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POLAR EFFECT ON METALLOPORPHYRIN-CATALYZED REACTION

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The isomerization rate of 2-carboxyquadricyclanes catalyzed by cobalt-porphyrin complexes was enhanced by introduction of a pyridyl group to the porphyrin ligand. This phenomenon is recognized to be due to a polar effect; an interaction between acid and base.

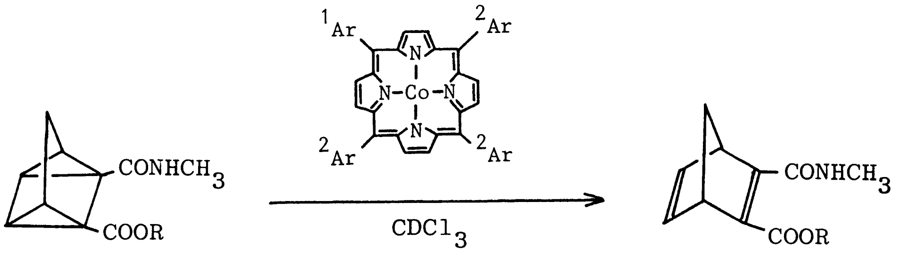
Metalloporphyrins play an important role in many bio-reactions (oxygen carrier, P-450 enzyme, photosynthesis, and so on), so many chemists are interested in metalloporphyrin chemistry.[1)] Metalloporphyrin-catalyzed reactions have attracted much attention from the viewpoints of wide applicability for organic syntheses and of elucidation of their reaction mechanisms. Metalloporphyrin-catalyzed reaction is controlled by perturbation to the central metal which is a reactive site and to the field around the central metal. The former consists of i) a variety of central metals; ii) axial ligands; iii) porphyrin ligands (for example, an electronic effect of substituents on the porphine ring through metal-nitrogen bonds). The latter consists of iv) steric effects; v) hydrophobic effects; vi) polar effects. Steric effects have been widely investigated by using ortho-substituted tetraaryl-metalloporphyrins, i.e., high selectivities in synthetic reactions (regio-, facial-, and enantio-selectivities)[2)] and inhibition of deactivating dimerization of oxo-metalloporphyrin which is an active intermediate on P-450 model reactions.[3)] Hydrophobic effects have also been reported in the P-450 reaction; the formation of the complex between iron porphyrin and dioxygen which is a precursor to oxo-iron-porphyrin.[1)] Polar effects, however, have never been discussed in metalloporphyrin-catalyzed reactions; an interaction between electron-donor and acceptor.[4)] Here, we will first report a polar effect on a metalloporphyrin-catalyzed reaction; isomerization reaction of quadricyclane derivatives 1 to norbornadiene derivatives 2 catalyzed by cobalt-porphyrin complexes.[5-7)]

The catalytic isomerization obeyed pseudo-first order, and we measured the apparent second order rate constants k in chloroform-d[10)] by means of ^{1}H-NMR.[11,12)] Using cobalt 5,10,15,20-tetraphenylporphyrin (Co-TPP) as the catalyst, the value of the rate constant of acid 1a to 2a (k_a) was nearly equal to that of ester 1b to 2b (k_b) (see Table 1, Run 1). When only one phenyl group of Co-TPP was substituted to a 2-pyridyl group,[13)] k_a was larger than k_b, i.e., k_a increased but k_b unchanged (Runs 1 and 2). Replacement of one p-tolyl group of cobalt 5,10,15,20-tetrakis(p-tolyl)porphyrin (Co-TTP) to a 2-pyridyl group showed the same behavior (Runs 3 and 4). Pre-addition of an acid 2a affected neither k_a nor k_b (Run 4). Coordination of the acid 1a or 2a to the pyridyl catalysts is not responsible for the specific increase of k_a. Therefore, introduction of the pyridyl group affects the isomerization of acid 1a to 2a.

Substitution of all four phenyl groups of Co-TPP to p-tolyl groups increased only k_a (Runs 1 and 3). The similar fact was observed by introducing methoxy groups (Runs 1, 5, 6, and 7).[14)] The k_a values in the isomerization by p-tolyl, p-anisyl, and m-anisyl substituted catalysts were larger than those by p-chlorophenyl and phenyl substituted catalysts, and all the k_b values by the above five catalysts were nearly equal (Runs 1, 3, 5, 6, and 8). In the phenyl, p-anisyl, and m-anisyl substituted catalysts (Runs 1, 5, and 6), comparison of the k_a values (p-anisyl > m-anisyl > phenyl) with the Hammett substituent constants (σ-value; m-methoxy > hydrogen > p-methoxy) indicates that the specific increase of k_a is not due to the electronic effect. Consequently, introduction of the electron-donating group may clearly increase the basicity of the catalyst and influences the rate constant k_a.

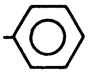
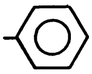
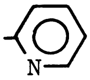
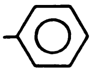
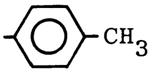
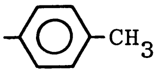
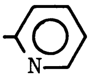
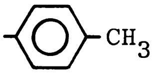
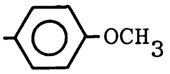
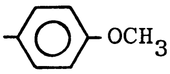
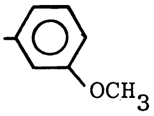
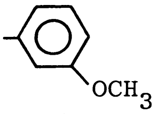
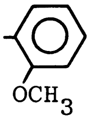
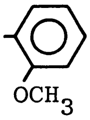
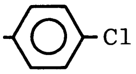
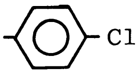
The above findings will reflect the fact that a polar interaction between catalysts and 1a accelerates the isomerization rate. Thus, the isomerization reaction of quadricyclane derivatives will serve as a model for elucidating the mechanisms of a variety of catalytic reactions concerned with metalloporphyrins.

Table 1. Rate constant k of isomerization of 1 to 2 (1 M = 1 mol dm^{-3})



1 (a:R=H; b:R=CH_3)

2

Run	^1Ar	^2Ar		$k_{1\rightarrow2}{}^{a)}/M^{-1}s^{-1}$	
				k_a (R = H)	k_b (R = CH_3)
1			(Co-TPP)	7.6[b)]	6.5
2				22.9	8.4
3			(Co-TTP)	16.7	7.7
4				26.8, ≃30[c)]	6.4, 6.5[c)]
5				15.2	7.1
6			d)	11.1	5.8
7			(Co-TAP)[d)]	>300	26.4
8				7.1	6.8

a) All the values were measured at 25 °C ([1] = 0.1 M, [cobalt porphyrins] = 1 x 10^{-4} M). b) See Ref. 9. c) Acid 2a was added ([2a] = 0.1 M). d) The catalyst was a mixture of atropisomers.

References

1) "The Porphyrins," ed by D.Dolphin, Academic Press, New York (1979), Vol. VII.

2) For example, an oxidation by iron porphyrins and PhIO; J.T.Groves and T.E.

Nemo, J.Am.Chem.Soc., 105, 5786, 6243 (1983); J.T.Groves and R.S.Myers, ibid., 105, 5791, (1983).

3) A.L.Balch, Y.Chan, R.Cheng, G.N.La Mar, L.L.-Grazynski, and M.W.Renner, J.Am. Chem.Soc., 106, 7779 (1984).

4) Polar effects were discussed in the stabilization of the complexes between iron porphyrins and dioxygen; M.P.Mims, A.G.Porras, J.S.Olson, R.W.Noble, and J.A.Peterson, J.Biol.Chem., 258, 14219 (1983); T.G.Traylor, N.Koga, and L.A. Deardurff, J.Am.Chem.Soc., 107, 6504 (1985).

5) J.Manassen, J.Catal., 18, 38 (1970).

6) R.R.Hautala, R.B.King, and C.Kutal, "Solar Energy; Chemical Conversion and Storage," Humana Press, Clifton, N.J. (1979), pp. 333-369.

7) In the catalytic reaction, the effects of i),5) ii),5) and iii)8) have already reported, and we also discussed the effects of iv) and v).9)

8) Z.Yoshida, Heterocycles, 21, 331 (1984).

9) K.Maruyama and H.Tamiaki, J.Org.Chem., 51, 602 (1986).

10) Chloroform-d was distilled, passed through an alumina column, and used.

11) K.Maruyama, H.Tamiaki, and S.Kawabata, J.Chem.Soc.,Perkin Trans.2, 1986, in press.

12) K.Maruyama, H.Tamiaki, and T.Yanai, Bull.Chem.Soc.Jpn., 58, 781 (1985).

13) It was known that a 2-pyridyl group was unable to coordinate the central cobalt metal as the axial ligands.5)

14) The k_b value in the isomerization by cobalt 5,10,15,20-tetrakis(o-anisyl)-porphyrin (Co-TAP) was also larger than that by Co-TPP (Runs 1 and 7), which might be due to a steric effect. In the ortho-anisyl substituted catalyst (Co-TAP), k_a was larger than k_b as well as in the meta- and para-anisyl substituted catalysts. The k_a values by Co-TAP is the largest in the isomerization of substituted quadricyclanes reported so far,11) and about 10^4 times larger than that by rhodium (I) catalyst.15) Therefore, the valence isomerization between 1a and 2a in an organic solvent will be a useful candidate for solar energy storage.6,15)

15) K.Maruyama, K.Terada, and Y.Yamamoto, J.Org.Chem., 46, 5294 (1981).

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