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LETTERS TO THE EDITORS

Chloro-*meso*-tetraphenylporphyrinatocobalt(III) as Catalyst for Quadricyclane Isomerization

There is considerable current interest in the catalytic isomerization of quadricyclane to norbornadiene, both in the context of mechanistic considerations (*1*) and of potential application to solar energy storage (*2*). In a recent paper in this Journal (*3*) Wilson and Rinker (WR) reported the kinetics of isomerization of quadricyclene to norbornadiene by *meso*-tetraphenylporphyrinatocobalt(II), $Co^{II}TPP$. After numerous trials, we failed to reproduce their result ($k^{(2)} = 3.0 \times 10^{+3}$ M^{-1} sec^{-1} at 25°C in chloroform)[1] with purchased $Co^{II}TPP$ or with $Co^{II}TPP$ synthesized according to the procedure of Rothemund and Menotti (*4*) or of Adler and co-workers (*5*). Our rates were invariably a hundredfold slower. The WR results were finally reproduced by following their procedure (*6*) which involved an intended purification of their crude product by Soxhlet extraction with carbon tetrachloride.

We now believe that the very active catalyst used by WR (at least in chloroform as solvent) is chloro-*meso*-tetraphenylporphyrinatocobalt(III) [$Co^{III}(TPP)Cl$], produced by reaction of $Co^{II}TPP$ with CCl_4 during reflux. This reaction was unknown and was not anticipated by WR.

Results in support of this conclusion are:

1. Authentic samples of $Co^{II}TPP$ synthesized in our laboratory and variously purified, or purchased (Strem Chemical) gave satisfactory analyses (No. 1–3 of Table I) and have electronic spectra which agree well with that reported by Dorough *et al.* (*7*). These crystalline materials (all maroon in color) give second-order rate constants for the isomerization of quadricyclane to norbornadiene of 30 ± 10 M^{-1} sec^{-1} in chloroform at room temperature. Such rate constants are consistent with the limited data reported by Manassen (*8*).

2. During reflux of $Co^{II}TPP$ with carbon tetrachloride the color of the solid changes slowly from maroon to violet. Simultaneously, absorption maxima of solutions of these solids in chloroform shift from 527 to 545 nm and from 410 to 435 nm. The electronic spectrum (Table 2) of a sample isolated after 30 hr of reflux agrees with that reported for the violet compound $Co^{III}(TPP)Cl$ (*9*). Analysis of this sample (No. 4 of Table 1) is satisfactory for $Co^{III}(TPP)Cl$, except for a possibly high chlorine analysis. Analysis of a sample which was used in the WR study (kindly provided by Professor Rinker) also indicates the presence of chlorine (No. 5 of Table 1).

3. Sample No. 4 gave a second-order rate constant of 2.5×10^3 M^{-1} sec^{-1} (room temperature) in chloroform, in reasonable agreement with WR. An authentic sample of $Co^{III}(TPP)Cl$, synthesized according to Sakurai *et al.* (*9*) gave the same second-order rate constant.

We suggest that the unusual variations in rate laws and rate constants in $CHCl_3$,

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[1] Derived from Fig. 7 in Ref. (*3*). There is a discrepancy between the values in Table 1 and Fig. 7. Apparently, the catalyst concentration in Table 1 should be $(2.1–27.3) \times 10^{-5}$ M.

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TABLE 1

Elemental Analyses[a] of Samples

Sample No.	Percent					Remarks
	C	H	N	Co	Cl	
1	79.10	4.53	8.26	—	—	Co^{II}TPP from Strem Chemical.
2	77.94	4.49	7.83	7.70	—	Co^{II}TPP prepared according to Ref. (*4*) and purified by column chromatography on alumina.
3	79.25	4.65	8.06	7.95	—	Co^{II}TPP prepared according to Ref. (*5*).
4	74.55	3.92	7.63	7.45	5.72	Sample No. 2 refluxed in CCl_4 for 30 hr, recrystallized from benzene/isooctane.
5	71.72	3.93	7.56	5.83	8.23	Sample provided by Prof. Rinker.
Calcd for						
Co^{II}TPP	78.68	4.20	8.34	8.77	0	
Co^{III}(TPP)Cl	74.73	3.99	7.92	8.33	5.01	

[a] By Galbraith Laboratories, Knoxville, Tenn.

TABLE 2

Electronic Spectra of Co^{III}(TPP)Cl in Methanol[a]

Preparation	Visible band	Soret band	UV band
Lit. (*9*)	$575_{sh}(3.8)$, $541_{max}(14.4)$, $505_{max}(3.5)$	$425.5_{max}(250)$	$313_{max}(17.0)$
This work, lit. (*9*) method	$575_{sh}(3.6)$, $540_{max}(13.9)$, $505_{sh}(3.9)$[b]	$426_{max}(252)$	$312_{max}(16.8)$
Sample No. 4 of Table 1	$575_{sh}(3.6)$, $540_{max}(15.0)$, $505_{sh}(4.4)$[b]	$426_{max}(264)$	$312_{max}(18.3)$

[a] Entries are wavelengths (nm) of absorption band maxima or shoulders and (molar extinction coefficients $\times 10^{-3}$).

[b] Measured in neutral methanolic solution at 5.0×10^{-5} *M*. According to K. Yamamoto (personal communication) this spectrum is acidity-dependent and slightly concentration-dependent.

CCl_4, and 1-chloronaphthalene reported by WR are related to the ionizability and coordinative unsaturation (*10*)[2] of Co^{III}(TPP)Cl. It is noteworthy that the catalytic activity of square pyramidal (*9*) d^6 Co(III) is much higher than that of square planar (*11*) d^7 Co(II) and the other metalloporphyrins and related complexes investigated by Manassen (*8*); it is not clear how this result may be reconciled with Manassen's interpretation of the electronic requirements for effective catalysis of quadricyclane isomerization. The behavior of the Co(III) catalyst will be the subject of further investigation.

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