

PHOTOSENSITIZED ISOMERIZATION OF NORBORNADIENE FOR SOLAR ENERGY STORAGE AND SUPPRESSION OF SIDE REACTION

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Photosensitized isomerization of norbornadiene to quadricyclene was investigated by using several photosensitizers such as toluene, acetone, acetophenone, benzophenone and α -naphthoquinone. The effect of wavelength on the quantum yield of quadricyclene and on the energy conversion efficiency was measured by using spectro-irradiator. The formation of byproduct polymer in the presence of photosensitizers was also studied. The formation of polymers during irradiation, which prevents the repeated use of energy storage material, was effectively suppressed by the addition of several phenolic substances into norbornadiene.

Introduction

Photochemical isomerization of norbornadiene (I) to quadricyclene (II) is regarded as one of the most promising reactions for the permanent storage of solar energy in the form of chemical energy^{1,4)} (Scheme 1). Its energy storage capacity, as much as 1190 J/g,³⁰⁾ makes this substance attractive for this purpose. There are, however, several difficulties which should be overcome to realize a practical energy-storage system from this reaction. Because norbornadiene has no absorption band corresponding to solar radiation, the utilization of longer-wavelength light by norbornadiene and the suppression of side reactions which cause the gradual degradation of the energy-storage material seem to be the most requisite for this system.²⁴⁾

Many research works have been carried out toward the efficient photoisomerization of norbornadiene to quadricyclene under sunlight. Two ways have been investigated to utilize longer-wavelength light. One is the use of suitable photosensitizers which assist the photoisomerization of norbornadiene to quadricyclene.^{1,10-12,18,25-27)} The other is the introduction of appropriate substituents into norbornadiene to extend the absorption band to longer wavelength.^{3-7,16,19,20,23,29,32)} But the latter way has such demerits as reduction of quantum yield, decrease in the amount of energy stored because of the increase in molecular weight, and increase of material cost owing to the complication of synthesis. Although the former

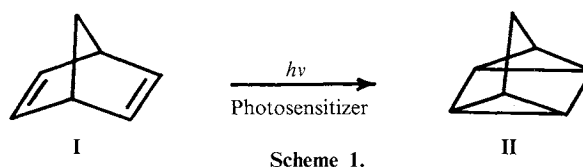
way has the possibility of contamination of the energy-storage material, it seems to be easy and economical for practical use.

A number of studies of photosensitizers for the isomerization of norbornadiene have been reported. However, they have not been oriented toward practical engineering but have emphasized chemistry. In many cases, 313 nm light from a mercury lamp and a very dilute solution of norbornadiene were used in the experiments, which are far from practical use for a solar system. In addition, the suppression of side reactions which is necessary for long-term repeated use of energy-storage material has never been reported.

We have studied the effect of wavelength in the presence of several photosensitizers on the quantum yield for the photoisomerization of norbornadiene to quadricyclene, on the energy-conversion efficiency and on the formation of byproduct polymers by using a spectro-irradiator and quartz cells. Furthermore, the effort was focused on the suppression of side reactions. Consequently, good prospects were found for the practical usage of this material for solar energy storage.

1. Experimental

Studies on the effect of wavelength of incident light



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were carried out by using a CRM-FA Spectro-Irradiator (Japan Spectroscopic Co. Ltd.), where 4.5 ml of cyclohexane solution of norbornadiene with a photosensitizer and with or without an inhibitor of side reaction in a 10×10 mm quartz cubette was irradiated by light of a given wavelength (15 nm in width) from a xenon light source. After irradiation, chemical yield and quantum yield of quadricyclene were determined by gas chromatography (Hitachi K53 Gas Chromatograph) by using an Apiezon L column at 70°C. The side reaction product, mainly composed of polymer, was obtained as a residue after distillation of volatile fraction. The incident energy of each wavelength was calibrated by output of an exposed vacuum-thermocouple.

2. Results and Discussion

Figure 1 shows the transmittances [%] of each cyclohexane solution of norbornadiene and photosensitizers. In Figs. 2 and 3, the results of norbornadiene photoisomerization in air by using several photosensitizers—toluene, acetone, acetophenone, benzophenone and α -naphthoquinone—are presented. Figure 2 shows the quantum yield for quadricyclene production and the energy conversion efficiency when various photosensitizers were used. And Fig. 3 shows the byproduct yields and the incident light energy. It can be seen that the photoisomerization of norbornadiene to quadricyclene occurred at the wavelength corresponding to the absorption band of the mixed solution.

The photoisomerization in the presence of a photosensitizer seemed to be explainable by the triplet state mechanism.^{15,21)} Figure 4 shows a schematic energy level diagram together with the excited singlet-state energy and the excited triplet-state energy of several photosensitizers.^{2,13,15,21,22,28,31)} After having been excited to a vibrational level of the excited singlet state ($^0S \rightarrow ^1S$), the photosensitizer molecule undergoes non-radiative intersystem crossing from singlet to triplet state (3S), and then transfers the energy to norbornadiene. Consequently, norbornadiene is excited to the triplet state (3NBD) and isomerizes to quadricyclene. Acetophenone has the highest quantum yield of the five photosensitizers (Fig. 2). It has a high efficiency (100%) in intersystem crossing and energy transfer, since there is a small separation between the excitation energies of its lowest excited singlet and triplet states, and its triplet excitation energy is higher than norbornadiene's.¹⁵⁾ The collisional energy transfer to norbornadiene should be more favorable for acetophenone than for such sensitizers as benzophenone and α -naphthoquinone having lower triplet energy, because acetophenone has higher triplet energy.⁹⁾ Both toluene and acetone have higher singlet or triplet energies and absorb shorter-

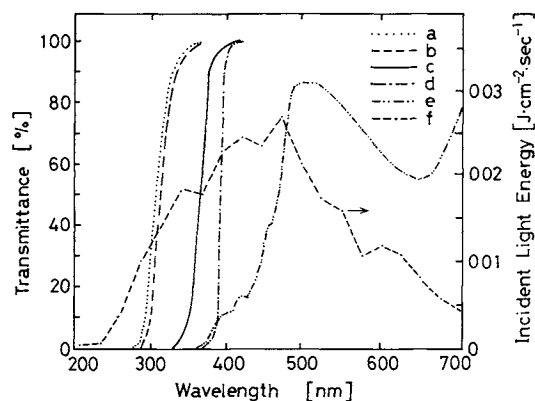


Fig. 1. Incident light energy and transmittance [%] of cyclohexane solution of norbornadiene and photosensitizer (reference: cyclohexane): (a), 1.0 mol/l norbornadiene with 100 mol% toluene; (b), 1.0 mol/l norbornadiene with 5 mol% acetone; (c), 1.0 mol/l norbornadiene with 5 mol% acetophenone; (d), 1.0 mol/l norbornadiene with 5 mol% benzophenone; (e), 1.0 mol/l norbornadiene with 5 mol% α -naphthoquinone; (f), incident light energy.

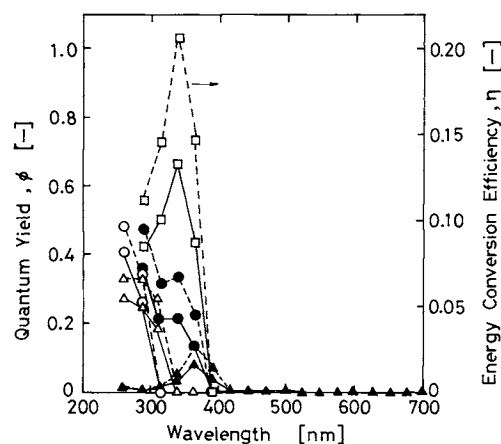


Fig. 2. Quantum yield for quadricyclene production and energy conversion efficiency: —, quantum yield ϕ ; ---, energy conversion efficiency η = (stored energy in the form of quadricyclene/incident energy), based on $\Delta H = 1190 \text{ J/g}^{30)}$; norbornadiene, 1.0 mol/l cyclohexane solution; ○, with 100 mol% toluene; △, with 5 mol% acetone; □, with 5 mol% acetophenone; ●, with 5 mol% benzophenone; ▲, with 5 mol% α -naphthoquinone; wavelength, central wavelength of incident light (15 nm in width).

wavelength light, whereas α -naphthoquinone has lower triplet energy than norbornadiene and also transfers the energy to norbornadiene with difficulty. When acetophenone was used as a photosensitizer, the increase in the extent of isomerization of norbornadiene to quadricyclene was almost linear with irradiation time till its 100% conversion, though a slight reduction of the isomerization rate was observed at higher conversion. However, when benzophenone was used the isomerization did not reach 100% conversion but stopped at about 85% conversion. Since benzophenone has lower triplet energy, a part of the energy would be

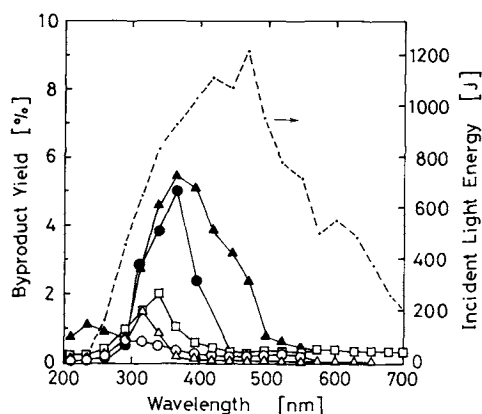


Fig. 3. Byproduct yield and incident light energy.

—, byproduct yield = 100 (byproduct [g]/norbornadiene [g]); ----, incident light energy. Refer to Fig. 2 for symbols ○, △, □, ●, ▲ and wavelength.

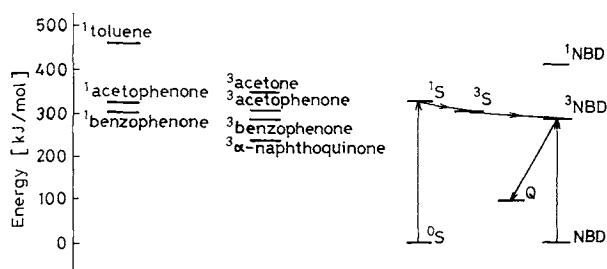


Fig. 4. Schematic energy level diagram and the excited singlet-state energy and excited triplet-state energy of several sensitizers.

transferred to quadricyclene via complex formation, resulting in norbornadiene regeneration.

The production of quadricyclene was limited to a relatively narrow wavelength range of ultraviolet region, while the byproduct was formed in a wide range. Polymers were thought to occupy the major part of byproduct in the isomerization reaction. No byproduct other than polymer was detected by gas chromatography. The polymers seem to be produced not only by the light irradiation but also to be formed independently of the irradiation. The oxygen dissolved in the reaction mixture accelerated the formation of the byproduct polymers, since the resultant polymers contained various amounts of oxygen. **Table 1** shows a typical composition of the polymers obtained when the experiment was carried out in air or under reduced pressure. When α -naphthoquinone, which should be a radical scavenger as well as a photosensitizer, was added, a considerable amount of byproduct was unexpectedly formed in place of quadricyclene compared with the cases of the other photosensitizers. Since the ultraviolet absorption spectrum of cyclohexane solution of norbornadiene and α -naphthoquinone showed a new absorption band at 650 nm which is absent in the spectra of the parent compounds (shown in **Fig. 5**), a complex between

Table 1. Results of elementary analysis of byproduct polymers

	C [%]	H [%]	N [%]	O [%]	Yield [%]
Polymer A*	72.76	7.00	0.09	20.15	9.8
Polymer B**	77.71	7.70	0.20	14.39	1.7
C***	91.30	8.70			

* Polymer A: byproduct polymer obtained in air by using acetophenone as a photosensitizer.

** Polymer B: byproduct polymer obtained under reduced pressure without photosensitizer.

*** C: theoretical value for norbornadiene (C_7H_8).

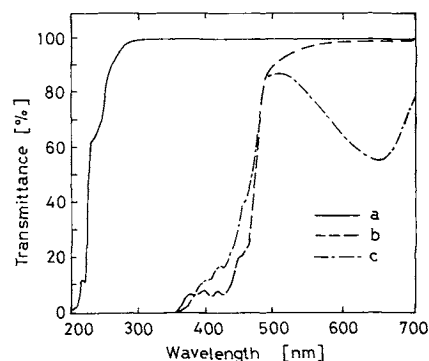


Fig. 5. Transmittance [%] of cyclohexane solution of norbornadiene and α -naphthoquinone (reference: cyclohexane). (a), 10^{-3} mol/l norbornadiene; (b), 5×10^{-2} mol/l α -naphthoquinone; (c), 1.0 mol/l norbornadiene with 5 mol% α -naphthoquinone.

norbornadiene and α -naphthoquinone must be formed in the solution. Since α -naphthoquinone has a lower triplet energy than norbornadiene (as is seen in **Fig. 4**), it could not transfer its triplet energy to norbornadiene but produced byproduct polymer via the complex. When benzophenone was used as a photosensitizer, a fair amount of byproduct was also obtained. As benzophenone is known to form a complex with quadricyclene,^{8,9,17} the byproduct is thought to be produced by the complex formation mechanism.

Formation of the polymers during irradiation was effectively suppressed by the addition of several phenolic substances (radical scavengers) into norbornadiene. **Table 2** shows the result of norbornadiene photoisomerization by using acetophenone as a photosensitizer and 2,6-di-*t*-butyl-*p*-cresol as an inhibitor of side reaction. After the irradiation, no byproduct polymer was found. Photoisomerization proceeded almost linearly until complete conversion was attained, but the rate was reduced slightly at higher conversion. The above results will contribute to the realization of a chemical conversion system for solar energy that allows the repeated use of the norbornadiene-quadricyclene system.

Table 2. Photoisomerization of norbornadiene to quadricyclene by using acetophenone (5 mol% for norbornadiene) as photosensitizer and 2,6-di-*t*-butyl-*p*-cresol (5 mol% for norbornadiene) as inhibitor of side reaction

Wave-length ^{a)} [nm]	Incident energy [J]	ϕ^b [—]	η^c [—]	Byproduct yield ^{d)} [%]
209	9	none	none	none
235	19	0.279	0.060	none
261	162	0.207	0.050	none
288	454	0.247	0.065	none
314	649	0.529	0.152	none
340	836	0.643	0.200	none
366	925	0.398	0.133	none
392	1038	0.008	0.003	none
418	1114	none	none	none
445	1071	none	none	none
471	1217	none	none	none
497	957	none	none	none
523	785	none	none	none
549	720	none	none	none
575	503	none	none	none
601	553	none	none	none
628	491	none	none	none
654	376	none	none	none
680	266	none	none	none
706	201	none	none	none

Norbornadiene: 1.0 mol/l cyclohexane solution.

^{a)} Central wavelength of incident light (15 nm in width).

^{b)} Quantum yield for quadricyclene production.

^{c)} Energy conversion efficiency η = (stored energy in the form of quadricyclene/incident energy), based on $\Delta H = 1190 \text{ J/g}$.³⁰⁾

^{d)} Byproduct yield = 100 (byproduct[g]/norbornadiene[g]).

Conclusions

The effect of wavelength on the quantum yield in the photosensitized isomerization of norbornadiene to quadricyclene, on the energy conversion efficiency and on the yield of byproduct polymer formation has been investigated by using several photosensitizers: toluene, acetone, acetophenone, benzophenone and α -naphthoquinone. The formation of byproduct polymers which prevent the repeated use of the energy-storage material was effectively suppressed by the addition of phenolic substances into norbornadiene. We are now carrying out large-scale solar energy conversion and storage experiments by using a 1-m² solar collector and 20 kg of norbornadiene solution with a photosensitizer and an inhibitor of side reaction.

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