INDUCED REACTIONS OF HALOGENS IN AQUEOUS SOLUTION

PART I. REACTIONS IN THE SYSTEM IODINE-THIOSULPHATE-NITRITE

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The reactions occurring in aqueous solutions containing I_2, $Na_2S_2O_3$ and $NaNO_2$ buffered to pH's in the neighbourhood of 6 have been studied by analytical methods. It is found that the thiosulphate is oxidized to both tetrathionate and sulphate, but that no significant amounts of nitrite are consumed. A mechanism is suggested for the nitrite-catalyzed reaction between $S_2O_3^{--}$ and I_2 which leads to the formation of sulphate.

Berthoud and Berger [1] noted that it was not possible to obtain the theoretical end-point in the titration of iodine with sodium thiosulphate in the presence of a nitrite and they subjected the matter to further study. They found, carrying out the titrations in acetate buffers by running the thiosulphate into solutions of iodine containing potassium nitrite, that the ratio of thiosulphate consumed to the amount theoretically required for formation of $Na_2S_4O_6$ was less than unity and tended towards a limiting value of 0·5 at high concentrations of nitrite and low concentrations of thiosulphate. They further stated that none of the thiosulphate was converted into sulphate, but this statement has been contradicted by Kurtenacker and Spielhaczek,[2] who found considerable sulphate in all solutions of iodine together with nitrite which they had decolorized with thiosulphate. In our work we have carried out measurements essentially similar to those of Berthoud and Berger, but with wider variation of experimental conditions, and have obtained results not in agreement with the conclusions of those investigators.

Experimental

The reactions occurring in systems containing I_2, $NaNO_2$ and $Na_2S_2O_3$ are extremely fast and cannot be followed kinetically. The method we have adopted therefore is to determine the stoichiometry of the *net* reaction under a variety of conditions, in the hope that the results would give some indication of the kinetics of the processes occurring. It is to be noted that, apart from the reaction between thiosulphate and iodine and the induced reaction involving the three reactants, there is the possibility in these systems of reaction between nitrite and iodine [3] and of reaction between nitrite and thiosulphate.[2] Neither of these reactions need be taken into account, however, as each is much too slow to exert any significant effect under the conditions of this work. The results we have obtained may conveniently be presented under two heads: (*a*) determination of the ratio

$$R = \frac{\text{molecules } I_2 \text{ consumed}}{\text{molecules } Na_2S_2O_3 \text{ consumed}},$$

(*b*) quantitative determination of the end-products of the reaction.

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[1] Berthoud and Berger, *J. Chim. physique*, 1928, **25**, 562.

[2] Kurtenacker and Spielhaczek, *Z. anorg. Chem.*, 1934, **217**, 321.

[3] Durrant, Griffith and McKeown, *Trans. Faraday Soc.*, 1936, **32**, 999.

All reaction mixtures were buffered to avoid complications due to free nitrous acid ; pH's between about 6 and 7·2 were used, most of the experiments being carried out in phosphate buffers, though a few determinations of *R* and most of the quantitative analyses of the end-products were effected using acetate buffers.

(I) Determinations of *R*. Values of *R* were obtained by adding known amounts of thiosulphate solution to buffered solutions containing iodine and nitrite, the amounts of thiosulphate being insufficient to decolorize all the iodine. The remaining iodine was then determined by addition of sodium arsenite and back-titration with iodine. Preliminary experiments showed that the values of *R* obtained in this way depend on (i) the rate at which the thiosulphate solution is run in, and (ii) the method of stirring during the addition, but are independent of (iii) the volume of thiosulphate run in under our experimental conditions and (iv) the time the reaction mixture is allowed to stand before addition of sodium arsenite. The last of these results implies that the reactions occurring in the system are fast and further that any reactions consuming I_2 in the systems which result, i.e. I_2—NO_2^-—$S_4O_6^{--}$ (or other sulphur compound formed from the $S_2O_3^{--}$) are negligibly slow. As regards effects (i) and (ii) neither is of large magnitude. For example, the effect on *R* of the rate of addition of $Na_2S_2O_3$ was tested by comparing the *R* values obtained (*a*) by running in the thiosulphate solution from a fast-flowing pipette (time required 3-4 sec.) with those (*b*) obtained by running in the thiosulphate drop by drop (time of addition about 70 sec.). Using the same method of stirring throughout, examples of the results obtained are :

$[KH_2PO_4] = 0·0375$; $[Na_2\,HPO_4] = 0·01875$; $[NaNO_2] = 0·075$;
$[\Sigma I_2]_{\text{init.}} = 0·0006$; $[KI] = 0·01$. Units are g. mol./l.

[Thiosulphate] (g. mol./l.)	*R*			
	3×10^{-3}	10^{-3}	2×10^{-4}	5×10^{-5}
Method (*a*) .	1·17	1·68	3·03	3·88
Method (*b*) .	1·19	1·66	2·86	3·57

These and other results show that the rate of addition of the thiosulphate has an influence on the value of *R*, that the effect is not pronounced, that with very low concentrations of thiosulphate the *R* values obtained by running in the thiosulphate " in bulk " are greater than those using drop-by-drop addition, while with higher concentrations (3×10^{-3} g. mol./l. and over) there is a tendency for the reverse statement to hold true. Similarly, the method of agitation of the solution during the addition of thiosulphate is found to exert a definite though not a very large effect. Thus in corresponding experiments, adding the thiosulphate drop-by-drop, values of *R* obtained were :

Method of Agitation	*R*	
Solutions hand-shaken .	3·27	2·07
Solutions motor-stirred .	3·49	2·29

The standard procedure adopted to determine *R* was as follows. Into a 300 ml. Erlenmeyer flask were introduced 5 ml. buffer solution, 5 ml. $NaNO_2$ solution, 20 ml. I_2—KI solution together with the volume of water necessary to make the average volume 40 ml., the average volume being defined as that of the reaction mixture when one-half of the pre-determined volume of thiosulphate solution had been added. The latter was run in drop by drop at approximately the same rate in each experiment (2 drops/sec.) and during the addition the reaction mixture was kept agitated by uniform hand-shaking. Blank experiments were also carried out in which water (instead of thiosulphate solution) was run into the buffered mixture of iodine and nitrite to find the corrections for any loss of iodine by vaporization or reaction with nitrite. A repeat of each experiment was carried out; the results show reproducibility of R values to within 1-2 %. It is further to be noted that the results obtained by any other standard procedure would present the same general picture as those to be given, though the individual R values in the two sets would in general differ to some extent.

All the experiments were carried out at room temperature (16°-20° C), no special precautions being needed to work within narrower limits as it was found that the R values are relatively insensitive to temperature. In general, lowering the temperature from 18° to 0° C diminishes R by about 10 %.

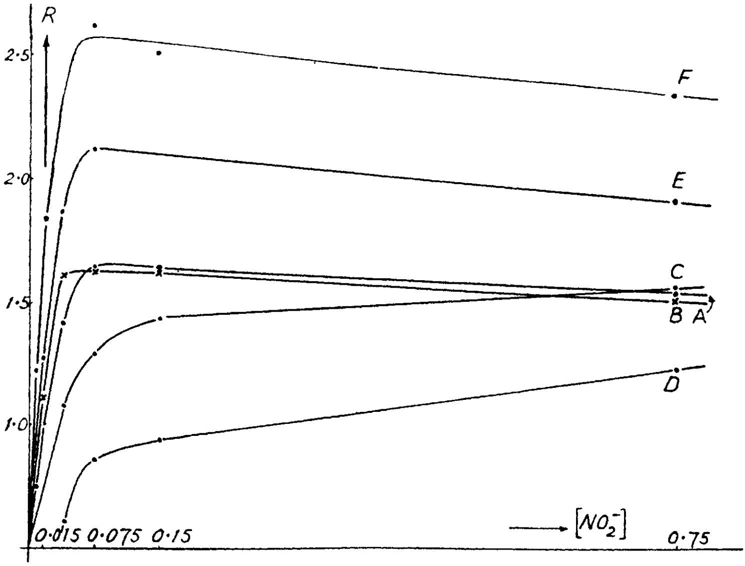

FIG. 1.

Series	[KH$_2$PO$_4$]	[Na$_2$HPO$_4$]	[ΣI$_2$]	[ΣI$^-$]	[S$_2$O$_3^=$] added
A	0·0375	0·0187	0·00061	0·01	0·001
B	0·0375	0·0187	0·00061	0·0025	0·001
C	0·0375	0·0187	0·00061	0·05	0·001
D	0·0375	0·0187	0·00061	0·25	0·001
E	0·0375	0·0187	0·0025	0·01	0·001
	[HAc]	[NaAc]			
F	0·125	0·00625	0·00025	0·01	0·00019

Concentrations in g. mol. or g. ion per litre.

Fig. 1-3 give an indication of the type of results obtained. It is found that:

(1) R values range between 0·5 and 4·0, the limiting value of 4·0 being approached using moderate concentrations of NO_2^- and running in a very dilute (M/20,000) solution of thiosulphate.

(2) Increase in concentration of NO_2^- in general increases R, but in the presence of low concentrations of I^- a maximum value of R is soon reached, beyond which further increase in [NO_2^-] has practically no effect.

(3) Increase in concentration of iodine increases R.

(4) Increase in [I^-] diminishes R, except at very low concentrations of I^- where no effect is found.

(5) Neither change in pH nor change of buffer constituents affects R within the limits of [H^+] of 10^{-6} to 5×10^{-8} g. ion/l.

(II) End-products of the Reaction. Qualitatively it was found, in disagreement with Berthoud and Berger,[1] that sulphate is always formed in the reaction between thiosulphate and iodine when nitrite is present, and that the sulphate formation is accompanied by an increase in acidity of the reaction mixture. Quantitative determinations were made of the tetrathionate and sulphate formed and acid liberated, together with iodine and thiosulphate consumed. It was unfortunately not feasible to trace the fate of the nitrite, but the quantitative data obtained prove that no appreciable amounts of nitrite can be consumed during the reaction. The method used to determine the other resultants was to run in thiosulphate into the buffered solution containing I_2 and NO_2^- until the colour of the iodine just disappeared. Aliquot portions of the resulting solution were then analyzed : (i) for sulphate by precipitation as $BaSO_4$ and weighing, (ii) for tetrathionate by addition of excess sulphite forming thiosulphate, which was titrated with iodine after addition of formaldehyde to bind the excess sulphite, and (iii) for increase in acidity by titration with standard NaOH, using phenolphthalein.

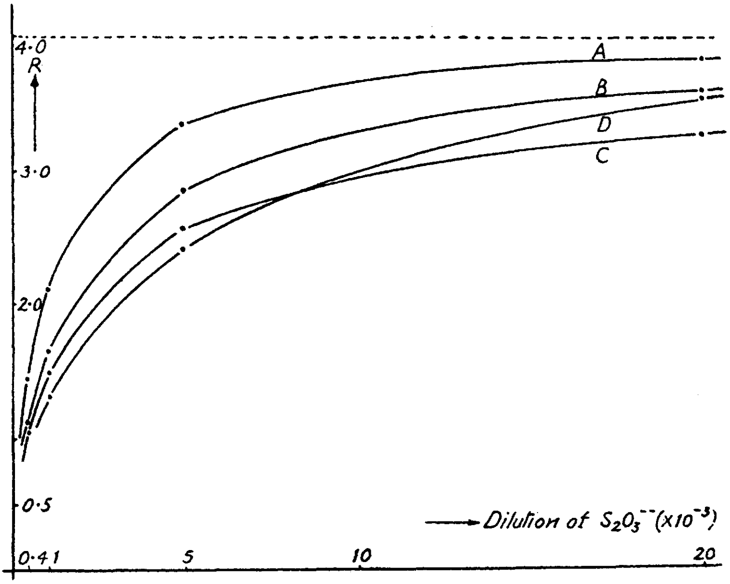

FIG. 2.

Series	$[KH_2PO_4]$	$[Na_2HPO_4]$	$[\Sigma I_3]$	$[\Sigma I^-]$	$[NO_2^-]$
A	0·0375	0·0187	0·0025	0·01	0·075
B	0·0375	0·0187	0·00061	0·01	0·075
C	0·0375	0·0187	0·00061	0·01	0·75
D	0·0375	0·0187	0·00025	0·01	0·075

Concentrations in g. mol. or g. ion per litre.

In order to avoid the possibility of decomposition of tetrathionate (with formation of sulphate) in hot solutions, sulphate was determined by precipitation of $BaSO_4$ in the cold. 3 % $BaCl_2$ solution was run very slowly with efficient stirring into the solution to be analyzed. After two hours' standing the precipitate was filtered, ignited and weighed. Blank experiments were carried out with known amounts of K_2SO_4 together with tetrathionate, KI, $NaNO_2$ and buffer constituents, each in concentration of the same order as those in the actual experiments. With weights of $BaSO_4$ precipitate of from 0·04 to 0·09 g., the blank experiments agreed with the theoretical to within about 1·5 %. For the estimation of tetrathionate also, appropriate blank experiments were made to find the conditions under which, by Kurtenacker's method, tetrathionate could be determined when present in low concentration (about 0·002 M) in presence of nitrite. The chief matter requiring attention is, as mentioned by Kurtenacker and Spielhaczek, the pH of the solution when the final titration of I_2 is effected. This pH had not to be less than about 5·4, and the blank experiments gave the amount of acetic acid that could safely be added to the solution before the final titration in order to obtain satisfactory results. It is considered that the estimations of tetrathionate should be accurate to within about 2 %.

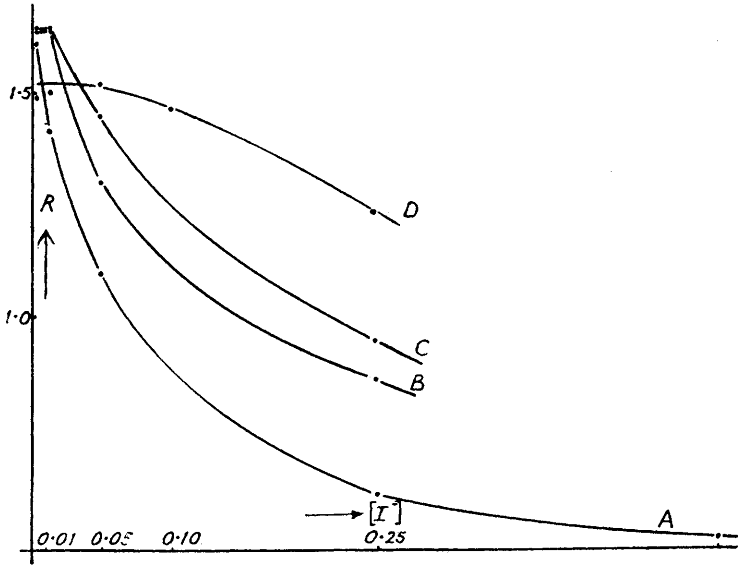

FIG. 3.

Series	$[KH_2PO_4]$	$[Na_2HPO_4]$	$[\Sigma I_2]$	$[NO_2^-]$	$[S_2O_3^=]$ added
A	0·0375	0·0187	0·00061	0·045	0·001
B	0·0375	0·0187	0·00061	0·075	0·001
C	0·0375	0·0187	0·00061	0·15	0·001
D	0·0375	0·0187	0·00061	0·75	0·001

Concentrations in g. mol. or g. ion per litre.

In these determinations, the concentration of iodine in g. mol./l. $[\Sigma I_2]$ in the original solution was varied from 0·003 to 0·03, $[I^-]$ from 0·01 to 0·12, $[NO_2^-]$ from 0·03 to 0·72 g. ion/l. The buffer ratio [NaAc]/[HAc] = 20/1 was used, though the concentrations of the buffer constituents were varied. A few experiments were also done with phosphate buffers in the ratio $[Na_2HPO_4]/[KH_2PO_4] = 1/2$. The concentration of added thiosulphate was varied between 0·0004 and 0·1 g. mol./l. Some of the results obtained in this way are given in Table I. ($\Delta S_4O_6^{--}$, ΔH^+, ΔSO_4^{--} = moles tetrathionate, moles acid, moles sulphate formed.)

The results as seen in Table I on page 310 and other results show that under all conditions :

(*a*) the ratio of moles H^+ formed to moles sulphate formed = 5·0 ;

(*b*) moles thiosulphate consumed = 2 (moles tetrathionate formed) + ½ (moles sulphate formed), i.e. no sulphur compounds other than tetrathionate and sulphate are produced ;

(*c*) moles I_2 consumed = moles tetrathionate formed + 2 (moles sulphate formed).

TABLE I

Temp. = 18° C ; [NaAc]/[HAc] = 20/1

Concentrations in Initial Solution g. mol. or g. ion per l.			Conc. of Added $Na_2S_2O_3$ g. mol./l × 10^3	Moles $S_2O_3^{--}$ Consumed × 10^4	Moles I_2 Consumed × 10^4	g. ion × 10^4		
$[\Sigma I_2]$	$[\Sigma I^-]$	$[NO_2^-]$				$\Delta S_4O_6^{--}$	ΔH^+	ΔSO_4^{--}
0·02655	0·1067	0·08000	24·22	27·29	19·10	12·97	15·44	3·104
0·03158	0·1263	0·06317	25·58	40·45	30·00	18·74	28·15	3·602
0·002045	0·04054	0·03243	5·070	4·177	3·624	1·881	4·34	0·881
0·002134	0·04348	0·03478	5·175	8·035	7·123	3·527	8·505	1·724
0·01491	0·0375	0·1000	2·656	7·682	11·93	2·899	20·36	4·158
0·01878	0·0250	0·7200	0·4124	3·894	9·390	—	21·32	4·383

It follows from these that the total reaction is compounded of two *net* processes, which occur in varying proportions dependent on the conditions, viz. :

$$2S_2O_3^{=} + I_2 \rightarrow S_4O_6^{--} + 2I^-, \quad . \quad . \quad . \quad . \quad (1)$$

and
$$S_2O_3^{--} + 4I_2 + 5H_2O + zNO_2^- \rightarrow 2SO_4^{--} + I^- + 10H^+ + zNO_2^-. \quad . \quad (2)$$

The nitrite is thus not permanently consumed, and so acts solely as a catalyst. For consumption of the nitrite to occur, it would be necessary to add to reactions (1) and (2), one or more of the following *net* processes :

$$I_2 + NO_2^- + H_2O \rightarrow NO_3^- + 2H^+ + 2I^-, \quad . \quad . \quad . \quad (3)$$

$$2NO_2^- + 2I^- + 2H_2O \rightarrow 2NO + 4OH^- + I_2, \quad . \quad . \quad (4)$$

$$2S_2O_3^- + 2NO_2^{--} + 2H_2O \rightarrow S_4O_6^{--} + 2NO + 4OH^-. \quad . \quad (5)$$

If any or all of these take place to a significant extent, however, the experimental results (*a*), (*b*) and (*c*) could not simultaneously hold true ; it must, therefore, be inferred that (1) and (2) are the sole *net* processes which have to be considered. On this basis, it follows that if in any experiment, x is the fraction of the thiosulphate converted into tetrathionate, and R is the ratio of

$$(\text{moles } I_2 \text{ consumed})/(\text{moles } Na_2S_2O_3 \text{ consumed}),$$

then $x = (8 - 2R)/7$, so that fraction of thiosulphate forming sulphate

$$= 1 - x = \frac{2R}{7} - \frac{1}{7}.$$

A plot of R against $(1 - x)$ should thus be a straight line with a slope of $2/7 = 0·286$. The results plotted in Fig. 4 show satisfactory agreement, the slope of the straight line plotted being 0·273.

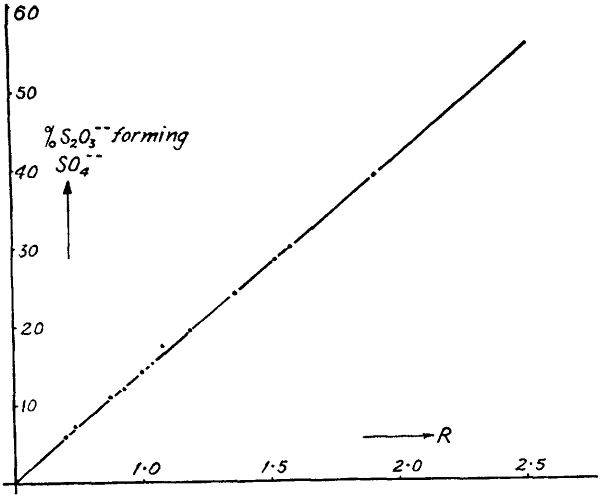

FIG. 4.

Discussion

The results given above show that in the presence of nitrite the reaction between iodine and thiosulphate leads not only to tetrathionate formation, but also to the production of sulphate, that with sufficiently dilute thiosulphate the fraction oxidized to sulphate approaches unity, and that no significant amount of nitrite is consumed in the change. The mechanism suggested by Berthoud and Berger [1] for the reactions in these systems need not be discussed, as it was based on an erroneous limit for *R*, and further it takes no account of sulphate formation. We propose the following mechanism, which will account qualitatively for most of our results and which is based on the hypothesis that the first product of the reaction between thiosulphate and iodine is, as suggested by Raschig,[4] the ion $S_2O_3I^-$.

(1*a*) $I_2 + S_2O_3^= \rightarrow S_2O_3I^- + I^-$,
(1*b*) $I_3^- + S_2O_3^= \rightarrow S_2O_3I^- + 2I^-$,
(2) $S_2O_3I^- + S_2O_3^= \rightarrow S_4O_6^= + I^-$,
(3) $S_2O_3I^- + NO_2^- \rightleftharpoons S_2O_3NO_2^- + I^-$,
(4) $S_2O_3NO_2^- + S_2O_3^= \rightarrow S_4O_6^= + NO_2^-$,
(5) $S_2O_3NO_2^- + I_2 + 3H_2O \rightarrow 2SO_3^= + 2I^- + 6H^+ + NO_2^-$,
(6) $SO_3^= + I_2 + H_2O \rightarrow SO_4^= + 2H^+ + 2I^-$.

All these reaction steps are regarded as fast reactions, but, to interpret our results, it is necessary to make the following assumptions in respect of relative rates : (i) that in presence of moderate concentrations of nitrite, tetrathionate formation via (3) and (4) is faster than via (2), and (ii) except at fairly high concentrations of iodide the equilibrium (3) lies well over to the right-hand side. Reactions (1*a*), (1*b*) and (2) are postulated as those taking place also when I_2 reacts with $S_2O_3^=$ in absence of NO_2^-, except that under these conditions it may also be necessary to take into account the reversals of (1*a*) and (1*b*) ; the reasons for the choice of this mechanism for the $I_2 - S_2O_3^{--}$ reaction will be given in a subsequent paper.

It is not possible to deal quantitatively with the reaction kinetics on the basis of this or of any other mechanism, since the part-reactions are so rapid that they are practically completed during the time of addition of the thiosulphate, so that the system is not a homogeneous one, but qualitatively this mechanism accounts for the experimental findings. The effect of concentration of added thiosulphate is seen to be in the sense that increasing dilution of thiosulphate will diminish tetrathionate formation (i.e. increase sulphate formation), since reactions (2) and (4) which produce tetrathionate will—due to the lowered concentration of $S_2O_3^=$—be more retarded than reaction (5) which leads to sulphate formation. The effect of increasing $[\Sigma I_2]$ is found experimentally to result in an increase of *R*, i.e. increased sulphate formation. This is due partly to an increased rate of reaction (5), and partly to the fact that the increase in the rates of (1*a*) and (1*b*) will cause a reduced concentration of $S_2O_3^=$ available for the tetrathionate-forming reactions (2) and (4). The effects of $[I^-]$ and $[NO_2^-]$ are to some extent bound together. We may consider them as follows. At low $[I^-]$, the reversal of process (3) may be neglected. At low $[I^-]$ and very low $[NO_2^-]$ much $S_4O_6^=$ is formed by reaction (2), but on increasing $[NO_2^-]$ the rate of reaction (3) increases and the concentration of $S_2O_3NO_2^-$ increases at the expense of that of $S_2O_3I^-$. If now a fair proportion of the resulting $S_2O_3NO_2^-$ reacts by (5) this will cause a sharp rise in *R* with increasing $[NO_2^-]$ as found experimentally. At higher concentrations of NO_2^-, however, a state will be reached when all the $S_2O_3I^-$ formed in (1*a*) and (1*b*) reacts by (3) to form $S_2O_3NO_2^-$ and reaction (2) does not occur. Under these conditions a certain fraction of the $S_2O_3NO_2^-$ reacts by (5), the remainder by (4) yielding a value of *R*

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[4] Raschig, *Ber.*, 1915, **48**, 2088.

which depends on the concentrations of I_2, I^- and thiosulphate. Increase of $[NO_2^-]$ beyond this limiting value should not affect R. This is approximately what is found experimentally, though there is a slight tendency for the R values to fall at higher values of $[NO_2^-]$ than the limiting. The effect of $[I^-]$ on R at moderate and high values of $[I^-]$ ($[I^-] > 0{\cdot}02$ g. ion/l.) is ascribed to the reduction by tri-iodide formation of the concentration of free iodine with consequent reduction in the rate of reaction (5), which leads to sulphate formation. The effect of increase of $[NO_2^-]$ at these concentrations of iodide will, in general, be similar to that at low $[I^-]$, except that we must now consider (3) to be an equilibrium and take account of the reversal. This will have the effect that the attainment of the concentration of NO_2^- at which the limiting value of R is reached is delayed, i.e. the mechanism will qualitatively predict the type of R — $[NO_2^-]$ curve found, namely, an initial more or less steep rise followed by a slow rise at higher concentrations of $[NO_2^-]$. There is, however, one experimental result which this mechanism does not account for, viz., the absence of any effect of $[I^-]$ on R at low values of $[I^-]$ ($[I^-] > 0{\cdot}02$) and not too low values of $[NO_2^-]$. The theory predicts that under all conditions R should decrease with increasing $[I^-]$ and we can suggest no satisfactory explanation of this anomaly.

In this system we have thus an example of selective direction of the course of reaction by catalysis, somewhat similar to the catalytic effect of molybdic acid on the reaction between thiosulphate and hydrogen peroxide, studied by Abel.[5] In that process, just as in the processes dealt with in this paper, the uncatalysed reaction leads to tetrathionate, the catalyzed process to sulphate. The mechanisms of the catalyses in the two cases would, however, appear to be very different.

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[5] Abel, *Z. Elektrochem.*, 1912, **18**, 705.