Possibility of Photochemical Energy Storage in the Norbornadiene - Quadricyclane System. Part II

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Abstract

Sensitization effect of an organic sensitizer propiophenone in the photoisomeric system norbornadiene - quadricyclane was investigated. Experimental data on the N - Q conversion for various concentrations of the sensitizer and irradiation times were given. Results confirmed a proposed kinetic model.

1.INTRODUCTION

Photorearrangement reaction of valence isomers norbornadiene (N) - quadricyclane (Q) is endoergic ($\Delta G > 0$), reversible and kinetically inert at ambient temperature (Scheme 1). These characteristics make it interesting and attractive as a potential mean for storage of light energy [1,2], especially, because some other criteria for practical use are fulfilled.



Scheme 1. The norbornadiene - quadricyclane photochemical system

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Specific capacity for energy storage is large ($\sim 10^6$ J/kg), as well as the reaction quantum yield when sensitization is performed. Simple initiation (thermal or catalytic, Δ) of the reverse reaction makes possible a complete and closed cycle available for an active solar system for storage energy of a non-thermal part of the solar spectrum.

Norbornadiene weakly absorbs in a shortwave region of the spectrum, bellow 230 nm [3]. This drawback can be eliminated by addition of a sensitizer, a molecule that takes part in a reaction only indirectly as a transferor of the excitation energy, or by incorporation of appropriate substituents into the norbornadiene molecule, which induces a bathochromic spectral shift.

Action of organic sensitizers is amply investigated in photochemistry [4].

In the present paper the N - Q isomerization reaction was studied at several propiophenone concentrations and irradiation times. The norbornadiene concentration was kept constant, $c_N=0.5$ M, chosen on the fact [5] that the quantum yield above this concentration changes little and gradually. Experimental data allow kinetic examination of the sensitization reaction.

2.EXPERIMENTAL

Experiments were carried out in the photochemical apparatus UV 17 F Helios Italquartz. It consists of the low pressure Hg lamp, ATE 215 M introduced into a quartz sheathing, which is centrally mounted through the grounded glass joint into a three-necked cylindrical photoreactor. The reactor was equipped with a Liebig condenser, thermometer and a nitrogen - inlet line for removing air atmosphere from the reactor. Stirring was performed with a magnetic stirrer.

The whole reactor was immersed into the water bath at the temperature up to 6° C, whereas the upper part of the apparatus (lamp socket) was cooled by an air stream.

A number of photons emitted during experiments in the ten milliliter photoisomeric system was determined by an actinometric experiment [6] in the reproducible region of the lamp operation, and yielded 7.740×10^{-6} Ein/min.

Chemicals (E.Merck - Darmstadt) commercially delivered, unpurified (p.a., z.Synth.) were used. Cyclohexane as a solvent was inert and transparent, although rather volatile.

Gas chromatographic analyses were carried out with a Hewlett-Packard gas chromatograph, HP 5890 Scrics II. The chromatograph was equipped with split/splitless injector, a fused silica capillary column (i.d. =0.32 mm, L=25 m), coated with cross linked methyl silicone gum (HP-1), and a flame ionization detector. Data acquisition and processing were performed by a HP Vectra QS 16S data station using a HP 3365 ChemStation software.

3.RESULTS AND DISCUSSION

3.1. Effect of the sensitizer concentration on the N - Q conversion

Photochemical conversion of norbornadiene to quadricyclane by 254 nm radiation was investigated in cyclohexane solutions, containing 0.02, 0.1, 0.3, 0.5 and 1.0 moles per liter of propiophenone. Norborndiene concentration was kept constant $c_N=0.5$ M. Irradiation times were 1, 3, 10, 30 and 90 minutes.

Experimental data on the N - Q conversion expressed as the millimolar concentration of quadricyclane, c_Q , produced by an action of corresponding mole number of photons, $n_{h\nu}$, (which is strictly proportional to irradiation time) are shown in Figure 1.



Figure 1. Log-log plot of quadricyclane, c_0 , vs. number of photons, $n_{h\nu}$

A series of straight lines is obtained. It can been seen that conversion increases with rising the propiophenone concentration up to 0.3 M, while for higher sensitizer concentrations it does not change significantly. At this limiting value the light absorption is complete.

3.2. Kinetic equation

Photochemical isomerization in the system $A \rightarrow B$, sensitized with a sensitizer S, can be represented as follows:

$$S \xrightarrow{hv} S$$
 (1)

$$S \xrightarrow{k_f} S$$
 (2)

$${}^{1}S \xrightarrow{k_{isc}} {}^{3}S \tag{3}$$

$$S \land \frac{k_t}{k_t} > A S$$
 (4)

$$A \xrightarrow{k_r} B \tag{5}$$

$$A \xrightarrow{k_p} A \tag{6}$$

The sensitizer S absorbs photons and turns into the singlet state, ${}^{1}S^{*}$. It can deactivate to its ground state by fluorescence or convert through the process of intersystem crossing into a corresponding triplet state, ${}^{3}S^{*}$. The latter transfers energy to the molecule A or deactivates to the ground state by phosphorescence. The molecule A may transform to the energy-rich (strained) isomer B or deactivate through the process of phosphorence. The processes of fluorescence, intersystem crossing, energy transfer from the sensitizer to the molecule A, isomerization reaction and phosphorescence are characterized with the rate constants k_{f} , k_{isc} , k_{t} , k_{r} , k_{p} , respectively.

Taking into account all these processes and applying quasi-steady state hypothesis with respect to concentrations of activated species $[A^*]$ and $[S^*]$, the following equation for the production of B or consumption of A can be obtained

$$\frac{dc_B}{dt} \frac{k_t k_r}{k_r k_p} \frac{Ic_A}{(k_{isc} k_f) k_t c_A}$$
(7)

Assuming that the energy transfer from the sensitizer to the molecule A is the rate controlling step, $(k_{isc} + k_f) >> k_t c_A$, the rate equation becomes first order with respect to [A]

$$\frac{dc_{B}}{dt} = \frac{k_{t}k_{r}}{k_{r}+k_{p}} \frac{Ic_{A}}{k_{isc}+k_{f}}$$
(8)

or, after integration

$$-\ln\left(1-x_{a}\right)=kIt\tag{9}$$

where x_A represents the fractional conversion of norbornadiene to quadricyclane, I - intensity of the radiation used.

Dependence of the norbornadiene concentration, expressed as fractional conversion x_{A_1} on the reaction time, according eq.9, is given in Figure 2.



Figure 2. Dependence of norbornadiene conversion on reaction time for different sensitizer concentrations

It can be seen that for propiophenone as the sensitizer the reaction is the first order with respect to norbornadiene concentration, that is in an agreement with the rate equation derived. Results confirm that the rate of the sensitization reaction [7] is controlled by the rate of energy transfer from propiophenone to norbornadiene and not by intersystem crossing of fluorescence.

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