

**MERCURY-PHOTOSENSITIZED *cis-trans* ISOMERIZATION OF OLEFINS IN THE GAS PHASE  
PHYSICAL CHEMISTRY EXPERIMENTS FOR THE ADVANCED UNDERGRADUATE LABORATORY**

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### Summary

Some of the most important problems and concepts evoked by the gas phase mercury( $\text{Hg}\{6(^3\text{P}_1)\}$ )-photosensitized *cis-trans* isomerization of olefins are reviewed through a set of five physical chemistry experiments for the advanced undergraduate laboratory. The nature and shape of the so-called 253.7 nm resonance line of mercury under various conditions are discussed. A short description of the  $\text{Hg}\{6(^3\text{P}_1)\}$ -photosensitized isomerization of 2-butene (previously proposed as a gas phase actinometer) is given. Quantum yields of other photochemical reactions are determined. Relative efficiencies of energy transfer from  $\text{Hg}\{6(^3\text{P}_1)\}$  atoms to various olefins are obtained by competitive photosensitizations of these compounds. The photostationary steady state (SS) concentration ratio  $\alpha_{\text{SS}} = [\textit{trans}] / [\textit{cis}]$  of a 1,2-disubstituted olefin is determined from the time dependence of the isomer concentration ratio. The ratio  $\alpha_{\text{SS}}$  is related to the relative cross section for energy transfer from  $\text{Hg}\{6(^3\text{P}_1)\}$  to the geometric isomers and to the natural decay ratio of the triplet olefin to the ground state *cis* or *trans* forms.

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### 1. Introduction

In spite of Draper's [1] pioneering work on the effect of sunlight on chlorine and hydrogen mixtures more than a century ago, photochemistry can be considered to be a very young science: the number of photochemical studies has increased exponentially over the last 20 years and the importance of photochemical events has been recognized in the fields of spectroscopy, physics, biology and medicine. Photochemical smog has become a household conversation topic. Nevertheless, photochemistry, and especially gas phase photochemistry, seldom appears in the programme of teaching laboratories.

In this work we present an experiment which concerns the mercury-photosensitized isomerization of olefins and is part of the physical chemistry

laboratory programme for third-year undergraduate students in Brussels. There are five separate parts (see later), each of which is suitable for one or two laboratory periods. Taken separately they provide an initiation to one of the following aspects of photochemistry.

### 1.1. Actinic light\*

The Grotthus–Draper Law, the first law of photochemistry, states that “only light which is absorbed can cause chemical change in matter” [2]. The first requirement is that the incident light be capable (energetics) of raising the substrate from its ground state to an excited state. Moreover, the absorption of an atomic spectral line depends on the shape of the emitted line (actinic light) compared with that of the absorption line of the atoms in their particular environment.

### 1.2. Gas phase actinometry

The two most important quantities to be determined in a photochemical experiment are the absorbed light intensity  $I_a$  and the number of molecules of product formed (or of substrate which have been transformed). A chemical actinometer is a reaction for which the quantum yield  $\Phi = \text{Reaction rate}/I_a$  is known accurately. For gas phase reactions such as photochlorinations or mercury photosensitizations, the most convenient actinometers are reactions of the same kind.

### 1.3. Determination of the quantum yield(s) of a photochemical reaction

Absorption of light or transfer of energy from a sensitizer produces an energy-rich molecule which may undergo one of a number of primary photochemical or photophysical processes resulting in its decomposition, isomerization or return to the ground state. We may distinguish the overall quantum yield  $\Phi$ , the individual product quantum yields  $\Phi_{xi}$  and the quantum yields  $\Phi_j$  of the primary photoprocesses.

### 1.4. Relative cross sections for energy transfer

The competitive mercury-photosensitized *cis*–*trans* isomerizations of two different compounds allow us to measure the relative efficiencies of energy transfer.

### 1.5. Photostationary ratio of *trans* to *cis* isomer concentrations

Prolonged photosensitization of either the *cis* isomer or the *trans* isomer of a molecule with a 1,2-disubstituted double bond causes the [*trans*]-to-[*cis*] ratio  $\alpha$  to evolve towards a photostationary steady state  $\alpha_{SS}$  which is generally different from the thermochemical equilibrium  $\alpha_{TE}$ .

The five parts are essentially independent of each other except for Parts 3 and 5 which require the absorbed light intensity determined in Part 2.

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\*In photochemistry the term “light” is used for electromagnetic radiation, even if the “light” is not visible. The terms photon and quantum are also used interchangeably.

Alternatively,  $I_a$  may be treated as a known quantity, supplied by the laboratory instructor.

## 2. Apparatus and general procedure

The apparatus is shown schematically in Fig. 1. The vacuum is monitored with a thermal conductivity gauge (lower limit approximately  $10^{-3}$  Torr). A cylindrical fused silica reaction cell (4 cm in diameter and 1 - 5 cm long) with a small drop of mercury in a side arm is connected (a) to a conventional high vacuum system, (b) to mercury manometers and (c) to a modified gas injection port of an Intersmat IGC 112 M gas chromatograph for on-line measurements in Parts 2 - 5. For maximum change in absorption (Fig. 2) and for convenience in the absorbed intensity and quantum yield measurements, a low pressure mercury resonance radiation source such as the Hanovia SC2537 lamp or the Mineralight UVSL 58 lamp should be used. The Mineralight lamps have the marked advantages that they are enclosed in an easily modified housing and that they do not heat up appreciably during operation. The lamp must nevertheless be lit about 20 min before use. A monochromator (Schoeffel QPM 30, quartz prism) equipped with a 1P28

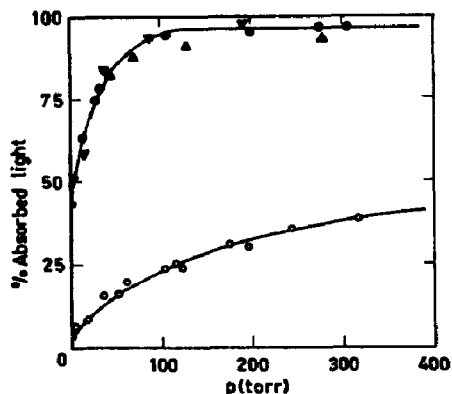
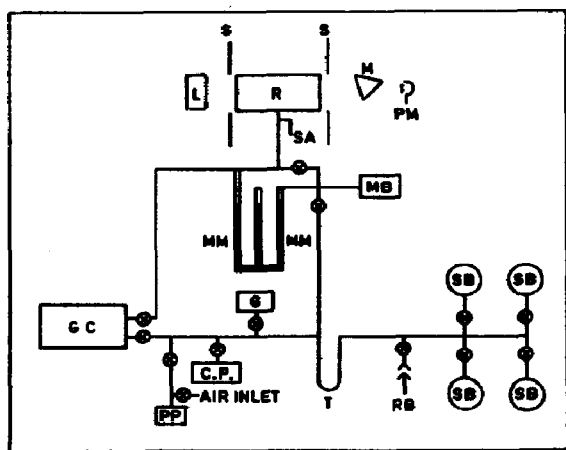


Fig. 1. The kinetic apparatus together with the gas chromatograph and the photomultiplier: L, mercury lamp (253.7 nm); S, screens; R, fused silica reaction cell; SA, side arm with mercury droplet; M, monochromator; PM, photomultiplier; MB, mixing bulb containing a mercury droplet; MM, mercury manometer; G, heat conductivity pressure gauge; C.P., cryogenic pump; PP, primary mechanical pump; GC, gas chromatograph; T, distillation trap; RB, removable bulb; SB, storage bulb for the liquid and gaseous compounds.

Fig. 2. The fraction of light absorbed (resonance line at 253.7 nm) by mercury at its saturating vapour pressure at 22 °C vs. the pressure of added (di)olefin: ●, ○, *cis*-2-butene; ▲, *cis*-1,3-pentadiene; ▼, *trans*-1,3-pentadiene; ○, Philips 93109 lamp; ●, ▲, ▼, Mineralight UVSL 58 lamp. The percentage of absorbed light is  $100(1 - R/R_{100})$  where  $R_{100}$  is the photomultiplier response when the cell is evacuated and all mercury vapour is carefully condensed at liquid nitrogen temperature;  $R$  is the photomultiplier response when the cell contains mercury at its saturating vapour pressure and a pressure  $p$  of the (di)olefin.

photomultiplier is placed behind the reaction cell. The photomultiplier response is recorded on a Houston Instruments Omniscrite recorder. A series of screens between the lamp and the cell and between the cell and monochromator partially collimates the light beam and also eliminates light which has not passed through the reaction cell. A mechanical shutter next to the lamp is used to interrupt the light beam. The photomultiplier must be protected from stray light as much as possible (the dark current in our set-up is  $30 \times 10^{-9}$  A and is about 5% of the response to the 253.7 nm radiation). The apparatus is evacuated, the 253.7 nm line is scanned manually and the monochromator is positioned at the maximum response. The monochromator slit width is reduced and the photomultiplier operates at about 1100 V.

The quantitative or relative analysis of 1,3-butadiene, *cis*- and *trans*-2-butene and *cis*- and *trans*-1,3-pentadiene is easily carried out on the gas chromatograph. Ours has a dual column and thermal conductivity detection. The column used in our laboratory is a 6 m long ( $\frac{1}{8}$  in diameter) column containing 30% silicone oil SISS SI 710 on 50 - 60 mesh Chromosorb P NAW, operated at 60 °C with a flow rate of 13 (cm<sup>3</sup> H<sub>2</sub>) min<sup>-1</sup>. The retention times of *trans*-2-butene, *cis*-2-butene, 1,3-butadiene, *trans*-1,3-pentadiene and *cis*-1,3-pentadiene are then 5 min, 5.5 min, 6.6 min, 11.5 min and 13 min respectively. If the analysis concerns only the separation of the *cis* and *trans* isomers of 2-butene, a better resolution is obtained at a lower column temperature (*i.e.* at 38 °C the retention times of *trans*- and *cis*-2-butene are 8 min and 9 min respectively).

### 3. Part 1: Actinic light

Atom-sensitized reactions involving the transfer of electronic energy from an excited atom (or direct chemical interaction of the excited atom with another atom or compound) are usually initiated by excitation of the atom with resonance radiation from a lamp containing the same element. Resonance radiation refers to light with a frequency such that it can be absorbed by atoms in the ground state and re-emitted with a high probability. The sodium D lines are a well-known example of resonance fluorescence.

Let us consider the ground state and the four lowest excited states of mercury:  $6(1S_0)$ ,  $6(3P_0)$ ,  $6(3P_1)$ ,  $6(3P_2)$  and  $6(1P_1)$ . Only the transitions to the  $1P_1$  state are allowed and the radiative lifetime of the state is very short, about  $3 \times 10^{-10}$  s. The radiative lifetime is defined as the average time that an atom would remain in the excited state before radiating in the absence of all perturbations (collisions, radiation etc.). The radiation occurs at 184.9 nm and is the true resonance radiation (fluorescence) of mercury. Transitions between the ground state and the triplet states violate the spin selection rule which requires that  $\Delta S = 0$ . In addition the transitions  $3P_0-1S_0$  and  $3P_2-1S_0$  are forbidden by the angular momentum selection rules since  $J = 0$  does not commute with  $J = 0$  and  $\Delta J = 2$  is not allowed. These "doubly forbidden" transitions were nevertheless observed and identified just over 50 years ago

using special experimental conditions. This is because the selection rules, which arise from assumed Russell–Saunders coupling, are strictly applicable only for the light elements. They hold approximately in the majority of cases, however, and are useful guidelines. For heavy atoms such as mercury, the designations singlet and triplet are not exactly applicable: the states have both singlet and triplet character [3]. Photosensitization with  $\text{Hg}\{6(^3\text{P}_1)\}$  nevertheless provides a convenient method of producing triplet state molecules of olefins, dienes etc.

When transitions from an excited state to all lower states (and conversely from all lower states to the excited state) are “forbidden”, the excited state is a metastable state. The forbidden nature of the transitions will generally manifest itself by relatively low probabilities for absorption to the state and a relatively long radiative lifetime for an atom in the metastable state. The true radiative lifetimes of the  $^3\text{P}_0$  and  $^3\text{P}_1$  states of mercury are about  $10^{-3}$  s and  $1.1 \times 10^{-7}$  s respectively. The radiative lifetime of the  $^3\text{P}_0$  state is so long that, as mentioned earlier, the transition  $^3\text{P}_0 \rightarrow ^1\text{S}_0$  is only observed under very special conditions. The lifetime of the  $^3\text{P}_1$  state allows for a reasonable number of collisions between the excited atom and the surrounding gas (approximately 8 at 10 Torr pressure) for competition between energy transfer and emission to occur.

The lifetime of the  $^1\text{P}_1$  state is very short and only radiation imprisonment due to the very high absorption coefficient allows us to use it as a photosensitizer. Also, since the transition occurs at 184.9 nm, its transmission requires high quality quartz and the absence of air (because water vapour and oxygen absorb) in the path travelled by the beam.

Because of these restrictions, when we speak of mercury photosensitization, reference is almost always to photosensitization by the  $^3\text{P}_1$  state and use of the “253.7 nm line”. The “line” actually consists of ten hyperfine components: the five even mass isotopes each have one line which is shifted by the isotopic shift, the odd isotopes have nuclear spins of  $\frac{1}{2}$  (199) and  $\frac{3}{2}$  (201) which give rise to two and three hyperfine components respectively. The splitting due to nuclear spin causes these lines to overlap with some of the other isotopic lines. Hyperfine splitting is very fine and cannot be observed with ordinary apparatus. It is large enough, however, to permit monoisotopic photosensitization [4].

The atomic lines have a “natural” width depending on the lifetime of the excited species and the energy of the transition (Heisenberg uncertainty principle). The “natural” width of the hyperfine component at 253.7 nm at half-intensity is predicted to be about  $3 \times 10^{-7}$  nm. The natural width is actually quite small compared with the “Doppler” width which is about  $2 \times 10^{-4}$  nm at 20 °C. Doppler broadening is caused by the relative motions of the atoms compared with the direction of propagation of the light; its importance increases with the square root of the absolute temperature.

In the lamp itself the most important phenomenon is the absorption and re-emission of the 253.7 nm radiation. Let us consider a single hyperfine component. Absorption occurs preferentially at the “centre” of the line

while emission is nearly gaussian. The importance of the process increases with the mercury pressure in the lamp: the line becomes broader and broader while the intensity at the line centre decreases rapidly. We thus obtain a so-called "reversed" line and the "253.7 nm radiation" from such a lamp will not be appreciably absorbed in a cell containing mercury vapour at room temperature. This is why only low pressure mercury lamps should (or can) be used as sources for mercury photosensitization.

In the reaction cell the profile of the absorption lines also depends on the pressure of added gases: this is known as Lorentz collision broadening. Obviously, the better the profiles of the absorption and incident emission lines superpose, the higher is the fraction of the incident light that will be absorbed in the reaction cell. Theory predicts a rapid increase of the fraction of light absorbed with increasing pressure of foreign gas up to a maximum, followed by a slow decrease at higher pressures. In Fig. 2 the fraction of light ( $\lambda = 253.7$  nm) absorbed in a reaction cell (length, 5 cm; diameter, 4 cm) containing mercury at its saturating vapour pressure at 22 °C is plotted against the pressure of different added olefins. The results obtained with the Mineralight UVSL 58 lamp indicate that 96% absorption is reached for pressures in excess of about 100 Torr. In contrast, the same measurements carried out with a Philips 93109 lamp correspond to a much lower fraction of light absorbed; in this latter case the fraction is still increasing at 300 Torr where it is less than 40%. The nature of the olefin does not affect the measurements significantly.

### 3.1. Suggested experiment

Evacuate the apparatus and check carefully for leaks by observing the behaviour of static vacuum. The lamp should have been on for at least 20 min and the shutter between it and the cell closed. Set the "zero response" for the photomultiplier dark current so as to allow for an eventual small drift and to give maximum remaining scale for the 100% response (the instructor may help with this from previous experience). Remove the shutter from in front of the lamp while monitoring the photomultiplier response  $R$  continuously. Close the cell.  $R$  will decrease to a constant value  $R'$ , the photomultiplier response when the cell contains mercury at its saturating vapour pressure (about  $10^{-3}$  Torr) at room temperature. To obtain the photomultiplier response  $R_{100}$  for 100% transmission through the empty cell, freeze the mercury in the side arm at liquid nitrogen temperature (77 K) and raise the nitrogen level progressively to prevent back diffusion into the cell. If no stopcock has been placed between the cell and the manometers, the tubing must be wrapped at a point between them with a pipe-cleaner (or surgical cotton) and cooled to 77 K to prevent the arrival of mercury in the cell.

Having obtained  $R_{100}$ , warm the mercury to room temperature.

Measure the variation of  $R$  caused by addition of an organic compound (any light molecule will do; however, if you plan on doing Parts 2 - 5, 1,3-butadiene, or the 2-butene or 1,3-pentadiene isomers should be used).

The compound should be added in steps of about 10 Torr up to 100 Torr and then by 100 Torr steps up to or near 1 atm. Repeat the measurements while removing the product from the reaction cell. Plot  $R/R_{100}$  against pressure to obtain the fraction of the 253.7 nm light absorbed and draw a smooth curve through the points. Compare the curves for different compounds. What percentage error would be caused by assuming that the absorbed light intensity at 10 Torr is the same as that in an actinometry experiment (Part 2) performed at 300 Torr in your particular case?

The results from several groups of students may be combined to increase the number of compounds studied and to give an indication of the dispersion and reliability of the results.

Under what experimental conditions is the lamp you have used suitable for studying triplet-mercury-photosensitized reactions?

If time permits, similar measurements may be carried out by setting the monochromator at the 313.0 nm line of mercury ( $^3D_2 \rightarrow ^3P_1$ ). What do you expect to observe?

#### 4. Part 2: Gas phase actinometry

The absorbed light intensity  $I_a$  can be determined from the difference between the incident and transmitted intensities if there is a parallel beam of light. These intensities can be measured using a calibrated phototube, photomultiplier or thermopile-galvanometer system. The total incident intensity can also be determined using a chemical actinometer such as potassium ferrioxalate if the light is nearly monochromatic. Then  $I_a$  may be calculated using the Beer-Lambert law if the absorption coefficient of the absorbing substance is known. For gas phase reactions it is more interesting to measure the light intensity by means of a reaction of the same type. This eliminates many possible errors and uncertainties arising from the particular apparatus used for the investigations.

Termonia and De Maré [5] have shown that the quantum yield of the mercury-photosensitized *cis*  $\rightarrow$  *trans* isomerization of 2-butene is 0.5 for butene pressures higher than 30 Torr. This reaction can therefore be used to measure the absorbed light intensity for mercury-photosensitized reactions.

With the apparatus described in Fig. 1 and a Mineralight UVSL 58 lamp there is no significant fragmentation for pressures of 2-butene exceeding about 30 Torr and up to 5% reaction. Typical reaction times are 2 h for 100 Torr of 2-butene; this yields 1% isomerization. Except for the small variation in the fraction of light absorbed (see Fig. 2), the percentage of isomerization is nearly inversely proportional to the substrate pressure. The rates obtained at different pressures are shown in Fig. 3: multiplying the rates by a factor of 2 (the quantum yield is 0.5) gives the absorbed light intensity. The shape of the curve in the figure is identical with that obtained, for the same lamp, for the fraction of light absorbed (see Fig. 2). Within the limits of experimental error,  $I_a$  is independent of pressure above 80 Torr.

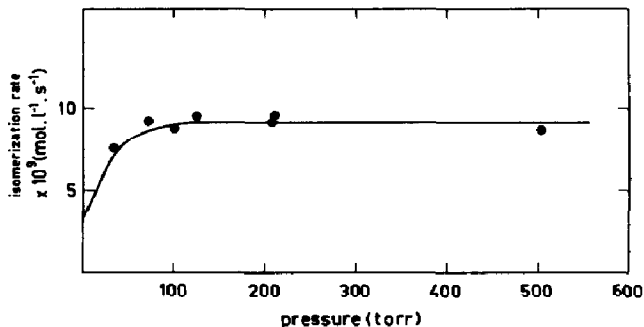


Fig. 3. Actinometry: the rate of the *cis* → *trans* isomerization under initial conditions (less than 3% conversion) vs. the *cis*-2-butene pressure. The rate is calculated from

$$\{(\% \text{ trans})_{t=t} - (\% \text{ trans})_{t=0}\} p / 100RTt$$

where  $t$  is the reaction time,  $p$  is the pressure,  $R$  is the gas constant and  $T$  is the absolute temperature. The % *trans* is calculated from the chromatographic peak areas (PA) of the *trans*- and *cis*-2-butene isomers:

$$\% \text{ trans} = 100 \frac{\text{PA}(\text{trans})}{\text{PA}(\text{trans}) + \text{PA}(\text{cis})}$$

The curve has been drawn with exactly the same shape as the upper curve in Fig. 2.

#### 4.1. Suggested experiment

Place high purity *cis*-2-butene (we use 2-butene from L'Air Liquide containing 0.48% of the *trans* isomer) in the reaction cell at a pressure higher than 80 Torr. Before irradiation, analyse a sample of the 2-butene on the gas chromatograph to obtain the exact percentage of the *trans* isomer in the sample. This is calculated by assuming that the catharometer response is the same for both isomers and that the peak area (PA) is directly proportional to the pressure of each isomer, *i.e.*

$$\% \text{ trans} = 100 \frac{\text{PA}(\text{trans})}{\text{PA}(\text{trans}) + \text{PA}(\text{cis})}$$

Irradiate the *cis*-2-butene with the light from the low pressure mercury lamp (which has been on for at least 20 min) for 1 h or according to the instructions you may receive. After this period, stop the illumination and remove a small fraction of the reaction mixture. This fraction should correspond to the gas contained in the non-illuminated dead space of the reaction cell (connection between the reactor, the manometer and the valve to the injection port). Perform three chromatographic analyses of the irradiated olefin: the amount of *trans*-2-butene formed during irradiation is obtained by multiplying the pressure by the difference in the percentage after and before irradiation. This yields a reaction rate in Torr per second; taking into account the gas law, this rate can be expressed in moles per litre per second. The absorbed light intensity is then obtained in einsteins (moles of quanta) per litre per second.



## 5. Part 3: Determination of the quantum yield(s) of a photochemical reaction

The energy-rich molecules formed by absorption of light or transfer of electronic energy from a photosensitizer undergo one of a number of primary photophysical or photochemical processes: emission of fluorescence or phosphorescence; intersystem crossing or internal conversion to a lower excited state (vibrationally excited ground state?) without change in total energy; deactivation by collision or by the walls; direct or spontaneous dissociation, often yielding products capable of inducing further reactions; reaction with other molecules; internal rearrangement or isomerization. This list is not exhaustive; it is obvious that the relative importance of these processes can lead to quantum yields that are lower or higher than unity.

The overall quantum yield  $\Phi$  is defined as the number of molecules of substrate S transformed per quantum (photon) absorbed. We may also distinguish the individual product quantum yields  $\Phi_{Xi}$ , where  $\Phi_{Xi}$  is the number of molecules of Xi formed per quantum absorbed. Similarly, the primary quantum yields  $\Phi_j$  give the fraction of the excited molecules (or atoms) participating in primary process  $j$ . It follows that, while  $\Phi$  and  $\Phi_{Xi}$  may be very small or very large,  $\sum_{j=1}^n \Phi_j = 1.0$ , where  $n$  is the total number of primary processes. If geometric isomerization is the only chemical process occurring in the photosensitization of a 1,2-disubstituted olefin, then  $\Phi = \Phi_{Xi}$  with  $Xi \equiv$  the geometric isomer. The quantum yield  $\Phi_T$  of the primary process leading to the formation of the triplet olefin may be determined by studying both isomers:

$$\Phi_T = \Phi(cis \rightarrow trans) + \Phi(trans \rightarrow cis)$$

If this quantum yield is far from unity it indicates the presence of other primary steps or the participation of secondary reactions.

The quantum yields of the *cis*  $\rightleftharpoons$  *trans* isomerizations of the 1,3-pentadienes have been determined for mercury and a large number of photosensitizers (most of them in solution). The energies of the triplet donors range from about 53 kcal mol<sup>-1</sup> up to that of mercury, 112.7 kcal mol<sup>-1</sup>. The lower energies correspond to "soft" conditions where only *cis-trans* isomerizations (or additions) are observed. For mercury photosensitization the triplet of the acceptor is initially formed with a large excess of vibrational and rotational energy; in that case additional reactions are observed, especially at low pressures (between 1 and 30 Torr) where the collisional relaxation of this excess energy is not complete.

### 5.1. Suggested experiment

Using the same experimental procedure as outlined in Part 2, measure the rates of the *cis*  $\rightarrow$  *trans* and *trans*  $\rightarrow$  *cis* mercury-photosensitized isomerizations of the 1,3-pentadienes. To avoid appreciable decomposition of the 1,3-pentadienes, study the photosensitized isomerizations at pressures higher than 30 Torr. Under these conditions the excited pentadiene undergoes enough collisions to remove excess vibrational and rotational energy so that

we observe only isomerization at low percentages of reaction. We used 1,3-pentadienes from Fluka; the *cis* isomer contains 0.37% *trans* as the only impurity; the *trans* isomer contains 0.06% *cis* and about 1% of an impurity identified as cyclopentene. Typical values of the quantum yields obtained under different conditions of pressure are shown in Fig. 4. Thus the product quantum yields are  $\Phi(cis \rightarrow trans) = 0.60 \pm 0.04$  and  $\Phi(trans \rightarrow cis) = 0.42 \pm 0.04$ . The total quantum yield  $\Phi$  is unity within experimental error ( $1.02 \pm 0.08$ ). This means that all the quanta initially absorbed by the mercury atoms are transferred to the 1,3-pentadiene [6].

From the rates and the absorbed light intensity determined in Part 2 (or supplied by the instructor), calculate the quantum yields of isomerization in your experiments. Your data can be discussed with respect to the following mechanism (Scheme I):

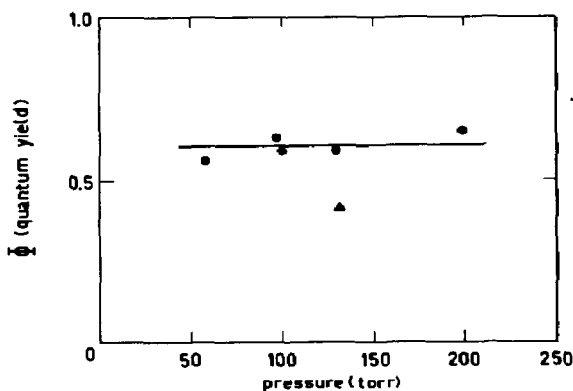
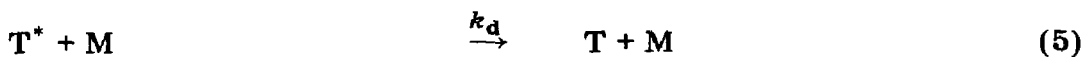
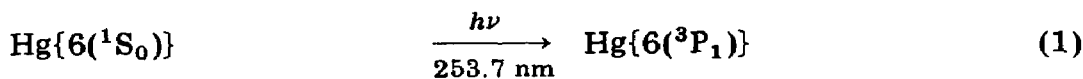


Fig. 4. Quantum yields of the *cis*  $\rightarrow$  *trans* (●) and *trans*  $\rightarrow$  *cis* (▲) mercury-photosensitized isomerizations of 1,3-pentadiene under initial conditions as a function of 1,3-pentadiene pressure. The reaction rates were obtained as described in the caption to Fig. 3; the absorbed light intensities were determined using 2-butene actinometry and the upper curve in Fig. 2.

where T is the vibrational-rotational relaxed lowest triplet state of 1,3-pentadiene and T\* is the vibrational-rotational excited lowest triplet state of 1,3-pentadiene. (As indicated by eqns. (2) and (3), the same triplet state is obtained from both *cis*- and *trans*-1,3-pentadiene.) M denotes any molecule capable of removing the excess vibrational-rotational energy from the excited pentadiene triplet T\*.

From this mechanism the initial rates (when starting with pure isomers and for low conversions) are given by

$$v(\textit{cis} \rightarrow \textit{trans}) = I_a k_2 / (k_2 + k_3) \quad (\text{II})$$

and

$$v(\textit{trans} \rightarrow \textit{cis}) = I_a k_3 / (k_2 + k_3) \quad (\text{III})$$

Thus from the ratio of the initial rates we determine  $k_2/k_3$ , the so-called natural decay ratio of triplet 1,3-pentadiene.

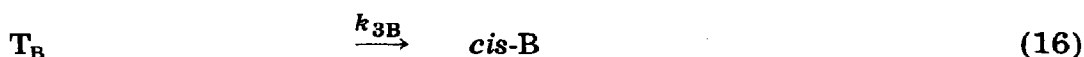
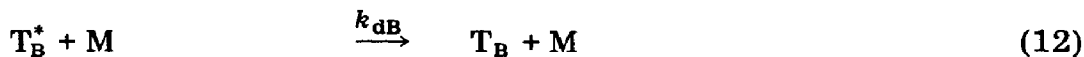
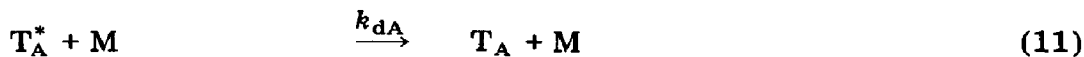
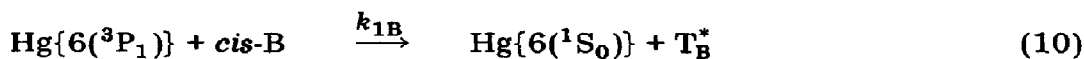
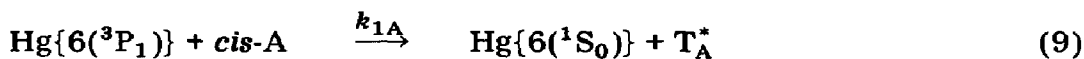
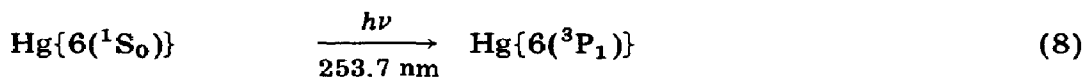
#### 6. Part 4: Relative cross sections for energy transfer

The number of collisions per unit time between a mercury atom and the molecules of added foreign gas can be calculated using gas kinetic cross sections and hard sphere approximations. As a first approximation the cross section of the excited mercury atom may be taken to be equal to that of the ground state atom to calculate a "rate" of collisions between the excited atom and the added gas. (Do you expect the cross section of the excited atom to be smaller or larger than that of the ground state atom? Why?) The second problem then involves the "efficiency" of energy transfer or of reaction: does every collision cause the triplet mercury atom to be deactivated or not? If not, how many collisions are necessary (on average) for deactivation to occur? These are difficult questions and many researchers have tried to answer them.

We can distinguish between "physical" quenching cross sections, which refer to the ability of a compound to reduce or "quench" the 253.7 nm mercury radiation at low pressures, and chemical quenching cross sections which are relative to the ability of a compound to quench a competing chemical photosensitized reaction. The reduction in the rate of formation of N<sub>2</sub> from the mercury photosensitization of N<sub>2</sub>O when trace quantities of another compound are added allows us to calculate a relative quenching cross section for the added compound. (The terms physical and chemical quenching are also used to designate quenching which does not and does lead to chemical reaction respectively.)

Thus if two olefins are irradiated together at 253.7 nm in the presence of mercury vapour, the probability that one of them accepts the energy from the excited mercury will depend on their relative concentrations and on their relative quenching cross sections.

Consider the mechanism (Scheme (IV)) for the competitive photo-sensitization of two *cis* compounds at pressures where collisional relaxation of excess vibrational and rotational energy is complete (see Part 3):



where  $\text{T}_i$  is the vibrational-rotational relaxed lowest triplet state of compound  $i$  and  $\text{T}_i^*$  is the vibrational-rotational excited lowest triplet state of compound  $i$ . The possibility of secondary energy transfer from one compound to the other is not considered [5, 6]. Assuming steady state concentrations for the intermediates, we obtain

$$\frac{v_A}{v_B} = \frac{k_{1A}}{k_{1B}} \frac{[A]}{[B]} \frac{k_{2A}/(k_{2A} + k_{3A})}{k_{2B}/(k_{2B} + k_{3B})} \quad (V)$$

where  $v_A$  and  $v_B$  are the initial rates of formation of the *trans* isomers of A and B respectively, and  $[A]$  and  $[B]$  are the concentrations.  $k_{1A}/k_{1B}$ , the ratio of the rate constants for energy transfer, is nearly equal to the ratio of the cross sections for energy transfer to A and B. (The ratio of the constants is proportional to the ratio of the relative velocities and therefore depends on the ratio of the reduced masses of the systems Hg-A and Hg-B.)  $k_2/(k_2 + k_3)$  is the probability that the triplet (di)olefin will yield the *trans* isomer on returning to the ground state. Such probabilities can be obtained from the literature or from Part 3 from the quantum yields of isomerization of the pure compounds: they are 0.5 and 0.6 for 2-butene and 1,3-pentadiene respectively. The ratio of the cross sections may be calculated from the slope of a plot of the ratio of the rates of isomerization against the ratio of the concentrations. It can be seen from Fig. 5 that the efficiency of transfer is almost the same for both compounds; this is not surprising since both transfers are exothermic (by at least 35 kcal mol<sup>-1</sup>).

### 6.1. Suggested experiment

Prepare a mixture of about 100 Torr total pressure of *cis*-2-butene and *cis*-1,3-pentadiene with relative concentrations in the range between 0.3 and 3.0. This may be done by introducing the minor component (say 35 Torr) into the cell first; evacuate the manifold and then bring the major component into the manifold at a pressure of about 200 Torr. Introduce it into the cell slowly up to the desired total pressure. The lamp should be started with the shutter in place and the reaction mixture should be allowed to stand for at least  $\frac{1}{2}$  h for diffusion and equilibration of the mixture before irradiation. Immediately before beginning irradiation, determine the exact percentage of the *cis* and *trans* isomers of both the 2-butene and the 1,3-pentadiene by gas chromatography (see Part 2). Irradiate the mixture for 1 h (or according to instructions) and proceed as in Part 2. The rates of isomerization are obtained from the peak areas and the partial pressures of the butene and pentadiene.

From the total peak areas and the partial pressures (determined manometrically upon introduction of the compounds) you may calculate the relative response of the chromatograph for 2-butene and 1,3-pentadiene.

## 7. Part 5: Photostationary ratio of *trans* to *cis* isomer concentrations

Prolonged photosensitization of molecules with a disubstituted double bond usually causes the ratio  $\alpha = [\textit{trans}] / [\textit{cis}]$  of the isomer concentrations to evolve towards a steady state ratio  $\alpha_{\text{SS}}$ . The mechanism (Scheme (I)) given for the isomerization of *cis*- and *trans*-1,3-pentadiene leads to the following rate equation when both isomers are present and step (4) is unimportant:

$$\frac{d[\textit{trans}]}{dt} = - \frac{d[\textit{cis}]}{dt} = \frac{I_a(k_1 k_2 [\textit{cis}] - k'_1 k_3 [\textit{trans}])}{(k_1 [\textit{cis}] + k'_1 [\textit{trans}])(k_2 + k_3)} \quad (\text{VI})$$

From this equation it can be seen that the rate equals zero (*i.e.* the *trans*-to-*cis* ratio no longer changes) when

$$[\textit{trans}] / [\textit{cis}] = k_1 k_2 / k'_1 k_3 \quad (\text{VII})$$

With the Mineralight UVSL 58 lamp it would require an excessively long time to reach this photostationary state (at least several weeks). Lamps giving a much higher light intensity can be used (*i.e.* the germicidal "original Hanau" NN 15/44 low pressure mercury lamp).

Another way of proceeding is to irradiate pure *cis*- and *trans*-1,3-pentadiene at a given pressure (approximately 130 Torr) for 1 night, for 3 days and for 1 week. The results are then analysed according to eqn. (VI). Indeed, if all the excited mercury atoms transfer their energy to the 1,3-pentadiene (Part 3) and geometric isomerization is the only major process occurring, the photostationary ratio will be equal to the ratio of the initial quantum yields for the *cis*  $\rightarrow$  *trans* and *trans*  $\rightarrow$  *cis* isomerizations multiplied by the ratio of the rate constants for the energy transfer to the *cis* and *trans* isomers. Rewriting eqn. (VI) and assuming that  $k_1 [\textit{cis}] + k'_1 [\textit{trans}]$  is nearly

constant, *i.e.* that the values of  $k_1$  and  $k'_1$  are not too different from each other, we have

$$+ \frac{d[\textit{trans}]}{dt} = - \frac{d[\textit{cis}]}{dt} = K[\textit{cis}] - K' \quad (\text{VIII})$$

which can be easily integrated:

$$\ln \left( \frac{K[\textit{cis}]_0 - K'}{K[\textit{cis}]_t - K'} \right) = Kt \quad (\text{IX})$$

where

$$K = \frac{I_a(k_1k_2 + k'_1k_3)}{(k_1[\textit{cis}] + k'_1[\textit{trans}])(k_2 + k_3)} \quad (\text{X})$$

and

$$K' = \frac{I_ak'_1k_3([\textit{cis}] + [\textit{trans}])}{(k_1[\textit{cis}] + k'_1[\textit{trans}])(k_2 + k_3)} \quad (\text{XI})$$

Assuming that  $k_1 \approx k'_1$  and replacing the concentrations by pressures, eqn. (IX) becomes

$$\ln \left\{ \frac{p(\textit{cis})_0/p(\textit{tot}) - \Phi_0}{p(\textit{cis})_t/p(\textit{tot}) - \Phi_0} \right\} = \frac{I_aRT}{p(\textit{tot})} t \quad (\text{XII})$$

where  $\Phi_0 (= k_3/(k_2 + k_3))$  is the quantum yield of the *trans*  $\rightarrow$  *cis* isomerization under initial conditions. Equation (XII) describes the kinetics of the isomerization whatever the isomer composition. Nevertheless, when the initial composition is too close to  $\alpha_{SS}$ , eqn. (XII), because of its structure and the experimental uncertainty, is no longer useful.

We performed two series of three experiments each, irradiating  $129 \pm 3$  Torr of 1,3-pentadiene (pure *cis* isomer for one series and pure *trans* isomer for the other) for 1 afternoon, 1 night and 1 week-end. The results are given in Table 1. These results can be plotted according to eqn. (XII) which predicts a straight line with slope  $I_aRT/p(\textit{tot})$ . Such a plot is shown in Fig. 6; the initial quantum yield ( $\Phi_0 = 0.42 \pm 0.04$ ) of the *cis*  $\rightarrow$  *trans* isomerization was taken from Part 3. It must be emphasized that this representation is rather sensitive to the value of  $\Phi_0$ . For  $\Phi_0 = 0.42$  both points at 4200 min are on the straight line with the correct calculated slope while for  $\Phi_0 = 0.40$  or  $\Phi_0 = 0.45$  they deviate significantly, one up and one down, from the straight line.

Thus eqn. (XII), with the value of  $\Phi_0$  obtained under initial conditions, correctly describes the experimental data at up to more than 20% isomerization. This supports the assumption that the efficiency of energy transfer from triplet mercury to both *cis*- and *trans*-1,3-pentadiene is the same. Then  $\alpha_{SS} = v(\textit{cis} \rightarrow \textit{trans})/v(\textit{trans} \rightarrow \textit{cis})$  or  $\alpha_{SS} = \Phi(\textit{cis} \rightarrow \textit{trans})/\Phi(\textit{trans} \rightarrow \textit{cis})$  under initial conditions. The results in Table 1 give  $\alpha_{SS} = 1.39$ ; the quantum yields, Part 3, lead to  $\alpha_{SS} = 1.43 \pm 0.20$ . These data can be compared with

TABLE 1

The *cis* → *trans* and *trans* → *cis* mercury-photosensitized isomerization of 1,3-pentadiene

<i>cis</i> → <i>trans</i>			<i>trans</i> → <i>cis</i>		
$p_0$ (Torr)	% <i>trans</i>	$t$ (min)	$p_0$ (Torr)	% <i>cis</i>	$t$ (min)
	0.37	0		0.06	0
130	3.18	308	132	1.61	240
127	10.32	1140	130	5.98	1000
127	28.22	4200	126	20.75	4230

The absorbed light intensity is  $1.82 \times 10^{-8}$  einsteins  $l^{-1} s^{-1}$ .

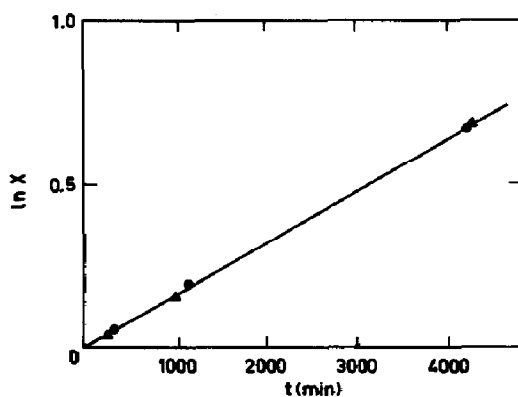
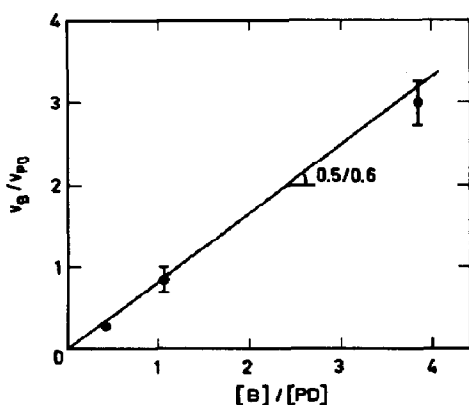


Fig. 5. Competitive mercury-photosensitized *cis* → *trans* isomerizations of 2-butene and 1,3-pentadiene: ratio of the initial rates  $v$  of isomerization against the ratio of the partial pressures of 2-butene (B) and 1,3-pentadiene (PD). The rates were obtained as described in the caption to Fig. 3. The straight line has been drawn with a slope corresponding to the ratio of the initial quantum yields.

Fig. 6. Mercury-photosensitized *cis* → *trans* (●) and *trans* → *cis* (▲) isomerizations of 1,3-pentadiene: evolution of the *cis* isomer with time.

$$X = \{p(\text{cis})_0/p(\text{tot}) - \Phi_0\} / \{p(\text{cis})_t/p(\text{tot}) - \Phi_0\}$$

where  $\Phi_0 = k_3/(k_2 + k_3)$  is the initial quantum yield of the *trans* → *cis* isomerization. The straight line has been drawn with a slope equal to  $I_a RT/p(\text{tot})$ , where  $I_a = 1.82 \times 10^{-8}$  einsteins  $l^{-1} s^{-1}$ ,  $R$  is the gas constant,  $T$  is the absolute temperature (295 K) and  $p(\text{tot}) = 129$  Torr.

the literature values  $\Phi(\text{cis} \rightarrow \text{trans})/\Phi(\text{trans} \rightarrow \text{cis}) = 1.29 \pm 0.10$  and  $\alpha_{SS} = 1.27 \pm 0.05$  obtained under long-time irradiation conditions [6].

### 7.1. Suggested experiment

This part will require the collaboration of several groups of students and each group will have to carry out accurate analyses on the gas chromato-

graph, either of the starting composition or of the final composition, or of both, of mixtures of *cis*- and *trans*-1,3-pentadiene. Two methods can be used.

### 7.1.1. Method A

If a high intensity and low pressure mercury lamp is available, you may approach the photostationary state directly. To avoid eventual complications due to the accumulation of minor products, this is usually done by successive approximations.

Fill the reaction cell with about 160 Torr of a 3:1 mixture of *trans*-1,3-pentadiene-*cis*-1,3-pentadiene using the method given in Part 4. After a suitable equilibrium time, analyse part of the mixture by chromatography to confirm the ratio determined manometrically. Eliminate any excess 1,3-pentadiene so as to have a final pressure of 130 Torr. Irradiate for 2 h (or as instructed). Eliminate the fraction of pentadiene corresponding to the dead space (see Part 2) and analyse the remaining mixture. You will observe that the ratio has decreased to a value  $\alpha_1$ , *i.e.* the amount of *cis*-1,3-pentadiene has increased. Repeat the procedure with a 0.3:1 ratio of *trans* isomer to *cis* isomer. The ratio will have increased to a value  $\alpha_2$ . The third experiment is then carried out with a ratio  $(\alpha_1 + \alpha_2)/2$  and evolves to  $\alpha_3$  which is greater than or less than  $(\alpha_1 + \alpha_2)/2$ . Let us assume that  $\alpha_3 > (\alpha_1 + \alpha_2)/2$ . Then the series 3.0,  $\alpha_1$ ,  $\alpha_3$ , ... , allows us to write  $\alpha_1 \geq \alpha_{SS} \geq \alpha_3$ . A new experiment with a ratio of *trans* isomer to *cis* isomer of  $(\alpha_1 + \alpha_3)/2$  can eventually narrow down the uncertainty in the value of the photostationary state. Unless the lamp is very intense and the radiation times are long, this can be a tedious process!

### 7.1.2. Method B

If a high intensity lamp is not available, the steady state ratio may be approached through two series of experiments such as those given in Table 1. This requires that a certain number of conditions be met.

(1) The experimental conditions must be chosen so that all the excited mercury atoms transfer their energy to acceptor molecules and collisional deactivation of the excess vibrational and rotational energy is complete. You must therefore choose a pressure greater than 30 Torr.

(2) Unless you measure the fraction of the incident light absorbed in the cell, you must use the same pressure for the *cis* and *trans* isomers in all experiments. This will also allow you to interpret your results using eqn. (XII) if  $I_a$  and  $\Phi_0$  are known.

(3) Geometrical isomerization should be the only major reaction of the acceptor. These three conditions are met for 2-butene and 1,3-pentadiene. If another acceptor is used, the light intensity (Part 2) should be determined or known to check the validity of eqn. (XII) and, from this, the validity of the reaction scheme.

The experimental procedure is the same as in Part 2. A pressure exceeding 80 Torr should be used to avoid corrections for the fraction of light absorbed.



Determine the ratio of the rates under initial conditions. To do this, irradiate one sample of the *cis* isomer and one sample of the *trans* isomer for a time such that the transformation  $(\% \text{ isomer})_{t=t} - (\% \text{ isomer})_{t=0}$  is between 1% and 5%. From these results you have

$$\alpha_{ss} = \frac{(\% \text{ trans formed})\{p(\text{tot})\}}{\text{time}} \frac{\text{time}}{(\% \text{ cis formed})\{p(\text{tot})\}} \quad (\text{XIII})$$

if the three conditions are met. If you know  $I_a$ , calculate  $\Phi(\text{cis} \rightarrow \text{trans})$ ,  $\Phi(\text{trans} \rightarrow \text{cis})$  and  $\Phi_{\text{tot}}$ .

Perform two more experiments with each isomer, with irradiation times a factor of 3 and a factor of 10 longer than that used for the determination of the initial rates. Interpret your results using eqn. (XII). Do both isomers give the same straight line with slope  $I_a RT/p(\text{tot})$ ? If so, or if not, what are the conclusions that you can draw from your results?

## 8. General conclusions

Although the apparatus described here is not inexpensive (cost about US \$10 000), it should be accessible to most undergraduate laboratories. The apparatus is also particularly convenient for any final-year projects in photochemistry because of its versatility. The chromatograph may also be used to teach gas chromatographic techniques. The total cost can be reduced somewhat by using a 253.7 nm interference filter instead of the monochromator; alternatively, if quartz lenses are available, the 253.7 nm beam may be rendered parallel and chemical filters [2] may be used.

The experimental technique is simple, requiring only a basic knowledge of vacuum techniques and gas phase chromatography. The results obtained are accurate and compare favourably with literature data.

The important principles of modern photochemistry introduced here are not an exhaustive list of the subjects which may be treated in discussions of the results. Comparison may be made with thermal reactions, radiation chemistry and atmospheric chemistry. For instance, the reactions of oxygen atoms, produced by the mercury photosensitization of  $\text{N}_2\text{O}$  (another actinometer since  $\Phi(\text{N}_2) = 1$ ) have recently received much attention [7].

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