Preliminary Note

Sensitized photoisomerization of limonene as a model for a light energy storage process

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1. Introduction

During the last decade, the photochemical reactions of organic compounds have been actively investigated in order to develop a convenient light energy storage system [1 - 5]. Among the many photochemical processes studied, valence photoisomerizations seem to be the most promising candidates for the storage of light energy, especially since these photoreactions give, in general, high storage enthalpies and stable photoproducts [6 - 12]. Recently, it has been suggested by Jones *et al.* [3] that limonene (1) is photoisomerized into 1,2-dimethyl-tricyclo[3.3.0.0^{2,7}]octane (2) according to the following reverse reaction:

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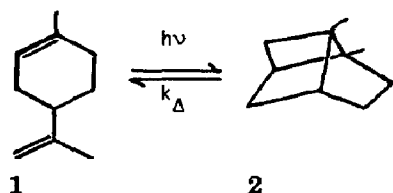
It is worth mentioning that the formation of the exocyclic isomer of limonene has also been reported to take place during its photoprotonation in methanolic solution [13] and, very recently, upon laser irradiation [14]. From the standpoint of the photochemical storage of light energy, limonene has the advantage of being widely available in nature and of already being used widely in industry.

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In the present work, we have studied the effect of photosensitizers on the quantum yield and kinetics of the valence photoisomerization of limonene in cyclohexane solution, in order to gain greater insight into the possibility of using this photoreaction as a light energy storage system.

2. Experimental details

2.1. Materials
Limonene (Aldrich) was purified using an Aerograph Autoprep A-700 gas chromatograph equipped with a Carbowax column 10 ft long. Analytical grade cyclohexane (Aldrich) was used. Copper(I) chloride (Aldrich), benzophenone and 9-xanthenone (J. T. Baker, photosensitizer grade) were used as received.

2.2. Methods
Cyclohexane solutions containing limonene (6.2×10^{-2} M) and sensitizer were irradiated in 1 cm quartz cuvettes using an Osram HBO 200 W high pressure mercury arc lamp placed in an Oriel model 6137 housing.

Samples were taken at suitable intervals and were analysed for limonene and photoproducts with a Varian 1200 gas chromatograph. An OV-101 column was used for the gas chromatography (GC) separation. For the identification of photoproducts, a Jeol JMS gas chromatograph—mass spectrometer interfaced to a computer was utilized. The mass spectra of limonene and the photoproduct P_1 are given in Table 1.

For the determination of photoisomerization quantum yields, a narrowband UV filter was used to isolate the wavelength of the irradiating light at 250 (± 10) nm. The light intensity was evaluated by potassium ferrioxalate actinometry [15, 16]. The value of the molar absorption coefficient of limonene at this wavelength (log $\epsilon_{250} = 1.36$) was taken into account in the calculation of the quantum yields.

3. Results and discussion

Limonene strongly absorbs light of wavelengths shorter than 250 nm, but it absorbs only weakly at wavelengths longer than 250 nm. Therefore, in order to test the usefulness of photoisomerization for storing solar energy, it was of interest to study sensitizers which absorb in the region 250 - 400 nm.

Using GC analysis, we found that two photoproducts P_1 (retention time $t_R^{P_1} = 11.4$ min; 90.3%) and P_2 ($t_R^{P_2} = 14.5$ min; 9.7%) were formed upon irradiation of limonene ($t_R^L = 9.0$ min) in cyclohexane solution at room temperature (298 K). The mass spectrum of the predominant photoproduct P_1 is significantly different from that of limonene (Table 1).

TABLE 1

Mass spectra of limonene and its photoproducts

m/e	Relative abundance[a] (%)	
	Limonene	Photoproduct P_1
27	19.8	30.0
28	7.3	25.0
29	9.4	19.0
39	33.3	40.5
40	9.4	16.0
41	28.1	68.0
42	4.2	22.0
43	6.2	100.0
50	4.2	18.0
51	12.5	12.0
52	7.3	—
53	27.1	24.0
55	9.4	33.0
63	4.2	—
65	9.4	—
66	4.2	—
67	47.8	—
68	100.0	65.0
69	9.4	43.0
77	19.8	15.0
78	6.2	—
79	30.2	26.0
80	14.6	—
81	12.5	25.0
91	22.4	19.0
92	22.4	12.0
93	75.0	51.5
94	21.9	20.0
95	9.4	22.0
105	8.3	—
107	18.7	—
108	6.2	19.5
117	6.2	25.0
119	9.4	12.0
121	37.5	8.0
122	3.1	—
136	31.2	12.0
137	3.1	—

[a]Values calculated relative to the most abundant peak (100.0%) of the mass spectrum.

The spectrum of P_1 includes three peaks at $m/e = 41$ (68%), 43 (100%) and 68 (65%); for the limonene the relative abundances of these ions are respectively 28%, 6.2% and 100%. The peak at $m/e = 43$ (which is the most abundant in the mass spectrum of P_1) can be attributed to a $C_3H_7^+$ ion formed during the fragmentation of a structure similar to that of photoiso-

mer 2. Such an ion could not be formed during the fragmentation of limonene or of its exocyclic isomer, as shown by the very small relative abundance of $m/e = 43$ (6.2%) in the mass spectrum of limonene. The peak at $m/e = 41$ is related to a $C_3H_5^+$ ion resulting probably from the loss of a hydrogen molecule from the $C_3H_7^+$ ion; the relative abundance of $m/e = 41$ is also smaller in the mass spectrum of P_1 than in that of limonene. The peak at $m/e = 68$ could be due to a $C_5H_8^+$ ion resulting from a dismutation reaction of P_1, which would take place also in the case of limonene, in agreement with the similar values of the relative abundance of this ion in the two mass spectra. Taking into account these results, we propose that the structure of P_1 corresponds to that of photoisomer 2. In order to confirm definitely this identification by nuclear magnetic resonance (NMR) spectroscopy, it will be necessary to synthesize and isolate larger quantities of P_1. Such an investigation is now under way and will be reported in more detail in a subsequent paper. The concentration of P_2 was too low to permit its identification.

Kinetic study of the photoisomerization of limonene shows that the photoreaction rate increases dramatically using 9-xanthenone as a sensitizer. Indeed, a 10% photoconversion ratio was reached after irradiation times of 64 min in the presence of 9-xanthenone ($\epsilon_{250} = 10^4$ M^{-1} cm^{-1}) and of 720 min in the absence of sensitizer. Other sensitizers, such as copper(I) chloride and benzophenone, which have been used previously for sensitizing the
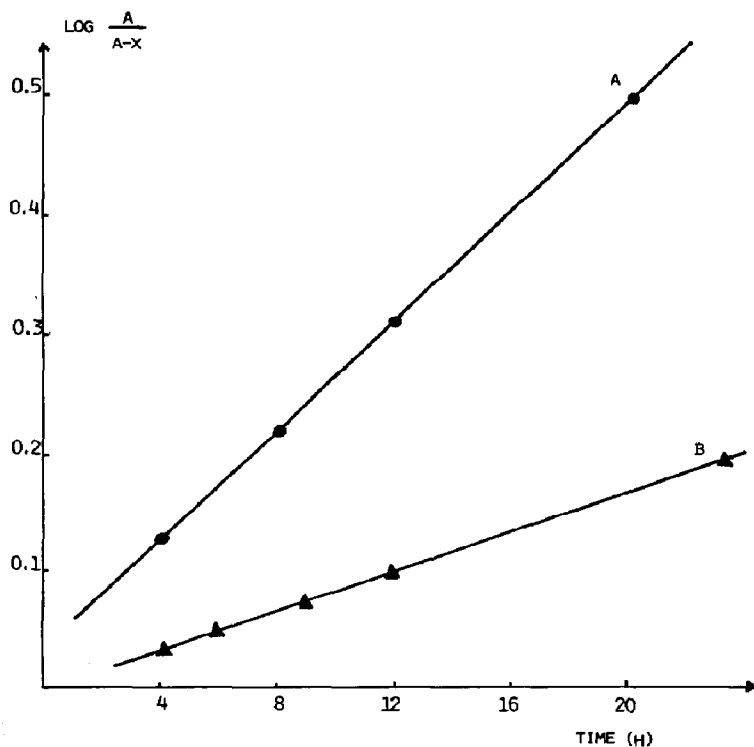

Fig. 1. Photoisomerization rates for 6.2×10^{-2} M limonene in cyclohexane solution at 298 K: curve A, in the presence of 9-xanthenone; curve B, without photosensitizer.

isomerization of norbornadienes [4], did not change significantly the photoisomerization rate of limonene. At the concentration of 6.2×10^{-2} M limonene, with the light intensities (wavelength of irradiation, 250 ± 10 nm) utilized in our experiments, we found that the rate was first order, *i.e.* a plot of $\log\{a/(a-x)\}$ against illumination time t was linear (Fig. 1). As expected, the overall first-order rate constant k_1 calculated from the slope of the log plots was about three times larger when the photoreaction was sensitized by 9-xanthenone ($k_1 = 3.84 \times 10^{-4}$ min^{-1}) than in the absence of sensitizer ($k_1 = 1.32 \times 10^{-4}$ min^{-1}) or when benzophenone was used.

We obtained significantly higher photoisomerization quantum yields ϕ_p for the 9-xanthenone-sensitized photoreaction ($\phi_p = 0.49 \pm 0.02$) than in the absence of sensitizer ($\phi_p = 0.17 \pm 0.02$).

That 9-xanthenone promotes a significant increase in the photoisomerization rates and quantum yields compared with benzophenone (or other sensitizers) can be attributed to the operation of a triplet–triplet energy transfer mechanism. Indeed, the triplet energy E_T of 9-xanthenone is about 310 kJ mol^{-1}, while for benzophenone $E_T = 288$ kJ mol^{-1} [17]. The difference in efficiency between the two sensitizers can be understood by taking into account that the triplet–triplet energy transfer process is efficient only if the
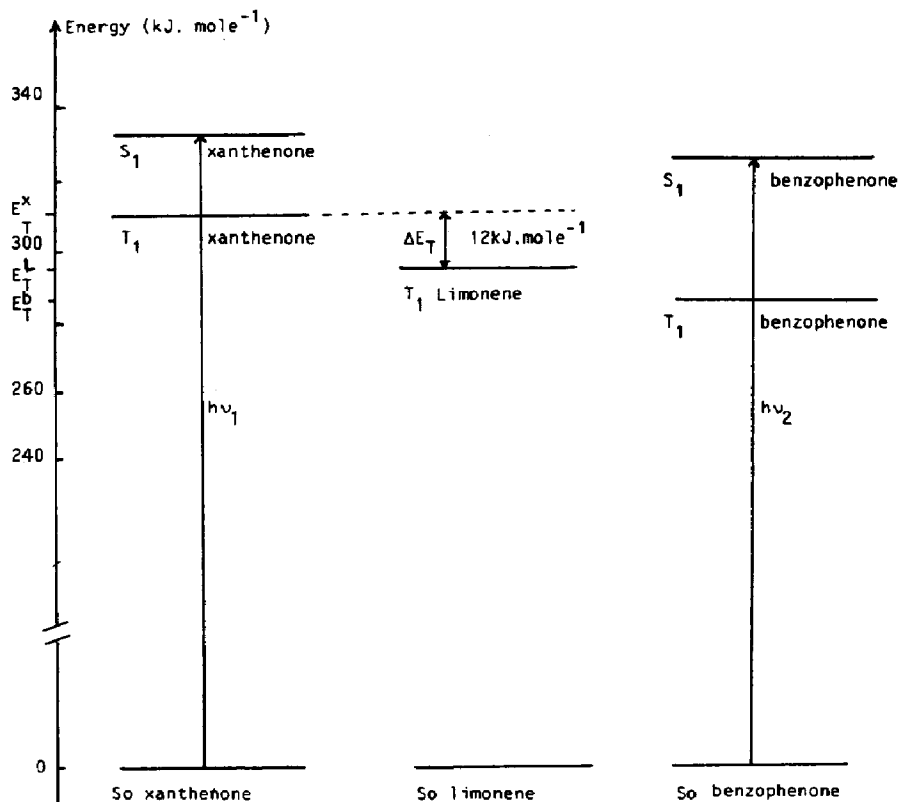

Fig. 2. Energy diagram of the triplet–triplet energy transfer process which occurs during the photoisomerization of limonene (E_T^b, triplet state energy level of benzophenone; E_T^L, triplet state energy level of limonene; E_T^x, triplet state energy level of xanthenone).

difference in energy ΔE_T between the triplet states of the donor and the acceptor conforms to the relation

$$\Delta E_T = E_T^{donor} - E_T^{acceptor} \gtrsim 12 \text{ kJ mol}^{-1} \tag{1}$$

In our case, this would mean that the triplet state energy level of limonene lies between the triplet energy levels of 9-xanthenone (E_T^X) and benzophenone (E_T^b), as shown in Fig. 2. The energy diagram allows us to predict that the limonene reactive triplet state should be characterized by an E_T^L value close to 295 kJ mol^{-1} (calculated from relation (1)).

The full characterization of the photoisomer P_1 is currently under way. We have also undertaken a study of the thermodynamic properties of the photoisomerization reverse reaction, and we are investigating the possibility of using other photosensitizers for shifting the action spectrum towards the visible.

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