

Redox reactions in non-aqueous media: determination of hydrazine and its organic derivatives with lead(IV) acetate

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Abstract. Lead(IV) acetate (in glacial acetic acid) has been described as an oxidimetric reagent for the determination of hydrazine and its organic derivatives in glacial acetic acid medium. The end-points have been detected visually using quinalizarin as an indicator and potentiometrically using platinum wire indicator electrode and modified-calomel reference electrode. The method is simple, accurate, reliable and widely applicable.

Keywords. Lead(IV) acetate ; hydrazine ; non-aqueous titration ; quinalizarin.

1. Introduction

The usefulness of non-aqueous redox methods for the determination of compounds which are insoluble in water, or react with water to undergo hydrolysis/oxidation or are decomposed by the media, *i.e.*, acids, bases, etc. of aqueous redox titrations, is well established. Hydrazine is a powerful reducing agent and majority of the analysis of hydrazine or its organic derivatives is based on this behaviour of hydrazino group. Although this group is readily oxidised, yet its oxidation in aqueous media is affected only under properly controlled conditions ; the nature and proportion of the oxidation products depend upon the nature of the oxidants and experimental conditions, *i.e.*, concentration of reactants, temperature, pH, etc. The oxidation of hydrazines in acidic medium even with moderate oxidising agents is slow, and in alkaline medium the compounds are quite susceptible to air oxidation. Many organic derivatives of hydrazine, especially those containing aryl groups are only sparingly soluble in water. The application of non-aqueous redox methods to the determination of hydrazine and its organic derivatives is of great interest and scope. Only limited efforts have been made to apply such methods to the analysis of these compounds.

The present communication reports the use of lead(IV) acetate (in glacial acetic acid) for the visual and potentiometric determination of hydrazine and its organic derivatives in glacial acetic acid medium. Quinalizarin has been found

to be a suitable indicator in visual titrations. The end-point is marked by a sharp colour change from red to blue except in cases of *p*-nitrophenylhydrazine and 2,4-dinitrophenylhydrazine where it is from red to bluish green. The potentiometric titrations were performed using platinum wire indicator electrode and a modified-calomel reference electrode. A sharp jump in potential was observed at the equivalence point in each titration.

2. Experimental

2.1. Apparatus

Potentiometric titrations were performed with a Toshniwal CLO6A potentiometer using bright platinum wire indicator electrode and modified-calomel (saturated methanolic potassium chloride solution instead of aqueous) reference electrode. The solutions were magnetically stirred during the titrations.

2.2. Standard lead(IV) acetate solution

Standard lead(IV) acetate, 0.05 N in glacial acetic acid was prepared by reacting Pb_3O_4 in glacial acetic acid (Berka *et al* 1960) and standardized iodometrically (Berka *et al* 1965).

2.3. Hydrazines

Carboxylic acid phenylhydrazides were prepared and purified by the method of Stempel and Schaffel (1942). Phenylhydrazine was distilled before use. *p*-nitrophenylhydrazine and 2,4-dinitrophenylhydrazine were recrystallised before use. Hydrazine hydrate was used as received.

2.4. Indicator solution

Quinalizarin (1,2,5,8-tetrahydroxy anthraquinone) indicator was used as 0.2% solution in glacial acetic acid.

2.5. Solvent

Glacial acetic acid (BDH, AR) was used as received.

2.6. Procedure

Aliquots (1–5 ml) of solution in glacial acetic acid of each hydrazine were taken in titration vessels. For visual titrations 20–30 ml of glacial acetic acid and 5–10 drops of quinalizarin indicator were also added. Each solution was titrated at room temperature (25°C) with standard (0.05 N) lead(IV) acetate to a colour change from red to blue (red to bluish green in case of *p*-nitrophenylhydrazine and 2,4-dinitrophenylhydrazine). Potentiometric titrations were performed using

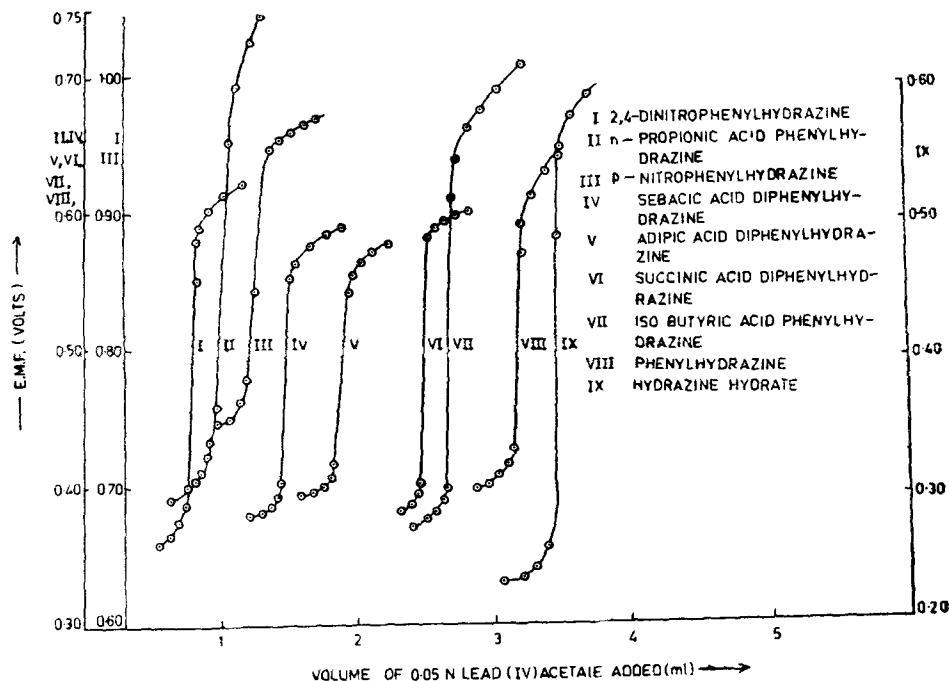


Figure 1.

platinum-modified calomel electrode assembly. A series of potentiometric titrations were performed with different amounts of each compound. Potentiometric titrations, one for each hydrazine, are represented by curves I to IX in figure 1.

From the volume of oxidant solution used corresponding to the end-points in visual and potentiometric titrations, the amount of each hydrazine was calculated. The results are given in table 1.

3. Results and discussion

The usefulness of lead(IV) acetate (in glacial acetic acid) in oxidimetry is well established. The oxidant had been used for the determination of a number of reducible compounds including some hydrazines (Ashworth 1964), but the analysis has been carried out in aqueous acidic media and that obviates one of the advantages of non-aqueous oxidimetry with lead(IV) acetate.

In the present work, the oxidant has been found to oxidise hydrazines smoothly in glacial acetic acid, permitting the use of quinalizarin indicator in visual titrations. Fluctuations in potentials were observed when saturated (aqueous) calomel electrode was used as reference electrode. When the titrations were, however, performed with a modified-calomel reference electrode, the potentials stabilized rapidly. That modified calomel is a suitable electrode for non-aqueous oxidimetry, is already shown by Verma and Kumar (1978). Drifts in potentials

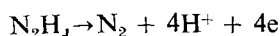
Table I. Determination of hydrazine and its organic derivatives with lead(IV) acetate.

Hydrazines	Values are mean of ten determinations with standard deviation (\pm)			
	Amount found*, mg		Amount found**, mg	
	Visual method	Potentiometric method	Visual method	Potentiometric method
Hydrazine hydrate	4.03, 0.088	4.01, 0.050	12.11, 0.082	12.08, 0.078
<i>n</i> -Propionic acid phenylhydrazide	4.04, 0.060	3.98, 0.058	11.91, 0.101	11.96, 0.083
<i>Iso</i> -butyric acid phenylhydrazide	3.96, 0.071	3.98, 0.065	11.90, 0.093	11.96, 0.059
Succinic acid diphenylhydrazide	4.00, 0.081	4.00, 0.077	11.90, 0.078	11.95, 0.072
Adipic acid diphenylhydrazide	3.97, 0.091	3.98, 0.072	12.09, 0.100	12.07, 0.088
Sebacic acid diphenylhydrazide	4.02, 0.091	4.02, 0.083	12.06, 0.088	12.05, 0.073
Phenylhydrazine	3.96, 0.092	12.11, 0.088
<i>p</i> -Nitrophenylhydrazine	3.95, 0.076	3.97, 0.075	11.96, 0.096	12.04, 0.088
2,4-dinitro-phenylhydrazine	3.96, 0.086	3.98, 0.081	12.08, 0.100	11.94, 0.078

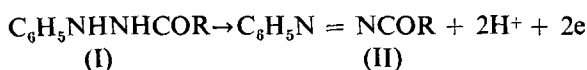
* Amount taken, 4 mg ; ** Amount taken, 12 mg.

in redox titrations in acetic acid medium using platinum-saturated (water) calomel electrode assembly have been described by many workers (Kratochvil 1966).

The results (table 1) indicate that whereas hydrazine is oxidised with a four-electron change, monosubstituted hydrazides (I)

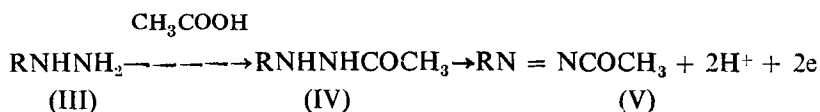


(*n*-propionic acid and *iso*-butyric acid phenylhydrazides as well as adipic acid-, succinic acid- and sebacic acid diphenylhydrazides) are oxidised with a two electron change per hydrazino group with the oxidant. That phenylhydrazides (I) could be oxidatively converted



to diazonium compounds (II), is already known (Zabicky 1970 ; Smith 1966). Lead(IV) acetate oxidises monosubstituted hydrazines (III) (phenyl-, *p*-nitro-

and 2,4-dinitrophenylhydrazines) also with a two-electron change. The course of reaction may be described as :



Phenylhydrazines (III) are first converted to hydrazides (IV) with the solvent before they are oxidised to the corresponding diazonium compounds (V) in the same manner as described for monosubstituted hydrazides earlier. This role of the solvent that it reacts with monosubstituted hydrazines to form the corresponding hydrazides is also known (Streuli and Averell 1970).

4. Conclusion

The proposed methods for the determination of hydrazine and its organic derivatives with lead(IV) acetate in glacial acetic acid medium are simple, accurate, reliable and of wide applicability. Since a solution of lead(IV) acetate prepared by the reaction of Pb_3O_4 with glacial acetic acid if stored in closed flask is highly stable even at dilutions (Zyka and Berka 1962), the method can be extended to the microdetermination of hydrazines.

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