THE OXIDATIVE DECARBOXYLATION OF POLYAMINOCARBOXYLIC ACIDS WITH LEAD DIOXIDE SUSPENSION IN NEUTRAL MEDIUM

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Summary—The reaction between a suspension of lead dioxide and polyaminocarboxylic acids in neutral medium at 80° has been examined titrimetrically and found to involve decarboxylation in which 3 moles of PbO_2 oxidize 1 mole of the acid, the products being 3 moles of CO_2, 3 moles of HCHO, 1 mole of ethylenediaminemonoacetic acid and 3 moles of Pb(II) followed by chelation of the 3 moles of Pb(II) by an additional 3 moles of EDTA.

The oxidation of the polyaminocarboxylic acids used as sequestering agents has found applications in analytical and environmental chemistry.[1,2] MacNevin et al.[3] have studied the homogeneous precipitation of ferric hydroxide through release of iron(III) from its EDTA-complex by destructive oxidation of the EDTA with hydrogen peroxide. Rao et al.[4] used the same idea in precipitating lead smoothly as lead sulphate, and Cartwright[5] precipitated bismuth phosphate in a similar manner.

Various reports have appeared on the oxidation of EDTA with potassium permanganate,[6,7] ceric sulphate,[8–10] manganese(III)[11] and lead dioxide in sulphuric acid medium.[12]

The extent of oxidation varies with the conditions used. Thus Carroll et al.[9] reported that at room temperature a 4-electron oxidation of EDTA took place but with increasing temperature and reaction time a 14-electron oxidation could be achieved. The last of these studies concluded that 4 moles of CO_2, 3 moles of formaldehyde and 1 mole of N-hydroxymethylethylenediamine are the products of the oxidation of 1 mole of EDTA with 4 moles of PbO_2, but these conclusions depended on certain assumptions. We have made an independent investigation of the oxidative decarboxylation of some commonly used polyaminocarboxylic acids with a suspension of lead dioxide in neutral medium. We consider the study interesting, as representing use of a heterogeneous reaction in analytical chemistry, and also in connection with determination of polyaminocarboxylic acids in waste-water treatment.

EXPERIMENTAL

Reagents

Solid lead dioxide of general reagent grade was dried and used without further purification. Its purity was determined

by a standard iodate method.[13] Ethylenediaminetetra-acetic acid (H_4EDTA), *trans*-1,2-diaminocyclohexane-*N,N,N′,N′*-tetra-acetic acid (H_4DCTA) and ethyleneglycol bis(aminoethyl ether) tetra-acetic acid (H_4EGTA) were all reagent grade, and were checked by complexometric titration[14] with 0.02*M* manganese sulphate. A carbonate-free stock solution of barium hydroxide was prepared by dissolving 40 g of the pure solid in 1 litre of boiled-out doubly distilled water, and filtering off all carbonate deposits. The solution was standardized with 0.1*M* hydrochloric acid.

Procedure

Different known weights of the dried solid lead dioxide were thoroughly mixed with a constant weight of solid polyaminocarboxylic acid (the acid being in excess), the weights being chosen to provide a wide range of molar ratios. The mixture was introduced into a reaction cell (25 cm long and 4 cm in diameter) connected in the middle of a series of ten CO_2-traps, each containing 25 ml of standard barium hydroxide solution. The first five traps removed all CO_2 from the air drawn into the system, and the second five trapped all the CO_2 released in the oxidative decarboxylation. The last trap was connected to a water pump, which was allowed to run for few minutes to remove all CO_2 from the system, then 50 ml of boiled-out doubly distilled water were introduced into the reaction cell, after which the temperature was slowly raised to 80°. The completion of the reaction was indicated by the complete disappearance of the dark brown lead dioxide.

Determination of the unreacted H_4A

At the end of the reaction the unreacted polyaminocarboxylic acid was determined by complexometric titration with 0.05*M* manganese sulphate, at pH 10 in the presence of ascorbic acid and with Eriochrome Black T as indicator. A blank was run under the same conditions to check that there was no other decomposition of the acid. The amount of the acid reacting with the lead dioxide was determined from the difference between the two titrations.

Determination of CO_2

The unreacted barium hydroxide solution in the last five traps was filtered to remove the barium carbonate, and titrated with 0.1*M* hydrochloric acid, with Methyl Orange as indicator. A blank was run with the same initial volume of barium hydroxide solution, and the difference was used for calculation of the amount of CO_2 released.

This amount was substantiated by gravimetric deter-

Table 1. Reacting ratio of PbO_2 and H_4A

| H_4A | Reaction mixture | | Molar ratio PbO_2/H_4A | |
	PbO_2, mmole	H_4A, mmole	Taken	Reacting ratio
H_4EDTA	0.029	0.342	0.085	0.729
	0.059		0.172	0.754
	0.085		0.251	0.748
	0.114		0.333	0.769
	0.163		0.476	0.751
	0.182		0.532	0.752
	0.969	3.023	0.320	0.765
	1.288	3.395	0.379	0.762
			Mean	0.754
H_4DCTA	1.051	3.057	0.343	0.736
	0.423	1.021	0.414	0.744
	0.525	1.216	0.432	0.762
			Mean	0.747
H_4EGTA	0.288	1.055	0.273	0.749
	0.354	1.121	0.316	0.741
	0.452	1.230	0.367	0.759
			Mean	0.750

Table 2. Reacting ratio of PbO_2 and H_4EDTA in $0.5M$ H_2SO_4

| Reaction mixture | | Molar ratio PbO_2/H_4A | |
PbO_2, mmole	H_4A, mmole	Taken	Reacting ratio
0.418	0.595	0.70	1.43
0.944		1.59	2.29
2.090		3.51	2.70
10.40	1.504	6.94	2.90

mination of the precipitated barium carbonate, by conversion into barium sulphate.

Determination of formaldehyde

The apparatus used for determination of CO_2 was also used for estimating the amount of formaldehyde released in the oxidative decarboxylation, the first five traps being filled with 10% sodium sulphite solution, to prevent oxygen from entering the system, and the last five traps with $0.1N$ sodium sulphite to absorb the formaldehyde produced.

The excess of sulphite was determined iodimetrically and compared with the value for a blank run, to give the amount of formaldehyde released.

RESULTS AND DISCUSSION

Stoichiometry

Solid lead dioxide in suspension reacts mildly with polyaminocarboxylic acids in neutral aqueous medium at 80°. The reaction can be monitored by titrating the unreacted H_4A with manganese(II). The lead(II) present as $PbEDTA^{2-}$ in the solution does not affect the titration.

The results (Table 1) indicate that 3 moles of PbO_2 react with 4 moles of polyaminotetracarboxylic acid, when the acid is present in large excess, 1 mole of the acid being oxidized, and the other three complexing the lead(II) produced.

However, when the reactants were mixed in molar ratio (PbO_2/H_4A) greater than 0.6 and both the

unreacted PbO_2 and H_4A were determined, the reaction was not complete even in $0.5M$ sulphuric acid medium, but approached a limiting molar ratio of 3 (Table 2), in agreement with the redox reaction proposed below; in this case there is insufficient H_4A to complex all the lead(II).

The results for the determination of lead(II) by flame atomic-absorption spectrometry and for CO_2 and HCHO are collected in Table 3. They show that 3 moles of CO_2 and 3 moles of HCHO are liberated when 3 moles of PbO_2 react with 4 moles of H_4A. This suggests that one mole of H_4A is destructively oxidized by reaction with 3 moles of PbO_2 to give a less reactive species, presumably a non-chelating agent, such as ethylenediaminemonoacetic acid in the case of H_4EDTA, and 3 moles of CO_2 and 3 moles of HCHO. The three moles of lead(II) produced are complexed by the other 3 moles of H_4A. Hence the *oxidative* reacting ratio is $1:1$ $PbO_2:H_4A$.

Mechanism of the reaction

The reaction mechanism suggested by Nagai et al.[12] for the oxidation is adopted here, but under our conditions the decarboxylation process proceeds only up to its third step. The first decarboxylation step can be treated as a three-stage reaction, as shown in (1)–(3) below, and the same mechanism applies for further decarboxylation.

The overall equation for complete decarboxylation of H_4EDTA, in short, can be represented as follows:

$$3Pb^{4+} + C_{10}H_{16}N_2O_8 \xrightarrow{+3H_2O} 3Pb^{2+}$$

$$+ 3CO_2 + 3HCHO + C_4H_{10}N_2O_2 + 6H^+$$
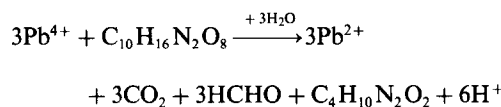
The difference between our results and those of Nagai et al.[12] can be attributed to the difference in experimental conditions and is supported by the fact

Table 3. Molar ratios of Pb(II) to H_4A, CO_2 to H_4A and HCHO to H_4A

| H_4A | Reaction mixture | | Molar ratios | | |
	PbO_2, mmole	H_4A, mmole	Pb^{2+}/H_4A	CO_2/H_4A	$HCHO/H_4A$
H_4EDTA	0.163	0.342	0.751	0.748	0.755
	0.182		0.752	0.752	0.749
	0.969	3.023	0.765	0.739	0.738
	1.288	3.395	0.762	0.761	0.764
H_4DCTA	1.051	3.057	0.736	0.752	0.759
	0.423	1.021	0.744	0.758	0.760
	0.525	1.216	0.762	0.741	0.739
H_4EGTA	1.122	3.455	0.734	0.762	0.751
	0.474	1.234	0.755	0.743	0.749
	0.511	1.474	0.745	0.753	0.750

that the reacting ratio of cerium(IV) to EDTA varies considerably with the experimental conditions.[9] Nagai *et al.* stressed that the fourth decarboxylation step was difficult and not completely achieved. We attempted to reproduce the conditions used by Nagai *et al.*, with an initial molar ratio of 4:1 (PbO_2/H_4A), but found that some PbO_2 was left unreacted and that the maximum reacting ratio was about 3.5:1, instead of the 4:1 reported by Nagai *et al.*[12] This indicates that the fourth decarboxylation step can take place, but not necessarily completely.

Comparison of these results with those reported for oxidation with permanganate and cerium(IV) shows clearly that the reactions depend very strongly on the conditions used.

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