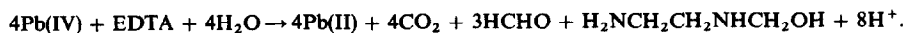


## STUDY OF THE OXIDATION OF ETHYLENEDIAMINETETRA-ACETIC ACID WITH LEAD DIOXIDE SUSPENSION IN SULPHURIC ACID

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**Summary**—The stoichiometry of the reaction between lead dioxide suspension and EDTA was studied by derivative polarographic titration and determination of the products. Four moles of Pb(IV) are reduced per mole of EDTA with moderate speed at room temperature in sulphuric acid solutions. Four moles of carbon dioxide and 3 moles of formaldehyde are the products of the oxidation of 1 mole of EDTA. One mole of *N*-hydroxymethylethylenediamine is also thought to be produced. The overall reaction may be written as



Ethylenediamine is also partly produced if a large excess of lead dioxide is used.

The investigation of the redox reactions of organic sequestering agents such as ethylenediaminetetra-acetic acid (EDTA) with various oxidizing agents has become increasingly important in analytical and environmental chemistry.<sup>1,2</sup> The kinetics and the reaction products of the oxidation of EDTA with Ce(IV)<sup>3</sup> and Mn(III)-EDTA<sup>4</sup> have been reported, but the stoichiometry of the reactions has not been made clear. Another report deals with the oxidative determination of EDTA with potassium permanganate,<sup>5</sup> but says nothing about the kinetics or the products.

Recently, in our laboratory, the redox reaction of lead dioxide suspension, prepared by hydrolysis of lead tetra-acetate, with sodium oxalate in nitric acid was investigated by derivative polarographic titration (conventional potentiometric titration at constant current, the "DPT" method) and determination of the reaction products.<sup>6</sup>

The present work applies the same methods to the redox reaction of lead dioxide suspension with EDTA in sulphuric acid. Four moles of Pb(IV) are reduced per mole of EDTA with moderate speed at room temperature in sulphuric acid media. Four moles of carbon dioxide and three moles of formaldehyde are produced from one mole of EDTA, and one mole of *N*-hydroxymethylethylenediamine is also thought to be produced.

These results are of interest from the viewpoint of heterogeneous reactions in analytical chemistry and also oxidative destruction of polyaminocarboxylic acids in waste-water treatment in environmental chemistry.

### EXPERIMENTAL

#### Reagents and apparatus

A 0.05*M* solution of lead tetra-acetate in glacial acetic

acid was standardized by potentiometric titration with sodium oxalate.<sup>7</sup> A 0.02*M* EDTA solution was prepared from the recrystallized dihydrate of the disodium salt. The formaldehyde solution was prepared by diluting commercial formalin and standardized by the sodium sulphite method. The ethylenediamine solution was standardized with hydrochloric acid.<sup>8</sup> Three potentiometers were used to measure the potentials of the anode and cathode vs. SCE, and the potential difference between anode and cathode. All titrations were performed at 25 ± 0.2°.

#### Determination of the reaction stoichiometry

The DPT method was used for determining the reacting ratios, as follows. A 100-ml electrolytic cell fitted with a rubber stopper was used as the reaction vessel, to which 5 ml of 2.5*M* sulphuric acid, 5 ml of 1*M* potassium nitrate, and 35 ml of distilled water were added. The solution was deaerated with nitrogen. Two platinum electrodes, 0.5 mm in diameter and 20 mm long, sealed in glass tubes, were inserted as the anode and cathode. The anode was electrolytically reduced to remove the oxide film on the platinum surface. Then 5.00 ml of 0.05*M* standard lead tetra-acetate solution were added followed by a known amount of standard EDTA solution, nitrogen was passed through the solution for 1 min, and the potential difference produced by the constant current polarization was measured after 1 min more. The waiting time before measurements of potential difference was made longer (3 min) in the neighbourhood of the end-point. The solution was stirred throughout the titration.

#### Determination of the products

Solutions of lead tetra-acetate and EDTA were mixed in 4:1 molar ratio in 0.25*M* sulphuric acid and allowed to stand for 30 min.

The lead sulphate was filtered off, then dissolved in a small amount of 5*M* ammonium acetate, and the solution was adjusted to pH 4–5 with dilute nitric acid and analysed for lead polarographically.

Particular attention was paid to measuring the amount of carbon dioxide evolved, since contamination with acetic

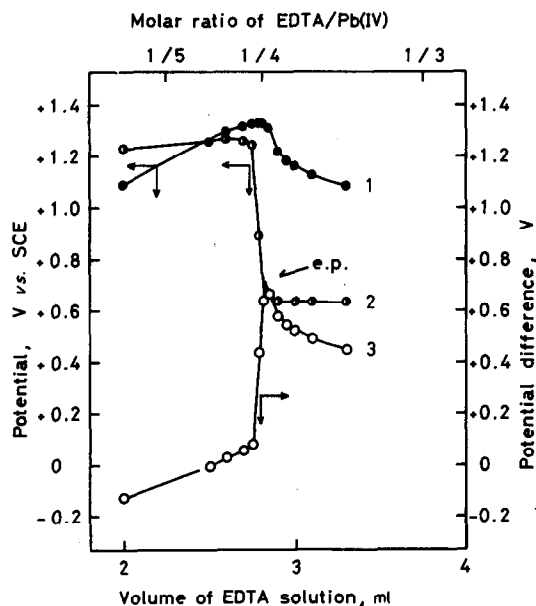


Fig. 1. Titration curve and potential changes of anode and cathode for 5.00 ml of  $4.55 \times 10^{-2} M$  lead tetra-acetate hydrolysed in 0.25M sulphuric acid and 0.1M potassium nitrate, and then titrated with  $2.02 \times 10^{-2} M$  EDTA. Current density 19 nA/mm<sup>2</sup>: ●: anode potential; ○: cathode potential; ○:  $\Delta E$ .

acid was unavoidable. The carbon dioxide evolved was first absorbed in two traps, each containing 50 ml of 0.005M barium hydroxide, a stream of nitrogen being passed through the system for 10 hr, as carrier gas. Then 4 ml of conc. nitric acid were added to the traps and the carbon dioxide evolved was transferred into another two traps with a stream of nitrogen. The excess of barium hydroxide in these two traps was titrated with hydrochloric acid. The flow-rate of nitrogen was 10 ml/min in both cases.

Formaldehyde was determined by distillation into a solution of Schiff's reagent or chromotropic acid followed by gravimetric determination with dimedone<sup>9</sup> or titration with iodine.<sup>10</sup>

Ethylenediamine was determined as follows. Lead tetra-acetate and EDTA solutions were mixed in sulphuric acid medium. Lead sulphate and lead dioxide were filtered off and most of the acetic acid was removed by steam distillation. Barium hydroxide crystals were added to remove most of the sulphuric acid and the barium sulphate was filtered off. Iodine and alkali were added to oxidize formal-

Table 1. Determination of carbon dioxide

Calcd., mM	Found, mM	Recovery %	Moles of CO <sub>2</sub>	
			Moles of EDTA	
4.94	4.32	87	3.5	
	5.31	107	4.3	
	4.47	90	3.6	
	4.79	97	3.9	
	4.41	89	3.6	
	4.59	93	3.7	
			Mean 3.8	

dehyde to formic acid and liberate ethylenediamine from *N*-hydroxymethylethylenediamine. The solution was then evaporated to small volume to remove excess of iodine and raise the efficiency of the subsequent steam-distillation. The solution was placed in a 200-ml Claisen flask, adjusted to pH 13 and steam-distilled. A known volume of hydrochloric acid of known concentration was added to the 400-500 ml of distillate, and the excess of acid was titrated potentiometrically with sodium hydroxide solution.

## RESULTS AND DISCUSSION

### Determination of reacting ratio

An example of the titration curve obtained by the DPT method is shown in Fig. 1. Curves 1 and 2 show the changes in the potential of the anode and the cathode, respectively. The reduction of lead dioxide and oxidation of OH<sup>-</sup> are the electrode reactions before the end-point, at the cathode and the anode, respectively. After the end-point, the reduction of the oxide film on the cathode and oxidation of EDTA are the electrode reactions at the cathode and the anode. Curve 3 is the titration curve giving the changes of potential difference ( $\Delta E$ ) between the anode and the cathode. A peak appears at the end-point, and gives the molar reacting ratio between Pb(IV) and EDTA. The optimum current density was obtained by measuring current-potential curves at both electrodes.

A wide range of current density at the anode is suitable, but a low current density at the cathode

Table 2. Determination of formaldehyde by dimedone method

Moles of Pb(IV)	HCHO, mmole		Moles of HCHO
	Moles of EDTA	Calcd.	
4	0.121	0.091 ± 0.004	3.0
5.4	0.180	0.141 ± 0.005	3.1
16	0.120	0.103 ± 0.005	3.4
32	0.090	0.077 ± 0.002†	3.4
	0.155	0.180 ± 0.010‡	3.5

\* Average and deviation are based on three replicates of each of four solutions, except where indicated.

† One solution, three replicates.

‡ Three solutions, three replicates of each.

Table 3. Determination of formaldehyde by iodimetry

Moles of Pb(IV)		HCHO, mmole		Moles of HCHO
Moles of EDTA	Calcd.	Found*	Moles of EDTA	
5.4	0.180	0.170 ± 0.001	3.8	
		0.181 ± 0.001	4.0	
		0.171 ± 0.002	3.8	
		0.177 ± 0.001	3.9	
		0.177 ± 0.003	3.9	
			Mean 3.9	

\* Average and deviation are based on three aliquots of the same solution.

(~25 nA/mm<sup>2</sup>) is preferable. The titration of 50 ml of  $4.55 \times 10^{-3}M$  lead dioxide suspension with  $2.02 \times 10^{-2}M$  EDTA at various current densities from 6.3 to 63 nA/mm<sup>2</sup> gave practically identical results, with a 4:1 mole ratio of Pb(IV) to EDTA. A sharp peak on the titration curve was obtained with 19–25 nA/mm<sup>2</sup> current density. However, the titration curves were liable to rise after the end-point when a current density below 19 nA/mm<sup>2</sup> was applied. The reacting ratio was also determined as a function of the concentration of Pb(IV), (1.00 or 2.00 ml of lead tetracetate solution) the acidity (0.05 or 0.5M sulphuric acid), and temperature (35 or 45°). The 4:1 ratio was found in all cases.

#### Products

The determination of Pb(II) was tested with a standard lead nitrate solution. The recovery was  $99 \pm 2\%$ . The determination of Pb(II) in the reaction solution confirmed the 4:1 reacting ratio.

The results for the determination of carbon dioxide are shown in Table 1. The calculated value listed is based on the assumption that all four carboxyl groups of EDTA are decarboxylated. The results indicate that four moles of carbon dioxide are produced per mole of EDTA.

The results for determination of formaldehyde by the dimedone method are shown in Table 2. The effect of other substances present (sulphuric acid, acetic acid, ethylenediamine, lead sulphate and lead diox-

ide) was studied beforehand, and the recovery of formaldehyde found to be  $99 \pm 1\%$ . Table 2 indicates that three moles of formaldehyde are produced per mole of EDTA if the ratio Pb(IV):EDTA = 4:1, and more than three if a large excess of lead dioxide is present.

The results for the determination of formaldehyde by iodimetry are also shown in Table 3. The effect of ethylenediamine was studied first. The recovery of formaldehyde was  $100 \pm 1\%$  in the presence of ethylenediamine in molar ratio between 1:4 and 3:4 to formaldehyde. The results appear to indicate that four moles of formaldehyde are produced per mole of EDTA. However, it has been reported<sup>10</sup> that the *N*-hydroxymethyl compounds of amines can be oxidized by iodine, and the *N*-hydroxymethyl group determined by iodimetry. *N*-Hydroxymethylethylenediamine has not been reported yet in the literature, but it would be formed between ethylenediamine and formaldehyde, and would also be determined by iodimetry. Therefore, it is supposed that three moles of formaldehyde and one mole of *N*-hydroxymethylethylenediamine are produced per mole of EDTA.

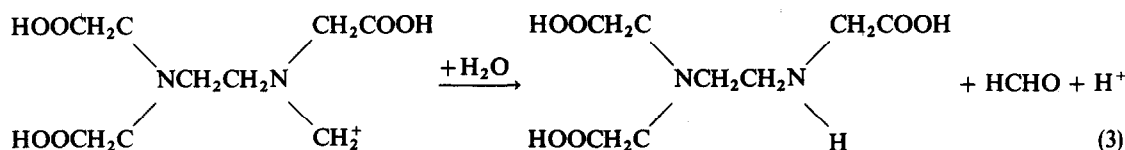
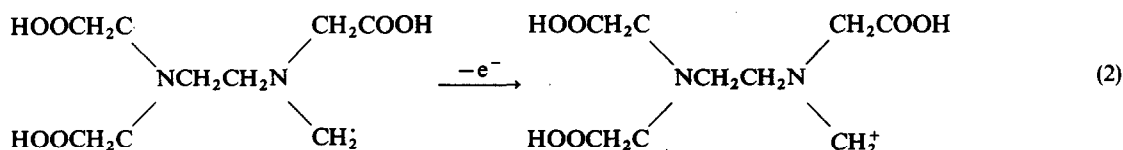
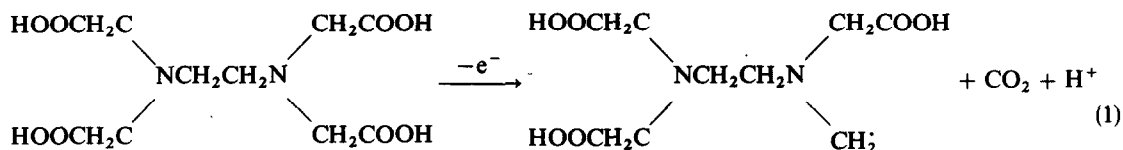
The results for determination of ethylenediamine are shown in Table 4. The calculated value is based on the assumption that one mole of ethylenediamine will be produced per mole of *N*-hydroxymethylethylenediamine. In preliminary experiments on the distillation method for the determination of ethylenediamine, the recovery for the complete procedure was about  $72 \pm 2\%$ . The results in Table 4 indicate that the value found is about 59% of the calculated value. Taking into account the recovery (72%) in the preliminary experiments, about 82% of the expected amount of ethylenediamine is found. It is therefore postulated that one mole of *N*-hydroxymethylethylenediamine is produced from one mole of EDTA and almost completely recovered as ethylenediamine.

Table 4. Determination of ethylenediamine

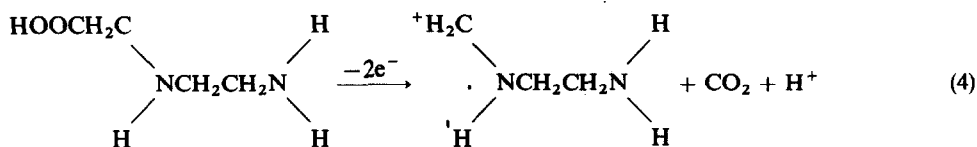
EDTA, mmole	Ethylenediamine		
	Calcd., mmole	Found, mmole	Recovery, %
0.180	0.180	0.109	61
		0.107	59
		0.104	58
		0.116	64
		0.102	57
		0.101	56
		Mean 0.107	59

#### CONCLUSIONS

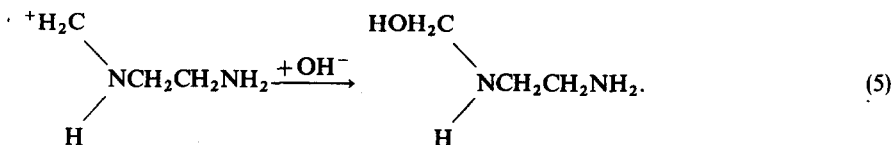
From the results above, the mechanism is suggested to be as follows. EDTA first loses one electron, with decarboxylation, and then a second electron before the detachment of formaldehyde by hydrolysis.



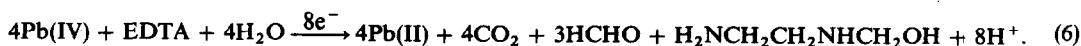
This sequence is repeated in the second and third steps. In the fourth step, it is supposed that after the decarboxylation of ethylenediamine-acetic acid, the hydrolysis does not occur easily,



and *N*-hydroxymethyl-ethylenediamine is produced by addition of  $\text{OH}^-$  owing to the abnormal Kolbe reaction.<sup>11,12</sup>



Therefore, the overall reaction may be written as



In the presence of a large excess of lead dioxide, the detachment of more than three moles of formaldehyde per mole of EDTA proceeds. This is of interest because it may be due to the effect of the adsorptive properties of the surface of lead dioxide.

The reaction is being investigated in media other than sulphuric acid.

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#### REFERENCES

- R. G. Clem and A. T. Hodgson, *Anal. Chem.*, 1978, **50**, 102.
- P. D. Goulden and D. H. J. Anthony, *ibid.*, 1978, **50**, 953.
- S. B. Hanna, S. Al-Hashimi, W. H. Webb and W. R. Carroll, *Z. Anal. Chem.*, 1969, **246**, 231.
- N. Tanaka, K. Gomi and T. Shirakashi, *Nippon Kagaku Kaishi*, 1975, 444.
- M. T. Beck, *Chemist-Analyst*, 1961, **50**, 14.
- S. Ito, T. Matsuda and T. Nagai, *Bunseki Kagaku*, 1977, **26**, 687.
- T. Nagai, T. Matsuda and N. Sugii, *ibid.*, 1971, **20**, 1412.
- E. F. Hillenbrand and C. A. Pentz, in *Organic Analysis*, Vol. 3, J. Mitchell, Jr., I. M. Kolthoff, E. S. Proskaner and A. Weissberger, eds., p. 142. Interscience, New York, 1956.
- J. H. Yoe and L. C. Reid, *Ind. Eng. Chem., Anal. Ed.*, 1941, **13**, 238.
- M. Imoto, H. Kakiuchi and K. Kou, *Horumuarudehido*, p. 414. Asakura, Tokyo, 1965.
- S. Tsutsumi and K. Koyama, *Denki Kagaku*, 1965, **33**, 407.
- T. Kitagawa and S. Tsushima, *Bunseki Kagaku*, 1966, **15**, 452.