

Solar Energy Storage: A Possible Use of Inclusion Compounds

A. GUARINO*, E. POSSAGNO, and R. BASSANELLI

Istituto di Chimica Nucleare, C.N.R., C.P. 10, I-00016 Monterotondo Stazione, Rome, Italy

(Received: 13 May 1986; in final form: 21 January 1987)

Abstract. Valence isomerization of norbornadiene to quadricyclene has been studied under different experimental conditions in order to develop a suitable system for solar energy storage.

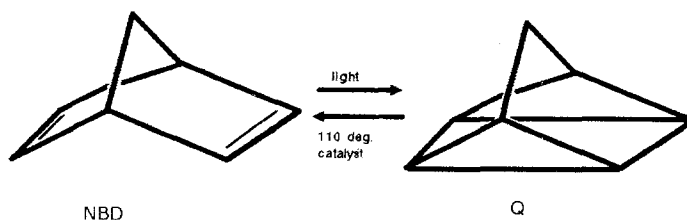
In particular, a device has been tested which exploits the sorbent properties of many inclusion compounds; norbornadiene and a suitable sensitizer are eluted through a column containing deoxycholic acid, under solar irradiation. The observed ratio of yield of quadricyclene vs. by-products is significantly favourable with respect to an analogous solar irradiation of norbornadiene and sensitizer in solution.

Key words: Inclusion compound, norbornadiene, quadricyclene, solar energy storage, photoisomerization, adsorption properties.

1. Introduction

Inclusion compounds are rather flexible systems, useful for a large variety of scientific and technological applications [1]. In particular, several phototransformations of molecules included as guests in specific hosts have been carried out [2, 3].

The present communication reports on a rather unusual use for an inclusion compound: the isomerization of norbornadiene to quadricyclene in the channels of deoxycholic acid, under solar irradiation. The interest for such a photoisomerization stems from the suggestion [4] of employing this process as part of a 'solar pump' able to store solar energy according to the process:



where NBD denotes norbornadiene and Q quadricyclene; the catalyzed back-reaction releases useful thermal energy.

Unfortunately, when this reaction is carried out in solution a large amount of by-products is formed during NBD conversion with a consequent decrease of the overall efficiency of the process. However, if the NBD isomerization is carried out

* Author for correspondence.

in the channels of deoxycholic acid (DCA) by exposing the crystals of the inclusion compound to solar light, a significant decrease has been observed in the amount of by-products formed in solution, (e.g. cyclo-hepta-1, 3, 5-triene, 6-methylfulvene and polymers) due to the steric hindrance imposed by the host lattice on the norbornadiene rearrangement to bulky molecules in comparison to its valence isomerization.

Given that NBD undergoes direct absorption of solar energy rather weakly, a second guest has been included as a sensitizer, i.e., pinacolone (3,3-dimethyl-2-butanone): this specific sensitizer has been chosen because it does not disturb the host cavity environment, as shown by X-ray studies [7].

However, to use an inclusion compound advantageously as part of a solar energy "pump" it is necessary to expose NBD and pinacolone in DCA to solar irradiation, to recover the reaction mixture and let the quadricyclene formed to react with a suitable catalyst to re-convert it to NBD with useful thermal energy release; at this point the system is ready for a new cycle.

In order to achieve this goal a well known property of inclusion compounds has been exploited, i.e., the sorbent ability of many of them, which is often used for separation of organic mixtures [8].

2. Experimental

2.1. MATERIALS

All materials were purchased commercially and further purified by VPC.

2.2. METHODS

(a) *Solution experiments:*

NBD or NBD and pinacolone were irradiated in spectral grade hexane and analyzed by VPC.

(b) *Inclusion compound on quartz-plate:*

The inclusion compound was prepared by adding to a methanolic solution of deoxycholic acid NBD or NBD and pinacolone. The crystals were washed with benzene, dried and exposed to sun between two quartz plates at a known separation. After irradiation the crystals were dissolved in methanol and analyzed by VPC.

(c) *Inclusion compound on column:*

A specific device has been used consisting of a pyrex column of suitable length and size with a hollow annular compartment filled with DCA: the column is joined by means of valves at its top with a reservoir containing NBD, pinacolone and a solvent inert to solar irradiation and at its bottom with a "catalytic chamber" which contains a Cu complex adsorbed on a zeolite-like material of suitable pore size. This chamber is surrounded by a water jacket equipped with temperature sensors. At the bottom of the catalytic chamber a second reservoir collects the eluted reaction mixture; this reservoir is then swapped with that placed at the top of the DCA containing column in order to repeat the process. The device is sketched in Figure 1.

In all cases the irradiation doses were carefully measured by a Lintronic solarimeter, (54, Bartholomew Close, London).

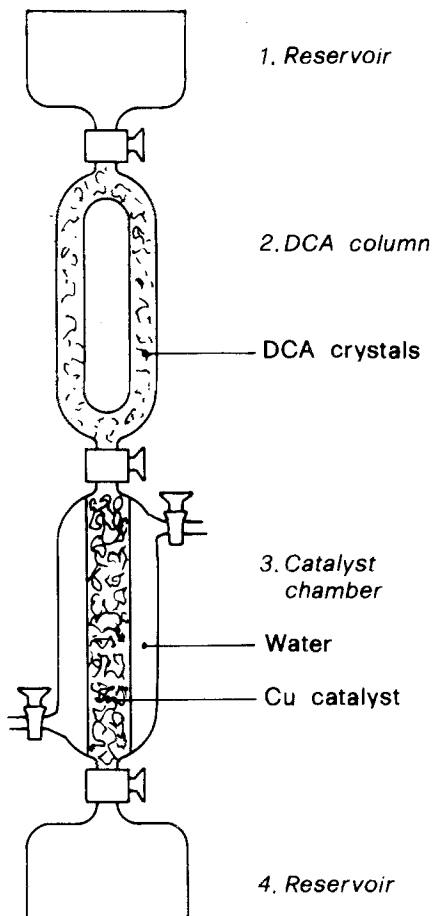


Fig. 1. (1) Reservoir containing NBD and pinacolone in hexane; (2) DCA crystals in the annular space of the column; only this section is exposed to sunlight; (3) the inside of the column is filled with a Cu complex adsorbed on a zeolite-like polymer; (4) reservoir containing the eluted reaction mixture. The various parts of this device are joined through detachable valves which control the flow of the liquids.

3. Results and Discussion

Table I reports the values of the observed conversion yields; in particular, the following results deserve comment:

- (i) The NBD isomerization to Q increases, at any dose, when pinacolone is present.
- (ii) When the system NBD and pinacolone is irradiated in hexane solution its conversion to Q is larger by a factor of 1.3 with respect to its irradiation as an inclusion compound on a quartz plate and lower by a factor of 1.6 with respect to its irradiation on a DCA column, which corresponds to the best obtained valence isomerization of the norbornadiene.
- (iii) When the system NBD and pinacolone is irradiated in hexane solution the yield of by-products is larger by a factor of 5.4 with respect to its irradiation as an inclusion compound on a quartz plate and larger by a factor of 3.8 with respect to its irradiation on a DCA column.

Table I. Solar irradiation of norbornadiene

System	Solution (hexane)	Q yield ^a		By-products yield ^a		
		DCA on quartz plate	DCA in pyrex column	Solution (hexane)	DCA on quartz plate	DCA on pyrex column
NBD	5.6	2.6	4.9	10.3	13.3	15.5
NBD + pinacolone	11.0	8.7	18.1	82.2	15.2	21.4

^a Calculated as % transformation of the starting norbornadiene, at a dose of 33.1 KW hr m⁻².

The decrease of "protection" towards the formation of by-products is a consequence of the different role of deoxycholic acid, passing from a crystalline inclusion compound to a sorbent phase: in the latter case the isomerization process occurs partly outside the host cavities with a larger probability of formation of bulky isomerization products; however, this unavoidable effect matches the significant increase of quadricyclene formation.

It is worth noting that the comparisons based on the data in Table I are qualitative: in fact, even though the incident light intensity is equal for the various systems studied, the actual number of photons absorbed depends on factors difficult to account for, like the amount of light scattering, the sample pathlength, etc.

Quite obviously, the sketched device is by no means a working model of a solar pump but a flexible and expedient system to test the various aspects of such a pump. For instance, the possibility of using columns of different shapes and sizes to expose to sun is under investigation; the use of other inclusion compounds as absorbent phases, e.g. NI(II)(4-picoline)₄(NCS)₂ and tri-*ortho*-thymotide is also being studied; analogously, norbornadiene and pinacolone will be replaced by substituted norbornadienes bearing solar energy absorbing chemical groups, in order to avoid the addition of sensitizers.

4. References

1. J. L. Atwood, J. E. D. Davies and D. D. MacNicol, (eds.): *Inclusion Compounds*, vol. 1-3, Academic Press, London (1984).
2. K. Hirao, A. Ando, T. Hamada, and O. Yonemitsu: *J. Chem. Soc., Chem. Commun.* 300 (1984).
3. A. Guarino, G. Occhiucci and A. Patacchiola: *J. Photochem.* **12**, 147 (1980).
4. R. R. Hautala, J. Little, and E. Sweet: *Solar Energy* **19**, 503 (1977).
5. R. Bassanelli and E. Possagno: *Proceedings of Xth IUPAC Symp. on Photochemistry*, Interlaken (CH), pp. 337 (July 1984).
6. R. Bassanelli and E. Possagno: *Proceedings of the XIIth Int. Conf. on Photochemistry*, Tokyo (Japan), pp. 509 (August 1985).
7. V. M. Coiro, F. Mazza, G. Pochetti, E. Giglio, and N. V. Pavel: *Acta Crystallogr.* **C41**, 229 (1985).
8. D. Sybilska and E. Smolkova-Keulemansova, in ref. [1], Vol. 3, p. 173.