Oxidation of Some Organic Acids Using Sodium Bismuthate in Aqueous and Acidic Media

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Summary: The study includes oxidation of lactic, citric, tartaric, malic, mandelic, α-hydroxy isobutyric and isobutyric acids by sodium bismuthate as an oxidising agent. The oxidation reactions were carried out in water, aqueous sulphuric (1-> 4N) or glacial acetic acid, using different molar proportions of sodium bismuthate. A tentative mechanism of oxidation is given and discussed.

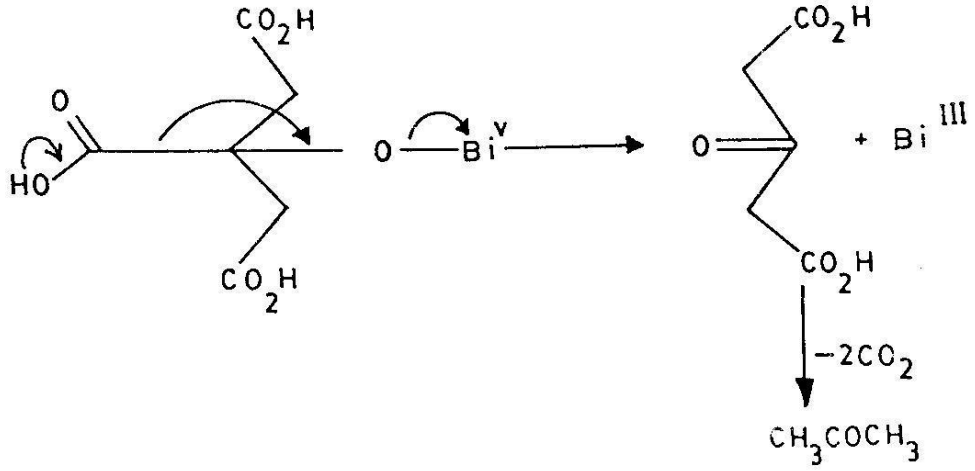
Sodium bismuthate in phosphoric acid smoothly and selectively effects oxidations similar to those brought about by lead tetra-acetate and periodic acid [1]. Few reports are available in literature concerning mainly its action as glycol splitting reagent [1,2] in presence of phosphoric acid.

Therefore, it seemed desirable to extend the work to other organic compounds which has not been investigated using sodium bismuthate as an oxidant.

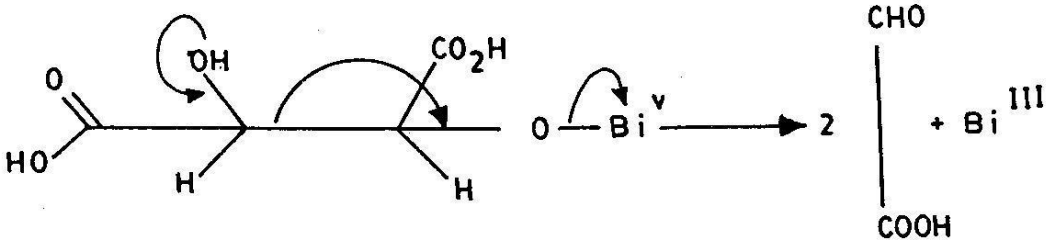
It is worth mentioning to report from this investigation that the effect of sulphuric acid is satisfactory as acidic medium in sodium bismuthate oxidation and has the same role as phosphoric acid.

Oxidation of lactic, citric, tartaric, malic, mandelic, α-hydroxy isobutyric and isobutyric acids in water, aqueous sulphuric (1 -> 4N) or glacial acetic acid is suggested to take place via a complex between the hydroxy moiety and the oxidising agent. This type of complex formation is similar to that reported in oxidation by pentavalent vanadium [3] or tetravalent lead [4].

Formation of acetone dicarboxylic acid and acetone in citric acid oxidation can be explained as follows:

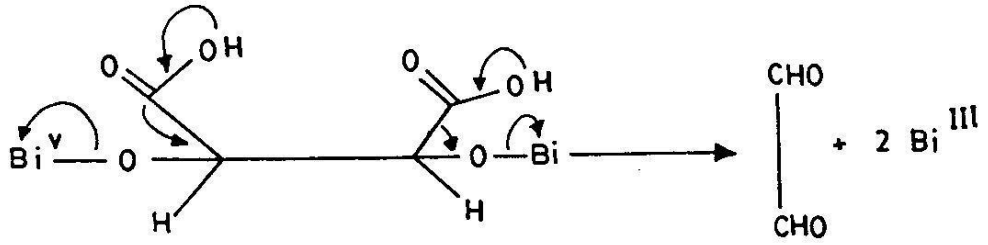


Since tartaric acid behaves as α,β-glycol type, therefore, formation of glyoxylic acid from D(+)-tartaric acid oxidation by Bi^{V} can be simplified as follows:



Using 2 moles of sodium bismuthate to 1 mol of tartaric acid, leads to the formation of glyoxal as follows:

Formation of methacrylic acid in oxidation of isobutyric acid by sodium bismuthate-water, indicates that sodium



As the molar proportions of sodium bismuthate increased over the substrate, no further oxidation seemed to take place.

Oxidation of α-hydroxy acids in aqueous sulphuric acid (1→ 4N) was found to proceed very rapidly as the concentration of sulphuric acid is increased, irrespective to the substrate concentration with 4N sulphuric acid. This could be explained on the basis that in acidic media, the bismuthate being more powerful as oxidising agent [5].

In presence of glacial acetic acid, as oxidation medium, the oxidation reaction was notably retarded in comparison with (1→ 4N) aqueous sulphuric acid. However, this effect being observed in lead tetra-acetate oxidation [4].

bismuthate is apparently able to cause dehydrogenation, i.e. acts as an oxidant.

In 1N aqueous sulphuric acid, sodium bismuthate oxidises isobutyric acid into pyruvic acid. This shows that methacrylic acid which was primarily formed, is now more susceptible to the oxidation by bismuthate in acidic media. As the concentration of sulphuric acid is increased, pyruvic acid easily undergoes decarbonylation to acetic acid.

Experimental

All the carbonyl oxidation products obtained were identified as

their 2,4-dinitrophenyl hydrazone derivatives (m.p. & mixed m.p.s with authentic specimens).

General procedure:

In 250 ml round bottom flask, Analar sodium bisuthate (0.1, 0.2 or 0.4 mole) was added in portion-wise within 1 hour to a stirred solution of organic substance (0.1 mole) in a proper oxidation solvent (100 ml, water, aqueous sulphuric acid 1→4N or glacial acetic acid). Stirring was continued for 1 hour at 30-35°C. The reaction mixture was then diluted with ice-cold water (300 ml) and filtered off several times in order to remove the inorganic bismuth compounds. The aqueous mother liquor was extracted with several portions of ether. The ether extracts was neutralized with aqueous sodium carbonate, washed with water and dried. Distillation of ether solution gave the neutral products. Acidification and ether extraction of the alkaline aqueous layer gave the acidic products. The results are included in Table 1-5.

Table-1: Products of oxidation the organic substance with sodium bismuthate (1:1, 1:2 or 1:4 mole) in water

Compound	Neutral products	Yield %	Acid products	Yield %
lactic acid $CH_3CHOH.COOH$	Acetaldehyde	60	---	
D(+)-Tartaric acid HOOC.CHOH.CHOH.COOH	---		Glyoxylic acid	33
Citric acid HOOC.CH_2.CHOH.COOH COOH	Acetone	10	Acetonedicarboxylic acid[a]	15
α-Hydroxy iso-butyric acid $(CH_3)_2COH.COOH$	Acetone	35	---	
DL-Malic acid HOOC.CH_2.CHOH.COOH	---		Oxalacetic acid	50
Mandelic acid $C_6H_5CHOHCOOH$	Benzaldehyde	55	---	
Isobutyric acid $(CH_3)_2CHCOOH$	---		methacrylic acid	25

(a) Its 2,4-dinitrophenyl hydrazone, m.p.318°C (Found:C,40.51;H,3.15; N,17.25. $C_{11}H_{10}N_4O_8$ requires C,40.49; H,3.07;N,17.18%).

Table-2: Products of oxidation the organic substance with sodium bismuthate (1:1 mole) in aqueous sulphuric acid (1->4N).

Compound	Neutral products	Yield %	Acidic products	Yield %
Lactic acid	Acetaldehyde	80	---	
D(+)-Tartaric acid	---		Glyoxylic acid	75
Citric acid	Acetone	30	---	
α-Hydroxy isobutyric acid	Acetone	55	---	
DL-Malic acid	Acetaldehyde	84	---	
Mandelic acid	Benzaldehyde	85	---	
Isobutyric acid	---		Formic acid,[b]	
			acetic acid and pyruvic acid	55

(b) Formic and acetic acids are increased over pyruvic acid as the concentration of sulphuric acid is increased.

Table-3: Products of oxidation the organic substance with sodium bismuthate (1:2 mole) in aqueous sulphuric acid (1->4N).

Compound	Neutral products	Yield %	Acidic products	Yield %
Lactic acid	Acetaldehyde	50[c]	Acetic acid	10[c]
		35[d]		18[d]
		15[e]		40[3]
		10[f]		55[f]
D(+)-Tartaric acid	Glyoxal	40[c]		
		55[d]	---	
		70[e,f]		
Citric acid	Acetone	50[c]		
		68[d]	---	
		65[e]		
		48[f]		
α-Hydroxy iso-	Acetone	60[c,d]		

Table-3 (Continued)

Compound	Neutral products	Yield %	Acidic products	Yield %
butyric acid		55[e]	---	
		40[f]		
DL-Malic acid	Acetaldehyde	60[c]	Acetic acid	10[c]
		50[d]		15[d]
		30[e]		28[e]
		10[f]		50[f]
Mandelic acid	Benzaldehyde	67[c]	Benzoic acid	10[c]
		60[d]		15[d]
		45[e]		40[e]
		30[f]		45[f]
Isobutyric acid	---		Formic and acetic acids	65-80[c-f]

c → f are oxidations in 1,2,3 and 4N, respectively.

Table-4: Products of oxidation the organic substance with sodium bismuthate (1:4 mole) in aqueous sulphuric acid.*

Compound	Neutral products	Yield %	Acidic products	Yield %
Lactic acid	---		Acetic acid	80
D(+)-Tartaric acid	---		Oxalic acid	75
Citric acid	Acetone	30	---	
α-Hydroxy iso-butyric acid	Acetone	24	---	
DL-Malic acid	---		Acetic acid	75
Mandelic acid	---		Benzoic acid	78
Isobutyric acid	---		Formic and acetic acids	80

* Oxidations in 1,2,3 or 4N sulphuric acid gave the same results.

Table-5: Products of oxidation the organic substance with sodium bismuthate (1:1 mole, 1:2 mole or 1:4 mole) in glacial acetic acid.

Compound	Neutral products	Yield %	Acidic products	Yield %
Lactic acid	Acetaldehyde	60	---	
D(+)-Tartaric acid	---		Glyoxylic acid	3
Citric acid	---		Acetonedicarboxylic acid	6
α-Hydroxy isobutyric acid	Acetone	38	---	
DL-Malic acid	---		Oxalacetic acid	5
Mandelic acid	Benzaldehyde	40	---	
Isobutyric acid	---		---	

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