

## Studies on the Kolbe Electrolytic Synthesis

### IX.\* Comparison between Anodic and Peroxydisulfate Oxidation of Carboxylates; Kinetics of Peroxydisulfate Decomposition in the Presence of Acetate Ion

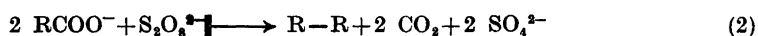
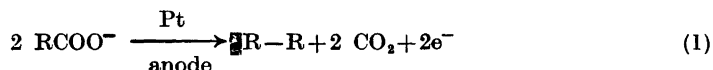
LENNART EBERSON, SYLVA GRÄNSE and  
BERIT OLOFSSON

*Department of Chemistry, University of Lund, Lund, Sweden*

The oxidation of ethyl *t*-butylmalonate ion, *t*-butylcyanoacetate ion, and *t*-butylmalonamate ion with peroxydisulfate ion in aqueous solution has been studied with respect to product distribution and the results compared with the anodic oxidation of the same substrates. The distributions of coupling products are closely similar in the two reactions. No products derived from cationic intermediates were detected in the peroxydisulfate reaction.

The kinetics of peroxydisulfate decomposition in the presence of acetate ion were also examined, using the pH-stat technique. From these results and the preparative studies it is concluded that the sulfate anion radical is the oxidizing species and that a chain reaction involving RCOO· (or R·) formed by attack of hydroxyl radicals on RCOO<sup>-</sup> is rather unlikely in this case.

The most important feature of the Kolbe electro-synthesis, formation of the coupling product R—R from RCOO<sup>-</sup> (eqn. 1) can be simulated in homogeneous medium by the oxidation of a carboxylate with peroxydisulfate ion (eqn. 2). Thus, Fichter and co-workers<sup>1-3</sup> were able to isolate coupling products from peroxydisulfate oxidation of ethyl malonate ion, ethyl methyl- and

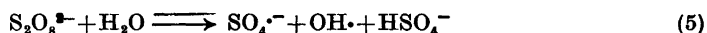


dimethylmalonate ion, and ethyl succinate ion, together with small amounts of what must now be recognized as products formed *via* disproportionation of

\* For part VIII in this series, see *Acta Chem. Scand.* 22 (1968) 2453.

intermediate radicals R. As an example,<sup>2</sup> ethyl dimethylmalonate ion on treatment with an equimolar amount of aqueous potassium peroxydisulfate at 100° gave diethyl tetramethylsuccinate (24 %) and a mixture of ethyl isobutyrate and ethyl  $\alpha$ -methylacrylate (yield was not given, but the saturated ester was the predominant product). In similar experiments with acetate ion, Glasstone and Hickling<sup>4</sup> obtained ethane and methane, products resulting from methyl radical coupling and hydrogen atom abstraction by methyl radicals, respectively. More recently,<sup>5</sup> bibenzyl has been obtained in 36 % yield from peroxydisulfate oxidation of phenylacetate ion and 1,1,2,2-tetra-phenylethane in 45 % yield from diphenylacetate ion.

Since these early investigations peroxydisulfate oxidations have been extensively studied from the mechanistic point of view.<sup>6,7</sup> For a number of substrates, including formate and oxalate ion, the rate of disappearance of peroxydisulfate ion has been shown to be first order in peroxydisulfate ion and zero order in substrate concentration. Although the nature of the rate-determining step is still under discussion, there is general agreement that the oxidizing species is the sulfate radical,  $\text{SO}_4^{\cdot-}$ , or in some cases also the hydroxyl radical,  $\text{HO}\cdot$ , both formed in the thermal decomposition of peroxydisulfate ion, either in a two-step process<sup>8</sup> (eqns. 3 and 4) or in a single step<sup>9</sup> (eqn. 5).



We have previously studied the Kolbe electrolysis of ethyl *t*-butylmalonate ion<sup>10</sup> and other *t*-alkylmalonates,<sup>11</sup> *t*-butylcyanoacetate ion,<sup>12</sup> and *t*-butylmalonamate ion<sup>13</sup> and found the coupling reaction to be predominant, partly because the intermediate radicals cannot disproportionate, partly because they are resistant towards further oxidation at the anode to form carbonium ions. In this paper, we wish to report a comparative study of the Kolbe electrolysis of these compounds in aqueous solution and the corresponding peroxydisulfate oxidation. Our aim has been to elucidate whether there is any significant difference in the chemical behavior between radicals generated at the anode and radicals formed in homogeneous solution under as closely similar conditions as possible. We were also interested to see if any carbonium ion mediated products are formed in the peroxydisulfate oxidations, since the formation of such products would have certain implications for the mechanism of peroxydisulfate oxidation. In this connection, the kinetics of peroxydisulfate ion in the presence of acetate ion have been studied.

## RESULTS

It must first be pointed out that several difficulties are encountered when the two reactions under investigation are to be compared under as closely similar experimental conditions as possible. The Kolbe reaction<sup>14</sup> is favored in organic solvents like methanol and *N,N*-dimethylformamide, (DMF), whereas the peroxydisulfate reaction has to be carried out in aqueous solution,

partly due to solubility problems, partly due to the fact that peroxydisulfate decomposition is strongly influenced by organic additives. The peroxydisulfate reaction has to be run at temperatures around 100°, whereas the Kolbe reaction generally is suppressed at high temperatures. The possibility that anodically generated radicals can be further oxidized at the anode to give cations must also be considered, although the substrates chosen here are fairly resistant in this respect. After preliminary experiments, the best compromise between the above-mentioned requirements was found in running the Kolbe reaction in water at pH 7 at 30° to an extent of 5 %, and the peroxydisulfate reaction in water at 100°, employing an initially neutral solution of the carboxylate and a ratio of  $[\text{RCOO}^-]/[\text{S}_2\text{O}_8^{2-}]$  of 5:1. This high ratio is necessary to maintain the pH of the solution reasonably constant during the whole reaction period. The peroxydisulfate decomposition reaction is accompanied by the liberation of two protons/peroxydisulfate ion and hence lower ratios will cause a decrease of the pH of the solution and formation of the free acid during the run. This in turn undergoes a slow decarboxylation under the reaction conditions employed. The use of a high ratio of  $[\text{RCOO}^-]/[\text{S}_2\text{O}_8^{2-}]$  is also desirable in order to avoid possible further oxidation of the products formed primarily.

Table 1 is a summary of the product distributions obtained in the oxidation of ethyl *t*-butylmalonate ion. Both reactions are remarkably clean, the coupling products accounting for about 95 % of the total product mixture. The minor components were not identified since it is sufficient for the purpose at hand to know that carbonium ion mediated products are not formed to any large extent.

In Table 2 we have summarized the yields of coupling products from the oxidation of *t*-butylcyanoacetate ion under different conditions. Unfortunately, the Kolbe reaction in water in this case gives low yields of coupling products but instead a large percentage of low-boiling components. Results from non-aqueous runs<sup>15</sup> have therefore been included in the table; in such media the

Table 1. Coupling products from the oxidation of ethyl *t*-butylmalonate ion.

Reaction	Total yield of coupling products, %	Diethyl 2,3-di- <i>t</i> -butylsuccinate Meso form, %	Racemic form, %
Kolbe reaction in water, analytical run at 30°, anode potential +2.5 V vs. SCE, 5 % of theoretical amount of charge passed	41 <sup>a</sup>	51	49
Kolbe reaction in methanol, preparative run at 30°	74 <sup>a</sup>	50	50
Peroxydisulfate oxidation in water at 100°, $[\text{RCOO}^-]/[\text{S}_2\text{O}_8^{2-}] = 5:1$	34 <sup>b</sup>	51	49

<sup>a</sup> Current yield. <sup>b</sup> Calculated according to the stoichiometry of eqn. 2 (see also below).

Table 2. Coupling products from the oxidation of *t*-butyleyoacetate ion.

Reaction	Total yield of coupling products, %	Coupling products		
		2,3-Di- <i>t</i> -butylsuccinonitrile Meso form, %	Racemic form, %	<i>N</i> -( <i>t</i> -butylacetyl)- <i>t</i> -butylglycinonitrile, %
Kolbe reaction in water, analytical run at 30°, anode potential +3.0 V vs. SCE, 5 % of theoretical amount of charge passed	Low <sup>a</sup>	21	31	48
Kolbe reaction in water <sup>15</sup>	5 <sup>a</sup> , 14 <sup>b</sup>	28	36	36
Kolbe reaction in methanol <sup>15</sup>	47 <sup>a</sup> , 61 <sup>b</sup>	21	28	51
Kolbe reaction in DMF <sup>15</sup>	7 <sup>a</sup> , 16 <sup>b</sup>	26	19	55
Kolbe reaction in CH <sub>3</sub> CN <sup>15</sup>	12 <sup>a</sup> , 37 <sup>b</sup>	24	22	54
Peroxydisulfate oxidation in water at 100°, [RCOO <sup>-</sup> ]/[S <sub>2</sub> O <sub>8</sub> <sup>2-</sup> ] = 1:1	38 <sup>c</sup>	32	21	47
Same, but ratio 2:1	40 <sup>c</sup>	27	34	39
Same, but ratio 5:1	23 <sup>c</sup>	25	45	30
Same, but ratio 20:1	31 <sup>c</sup>	25	48	27

<sup>a</sup> Current yield. <sup>b</sup> Calculated on the basis of eqn. 1. <sup>c</sup> Calculated on the basis of eqn. 2.

products are formed in much higher yields and coupling predominates. However, the results from aqueous runs provide at least a qualitative indication of how anodically generated  $\alpha$ -cyanoalkyl radicals behave in this medium. In contrast to the anodic oxidation in water, peroxydisulfate oxidation of *t*-butyleyoacetate ion in water at 100° gave coupling products *exclusively* with no other products detectable.

Finally, Table 3 summarizes the results obtained in the oxidation of *t*-butylmalonamate ion. Here the Kolbe reaction did not give any products in aqueous medium, probably due to the fact that the anode is covered by the exceedingly difficultly soluble 2,3-di-*t*-butylsuccinic diamides (even in

Table 3. Coupling products from the oxidation of *t*-butylmalonamate ion.

Reaction	Total yield of coupling products, %	Coupling products	
		2,3-di- <i>t</i> -butylsuccinic diamide Meso form, %	Racemic form, %
Kolbe reaction in methanol <sup>13</sup>	25 <sup>a</sup> , 55 <sup>b</sup>	67	33
Peroxydisulfate oxidation in water at 100°, [RCOO <sup>-</sup> ]/[S <sub>2</sub> O <sub>8</sub> <sup>2-</sup> ] = 5:1	41 <sup>c</sup>	73	27

<sup>a</sup> Current yield. <sup>b</sup> Calculated on the basis of eqn. 1. <sup>c</sup> Calculated on the basis of eqn. 2.

Table 4. Rate of decomposition of peroxydisulfate ion in water at 80.0°;  $[S_2O_8^{2-}] = 4.8 \times 10^{-4}$  M.

pH	Rate constant, <sup>a</sup> min <sup>-1</sup>	pH	Rate constant, <sup>a</sup> min <sup>-1</sup>
5.1	0.010	7.6	0.012
5.6	0.012	8.1	0.013
6.1	0.013	8.6	0.010
6.6	0.013	9.1	0.008
7.1	0.012	9.6	0.006

<sup>a</sup> Mean value from 3–6 runs; the probable error is  $\pm 10$  %.

methanol, the current efficiency for the Kolbe reaction with malonic acids<sup>13</sup> is rather low, so this behavior was not unexpected), so we have to base the comparison on product distributions from methanolic runs. Again, the peroxydisulfate reaction was very clean; only coupling products were observed and thus no incursion of carbonium ions has occurred in this system either.

Next, we turned our attention to the study of the kinetics of peroxydisulfate decomposition in water alone, with acetate ion present, and with the above-mentioned substrates present. The kinetics could be conveniently followed by the pH-stat technique, enabling the determination of rate constants in the otherwise difficultly accessible pH region between 5 and 10 in very dilute solution with no other species than those participating in the reaction and sodium ions from the added titrating solution present.

Table 4 lists rate constants for the decomposition of peroxydisulfate ion in water alone at different hydrogen ion concentrations at 80.0°, obtained by the pH-stat technique.

Next, the kinetics of the reaction were examined with acetate ion present. As Table 5 shows, this reaction exhibits the characteristics of many other peroxydisulfate oxidations,<sup>6</sup> *i.e.*, the reaction is first order in  $[S_2O_8^{2-}]$  and zero order in substrate, but nevertheless the rate constant in the presence of substrate is appreciably larger than that observed for the decomposition in

Table 5. Rate of decomposition of peroxydisulfate ion in water at 80.0° in the presence of acetate ion; pH=7.6,  $[S_2O_8^{2-}] = 4.8 \times 10^{-4}$  M.

$[CH_3COO^-]/[S_2O_8^{2-}]$	Rate constant, <sup>a</sup> min <sup>-1</sup>
2.00	0.034
4.00	0.033
10.0	0.025
20.0	0.028
30.0	0.027
40.0	0.029

<sup>a</sup> Mean value from 3–5 runs; probable error is  $\pm 10$  %.

Table 6. Rate of decomposition of peroxydisulfate ion in water at 80.0° in the presence of  $t\text{-C}_4\text{H}_9\text{CH(X)COO}^-$ ; pH = 7.6,  $[\text{S}_2\text{O}_8^{2-}] = 4.8 \times 10^{-4}$  M,  $[\text{RCOO}^-]/[\text{S}_2\text{O}_8^{2-}] = 20.0$ .

X	Rate constant, <sup>a</sup> min <sup>-1</sup>
COOEt	0.035
CN	0.031
CONH <sub>2</sub>	0.012

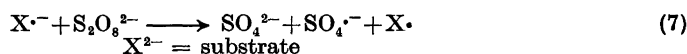
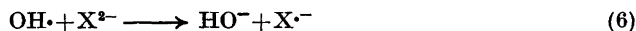
<sup>a</sup> Mean value from three runs; probable error  $\pm 10$  %.

water alone. Finally, Table 6 gives rate constants for peroxydisulfate decomposition in the presence of a large excess of the substrates studied in this paper.

#### DISCUSSION

**Peroxydisulfate oxidation.** The preparative results (Tables 1–3) from peroxydisulfate oxidation of ethyl *t*-butylmalonate ion, *t*-butylcyanoacetate ion, and *t*-butylmalonamate ion demonstrate that the products are exclusively derived from radical coupling and that no products formed *via* cations were detected. The yields of coupling products, based on the stoichiometry of eqn. 2, fall in the region between 25 and 40 %.

The first problem at hand is to identify the oxidizing species. From the kinetic behavior of peroxydisulfate decomposition in the presence of acetate ion one can see that this reaction conforms to the behavior of other peroxydisulfate oxidations, being first order in  $[\text{S}_2\text{O}_8^{2-}]$  and zero order in  $[\text{CH}_3\text{COO}^-]$  with a considerably higher rate constant than for the decomposition in water. This type of kinetics has been explained in terms of a chain reaction<sup>6</sup> where initially formed hydroxyl radicals (eqns. 3 and 4 or 5) attack the substrate to form new radicals, which in their turn induce the decomposition of peroxydisulfate ions (eqns. 6 and 7).

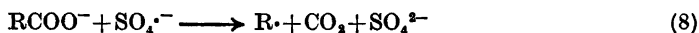


With  $\text{X}^{2-}$  equal to  $\text{RCOO}^-$ ,  $\text{X}\cdot^-$  would be the  $\text{RCOO}\cdot$  radical (or, in view of the instability of such radicals,<sup>16</sup> its decarboxylation product, R.) and X then equal to  $\text{RCOO}^+$  (or, more likely,  $\text{R}^+$ ).

The results from the peroxydisulfate oxidations (Tables 1–3) are, however, seriously in disagreement with this mechanism. Firstly, no carbonium ion mediated products are formed from the carboxylates studied above, nor have such products (methanol and/or formaldehyde) been detected among the products formed in the peroxydisulfate oxidation of acetate ion.<sup>4</sup> Secondly, we tested the possibility that hydroxyl radicals might be the oxidizing species

by treating *t*-butylcyanoacetate ion with Fenton's reagent,<sup>17</sup> a known hydroxyl radical generating system, at pH 4.5 in aqueous solution. No coupling products were obtained in this reaction.

Thus, the sulfate radical in all probability is the oxidizing species in the peroxydisulfate oxidation of carboxylates (eqn. 8) and, since no products



derived from carbonium ions are observed, the radicals R· cannot propagate a chain reaction as depicted in eqns. 6 and 7.

It was originally hoped that the yields of coupling products would provide some information regarding the nature of the initial step. The homolytic cleavage of peroxydisulfate ion to form two sulfate radicals (eqn. 3) would evidently give twice the yield of coupling products than the rate-determining step favored by Fronæus and Östman<sup>9</sup> (eqn. 5), in which only one sulfate radical per peroxydisulfate ion is formed. However, the yield of coupling products, based on the formation of two sulfate radicals per peroxydisulfate ion, never exceeded 50 % and hence no conclusions can be drawn. It has recently been shown<sup>18</sup> that sulfate radicals generated by photolysis of aqueous potassium peroxydisulfate solution react very fast thermally with acetate and formate, in fact so fast that the rate constants could not be determined. Other substrates, such as methanol and ethanol, react with sulfate radicals according to second-order kinetics with rate constants of the order of  $10^8 \text{ M}^{-1}\text{sec}^{-1}$  at room temperature.

The rate constants for the decomposition of peroxydisulfate ion in water (Table 4) are somewhat higher than those reported by other investigators (for compilations of rate constants, see Refs. 6, 7). It is, however, difficult to compare our values with the literature values for a number of reasons. Many of the literature values have been obtained from runs on initially neutral solutions of peroxydisulfate, in which cases the hydrogen ion catalyzed decomposition during the later stages of the run necessitates an extrapolation procedure to evaluate the rate constant of the uncatalyzed reaction. Moreover, it is known<sup>6,7</sup> that the rate constant increases with decreasing peroxydisulfate ion concentration. In this work, the concentration range is 10–100 times lower than normally employed. Finally, the fact that other investigators have had to use buffers in the difficultly accessible pH region between 5 and 10 might account for part of the difference.

*Comparison with the Kolbe reaction.* Tables 1–3 clearly show that radicals generated in the homogeneous peroxydisulfate and the heterogeneous Kolbe oxidation undergo the coupling reaction to form very similar product mixtures. From ethyl *t*-butylmalonate ion, the coupling product consists of a 1:1 mixture of diethyl meso- and rac-2,3-di-*t*-butylsuccinate irrespective of how the radical is formed. Kolbe coupling of *t*-butylcyanoacetate ion gives ratios of meso- to rac-di-*t*-butylsuccinonitrile in the range of 0.5–1.5, depending on the solvent used, whereas the peroxydisulfate oxidation gives ratios in the same range, depending on the concentration ratios employed. Similarly, the ratio between C-to-C- and C-to-N-coupling products varies slightly in both reactions, depending on the reaction conditions employed. It is difficult to

rationalize these variations, but it is important to note that they are fairly small and are found in both the homogeneous and heterogeneous process.

Finally, the composition of the product mixtures from peroxydisulfate and Kolbe oxidation of *t*-butylmalonamate ion are nearly identical, although it must be noted that the solvents differ in this case.

The implications of the similarity with regard to product distribution between the Kolbe and peroxydisulfate oxidation of carboxylates have been discussed elsewhere.<sup>19</sup>

### EXPERIMENTAL

*Kolbe electrolyses.* The electrolyses were run in a micro-cell using a 0.02 cm<sup>2</sup> Pt wire as the anode and a piece of Pt foil as the cathode. The electrolyte was a solution of 10 mmoles of the acid in 5.0 ml of 2.0 M aqueous sodium hydroxide, adjusted to pH 7. The electrolyses were performed at a constant anode potential, maintained by an AMEL model 557 potentiostat connected with the model 558 Integrator from the same company. When 5.0 % of the theoretical amount of charge had been passed through the solution, products were taken up in ether and the ether solution was analyzed by VPC on a 2 m × 0.3 cm 5 % neopentylglycolsuccinate on Chromosorb P column using 2-acetoxybiphenyl as a standard (Perkin-Elmer 880 gas chromatograph, equipped with a disc integrator). The product from the electrolysis of *t*-butylmalonamate ion in methanol was analyzed after conversion to the corresponding dinitriles by treatment with POCl<sub>3</sub>, a procedure known to preserve the configurational integrity of the primary product.<sup>18</sup>

*Peroxydisulfate oxidations.* The coupling products were identified by isolation and comparison with authentic samples in preparative runs, using solutions 1 M in carboxylate and 1 M in potassium peroxydisulfate, which were kept at the boiling point for 30 min.

Analytical runs were made on solutions of 10 mmoles of the acid, dissolved in 5.0 ml of 2.0 M aqueous sodium hydroxide. After addition of the appropriate amount of potassium peroxydisulfate (usually 2 mmoles) the solution was kept at 100° for 30 min. Products were isolated and analyzed as before.

*Oxidation of *t*-butylcyanoacetate ion by Fenton's reagent.* *t*-Butylcyanoacetic acid (10 mmoles) was dissolved in a solution of NaH<sub>2</sub>PO<sub>4</sub>·H<sub>2</sub>O (138 mg) and Na<sub>2</sub>HPO<sub>4</sub>·7 H<sub>2</sub>O (455 mg). The final pH of this solution was about 4.5. Then 30 % H<sub>2</sub>O<sub>2</sub> (1 ml, 10 mmoles) and ferrous sulfate solution (10 moles dissolved in 6.0 ml of water) were added to the rapidly stirred solution by means of two syringes, automatically operated so as to deliver the two reagents at the same rate (about 1 mmole of each per min). The temperature of the reaction mixture was about 20°. The reaction mixture was extracted by ether (3 × 10 ml) and the ether solution washed with sodium bicarbonate solution. After concentration to about 2 ml, the solution was analyzed by VPC for coupling products. None of the possible coupling products was detectable even at high attenuations.

*Kinetics of peroxydisulfate decomposition.* The kinetic studies were performed in a closed thermostated vessel of a volume of about 120 ml. Care was taken to ensure that no other organic material than a Teflon-covered stirring magnet was in contact with the solution or the vapor above it. Prior to use, the vessel was conditioned<sup>7</sup> by running several peroxydisulfate compositions on it.

Water (100 ml, distilled twice in an all-quartz apparatus) was allowed to reach thermal equilibrium in the vessel, in the appropriate cases with carboxylate added. Then the pH was adjusted to a preset value by means of a Radiometer pH-stat apparatus (SBR2c titrigrph, SBULa syringe burette, and TTT1a titrator). Potassium peroxydisulfate solution (13 mg in 0.5 ml of water) was injected into the rapidly stirred solution, and the decomposition rate followed by recording *vs.* time the amount of sodium hydroxide (0.1 M) added to maintain the pH of the solution at the constant, preset value. The rate constants were evaluated by Guggenheim plots.



*Acknowledgements.* One of the authors (L.E.) is grateful to the Swedish Natural Science Research Council for generous financial support, and to Professor S. Fronæus at the Department of Physical and Inorganic Chemistry, University of Lund, for valuable discussions.

## REFERENCES

1. Fichter, F. and Heer, J. *Helv. Chim. Acta* **18** (1935) 704.
2. Fichter, F. and Heer, J. *Helv. Chim. Acta* **18** (1935) 1276.
3. Fichter, F. and Heer, J. *Helv. Chim. Acta* **19** (1936) 149.
4. Glasstone, S. and Hickling, A. *J. Chem. Soc.* **1934** 1878.
5. Horii, Z. and Sakurai, K. *J. Pharm. Soc. Japan* **77** (1957) 1.
6. House, D. A. *Chem. Rev.* **48** (1962) 185.
7. Hakoila, E. *Ann. Univ. Turku Ser. A* **66** (1963).
8. Kolthoff, I. M. and Miller, I. K. *J. Am. Chem. Soc.* **73** (1951) 3055.
9. Fronæus, S. and Östman, C. O. *Acta Chem. Scand.* **9** (1955) 902.
10. Ebersson, L. *Acta Chem. Scand.* **13** (1959) 40.
11. Ebersson, L. and Sandberg, B. *Acta Chem. Scand.* **20** (1966) 739.
12. Ebersson, L. *J. Org. Chem.* **27** (1963) 2329; Ebersson, L. and Nilsson, S. *Acta Chem. Scand.* **22** (1968) 2453.
13. Ebersson, L. *Acta Chem. Scand.* **17** (1963) 1196.
14. For recent reviews, see: Vijh, A. K. and Conway, B. E. *Chem. Rev.* **54** (1968) 623; Ebersson, L. In Patai, S. *Chemistry of Carboxylic Acids*, Wiley, London 1968, Chap. 6. *In press.*
15. Ebersson, L. and Nilsson, S. *Acta Chem. Scand.* **22** (1968) 2453.
16. Braun, W., Rajkenbach, L. and Eirich, F. R. *J. Phys. Chem.* **66** (1962) 1591.
17. Coffmann, D. D., Jenner, E. L. and Lipscomb, R. D. *J. Am. Chem. Soc.* **80** (1958) 2864.
18. Dogliotti, L. and Hayon, E. *J. Phys. Chem.* **71** (1967) 2511.
19. Ebersson, L. *Electrochim. Acta* **12** (1967) 1473.

Received March 21, 1968.