Stannane was prepared according to the method of Emeléus and Kettle.[4] The melting point was determined to be −146° and the boiling point −52.5° (lit.[5] mp −150°; bp −51.8°). The solubility of stannane at ~78° (Dry Ice–acetone) was found to be 1.4 g/100 ml in ethyl ether, 1.8 g/100 ml in hexane, 2.4 g/100 ml in tetrahydrofuran, and 7.7 g/100 ml in carbon disulfide.

When stannane was added to a suspension of lithium hydride in dioxane or sodium hydride in mineral oil at liquid nitrogen temperature and allowed to come to room temperature, no reaction could be detected. In both cases over 95% of the stannane was recovered so that it is clear that stannane did not form a complex hydride.

A survey of the reactivity of stannane with a selection of organic functional groups was conducted. Stannane was condensed into a tube containing the substrate at liquid nitrogen temperature, and the mixture was brought over a period of several hours to room temperature by sequential transfer through a series of freezing mixtures of increasing temperature. Stannane did not react with aniline, triethylamine, dimethylacetamide, ethylacetamide, or ethyl acetate. Nitrobenzene was reduced to aniline in 94% yield (all identity and yield data by vpc). Benzaldehyde was reduced quantitatively to benzyl alcohol while acetone was reduced to isopropyl alcohol in a 71% yield. The reaction with benzyl chloride was complex, but a 10% yield of toluene was detected.

In contrast to the clean reduction of nitrobenzene, only a 29% yield of isopropylamine was obtained in the reduction of 2-nitropropane, and the reduction was accompanied by extensive decomposition of stannane. This difference is understandable in light of the demonstration that isopropylamine was found to catalyze the decomposition while aniline was without effect. Attempts to form a complex with the ligand N,N,N′,N′-tetramethylethylenediamine in tetrahydrofuran yielded only the decomposition products of stannane. When the aliphatic chelating agent was replaced with 1,10-phenanthroline or 2,2′-bipyridine, no reaction could be demonstrated and stannane was recovered in high yield.

Stannane reacted with boron trifluoride etherate to give quantitative yields of stannic fluoride and presumably diborane. With glacial acetic acid the major product was tin metal, but about 4% of the tin was found as a complex tin(IV) acetate. We have confirmed literature reports[1] that stannane is unaffected by dilute aqueous acid and alkali. However, stannane was decomposed by 2.5 *N* NaOH to give tin metal as the main product. About 8% of the tin was found in solution as stannate ion. With concentrated hydrochloric acid an initial precipitate of tin was observed; then the metal dissolved and the major product isolated was stannous chloride.

Stannane added to the double bond of acrylonitrile even though no reaction could be detected with methyl acrylate. When stannane (2.8 g, 0.023 mole) and inhibitor-free acrylonitrile (10 g, 0.20 mole) were condensed into a trap held at liquid nitrogen temperature (−195°) and the temperature was allowed to rise to room temperature, 2.6 g (34%, 0.008 mole) of tetrakis-(2-cyanothyl)tin[6] was isolated from the residue by distillation of the excess acrylonitrile.

Simple, unactivated olefins would not add stannane across the double bond in the absence of catalyst. We found, however, that cobalt naphthenate di-*t*-butyl peroxide (or *t*-butyl hydroperoxide), palladium (10% on charcoal), or hexachloroplatinic acid were effective in catalyzing the addition of stannane to a number of terminal olefins and at least one internal olefin. This addition was remarkably clean in that no alkyltin hydrides could be detected. In every case only the tetraalkyltin was found.

In a typical example, a trap held at liquid nitrogen temperature was charged with 60 mg of di-*t*-butyl peroxide, 150 mg of a 6% solution of cobalt naphthenate in mineral spirits, and butene-1 (6.0 g, 0.11 mole). Stannane (2.6 g, 0.021 mole) was then condensed in the trap, and the whole was allowed to come up to room temperature. The liquid residue weighed 2.4 g (34%, 0.07 mole). Vpc analysis showed it to be 99% tetrabutyltin and its infrared spectrum was free of any bands attributable to Sn–H bonds. Under the same conditions the following additional olefins reacted (the figure in parentheses is the per cent conversion of stannane to tetraalkyltin as determined by vpc): ethylene (34), propylene (20), isobutylene (14), octene-1 (6), and cyclohexene (20).

Acknowledgment. We thank Mr. John Saraka, Jr., for his technical assistance in these investigations and Messrs. I. L. Simmons and P. D. Brannigan and their colleagues for their analytical support.

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Received December 13, 1969

On the Mechanism of the Kolbe Electrosynthesis. A Comment on a Paper by Reichenbacher, Liu, and Skell

Sir:

Some years ago[1] it was proposed that the Kolbe electrosynthesis might occur *via* a concerted electron transfer and loss of CO_2 rather than the commonly

$$RCOO^- \rightarrow [R\cdots\cdots CO_2\cdots\cdots e^-(\text{anode})]^{\ddagger} \rightarrow R\cdot + CO_2 + e^- \quad (1)$$

assumed rate-determining step,[2] discharge of $RCOO^-$ to form $RCOO\cdot$ with subsequent decarboxylation of this species. Reichenbacher, Liu, and Skell[3] have recently determined "relative rate constants," k/k',[4]

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(1) L. Eberson, *Acta Chem. Scand.*, 17, 2004 (1963).

(2) For a discussion, see A. K. Vijh and B. E. Conway, *Chem. Rev.*, 67, 623 (1967); L. Eberson in "Chemistry of the Carboxyl Group," S. Patai, Ed., John Wiley & Sons, Inc., New York, N. Y., 1969, Chapter 6.

(3) P. H. Reichenbacher, M. Y. Liu, and P. S. Skell, *J. Am. Chem. Soc.*, 90, 1816 (1968).

(4) Defined as $(\log [RCOO^-]_{final} - \log [RCOO^-]_{initial})/(\log [R'COO^-]_{final} - \log [R'COO^-]_{initial})$, potassium pentanoate being the reference compound.

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).

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Received March 8, 1969

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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