Exothermic Isomerization of Water-soluble Quadricyclanes to Norbornadienes by Soluble and Insoluble Catalysts

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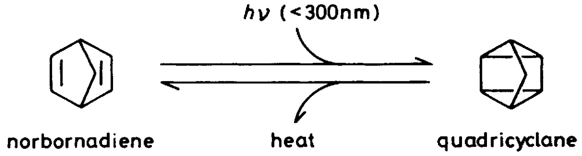
Water-soluble quadricyclane derivatives (**1**) were stable in an aqueous sodium carbonate solution, but addition of a catalytic amount of water-soluble cobalt porphyrin complexes (**3**) induced rapid and quantitative isomerization of (**1**) to norbornadiene derivatives (**2**) under release of heat. Insoluble catalysts (**4**) prepared by adsorption of Co-TPP† or Co-Pc on activated carbon were similarly active as the soluble analogues. They were stable enough to keep high activities for recycling use.

Valence isomerization between norbornadiene and quadricyclane is of much interest as a means of solar energy storage.[1–4] The system consists of two processes: (i) endothermic photoisomerization, and (ii) exothermic reverse isomerization. For (i), much effort has been applied to enable norbornadiene to absorb sunlight efficiently.[5] For (ii), many workers have examined a great many catalysts and have found that some induce rapid quantitative isomerization of quadricyclane to norbornadiene.[2,3,6,7] Efficient catalysts include metal compounds (Fe,[2] Co,[2,4,8] Ni,[2,3,9–11] Mo,[10,12] Rh,[2,3,11,13–16] Pd,[3,14–18] Ag,[15,19,20] Sn,[18,21] W,[12] Pt,[3,14] and Hg[22]), oxidizing reagents,[23] acids,[20,24] and others.[25] Most of them are soluble in reacting media, and for such soluble catalysts a great many practical difficulties have to be overcome: (i) control of the reaction, and (ii) recovery of the catalyst for recycling. Insoluble catalysts have therefore been studied to avoid the above problems. These were $SnCl_2$,[26] $CuSO_4$,[26] SiO_2,[20] Al_2O_3,[27] and industrial solid acids[24] including Co,[8c,28] Pd,[29] and Sn[21] salts immobilized on several supports (cross-linked polystyrene or aluminium oxide). However, the activities of the insoluble catalysts were generally low and the immobilized catalysts had much lower activities than the corresponding soluble catalysts. In all of the catalytic isomerizations investigated so far, organic solvents were used. This is a practical disadvantage because of their flammability, toxicity, and expense; to overcome this we first tried water as the reacting medium. However, water is apt to react with the cyclopropane or cyclobutane ring of the quadricyclane molecule.[16,30] Almost all of the catalysts reported so far were not only unstable in water[31] but also induced addition of water to the quadricyclane moiety.[10] In order to avoid such difficulties, we selected the combination of stable water-soluble quadricyclane derivatives (1) and water-insoluble cobalt porphyrin complex catalysts. Water-insoluble cobalt porphyrin complexes were adsorbed on activated carbon. The activities of the water-insoluble catalysts were higher than those of the corresponding soluble catalysts. The above findings were outlined in preliminary reports,[32] and we now report the details in this paper. Factors controlling activities and stabilities of insoluble catalysts were examined.

Results and Discussion

We prepared quadricyclanes (**1**) in which carboxyl and amido groups were introduced to one of the two sides of quadricyclane molecule.[4,5a] The compounds (**1**) were so stable in aqueous sodium carbonate solution that we could induce no thermal isomerization of (**1**) to the norbornadienes (**2**), no hydrolysis of amides (**1**) to acids and amines,[33] and no addition of water to (**1**),[16,30] even at reflux temperature (4 h). We searched for a catalyst which would induce the rapid isomerization of (**1**) to (**2**). The catalyst should be stable, but should induce rapid



isomerization in water without affording by-products (solvent adducts,[10,15,16,19b] catalyst adducts,[19b,25b] dimers,[9a,13b] and polymers[12]). We found that water-soluble cobalt porphyrin complexes (**3**) satisfied the above requirements. For example, when a catalytic amount of Co-TPPC (**3c**) was added to an aqueous sodium carbonate solution of (**1a**), (**1a**) suddenly and quantitatively isomerized to (**2a**) with the release of heat, even in the presence of air.[34] The isomerization rate was first-order for (**1**), but the observed first-order rate constant was proportional to the initial concentration of (**3**). This means that the total reaction was pseudo-first-order. Therefore, the reaction could obey a Michaelis–Menten mechanism under the condition that the Michaelis constant K_m was much larger than the concentration of (**1**) [equation (1)].[35]

$$(\mathbf{1}) + (\mathbf{3}) \underset{k_{-1}}{\overset{k_{+1}}{\rightleftharpoons}} (\mathbf{1})\cdots(\mathbf{3}) \xrightarrow{k_{+2}} (\mathbf{2}) + (\mathbf{3})$$

$$\begin{aligned} \mathrm{v} = -\frac{\mathrm{d}[(\mathbf{1})]}{\mathrm{d}t} &= \frac{k_{+2}[(\mathbf{3})]_0[(\mathbf{1})]}{K_m + [(\mathbf{1})]};\ [K_m = (k_{-1} + k_{+2})/k_{+1}] \\ &= \frac{k_{+2}[(\mathbf{3})]_0[(\mathbf{1})]}{K_m};\ (K_m \gg [(\mathbf{1})]) \\ &\fallingdotseq k[(\mathbf{3})]_0[(\mathbf{1})];\quad (k = k_{+2}/K_m) \end{aligned}$$

Equation (1)

From Table 1, it can be seen that the rate constant k of isomerization of (**1b**) to (**2b**) using catalyst (**3**) was slightly higher than that of (**1a**) to (**2a**) with the same catalyst. The catalytic activities of (**3a**—**c**) in an aqueous alkaline solution were nearly equal to that of Co-TPP in organic solvent and there was no difference among the rate constants in aqueous $NaHCO_3$, in aqueous Na_2CO_3, and in aqueous NaOH. Therefore, water, hydroxide anion, and carbonate anion did not

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† The following abbreviations are used in this paper; TPP = 5,10,15,20-tetraphenylporphyrin dianion, TPPS = 5,10,15,20-tetrakis-(*p*-sulphophenyl)porphyrin dianion, TPPC = 5,10,15,20-tetrakis-(*p*-carboxyphenyl)porphyrin dianion, TMPyP = 5,10,15,20-tetrakis-(4-*N*-methylpyridyl)porphyrin dianion, HP = hematoporphyrin dianion, Pc = phthalocyanine dianion, PcS_1 = monosulphophthalocyanine dianion, PcS_4 = 4,4′,4″,4‴-tetrasulphophthalocyanine dianion, PcC_4 = 4,4′,4″,4‴-tetracarboxyphthalocyanine dianion.

Table 1. Second-order rate constant k^a by soluble catalyst (**3**)

Soluble Catalyst		$k_{(1)\rightarrow(2)}/\text{M}^{-1}\ \text{s}^{-1}$	
		(**1a**) (R = Me)	(**1b**) (R = Ph)
Co-TMPyP	(**3a**)	4	10
Co-TPPS	(**3b**)	5	10
Co-TPPC	(**3c**)	3	7^b
Co-HP	(**3d**)	0.9	2
Co-PcS$_4$	(**3e**)	0.3	0.3
Co-PcS$_1$	(**3f**)	0.03	0.03
Co-PcC$_4$	(**3g**)	0.8	0.8
Co-TPP		8^c	6^d

[a] k was measured by means of ^{1}H n.m.r. {[(**1**)] = 0.1 M, in 0.5M-Na_2CO_3–D_2O, at 25 °C}. [b] See ref. 5. [c] In $CDCl_3$. [d] In CD_3COCD_3.

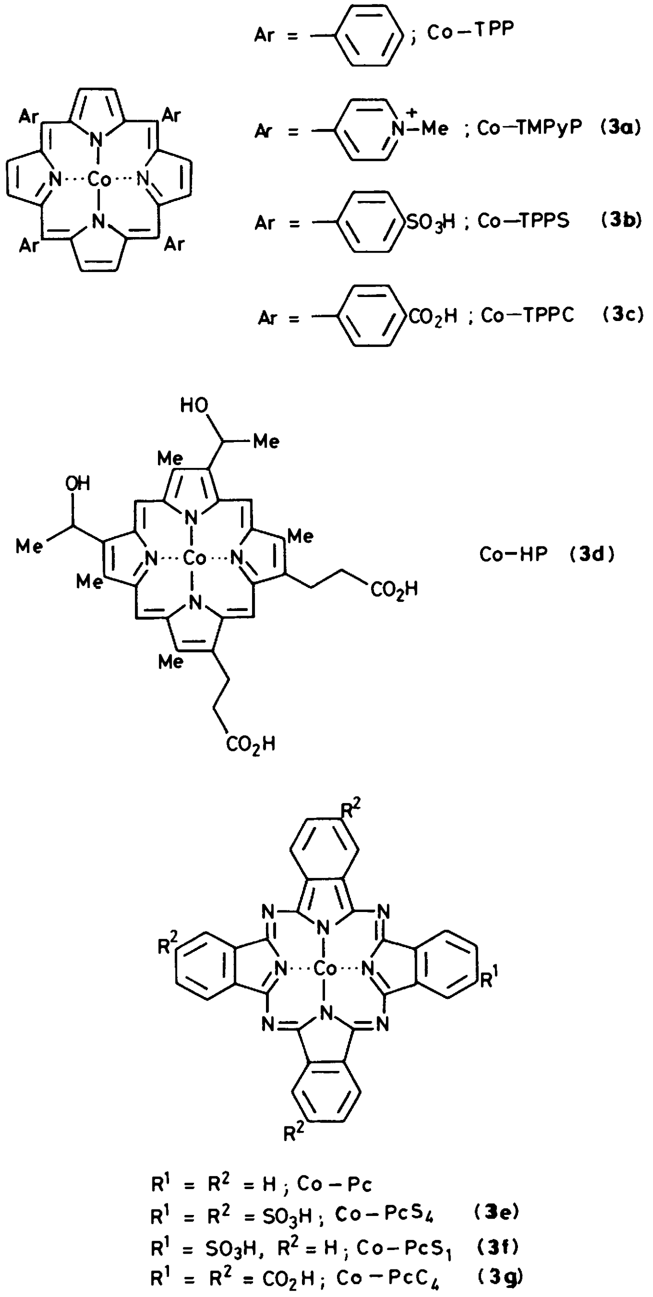
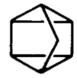
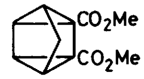
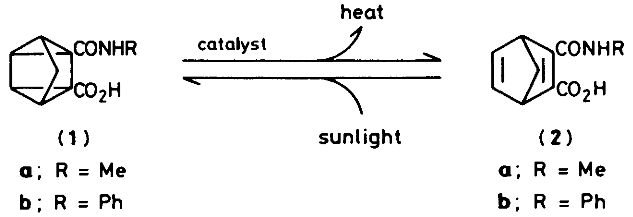


Figure 1. Catalysts

Table 2. Heat of isomerization $-\Delta H$ of quadricyclanes to norbornadienes

Quadricyclane	$-\Delta H$/kJ mol^{-1}	Conditions
(**1a**)	52 ± 4	Co-TPPC–aqueous NaOH
(**1b**)	59 ± 4	Co-TPPC–aqueous NaOH^a
(**1b**)	59 ± 2	Co-HP–aqueous NaOH
	81 ± 1 89 ± 1	Co-TPP–C_6H_6 thermolysis–toluene^b
	77 ± 1	thermolysis–toluene^b

[a] See ref. 4. [b] See ref. 37.



affect the catalytic isomerization. In aqueous ammonia, however, we observed very low activity, and in the water-soluble system, as reported in organic solvent by Manassen,[8a] addition of pyridine and 4-picoline suppressed the activity. 2-Picoline did not suppress the activity. Addition of compounds able to coordinate to the central metal (Co) interfered greatly with the catalytic isomerization. These facts indicate that the reactive sites of the water-soluble catalyst are the axial sites of the cobalt complex. The rate constant in the isomerization by cationic catalyst (**3a**) was equal to that in the isomerization by the anionic one, (**3b**). Thus, any electrostatic interaction between (**3**) and the anion of (**1**) could be small. On the other hand, the cobalt porphyrin complexes (**3a**—**d**) showed larger activities than the cobalt phthalocyanine complexes (**3e**—**g**). Catalysts (**3a**—**c**) possessing phenyl groups at the *meso* positions showed larger activities than (**3d**), whose *meso* positions were non-substituted. Similarly, cobalt complex (**3e**) having many polar substituents showed a higher activity than the less substituted (**3f**). Therefore, catalysts able to aggregate in water[36] showed lower activities.

By adding (**3c**) to a sodium hydroxide solution of (**1**), the heats of isomerization of (**1a**) to (**2a**) and that of (**1b**) to (**2b**) were confirmed to be 52 and 59 kJ mol^{-1}, respectively. These values are about 20 kJ mol^{-1} smaller than the heat of isomerization of quadricyclane to norbornadiene (determined in benzene solution using Co-TPP as the catalyst). This is reasonable, considering the fact that the heat of isomerization of dimethyl quadricyclane-2,3-dicarboxylate to dimethyl norbornadiene-2,3-dicarboxylate is about 10 kJ mol^{-1} smaller than that of quadricyclane to norbornadiene observed by thermolysis experiments[37] (see Table 2). Introduction of substituents onto the quadricyclane skeleton decreases the heat of isomerization.[38]

In order to increase activities and stabilities of catalysts as well as their availabilities, we tried to prepare insoluble catalysts by immobilizing cobalt porphyrin complexes. Several immobilizing methods with some varieties of several supports were examined (see Experimental section). It was found that adsorption on activated carbon (**4a**,**b**) was most effective. For example, when 2.6 mg of insoluble catalyst (**4a**) [Co-Pc/activated carbon (DIAHOPE) = 6.4 mg/l g] was added to 1 ml of 0.1M-(**1a**) in 0.5M-aqueous Na_2CO_3, the half life of (**1a**) was about 13 min at 25 °C [Co-Pc/(**1a**) = 1/3 400]. Insoluble catalysts have two

Table 3. Apparent second-order rate constant k and k'[a] with insoluble catalyst (4)

Insoluble catalyst		Co content/%	(1a) (R = Me) $k'/10^{-5}(g/l)^{-1}\ s^{-1}$	(1a) (R = Me) $k/M^{-1}\ s^{-1}$	(1b) (R = Ph) $k'/10^{-5}(g/l)^{-1}\ s^{-1}$	(1b) (R = Ph) $k/M^{-1}\ s^{-1}$
Darco G-60[b] ··· Co-Pc	(4a)	0.041	6.2 ± 0.7	8.8 ± 1.0	2.5 ± 0.2	3.5 ± 0.3
Darco G-60[b] ··· Co-Pc	(4a)	0.168	16.2 ± 0.5	5.7 ± 0.2	6.4 ± 1.8	2.3 ± 0.6
Darco G-60[b] ··· Co-TPP	(4b)	0.025	7.5 ± 0.2	17.9 ± 0.5	5.6 ± 1.1	13.5 ± 2.6
Darco G-60[b] ··· Co-TPP	(4b)	0.125	18.0 ± 0.6	8.5 ± 0.3	13.1 ± 1.0	6.2 ± 0.5
Amberlite 200C[c] ··· Co-TPP	(4c)	0.03			0.31 ± 0.02	0.61 ± 0.04
Amberlite 15[c] ··· Co-TPP	(4d)	0.06			0.19 ± 0.03	0.19 ± 0.03
Amberlite IRA-45[d] ··· Co-TPP	(4e)	0.27			0	0
Amberlite XAD-7[e] ··· Co-TPP	(4f)	0.05			0.29 ± 0.04	0.34 ± 0.05
Amberlite XAD-8[e] ··· Co-TPP	(4g)	0.09			0.42 ± 0.07	0.28 ± 0.05

[a] The rate constants k and k' were measured by means of ^{1}H n.m.r. {[(1)] = 0.1M, in 0.5M-Na_2CO_3–D_2O, at 25 °C}. [b] Activated carbon. [c] Sulphonated cross-linked polystyrene. [d] Aminomethylated cross-linked polystyrene. [e] Cross-linked polyacrylic ester.

advantages: (i) the isomerization reaction is easy to control, and (ii) after completion of isomerization the catalyst is easily separated from the solution to prevent undesirable further photoreactions. In addition, insoluble catalysts (**4a**) have two other merits, as follows: they are stable in aqueous alkaline solution and are easily prepared, the preparation procedure only requiring the stirring of the starting materials in tetrahydrofuran (THF) at room temperature. Since water-insoluble cobalt porphyrin complexes were adsorbed on activated carbon by hydrophobic bonding, we observed no detachment of the complexes from activated carbon during the reaction. Though the system using a water-insoluble catalyst was heterogeneous, it might be treated in approximation as a homogeneous one by vigorous stirring.* We thus investigated the kinetics.

The isomerization rate induced by (**4a**) could obey the Michaelis–Menten mechanism in which the product (2a) plays the role of competitive inhibitor [equation (2)].[35] It was

$$\textbf{(1a)} + \textbf{(4a)} \underset{k_{-1}}{\overset{k_{+1}}{\rightleftarrows}} \textbf{(1a)} \cdots \textbf{(4a)} \xrightarrow{k_{+2}} \textbf{(2a)} + \textbf{(4a)} \overset{K_i}{\rightleftarrows} \textbf{(2a)} \cdots \textbf{(4a)}$$

$$\mathrm{v} = -\frac{d[\textbf{(1a)}]}{dt} = \frac{k_{+2}[\textbf{(4a)}]_0[\textbf{(1a)}]}{K_m(1 + [\textbf{(2a)}]/K_i) + [\textbf{(1a)}]}$$

$$\fallingdotseq \frac{k_{+2}[\textbf{(4a)}]_0[\textbf{(1a)}]}{K_m + [\textbf{(1a)}]_0}; \ (K_m \sim K_i)$$

$$= k[\textbf{(4a)}]_0[\textbf{(1a)}]; \ [k = k_{+2}/(K_m + [\textbf{(1a)}]_0)]$$

Equation (2)

confirmed that the Michaelis constant K_m, the dissociation constant K_i, and k_{+2} were 62mM, 90mM, and 2.3 × $10^{-5}M(g/l)^{-1}\ s^{-1}$ respectively (**4a**; Co-Pc/Darco G-60 = 20 mg/l g, at 25 °C). The K_m of soluble catalyst (**3**) {$K_m \gg$ [(**1a**)]} is larger than that of the insoluble catalyst. This may reflect high adsorption ability of activated carbon used as a support. Since Michaelis constants $[(k_{-1} + k_{+2})/k_{+1}]$ are always larger than dissociation constants K_m' (k_{-1}/k_{+1}) of complexes between catalysts and substrates, the dissociation constant K_i (90mM) of a complex between (**2a**) and (**4a**) is larger than the dissociation constant K_m' (<62mM) of a complex between (**1a**) and (**4a**). This fact indicates that the co-ordination ability of quadricyclane derivative (**1a**) with the cobalt complex (**4a**) is about 1.5 times larger than that of norbornadiene derivative (**2a**) with (**4a**). The results are contrary to expectations, since it is known that silver ion complexes with olefins much more easily than with cyclopropyl compounds.[19a] When we simulated the reaction by using the observed values K_m, K_i, and k_{+2}, the initial reaction rate nearly obeyed pseudo-first-order kinetics; the observed initial rate was in fact pseudo-first-order within experimental error. Based on the above results we measured the apparent second-order rate constants. These are discussed below.

Unlike the reactions using (**3**), the rate constant of isomerization of (**1a**) to (**2a**) by catalyst (**4**) was slightly higher than that of (**1b**) to (**2b**) by the same catalyst (Table 3). By comparing the estimated rate constants of insoluble catalysts k ($M^{-1}\ s^{-1}$) with those of soluble catalysts, both soluble and insoluble cobalt porphyrins (**3a**—**d**) and (**4b**) showed nearly the same activities. But insoluble cobalt phthalocyanine (**4a**) showed higher activity than soluble catalysts (**3e**—**g**), in spite of its lower mobility.† The increased catalytic activity of cobalt phthalocyanine by adsorption on activated carbon may be due to the following. Water-soluble cobalt phthalocyanines (**3e**—**g**) easily aggregate, resulting in lower activities, but water-insoluble cobalt phthalocyanine (**4a**) cannot aggregate because of its immobilization on activated carbon. Since there is little difference between the activities of immobilized cobalt porphyrin (**4b**) and those of immobilized cobalt phthalocyanine (**4a**), cobalt phthalocyanine has essentially the same activity as cobalt porphyrin. In the case of the immobilized catalysts investigated so far, it has been reported that immobilization decreased the activities,[8c,21,28,29] but in our case the activity did not decrease.

Figure 2 shows that the rate constant k' reaches a maximum with increasing weight percent of Co-Pc on activated carbon. At about 1.5 weight percent of Co-Pc it apparently seems to be that all the surface of activated carbon is covered with Co-Pc. This is not true, however, because the activity showed no change by additional adsorption of copper phthalocyanine (Cu-Pc) which by itself showed no activity for the isomerization as given in Table 4. We may explain the saturation phenomenon by taking into consideration the fact that the number of contacts between (**1a**) and (**4a**) per unit time is limited and thus that the amount of (**1a**) which is able to isomerize to (**2a**) within unit time is limited,

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* Under a constant concentration of (**1**), the initial rate was proportional to the added amount of the insoluble catalyst per unit volume of the solution, *i.e.*, the initial estimated concentration of the insoluble catalyst $[(\textbf{4})]_0$.

† The water-insoluble cobalt complex had no activity, but adsorption of the complex onto an activated carbon support induced the catalytic activity. We have obtained maximum k, 29 $M^{-1}\ s^{-1}$ (**4a**; Co-Pc/DIAHOPE = 6.4 mg/l g) under the conditions of [(**1a**)] = 0.1M and 25 °C.

Table 4. The effect on the catalytic activity of (**4a**)[a] of the addition of phthalocyanine complexes

1st adsorption (weight %)	2nd adsorption (weight %)	$k'^{b}/10^{-5}$ (g/l)$^{-1}$ s^{-1}
0.5% Co-Pc	none	2.4
0.5% Co-Pc	3.0% Cu-Pc	2.1
0.5% Co-Pc	3.0% H_2-Pc	2.1
3.0% Co-Pc	none	9.6
3.0% Co-Pc	3.0% Cu-Pc	6.6
3.0% Cu-Pc	none	0
3.0% Cu-Pc	0.5% Co-Pc	3.4
3.0% Cu-Pc	3.0% Co-Pc	8.4

[a] Darco G-60 was used as the support. [b] k' of isomerization of (**1a**) to (**2a**) was measured by means of ^{1}H n.m.r. {[(**1a**)] = 0.2M, in 0.5M-aqueous Na_2CO_3, at 25 °C}.

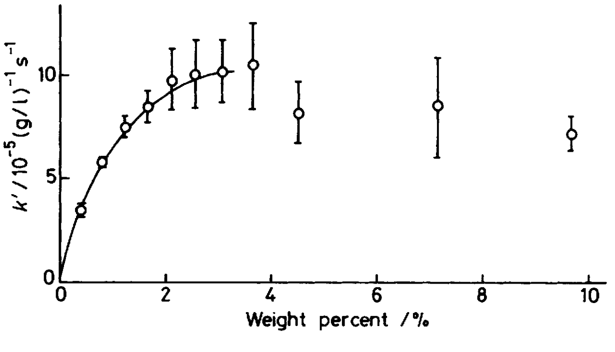


Figure 2. Apparent second-order rate constant k'^{a} dependent upon weight percent of Co-Pc on activated carbon

[a] k' of isomerization of (**1a**) to (**2a**) induced by (**4a**) (Co-Pc/Darco G-60) was measured by means of ^{1}H n.m.r. {[(**1a**)] = 0.2M, in 0.5M-Na_2CO_3–D_2O, at 25 °C}.

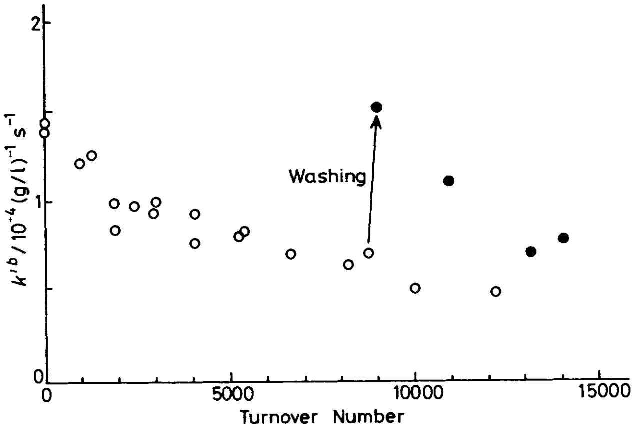


Figure 3. Recycling study on the insoluble catalyst (**4a**)[a]

[a] Co-Pc/Darco G-60 = 20 mg/l g. [b] k' of isomerization of (**1a**) to (**2a**) was measured by means of h.p.l.c. {[(**1a**)] = 0.1M, in 0.5M-aqueous Na_2CO_3, at 25 °C}. ○, original decay of catalytic activity. ●, decay of catalytic activity after washing by THF.

depending on the properties of the support. The rate constant k' of isomerization of (**1a**) to (**2a**) by (**4a**) reached a maximum at about 3 weight percent.

Immobilization allows us to recycle insoluble catalysts. We examined the stability and activity of (**4a**) after recycling. From Figure 3, the activity of (**4a**) decreased gradually with increasing turnover number. In fact, the activity of (**4a**) [Co-Pc/activated carbon (Darco G-60) = 20 mg/l g] fell to half in about 10^4 turnovers. However, simple washing of the used (**4a**) by refluxing THF fully recovered its activity. This indicates that a chemical change in the catalyst (oxidation of the central metal or the porphyrin ligand, and so on) is not responsible for the reduction of the activity, but that this may be due to adsorption of some inhibitors on the surface of (**4a**). The catalyst (**4a**) was so stable that no detachment of cobalt complexes from the support occurred, even over 1.5 × 10^4 turnovers. Bubbling air or oxygen into an aqueous suspension of (**4a**) affected the activity little, whereas the activities of the soluble catalysts (**3**) decreased significantly on similar treatment.[34]

As the catalyst supports, several ion-exchange resins (**4c,d**) and adsorbents (**4f,g**) could be also used instead of activated carbon. But the activities of the insoluble catalysts (**4c,d,f,g**) were lower than that of the corresponding insoluble catalyst (**4b**) (see Table 3). The other catalysts, such as (**4e**), adsorbed on supports having amino or pyridyl groups, showed no activity.

In addition, we examined a method of immobilization using covalent bonding. As the support, we used cross-linked polystyrene which was chemically highly reactive, but stable in aqueous alkaline solution. Amide (**5a**) and ester (**5b**) were not used because of detachment of cobalt porphyrin complexes from the cross-linked polystyrene support by hydrolysis in an aqueous alkaline solution. However, ketone (**5c**), quaternary salts (**5d**—**f**), and amine (**5g**) were effective and stable under the same conditions. From Table 5 the estimated activities k (M^{-1} s^{-1}) of (**5c**—**g**) were independent of the immobilizing linkages and porphyrin ligands. The properties of the supports affected the activities of catalysts more than did the structural change of the cobalt porphyrin derivatives. The presence of pyridyl (**5e**) and amino groups (**5f,g**) affected the activities little.

Experimental

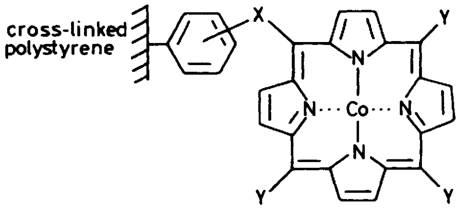
Apparatus.—^{1}H N.m.r. spectra were recorded on a JEOL JMN-PS-100 instrument. U.v. and visible spectra were measured with a Shimadzu UV-200 spectrometer. H.p.l.c. analysis was carried out with a Waters liquid chromatograph containing a C_{18} column (0.02M-aqueous AcOH–MeCN). The elemental analyses of C, H, N, and Cl were performed at the Microanalysis Center of Kyoto University, and that of Co was done at MES Testing & Research Center.

Materials.—Reagent-grade solvents were simply distilled and used. All acids, bases, salts, and adsorbents were commercially available and used without further purification. Quadricyclane,[39] (**1a,b**),[5a] (**2a,b**),[5a] (**3a**—**d**),[40] Co-TPP,[40] (**3e**),[41] (**3g**),[42] (**5b,c**),[43] and (**5g**)[43] were synthesized according to the procedures given in the literature. Compound (**3f**) was supplied from Mitsui Toatsu Chemical Inc. (dye; C.I. Vat Blue 29, C.I.74140) and DIAHOPE (activated carbon) was supplied from Mitsubishi Chemical Industries Ltd.

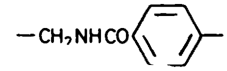
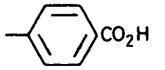
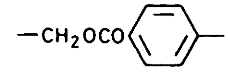
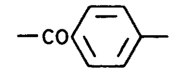
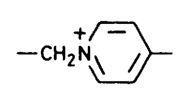
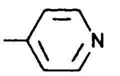
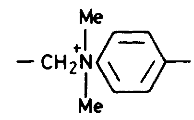
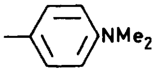
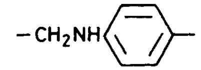
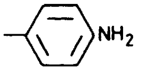
Preparation of Insoluble Catalysts.—*Catalyst* (**4a**). A typical preparation is given. THF (2 000 ml), commercially available Co-Pc (299 mg), and activated carbon (Darco G-60, 14.85 g) were mixed together and stirred overnight at room temperature. After that, insoluble matter was filtered off, washed with water and THF until the filtrate contained little of Co-Pc, and dried *in vacuo*. Insoluble (**4a**) (Co-Pc/Darco G-60 = 20 mg/l g) was obtained. All immobilization ratios were determined by measurement of the weight of the starting materials and the u.v. spectra of the filtrate solution and/or elemental analyses of N and Co.

Catalysts (**4b**—**g**). To a THF solution of Co-TPP were added adsorbents and the suspensions were refluxed overnight under

Table 5. Apparent second-order rate constant k and k'^a of isomerization of (**1b**) to (**2b**) induced by the insoluble catalyst (**5**)



(**5**)

-X-	-Y		Co content/%	k'/ $10^{-6}(g/l)^{-1}$ s^{-1}	k/ M^{-1} s^{-1}
		(**5a**)		b	b
	//	(**5b**)		b	b
	//	(**5c**)	0.20	3.7 ± 0.2	0.11 ± 0.01
		(**5d**)	0.27	5.0 ± 0.4	0.11 ± 0.01
//		(**5e**)	0.20	3.3 ± 0.2	0.10 ± 0.01
//	//	(**5e**)	1.03	6.1 ± 0.6	0.035 ± 0.003
		(**5f**)	0.11	3.3 ± 0.9	0.16 ± 0.05
		(**5g**)	0.75	3.8 ± 0.3	0.030 ± 0.002

[a] k and k' measured by ^1H n.m.r. {[(**1b**)] = 0.1M, in 0.5M-Na_2CO_3–D_2O, at 25 °C}. [b] k and k' not determined because of leakage of Co complex from the support.

nitrogen in the dark and then filtered. The insoluble catalysts (**4b**—**g**) were washed with water and methanol, and dried *in vacuo*.

Catalyst (**5a**). To 50 ml of a dimethylformamide solution of H_2TPPC (100 mg, 0.13 mmol) and dicyclohexylcarbodi-imide (20 mg, 0.1 mmol) was added 100 mg of aminomethylated polystyrene (Protein Research Foundation; divinylbenzene 1%, 100—200 mesh, NH_2 0.63 mmol/g), heated overnight at 60 °C under nitrogen, filtered, and washed with aqueous Na_2CO_3 and water. All free porphyrin base bonding covalently with cross-linked polystyrene was metallated by refluxing in acetic acid with excess of cobalt acetate for several hours under nitrogen, followed by filtering. Brown beads were also washed and dried *in vacuo*.

Catalyst (**5d**). To 5 ml of a chloroform suspension of 5-(4-pyridyl)-10,15,20-tris-(*p*-tolyl)porphyrin (50 mg, 0.076 mmol)[44] was added 30 mg of chloromethylated polystyrene (Cl 7.6 mmol/g) synthesized[45] from macroporous polystyrene (Aldrich Chemical Co.; 22—50 mesh), heated for 1 day at 210 °C in a sealed tube, filtered, and washed with aqueous HCl and water. Dark brown beads were metallated, filtered, washed, and dried *in vacuo* (Found: N, 0.44; Co, 0.27%).

Catalyst (**5e**). 50 ml of a chloroform suspension of 5,10,15,20-tetraki-(4-pyridyl)porphyrin[46] (30 mg, 0.049 mmol) and chloromethylated polystyrene (100 mg, Cl 7.6 mmol/g) were treated in a similar manner as for the synthesis of (**5d**) (Found: N, 0.36; Co, 0.20%), under the same conditions except using 30 mg of chloromethylated polystyrene (Found: N, 2.42; Co, 1.03%).

Catalyst (**5f**). 100 ml of a chloroform suspension of 5,10,15,20-tetrakis-(*p*-dimethylaminophenyl)porphyrin[47] (30 mg, 0.038 mmol) and chloromethylated polystyrene (30 mg; Cl 7.6 mmol/g) was treated in a similar manner as for the synthesis of (**5d**) (Found: N, 0.29; Co, 0.11%).

Measurement of Rate Constants.—^1H *N.m.r. spectral analysis.* An Na_2CO_3–D_2O solution of (**1**) was added to an Na_2CO_3–D_2O solution of (**3**) or solids of (**4**) and (**5**) in a n.m.r. sample tube at 25 °C. The sample tube was put quickly into a n.m.r. probe. Signals of (**1**) and (**2**) were integrated at an appropriate time interval. In the case of insoluble catalysts (**4**) and (**5**), the tube was vigorously shaken throughout the measurement. Molar quantities of (**1**) and (**2**) were calculated and $-\ln[(1)]/[(1)]_0$ was plotted *versus* time. The pseudo-first-order rate constant was determined from a slope of the straight line thus obtained. The second-order rate constant was determined by dividing the pseudo-first-order rate constant by initial concentration of (**3**) (k; $\text{M}^{-1}\ \text{s}^{-1}$) or estimated initial concentrations of (**4**) and (**5**) (k; $\text{M}^{-1}\ \text{s}^{-1}$, k'; $(\text{g/l})^{-1}\ \text{s}^{-1}$) and was an average value of three measurements at least.

H.p.l. chromatogram analysis. An Na_2CO_3–H_2O solution of (**1**) was added to (**4**) or (**5**) in a tube at 25 °C. The suspension was vigorously shaken and sampled at an appropriate interval. Molar quantities of (**1**) and (**2**) were determined by measuring each area of liquid chromatogram. A second-order rate constant was determined in a similar manner as for ^1H n.m.r. spectral analysis.

Recycling of (**4a**). 30 ml of an Na_2CO_3–H_2O solution of (**1a**) was added to 100 mg of (**4a**) (Co-Pc/Darco G-60 = 20 mg/l g) at 25 °C. The suspension was vigorously stirred and k was determined by means of h.p.l.c. After stirring overnight, isomerization ratio was determined, and used (**4a**) was filtered, dried *in vacuo*, and re-used for the above isomerization.

Measurement of Heat of Isomerization.—A 1M-aqueous sodium hydroxide solution of (**1**) was prepared and water-soluble cobalt porphyrin complex was added to 1.0 ml of the solution. The temperature change of the solution was measured by using a corrected copper–constantan thermocouple in a thermostat. The specific heat of the solution was estimated as 4.0 $\text{J g}^{-1}\ \text{K}^{-1}$. The heat of solution by catalyst was corrected from the blank experiment and its radiative heat was corrected by an application of Newton's law of cooling. Based on the assumption pseudo-first-order rate constant k_1 does not change during the exothermic reaction, the following two equations are given.

$$Q + Q_3 = Q_1\,[1 - \exp(-k_1 t)] + Q_2 \qquad (3)$$

$$\mathrm{d}Q_3/\mathrm{d}t = k_2 Q \qquad (4)$$

Q = heat measured at t (J)
Q_1 = heat of isomerization (J)
Q_2 = heat of solution (J)
Q_3 = radiative heat at t (J)
t = time from addition of catalyst (min)
k_1 = pseudo-first-order rate constant of isomerization of (**1**) to (**2**) (min^{-1})
k_2 = first-order rate constant of cooling reaction (min^{-1})

By solving equations (3) and (4) under the initial condition that Q_1 at $t = 0$ is Q_2, the following equation is obtained.

$$Q = k_1 Q[-\exp(-k_1 t) + \exp(-k_2 t)]/(k_1 - k_2) + Q_2\exp(-k_2 t) \qquad (5)$$

In our experiment k_1 was much larger than k_2, and so

$$Q = -Q_1\exp(-k_1 t) + (Q_1 + Q_2)\exp(-k_2 t) \qquad (6)$$

is obtained. Immediately after addition of catalyst, (**1**) isomerized into (**2**) rapidly and t is so small that $\exp(-k_2 t)$ is nearly one, so equation (6) may be written as follows

$$Q = -Q_1\exp(-k_1 t) + Q_1 + Q_2 \qquad (7)$$

$$\ln(Q_1 + Q_2 - Q) = \ln Q_1 - k_1 t \qquad (8)$$

After the temperature of the solution reaches a maximum, t is so large that $\exp(-k_1 t)$ is negligible, so equation (6) may be converted into

$$Q = (Q_1 + Q_2)\exp(-k_2 t) \qquad (9)$$

$$\ln Q = \ln(Q_1 + Q_2) - k_2 t \qquad (10)$$

From equations (8) and (10) or from equation (10), real heat corrected of isomerization of (**1**) to (**2**) ($Q_1/[(\mathbf{1})]_0$) was determined. An average value of over three measurements was given.

Examination of Catalytic Activities.—Metal complex. Catalytic activities for the isomerization of (**1b**) to (**2b**) induced by several metal complexes were followed by means of ^1H n.m.r. and the metal complexes were classified into three groups.

Class 1: (**1b**) isomerized to (**2b**) after standing for 6 h at room temperature; cobalt 5,10,15,20-tetrakis-(*p*-hydroxyphenyl)porphyrin.

Class 2: (**1b**) isomerized to (**2b**) after standing for 6 h at 60 °C; cyanocobalamin, chlorobis(dimethylglyoximato)-pyridine cobalt, dichloro-(1,4,8,11-tetra-azacyclotetradecane)-cobalt, bis(acetylacetonato)diaquacobalt, Fe-HP, Fe-PcS_1, and Ni-PcS_1.

Class 3: (**1b**) did not isomerize to (**2b**) after standing for 6 h at 60 °C; cobalt acetate, cobalt sulphate, *trans*-dichlorobis-(ethylenediamine)cobalt chloride, Mn-HP, Ni-HP, Cu-HP, Zn-HP, Mn-PcS_1, Cu-PcS_1, and Zn-PcS_1.

Support. Catalytic activities for isomerization of (**1b**) to (**2b**) induced by Co-TPP adsorbed on several supports were followed by means of ^1H n.m.r. and the supports were classified into three groups.

Class 1: (**1b**) isomerized to (**2b**) after standing for 1 h at room temperature; activated alumina, cross-linked polymethacrylic acid, Florisil, magnesium silicate, and silica gel (none-substituted, octadecyl-substituted).

Class 2: (**1b**) isomerized to (**2b**) after standing for 24 h at room temperature; activated clay, calcium oxide, calcium phosphate, magnesium oxide, Nafion, and talc.

Class 3: (**1b**) did not isomerize to (**2b**) after standing for 72 h at room temperature; barium sulphate, calcium carboxylate, carborundum, Celite, cellulose, cross-linked polystyrene (none-substituted), Kieselguhr, quartz sand, and Sephadex.

Cationic polymers (Dowex 1, Amberlite 400 and 900) were not effective as supports because of adsorption of (**1b**) and (**2b**) onto the supports.

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