INDUCED REACTIONS OF THE HALOGENS IN AQUEOUS SOLUTION

PART II. REACTIONS IN THE SYSTEMS I_2—$S_2O_3^{--}$—N_3^- AND I_2—$S_4O_6^{--}$—N_3^-

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The reaction between NaN_3 and I_2 in aqueous solution with liberation of N_2 is induced by both $Na_2S_2O_3$ and $Na_2S_4O_6$, and studies of both processes have been made over fairly wide ranges of conditions. The induction by $Na_2S_4O_6$ which yields H_2SO_4 and N_2 is slow, and kinetic measurements have been made by determining the rates of consumption of iodine and of production of N_2. The effect of $[I^-]$ on both rates is characterized by a pronounced minimum in the region of $[I^-] = 0{\cdot}01$-$0{\cdot}02$. The results are accounted for in terms of a chain mechanism, involving the intermediates $S_2O_3I^-$ and $S_2O_3N_3^-$ (or $S_2O_3^-$), with different primary steps in the regions of low $[I^-]$ and high $[I^-]$. The latter correspond to the first steps in reactions which have been found to take place in absence of N_3^-, viz. the reaction between $S_4O_6^{--}$ and I_2 in presence of very low $[I^-]$ and the reaction between $S_4O_6^{--}$ and I^-. The former of these has been studied kinetically but as yet no mechanism is proposed for it.

The products of reaction in $S_2O_3^{--}$—I_2—N_3^- systems include $S_4O_6^{--}$, H_2SO_4 and N_2. The reactions are too fast to follow by ordinary kinetic methods and experimental work has been limited to investigation of the over-all stoichiometry and of the relation between I_2 consumed to $Na_2S_2O_3$ consumed under a variety of conditions. A possible chain mechanism for the reaction is suggested. Based on this work an experimental method was evolved by means of which the rate of the direct reaction between $Na_2S_2O_3$ and I_2 could be measured in mixtures containing excess I_2, and a reaction mechanism derived from these data is proposed for the I_2—$S_2O_3^{--}$ reaction. The mechanism suggested is

$$S_2O^{--} + I_2 \rightleftarrows S_2O_3I^- + I^-,$$

followed by

$$S_2O_3I^- + S_2O_3^{--} \rightarrow S_4O_6^{--} + I^-.$$

Raschig [1] [2] discovered that the addition of small amounts of $Na_2S_2O_3$ (or Na_2S) induces a vigorous reaction between I_2 and NaN_3 in aqueous solution, nitrogen being evolved; in absence of the catalyst no reaction between I_2 and NaN_3 can be detected. Though the induced reaction has been used as a means of estimating azide and as a sensitive test for the detection of various compounds of sulphur, no detailed quantitative study of the process appears to have been made, and insufficient data exist to throw much light on its mechanism. Published work bearing on these induced reactions may be briefly summarized. Raschig carried out a few qualitative measurements on the system I_2—$S_2O_3^{--}$—N_3^- and showed that H_2SO_4 is one of the resultants of the reactions which occur. He also showed that in the system $S_2O_3^{--}$—I_2 there is formed a catalyst whose life under certain conditions can be of the order of minutes. Browne

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[1] Raschig, *Chem.-Ztg.*, 1908, **32**, 1203.
[2] Raschig, *Ber.*, 1915, **48**, 2088.

and Hoel[3] investigated the reaction between KN_3 and I_2 induced by CS_2 and concluded that the probable mechanism is :

$$KN_3 + CS_2 \rightarrow KSCSN_3$$
$$2KSCSN_3 + I_2 \rightarrow (SCSN_3)_2 + 2KI$$
$$(SCSN_3)_2 + 2KN_3 \rightarrow 2KSCSN_3 + 3N_2.$$

The mechanism was supported by the preparation and isolation of the two intermediates $KSCSN_3$ and $(SCSN_3)_2$, together with the observation that the addition of small amounts of either of these two substances to a KN_3—I_2 mixture free from CS_2 results in a vigorous oxidation of the azide. Friedman[4] has studied the reaction between NaN_3 and I_2 induced by a number of sulphur-containing compounds, including $Na_2S_2O_3$. By measuring the N_2 evolution from a Barcroft apparatus he determined the ratio (U) of moles NaN_3 decomposed to moles of sulphur compound consumed. In general, a very rapid evolution of N_2 occurred in the first few minutes, followed by a much slower evolution subsequently. The fast reaction was ascribed to the action of the R—SH compound in initiating a chain whose chain-breaking process was the conversion of the R . SH molecule into the disulphide R—S—S—R ; the much slower reaction to a reaction between NaN_3 and I_2 induced by the disulphide. Only one experiment with $Na_2S_2O_3$ was carried out ; the value of U obtained for the fast initial reaction under the conditions of this experiment was about 11. Though Raschig,[2] Friedman[4] and Weiss[5] have advanced mechanisms for the induced reaction in the system I_2—$S_2O_3^{--}$—N_3^-, none is supported by adequate experimental evidence. In the present work we have carried out over a fairly wide range of conditions experiments on the reactivity of these systems ; we have further studied the analogous system I_2—$S_4O_6^{--}$—N_3^-, the direct I_2—$S_2O_3^{--}$ reaction in absence of azide, and the reaction between $S_4O_6^{--}$ and I_2 which is found to take place at very low concentrations of iodide. By correlation of all the data, it has been possible to advance mechanisms, which, though in some respects speculative, account satisfactorily for the reactivity of these systems.

Experimental

System I_2—$S_2O_3^{--}$—N_3^-.—Owing to the great rapidity of the reactions in these systems, kinetic methods are not available to follow them ; our work has thus been confined to determining the stoichiometry of the reaction and the amount of reaction induced by unit amounts of thiosulphate under a variety of conditions. The data thus comprise determinations of the ratio R of (moles I_2 consumed)/(moles $Na_2S_2O_3$ consumed) and quantitative estimation of the end-products of the reaction.

Values of R were determined by running small amounts of thiosulphate solution into solutions containing azide and iodine, buffered with acetic acid—sodium acetate, and determining the excess iodine by addition of sodium arsenite and back-titration with standard iodine. This method is similar to that employed in the study of the I_2—$S_2O_3^{--}$—NO_2^- system described in Part I of this series,[6] and, except that the I_2—$S_2O_3^{--}$—N_3^- system is the more sensitive to variation in experimental method, similar remarks in regard to the effect on R of the method of adding thiosulphate and of mode of stirring apply to both systems. As described in Part I, here also in order to obtain comparable and reproducible results, a standard procedure was adopted, which consisted in the addition of the thiosulphate solution drop by drop at the rate of approximately one drop per second into the remainder of the reaction mixture, which was briskly swirled by hand during the addition. As the system (either in presence or absence of $S_2O_3^{--}$) is not light-sensitive, and as the R values are not very temperature-dependent, non-thermostatted reaction flasks of clear glass were used, and the

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[3] Browne and Hoel, *J. Amer. Chem. Soc.*, 1922, **44**, 2106.
[4] Friedman, *J. prakt. Chem.*, 1935, **146** (ii), 179.
[5] Weiss, *Trans. Faraday Soc.*, 1947, **43**, 119.
[6] Griffith and Irving, *ibid.*, 1949, **45**, 305.

data obtained relate to room temperature, from 17° to 20° C. Fig. 1-4 are representative of the results obtained. These and other data show that values of R found range from 0·5 (the limiting value in absence of N_3^-) to 50, though higher values could result by extending the range of conditions of experiment. They increase with increasing $[N_3^-]$ and with increasing $[I^-]$, in each case the increase being the more marked at low concentrations. R increases with decreasing concentration of added $S_2O_3^{--}$, the increase being the greater at low $[S_2O_3^{--}]$. The effect of variation of $[\Sigma I_2]$ on R is inappreciable, while, in general, decrease of temperature from 18° to 1° C increases R by about 20 %. Increase in $[H^+]$ tends to diminish R. As in the presence of sufficient strong mineral acid the oxidation of azide is completely inhibited, it appears that HN_3 does not react with I_2 in the presence of $Na_2S_2O_3$ and that reaction occurs only with free N_3^- ion. The observed decrease of R with increase of H^+ in the range tested in our experiments can be ascribed mainly, if not entirely, to the corresponding decrease in the effective $[N_3^-]$ due to increase in the ratio $[HN_3]/[N_3^-]$. It may finally be noted here that, as dealt with later, $S_4O_6^{--}$ also catalyzes the reaction between NaN_3 and I_2, but, compared with the $S_2O_3^{--}$ catalysis, the speed of the reaction involving $S_4O_6^{--}$ is very small and catalysis by $S_4O_6^{--}$ can be entirely neglected under the conditions of the experiments of this section.

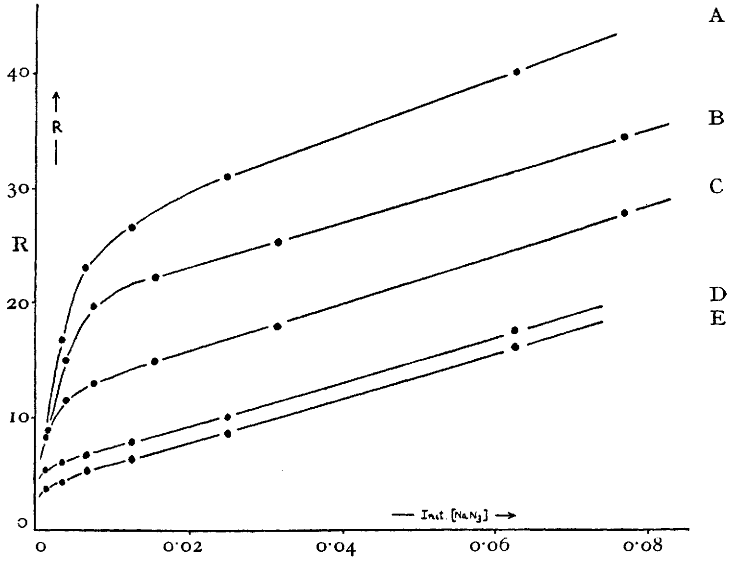

FIG. 1

Series	Init. $[I^-]$
A	0·2500
B	0·06153
C	0·01230
D	0·00200
E	Nil

In all Series :—

Init. $[\Sigma I_2]$ = 0·000250 or 0·000300

$$\text{Init.}\ \frac{[NaAc]}{[HAc]} = \frac{0{\cdot}01250}{0{\cdot}00625}\ \text{or}\ \frac{0{\cdot}01538}{0{\cdot}00769}$$

$[Na_2S_2O_3]$ added = N/10,000

Quantitative estimation of the end-products showed that the *net* reactions taking place are :

$$2N_3^- + I_2 \rightarrow 3N_2 + 2I^- \quad . \quad . \quad . \quad . \quad (1)$$

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

$$S_2O_3^{--} + 4I_2 + 5H_2O \rightarrow 2SO_4^{--} + 10H^+ + 8I^- . \quad . \quad . \quad (3)$$

The experiments were carried out by addition of $Na_2S_2O_3$ solutions to mixtures of known composition of I_2, KI, NaN_3 and buffer constituents until all the I_2 present had been exactly consumed, followed by analysis of the resulting colourless solution and/or by the measurement of N_2 evolved. $S_4O_6^{--}$ was determined by the method of Kurtenacker and Goldberg,[7] consisting in the reduction of $S_4O_6^{--}$ to $S_2O_3^{--}$ by KCN, addition of mineral acid and titration of the $S_2O_3^{--}$ with standard I_2. Unfortunately, for the range of concentrations of $S_4O_6^{--}$ M/800-M/4000, in which chief interest lies, it was not found possible to obtain results with an accuracy better than ± 5 %; with stronger solutions data of reasonable accuracy could be obtained and determinations of $S_4O_6^{--}$ were made in solutions in which $S_4O_6^{--}$, as end-product, was present in concentrations exceeding M/800. Sulphate was determined by precipitation as $BaSO_4$ and weighing; to avoid any possible decomposition of tetrathionate the precipitation was effected in the cold, blank experiments being made to find the best conditions for accurate analyses. Estimations of $S_4O_6^{--}$ and SO_4^{--} in the solutions resulting from the running-in of N/50 thiosulphate into various mixtures of the other reactants showed that at least 98 % of the S in the $S_2O_3^{--}$ was accounted for as $S_4O_6^{--}$ and SO_4^{--}. In view of the estimated experimental errors in the two determinations it is not considered that the remaining 2 % is of significance, and the most probable conclusion is that in the induced reaction the only products containing S are $S_4O_6^{--}$ and SO_4^{--}. This view is supported by the results of experiments in which the N_2 evolved was measured in a nitrometer. Table I summarizes the data of some experiments in which thiosulphate was run into the reaction mixture of the composition indicated until the iodine was decolorized, the evolved N_2 measured and the SO_4^{--} in the colourless solution determined. In the last two columns are given the percentages of $S_2O_3^{--}$ converted to SO_4^{--} obtained (*a*) by direct determination of $BaSO_4$ and (*b*) from the amount of N_2

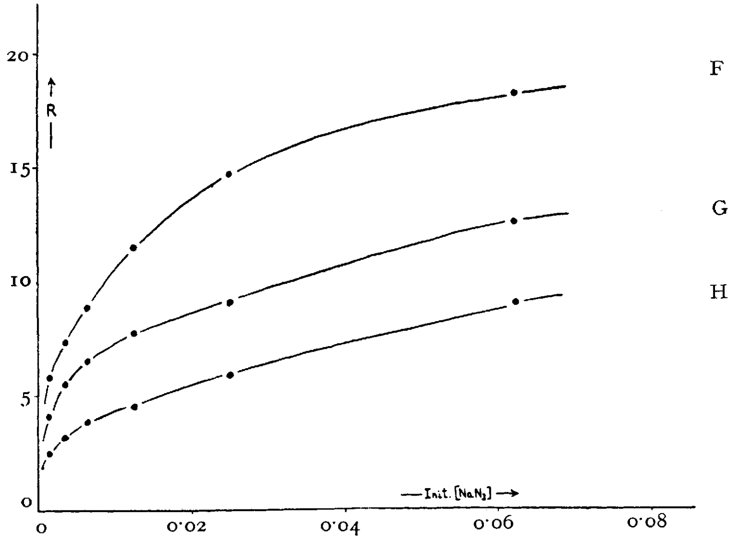

FIG. 2

Series	$[Na_2S_2O_3]$ added
F	N/10,000
G	N/1,000
H	N/200

In all Series:—

Init. $[\Sigma I_2] = 0{\cdot}002786$

Init. $[I^-] = 0{\cdot}007500$

Init. $\dfrac{[NaAc]}{[HAc]} = \dfrac{0{\cdot}01250}{0{\cdot}00625}$

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[7] Kurtenacker and Goldberg, *Z. anal. Chem.*, 1927, **166**, 177.

evolved assuming that the only *net* processes occurring are (1), (2) and (3). The agreement between the two is regarded as sufficient to justify the assumption made.

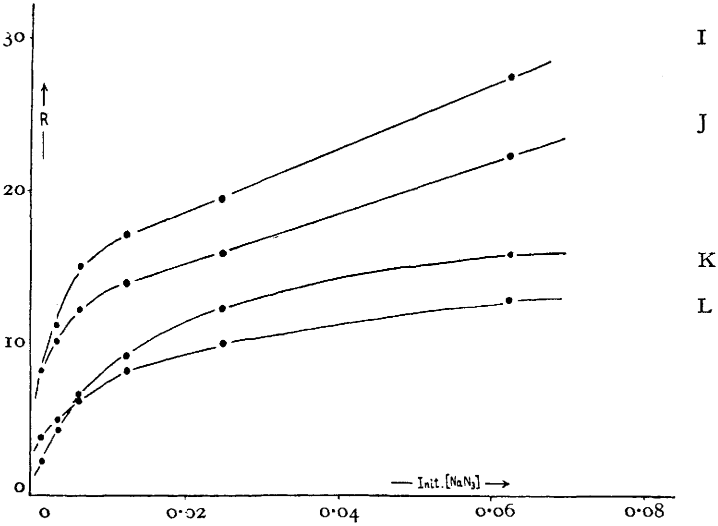

Fig. 3

Series	Temp.	Init. [H+]
I	1° C	$1{\cdot}8 \times 10^{-6}$
J	Room	$1{\cdot}8 \times 10^{-6}$
K	1° C	$90{\cdot}0 \times 10^{-6}$
L	Room	$90{\cdot}0 \times 10^{-6}$

In all Series :—

Init. $[\Sigma I_2] = 0{\cdot}00025$

Init. $[I^-] = 0{\cdot}0100$

$[Na_2S_2O_3$ added$] = N/10{,}000$

Some experiments were also made to determine the increase of acidity of the reaction mixture, the stoichiometric relation (3) requiring the formation of 10 moles of H+ for each mole of $S_2O_3^{--}$ oxidized to sulphate. The results obtained were only about one-half to three-quarters of the expected values, but the discrepancies are due to loss of the very volatile HN_3 when the reaction is carried out in open flasks or beakers. In a closed apparatus with a trap containing NaOH solution through which passed the evolved N_2 together with any HN_3 in the gaseous phase, the results found were in reasonable agreement with the theoretical values.

TABLE I

Initial Concentrations (g.-mole (or g.-ion)/l.)					Conc. of added $S_2O_3^{--}$ (approx.)	% $S_2O_3^{--}$ converted to SO_4^{--}	
$[\Sigma I_2]$	$[I^-]$	$[N_3^-]$	[NaAc]	[HAc]		(*a*)	(*b*)
0·02858	0·1143	0·07143	0·01429	0·007143	N/1000	60·6	59·8
0·02500	0·1000	0·1250	0·01250	0·006250	N/1000	50·8	53·7
0·02858	0·5714	0·07143	0·01429	0·007143	N/1000	50·0	48·9
0·02500	0·5000	0·1250	0·01250	0·006250	N/1000	42·5	41·4
0·02858	0·1143	0·07143	0·01429	0·007143	N/500	42·1	42·4
0·02858	0·1143	0·07143	0·01429	0·007143	N/200	23·5	25·2
0·02858	0·1143	0·07143	0·01429	0·007143	N/100	17·0	18·3

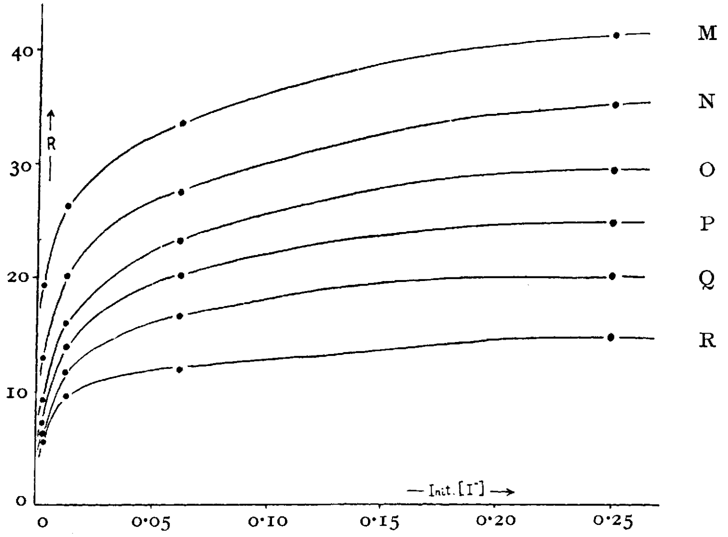

FIG. 4

Series	Init. $[NaN_3]$
M	0·0700
N	0·0400
O	0·0200
P	0·0100
Q	0·0050
R	0·0025

In all Series :—

Init. $[\Sigma I_2]$ = 0·00025 or 0·00030

Init. $\frac{[NaAc]}{[HAC]} = \frac{0·01250}{0·00625}$ or $\frac{0·01538}{0·00769}$

$[Na_2S_2O_3]$ added = N/10,000

The results of experiments of the type of those in Table I are briefly summarized in Table II, in which P is the percentage of the $S_2O_3^{--}$ converted into SO_4^{--} and Q' is the ratio of moles of N_3^- decomposed to moles of $S_2O_3^{--}$ converted into SO_4^{--}. The table gives the effect of increasing the concentrations of N_3^-, I^-, ΣI_2 and $S_2O_3^{--}$ on these variables.

TABLE II

	$[N_3^-]$	$[I^-]$	$[\Sigma I_2]$	$[S_2O_3^{--}]$
P	Nearly independent	Nearly independent	Increases slightly	Marked decrease more marked at low $[S_2O_3^{--}]$
Q'	Increases slightly	Increases slightly	Independent	Independent

The Reaction between $Na_2S_2O_3$ and I_2.—Raschig [2] has shown that a solution prepared by adding thiosulphate solution to an excess of a solution of iodine (*e.g.* a mixture of equimolar amounts of I_2 and $Na_2S_2O_3$) retains some catalytic activity, as measured by its action when poured into a solution of NaN_3, for a time of 1-2 min. He suggested that the direct reaction between I_2 and $Na_2S_2O_3$ proceeds via the mechanism :

$$S_2O_3^{--} + I_2 \rightarrow S_2O_3I^- + I^-$$
$$S_2O_3I^- + S_2O_3^{--} \rightarrow S_4O_6^{--} + I^-,$$

and that the catalytic activity of a mixture of I_2 and $Na_2S_2O_3$ such as the one mentioned above is due to the presence of the catalyst $S_2O_3I^-$, which under certain conditions has a detectable life-period, and which, it is presumed, can initiate reactions leading to the oxidations of azide. As the mechanism of the direct I_2—$Na_2S_2O_3$ reaction is of prime importance in formulating a mechanism, of the reactions in the system I_3^-—$S_2O_3^{--}$—N_3^-, we have attempted to obtain quantitative data from experiments of the type which Raschig carried out qualitatively, i.e. we have carried out determinations of the rate of reaction in mixtures of $Na_2S_2O_3$ and excess I_2. The rate of this direct reaction we have found to be strongly accelerated by increase of $[I^-]$, but, by working with mixtures containing I_2 and $Na_2S_2O_3$ of initial concentrations of the order of M/2000 and KI of initial concentrations of the order M/600-M/150, it has been found possible to measure the reaction rate over periods of two hours or more.

The experiments were made by adding $Na_2S_2O_3$ solution to an excess of an I_2–KI solution in a thermostatted flask, withdrawing samples from time to time, and determining the concentration of " active " $S_2O_3^{--}$ in each sample. The " active " $S_2O_3^{--}$, designated by $\Sigma S_2O_3^{--}$, is defined as the $S_2O_3^{--}$ not converted into $S_4O_6^{--}$, i.e. it is the sum of the free unchanged $S_2O_3^{--}$ together with the $S_2O_3^{--}$ present in the form of some active intermediate, such as, for example, the $S_2O_3I^-$ intermediate postulated by Raschig. The concentration of $\Sigma S_2O_3^{--}$ in each sample was determined from the extent of reaction, measured in terms of consumption of iodine, when the sample was added to a standard " indicator " mixture of I_2, KI, NaN_3 and buffer. Empirically an " indicator " mixture was sought, whose sensitivity (i.e. R value = moles ΣI_2 consumed in the mixture per mole of $S_2O_3^{--}$ added) was fairly constant for the range N/4000-N/20,000 of concentration of added thiosulphate. Such an " indicator " was found in a mixture of the composition :

$[\Sigma I_2] = 0{\cdot}0250$; $[I^-] = 0{\cdot}125$; $[N_3^-] = 0{\cdot}125$; $[NaAc] = 0{\cdot}025$; $[HAc] = 0{\cdot}0125$, as is shown by the following R values found when 24·75 ml. of solutions of $Na_2S_2O_3$ of various strengths were run under standardized conditions * into 50 ml. of the " indicator."

Conc. of added $Na_2S_2O_3 \times 10^4$	2·488	1·986	1·192	0·9930	0·4965
R	42·24	42·99	44·51	42·46	44·65
				(Mean R = 43·65)	

Thus by running a 24·75 ml. sample of the reacting mixture of $Na_2S_2O_3$ and I_2 into 50 ml. of this " indicator " under the same standard conditions and determining the moles iodine consumed (x) in the " indicator," we obtain the concentration in the sample of " active " $S_2O_3^{--}$, viz. :

$$[\Sigma S_2O_3^{--}] = \frac{x \times 1000}{24{\cdot}75 \times 43{\cdot}35}.$$

The data obtained in this way for a typical reaction mixture are shown in Table III.

From this and the other experiments it was found that the decrease in $[\Sigma S_2O_3^{--}]$ with time follows a bimolecular course, and bimolecular velocity constants k_{bi} (l. moles^{-1} min.$^{-1}$) were calculated from " point to point " in each experiment. The results are summarized in Table IV.

The fifth column of Table IV gives the mean values of k_{bi}, found in experiments classified into four groups according to ionic strength and temperature. Inspection of these values shows that the rate of reaction as given by the k_{bi}'s is strongly accelerated by $[I^-]$ and is retarded by $[\Sigma I_2]$. This behaviour can be accounted for in terms of Raschig's mechanism slightly modified. We postulate the mechanism to be

$$S_2O_3^{--} + I_2 \rightleftarrows S_2O_3I^- + I^- \quad . \quad . \quad . \quad . \quad (4)$$

$$S_2O_3I^- + S_2O_3^{--} \rightarrow S_4O_6^{--} + I^-, \quad . \quad . \quad . \quad (5)$$

with (4) a rapidly established equilibrium well over to the right-hand side, and (5) the rate-determining reaction. On this basis, if k_2 is the velocity constant

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* 24·75 ml. of the $Na_2S_2O_3$ solution was delivered from a fast-flowing pipette (time of delivery 4 sec., with no drainage time) into 50 ml. of the " indicator " contained in a 250 ml. Erlenmeyer flask, the flask being briskly swirled by hand during the mixing process. Excess of standard As_2O_3 solution was then added and the excess back-titrated with standard iodine.

of reaction (5), K the equilibrium constant of (4), i.e. $K = \frac{[S_2O_3I^-][I^-]}{[S_2O_3^{--}][I_2]}$ and K_3 the tri-iodide equilibrium constant $\frac{[I^-][I_2]}{[I_3^-]}$, it follows that

$$\frac{d[S_4O_6^{--}]}{dt} = k_2[S_2O_3I^-][S_2O_3^{--}] = \frac{k_2[S_2O_3I^-]^2[I^-]\{K_3 + [I^-]\}}{KK_3[\Sigma I_2]}.$$

If it be assumed that equilibrium (4) is nearly completely over to the right, then $[S_2O_3I^-]$ can be identified with $[\Sigma S_2O_3^{--}]$ measured during each run. Hence

$$\frac{d[S_4O_6^{--}]}{dt} = k_{b1}[\Sigma S_2O_3^{--}]^2 = \frac{k_2[\Sigma S_2O_3^{--}]^2[I^-]\{K_3 + [I^-]\}}{KK_3[\Sigma I_2]}$$

and
$$\frac{k_{b1}[\Sigma I_2]}{[I^-]\{K_3 + [I^-]\}} = \frac{k_2}{KK_3} = \text{const.} = k_\alpha \text{ (say)}.$$

TABLE III

Temp. = 20° C
Ionic strength (μ) = 0·100

Initial concentrations (g.-mole (or g.-ion)/l.)

$$\begin{cases} [\Sigma I_2] = 0{\cdot}0006600 \\ [\Sigma I^-] = 0{\cdot}001667 \\ [S_2O_3^{--}] = 0{\cdot}0003164 \\ [NaNO_3] = 0{\cdot}09733 \end{cases}$$

Time (min.)	Δt	$x \times 10^4$ *	$[\Sigma S_2O_3^{--}] \times 10^4$	$\Delta[\Sigma S_2O_3^{--}] \times 10^4$	$k_{b1} \times 10^{-2}$
1·00		2·024	1·886		
	4·00			0·267	2·19
5·00		1·737	1·619		
	8·00			0·362	2·22
13·00		1·349	1·257		
	16·00			0·3711	2·08
29·00		0·9504	0·8859		
	32·00			0·3506	2·31
61·00		0·5744	0·5353		

Thus if the experimental values of k_{b1} are multiplied by the factor

$$[\Sigma I_2]/[I^-]\{K_3 + [I^-]\} \ (= F),$$

the values of the product k_α should be constant. The seventh and eighth columns of Table II give the mean concentrations during the runs of $[\Sigma I_2]$ and $[I^-]$ (corrected for tri-iodide formation using $K_3 = 1{\cdot}20 \times 10^{-3}$ at 20° and $1{\cdot}57 \times 10^{-3}$

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* It is to be noted that to obtain values of x it is necessary to know the $[\Sigma I_2]$ in the sample of reaction mixture. It is, however, not possible to calculate this quantity until both the mechanism of the I_2—$S_2O_3^{--}$ reaction and the amount of $S_2O_3^{--}$ in the sample are known. Hence, to obtain an approximate value of the iodine in the sample the assumption was made that the I_2—$S_2O_3^{--}$ reaction had gone to completion. Thus, for the reaction mixture of Table III the $[\Sigma I_2]$ at completion is given by 0·0006600 − 0·0003164/2 = 0·0005018; a 24·75 ml.-sample at completion thus contains $0{\cdot}1242 \times 10^{-4}$ moles I_2, and this value is used throughout in obtaining x. This procedure, though an approximation, introduces only a small error, since the consumption of iodine in the " indicator " is large compared with the amount of iodine in the sample. In the experiment of Table III, by the time the first sample was removed $[\Sigma S_2O_3^{--}]$ had fallen from 0·0003164 to 0·0001886 moles/l., that is, during the mixing process and the following minute the reaction had proceeded to nearly half completion, and after this initial disturbance the comparatively slow rate was measurable. An effect of this magnitude—up to two-thirds completion of the reaction by the time of taking the first sample—was observed in the majority of the experiments, and is discussed later. In the experiment of Table III the value of the amount of iodine in the first sample thus cannot differ by more than about $0{\cdot}07 \times 10^{-4}$ moles from the value $0{\cdot}1242 \times 10^{-4}$ moles calculated on the basis that the reaction had gone to completion. This possible error of $0{\cdot}07 \times 10^{-4}$ is an error in the value $x = 2{\cdot}024 \times 10^{-4}$, i.e. an error of about 3·5 %; the error in succeeding samples is progressively less.

TABLE IV

Temp. = 20° C (except for Group D)

Initial concentrations (g.-mole (or g.-ion)/l.)				k_{b1} × 10^{-2}	$[\Sigma S_2O_3^{--}]_m$ × 10^4	$[\Sigma I_2]_m$ × 10^4	$[I^-]_m$ × 10^3	k_α × 10^{-4}	k_2 × 10^{-3}
$[\Sigma I_2]$ × 10^4	$[\Sigma I^-]$ × 10^3	$[S_2O_3^{--}]$ × 10^4	μ*						
Group A									
6·51	1·67	6·43	0·0036	1·23	1·34	2·63	2·15	0·449	3·39
6·51	1·67	3·22	0·0026	0·743	1·53	4·14	1·74	0·599	4·34
6·51	1·67	1·63	0·0022	0·606	1·16	5·11	1·55	0·730	5·23
3·27	1·67	1·63	0·0022	0·987	0·98	1·96	1·71	0·388	2·92
6·64	6·67	6·60	0·0087	8·55	1·14	2·77	7·09	0·403	4·79
6·64	6·67	3·32	0·0077	5·32	1·33	4·32	6·63	0·442	4·30
6·64	6·67	1·65	0·0072	3·99	1·03	5·30	6·39	0·436	3·90
3·30	6·67	3·27	0·0077	13·28	0·69	1·33	6·88	0·317	5·67
3·30	6·67	1·63	0·0072	8·61	0·77	2·10	6·65	0·347	4·45
Group B									
6·55	1·67	6·54	0·064	3·63	1·00	2·78	2·14	1·41	6·38
6·54	1·67	3·29	0·064	2·07	1·17	4·31	1·74	1·74	7·38
6·54	1·67	1·64	0·064	1·73	0·95	5·25	1·54	2·16	8·99
6·63	6·67	6·60	0·064	17·57	0·86	2·90	7·08	0·870	7·88
6·61	6·67	3·32	0·064	10·58	1·05	4·45	6·62	0·908	6·06
6·63	6·67	1·65	0·064	8·69	0·88	5·37	6·38	0·965	5·79
Group C									
6·59	1·67	6·32	0·100	3·81	1·05	2·90	2·11	1·58	7·10
6·60	1·67	3·16	0·100	2·20	1·21	4·41	1·72	1·93	8·15
6·57	1·67	1·66	0·100	1·80	1·03	5·23	1·54	2·24	9·32
6·61	6·67	6·60	0·100	21·22	0·69	2·96	7·07	1·08	9·59
6·63	6·67	3·32	0·100	14·31	0·89	4·53	6·61	1·25	8·29
6·64	6·67	1·65	0·100	11·78	0·81	5·41	6·38	1·32	7·90
Group D (Temp. = 30°)									
6·57	1·67	6·62	0·0036	1·79	1·31	2·60	2·18	0·568	5·50
6·57	6·67	6·62	0·0086	10·02	1·08	2·72	7·11	0·440	6·23

at 30°), and the ninth column the derived values of k_α. Inspection of these values shows that in each of the groups, the values of k_α tend to increase with increase of $[\Sigma I_2]_m$ and to fall with increase of $[I^-]_m$, and hence to increase with increasing F. These discrepancies indicate that the equilibrium position of (4) is not so far over to the right-hand side as has been assumed above; from the deviations we may obtain approximate values of K and k_2 as follows.

By definition of K we have

$$\frac{[S_2O_3I^-]}{[S_2O_3^{--}]} = KK_3F = K'F,$$

where $K' = KK_3$. Further,

$$k_2[S_2O_3I^-][S_2O_3^{--}] = k_{b1}[\Sigma S_2O_3^{--}]^2$$

and

$$[\Sigma S_2O_3^{--}] = [S_2O_3I^-] + [S_2O_3^{--}],$$

from which

$$k_2 = \frac{k_{b1}(1 + K'F)^2}{F}.$$

By trial and error values of K' are found which on substituting in the above equation makes k_2 most constant in each group. The values of K' so derived are 0·7 for the experiments of Group A and 0·4 for the experiments of Groups

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* For reaction mixtures with $\mu > 0·01$, the ionic strength was increased to the indicated value by addition of $NaNO_3$.

B and C. These correspond to values of K of about 580 for Group A, and 330 for Groups B and C. We shall assume that K for Group D is also 580, giving $K' = KK_3 = 0{\cdot}9$ With these values of K', the k_2's given in the last column of Table IV were calculated from the observed values of k_{b1}. Though some slight errors are involved in this procedure, since the values of $[\Sigma I_2]_m$ and $[I^-]_m$ (and hence also of F), all based on the assumption that the equilibrium (4) lies nearly completely over to the right, are not now quite correct, the experimental data are not sufficiently accurate to warrant more elaborate calculations, but it is considered that, as they stand, they provide substantial evidence for the mechanism proposed and that they yield values of K and k_2 of the rough order of magnitude of those summarized in Table V.

TABLE V

Ionic Strength	Temp. (°C)	K	$k_2 \times 10^{-3}$
0·002-0·008	20	580	4·3
0·06	20	330	7·1
0·10	20	330	8·4
0·002-0·008	30	(580)	5·9

It is to be noted that on the basis of the mechanism $[\Sigma I_2]$ should increase over the period of reaction for which measurements can be made. This follows because after the initial rapid formation of $S_2O_3I^-$, reaction (5) is maintained by the re-conversion of part of the $S_2O_3I^-$ back into $S_2O_3^{--}$ and I_2 by the reverse reaction in equilibrium (4), and hence $[\Sigma I_2]$ increases. The predicted rise in $[\Sigma I_2]$ during the course of reaction was found and followed experimentally by measuring the light absorption of an I_2—$Na_2S_2O_3$ mixture by means of a Hilger Spekker absorptiometer. For example, with a reaction mixture of initial composition

$$[\Sigma I_2] = 0{\cdot}000657,\ [\Sigma I^-] = 0{\cdot}00267,\ [S_2O_3^{--}] = 0{\cdot}000649,$$

reacting at room temperature (*ca.* 18°) in a cell of 1 cm. thickness, the following values of αcd were obtained, using a violet filter.

Time (min. from start) .	2·0	5·0	10·0	20·0	30·0	40·0
αcd	0·401	0·406	0·410	0·430	0·438	0·440

Though a part of this increase in αcd with time may be due to an increase in $[\Sigma I^-]$, leading to an increased ratio of $[I_3^-]/[I_2]$ and, since $\alpha_{I_3^-} > \alpha_{I_2}$ for $\lambda = 4300$Å, to an increased absorption of light, it is not difficult to show that the effect is much too big to be accounted for in this way, and we can conclude that the main part of the increase must be due to an increase in $[\Sigma I_2]$, as predicted by the mechanism.

To test the validity of the experimental method for determining $[\Sigma S_2O_3^{--}]$ in reacting mixtures of I_2 and $S_2O_3^{--}$, a few of the experiments of Table III were repeated, but instead of running samples into the I_2—KI—NaN_3 " indicator " mixture, the latter was replaced by a suitable I_2—KI—$NaNO_2$ mixture. A study of the reactivity of $S_2O_3^{--}$—I_2—NO_2^- systems[6] has shown that R values between 0·5 and a maximum of 4·0 are obtainable. Hence by employing a procedure analogous to that described above, it is possible to determine the $[\Sigma S_2O_3^{--}]$ in each sample of a reacting $S_2O_3^{--}$—I_2 mixture from the extent of reaction induced in an I_2—KI—$NaNO_2$ " indicator " mixture. The sensitivity of the " indicator," however, is very low, and the data are subject to considerable error, yet the method yields approximate values of k_{b1} which are found to be in reasonable agreement with those given above.

Other mechanisms have been considered, e.g.

$$(a)\ S_2O_3^{--} + I_2 \rightleftharpoons S_2O_3I^- + I_2,$$

followed by

$$2S_2O_3I^- \rightarrow S_4O_6^{--} + I_2,$$

and (*b*) the mechanism suggested by Weiss,[5]

$$S_2O_3^{--} + I_2 \rightleftharpoons S_2O_3^- + I^- + I$$

followed by

$$2S_2O_3^- \rightarrow S_4O_6^{--}$$

and

$$I + I \rightarrow I_2,$$

but none is consistent with the experimental data ; hence the mechanism

$$S_2O_3^{--} + I_2 \rightleftharpoons S_2O_3I^- + I^- ;$$
$$S_2O_3I^- + S_2O_3^{--} \rightarrow S_4O_6^{--} + I^-$$

appears to us to be the most likely course of the reaction between thiosulphate and iodine.

System I_2—$S_4O_6^{--}$—N_3^-.—The reactions occurring in these systems are measurably slow and can be followed by ordinary kinetic methods, if the concentrations of reactants are not too high, and determinations of the rate of reaction have been made at 20° and 30° C in the presence of acetate buffers. Analysis of the end-products showed that the only *net* processes taking place are :

$$2N_3^- + I_2 \rightarrow 3N_2 + 2I^- \quad . \quad . \quad . \quad . \quad (6)$$

and $$S_4O_6^{--} + 7I_2 + 10H_2O \rightarrow 4SO_4^{--} + 14I^- + 20H^+ . \quad . \quad . \quad (7)$$

This was shown by preparing reaction mixtures of compositions similar to those employed in the kinetic experiments and allowing the reaction to proceed to completion at 20°, that is, until all the initial iodine had been consumed, sufficient NaN_3 being present to ensure an excess of this salt at the end of the run. The total volume of N_2 evolved was measured in a nitrometer and the sulphate in the resulting colourless solution was determined by precipitation and weighing as $BaSO_4$. Table VI shows the type of result obtained.

TABLE VI

Temp. = 20° ; $[\Sigma I_2]_{init.} = 0{\cdot}001974$; [HAc] = 0·0333 ; [NaAc] = 0·0333
Conc. in g.-mole (on g.-ion)/l.

$[N_3^-]_{init.}$	$[S_4O_6^{--}]_{init.}$	$[I^-]_{init.}$	% $S_4O_6^{--}$ converted into SO_4^{--}	
			(α)	(β)
0·004167	0·01667	0·100	0·423	0·465
0·008333	0·008333	0·100	0·488	0·448
0·008333	0·008333	0·050	0·546	0·534

In the last two columns are given the percentage conversions of the initial tetrathionate into sulphate, (α) as given directly by sulphate determination, and (β) as inferred from the volume of N_2 evolved and total iodine consumed on the basis of (6) and (7) being the sole *net* reactions.

For kinetic measurements at 20° it was found that reaction mixtures containing $[\Sigma I_2]$, $[NaN_3]$ and $[Na_2S_4O_6]$ in the range 0·0004-0·002 M gave conveniently measurable rates. The data of the analyses quoted above show that the percentage conversion of $Na_2S_4O_6$ into Na_2SO_4 in such mixtures is very small. Hence it was not practicable to measure the rate of sulphate formation during a run either by determination of SO_4^{--} formed or of $S_4O_6^{--}$ remaining. The rate of sulphate formation had therefore to be obtained indirectly as follows. Reaction mixtures were divided into two portions. From one portion samples were removed from time to time, $[\Sigma I_2]$ in the samples determined by titration, and hence the over-all rate of reaction in terms of $[\Sigma I_2]$ determined. The other portion was placed in a Warburg apparatus, the rate of evolution of N_2 determined, and hence, in terms of eqn. (6), the rate of consumption of I_2 used in oxidizing NaN_3. Subtraction of this latter rate from the over-all rate of iodine consumption gives the rate of iodine consumed in oxidizing tetrathionate, and one-seventh of this is rate of disappearance of tetrathionate.

Preliminary measurements of the over-all rate showed that variation of $[I^-]$ has a striking effect on the rate. With zero initial $[I^-]$ a comparatively high rate of reaction is found. Increase of $[I^-]$ strongly retards the reaction, until a minimum is reached in the region of $[I^-]$ between 0·01 and 0·02 M. Increase of $[I^-]$ beyond this region progressively accelerates the reaction, the rate becoming about proportional to $[I^-]^2$ when $[I^-] = 0{\cdot}4$. Fig. 5 illustrates this behaviour for reaction mixtures at 20° containing initially

$$[\Sigma I_2] = 4{\cdot}10^{-4}, \qquad [N_3^-] = [S_4O_6^{--}] = 1{\cdot}67 \times 10^{-3},$$
$$[NaAc] = 3{\cdot}33 \times 10^{-2}, \qquad [HAc] = 1{\cdot}67 \times 10^{-2},$$

with varying [I⁻]. In the plot the rate is expressed as $k_{0(\Sigma I_2)} = -\frac{\Delta[\Sigma I_2]}{\Delta t}$ measured for the first time interval. It thus appears probable that at least two mechanisms are operative, one predominating in the region of very low [I⁻], with the rate retarded by I⁻, and the other predominating in the region of medium and high [I⁻], with the reaction catalyzed by I⁻. This conclusion receives support from the discoveries (*a*) that I_2 reacts with $Na_2S_4O_6$ in absence of NaN_3 in solutions of very low I⁻ content and, (*b*) that at high concentrations of reactants a reaction between $Na_2S_4O_6$ and I⁻ can be detected, also in absence of NaN_3. These direct reactions are discussed later in this paper; for the present we shall assume that two distinct mechanisms operate in the reactions in I_2—$S_4O_6^{--}$—N_3 mixtures and deal separately with the data pertaining to the regions of [I⁻] above and below 0·01 M.

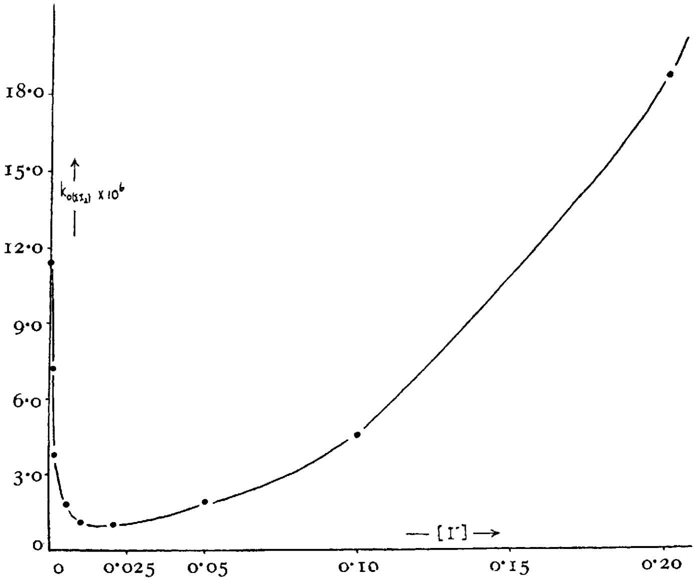

FIG. 5

TABLE VII

Temp. = 20° C; [NaAc] = 0·0333; [HAc] = 0·0167 g. mole/l.

Initial concentrations (g.-mole (or g.-ion/l.)				$k_{0(\Sigma I_2)} \times 10^6$	$k_{\mathrm{uni}(N_3^-)} \times 10^3$	$k_{0(S_4O_6^{--})} \times 10^7$	Q_0
$[\Sigma I_2] \times 10^4$	$[I^-]$	$[N_3^-] \times 10^3$	$[S_4O_6^{--}] \times 10^4$				
8·28	0·40	1·67	3·33	7·73- 3·39	8·63	1·28	73·0
4·09	0·20	1·67	16·7	15·9 -11·4	18·1	3·45	53·7
4·09	0·20	1·67	8·33	7·93- 5·92	9·59	1·44	84·6
16·49	0·20	0·833	3·39	1·57- 0·77	3·28	0·44	32·0
16·49	0·20	3·33	8·49	10·5 - 5·12	6·11	1·68	70·1
4·09	0·10	1·67	17·0	4·49- 3·89	4·77	1·40	43·5
8·25	0·05	1·67	33·8	4·70- 2·77	4·75	1·33	41·0
16·47	0·05	0·833	33·3	3·20- 1·84	5·21	1·39	21·4
4·09	0·05	3·33	17·0	3·20- 2·93	1·61	0·86	49·2
4·08	0·02	1·67	16·7	1·00- 0·73	0·74	0·37	29·2

Table VII summarizes the results of some of the experiments (about one-third of the total) carried out at medium and high $[I^-]$. In this table $k_{0(\Sigma I_2)}$ and $k_{0(S_4O_6^{--})}$ are zero-molecular constants with respect to ΣI_2 and $S_4O_6^{--}$ respectively. The former of these was found to fall slightly during a run; in the Table are given the first and last values determined. The rate of evolution of N_2 was found to be unimolecular with respect to N_3^- and the Table gives mean values for each experiment of

$$k_{\text{uni}(N_3^-)} = \frac{1}{t_2 - t_1} \log_e \frac{[N_3^-]_1}{[N_3^-]_2}.$$

The last column gives values of the ratio

$$Q_0 = (\text{moles NaN}_3 \text{ decomposed})/(\text{moles Na}_2\text{S}_4\text{O}_6 \text{ consumed})$$

over the time the reaction was followed.

From these and other data not listed, it is found that the dependence of the various rates measured on the concentration of reactants and of iodide in this region of $[I^-]$ is as summarized in Table VIII.

TABLE VIII

	Dependence on			
	$[\Sigma I_2]$	$[I^-]$	$[N_3^-]$	$[S_4O_6^{--}]$
Overall rate of consumption of I_2	Independent	$\propto [I^-]^x$ $2 > x > 1$	$\propto [N_3^-]^y$ y slightly less than 1	Proportional
Rate of NaN_3 decomposition	Independent	$\propto [I^-]^x$ $2 > x > 1$	Proportional	Proportional
Rate of consumption of $Na_2S_4O_6$	Independent	Proportional	$\propto [N_3^-]^z$ z approx. 0·5	Proportional
Q_0	Independent	Increases slightly with inc. $[I^-]$	$\propto [N_3^-]^z$ z approx. 0·5	Independent

We have also made a number of similar kinetic experiments in N_3^-—$S_4O_6^{--}$—I_2 systems in the presence of low concentrations of iodide ($[\Sigma I^-]_{\text{init.}} < 0{\cdot}006$). These yielded values of Q_0 in the range from 10 to 45, with rates of reactions markedly retarded by I^-. Since here there is a considerable increase of $[I^-]$ during each run, it has so far been found difficult to make an exact assessment from the data of the effect of concentrations of ΣI_2, $S_4O_6^{--}$, N_3^- and I^- on the rates of reaction; consequently we shall not deal further at present with the reactivity of such systems in presence of low $[I^-]$.

The Reactions between $S_4O_6^{--}$ and I^- and $S_4O_6^{--}$ and I_2.—As indicated earlier, $S_4O_6^{--}$ is found to react directly under certain conditions both with I^- and I_2, and these reactions (or their initial steps) must play important roles in the reactivity of the system $S_4O_6^{--}$—I—N_3^- in the regions respectively of high and low $[I^-]$. Both reactions are complicated, particularly the $S_4O_6^-$—I^- reaction, on which we have made only a few qualitative measurements. The $S_4O_6^{--}$—I_2 reaction can only be measured at very low concentrations of iodide; for it we have obtained some quantitative data, but not sufficient to establish a mechanism.

Dealing first with the $S_4O_6^-$—I^- reaction, the following experiment indicates the formation during the course of the reaction of appreciable amounts of a substance which reacts rapidly with iodine or induces azide to do so. To 130 ml. of a solution of composition:

$$[\Sigma I_2] = 0{\cdot}000413, \quad [I^-] = 0{\cdot}200, \quad [N_3^-] = 0{\cdot}00667,$$
$$[\text{NaAc}] = 0{\cdot}0333, \quad [\text{HAc}] = 0{\cdot}0167$$

at 20° C were added 20 ml. M/400 $Na_2S_4O_6$ in 1·5 M KI solution, which had previously been heated to 65° C for 30 min. and then cooled to 20° C. However, even before all the $Na_2S_4O_6$ solution had been added, all the iodine in the reaction mixture was completely consumed. In an identical reaction mixture, but without pre-heating of the $Na_2S_4O_6$ with KI, the time required for complete consumption of the iodine was over an hour. Qualitative tests showed that the mixture of $Na_2S_4O_6$ and KI used above after heating would itself react with iodine and also contained sulphate and H^+. A few attempts were made to follow the course of the direct reaction between $S_4O_6^{--}$ and I^- at 20°, using fairly high concentrations of reactants ($[I^-] = 1·00$; $[S_4O_6^{--}] = 0·02$-$1·00$), by titrating samples with I_2. Using unbuffered solutions, the reaction followed a marked autocatalytic course; in phosphate or acetate buffers, the rates of reaction were much less and the degree of autocatalysis not so pronounced. Among the ultimate products are H_2S, free S, SO_4^{--} and H^+. Of chief interest for our purpose of discussing the mechanism of the reactions in I_2—$S_4O_6^{-}$—N_3^{-} systems is the fact that a direct reaction between $S_4O_6^{--}$ and I^- does take place at 20° and that one of the products in the early stages of the reaction is a compound which reacts immediately with I_2. This product is not SO_3^{--} and is most probably $S_2O_3^{--}$.

On the reaction between $S_4O_6^{--}$ and I_2, which yields SO_4^{--}, H^+ and I^-, we have carried out kinetic measurements at 20° C in presence of acetate buffers and in the presence of initial $[\Sigma I^-]$ ranging from zero to 0·009. The reaction was followed by determination of $[\Sigma I_2]$ by titration in samples withdrawn from time to time. Table IX summarizes the results.

TABLE IX

Temp. = 20°; [NaAc] = 0·0250; [HAc] = 0·0125 g. mole/l.

Initial Concentrations (g.-mole (or g.-ion)/l.)			$k_{uni} \times 10^2$	$[I^-] \times 10^4$		$k^1 \times 10^3$
$[\Sigma I_2] \times 10^4$	$[S_4O_6^{--}] \times 10^3$	$[\Sigma I^-] \times 10^4$		First sample	Last sample	
3·36	0·937	Nil	2·80-0·84	0·750	5·56	5·89
3·36	1·87	Nil	4·37-1·33	0·930	5·45	5·00
*3·36	1·87	Nil	4·26-1·50	1·08	5·63	5·24
6·72	1·87	Nil	3·25-0·51	1·62	10·77	4·91
3·36	3·75	Nil	7·16-2·05	1·43	5·61	4·27
6·51	3·75	Nil	5·09-0·81	1·66	10·76	3·96
3·25	7·50	3·06	5·37-1·51	3·18	9·00	3·24
3·25	15·0	3·06	7·73-2·28	3·44	8·87	2·60
3·33	15·0	8·66	3·23-1·39	7·68	14·55	2·99
3·33	30·0	8·66	4·64-2·18	8·03	14·58	2·38
†3·17	0·937	Nil	9·32-3·82	1·69	5·72	29·7
†6·35	1·87	Nil	7·35-2·40	3·13	12·03	23·5

* [NaAc] = 0·0250, [HAc] = 0·0025 g.-moles/l.; † Temp. = 20°.

In the fourth column of Table VIII are given first-order constants (k_{uni}) with respect to ΣI_2. These fall markedly in each run; the values given are those relating to the first and last time intervals in each experiment. The concentration of tetrathionate in all these experiments decreases only slightly, and the fall in k_{uni} with time is thus probably to be referred to the large increase in $[I^-]$ which occurs in each run; columns 5 and 6 give the concentrations of I^-, corrected for tri-iodide formation, in the first and final samples taken from the reaction mixture. Comparison of the results of Expt. (2) and (3) indicates that $[H^+]$ has no significant effect on the rate over the range of $[H^+]$ tested. Insufficient work has been done to derive the exact dependence of the rate on the concentrations of reactants and of iodide, but application of the equation,

$$k' = k_{uni}\frac{\{K_3 + [I^-]_m\}[I^-]_m}{K_3}[S_4O_6^{--}]_m^{-1},$$

where $[I^-]_m$ and $[S_4O_6^{--}]_m$ are the mean concentrations of free I^- and $S_4O_6^{--}$ respectively in the time interval for which k_{uni} was determined and K_3, the tri-iodide equilibrium constant, has the values 0·0012 at 20° and 0·00157 at 30°, appears to give reasonable constancy of k' in each experiment. The mean values of k' are given in the last column; it is seen that these fall as $[S_4O_6^{--}]$ is increased. However, in these experiments the increase in $[S_4O_6^{--}]$ was accompanied by an increase in ionic strength, and thus there is a possibility that the fall in k' may be referred to an effect of ionic strength. Further work will thus be necessary before the mechanism of this reaction can be usefully discussed. These preliminary experiments show, however, that tetrathionate is oxidized by I_2 at low concentrations of I^-; the initial step (or steps) of this reaction will form the catalyst which is responsible for the reaction between I_2 and N_3^- induced by $Na_2S_4O_6$ at very low concentrations of iodide.

Reaction Mechanisms

It is convenient first to deal with the mechanism of reaction in I_2—$S_4O_6^{--}$—N_3^- systems, for which quantitative measurements of rates of reaction have been obtained over a fairly wide range of conditions. As there are grounds for the belief that the reactivity of these systems is closely linked with that of I_2—$S_2O_3^{--}$—N_3^- systems, for which direct kinetic measurements are not available, the mechanism of the latter can best be discussed in the light of the mechanism adopted for the former.

Discussing first the kinetics of the reactions in I_2—$S_4O_6^{--}$—N_3^- systems in the presence of medium and high $[I^-]$, one of the outstanding features of the experimental data (see Table VII) is the large values of Q_0 obtained. Thus, depending on the conditions, 20-100 moles of NaN_3 are oxidized to N_2 per mole of $Na_2S_4O_6$ oxidized to sulphate. It is therefore considered that the mechanism of N_3^- decomposition involves a reaction chain. A plausible and simple chain mechanism is the following:

$$S_4O_6^{--} + I^- \underset{\dashleftarrow}{\xrightarrow{k_1}} S_2O_3^{--} + S_2O_3I^- \quad . \quad . \quad . \quad (1)$$

$$S_2O_3^{--} + I_2 \underset{\dashleftarrow}{\xrightarrow{k_2}} S_2O_3I^- + I^- \quad . \quad . \quad . \quad (2)$$

$$S_2O_3I^- + N_3^- \xrightarrow{k_3} S_2O_3N_3^- + I^- \quad . \quad . \quad . \quad (3)$$

$$S_2O_3N_3^- + N_3^- \xrightarrow{k_4} S_2O_3^{--} + 3N_2 \quad . \quad . \quad . \quad (4)$$

$$S_2O_3N_3^- \xrightarrow{k_5} SO + SO_2 + N_3^- , \quad . \quad . \quad (5)$$

(followed by rapid oxidation of SO and SO_2 by I_2 to sulphate). The initial step postulated is the slow reaction (1), which is the reverse of the second reaction assumed to take place when I_2 reacts with $S_2O_3^{--}$. It receives some justification from the fact given above that at high concentrations a reaction between $S_4O_6^{--}$ and I^- can be detected, yielding a product (probably $S_2O_3^{--}$) which reacts rapidly with I_2. In the absence of N_3^- and with moderate and low concentrations of $S_4O_6^{--}$ and I^- reaction (1) is not detectable, and the equilibrium lies nearly completely over the left. In the presence of I_2 and N_3^-, however, the small amounts of $S_2O_3^{--}$ and $S_2O_3I^-$ are immediately converted into the intermediate $S_2O_3N_3^-$ by the fast reactions (2) and (3). Since in $S_2O_3^{--}$—I_2—N_3^- systems the reactions are practically instantaneous, it follows that after the slow process (1) forming $S_2O_3^{--}$, all the succeeding reactions must be very rapid. Processes (2), (3) and (4) constitute the chain. Consideration of the experimental data leads to the conclusion that the chain-breaking process is probably closely linked with the formation of sulphate, and, after the consideration of other possibilities, process (5) is suggested. This mechanism yields, by the assumption of stationary state concentrations for $S_2O_3^{--}$, $S_2O_3I^-$, and $S_2O_3N_3^-$ expressions for $k_{0(\Sigma I_2)}$, $k_{\text{uni}(N_3^-)}$, $k_{0(S_4O_6^{--})}$ and Q_0 which can be compared in respect of their dependence on concentration variables with the experimental data summarized in Table VIII. It is found in this way that the mechanism satisfies most of the data, but does not account for the observed increase of rate of $S_4O_6^{--}$ consumption with increase of $[N_3^-]$ nor for the observed dependence of rates of consumption of ΣI_2 and of decomposition of N_3^- on the concentration of iodide. These defects may be remedied on the basis of the above scheme by the addition of further reactions to the mechanism. It appears that (*a*) one must postulate the occurrence of an additional sulphate-forming reaction whose velocity is increased by increase of $[N_3^-]$ but which does not result in decomposition of N_3^-, and (*b*) there exists an extra enhancing effect of $[I^-]$ on the chain which is not taken account of by reactions (1)-(5). These considerations lead us to postulate the following additional reactions to the scheme :

$$S_4O_6^{--} + I^- + N_3^- \xrightarrow{k_6} \text{(S-intermediate)} \xrightarrow{+I_2+H_2O} \text{sulphate} \quad . \quad (6)$$

$$S_2O_3N_3^- + I^- \underset{}{\overset{K_7}{\rightleftarrows}} S_2O_3N_3I^{--} \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

$$S_2O_3N_3I^{--} + N_3^- \xrightarrow{k_8} S_2O_3^{--} + I^- + 3N_2 \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Here process (6) is represented in a purely formal manner, and process (7) is regarded as a maintained equilibrium. With these additions to reactions (1)-(5), the following rate expressions are obtained, if it is assumed for simplicity that reactions (4) and (8) have equal intrinsic speeds,* i.e. $k_4 = k_8$:

$$k_{0(\Sigma I_2)} = [S_4O_6^{--}][I^-]\left\{\frac{2k_1k_4[N_3^-](K_7 + [I^-])}{k_5K_7} + 7(k_6[N_3^-] + k_1)\right\}$$

$$k_{\text{uni}(N_3^-)} = \frac{4k_1k_4[S_4O_6^{--}][I^-](K_7 + [I^-])}{k_5K_7}$$

$$k_{0(S_4O_6^{--})} = [S_4O_6^{--}][I^-](k_6[N_3^-] + k_1)$$

$$Q_0 = \frac{4k_1k_4[N_3^-](K_7 + [I^-])}{k_5K_7(k_6[N_3^-] + k_1)}.$$

Qualitatively these equations are in accord with the experimental findings as given in Table VIII, and quantitatively they reproduce the data (Table VII) fairly well with the following values of the constants :

$$k_1 = 0{\cdot}00045\ ;\quad k_4/k_5 = 9500\ ;\quad k_6 = 0{\cdot}349\ ;\quad K_7 = 0{\cdot}11,$$

all based on concentrations in moles/litre, and time in minutes. It may be noted that an alternative chain to the one given above is equally probable, as the two are kinetically indistinguishable. This is :

$$S_2O_3I^- + N_3^- \longrightarrow S_2O_3^- + I^- + 3/2N_2 \quad . \quad . \quad . \quad (3a)$$

$$S_2O_3^- + N_3^- \longrightarrow S_2O_3^{--} + 3/2N_2 \quad . \quad . \quad . \quad (4a)$$

$$S_2O_3I^- + I^- \longrightarrow S_2O_3I_2^{--} \quad . \quad . \quad . \quad . \quad . \quad . \quad (7a)$$

$$S_2O_3I_2^{--} + N_3^- \longrightarrow S_2O_3^{--} + I^- + 3/2N_2 \quad . \quad . \quad (8a)$$

$$S_2O_3^- \longrightarrow SO + SO_2^- \longrightarrow \text{sulphate.} \quad . \quad . \quad . \quad (5a)$$

Here, instead of $S_2O_3N_3^-$, the postulated chain carrier is the radical ion $S_2O_3^-$, whose existence has previously been postulated by several investigators, for example by Evans and Baxendale.[8]

As regards the reaction in the region of very low $[I^-]$, it is possible that the same intermediates $S_2O_3I^-$ and $S_2O_3N_3^-$ take part, but until further data are obtained for the reaction and for the reaction between $S_4O_6^{--}$ and I_2 in absence of N_3^-, the reaction mechanism cannot be profitably discussed.

Turning now to the reactivity of I_2—$S_2O_3^{--}$—N_3^- systems, for which the experimental data have been given in Fig. 1-4, and Tables I and II,

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* If this assumption is not made, no essential difference in the form of the resulting expression ensues.

[8] Evans and Baxendale, *Trans. Faraday Soc.*, 1946, **42**, 197.

the formulation of a reaction mechanism in absence of quantitative rate measurements presents difficulties, though some help is afforded from the fact that the proposed steps must be reconcilable with the data for the direct I_2—$Na_2S_2O_3$ reaction and the I_2—$Na_2S_4O_6$—NaN_3 induced reaction considered above. The following tentative mechanism, all the steps of which, except (11)-(13), have been previously put forward, is suggested :

$$S_2O_3^{--} + I_2 \longrightarrow S_2O_3I^- + I^- \qquad . \quad . \quad . \quad (1)$$

$$S_2O_3I^- + S_2O_3^{--} \longrightarrow S_4O_6^{--} + I^- \qquad . \quad . \quad . \quad . \quad (2)$$

$$S_2O_3I^- + N_3^- \longrightarrow S_2O_3N_3^- + I^- \qquad . \quad . \quad . \quad (3)$$

$$S_2O_3N_3^- + N_3^- \longrightarrow S_2O_3^{--} + 3N_2 \qquad . \quad . \quad . \quad (4)$$

$$S_2O_3N_3^- + I^- \rightleftarrows S_2O_3N_3I^{--} \qquad . \quad . \quad . \quad . \quad (7)$$

$$S_2O_3N_3I^{--} + N_3^- \longrightarrow S_2O_3^{--} + I^- + 3N_2 \qquad . \quad . \quad (8)$$

$$S_2O_3N_3^- \longrightarrow SO + SO_2 + N_3^- \qquad . \quad . \quad . \quad (5)$$

$$(SO \text{ and } SO_2 \text{ oxidized by } I_2 \text{ to } SO_4^{--})$$

$$S_2O_3N_3^- + S_2O_3N_3^- \longrightarrow S_4O_6^{--} + 3N_2 \qquad . \quad . \quad . \quad (11)$$

$$S_2O_3I^- + S_2O_3N_3^- \longrightarrow S_4O_6^{--} + 3/2N_2 + 1/2\, I_2 \qquad . \quad (12)$$

$$S_2O_3^{--} + S_2O_3N_3^- \longrightarrow S_4O_6^{--} + N_3^- \qquad . \quad . \quad . \quad (13)$$

It has been mentioned earlier that the values of *R* obtained depend to a considerable extent on the method of addition of $Na_2S_2O_3$ to the rest of the reaction mixture and on the mode of agitation during the addition. The process of mixing is thus of importance, and it is even possible that the total reaction occurs in the immediate vicinity of the regions in which the drops of $Na_2S_2O_3$ solution meet the remainder of the reaction mixture, so that the reaction is practically completed before the solution is homogeneous. The initial steps in the reaction are the same as those in the direct I_2—$S_2O_3^{--}$ reaction. For the latter we have evidence that the rate of formation of $S_4O_6^{--}$ is much greater initially than would be anticipated from the subsequent course of reaction ; the probable explanation is that during the mixing process owing to high local concentrations of $S_2O_3^{--}$ and $S_2O_3I^-$ the rate of reaction (2) is much enhanced, with the consequence that one-half to two-thirds of the thiosulphate has disappeared before the first reading can be taken, though the subsequent course of the reaction may be quite slow. In the presence of azide this tendency for the reaction to take place before the solution can become homogeneous must be considerably greater, because in place of the slow reaction (2), the much faster reaction (3) together with its successors occurs. In presence of moderate and high $[N_3^-]$ reaction (2) will be practically eliminated, and most of the tetrathionate which is then formed, must result from other processes. We must therefore postulate the occurrence of reactions such as (11)-(13) (and possibly also similar reactions with the complex $S_2O_3N_3I^{--}$ replacing $S_2O_3N_3^-$) as chain-breaking reactions forming $S_4O_6^{--}$, at least one of these being intrinsically much faster than (2). The chain-continuing processes we postulate are the same as those in $S_4O_6^{--}$—I_2—N_3^- systems in presence of moderate and high $[I^-]$, as also is the chain-breaking process forming SO_4^{--}. Considering the two systems, in both we have the same active intermediates, $S_2O_3^{--}$, $S_2O_3I^-$, $S_2O_3N_3^-$ and $S_2O_3N_3I^{--}$. In the $Na_2S_4O_6$—I_2—NaN_3 system these active bodies are true intermediates in the sense that their concentrations are extremely low and may be kinetically regarded as stationary. In $Na_2S_2O_3$—I_2—NaN_3 systems, however, the addition of $Na_2S_2O_3$ to the reaction mixture is equivalent to the addition of active catalyst in concentration very much higher than that of a true intermediate. The total reaction is complete within a very short time and probably within a limited volume, and the concentration of " active $S_2O_3^{--}$ " is thus falling during this short time from its initial value to zero. Hence the concentration of the catalysts cannot be regarded as kinetically stationary, and it is not possible to deal quantitatively with this or any other mechanism. It is clear, however, that the " average " concentration of the catalysts must be very much higher in these systems than in $S_4O_6^{--}$—I_2—N_3^- systems, and that, though reactions (11)-(13) might be of importance in the former they, and also reaction (2), may not need to be considered in the latter systems.

Reference may be made to one feature of the scheme. The effect of increase of $[I^-]$ is to increase the chain length (i.e. increase R) ; the mechanism accounts for this by the assumption of equilibrium (7) together with the postulate that the complex $S_2O_3N_3I^{--}$ does not decompose as readily as $S_2O_3N_3^-$ to give products (SO and SO_2) easily oxidized by I_2 to sulphate. It is found, however, that the other halide ions Br^- and Cl^- also exert a similar, but smaller effect, on the value of R, while NO_3^- has no effect. Thus for a certain reaction mixture (containing 0·002 M KI) the value of R obtained was 11·6 ; for the same mixture but with addition of KI or KBr or KCl, or KNO_3 to make each concentration of salt 0·248 M, the values of R were respectively 35·7, 21·8, 13·0 and 11·6. This observation thus lends some support to the assumption of the formation of complex, not specific to iodide, formed between halide and some reacting entity.

So far as the nature of the reaction permits a judgment to be made, the experimental data can be qualitatively interpreted in terms of this mechanism. It is realized, however, that further work employing more refined technique and with closer attention to the mixing process will be necessary before this or any other mechanism can be adequately tested ; for the present we may perhaps claim that the above scheme (or the alternative with the radical ion $S_2O_3^-$ replacing $S_2O_3N_3^-$) does not conflict with any of the available evidence obtained from studies of both $S_2O_3^-$ and $S_4O_6^{--}$ systems, and has at least some claims for consideration.

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