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PHOTOISOMERIZATION OF 7-SUBSTITUTED NORBORNADIENE-CYCLODEXTRIN INCLUSION COMPLEXES

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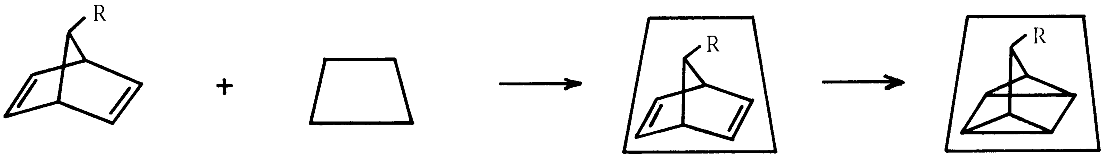
The photoisomerization of 7-substituted norbornadiene-cyclodextrin inclusion complexes, in which the substituents are t-butoxyl, acetoxyl, and hydroxyl groups, gave 7-substituted quadricyclene-cyclodextrin inclusion complexes.

Norbornadiene(NBD) is known as a promising energy storage material,$^{1)}$ but it has a well-known defect that it has no absorption bands corresponding to the solar light spectrum. Therefore the sunlight can not be used for photoisomerization of NBD without a photosensitizer. Another demerit lies in its disagreeable smell for the practical usage.

Many derivatives of NBD have been synthesized to get rid of such difficulties, and it is sure that the limited success was achieved to overcome such demerits.

We have also synthesized several NBD derivatives, as is shown below, but our main purpose of this report is to find another way of approach to the solution of these difficulties.$^{2)}$



1 cyclodextrin **2** **3**

1a: R=H; **1b**: R=OH
1c: R=OCOCH$_3$
1d: R=O(CH$_3$)$_3$

We have noticed that NBD and its derivatives can form clathrate compounds with several cyclodextrins(CD).$^{3)}$ The NBDs(**1a**-d) were included in β-CD and converted to the pulverized form, and had no smell any more. Table 1 shows the yields of inclusion complexes(**2a**-d) which were obtained when NBDs and β-CD were equimolecularly added.$^{4)}$

Figure 1 shows the ultraviolet absorption spectra of β-CD, NBD, and their clathrate. By inclusion no new absorption bands appeared. Therefore, photosensi-

Table 1. The yields of 7-substituted norbornadiene inclusion complexes

	R	Photosensitizer[a)]	β-CD-complexes Yield/%
1a	H	-	22.3
1a	H	Acetophenone	23.4
1b	OH	"	16.4
1c	$OCOCH_3$	"	17.9
1d	$OC(CH_3)_3$	"	50.7

a) 1a-1d: 5.7×10^{-3} mol, β-CD: 5.7×10^{-3} mol, acetophenone: 4.37×10^{-4} mol, in 350 ml water.

tizer was necessary for the practical photoisomerization.

Acetophenone was included as photosensitizer in the inclusion complexes by mixing with NBDs when the inclusion complexes were prepared. The spectrum of the inclusion complex 2a is shown in Fig. 1. At present, we do not know whether a NBD molecule and an acetophenone molecule occupied separate β-CD molecules or they were occasionally included in one β-CD molecule. But it was ascertained that acetophenone also formed clathrate with β-CD.

The irradiation was performed in the powder state of the inclusion complexes. The results were shown in Table 2. The solar irradiation converted the guest molecules(1a-d) to quadricyclenes in 3a-d, and the effect of adding acetophenone was clearly observable in Table 2. In this case the samples were spread thinly in a Petri dish in air.[5)] The quadricyclenes produced were included in the cave of β-CD as guests, because pure quadricyclenes were confirmed to form clathrates with β-CD(when the corresponding quadricyclenes and β-CD were equimolecularly added, the yields of 3a-d were 12-72%).

Figure 2 shows the change of yield of 3a and the efficiency of energy utilization on irradiation of 2a. The 340 nm light from spectroirradiator (Jasco CRM-FA) was used for the experiments. Since the powder was not stirred, the rate of conversion decreased with time and reached a constant value. But the quantum yield for the conversion seemed to be nearly equal to that of the naked NBD.[6)]

The dependency of the quantum yield on the wavelength of Xenon light is shown in Fig. 3. Wavelength up to 390 nm was effective for converting 2a

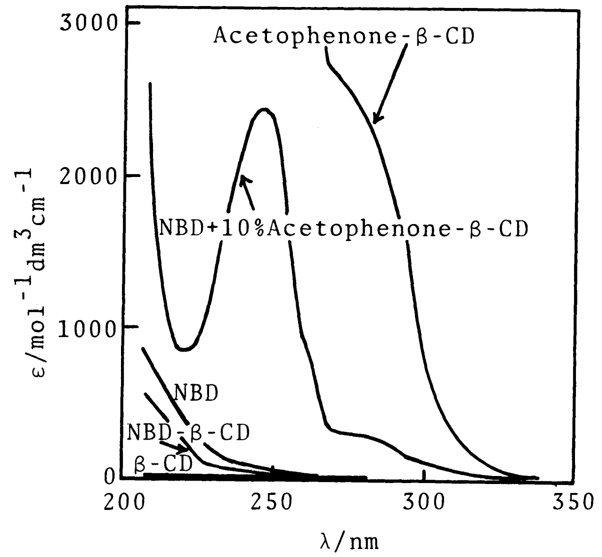


Fig. 1. UV spectra of inclusion complex.

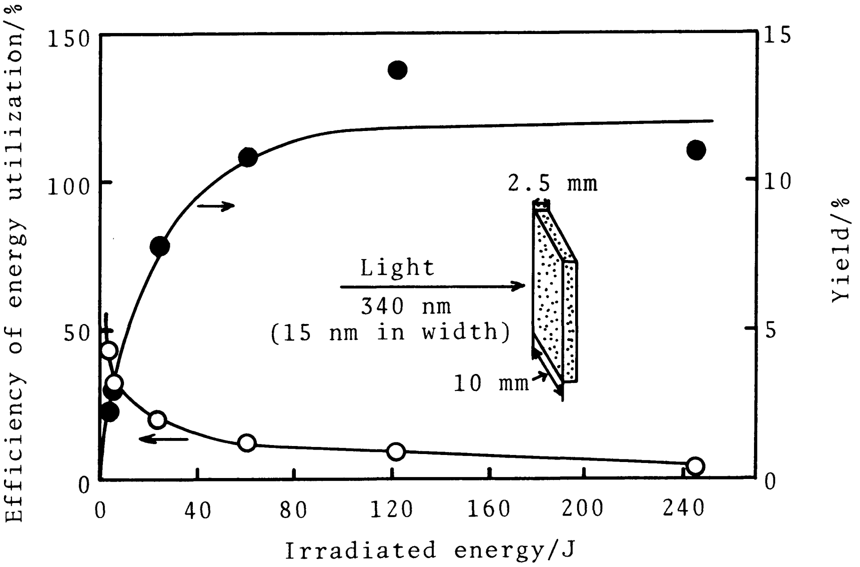


Fig. 2. The change of yield of 3a and the efficiency of energy utilization on irradiation of 2a: the efficiency of energy utilization = quadricyclene(mol)/photon(mol).

to 3a. The quantum yield was calculated at 20 J irradiation(Fig. 2).

The value of the quantum yield was about a half or one third of those of the naked NBD. The reflection by powder hampered the intrusion of light into the inside direction, while the inherent quantum yield may not change whether NBD is included or not, as Fig. 2 shows.

Since the inclusion complex 2a was soluble in water, the photoisomerization of guest NBD was also achieved in an aqueous solution(Table 2). Similarly, the photoisomerization reaction could be performed in fluid state by using water suspension without side reaction. Therefore, the NBDs 1a-d included in β-CD were found to be photoisomerized to the corresponding included quadricyclenes in the solid state, in the aqueous solution, and also in the water suspension.

Table 2. Photoisomerization of 7-substituted norbornadiene-β-cyclodextrin inclusion complexes under solar irradiation.

	R	Time/h	Quadricyclene/%	Remarks
2a	H	7 (May '83)	3.4	a)
2a	H	7 (May '83)	2.2	a)
2a	H	7 (Oct.'82)	26.2	b)
2a	H	6 (Oct.'82)	39.8	b)
2a	H	6 (Oct.'82)	9.4	c)
2b	OH	6 (Jan.'83)	22.3	b)
2c	$OCOCH_3$	6 (Jan.'83)	17.2	b)
2d	$OC(CH_3)_3$	6 (Jan.'83)	4.9	b)

a) No sensitizer. b) Acetophenone was included when the complex was prepared(See Table 1). c) Aqueous solution of 2a was irradiated.

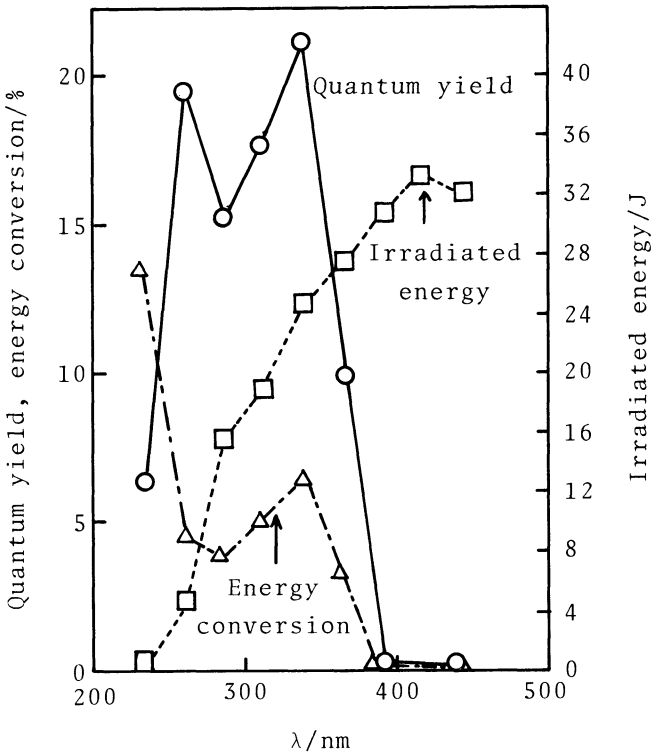


Fig. 3. Quantum yields for the conversion of norbornadiene-β-CD to quadricyclene-β-CD.

The reverse exothermic reaction also proceeded likewise in the presence of appropriate catalysts, which will be reported separately.

Another problem is the migration of excitation energy. The fact that the addition of small amount of acetophenone was effective for conversion of **2a** to **3a** with high yield would suggest that the excitation energy was transferred through fairly large distance. We are now trying to make a modified CD which is effective for long range photosensitization of NBD, according to this principle.

References
1) R. R. Hautala, J. Little, and E. Sweet, Solar En., 19, 503 (1977).
2) T. Yumoto, K. Hayakawa, K. Kawase, H. Yamakita, and H. Taoda, US pat. 584739 (1984).
3) D. C. Rideout and R. Breslow, J. Am. Chem. Soc., 102, 7816 (1980).
4) A mixed solution of 0.52 g of NBD and 0.05 g of acetophenone was poured into 350 ml of the saturated aqueous solution of β-CD with stirring. The precipitated crystals were separated by filtering and dried.
5) The powdery inclusion compound was uniformly spread in the quartz cell(2.5x10x40 mm) and exposed to 340 nm light.
6) H. Taoda, K. Hayakawa, and K. Kawase, Proceedings of the Eighth Biennial Congress of the International Solar Energy Society, 2038 (1983).

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