Torr, room temperature, 26.9°; □, 1,3-butadiene at 738 Torr, room temperature, 26.9°; vapor pressure of 1,3-butadiene 2650 Torr at 26.9°.

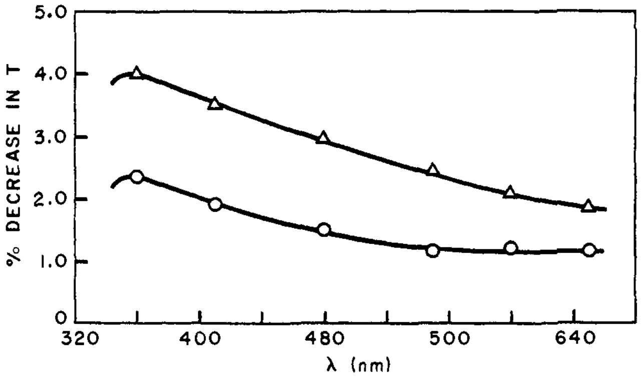

Figure 7. Effect of temperature on the internal reflection spectrum of *cis*-1,3-pentadiene. Decrease in transmitted intensity upon vaporization. Cell 2. △, Room temperature ~19°, pressure of diene, 269 Torr; ○, room temperature ~23°, pressure of diene, 273 Torr; vapor pressure of diene 295 Torr at 19°, 347 Torr at 23°.

The first substance used in IRS cell 2 was *n*-pentane at 364 Torr. The vacuum line had been outgassed for more than two weeks before this cell was connected to the line for filling. The decrease in intensity of light transmitted through the Pyrex light pipe upon vaporization was 1.0% at 365, 430, and 500 nm; monochromator slit widths were selected to give band half-widths of ~15, ~40, and ~60 nm, respectively. Apparently the adsorbed multilayer film causes a decrease in reflectivity which is independent of wavelength in nonabsorbing regions of the spectrum. This is also seen for *cis*-1,3-pentadiene in the wavelength region extending from 570 to 650 nm. This wavelength independent reflectivity decrease in nonabsorbing regions may be a manifestation of surface irregularities resulting from the multilayer film.

After using cell 2 for the spectra of dienes, the spectrum taken using it with *n*-pentane showed a wavelength dependence (Figure 8). Magnitudes of intensity changes with sample vaporization taken relative to a particular wavelength in the spectrum appeared to be the same as for the diene. The spectrum was unchanged on rinsing the cell with liquid *n*-pentane. The wavelength dependence was also observed using new cells upon vaporization of carbon tetrachloride (63 Torr) or *n*-pentane (400 Torr), even though the only diene to which the cells were exposed was residual material in the vacuum line. These results indicate that diene is strongly adsorbed on the Pyrex light pipe. This strongly adsorbed material absorbs light even at low diene pressures, but the nature of the IRS measurement is such that only the enhancement of absorption due to the multilayer is observed.

The wavelength dependence shown for a Pyrex light pipe on which diene is strongly adsorbed appears independent of the substance forming the multilayer; similar results were noted with *cis*-1,3-pentadiene, 1,3-butadiene, *cis,trans*-2,4-hexadiene, *n*-pentane, carbon disulfide, and carbon tetrachloride. It is clear that the multilayer does not absorb light. It is also unlikely that these observations result from a phenomenon akin to a solvent effect.

A qualitative measure of the enhancement of light absorption by the multilayer is gotten in the following manner. Data in Tables III and IV indicate that similar rates of isomerization are observed using conventional photolysis and IRP (taking account of the different light intensities in the two cases). It follows that the rate of light absorption is the same in the two cases. In the experiment which attempted to observe *cis*-1,3-pentadiene adsorbed on Pyrex by transmission spectroscopy, no absorbance change was observed; this places an upper limit of 0.002 on the absorbance in the conventional photolyses. Therefore, physically adsorbed *cis*-1,3-pentadiene increases the absorbance at 366 nm by a factor of at least 2.5.

The reflectivity in total internal reflection shows a dependence on the index of refraction in the rarer medium; the reflectivity decreases with an increase in the refractive index of the rarer medium.[16] During blanks the rarer medium has the index of refraction of vacuum. On vaporization, the index of refraction increases; for example, the index of refraction of *n*-pentane at 0° and 1 atm is 1.001711 relative to vacuum.[17] The refractive index change undoubtedly has some effect; however, the temperature and pressure dependence indicate its relative importance must be small in the present experiments.

It is suggested that the important effect of the multilayer is to extend the boundary at which reflection takes place. This may enhance absorption by increasing the electric field amplitude in the light-absorbing layer of diene strongly adsorbed on Pyrex. Hansen has provided formulas permitting the computation of the absorbance of a multiphase stratified medium if the optical constants and certain other conditions are specified.[18] In the absence of an estimate of the extinction coefficient of the strongly adsorbed diene, it is possible to calculate the enhancement of absorption as the ratio of mean square electric fields for different distances from the totally reflecting interface (that is, for different multilayer thicknesses), provided the polarization, wavelength, and angle of incidence of the light are specified.[19] It is assumed that the multilayer has the same index of refraction as Pyrex. An enhancement factor of 2.5 requires a multilayer of thickness >400 Å, which seems high in view of data in the literature. Thicknesses of multilayers on planar glass surfaces as great as hundreds of angstroms have been measured for water and isopropyl alcohol near their saturation pressures.[20] Similar observations have been made for nonpolar compounds, *e.g.*, benzene and carbon tetrachloride.[21]

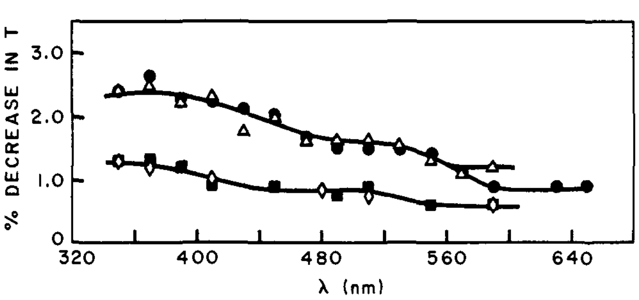

Figure 8. Internal reflection spectra taken with *n*-pentane and carbon disulfide. Decrease in transmitted intensity upon vaporization. ◊, ■, *n*-pentane, 399 Torr, before and after rinsing with liquid *n*-pentane; cell 2, room temperature. 26°, △, *n*-Pentane at 490 Torr; cell 3, room temperature, 27.5°. ●, Carbon disulfide at 298 Torr; cell 3, room temperature, 25.7°; vapor pressures *n*-pentane, ~630 Torr at 27°; carbon disulfide, ~363 Torr at 25.7°.

The lack of a sufficient number of independent data precludes a more quantitative interpretation of the IRS results. The relative contributions made to the internal reflection spectrum by strongly adsorbed diene molecules and by physically adsorbed multilayers will be the subject of further investigation.[22]

Because a quantitative assessment of the enhancement of light absorption due to multilayer adsorption is impossible, the IRS results cannot be used to derive accurate extinction coefficients or quantum yields. Some limits are set by other data. From transmission spectroscopy, the upper limit to the fraction of light absorbed by *cis*-1,3-pentadiene on two Pyrex interfaces is <0.005. At 0.6 Torr the rate of cis to trans is ~0.00001 times the flux of incident 366 nm radiation. Therefore, $\phi_{c\rightarrow t} > 0.002$. If, on the other hand, one assumes that $\phi_{c\rightarrow t} = 0.5$, that at 0.6 Torr of *cis*-1,3-pentadiene the surface concentration is 1 *M* (0.1 that of the bulk liquid), and that the optical path length through adsorbed *cis*-1,3-pentadiene is 1 nm, then $\epsilon \approx 200$ at 366 nm.

**Light Absorber.** The observation that, for equal incident intensity, 366-nm radiation is more efficient

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(16) W. N. Hansen, *Spectrochim. Acta*, 21, 815 (1965).

(17) "Handbook of Chemistry and Physics," 42nd ed, The Chemical Rubber Publishing Co., Cleveland, Ohio, 1960, p 2944.

(18) W. N. Hansen, *J. Opt. Soc. Amer.*, 58, 380 (1968).

(19) In a cylindrical rod, the angles of incidence range from a minimum angle (~50° in these experiments, determined by orientation of the rod to the incident beam) to grazing.

(20) U. Garbatski and M. Folman, *J. Chem. Phys.*, 22, 2086 (1954); *J. Phys. Chem.*, 60, 763 (1955).

(21) B. V. Deryagin and Z. M. Zorin, *Proc. Int. Congr. Surface Activity*, 2, 145 (1957). It appears that in the study by these investigators pressures nearer saturation were required to obtain multilayers 400 Å thick. This may reflect different surface characteristics due to different glass compositions and/or different surface preparations, or may point up errors in pressure estimates in the present work.

(22) Some confidence in the method is provided by the observation of an enhancement spectrum of methylene blue on Pyrex. Vaporization of *n*-pentane to give a pressure of ~400 Torr in an IRS cell with a light pipe coated with methylene blue causes a decrease in light intensity transmitted by the pipe at wavelengths absorbed by methylene blue.

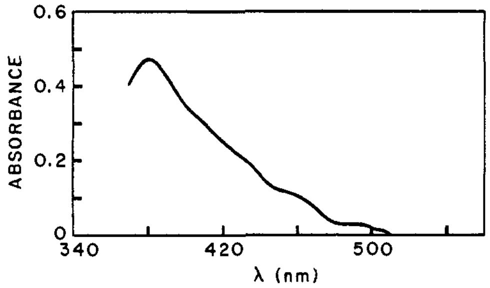

Figure 9. Absorption spectrum of *cis*-1,3-pentadiene in ethyl iodide.

than somewhat shorter or longer wavelengths in promoting the isomerization is consistent with the light absorber being strongly adsorbed diene with the absorption spectrum shown in Figure 4. Additional assumptions are required to account for the relatively small photochemical effects of the 404.5- and 435.8-nm emission lines, since the internal reflection spectrum of strongly adsorbed diene shows considerable absorption at these wavelengths.

It is of course not certain that the substance giving rise to the observed absorption is involved in the photochemical reaction. Isomerization occurs at comparable rates in quartz and Pyrex vessels, so there is no indication that a specific surface characteristic is required. The per cent conversion of cis to trans is a linear function of photolysis time with zero intercept for conversions less than 7%. It is therefore doubtful that a product of the reaction acts as sensitizer.

The possibility that a low concentration of impurity acting as a sensitizer could account for the photoisomerization cannot of course be completely excluded, but every test for impurity effects yielded negative results. The rate of photoisomerization measured with vapor (3.9 Torr of cis) taken from a liquid sample of cis purified by gas chromatography is the same as that measured with vapor taken from an unpurified sample obtained more than a year after the first sample was purchased. It is unlikely that the impurity concentration would be the same in the two cases. The average of seven results obtained with the purified samples was $5.93 \times 10^{12}$ molecules $sec^{-1}$; the average of five results obained with the unpurified material was $5.91 \times 10^{12}$ molecules $sec^{-1}$. The relative amount of an impurity would very likely be dependent on the temperature at which the diene vapor is taken from the liquid, but no trend was noted in the photoisomerization rate at 3.9 Torr cis when vapor was taken from the liquid over the temperature range −65.2 to −24.4°. The reaction rate shows long term reproducibility; it is improbable that this would be observed with an impurity acting as sensitizer. More than twenty different vessels of various configuration have been employed in this study. Since photoisomerization occurred at comparable rates in each case (though a vessel dependence is noted), the phenomenon is not peculiar to select apparatus.

Treatment of the cell with various cleaning agents ($CH_3OH$–KOH, $H_2SO_4$–$HNO_3$, $HNO_3$, $O_2$) did not significantly decrease the rate of photoisomerization; in fact, higher rates were generally noted after such treatments. This is inconsistent with the notion that the reaction might be promoted by sensitization at the wall of a dirty cell. In one series of experiments the rate of photoisomerization was measured using newly constructed portable cells and a newly constructed manifold; the manifold was isolated from the remainder of the line by a trap maintained at −78°. Similar rates were noted using old and new apparatus. This argues against the possibility of a line contaminant acting as sensitizer. In summary, it is highly improbable that impurity effects are significant.

Accepting that strongly absorbed diene gives rise to the observed absorption and photoisomerization, there is still no definite identification of the surface chromophore. A spectrum showing absorption over the wavelength range 600–300 nm has been reported for 2-butene and ethylene on hydrated silica–alumina or dissolved in $H_2SO_4$–HOAc solution.[23] The bands at 380, 465, and 560 nm were identified with a charge transfer complex formed between the olefin and Brönsted acid sites. This interpretation has been questioned.[24,25] Brönsted acid sites are thought to result from adsorption of water.[26] Since, in the present experiments, cells were evacuated at room temperature, it is likely that adsorbed water remained on the Pyrex surface. The transition of interest occurs at wavelengths which are too long to be attributed to an allylic carbonium ion.[27] Further, if surface carbonium ions were dominant, dark reactions would be expected. None are observed even at 110–116°. The rate of isomerization and polymerization of butenes on porous glass is decreased by acid leaching.[28] In the present experiments, acid treatment did not decrease the rate of photoisomerization; hence, active sites must not be dependent on the presence of components such as alumina or zirconia.

The apparent similarity between the internal reflection spectrum of *cis*-1,3-pentadiene and that obtained in ethyl iodide solution (Figure 9) suggests that the adsorption of the diene on Pyrex might cause perturbations which make the transitions $S_0 \rightarrow T_1$ allowed. In another case, that of *s*-trinitrobenzene adsorbed on $CaF_2$, ZnO, or MgO, perturbations which make $S_0 \rightarrow T_1$ allowed have been invoked.[29] Charge transfer interactions are thought important in mixing singlet and triplet states of the donor.[30] Excitation of the diene triplet by direct absorption cannot easily account for the fact that 404.5 and 435.8 lines have less photochemical effect than predicted on the basis of the internal reflection spectrum, relative intensities emitted by the lamp at these wavelengths, and the generally accepted geometry of diene triplets.[31]

**Mechanism.** The rate of isomerization is plotted as a function of the initial pressure of 1,3-pentadiene in Figure 10. The pressure dependence in the quartz vessel is similar but the rate levels off at a pressure of

(23) A. N. Webb, *Actes Congr. Int. Catal., 2nd*, 1289 (1961).

(24) A. Terenin in *Advan. Catal. Relat. Subj.*, **15**, 267 (1964).

(25) H. P. Leftin in "Carbonium Ions," Vol. I, G. A. Olah and P. v. R. Schleyer, Ed., Interscience, New York, N. Y., 1968, p 353ff.

(26) L. H. Little, "Infrared Spectra of Adsorbed Species," Academic Press, New York, N. Y., 1966, p 181.

(27) G. A. Olah, C. U. Pittman, and M. C. R. Symons in "Carbonium Ions," Vol. I, G. A. Olah and P. v. R. Schleyer, Eds., Interscience, New York, N. Y., 1968, p 153ff.

(28) L. H. Little, H. E. Klauser, and C. H. Amberg, *Can. J. Chem.*, **39**, 42 (1961).

(29) Reference 24, p 227.

(30) H. Tsubomura and R. S. Mulliken, *J. Amer. Chem. Soc.*, **82**, 5966 (1960).

(31) J. Saltiel, L. Metts, and M. Wrighton, *ibid.*, **91**, 5684 (1969).

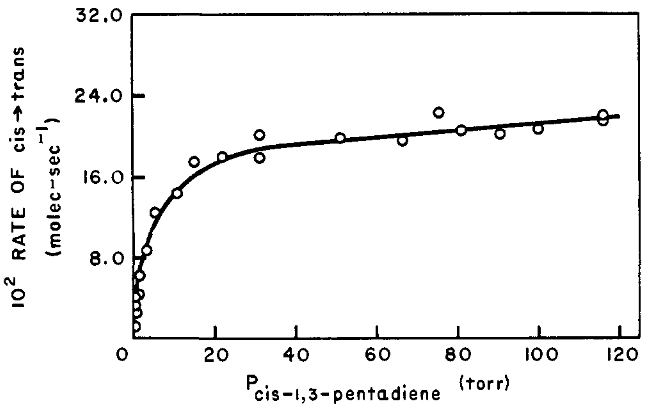

Figure 10. Isomerization rate *vs.* pressure of *cis*-1,3-pentadiene, $T \sim 35°$.

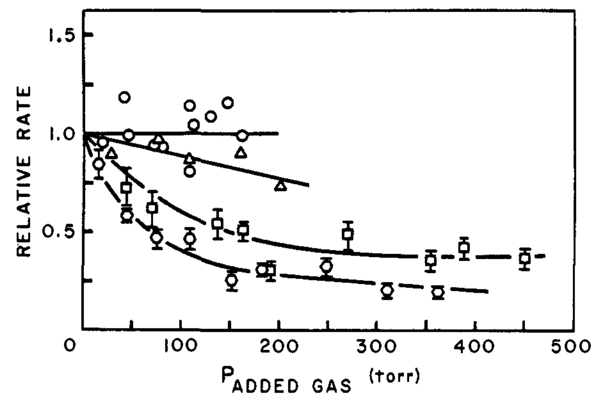

Figure 11. Effect of added gases on isomerization rate: ○, *n*-pentane; △, *cis*-2-pentene; □, oxygen; ○, 1,3-butadiene ($T \sim 35°$).

about 10 Torr. The pressure dependence seen in IRP is apparently similar to that in conventional photolysis. The effect of added gases on the rate of isomerization is illustrated in Figure 11. The results obtained with *n*-pentane as added gas in photolysis of *cis*-1,3-pentadiene indicate that vibrational relaxation cannot account for the dependence of rate on pressure. The effects seen with 1,3-butadiene and oxygen as added gas are consistent with quenching of an electronically excited species. It appears that the only excited electronic state of 1,3-pentadiene accessible with 366 nm radiation is the lowest triplet.[32]

Extended photolyses were carried out to define limits of the isomeric composition of the photostationary state. Illumination of a sample of cis initially 0.22 Torr for 166 hr formed a mixture 65.2% trans. Illumination of a sample of trans initially 0.37 Torr formed a mixture 70.3% trans. It is unlikely that the isomerization is promoted by a free radical or ionic intermediate because the composition of the photoequilibrium mixture (65–70% trans) differs considerably from thermodynamic equilibrium (83% trans).[33]

The following elementary processes are considered for their possible importance in the reaction mechanism.

$$\mathrm{S} + cis\text{-}\mathrm{D} \longrightarrow \mathrm{SD} \tag{1}$$
$$\mathrm{SD} + h\nu \longrightarrow (\mathrm{SD})^* \tag{2}$$
$$(\mathrm{SD})^* \longrightarrow \mathrm{SD} \tag{3}$$
$$(\mathrm{SD})^* + cis\text{-}\mathrm{D} \longrightarrow \mathrm{SD} + \mathrm{D}^* \tag{4}$$
$$(\mathrm{SD})^* \longrightarrow \mathrm{S} + \mathrm{D}^* \tag{5}$$
$$\mathrm{D}^* \longrightarrow cis\text{-}\mathrm{D} \tag{6}$$
$$\mathrm{D}^* \longrightarrow trans\text{-}\mathrm{D} \tag{7}$$

The symbolism is as follows: D = 1,3-pentadiene; S = surface site on which adsorption occurs to produce a light absorbing species; D* = reactive diene intermediate; $\theta$ = fraction of active sites to which D is adsorbed; $I_a$ = rate of light absorption; $I_0$ = incident intensity. A set of analogous equations can be written for trans to cis.

At equilibrium, in the dark

$$\theta = \frac{k_1[\mathrm{D}]}{k_{-1} + k_1[\mathrm{D}]}$$

IRS data indicate that complete coverage of sites which lead to light absorbing species occurs for diene pressures much lower than those used in photolysis experiments. Therefore, under conditions of photolysis, $k_1[\mathrm{D}] \gg k_{-1}$. Neglecting $k_{-1}$, the fraction of active sites to which diene is adsorbed during photolysis is given by

$$\theta = \frac{k_1[\mathrm{D}]}{k_1[\mathrm{D}] + \dfrac{k_2k_5I_0}{k_3 + k_5 + k_4[\mathrm{D}]}}$$

For the small fraction of light which is absorbed, $I_a = k_2\theta I_0$, where $k_2$ is the attenuation coefficient of *cis*-1,3-pentadiene on Pyrex. In this scheme the steady-state concentration of excited surface species is given by

$$[(\mathrm{SD})^*] = \frac{k_1k_2I_0[\mathrm{D}]}{k_1k_4[\mathrm{D}]^2 + k_1(k_3 + k_5)[\mathrm{D}] + \dfrac{k_2k_4k_5I_0[\mathrm{D}]}{k_3 + k_5 + k_4[\mathrm{D}]} + \dfrac{(k_3 + k_5)k_2k_5I_0}{k_3 + k_5 + k_4[\mathrm{D}]}} \tag{I}$$

It seems reasonable to expect a direct proportionality between [(SD)*] and reaction rate. Accordingly, for pressures <15 Torr, terms in the denominator of (I) which increase with [*cis*-D] must be of the same magnitude as the one which does not. This implies that for [*cis*-D] = constant (in the low pressure region), the dependence of rate on intensity should not be linear, contrary to what is observed. That is, photodesorption (step 5) must be slow relative to steps 3 and 4, and therefore even under photolytic conditions, $\theta \approx 1$. The hypothesis that isomerization might occur at the surface followed by photodesorption is similarly excluded by the intensity dependence.

The pressure dependence can be accounted for most simply by energy transfer from excited surface species to 1,3-pentadiene, followed by unimolecular decay to either isomer in the ground state. Additional assumptions are required to account for the wavelength dependence. It is possible that surface complexes have different electronic levels depending on the site to which the diene is adsorbed. Those which absorb 366 nm radiation possibly have triplet levels sufficiently high in energy to populate 1,3-pentadiene triplets, whereas those surface species excited by 404.5- and 435.8-nm radiation have triplets too low for such energy transfer.

(32) R. Srinivasan, *Advan. Photochem.*, 4, 113 (1966); L. M. Stephenson, D. G. Whitten, and G. S. Hammond in "The Chemistry of Ionization and Excitation," G. R. A. Johnson and G. Scholes, Ed., Taylor and Francis, London, 1967, p 35.

(33) K. W. Egger and S. W. Benson, *J. Amer. Chem. Soc.*, 87, 331 (1965).

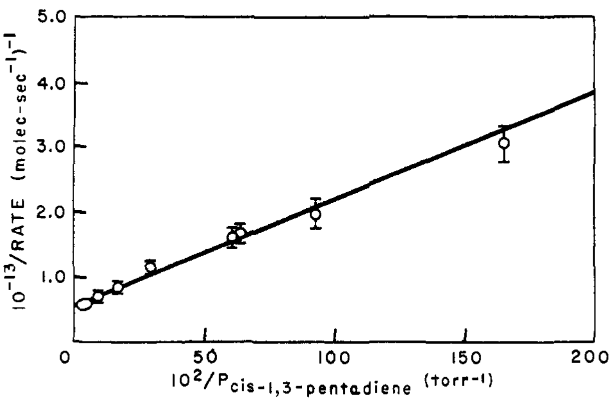

Figure 12. Reciprocal isomerization rate *vs.* reciprocal pressure of *cis*-1,3-pentadiene.

In this hypothesis, step 4 must embody the following processes.

$$(SD)^* \longrightarrow {}^3(SD) \qquad (4a)$$

$$^3(SD) \longrightarrow (SD) \qquad (4b)$$

$$cis\text{-}D + {}^3(SD) \longrightarrow {}^3D + SD \qquad (4c)$$

The rate law derived on this basis (assuming $\theta = 1$) is

$$\text{rate}_{c\to t} = \frac{k_7 k_{4a} k_{4c} k_2 I_0[cis\text{-D}]}{(k_{4b} + k_{4c}[cis\text{-D}])(k_3 + k_{4a} + k_5)(k_6 + k_7)}$$

The form of the rate law is unchanged if (4c) involves physically adsorbed diene. It should be noted that two types of adsorption are suggested here. In the first type light absorbing species are formed between "active" sites on the Pyrex surface and 1,3-pentadiene. This type of adsorption is complete at very low pressure. This second type of adsorption possibly important in eq 4c is physical and readily reversible. A plot of 1/rate *vs.* 1/*P* using data presented in Figure 10 for pressures ranging from the highest down to 0.54 Torr appears to be linear as required by this mechanism (Figure 12).

To account for the effect of added gases oxygen and 1,3-butadiene, eq 4d is included.

$$^3(SD) + M \longrightarrow OUT \qquad (4d)$$

For constant [*cis*-D], a plot of (rate without added gas)/(rate with added gas) *vs.* pressure of added gas should give a straight line with an intercept of unity. This is the case within the error limits of the data in Figure 11. A competitive adsorption mechanism probably could explain the data as well.

**Acknowledgments.** We are grateful to Professor T. Kuwana for use of equipment in his laboratory, to Professors N. Winograd and H. Blount III for helpful discussions of IRS, to referee I for useful calculations, and to the Environmental Protection Agency for Financial Support through Grant AP-00931.

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# Quenching of Excited States by Stable Free Radicals. II.[1] On the Mechanism of Triplet Quenching by Di-*tert*-butyl Nitroxide

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*Received June 26, 1972*

**Abstract:** The overall rate constants ($k_q$) for the quenching of a number of aromatic hydrocarbon and ketone triplets by di-*tert*-butyl nitroxide (DTBN) in fluid solution have been measured. The values of $k_q$ decrease in the order stilbene ≈ diffusion controlled > ketones > hydrocarbons, and show no correlation with triplet energies. The data are consistent with vibrational relaxation of the triplet *via* intersystem crossing to the ground-state vibrational manifold, which is made spin allowed by electron spin exchange with DTBN. This behavior of DTBN is contrasted with triplet quenching by other paramagnetic species, and several potential applications to photochemistry are discussed.

The deactivation of electronically excited molecules by paramagnetic species is a phenomenon which has received widespread interest from spectroscopists and photochemists for some time. It may reasonably be expected that transitions which are normally spin forbidden will become at least partially spin allowed in the presence of a paramagnetic quencher, providing pathways for deactivation are not available to diamagnetic quenchers or to the excited molecule itself. Clear-cut experimental evidence regarding the nature of paramagnetic quenching has been difficult to obtain, however, because of the variety of competing processes and experimental complications encountered in many studies. For instance, molecular oxygen, that most ubiquitous of paramagnetic molecules, is an exceedingly efficient quencher of photoexcited singlets and triplets.[3,4] This

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(1) Part I: R. A. Caldwell and Robert E. Schwerzel, *J. Amer. Chem. Soc.*, **94**, 1035 (1972).

(2) Address correspondence to this author at the Department of Chemistry, the University of Texas at Dallas, Box 30365, Dallas, Tex. 75230.

(3) (a) A. N. Terenin, "Photochemistry of Dyes and Related Organic Molecules," translation by Kresge-Hooker Science Library, Academy of Sciences Press, Moscow, 1947, Chapter 7; (b) D. R. Snelling, *Chem. Phys. Lett.*, **2**, 346 (1968).

(4) (a) R. Livingston and D. Tanner, *Trans. Faraday Soc.*, **54**, 765 (1958); (b) D. F. Evans, *J. Chem. Soc.*, 2753 (1959); (c) G. Porter and P. West, *Proc. Roy. Soc., Ser. A*, **279**, 302 (1964).