The Oxidation of Iodide to Iodite and the Reduction of Iodate to Iodite in Iodine Solutions of Permanganate and Some of the Carboxylic Acids

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The oxidation of iodide at low concentrations has been the subject of much recent interest. A number of oxidation products are possible, but some of which might be unstable. Such a possibility has already been indicated by Kahn and Wahl[1] and by Eiland and Kahn[2] in the oxidation of iodine by dichromate and cerium(IV). A number of the oxidation products of iodine from +1 to +5 states are possible if the oxidation is suitably carried out. However, iodate seems to be one of the most important products in all the oxidations reported by the above authors, and also in those reported by Musakin and Puchkov[3] and by one of the present authors[4] in permanganate oxidations.

During a kinetic study of the reduction of permanganate by citric and malonic acids in the presence of low concentrations of iodide, it has been reported by Misra and Gupta[5] that the reaction mixtures, even after becoming colourless, have some oxidant which could be determined iodometrically. This was suspected to be iodite. This observation necessitated a systematic attempt to identify this oxidant and to ascertain the mechanism by which it is produced. Similar observations have been reported by a number of workers[6-10] in the oxidation of oxalic acid by permanganate in

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[1] M. Kahn and A. C. Wahl, *J. Chem. Phys.*, **21**, 1185 (1953).

[2] H. M. Eiland and M. Kahn, *J. Phys. Chem.*, **65**, 1317 (1961).

[3] A. P. Musakin and L. V. Puchkov, *Zh. Neorg. Khim.*, **4**, 483 (1959).

[4] Y. K. Gupta, *J. Inorg. Nucl. Chem.*, **19**, 179 (1961).

[5] Y. K. Gupta and D. D. Misra, *Bull. acad. polon. sci.*, **9**, 379 (1961).

[6] Y. K. Gupta and S. Ghosh, *Z. physik. Chem.*, **208**, 368 (1958).

[7] H. Taube, *J. Am. Chem. Soc.*, **70**, 1216 (1948).

[8] F. Oberhauser and W. Hensinger, *Ber.*, **61B**, 521 (1928).

[9] P. S. Macmohan and B. B. Lal, *J. Ind. Chem. Soc.*, **20**, 143 (1943).

[10] H. Wieland and W. Zilg, *Ann.*, **530**, 257 (1937).

the absence of iodine, wherein hydrogen peroxide has been said to be formed.

Not much is known about iodite. Landolt[11] suspected the intermediate formation of iodite during the reduction of iodate. Lievin[12] and Guiseppe[13], from a study of the order of the conversion of hypoiodites into iodates, suspected the intermediate formation of iodite. Josien[14] found the existence of iodite in silver nitrate-iodine solutions by an analytical method. Kireev[15] reported the existence of silver iodite. The compound has not been isolated so far. Attempts have been made to discover a qualitative test to distinguish it from iodate or periodate, but no definite conclusions could be arrived at for want of this compound in the pure state.

It will be suggested in the present paper that, when permanganate is added to small amounts of iodide in aqueous solutions of citric or malonic acid, iodate is first formed and that this is subsequently reduced to iodite by the intermediate oxidation products of the acid. It will further be shown that iodate also is reduced to iodite in such solutions by the oxidation products of the acids.

Experimental

All the chemicals were of B.D.H.A.R. quality; the malonic acid made by Riedel. Distilled water was freshly boiled and cooled for preparing stock solutions and reaction mixtures.

Requisite quantities of the citric or malonic acid and potassium iodide were mixed, a permanganate solution was added, and the mixture was thoroughly shaken. The reaction mixtures were preferably kept overnight, whereupon they became colourless. The oxidising capacity of the mixtures was determined iodometrically by titrating 10 ml. of the mixture against N/100 thiosulphate using a 10—15% solution of iodide and 2 N sulphuric acid. The temperature varied between 15—20°C.

In the case of citric acid and higher concentrations of iodide, when a precipitate was obtained the mixture was filtered and the oxidising capacities of the filtrate and of the precipitate were determined separately.

For reactions with iodate, permanganate and the organic acid were mixed and allowed to become colourless, and then a requisite quantity of iodate was added. Ten or twenty-five milliliters aliquots were determined for the oxidant iodometrically using 10% potassium iodide. The determinations were repeated after 8, 24 and 48 hr. Analytical measurements were also made in cases when iodate was added before the permanganate.

In the case of malonic acid, a few experiments were carried out by adding iodate to the reaction mixture when the permanganate colour had just disappeared and there remained a reddish orange colour.

When iodide is oxidised to iodite or iodate, iodine is the intermediate product; it may react with the organic acid or with its oxidation products (by permanganate). The substitution products may remain in the solution or may be thrown out of the solution, but all of them give back iodine in acidified solutions of potassium iodide and hence can be determined iodometrically. A few qualitative experiments were made to ascertain this, as Table I shows. Tests for iodate or iodide and iodometric measurements were made only in colourless solutions. In columns 4, 5 and 6 the permanganate and the acid were allowed to react in the presence of iodate or iodide or aqueous iodine, and then the tests were made. In the experiments of column 7, aqueous iodine was added after the permanganate-acid mixture had become colourless. The concentrations of the reactants used were as will be shown in subsequent tables.

It was found that malonic and pyruvic acids could immediately react with the aqueous iodine and give back the latter when acidified potassium iodide was added. The reaction of iodine with other acids is slow and photochemical. Such an oxidation of citric acid by iodine has been reported by a number of workers,[16-21] but little has been said about the reaction between iodine and the oxidation products of citric acid. Mecmohan and Srivastava[22] and Bakore and Bharadwaj[23] have mentioned the formation of tetraiodoacetone and hexaiodoacetone. Similarly, a number of workers[24-30] have studied the reaction between iodine and malonic acid, but nothing has been said about the oxidation products of malonic acid. Kappanna and Talati[31] reported a slower reaction between malonate ion and iodine in the presence of hydrogen or iodide ions — a fact which indicates that the reaction is reversible and that, under appropriate conditions, iodine may not react with malonic acid

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[11] H. Landolt, *Sitzber Akad. Bodin.*, **1885**, 249.

[12] O. Lievin, Memoires et Travaux des Facultes Catholiques de Lille (1923).

[13] D. Guiseppe, *Boll. Chim. farma.*, **78**, 117 (1939); *Chem. Abstr.*, 33, 7652 (1939).

[14] M. L. Josien, *Compt. rend.*, **216**, 842 (1943).

[15] V. Kireev, *Acta Physicochem., U. R. R. S.*, **20**, 905 (1943).

[16] P. S. Macmohan and T. N. Srivastava, *J. Ind. Chem. Soc.*, **20**, 307 (1943).

[17] N. R. Dhar, *J. Chem. Soc.*, **111**, 699 (1917).

[18] A. N. Dey and N. R. Dhar, *Z. Electrochem.*, **32**, 586 (1926).

[19] R. P. Sanyal and N. R. Dhar, *Z. anorg. Chem.*, **139**, 161 (1924).

[20] N. R. Subbaratnam and A. K. Bhattacharya, *Saugor Univ. J. (India)*, Part 2, Nos. 4, 5 (1954).

[21] J. L. Mukherji and C. M. Kakati, *J. Ind. Chem. Soc.*, **24**, 361 (1947).

[22] P. S. Macmohan and T. N. Srivastava, ibid., **23**, 261 (1946).

[23] G. V. Bakore and S. D. Bharadwaj, *Proc. Natl. Inst. Sci. (India)*, **29A**, 90 (1963).

[24] T. N. Srivastava, *Current Sci.*, **15**, 249 (1946).

[25] R. W. West, *J. Chem. Soc.*, **1924**, 125.

[26] J. O. Halford and L. C. Anderson, *J. Am. Chem. Soc.*, **58**, 736 (1936).

[27] S. L. Bafna, K. P. Govindan and W. V. Bhagwat, *J. Sci. Industr. Res. (India)*, **IIB**, 376 (1952).

[28] S. L. Bafna, W. V. Bhagwat and M. A. Tilak, ibid., **IIB**, 231 (1952).

[29] V. M. Bhale, S. L. Bafna and W. V. Bhagwat, *Z. physik. Chem.*, **12**, 298 (1957).

[30] R. M. Verma and S. Bose, *J. Ind. Chem. Soc.*, **38**, 899 (1961).

[31] A. N. Kappanna and E. R. Talati, ibid., **28**, 675 (1951).

TABLE I.

(1) Acid	(2) Reaction with iodate	(3) Reaction with aq. I_2	(4) $KMnO_4$-Acid (KIO_3) test for		(5) $KMnO_4$-Acid (KI) test for		(6) $KMnO_4$-Acid (aq. iodine) test for		(7) $KMnO_4$-Acid → colourless. aq·I_2 added. Whether I_2 obtained back from colourless solution
			Iodate (iodite) ?	Iodide	Iodate (iodite) ?	Iodide	Iodate (iodite) ?	Iodide	
Citric	No	Slow	Yes	No	Yes	No	Yes	No	Yes
Lactic	No	Slow	Yes	No	Yes	No	Yes	No	Yes
Maleic	No	Slow	No	Yes	No	Yes	No	Yes	—
Malic	No	Slow	Yes	No	Yes	No	Yes	No	Yes
Malonic	No	Fast*	Yes	No	Yes	No	Yes ?	No	Yes
Oxalic	No	Slow	No	Yes	No	Yes	No	Yes	—
Pyruvic	Slow	Fast*	No	No	No	No	No	Yes ?	—
Tartaric	No	Slow	No	Yes	No	Yes	No	Yes	—

* Iodine was quantitatively obtained back from colourless solutions.

TABLE II. OVERALL VOLUME OF THE REACTION MIXTURE: 50 ml.

$KMnO_4$ N	Malonic acid, M	Oxidant (N) for KI (N)				Citric acid, M		
		2×10^{-4}	4×10^{-4}	1×10^{-3}	2×10^{-3}			
0.02	0.08	8×10^{-4}	15.6×10^{-4}	3.92×10^{-3}	6.40×10^{-3}**	7.6	15.8	3.58**
	0.04	8	16.3	4.06	6.70**	8.2	16.0	3.78**
	0.02	8	15.8	4.06	6.78**	8.2	16.2	3.90
	0.008	11.2*	19.2*	3.78**	6.10**	8.4	16.4	4.06
0.01	0.08	7.6	16.4	3.92	5.82**	8.2	15.2	
	0.04	8.4	16.8	3.96	6.10**	8.4	15.6	
	0.02	8.4	16.4	4.02	6.26**	8.0	16.4	
	0.008	10.4*	16.0	3.24**	5.35**	8.0	16.0	

* More than the expected four times the iodide.
** Less than the expected four times the iodide.

at all or that the reacted iodine may be set free from the substitution product.

Iodometric determinations in colourless mixtures are based on the above observations and on the fact that iodite, being an oxidising substance, will also liberate iodine from acidified iodine solution. However, a qualitative distinction between two such determinations can always be made. The organic acid is treated with the permanganate until the mixture becomes colourless. If iodine solution in water or dilute potassium iodide is then added, it reacts to give colourless solutions. These mixtures do not give back iodine when more potassium iodide is added, though the medium is acidic. Iodine is obtained only when dilute hydrochloric acid or dilute sulphuric and is added. On the other hand, colourless mixtures containing iodate liberate iodine instantaneously on the addition of potassium iodide. The two processes are quite different. In the latter there is an oxidant which liberates the iodine, whereas in the former it is a substitution product of the iodine which gives back iodine, probably by displacement.

Results and Discussion

For low concentrations of iodide ($<10^{-3}$ N) the oxidant produced is always four times the original iodide. This points to the existence of iodite in these colourless solutions. These solutions do not respond to the test for iodide. Some mixtures show the presence of iodate, while others do not, but all of them respond to this test after a couple of days. Qualitative tests for iodite, though not yet known, are likely to be similar to those of iodate, and, hence, in all probability, a positive thiocyanate test[32] can be obtained in all cases. The test is not administered in some cases in the beginning because when citric or malonic acid is oxidised by permanganate, a number of stable and unstable products may be formed which may then exist in colourless solution. When the test is applied, liberated iodine reacts with one or more of these intermediate products, and the blue colour with the starch is not obtained or it appears for only a short time. Afterwards these unstable products decompose and disappear and iodate test produces a positive response.

The data for the reduction of iodate by the oxidation products of the organic acids is given in Tables III, IV and V. In almost all

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32) F. Feigl, "Spot Tests in Inorganic Analysis," Elsvier Publishing Co. (1958).

TABLE III.

Citric acid: 0.08 M; 5 ml. of $KIO_3 \equiv 3.08$ ml. of 0.05 N $Na_2S_2O_3$; KIO_3 added after the reaction mixture was colourless. Figure in parentheses give the oxidant values when KIO_3 was added before the addition of the permanganate

KIO_3 in ml. of $Na_2S_2O_3$	Oxidant in the reaction mixture after 24 hr. in ml. of $Na_2S_2O_3$		
	$KMnO_4$: 0.01 N	$KMnO_4$: 0.02 N	$KMnO_4$: 0.04 N
0.616	0.44 (0.42)	0.42 (0.42)	— (0.42)
1.23	0.89 (0.85)	0.85 (0.83)	0.82 (0.82)
2.46	1.99* (1.68)	1.71 (1.64)	1.66 (1.64)
4.93	3.90* (3.38)	3.70* (3.30)	3.37 (3.30)
12.32	— (9.28)*	9.74* (8.30)	8.30 (8.30)
15.40	— —	— (10.32)	10.45 (10.28)
18.48	— —	— (12.30)	12.37 (12.32)

* More than the expected 2/3 of iodate added.

TABLE IV.

Malonic acid: 0.16 M; KIO_3 added immediately after the disappearance of the pink colour of the permanganate

KIO_3 in ml. of $Na_2S_2O_3$	Oxidant after 24 hr. in ml. of $Na_2S_2O_3$		KIO_3 in ml. of $Na_2S_2O_3$	Oxidant after 24 hr. in ml. of $Na_2S_2O_3$	
	$KMnO_4$: 0.02 N	$KMnO_4$: 0.04 N		$KMnO_4$: 0.06 N	$KMnO_4$: 0.08 N
5.09	3.45	3.02**	5.04	2.73**	2.52**
10.18	6.82	6.49	10.08	5.83**	5.50**
15.27	10.36	10.12	20.16	13.32	13.20
20.36	14.28	13.68	25.20	16.75	16.75
30.54	23.79*	21.45	30.24	20.28	20.15
5 ml. of $KIO_3 \equiv 5.09$ ml. of 0.02 N thiosulphate			5 ml. of $KIO_3 \equiv 5.04$ ml. of 0.02 N thiosulphate		

* More than the expected 2/3 of iodate.
** Less than the expected 2/3 of iodate.

TABLE V.

Malonic acid: 0.1 M; 5 ml. of $KIO_3 \equiv 5.09$ ml. of 0.02 N $Na_2S_2O_3$; KIO_3 added before the addition of $KMnO_4$

KIO_3 in ml. of $Na_2S_2O_3$	Oxidant after 24 hr. in ml. of thiosulphate		
	$KMnO_4$: 0.01 N	$KMnO_4$: 0.025 N	$KMnO_4$: 0.05 N
5.09	3.50	3.40	2.60**
10.18	7.40*	6.80	5.60**
15.27	11.40*	10.20	8.90**
20.36	16.70*	14.00	11.80**
30.54	21.40	21.40	20.20

* More than the expected 2/3 of iodate.
** Less than the expected 2/3 of iodate.

cases, subject to the conditions of mixing and the concentration of the reactants, the oxidising capacity of the original iodate is reduced to 2/3 (oxidising capacity), a fact which points to the reduction of iodate to iodite.

Higher iodometric values than the expected 2/3 of the added iodate are obtained only in cases where the reducing intermediates (the oxidation products of the organic acid) are not present in sufficient concentration, i.e., when there is less permanganate or comparatively more original iodate. In a few cases (Tables IV and V) the reduction of iodate seems to have gone further than the stage of iodite and the iodometric values are less than the expected 2/3 of the original iodate. This obviously happens when there is less iodate and when the reducing intermediates are formed in sufficient concentration. The mixtures are colourless and do not respond to the tests of iodide. Some of the iodate, therefore, appears to have been reduced to hypoiodite. A possibility of iodite disproportionating in a mixture of iodate and hypoiodite, with the same oxidising capacity as iodite, is ruled out because the reaction mixtures, even on heating, do not show any visible colour change or other reactions giving tests for iodide, a product which is well known to be formed by heating a solution of hypoiodite. An ammonia test[32] was negative.

The iodometric determinations were made 2, 8, 24 and 48 hr. after the addition of iodate. It was found that the reduction to iodite was not complete in two hours. It was, however, complete the next day. In the case of iodate experiments, difficulty was encountered in carrying out the iodometric titrations. The blue colour of the iodine-starch complex appeared again and again. However, no such difficulty was met with after 2 or 3 days nor in the case of malonic acid, even in the beginning. This difficulty is linked with the formation of the oxidation products of the organic acid. These products, existing in solution, react with the iodine liberated from the acidified potassium iodide for the purpose of titration; this iodine is retrieved only slowly. In the case of malonic acid, iodine is readily obtained even from the substituted products, and there is no difficulty during the titration. The oxidation products of citric acid disappear after 2 or 3 days, and once again there is no difficulty in titration.

The experiments with iodate were carried out by adding it after the permanganate-acid mixture had become colourless, and also by adding it to the acid before the addition of the permanganate. This was done in order to ascertain the degree of the stability of the oxidation products of the organic acid. It would appear from the results that the oxidation products of citric acid are more stable than those of the malonic acid. In the case of malonic acid, when iodate is added after the acid-permanganate mixture becomes colourless, a little iodate is reduced to iodite. Macmohan and Srivastava[16] have reported that acetone dicarboxylic acid — a product of oxidation of citric acid — is fairly stable, whereas the corresponding oxidation products of malonic acid are not stable.

Experiments were also carried out by adding iodate when the acid-permanganate mixtures had just lost the characteristic colour of the permanganate and become reddish orange, due probably to the formation of colloidal manganese dioxide[33] and tripositive manganese complexes.[34-38] The results were the expected 2/3 of the original iodate.

An interesting observation made in the case of malonic acid was the persistence of a light yellow colour when iodate was added in a sufficient concentration before the acid-permanganate mixture had become colourless. It was not due to iodine; probably manganese(III) complexes of malonic acid persisted in the solution. It, therefore, appears that the reduction of manganese(III) by malonic acid is very slow and that it is mainly brought about by its oxidation products. Irrespective of the nature of these products, whether they be radicals[37] or tartronic and glyoxalic acids,[39-41] they are all oxidised by iodate, and the colour of manganese(III) complexes tends to persist.

In the case of citric acid when higher concentrations ($>10^{-3}$ N) of iodide are employed, a light yellow precipitate is obtained, presumably a substitution product of citric acid with iodine, by a mechanism which will be given latter. This substance gives back its iodine in the presence of 15—20% potassium iodide and 1—2 N sulphuric acid, though not as quickly as the similar soluble product of malonic acid. The iodine in the yellow solid and the oxidising capacity of the filtrate are separately determined, and from this the total iodide is calculated. Table VI shows these results.

The fourth column gives the oxidant values of iodine in the +3 oxidation state (iodite), and column 6 gives those of iodine in its normal state (iodine-substituted oxidised species of the acid). The total of the iodine and iodide is obtained by dividing column 4 by four and adding it to column 6. The results show many deviations because of the crude method employed for the determination of iodine in the solid. The results of the individual columns are generally not reproducible, although those of the last column are fairly so in the 15—20°C temperature range (not at higher temperatures). Two or three iodine-substituted products are posssible in this case; if the concentration of such a soluble product is fairly comparable to that of the solid product, the present calculations would not give the expected results. However,

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[33] Y. K. Gupta and R. Dutta, *Bull. acad. polon. sci.*, **7**, 821 (1959).

[34] G. H. Cartledge and R. M. Nichols, *J. Am. Chem. Soc.*, **62**, 3057 (1940).

[35] J. Meyer and W. Schramm, *Z. anorg. Chem.*, **123**, 56 (1921).

[36] H. Taube, *J. Am. Chem. Soc.*, **70**, 3926 (1948).

[37] A. Y. Drummond and W. A. Waters, *J. Chem. Soc.*, **1954**, 2456.

[38] T. N. Srivastava, *Z. anorg. u. allgem. Chem.*, **288**, 288 (1956).

[39] W. H. Hatcher and C. R. West, *Trans. Roy. Soc., Canada*, **21** (III), 269 (1927).

[40] M. Cantley, L. Hough and A. O. Pettit, *Chem. Ind.*, **1959**, 1126.

[41] J. Courtois, *Ann. pharm. franc.*, **7**, 77 (1949).

TABLE VI.

Volume of the reaction mixture: 50 ml.; All values in ml. of 0.01 N thiosulphate

KI in ml. of $Na_2S_2O_3$	$KMnO_4$ N	Citric acid M	Oxidant in the filtrate ml.	Iodine in the filtrate (1/4 of 4th. column)	Oxidant or iodine in the ppt.	Total of iodide and iodine found	% Deviation
10	0.02	0.08	29.80	7.45	2.70	10.1	+ 1.5
		0.04	32.00	8.00	1.40	9.40	− 6.0
		0.02	34.48	8.62	0.26	8.88	−11.2
	0.01	0.08	17.40	4.35	6.70	11.05	+10.5
		0.04	20.20	5.05	5.60	10.65	+ 6.5
		0.02	22.52	5.64	3.37	9.00	−10.0
20	0.02	0.08	28.20	7.05	17.40	24.45	+22.20
		0.04	31.00	7.75	14.40	22.15	+10.75
		0.02	41.20	10.30	8.50	18.80	− 6.0
	0.01	0.08	4.40	1.10	19.80	20.90	+ 4.5
		0.04	8.40	2.10	18.60	20.70	+ 3.5
		0.02	12.00	3.00	15.00	18.00	−10.0

the regular increase or decrease in the values of this table does point to the correctness of the procedure adopted for the calculation.

It may thus be seen that, for low concentrations of iodide, the oxidant is always four times the equivalents of initial iodide, indicating the presence of the +3 state of iodine. The following reactions appear to take place:

$$MnO_4^- + \text{organic acid} \rightarrow Mn^{3+}\ (\text{complex}) + \text{oxidation products of acid} \qquad (1)$$

$$I^- + MnO_4^- \rightarrow I^0 + MnO_2 \qquad (2)$$

$$I^0 + MnO_4^- \rightarrow IO_3^- + MnO_2 \qquad (3)$$

$$I^0 + \text{organic acid} \rightarrow \text{substitution products} \qquad (4)$$

$$I^0 + \text{oxidation product of acid} \rightarrow \text{substitution products} \qquad (5)$$

$$IO_3^- + \text{oxidation products of acid} \rightarrow IO_2^- \qquad (6)$$

$$MnO_2 \text{ or } Mn(III) + \text{acid or its products} \rightarrow Mn(II) + \text{products} \qquad (7)$$

It would be reasonable to conclude, from the experiments on iodate (Tables III to V) and from the fact that permanganate is a strong oxidant, that iodate is first formed and that it is subsequently reduced to iodite. This could have been verified had it been possible to make a number of determinations of the oxidant (Table II) immediately after the addition of permanganate to the iodide-acid mixture. The iodometric determinations could be made, however, only when coloured manganese(III) complexes were reduced to colourless manganese(II) or its complexes. By the time this happens, iodate, even if formed earlier, has been reduced to iodite. The presence of iodate has been found[42] also when small amounts of iodide are oxidised by the permanganate in a sulphuric acid solution.

The first reaction of the above scheme has been reported[18,19,33,37,43-46] to be slow, but 2 is fairly fast.[4,5] The fate of iodine is now determined by reaction 3 on one hand, and by reactions 4 and 5 on the other. Ordinarily if the concentration of iodide is low, reaction 3 is predominant, which through 6 yields iodite; but if the concentration of malonic acid is also low, reactions 1, 4, 5, 6 and 7 would be insignificant and iodate will be the final product, giving oxidant values higher than the expected value of four times the original iodide. In some such cases manganese(IV) oxide was also precipitated.

If the concentration of iodide is increased, more iodine is produced and reactions 4 and 5 compete with 3. Part of the iodine gives substitution products with the acid and its oxidised species and, hence, is not raised to the +5 state by the permanganate. Consequently, the iodometric results are lower than expected for higher concentrations of iodide.

Citric acid seems to yield at least two oxidation products, one of which gives a soluble substituted product and the other, an insoluble one. These two products are obtained together if the temperature of the reaction is 25°C or higher, but at 20°C or lower, only a solid product can be obtained if the concentrations of iodide and citric acid are high. This yellow

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[42] Y. K. Gupta, unpublished work.

[43] Y. K. Gupta and R. S. Awasthi, *Proc. Natl. Acad. Sci. (India)*, **29A**, 331 (1960).

[44] L. Cabrera and C. Del Rio, *Anales. real Soc. espan fis. y quim (Madrid)*, **49B**, 263 (1953).

[45] V. M. Bhale, S. Mohammad, W. V. Bhagwat and S. L. Bafna, *J. Sci. Indust. Res. (India)*, **12B**, 521 (1953).

[46] A. Y. Drummond and W. A. Waters, *J. Chem. Soc.*, **1953**, 453.

product has properties similar to the tetraiodoacetone[47] reported to be formed under very similar conditions. The oxidation products of citric acid[48,49] are acetone, and acetonedicarboxylic, formic and oxalic acids. The solid product may be an iodine compound of one of these. Further work on this compound is in progress. In the case of malonic acid, the substitution product is soluble and is reported to be diiodomalonic acid.[29,43] Thus citric and malonic acids provide the products for the reduction of iodate to iodite and also prevent the accumulation of manganese dioxide, a product obtained from the reduction of permanganate. The organic acids react with it, giving soluble manganese(III) complexes.

Experiments with malic acid give somewhat similar results, but under limited conditions. The concentration ranges studied were:

Malic acid	$KMnO_4$	KI
$4—32\times10^{-2}$ M	$1—4\times10^{-2}$ N	$2—20\times10^{-4}$ N

In most cases the oxidant was found to be 4 to 6 times the original concentration of iodide, which corresponds to the situation of iodite or iodate or a mixture of the two, depending on the relative concentrations of malic acid and the permanganate. Permanganate should be more than ten times the concentration of iodide; otherwise the iodide is not likely to be oxidised beyond the stage of iodine. Reactions with iodate show its oxidising capacity reduced to 2/3 iodometric values only when the concentrations of the permanganate and the acid are high. At other concentrations, reduction does invariably take place in all cases, but not always to the extent expected.

Experiments with lactic acid and iodate reveal that the latter is not reduced by the permanganate-oxidation products of the acid. Experiments with iodine show that it is partly oxidised to iodate and partly to iodite.

Summary

Permanganate oxidises small amounts of iodide to iodite in the presence of malonic, citric or malic acid. The colourless reaction mixtures always have an oxidising capacity equivalent to four times the concentration of the iodide originally taken. In mixtures of permanganate and one of these acids, iodate is reduced to its 2/3 oxidising capacity, showing the formation of iodite. A mechanism for this has been suggested. Iodine is the product in the first stage of the oxidation of iodide, which is further oxidised to iodite or iodate or which may react with the oxidation products of the organic acids. Citric acid probably gives a number of such iodinated products, one of which is solid.

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