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INSOLUBLE CATALYST FOR HEAT-GAIN IN A WATER-SOLUBLE SOLAR ENERGY STORAGE SYSTEM

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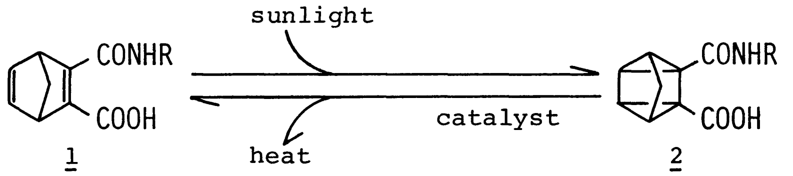
By action of insoluble catalysts, cobalt tetraphenylporphyrin or cobalt phthalocyanine adsorbed on activated carbon, water-soluble quadricyclane derivative was isomerized to norbornadiene derivative under release of heat in an alkaline solution. The activities of these insoluble catalysts were as high as those of water-soluble catalysts.

Solar energy storage based on the valence isomerization has attracted much attention from the viewpoint of the exploitation of renewable energy resources. The most important point is that desirable amounts of stored solar power can be released at any occasion. Valence isomerization between norbornadiene and quadricyclane is one of the most hopeful systems for solar energy storage. Therefore, this system has been studied by many chemists.1) Many soluble catalysts applicable for the exothermic reaction of quadricyclane to norbornadiene have been investigated.1,2) Soluble catalysts, however, have two inevitable disadvantages: i) isomerization reaction by soluble catalysts is hard to control; ii) soluble catalysts can hardly be free from quadricyclane in photoisomerization reservoir, and under the conditions heat-releasing back reaction occurs at an undesirable time. A few insoluble catalysts immobilized a soluble catalyst on a support were reported,1a,2b,3) but activities of the immobilized catalysts were much lower than those of the corresponding soluble catalysts. In our previous paper,4) a water-soluble solar energy storage system was reported (Fig. 1). Stable but energy rich quadricyclane derivative 2 was isomerized to norbornadiene derivative 1 by action of a water-soluble cobalt porphyrin complex. Here, we shall report highly efficient, easily available, and insoluble catalysts for a



(1a:R=Ph;1b:R=CH_3) (2a:R=Ph;2b:R=CH_3)

Fig. 1. A water-soluble solar energy storage system.

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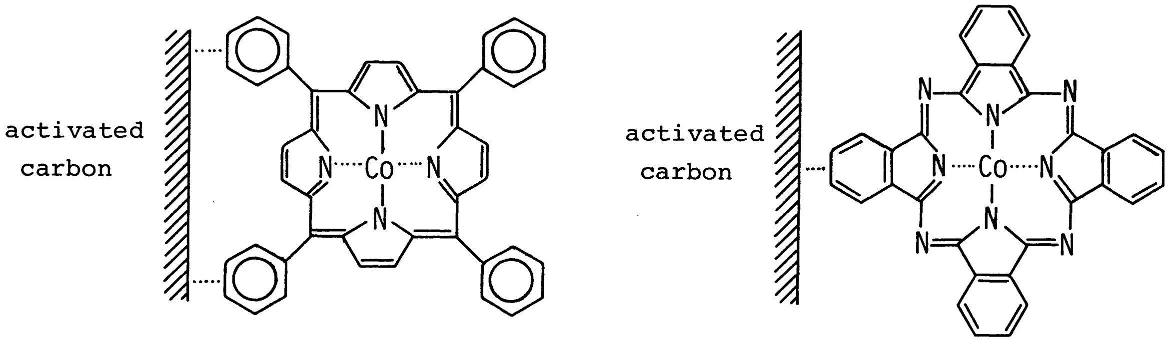
We synthesized insoluble catalysts 3a, b (Fig. 2) as follows. Activated carbon (Darco G-60) was added into a tetrahydrofuran solution of cobalt tetraphenylporphyrin (Co-TPP) and the suspension was refluxed for several hours. After cooling, Co-TPP adsorbed on activated carbon (3a) was filtered and dried. In a similar manner, cobalt phthalocyanine (Co-Pc) adsorbed on activated carbon (3b) was prepared by stirring at room temperature instead of reflux.

Quadricyclane derivative 2 was so stable even in a boiling aqueous sodium carbonate solution, but by addition of the insoluble catalysts 3a, b in the solution at room temperature, compound 2 was quantitatively isomerized to the isomer 1 under release of heat even in the presence of air. After the completion of the isomerization, the used insoluble catalyst was recovered by filtration and the filtrate containing only norbornadiene derivative 1 was used for the photoisomerization. No leak of Co-TPP or Co-Pc from 3a or b to the solution was detected because of strong adsorption of cobalt complexes on activated carbon. The catalytic reaction rate was proportional to the amount (weight used) of the insoluble catalyst (Fig. 3) and was pseudo-first order as well as that in the



3a 3b

Fig. 2. Insoluble catalysts 3.

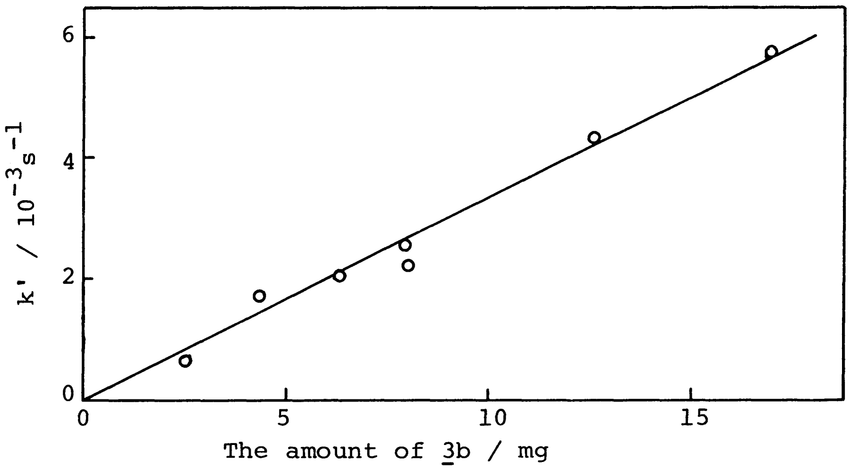


Fig. 3. Rate constant k' a) dependent on the amount of 3b. b)

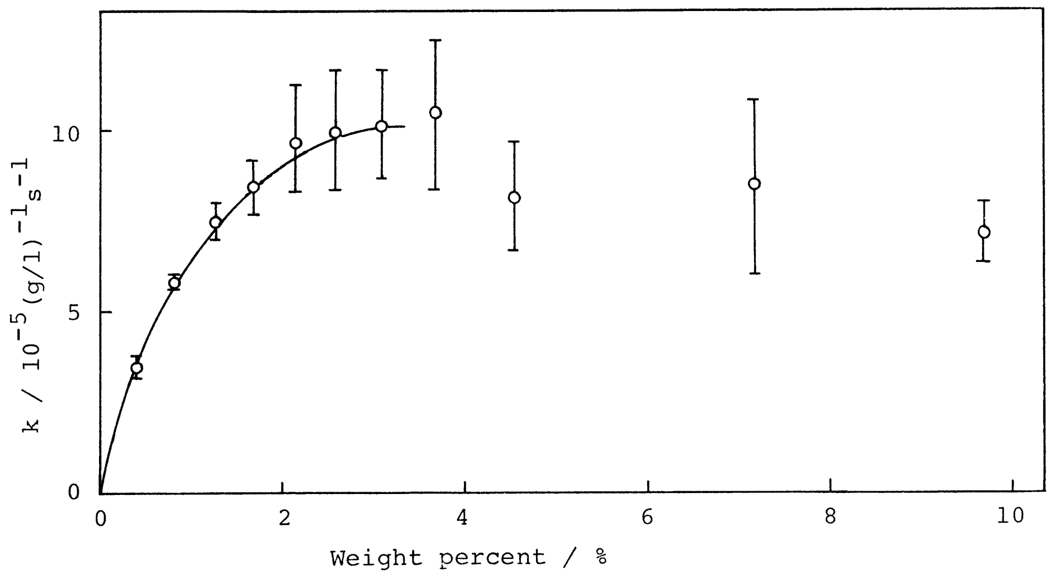
a) In the case of catalytic isomerization of 2b to 1b in 0.3 ml Na_2CO_3 aq., at 25 °C ([2b]=0.2 mol/l).
b) Co-Pc/Darco G-60=22 mg/1 g.

isomerization reaction by a water-soluble catalyst. The pseudo-first order rate constants of the isomerization are tabulated in Table 1. From Table 1, the activity of insoluble 3a is as high as that of soluble Co-TPPS and the activity of insoluble 3b is much higher than that of soluble Co-PcS in spite of its less movability. This reason may be due to the following. Co-PcS is easy to aggregate in water but Co-TPPS can hardly aggregate,[5)] and so Co-PcS in water has lower activity than Co-TPPS. In the case of insoluble catalyst, both Co-TPP molecules in 3a and Co-Pc molecules in 3b cannot aggregate because of their immobilization on activated carbon. Monomeric Co-Pc molecules in 3b were more effective for the isomerization than aggregated Co-PcS. From Fig. 4, we can estimate that the layer of Co-Pc on activated carbon (Darco G-60) is in the state of monolayer up to about 1.5 weight percent. These are supported by the fact that crystals of Co-TPP and Co-Pc had no activity themselves in a water-soluble system because of the complete aggregation.

Table 1. Rate constant k a) of 2a to 1a in Na_2CO_3 aq.

Catalyst	$k/(g/l)^{-1}s^{-1}$	$k/(mol/l)^{-1}s^{-1}$
3a b)	$(5.6 \pm 1.1) \times 10^{-5}$	13 ± 3
3b c)	$(2.1 \pm 0.6) \times 10^{-5}$	3 ± 1
Co-TPPS d)	——	10
Co-PcS e)	——	0.03

a) The values were measured by NMR technique at 25 °C([2a]=0.1 mol/l). b) Co-TPP/Darco G-60 = 2.8 mg/1 g. c) Co-Pc/Darco G-60 = 4.0 mg/1 g. d) Cobalt tetra-(p-sulfophenyl)porphyrin.
e) Cobalt phthalocyanine monosulfonic acid; dye, C.I.74140.



a) In the case of catalytic isomerization of 2b to 1b at 25 °C ([2b]=0.2 mol/l).

Fig. 4. Rate constant $k^{a)}$ dependent on weight percent of Co-Pc on activated carbon.

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