for anodic oxidation of 13 potassium alkanecarboxylates in alkaline aqueous and methanolic solution using a competition method. From mechanism 1 it was predicted that carboxylates giving tertiary radicals would react much faster than those giving primary radicals, whereas the discharge mechanism would not imply any large difference in this respect. Experimentally, the k/k' values turned out to be essentially the same[5] independent of the structure of R, and hence it was concluded that mechanism 1 could not be valid.

While it is possible to criticize mechanism 1 from other points of view,[2] we wish to point out that the use of competition methods, although very useful in homogeneous solution chemistry, is a very risky procedure when applied to electrode processes. As will be shown below, several important factors militate against the use of the k/k' values referred to above in any discussion of the mechanism of the Kolbe process.

(1) Experimentally, it was necessary to conduct the electrolyses in alkaline medium. It has, however, long been recognized that alkaline media tend to favor the formation of carbonium ions in the anodic oxidation of $RCOO^-$. Since no product studies were performed and the mechanism of carbonium ion formation is still largely unknown,[2] it is difficult to establish whether the k/k' values relate to the reaction under discussion, formation of radicals by anodic oxidation of $RCOO^-$.

(2) One also has to consider the possibility that the electrolyses were run under conditions at which the diffusion rate of the competing carboxylate ions from the solution bulk toward the electrode might determine the rate of the reaction. In such a case the k/k' value will simply reflect the ratio between the diffusion coefficients of the species involved and bear no relation to the ratio between the electrochemical rate constants. Since diffusion coefficients of different $RCOO^-$ differ only by a factor of ≈ 0.7 when R is changed from methyl to heptyl,[6] diffusion or near-diffusion control might possibly explain the low sensitivity of k/k' to changes in R. This is a point which needs further clarification.

(3) Adsorption effects might play an important role, as indicated by the observed trends in the variation of k/k' with changes in R and medium. In aqueous solution k/k' was found to increase with increasing molecular weight of the ion. This phenomenon could possibly be due to differences in adsorption isotherms for different ions; it is known[7] that adsorption of organic compounds from aqueous solution is much more extensive than from methanolic solution and that adsorption increases with increasing molecular weight. Hence a factor involving the ratio between the adsorption isotherms of the two competing ions should be taken into account.

(4) Assuming for a moment that diffusion and adsorption effects could be neglected, k/k' would still not be a measure of the ratio between the actual rate constants of the rate-determining step. According to absolute reaction rate theory, the rate constant of an anode process $k(E)$ at anode potential E is given by eq 2, where k_s is the electrochemical rate constant at the

$$k(E) = k_s \exp\{(1 - \alpha)(nF/RT)(E - E_s)\} \qquad (2)$$

standard potential E_s of the process, n is the number of electrons transferred in the rate-determining step, α is the transfer coefficient, and F, R, and T have their usual meaning. Clearly, the rate constant of interest is the potential-independent k_s, and it is easily shown that the ratio k_s/k_s' for two competing reactions cannot be obtained from k/k' without a knowledge of the values of E_s and E_s'. These are in principle possible to calculate from appropriate thermodynamic data,[1] but unfortunately accurate such data are not available for most of the reactions studied by Reichenbacher, Liu, and Skell.

(5) It has recently[8] been shown that eq 2 cannot be valid under conditions of high overpotentials ($E - E_s$), since the maximum possible rate of an electrode process, even in the complete absence of any transport control, is dependent upon the collision frequency of solute species with the electrode surface. Under these conditions eq 2 is replaced by an expression in which the diffusion coefficient is the only important parameter in determining $k(E)$. Now one of the most characteristic features of the Kolbe process is that it requires a very high overpotential to proceed at a measurable rate, and it therefore follows that this problem has to be considered in a discussion of rate data. The decrease of the Tafel slope at high anode potential observed by Conway and Vijh[9] for anodic oxidation of acetate ion in aqueous solution is an indication that it might be important.

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[5] This was true for all cases in methanol, whereas in water an increase in k/k' with increasing molecular weight was noted.

[6] Diffusion coefficients were calculated from the limiting equivalent conductances Λ_0 for $RCOO^-$ (International Critical Tables, Vol. 6, McGraw-Hill Book Co., Inc., New York, N. Y., 1929, p 259) through the expression $D = 2.67 \times 10^{-7}\Lambda_0/z$, where z is the charge of the ion (I. M. Kolthoff and J. J. Lingane, "Polarography," Vol. 1, Interscience Publishers, New York, N. Y., 1952, p 50 ff)

[7] For example, see B. J. Piersma and E. Gileadi, "Modern Aspects of Electrochemistry," Vol. 4, J. O'M Bockris and B. E. Conway, Ed., Butterworth and Co. (Publishers), Washington, D. C., 1966, p 47.

[8] K. B. Oldham, *J. Electroanal. Chem.*, **16**, 125 (1968); *cf.* also J. M. Hale, *ibid.*, **19**, 315 (1968).

[9] B. E. Conway and A. K. Vijh, *Z. Anal. Chem.*, **224**, 160 (1966).

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The Structure and Properties of μ-Oxo-bis(tetraphenylporphineiron(III))

Sir:

The interest both in binuclear iron(III)[1] species and in iron(III) porphyrins[2] prompts us to report the syn-

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[1] (a) W. M. Reiff, G. J. Long, and W. A. Baker, Jr., *J. Amer. Chem. Soc.*, **90**, 6347 (1968); (b) E. Fleischer and S. Hawkinson, *ibid.*, **89**, 720 (1967); (c) M. Gerloch, J. Lewis, J. Mabbs, and A. Richards, *Nature*, **212**, 809 (1966); (d) M. Gerloch, E. D. McKenzie, and A. Towl, *ibid.*, 220, 906 (1968); (e) H. Schugar, A. Hubbard, J. Anson, and H. Gray, *J. Amer. Chem. Soc.*, **91**, 71 (1969); (f) J. Lewis, J. Mabbs, and A. Richards, *J. Chem. Soc.*, 1014 (1967); (g) S. J. Lippard, H. Schugar, and C. Walling, *Inorg. Chem.*, **6**, 1825 (1967); (h) G. M. Bancraft, A. G. Maddock, and R. P. Randl, *J. Chem. Soc., A*, 2939 (1968).

[2] (a) E. Fleischer, C. Miller, and L. Webb. *J. Amer. Chem. Soc.*, **86**, 2342 (1964); (b) J. L. Hoard, M. J. Hamor, T. A. Hamor, and W. S. Caughey, *ibid.*, **87**, 2312 (1965); (c) D. Koenig, *Acta Cyrst.*, **18**, 663 (1965); (d) L. Webb and E. Fleischer, *J. Amer. Chem. Soc.*, **87**, 667 (1965); (e) L. Vogt, A. Zalkin, and D. Templeton, *Inorg. Chem.*, **6**, 1725 (1967); (f) J. Jordan and T. M. Bednorski, *J. Amer. Chem. Soc.*, **86**, 5690 (1964); (g) J. O. Alben, W. H. Fuichsman, C. A. Beaudreau, and W. S. Caughey, *Biochemistry*, **7**, 624 (1968); (h) K. Fenkart and C. Brubaker, Jr., *J. Inorg. Nucl. Chem.*, **30**, 3245 (1968).

thesis, characterization, and structure of the metalloporphyrin dimer, μ-oxo-bis(tetraphenylporphineiron(III)).

The complex was prepared by dissolving 0.5 g of tetraphenylporphine- (TPP) iron(III) chloride[3] in 60 ml of chloroform; potassium hydroxide solution (50 ml of 25%) was added and the mixture stirred for 1 hr. The chloroform layer was separated from the water layer, and it was chromatographed twice on a column packed with *dry* activated alumina and eluted with chloroform.

The first fraction that came off the column was the Fe-TPP-Cl and the second fraction the O-(Fe-TPP)$_2$ dimer. The dimer material was recrystallized from a xylene–chloroform mixture. *Anal.* Calcd for O-(Fe-TPP)$_2$·xylene, $C_{96}H_{66}N_8OFe_2$: C, 79.01; H, 4.54; N, 7.75; O, 1.10; Fe, 7.75. Found: C, 79.20; H, 4.49; N, 7.84; O, 0.80; Fe, 7.66. The main difference in the ir spectra of the Fe-TPP-Cl and O-(Fe-TPP)$_2$ are two peaks at 892 (m) and 878 (s) cm^{-1}. This is in the region where the antisymmetric Fe–O–Fe stretch is expected to occur.[1] The visible absorption spectrum of Fe^{III}TPP-Cl in chloroform has peaks at 3780, 4150, 5095, 5775, 6565, and 6905 Å with extinction coefficients of 58 × 10^3, 108 × 10^3, 13 × 10^3, 3.3 × 10^3, 2.8 × 10^3, and 3.1 × 10^3 M^{-1} cm^{-1}, respectively.[4]

The visible spectrum of the dimer, O-(Fe-TPP)$_2$, in benzene has peaks at 4080, 5715, and 6120 Å with extinction coefficients of 120 × 10^3, 10.7 × 10^3, and 4.8 × 10^3 M^{-1} cm^{-1}, respectively. (The extinction coefficients of the dimer are based on a molecular weight of one-half the dimer so comparison with the Fe-TPP-Cl monomer is reasonable.) A transformation between the dimer and monomer can easily be carried out by adding concentrated hydrochloric acid to a solution of the dimer.[5]

$$\text{O-(Fe}^{\text{III}}\text{-TPP)}_2 + 2\text{HCl} \rightleftharpoons 2\text{Fe}^{\text{III}}\text{-TPP-Cl} + \text{H}_2\text{O}$$

The Fe^{III}TPP will react with strong bases such as pyridine[6,7] to form the bispyridine adduct, while the dimer does not show any reaction with pyridine.

The magnetic susceptibility of these compounds was determined by Faraday method using HgCo(SCN)$_4$ as a standard. The following values of the effective magnetic moment[8] were determined for Fe^{III}-TPP-Cl: μ_{eff} = 5.87 (293°K), 5.81 (194°K), and 5.72 (77°K); for the O-(Fe-TPP)$_2$ dimer, μ_{eff} = 1.15 (293°K), 0.76 (195°K), and 0.45 (77°K) (the μ_{eff}'s are per iron atom for both the monomer and dimer). The magnetic susceptibility of Fe^{III}-TPP-Cl follows the Curie–Weiss law, $\chi_m = C/(\theta + T)$ where $\theta = 8°$. This indicates the iron has a spin of $^5/_2$ and is in a high-spin state;[9] this has been observed for other Fe(III) porphyrins.[10] The dimer's magnetic properties definitely indicate an antiferromagnetic interaction between the two iron ions of the dimer.

The structure of the dimer was ascertained by an X-ray diffraction study. The crystal belongs to the orthorhombic system, acentric space group C2cb (No. 41, "International Tables of Crystallography," orientation $\bar{c}$ba) and has cell constants a = 15.12, b = 25.06, c = 18.04 Å with four dimer molecules per unit cell (d_{obsd} = 1.31 g/cm^3, d_{calcd} = 1.313 g/cm^3). This requires the dimer to be on a crystallographic twofold axis. The structure was determined using 2011 observed Cu Kα data;[11] the present R factor for all the data after least-squares refinement of all 50 atoms employing isotropic temperature factors is 9.8%.[12] The X-ray study confirms the formulation of the compound as a O-(Fe^{III}-TPP)$_2$ dimer; the twofold axis is perpendicular to the Fe–Fe direction. The main features of interest in the structure of the dimer are that the Fe–O–Fe angle is 168° and the Fe(III)–O bond distance is 1.76 Å. The two porphyrin rings are not parallel but tilted because of the bent Fe(III)–O–Fe(III) angle. The iron atom is 0.48 Å out of the plane of the four pyrrole nitrogens toward the oxide atom. The rest of the tetraphenylporphine structure is similar to other studied porphyrins.[2] Previously determined structures of binuclear M–O–M systems show that in phthalocyanatopyridinemanganese(III) μ-oxo-phthalocyanatopyridinemanganese(III),[2e] the Mn–O–Mn angle is 178° with a Mn(III)–O bond distance of 1.71 Å; in Fe-(salen)$_2$-O-(py)$_2$[1d] (salen = bissalicylideneethylenediamine) the Fe–O–Fe angle is 139° with a bond distance of 1.79 Å; in [(HEDTA)Fe-O-Fe(HEDTA]$^{2-}$, where HEDTA is N-hydroxyethylethylenediamine triacetate,[1g] the Fe–O–Fe angle is 165°, with a Fe–O bond distance of 1.79 Å.

We intend to investigate further the various bond parameters and magnetic properties of this class of compounds in order to give a detailed interpretation of the observed data.

The magnetochemistry of iron containing porphyrins has been extensively studied especially in the case of the hemoproteins.[13] It is known that hydroxide has an anomalous effect on the spectral and magnetic properties of the hemoproteins, although it seems unlikely that dimer structures form in these cases due to the steric interference of the protein.[14,15]

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[3] G. D. Dorough, J. R. Miller, and F. Huennekens, *J. Amer. Chem. Soc.*, 73, 4315 (1951). We use dimethylformamide as the solvent in the preparation of the FeTPP-Cl. *Anal.* Calcd for $C_{44}N_4H_{28}FeCl$: C, 75.06; H, 4.00; N, 7.96; Fe, 7.93; Cl, 5.04. Found: C, 74.67; H, 4.17; N, 8.05; Fe, 7.79; Cl, 4.95.

[4] These agree with the literature values for this compound (see ref 3).

[5] If a base such as triethylamine is added to a solution of the Fe^{III}TPP-Cl the monomer is transformed into the dimer O-(Fe(III)-TPP)$_2$.

[6] Fe^{III}TPP-Cl dissolved in pyridine gives an absorption spectrum with maxima at 4420, 5090, 5295, 6550, and 6975 Å with extinction coefficients of 138 × 10^3, 10 × 10^3, 10 × 10^3, 1.9 × 10^3, and 2.4 × 10^3 M^{-1} cm^{-1}, respectively. The iron dimer, O-(Fe-TPP)$_2$, shows no change in its visible spectrum when dissolved in pyridine.

[7] L. M. Epstein, D. Straub, and C. Maricondi, *Inorg. Chem.*, **6**, 1720 (1967).

[8] $\mu_{eff} = 2.83\sqrt{\chi_M T}$ BM, where χ_M has been corrected for a diamagnetic correction of the TPP of 370 × 10^{-6} cgs.

[9] A more thorough temperature dependence of the magnetic susceptibilities is now under investigation in order to get better magnetic parameters.

[10] W. P. Hambright, A. N. Thorpe, and C. C. Alexander, *J. Inorg. Nucl. Chem.*, 30, 3139 (1968).

[11] There are 676 "zero" data that have not as yet been included in the refinement. The data were collected with a PAILRED automatic diffractometer employing Cu Kα radiation; all peaks 2θ < 100° were collected. The crystal was 0.1 × 0.2 × 0.2 mm^3 in size; an absorption correction has not yet been applied to the data.

[12] The refinement included the anomalous scattering of the iron atom; the refinement is almost complete. The difference map is relatively clean with background noise of about 1 e Å^3. In further refinement, the use of rigid-body refinement will be employed with the four pyrrole and four phenyl groups held as rigid bodies.

[13] (a) J. Bettlestone and P. George, *Biochemistry*, 3, 707, (1964); (b) P. George, J. Bettlestone, and J. S. Griffith, *Rev. Mod. Phys.*, **44 1**, (1964); (c) "Hemes and Hemoproteins," B. Chance, R. Esterbrook, and T. Yonetai, Ed., Academic Press, New York, N. Y., 1966.

[14] We are currently investigating the water-soluble porphyrin Fe^{III}(N-methylated)tetrapyridylporphine to better understand the behavior of these systems in water media.

Acknowledgment. We wish to thank Larry Sklar for his skillful help in the synthesis and purification of some of the porphyrins described in the paper. This work was supported by grants from the National Institutes of Health and National Science Foundation.

(15) Note Added in Proof. It has been brought to our attention that the structure of the O-(Fe-TPP)$_2$ dimer has been independently determined by X-ray diffraction at Cornell University by A. B. Hoffman, D. M. Collins, V. M. Day, and J. L. Hoard. Their results are in agreement with ours; a future joint publication will result employing their more accurate and extensive data (3500 reflections with Mo Kα radiation).

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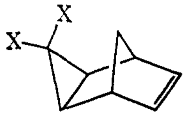
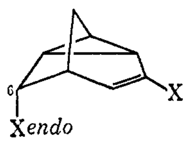
The Reaction of *exo*-Tricyclo$[3.2.1.0^{2,4}]$octene with Rhodium Catalysts

Sir:

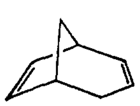
Noble metal catalysts, which effect the hydrogenation and isomerization of olefins and cyclopropanes, in the absence of hydrogen effect other reactions. We have been studying such reactions and report below on the action of some rhodium catalysts on *exo*-tricyclo$[3.2.1.0^{2,4}]$octene (Ia).[1] Others have recently found that some transition metals catalyze valence tautomerizations,[2] and this catalysis has been attributed without evidence to molecular orbital symmetries, the assumption being that the reactions are concerted electrocyclic processes.[2,3] But the experiments described below show that this assumption may be false: at least in the case reported here products and intermediates are formed that have no place in the previous mechanistic scheme and must be accounted for in a different way.

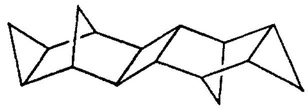
When Ia is warmed (90°, 2 hr) with 1.3 mol % tris(triphenylphosphine)rhodium(I) chloride[4] it is quantitatively converted into a mixture[5] consisting of 62% IIa,[6] 32% III,[7] and 6% IV;[8] with 5% rhodium on carbon (130°, 2 days) a similar mixture forms (25% IIa, 55% III, 20% IV) plus a dimerization product consisting mainly of a substance that will be described separately, mp 131–132°, isolated in *ca.* 15% yield, and assigned structure V.[9] In the absence of the catalysts no reactions occur.


Ia, X = H
b, X = D


II


III


IV


V

Although III is formally related to I by an electrocyclic reaction, II is not. Nevertheless, with tris(triphenylphosphine)rhodium chloride the rearrangement of I to both II and III is intramolecular, and the conversion of Ib to IIb is stereospecific.

The evidence for the stereospecificity of the rearrangement is that the nmr spectrum of IIb formed from Ib (93.8% d_2, 5.4% d_1, 0.8% d_0)[1a,10] is similar to that of IIa except that the resonance of the 6-*endo* proton, which in IIa appears as a doublet (J = 11 Hz) at τ 9.31 of intensity 2,[6c,8b,11] appears as a doublet of exactly half the intensity (calcd 1.035; found 1.04),[12] and that the resonance of the olefinic protons, which in IIa appears as a triplet of peaks of relative intensity 2 separated by 7.2 Hz at τ 4.18, is replaced by a doublet of peaks of intensity 1.01 (calcd 1.035) separated by 4 Hz.[13]

The evidence that the rearrangement of I to II and III is intramolecular is that, as shown in Table I, the reaction of a mixture of unlabeled and doubly labeled I (Ia plus Ib) gave only unlabeled and doubly labeled II and III.[14]

Table I. Deuterium Distribution in Starting Material I and Products II and III[a]

	I, %	II, %	III, %
d_0	41	57	30
d_1	3	3	4
d_2	55	40	66
d_3			0.3

[a] The latter after 1 hr at 60° in the presence of 1.2 mol % tris(triphenylphosphine)rhodium chloride (16% reaction).

The implication of the facts described above is that the catalyst, $[(C_6H_5)_3P]_3RhCl$, reacts with I to give either

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(1) (a) H. E. Simmons, E. P. Blanchard, and R. D. Smith, *J. Am. Chem. Soc.*, **86**, 1347 (1964); (b) W. von E. Doering and W. Grimme, quoted in K. B. Wiberg and G. R. Wenzinger, *J. Org. Chem.*, **30**, 2278 (1965), footnote 10; (c) K. Tori and M. Ohtsuru, *Chem. Commun.*, 886 (1966).

(2) H. Hogeveen and H. C. Volger, *J. Am. Chem. Soc.*, **89**, 2486 (1967); *Chem. Commun.*, 1133 (1967); H. C. Volger and H. Hogeveen, *Rec. Trav. Chim.*, **86**, 830 (1967); H. C. Volger, H. Hogeveen, and M. M. P. Gaasbeek, *J. Am. Chem. Soc.*, **91**, 218 (1969); W. Merk and R. Pettit, *ibid.*, **89**, 4788 (1967).

(3) F. D. Mango and J. H. Schachtschneider, *ibid.*, **89**, 2484 (1967).

(4) (a) J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc.*, *A*, 1711 (1966); (b) M. A. Bennett and P.A. Longstaff, *Chem. Ind.* (London), 846 (1965).

(5) Each component is unchanged when similarly treated.

(6) (a) W. von E. Doering and W. R. Roth, *Tetrahedron*, **19**, 715 (1963); (b) C. A. Grob and J. Hostynek, *Helv. Chim. Acta*, **46**, 1676 (1963); (c) R. R. Sauers and A. Shurpik, *J. Org. Chem.*, **33**, 799 (1968).

(7) (a) N. A. LeBel and R. N. Liesemer, *J. Am. Chem. Soc.*, **87**, 4301 (1965); (b) P. K. Freeman, D. G. Kuper, and V. N. M. Rao, *Tetrahedron Lett.*, 3301 (1965).

(8) (a) J. M. Brown and J. L. Occolowitz, *J. Chem. Soc.*, *B*, 411 (1968); (b) W. R. Moore, W. R. Moser, and J. E. LaPrade, *J. Org. Chem.*, **28**, 2200 (1963); (c) S. Winstein, M. Ogliaruso, M. Sakai, and J. M. Nicholson, *J. Am. Chem. Soc.*, **89**, 3656 (1967); (d) C. Cupas, W. E. Watts, and P. von R. Schleyer, *Tetrahedron Lett.*, 2503 (1964).

(9) Related structures: T. J. Katz, J. C. Carnahan, Jr., and R. Boecke, *J. Org. Chem.*, 32, 1301 (1967).

(10) CD_2I_2: S. Winstein, E. C. Friedrich, R. Baker, and Y. Lin, *Tetrahedron Suppl.*, **8**, **Part II**, 621 (1966).

(11) C. F. Huebner, E. Donoghue, L. Dorfman, F. A. Stuber, N. Danieli, and E. Wenkert, *Tetrahedron Lett.*, 1185 (1966).

(12) Because the peak at τ 9.31 is a doublet, none of the product in which the positions of the hydrogen and deuterium at C-6 are interchanged can be significantly present.

(13) Whether one specifically labeled isomer IV is (like III) formed from Ib has not yet been determined, initial experiments having been thwarted because a minor side product of the Simmons–Smith reaction of norbornadiene[1a] seems to be IV!

(14) With rhodium on carbon as catalyst, there was considerable intramolecular scrambling.