

Reduction of Selenous Acid with Carboxylic Acids

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Inhaltsübersicht

Es wird über die Reduktion von seleniger Säure durch Karbonsäuren in Gegenwart von Kaliumpermanganat und Salzsäure berichtet. Die Versuchstemperaturen liegen bei 50 und 70° C. Es wird festgestellt, daß die Reduktion analog der von Goldchlorid verläuft.

Summary

Reduction of selenous acid by certain carboxylic acids in presence of small quantities of KMnO_4 has been studied. The observed enhanced reducing power of the carboxylic acids treated with KMnO_4 towards selenous acid has been explained as being due to the formation of intermediate oxidation products of varying degree of stability, which strongly reduce selenous acid. In a few cases the presence of definite oxidation products has been indirectly proved. The results obtained are, in general, similar to those of gold chloride-carboxylic acid reactions studied by MACMAHON and SRIVASTAVA¹).

Introduction

It has been shown by a number of workers that when oxalic acid is treated with small quantities of KMnO_4 , it acquires enhanced reducing power towards certain metallic salts like HgCl_2 and AuCl_3 , a phenomenon which has been explained as being due to the production of "activated oxalic acid". MACMAHON and SRIVASTAVA¹) investigated in detail the behaviour of other simple polycarboxylic acids when similarly treated with KMnO_4 in order to find out whether they became activated i. e. whether their power of reducing certain metallic salts was enhanced.

These reactions were previously studied by DHAR²) who found that addition of KMnO_4 promoted reactions with HgCl_2 , gold chloride sodium selenite etc., and thus regarded them as examples of chemical induction, where KMnO_4 was supposed to act an inductor. MACMAHON and SRIVASTAVA, however, showed that these can not be regarded as induced reactions, since they found that the same reducing power was retained in solution when gold chloride was added after all the permanganate had

¹) MACMAHON and SRIVASTAVA, J. Indian chem. Soc. **20**, 307 (1943).

²) DHAR, J. chem. Soc. London **11**, 699 (1917).

been used up by reaction with the carboxylic acid (reduced to the Mn(II) state). They concluded from these observations that the reducing power acquired by the solution was due to the formation of intermediate oxidation products of varying degree of stability, formed by reaction of KMnO_4 on the acid, which reduce gold chloride very rapidly.

The present investigation was carried out in order to ascertain whether the reduction of selenous acid by the carboxylic acids in presence of KMnO_4 can also be explained in a similar manner.

Experimental

For the study of these reactions pure organic acids were recrystallised from conductivity water. Other reactants used were of analytically pure variety and the solutions were prepared in conductivity water. Malic, citric, tartaric, malonic, maleic, lactic and glycollic acids were thus studied. Reaction with oxalic acid could not, however, be studied in detail as it does not appreciably reduce selenous acid even when treated with KMnO_4 .

Suitable concentrations of the reactants were employed and the reactions were studied in all cases at 50°C excepting in the case of lactic and glycollic acids where the temperature had to be raised to 70°C , so as to obtain suitable rates of reduction. The concentrations of the carboxylic acids in solution through-out the investigation was generally kept M/4 and that of selenous acid as M/125. The reactions were studied in presence of a suitable concentration of HCl, as in its absence of reduction was extremely slow. Moreover, in the absence of HCl the coagulation of colloiddally precipitated selenium did not take place rapidly and hence the time of reduction observed was not sharp. Usually for experiments with malic, tartaric, malonic and maleic acids the concentrations of HCl in solution was N/5 and that with citric, glycollic and lactic acids was normal. In general, other factors remaining equal, the rate of reduction was accelerated by the increase in the concentration of HCl.

The reactions were studied in well-cleaned test tubes placed in a bath of constant temperature and the time of reduction was noted for an arbitrarily selected depth of colour of reduced colloidal selenium to appear. The results are thus only comparative and qualitative in nature. For some of the reactions studied in the absence of atmospheric oxygen an apparatus used by MAC MAHON and LAL³⁾ was employed.

Effect of KMnO_4

It was observed that unlike reactions between gold chloride and carboxylic acids, the reactions with selenous acid proceed almost with negligible velocity in the absence of KMnO_4 , excepting with malonic and glycollic acids where measureable rate was observed even without KMnO_4 . The addition of KMnO_4 in all cases accelerated the reaction and it was observed that when selenous acid in HCl was added to the solution just after the KMnO_4 was reduced by organic acids (i. e. reduced to Mn(II) state) the rate of reduction was at its maximum. By increasing the quantity of KMnO_4 the rate of reaction was still further increased. The results obtained are given in Table I. The time of reduction recorded in these observations is in minutes unless stated otherwise.

³⁾ MAC MAHON and LAL, J. Indian chem. Soc. **20**, 143 (1943).

Table I

Carboxylic acid	Without KMnO_4	KMnO_4 added together with H_2SeO_3 (Conc. of KMnO_4 N/250)	H_2SeO_3 in HCl added after decolourisation of KMnO_4 (Concs. of KMnO_4)			
			N/500	N/250	N/125	2 N/125
Malic	about 6 hrs.	45	—	18	13	6
Citric	about 24 hrs.	48	36	24	18	13
Tartaric	very slow	60	34	8	4	3
Malonic	90	60	57	53	48	45
Maleic	very slow	40	—	32	22	12
Lactic	about 8 hrs.	25	—	22	14	8
Glycollic	34	28	—	26	24	23

Effect of other factors

The effects of changing other factors like temperature and the concentration of the reactants were also studied and in general results similar to gold chloride-carboxylic acid reaction were obtained. In order to obtain comparative results, the suitable amount of selenous acid — HCl mixture was always added just after the KMnO_4 was used up by the organic acids. The values obtained are only relative and hence not given.

As expected an increase in the temperature and the concentration of the reactants results in an increase in the rate of reduction. But contrary to the gold chloride-carboxylic acid reaction, these reactions with selenous acid are not affected by light and by the presence of atmospheric oxygen. Comparative experiments were performed in dark, diffused light and in sunlight but without any appreciable change in the time of reduction. Similarly experiments performed in air and in an atmosphere of nitrogen showed no change in the time of reduction. The addition of NaCl, other neutral salts and Mn(II) salts in equivalent concentrations produces very little effect on the rate of reduction. Also potassium persulphate, another oxidising agent used by DHAR as an inductor, did not produce any effect.

Change in reducing power of the decolourised solutions (KMnO_4 and carboxylic acids) with time.

Suitable amount of selenous acid in HCl was added to the aqueous solutions of the carboxylic acids previously treated with KMnO_4 at varying intervals of time after the decolourisation of KMnO_4 (N/250) and time taken for reduction noted. The results are given in Table II.

Table II

Time	Malic	Citric	Tartaric	Malonic	Maleic	Lactic	Glycollic
Immediately	18	24	8	53	32	22	26
After 5 min.	22	26	8	60	35	22	26
After 10 min.	30	30	9	75	40	22	26
After 20 min.	50	34	10	90	50	22	26
After 30 min.	150	39	12	—	120	22	26
After one hour	very slow	48	very slow	—	very slow	22	26
After two hours	—	69	—	—	—	24	27
After 24 hours	—	very slow	—	—	—	26	28

It appears from Tables I and II that when carboxylic acids are treated with KMnO_4 , they are oxidised to various products which possess enhanced reducing power towards selenous acid. These oxidation products possess varying degree of stability and decompose in all cases in solution on keeping excepting those formed with lactic and glycollic acids, in which the enhanced reducing power of the solution does not change with time. The results are thus similar to those obtained for gold chloride-carboxylic acid reaction.

It has further been possible to confirm the presence of definite unstable oxidation products in certain cases. For example in the case of citric acid it is well known that the acid is finally oxidised by KMnO_4 to formic acid with intermediate formation of acetone-dicarboxylic acid. This was prepared by the method of PEOHMANN and was recrystallised with ether. The pure acid was found to reduce selenous acid instantaneously. Further, the acid was added to a solution of citric acid, in amount equivalent to KMnO_4 used up, along with equivalent amount of Mn(II) salt and the mixture was treated with selenous acid in HCl at various intervals of time under same conditions as in Table II. It was observed that the reducing power of the solution slowly decreased at the same rate as for citric acid treated with KMnO_4 in Table II.

Similarity the behaviour of KMnO_4 treated tartaric acid as shown in Table II could be reproduced by an aqueous solution containing tartaric acid, Mn(II) and dioxymaleic acid in quantities corresponding to KMnO_4 used up. Dioxymaleic acid been has suggested as the intermediate compound formed by the oxidation of tartaric acid with KMnO_4 by FENTON⁴). These results definitely suggest that the enhanced reducing power acquired by carboxylic acids treated with KMnO_4 is due to the presence of unstable oxidation products.

It has not been possible so far to definitely identify the oxidation products in cases of malic, maleic and malonic acids. In all probability the enhanced activity of malic acid is due to the intermediate formation of oxaloacetic acid which has been suggested as its oxidation product by DENIGES⁵). The greater reducing power of maleic acid treated with KMnO_4 may be due to mesotartaric acid as suggested by TANATAR⁶), KEKULÉ and ANSCHUETZ⁷). In the absence of pure samples of these acids the results could not be confirmed. The intermediate oxidation product in the case of malonic acid appears to be very unstable and disappears within a very short time and hence its identification was more difficult.

In cases of lactic and glycollic acids, the oxidation products formed by the action of KMnO_4 appeared to be quite stable and the reducing power of the oxidised solutions does not change with time. CHAPMAN and SMITH⁸) suggested that when lactic acid is oxidised by aqueous solutions of KMnO_4 , acetaldehyde, acetic acid, oxalic acid and carbon dioxide are formed. These products do not show any reducing power towards selenous acid excepting acetaldehyde which when added in equivalent quantities gave the same time of reduction as in Table I. Also the reducing power of an aqueous solution containing lactic acid, Mn(II) and acetaldehyde in equivalent quantities towards selenous acid-HCl mixture does not change with time on keeping, which suggests that the enhanced reducing power of KMnO_4 treated lactic acid is due to the presence of acetaldehyde. The oxidation of glycollic acid by KMnO_4 gives formic acid with intermediate formation of

4) FENTON, J. chem. Soc. London **56**, 899 (1894).

5) DENIGES, C. R. hebdomadaire des Séances Acad. Sci. **130**, 32 (1900).

6) TANATAR, Ber. deutsch. chem. Ges. **13**, 1383 (1880).

7) KEKULÉ and ANSCHUETZ, Ber. deutsch. chem. Ges. **14**, 714 (1881).

8) CHAPMAN and SMITH, J. chem. Soc. London **20**, 301 (1867).

glyoxylic acid. The latter when added in equivalent quantities reduces selenous acid at the same rate as in Table I. The reducing power of this acid also does not appreciably change in solution with time.

Thus the present investigation appears to show that similar to goldchloride-carboxylic acid reaction, KMnO_4 does not act as an inductor in these reaction with selenous acid, but the high reactivity of the KMnO_4 treated carboxylic acids is due to the presence of intermediate oxidation products which reduce selenous acid very rapidly.

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