

PHOTOSENSITIZED ISOMERIZATIONS OF DIDEUTEROETHYLENES

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INTRODUCTION

Photosensitization is an effective technique for the production of excited states of molecules which do not absorb the light of appropriate wavelengths. Especially in the gas phase, mercury photosensitization had widely been used to investigate the reactions of various radicals and of electronically excited states. The electronic energy available for transfer from the excited mercury atom (3P_1) is 4.9 eV/molecule.

Among hydrocarbons, ethylene is one of the most investigated compounds from both experimental and theoretical points of view. At present, we know that only a few excited states of ethylene can be attained by the absorption of the energy less than 4.9 eV. Nevertheless we are still in a position to accumulate significant new experimental data on this molecule.

MERCURY PHOTOSENSITIZED DECOMPOSITION OF ETHYLENE

By mercury photosensitization, ethylene decomposes into hydrogen and acetylene, which are apparently formed through a molecular process¹. According to Cvetanović and Callear, the mercury photosensitization of the mixture of normal ethylene (C_2H_4) and deuterated ethylene (C_2D_4) yields H_2 , D_2 , C_2H_2 and C_2D_2 but practically no HD and C_2HD . These workers also studied the pressure dependence of the reaction and concluded that the following "two excited state mechanism" is the most likely one.



Here, E^* and E^{**} are the two excited states of ethylene. The former is probably the lowest triplet state and the latter is another excited state of unspecified character which is the precursor for decomposition. Callear and Cvetanović postulated that this speculative state might be that of an ethyldene radical, because they found asymmetrical ethylene ($CH_2=CD_2$) as a reaction product by starting from *cis*-dideuteroethylene (*cis*-CHD=CHD). Setser, Rabinovitch and Placzek² reinvestigated this process with *trans*-dideuteroethylene as the starting compound and confirmed that the pressure

dependence of the reaction was interpretable in terms of the two excited state mechanism. They named E^{**} a "scrambled" state.

PHOTOSENSITIZED ISOMERIZATIONS BY ORGANIC COMPOUNDS

The next step is to use different photosensitizers for this reaction. Benzene is well known to have absorption at around 2600 Å. The electronic state is assigned to be $^1B_{2u}$. Below this state, there are at least two triplet states, $^3E_{1u}$ and $^3B_{1u}$. The latter level is lower and lies at about 3.6 eV.

Recently, several papers revealed that benzene photosensitization could successfully be applied to reactions requiring small activation energies. Our laboratory³ also showed that *cis-trans* isomerizations of butene-2 and pentene-2 do occur by the benzene photosensitization. Dideuteroethylene was also used as the reactant⁴. In this case, isomerization was observed as expected but no noticeable decomposition was detected. *Figure 1* shows the infrared spectrum of the reaction product obtained by benzene photosensitization of *trans*-dideuteroethylene. Obviously, *cis*- and *asym*-ethylene are produced but no acetylene is formed. If it were present in the product,

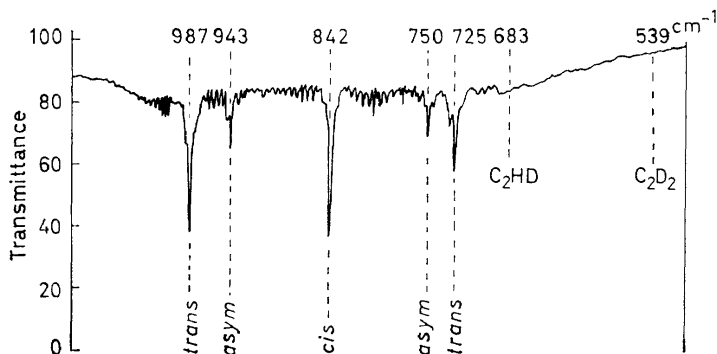


Figure 1. The infrared spectrum of the product of benzene photosensitized reaction of *trans*-dideuteroethylene. (3.0 mm ethylene and 2.0 mm benzene irradiated by a low pressure mercury lamp for 65 min.)

the absorption peaks at 729 (C_2H_2), 683 (C_2HD) and 539 cm^{-1} (C_2D_2) should appear in the spectrum.

In place of benzene, we tried to use several other organic compounds as photosensitizers⁵. Qualitative results are summarized in *Table 1*. Unfortunately, more than a half of the sensitizers used decomposed and deposited coloured materials on the window of the reaction cell. Using eight stable aromatic compounds, we studied the pressure dependence of the reaction. The ratios of the initial rate of formation of *asym*- to *cis*-isomer are plotted in *Figure 2* as a function of the pressure. In these reactions, again no decomposition was observed. As obviously seen in *Figure 2*, the rate of formation of *asym*-ethylene relative to that for production of *cis*-ethylene decreases with decreasing triplet state energies of photosensitizers. To explain this trend, we have to consider the low-lying energy levels of ethylene.

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Table 1. Qualitative observations of the photosensitized isomerization of dideuteroethylene

| Sensitizer | Energy of the lowest triplet (kcal/mole) | <i>cis-trans</i> isomerization | H-atom scrambling | Decomposition of sensitizer |
|------------------|--|--------------------------------|-------------------|-----------------------------|
| Benzene | 84.4 ^a | yes | yes | no |
| Fluorobenzene | 84.4 ^a | yes | yes | no |
| Benzotrifluoride | 83.3 ^a | yes | yes | no |
| Toluene | 82.9 ^a | yes | yes | no |
| <i>o</i> -Xylene | 82.1 ^b | yes | yes | no |
| Chlorobenzene | 81.7 ^a | yes | | yes |
| <i>m</i> -Xylene | 81.0 ^b | yes | yes | no |
| <i>p</i> -Xylene | 80.4 ^b | yes | yes | no |
| Mesitylene | 80.1 ^b | yes | yes | no |
| Aniline | 77 ^c | yes | | yes |
| Benzonitrile | 76.9 ^a | yes | | yes |
| Pyrazine | 75.9 ^d | yes | | yes |
| Acetophenone | 74.2 ^a | yes | | yes |
| Phenylacetylene | 72.0 ^a | yes | | yes |
| Naphthalene | 60.9 ^e | ? | | no |
| Nitrobenzene | 60 ^c | | | yes |

^a D. F. Evans. *J. Chem. Soc.* 2753 (1959).

^b Y. Kanda and R. Shimada. *Spectrochimica Acta* **17**, 279 (1961).

^c N. J. Turro, *Molecular Photochemistry*, Benjamin, 1965.

^d L. Goodman. *J. Mol. Spectroscopy* **6**, 109 (1961).

^e D. S. McClure. *J. Chem. Phys.* **19**, 670 (1951).

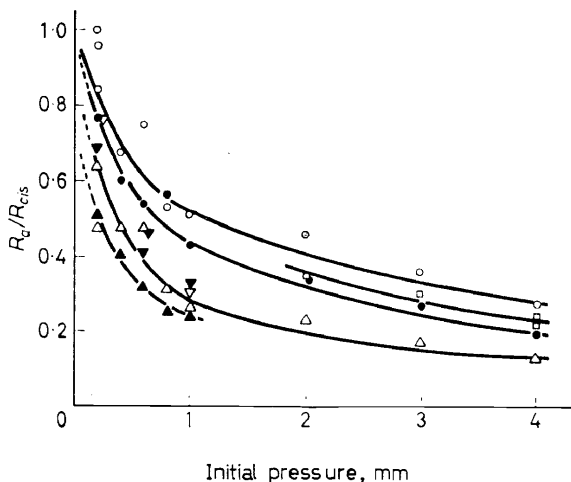


Figure 2. Plots of the ratio ($R_{\text{asym}}/R_{\text{cis}}$) as a function of the initial pressure. (○ Benzene, ● Toluene, ▽ *o*-Xylene, ▼ *m*-Xylene, △ *p*-Xylene, ▲ Mesitylene, □ Fluorobenzene)

THE LOW-LYING ENERGY LEVELS OF ETHYLENE

The energy diagram shown in Figure 3 is the same as already reported³ except that there are small corrections of the energy levels of acetylene and hydrogen. The lowest triplet state has a minimum at 1.9 eV (44 kcal), which is subject to large error because of the rough estimation. We recently studied the photosensitized *cis-trans* isomerization of butene-2 in cyclohexane at room temperature⁶. In the liquid phase, low volatile compounds having low

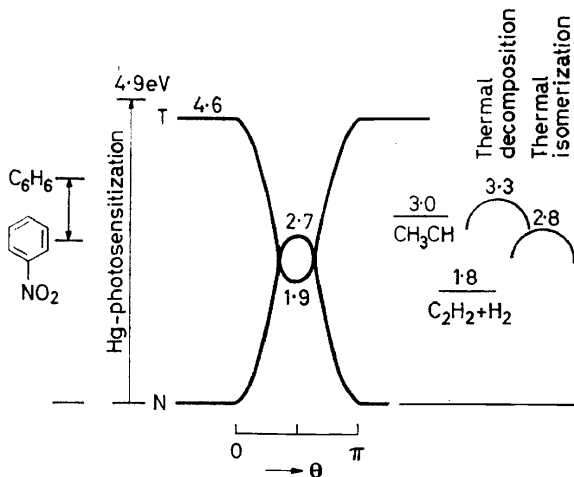


Figure 3. The energy diagram of ethylene

triplet state energies can be used as photosensitizers. Figure 4 shows the quantum yield of the *cis-trans* isomerization as a function of the triplet state energy. Although interpretation of the results is complicated by factors

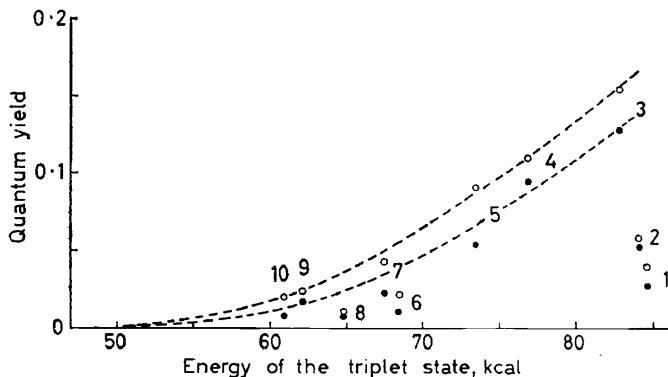


Figure 4. Plots of the quantum yield of *cis-trans* isomerization in cyclohexane as a function of the triplet state energy of photosensitizer. (O from *cis* to *trans*, ● from *trans* to *cis*)

such as the lifetime of triplet state and the efficiency of intersystem crossing of the excited state of photosensitizer, the energy required to effect *cis-trans* isomerization does not seem smaller than 2.1 eV (50 kcal).

A SIMPLE CALCULATION OF THE RELATIVE RATE OF THE REACTION [2]

The excited state of ethylene (E^*) primarily produced by photosensitizations may be the triplet state shown in Figure 3. This is based on the usually accepted assumption that the photosensitization occurs by triplet-triplet energy transfer, although there are still some uncertainties. If the transfer mechanism is assumed, E^* should have some vibrational energy when

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produced. Consequently, reaction (2) is a typical unimolecular reaction and the rate might be discussed by the classical theory of Kassel.

$$k = A(1 - \epsilon_0/\epsilon)^{s-1}$$

Here, ϵ_0 is the minimum vibrational energy required for the reaction (2) and may be approximated to be the difference between the energy of an ethylidene radical and the minimum energy of the triplet state, i.e. $\epsilon_0 = 69 - 50 = 19$ kcal. The quantity ϵ is the excess vibrational energy of the triplet state formed initially by energy transfer. In the case of benzene, ϵ may be as large as $84.4 - 50 = 34.4$ kcal. s is the number of the "effective" oscillators.

In mercury and benzene photosensitizations, the values of k have been obtained experimentally to be 3.1×10^9 and 8.2×10^7 s⁻¹ respectively, on the assumption that the collision diameter of the deactivating process [reaction (3)] is 4.95 Å. Thus, A and s are calculated to be 5.4×10^{10} s⁻¹ and 9. With these values and with relative values of k obtained in the present experiments, the triplet state energies of photosensitizers can be calculated using the above equation. The results are summarized in Table 2 in comparison with the spectroscopic values.

Table 2. Relative rates of reaction (2) and energies of the lowest triplet states†

| Sensitizer | Relative rate | Triplet state energy (kcal) | |
|------------------|---------------|-----------------------------|---------|
| | | Present | Optical |
| Benzene | 1.00 | (84.4) | 84.4 |
| Toluene | 0.65 ± 0.04 | 83.0 ± 0.2 | 82.9 |
| <i>p</i> -Xylene | 0.43 ± 0.03 | 81.8 ± 0.2 | 80.4 |
| Mesitylene | 0.27 ± 0.04 | 80.7 ± 0.4 | 80.1 |
| Fluorobenzene | 0.82 ± 0.2 | 83.7 ± 0.8 | 84.4 |
| Benzotrifluoride | 0.30 ~ 0.45 | 81.4 ± 0.5 | 83.3 |

† Calculation has not been made for *o*- and *m*-xylene, because of the scarcity of the data.

CADMIUM PHOTSENSITIZED ISOMERIZATION

It is well known that cadmium can be used as a photosensitizer⁷ in the similar manner as mercury. The reaction system, however, has to be heated up to obtain suitable vapour pressure of the metal. This may complicate the analysis of the data. The electronic excitation energy of a cadmium (³P₁) atom is 3.8 eV.

Figure 5 shows the ratios of the initial rate of formation of *cis*-isomer to that of *asym*-isomer, as a function of the initial pressure. Again, practically no decomposition was observed, i.e. the rate of decomposition was roughly 0.1 per cent of that of isomerization. Therefore, the two excited state mechanism which has successfully been applied to other photosensitizations, may explain the results shown in Figure 5. However, if the mechanism is strictly applied to the data, the intercept of the curves should be unity, while experimentally it seems greater than unity.

This trend is also seen in photosensitization by organic compounds although the effect is partly obscured by experimental errors. In *Figure 2* the curves do not always approach 1.0 as the pressure approaches zero. These results lead us to speculate that the vibrationally excited triplet state (E^*) does not always cross over to E^{**} even if it is not collisionally stabilized,

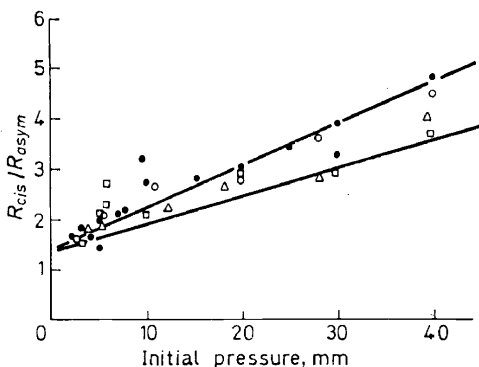


Figure 5. Plots of the ratio (R_{cis}/R_{asy} of cadmium photosensitization) as a function of the initial pressure. (● 275°C, ○ 300°C, △ 325°C, □ 350°C)

but may change to another state which undergoes only *cis-trans* isomerization. This state is, of course, unknown but might be the vibrationally excited ground state. If so, this process may be called "intramolecular deactivation".

Recently, Worsham and Rice⁸ reported that the quantum yield of the decomposition of azoethane was less than unity at the pressure of zero and that this could be explained by unimolecular deactivation. Such observations may actually be rather numerous, but the possible error connected with the light intensity measurement may have precluded the detailed investigation. The present result is free from the error of the light intensity measurement. Obviously, this postulation needs further investigations.

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