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INDUCED REACTIONS OF THE HALOGENS IN AQUEOUS SOLUTION

PART III. REACTIONS IN THE SYSTEMS $N_3 - Br_2$, $N_3 - Br_2 - S_2O_3^-$ AND $N_3 - Br_2 - S_4O_6^-$

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Received 9th December, 1948

This paper deals with the kinetics of (a) the uncatalyzed reaction in aqueous solution between NaN₃ and Br₃ and (b) of the same reaction in presence of Na₂S₂O₃ or Na₂S₄O₆. Measurements of the speed of the direct reaction (a) at temperatures o⁶, 10⁶ and 20[°] under a variety of conditions indicate that the mechanism is (I) N₃⁻ + Br₂ \longrightarrow N₃Br₃ \longrightarrow N₃Br + Br⁻; (II) N₃Br + N₃⁻ \longrightarrow 3N₂ + Br⁻, with the equilibria (I) rapidly established and (II) the rate-determining reaction. Support for the existence of strong complex formation which must be assumed to account for N₃⁻ + Br₂ \longrightarrow N₃Br + Br⁻ by partition and spectrophotometric methods, and, in general, the results can be quantitatively interpreted in terms of the mechanism.

(b) In the presence of $Na_2S_2O_3$ or $Na_2S_4O_6$ the reactions in systems containing NaN_3 and Br_2 are extremely rapid. Together with the fast oxidation of $Na_2S_2O_3$ or $Na_2S_4O_6$ to sulphate there is a concomitant rapid induced oxidation

of N_3^- by Br_2 . Determinations of the ratio of moles N_3^- oxidized to moles $Na_3S_2O_3$ (or $Na_2S_4O_6$) oxidized show that there is a strong parallelism between the action of $Na_2S_2O_3$ and that of $Na_2S_4O_6$. Values of this ratio increase with increasing dilution of $Na_2S_2O_3$ ($Na_2S_4O_6$); the high values obtained (up to 110) indicate a chain mechanism for the induced reaction. A mechanism of such a type, applicable to both inducing agents and involving $S_2O_3B_7^-$ and $S_2O_3N_3^-$ as intermediates, is suggested

In Part II of this series of papers,¹ the induced reactions in the systems I_2 — N_3 — S_2O_3 — (S_4O_6) were considered; this paper deals with the reactivity of the analogous systems with bromine replacing iodine. Since, however, bromine also reacts directly with azide, it has been necessary first to study the non-induced reaction in the attempt to elucidate its kinetics.

A. Kinetics of the Reaction Between Bromine and Azide in Aqueous Solution

When sodium azide is added to an aqueous solution of bromine, the colour of the mixture at once fades to a pale-straw, and nitrogen is evolved according to the over-all equation :

$$NaN_3 + Br_2 \rightarrow 2NaBr + 3N_2. \qquad (1)$$

The reaction is kinetically measureable at ordinary temperatures and a few determinations of the rate have been made by Spencer,² who followed the course of reaction iodometrically at a temperature of 15° C. No quantitative treatment of his data was attempted, but the following reaction mechanism was suggested :

 $NaN_3 + Br_2 + H_2O \rightarrow HN_3 + HOBr + NaBr$. (a)

$$HOBr + 2HN_3 \rightarrow 3N_2 + H_2O + HBr$$
 . (b)

 $HOBr + 2NaN_3 \rightarrow 3N_3 + NaOH + NaBr,$. . (c)

in which (a) is very fast, (b) and (c) relatively slow and rate-determining, with (c) faster than (b). We have carried out measurements of the rate of reaction over a wider range of conditions than Spencer's, with the result that his mechanism is not considered to be satisfactory, and should be replaced by one in which the compound N_3Br is an intermediate. We have also carried out a few experiments on the kinetics of the reaction between Cl_2 and NaN_3 in aqueous solution; these indicate that the mechanism of this reaction is analogous to that of the bromine reaction.

Experimental

The reaction between Br_2 and NaN_3 has been followed at temperatures of o° , $1o^\circ$ and $2o^\circ$ C in unbuffered solutions, in presence of phosphate buffers, in presence of mineral acid, with and without the addition of KBr, and in presence and absence of neutral salt (KNO₃). Two methods of determining the extent of reaction have been used. In the one mostly employed, the rate of decrease of concentration of bromine was determined by pipetting off samples of the reaction mixture, running these into acidified KI solution and titrating the liberated iodine with thiosulphate. (Provided enough mineral acid is present, azide does not interfere with the iodine-thiosulphate titration.) In some experiments the course of the reaction has been determined by measuring the rate of evolution of nitrogen, using for this purpose a modified Warburg apparatus. Satisfactory agreement between the rates inferred for a given reaction mixture from the two methods shows that the stoichiometry of the net reaction is as given by eqn. (1).

We define the rate of reaction in terms of the equation,

$$-\frac{\mathrm{I}}{2}\frac{\mathrm{d}[\Sigma\mathrm{N}_3^-]}{\mathrm{d}t} = -\frac{\mathrm{d}[\Sigma\mathrm{Br}_2]}{\mathrm{d}t} = k_{bi}[\Sigma\mathrm{N}_3^-][\Sigma\mathrm{Br}_2] \quad . \qquad . \qquad (2)$$

¹ Dodd and Griffith, Trans. Faraday Soc. (preceding paper).

² Spencer, J. Chem. Soc., 1925, 127, 216.

though the kinetics are more complex than given by this equation, in which $[\Sigma N_3^-]$ and $[\Sigma Br_2]$ are the concentrations (moles/litre) of total azide and total bromine respectively, and t is in minutes. k_{bi} is now found experimentally to be dependent on the concentration of bromide in the system, but also, and even to a greater extent, on the ratio of $[\Sigma N_3^-]/[\Sigma Br_2]$. For example it is found that when in a given experiment $[\Sigma N_3^-]/([\Sigma Br_2]) > 1$, k_{bi} increases during the run; when $[\Sigma N_3^-]/(2[\Sigma Br_2]) < 1$, k_{bi} decreases; and in systems in which $[\Sigma N_3^-]/(2[\Sigma Br_2]) = 1$, k_{bi} increases with increasing ratio of $[\Sigma N_3^-]/(2[\Sigma Br_2])$, and we have therefore determined values of k_{bi} as a function of this ratio. The experiment, details of which are given in Table I, is typical of the type of result obtained.

ΤA	BL	Æ	Ι

Temp. $= 20^{\circ} \text{ C}$;	$[\Sigma Br_2]_{init}$.	= 0 · 007087 ;	$[\Sigma N_3]_{init.} = 0.008;$
[KBr]init.	= 0.100.	Conc. in moles	or g. ions/l.

<i>t</i> (min.)	$t_2 - t_1 \ (\min.)$	10 ³ [ΣBr ₃]	$10^{8} [\Sigma N_{3}^{-}]$	$[\Sigma N_{\bar{3}}]/2[\Sigma Br_2]$	koi
2·27 30·68	28·41 46·42	7.003 6.630	7·832 7·086	0.5354 0.5182	0*259 0*225
77·10 152·27	75.17	5.669	5·164	0.4782	0·206
244·65 355·73	111.08	5·219 4·860	4·264 3·546	0.3875	0.162

Here the values of k_{bi} are worked out for each time interval, together with the corresponding mean values of the ratio $[\Sigma N_3^-]/(2[\Sigma Br_2])$.

Fig. I shows some of the results obtained at a temperature of 20° from experiments with three different initial concentrations of KBr, the values of k_{bi} being plotted as a function of $[\Sigma N_3^-]/(2[\Sigma Br_2])$. It is doubtless true that k_{bi} depends not only on this ratio, but also on the absolute values of the concentrations of reactants. In all these experiments, however, $[\Sigma Br_2]_{init.}$ was approximately constant, varying between 0.006 and 0.008, and thus during the course of the experiments $[\Sigma Br_2]$ lay in the range of concentrations between 0.008 and about 0.002; over this range of concentration of ΣBr_2 the results show that k_{b_1} is to a sufficiently good approximation a function only of $[\Sigma N_3^-]/(2[\Sigma Br_2])$ at constant [Br-]. Curves of shapes similar to those shown in Fig. 1 are also obtained from experiments at 10° and 0° C. It is seen that for small values of $[\Sigma N_3]/(2[\Sigma Br_2])$ the values of k_{bi} (and of rates of reaction) are very small, for values of the same ratio in the neighbourhood of 0.5 to 1.0 there is a rapid rise in k_{bi} as the ratio is increased, and that the curve for each concentration of Br- reaches a limiting value at high values of $[\Sigma N_3]/(2[\Sigma Br_3])$, the limiting value decreasing with increasing [Br-]. Fig. 1 also shows that in general the reaction is retarded by bromide, except at low values of the ratio $[\Sigma N_3^-]/(2[\Sigma Br_2])$. A few experiments have been carried out to determine the effect of ionic strength μ on the reaction rate. In two series of experiments, both with $[Br-]_{init}$ = zero, the one with $\mu = 0.02$ and the other (by addition of KNO₃) with $\mu = 0.12$, the plots of k_{bi} against $[\Sigma N_3]/(2[\Sigma Br_2])$ fall on the same curve, showing that the effect of ionic strength is here inappreciable. However, an effect can be detected by employing a larger increase in μ . Thus it is found that in the presence of 0.1 M KBr increasing the ionic strength from

It is found that in the presence of o'I M KBF increasing the fond strength from o'22 to o'82 by addition of KNO₃ increases the rate of reaction by about 17 %. The effect of [H⁺] on the rate is found to be nil in the region of pH 7. Thus, in three experiments in which $\mu = o'82$ and [Br⁻] = o'I, (a) with the solution unbuffered, (b) in the presence of o'I M Na₂HPO₄ + o'2 M KH₂PO₄, and (c) in the presence of o'I M Na₂HPO₄ + o'4 M KH₂PO₄, the values of k_{bt} compared at the same ratios of [ZN_3^{-}]/(2[ZBr_2]) were found to be the same. Even at still higher pH's where the hydrolysis of Br₂ might be expected to be considerable, the rate is still found to be the same as in the unbuffered solution. For





A: zero initial KBr B: 0.1 M KBr C: 0.2 M KBr

example, the same rates were found at 10 $^{\circ}$ C in two reaction mixtures each containing initially

 $0.006 \text{ M Br}_2 + 0.040 \text{ M NaN}_3 + 0.1 \text{ M KBr},$

but mixture (1) containing in addition 0.75 M NaNO₃ and mixture (2) 0.2444 [M Na₂HPO₄ + 0.0056 M KH₂PO₄. If we assume that the *only* equilibria we need take into account in these solutions are :

$$\begin{array}{c} \operatorname{Br}_2 + \operatorname{H}_2 O \xrightarrow{\longrightarrow} \operatorname{HOBr} + \operatorname{H}^+ + \operatorname{Br}^- \\ \operatorname{N}_3^- + \operatorname{H}_2 O \xrightarrow{\longrightarrow} \operatorname{HN}_3 + \operatorname{OH}^- \\ \operatorname{Br}_3^- \xrightarrow{\longrightarrow} \operatorname{Br}_2 + \operatorname{B}_7^- \\ \operatorname{H}_2 \operatorname{PO}_4^- \xrightarrow{\longrightarrow} \operatorname{H}^+ + \operatorname{HPO}_4^{--}, \end{array}$$

together with, in (2),

we calculate, using the values: ionization constant of $HN_3 = I\cdot8 \times Io^{-5}$, hydrolytic constant of bromine = $I\cdot45 \times Io^{-9}$, second ionization constant of phosphoric acid (at $\mu = o\cdot8$) = $3\cdot0 \times Io^{-7}$, and equilibrium constant for tribromide decomposition = $o\cdot057$, the following initial concentrations in the two reaction mixtures:

[HOBr] [HN₃] [H⁺] [N₃⁻] [Br₂] [Br₃⁻] Reaction mixture (1): $2 \cdot 58 \times 10^{-4} 2 \cdot 58 \times 10^{-4} 1 \cdot 17 \times 10^{-7} 3 \cdot 97 \times 10^{-2} 2 \cdot 08 \times 10^{-3} 3 \cdot 66 \times 10^{-3}$ Reaction mixture (2):

$$2^{.59} \times 10^{-3}$$
 $1^{.5} \times 10^{-5}$ $6^{.9} \times 10^{-9}$ $4^{.00} \times 10^{-2}$ $1^{.24} \times 10^{-3}$ $2^{.17} \times 10^{-3}$

Inspection of these figures shows that if these are the only equilibria concerned, Spencer's view that the reaction rate is determined chiefly by the product [HOBr][N₃] (or [HOBr][N₃]²) cannot be maintained. However, the fact that the same rate is observed in these two experiments is to be regarded as an indication that the basis of the calculation is incorrect, and that strong formation of some other compound must be assumed. We shall show that the probable equilibrium is

 $Br_2 + N_3 \xrightarrow{-} N_3 Br + Br_,$

with the equilibrium well over to the right-hand side; introduction of this into the scheme will make it possible for the concentrations of the rate-determining constituents in reaction mixtures (1) and (2) to be practically the same.

Although, as the above results show, variation of $[H^+]$ in the region of pH from about 6.3 to 8.4 has no influence on the rate of reaction, increase of $[H^+]$ does retard the reaction at lower pH's, i.e. when mineral acid is added giving a pH of 5 or less, so that significant amounts of azide are present as HN_3 . Later reference will be made to this. Finally, it may be noted that in strong alkaline solution, when all the bromine is present as OBr^- , no reaction with N_3^- can be detected.

Complex Formation in Br_2 --N₃ Mixtures.-Spencer² has prepared and isolated the compound N₃Br by passing bromine vapour over solid sodium azide, and has examined its properties; the methods of determining N₃Br given below are essentially those of Spencer, and shown by him to give accurate results. Assuming that the equilibrium

$$N_3 + Br_2 \xrightarrow{\longrightarrow} N_3 Br + Br_2$$

is set up in aqueous solution, and that this equilibrium (together with the tribromide equilibrium) is the only one that needs to be taken into account, attempts have been made to determine the equilibrium constant

$$K = \frac{[\mathrm{N_3Br}][\mathrm{Br}_-]}{[\mathrm{Br}_2][\mathrm{N_3}]}$$

by two methods, (a) by partition methods with CCl_4 as the second phase, and (b) by spectrophotometric determination of the concentration of bromine.

(a) If a mixture of N_3^- and Br_2 in aqueous solution be shaken with CCl₄, analysis of the CCl₄ layer shows that it contains both bromine and nitrogen. If the free bromine in the CCl₄ layer be determined by spectrophotometric means (i.e. assuming that N_3Br or any other complex does not absorb), it is then found that the ratio of atoms of nitrogen to atoms of the remainder of the bromine is 3/r, showing that the CCl₄ has extracted from the aqueous layer a mixture of bromine and a compound of empirical formula N_3Br . There is thus good ground for the view that N_3Br must also be present in the aqueous layer. In the partition method used for determining K, a CCl₄ solution containing N_3Br and Br_2 was prepared as above and this solution was shaken with an aqueous solution of KBr of known strength until equilibrium was attained. The CCl₄ solution was analyzed both before and after shaking as follows: (i) by running a sample into acidified KI and titrating with thiosulphate, (ii) by treating a sample with NaOH containing H_2O_2 and titration of the excess alkali with acid, (iii) a portion of the neutral solution formed in (ii) was titrated with AgNO₃ using K_2CrO_4 indicator, (iv) the remainder of the solution formed in (ii) was treated with excess AgNO₃, the solution boiled with HNO₃ to decompose the AgN₃ and drive off the HN₃ formed, and the cooled solution titrated with KCNS. The aqueous layer after equilibrium with the CCl₄ layer was attained was analyzed for $[\Sigma Br_2] + [N_3 Br]$ by treating a sample with acidified KI solution and titrating with thiosulphate. The experiments carried out at zo° C by this method yielded a value of K of about 200, and a value for the partition coefficient of N₃Br between CCl₄ and H₂O of about 24. The value of

$$K_{3} = \frac{[\mathrm{Br}_{2}] [\mathrm{Br}^{-}]}{[\mathrm{Br}_{3}]}$$

was taken to be 0.057.³

(b) More experiments have been done and probably a more accurate value of K obtained with the spectrophotometric method. Solutions of known content of bromine, bromide and azide were prepared—in all of them $[\mathbb{Z}Br_2]$ had to be greater than $[\mathbb{Z}N_3^-]$ in order to cut down the rate of reaction—and their light absorptions immediately determined and compared with those of solutions of identical content of bromine and bromide in absence of azide. The absorption measurements were made at room temperature (about 18° C) either with a "Spekker" absorptiometer using blue and violet light or with a Beckmann absorptiometer at three wavelengths 4300, 4400 and 4700 Å, the total concentration of bromine (i.e. $[Br_2] + [Br_3] + [N_3Br]$) being between 0.003 and 0.0003. Assuming that absorption by N_3Br is negligible, the results of Table II were obtained.

³ Griffith, McKeown and Winn, Trans. Faraday Soc., 1932, 28, 752.

TABLE II .--- VALUES OF K

$$\begin{bmatrix} [KBr] &= 0.05 \\ K &= 221, 245, 235, 321, 234, 321, 320, 261 \\ [KBr] &= 0.10 \\ \end{bmatrix}$$
 Mean : 270 ± 10

K = 304, 272, 274, 339, 277, 306, 279, 289, 283, 433, 316, 388, 282, 390[KBr] = 0.20

$$\vec{K} = 267, 303, 293, 303, 325, 291, 424, 332, 388, 341, 328, 427, 455$$

Mean: 344 ± 11

Though the values of K are not very concordant, the divergences are probably within the experimental errors of the method; it is seen that the experiments indicate strong complex formation, with a value of K in the neighbourhood of 300, a value in moderate agreement with the estimate of 200 given by the partition experiments. There is also an indication from the figures of the table that K, as calculated, increases somewhat with increasing concentration of bromide. In these experiments no corrections for the hydrolysis

$$N_3 + Br_9 + H_9O \xrightarrow{\longrightarrow} HOBr + HN_3$$

have been made; these would be small and would, in general, have the effect of reducing K by 2-3 %.

Reaction Mechanism

The type of curves shown in Fig. 1 for the variation of k_{bi} with the ratio $[\Sigma N_a^-]/(2[\Sigma Br_a])$ is consistent with the mechanism :

$$N_3^- + Br_2 \xrightarrow{\longrightarrow} N_3 Br + Br^-$$
 . . (I)

$$N_3Br + N_3^- \longrightarrow 3N_2 + Br^-$$
, . . (II)

with (I) a maintained equilibrium and (II) the rate-determining reaction. If, as we have found to be the case, the equilibrium constant of (I) is high, so that under our experimental conditions there is a large immediate conversion of the reactants into N_3Br , the general form of the curves is easily accounted for. At high ratios of $[\Sigma N_3]$ to $[\Sigma Br_2]$ practically all the bromine is present as N_3Br , and $[N_3]$ is nearly equal to $[\Sigma N_3]$; the rate of reaction will thus become proportional to $[\Sigma N_3]$ $[\Sigma Br_2]$, i.e. k_{bi} will be a constant in this region. At low ratios of $[\Sigma N_3]$ to $[\Sigma Br_2]$ practically all the azide is present as N_3Br , and as there is very little N_3 left for reaction (II) to occur, the rate of reaction will be very small. The effect of Br⁻ at these low ratios of $[\Sigma N_3^-]$ to $[\Sigma Br_2]$ is also consistent with the mechanism. But the effect of Br- at high ratios of $[\Sigma N_3]$ to $[\Sigma Br_2]$ is not accounted for; the scheme as written above predicts that at all bromide concentrations the same limiting value of k_{bi} at high ratios of $[\Sigma N_3]$ to $[\Sigma Br_2]$ should be attained, whereas experimentally the limiting value decreases with increasing concentration of bromide. The discrepancy may be removed by the assumption of an additional equilibrium forming the complex N_3Br_3 , i.e. by writing instead of (I),

$$N_3^- + Br_2 \xrightarrow{\longrightarrow} N_3 Br_2^- \xrightarrow{\longrightarrow} N_3 Br + Br^-$$
. (Ia)

The magnitude of

$$K' = \frac{[\mathbf{N}_{3}\mathbf{B}\mathbf{r}_{2}^{-}]}{[\mathbf{N}_{3}\mathbf{B}\mathbf{r}] [\mathbf{B}\mathbf{r}^{-}]}$$

may be estimated from the experimental data from which Fig. I was constructed. At 20° C the limiting k_{bl} 's for $[Br^-] = 0.2$, 0.1 and approximately zero are about 0.75, 0.87 and 1.06 respectively. On the basis that the concentration of $N_3Br_2^-$ is negligible in the solution with $[Br^-] \approx 0$ and on the assumption that $N_3Br_2^-$ does not react further with N_3^- , the ratio of concentrations of $N_3Br_2^-$ to N_3Br in the limit at the other bromide concentrations may be calculated, and it is found that K' = 2.18for $[Br^-] = 0.1$ and 2.07 at $[Br^-] = 0.2$, i.e. K' has a value of about 2.1. Some support to the presumed existence of the complex $N_3Br_2^-$ and to

a value of K' of this magnitude is afforded by the spectrophotometric determinations of the equilibrium constant K. It can be shown that if $N_3Br_2^-$ formation occurs, the apparent K's as calculated from the spectrophotometric determinations should increase with increasing concentration of bromide; the increase which is in fact found is of the order of magnitude corresponding to that which a K' of 2·I would produce.

On the basis of this mechanism the velocity constant k of the ratedetermining reaction (II) at 20° has the value 1 of, the limiting value of k_{bi} at very low concentrations of bromide; further, the value of k_{bi} in any other reaction mixture at 20° is given by:

$$k_{bi} = \frac{k[\mathrm{N}_{3}\mathrm{Br}] [\mathrm{N}_{3}^{-}]}{[\Sigma \mathrm{Br}_{3}] [\Sigma \mathrm{N}_{3}^{-}]},$$

in which $[N_3Br]$ and $[N_3^-]$ are the actual concentrations of the reactants in the system. These concentrations have been calculated for the experiments of Fig. 1, using the values K = 300, $K' = 2 \cdot 1$, $K_3 = 0.057$, and hence calculated values of k_{bi} derived. The results are shown in Fig. 2, in which the observed and calculated k_{bi} 's are plotted for three



series of experiments at 20°. It is seen that the agreement between theory and experiment is fairly good, and substantiates the mechanism. A still better agreement could probably be obtained by appropriate slight alterations in the values of the constants k, K and K'.

The temperature coefficient of k_{bi} between 10° and 20° under conditions of low [Br-] and of high ratios of $[\Sigma N_3^-]/2[\Sigma Br_2]$ is found to be 3.21; under such conditions the observed temperature coefficient is that of the rate-determining reaction (II), whose velocity coefficient is k. The reaction

 $N_3Br + N_3^- \longrightarrow 3N_2 + Br^-$

has thus an energy of activation of 19.2 kcal. Though it is not possible

to derive from the data any estimate of the effect of temperature on the equilibrium constant K, the temperature dependence of K' can be obtained. Thus at high ratios of $[\Sigma N_3]/[\Sigma Br_2]$ and at a bromide concentration of 0.1 the temperature coefficient between 10° and 20° of k_{bi} is found to be 3.59; combination of this with the previously-mentioned temperature coefficient of 3.21 leads to a value of K' of 3.5 at 10° compared with 2.1 at 20°.

Finally, a few kinetic experiments have been carried out in which, by addition of HCl, a considerable fraction of the azide was converted into HN₃, so that the azide in the reaction mixture was present partly as N_3^- , partly as HN₃ and partly as N₃Br. It is not considered necessary to give details of these; they are entirely consistent with the view that the rate of reaction between HN₃ and N₃Br is negligible compared with that between N_3^- and N₃Br.

B. Induced Reactions in the Systems $Br_2-N_3-S_2O_3$ and $Br_2-N_3-S_4O_6$

The reaction between NaN₃ and Br₂ can be catalyzed by either Na₂S₂O₃ or Na₂S₄O₆. The catalyzed reactions take place practically instantaneously, so that they cannot be followed kinetically. They are also as fast, so far as can be judged, under conditions for which the direct reaction between NaN₃ and Br₂ is very slow, such as, for example, when $[\Sigma Br_2] = [\Sigma N_3]$.

Experimental

Under conditions approximating to those used in the main series of experiments we have found that the *net* reactions occurring in these systems are :

$$Br_2 + 2N_3 \longrightarrow 3N_2 + 2Br^-$$
 . . . (1)

and either

$$S_2O_3^- + 4Br_2 + 5H_2O \longrightarrow 2SO_4^- + 8B\bar{r} + 10H^+$$
 (2)

or

$$S_4O_6^{--} + 7Br_2 + 10H_2O \longrightarrow 4SO_4^{--} + 14Br + 20H^+.$$
 (3)

This was shown by running an excess of bromine solution of known concentration drop by drop into a solution of thiosulphate (or tetrathionate) and azide in presence of phosphate buffer ($[KH_2PO_4]/[Na_2HPO_4] = 4/I$), and measuring the nitrogen evolved in a nitrometer. The excess bromine was then estimated by addition of sodium arsenite and back-titration with iodine. The amount of bromine consumed was compared with that estimated on the basis of the above equations; several experiments of this type were done and in all very satisfactory agreement between the observed and calculated bromine consumptions was found.

When bromine and thiosulphate react in absence of azide, there may or may not be, depending on the conditions of reaction, complete conversion of the thiosulphate into sulphate. If thiosulphate is run drop by drop into a bromine solution, buffered as above, between 99 and 100 % of the thiosulphate is oxidized to sulphate; if, however, the thiosulphate is run in quickly the odour of H_2S is apparent, and the amount of thiosulphate needed to decolorize the bromine is greater than for drop-by-drop addition. Also when bromine is run into a solution of thiosulphate H_2S formation ensues, especially when the ratio (moles Br_2)/(moles $S_2O_3^{--}$) is less than 4/1. Thus in two experiments in which oro5 M Br₂ was run quickly into oro1 M thiosulphate in presence of phosphate buffer, the results of analyses of the resulting solutions were :

(Mixture (i): (Moles
$$Br_2$$
)/(Moles $S_2O_3^-$) = 2/I;
Mixture (ii): (Moles Br_2)/(Moles $S_2O_3^-$) = 3/I).

/i\

(;;)

									(1)	(11)
Pe	rcent	age of o	origina	1 S ₂ O ₃	remaining				9.2	1.65
	,,	- ,,	,,	- ,, ⁻	converted t	$O_4O_6^{}$			53.0	43 · 58
	,,	,,	,,	,,	,,	SO3 .		•	0.0	0.42
The r	esulti	ng solu	itions :	were clo	e ar, n o sulph	ur separa	ating out	, bu	t in e	ach the
odour	of F	IS was	s appa	rent.	Analyses for	H,S, SC) ⁻ and	othe	er com	pounds

containing S (such as $S_3O_6^-$ and $S_5O_6^-$) were not carried out, but if it be assumed that the sulplur not otherwise accounted for is present only as H_2S and SO_4^- , the percentag conversions are : (:) 1::1

These results would appear to show that under the stated conditions, $Na_2S_4O_6$ is the main primary product of the reaction between Br_2 and $Na_2S_2O_3$; in presence of excess Br_2 , tetrathionate is, of course, very rapidly oxidized to sulph-ate. As already mentioned, however, H_2S formation is not detectable under our experimental conditions in the presence of azide, even when the bromine is run into the thiosulphate. The difference between the two sets of results may be due either to (a) sodium azide inhibiting H_2S formation by being very reactive towards intermediaries which might otherwise form H_2S or (b) possibly to the circumstance that the concentration of $S_2O_3^-$ was considerably smaller in the experiments with azide than in those with no azide present.

The main body of experiments in this work consists of the determination under a variety of conditions of the ratio (R) of

(moles Br_2 consumed)/(moles $S_2O_3^-(S_4O_6^-)$ consumed).

These determinations can be quickly carried out with negligible interference from the direct $Br_2 - N_3$ reaction provided that the ratio of azide to bromine present is not too great. Three methods have been employed to determine R:

- (a) by running a solution containing both N_3^- and $S_2O_3^-(S_4O_6^-)$ into a buffered solution containing bromine and bromide ;
- (b) by running a solution of $S_2O_3^{--}(S_4O_6^{--})$ into a buffered mixture of Br_2 , $Br-and N_3^-$;
- (c) by running a bromine-bromide solution into a buffered mixture of $S_2O_3^-(S_4O_6^-)$ and N_3^- .

The data obtained by method (c), though in general agreement with those of the other methods, need not be presented, as the R values which result are not so conveniently comparable with each other. In methods (a) and (b) the amount of inducing agent added was insufficient to cause consumption of all the bromine. Sodium arsenite was added immediately after the addition of the inducing agent and the excess arsenite estimated by titration with iodine solution. The volume of reagent run in was sufficient to bring the average volume of the reaction mixture in each experiment up to 40 ml., the average volume being that when one-half of the volume of inducing agent had been run in. During the drop-by-drop addition the reaction mixture was kept well-stirred by hand agitation, reproducible R values being obtained if the rate of addition of inducing agent and the vigour of stirring were kept approximately constant. In order to correct for any loss of bromine by vaporization or by reaction with im-purities, blank experiments were carried out for all runs, water being run in instead of the inducing agent. Buffering throughout was effected by a phosphate buffer $([KH_2PO_4]/[Na_2HPO_4] = 4/I)$. When $S_2O_3^-$ is the inducing agent R is defined as

(moles Br_2 consumed)/(moles S_2O_3 consumed);

in order to compare these values with those using $S_4O_6^{--}$ as the inducing agent, it is convenient to define the latter as

(moles Br_2 consumed)/(2 × moles $S_4O_6^{--}$ consumed),

the comparison being then made for equivalent amounts of sulphur. Thus, in the comparison being then made for equivalent amounts of suppur. Thus, in absence of azide the value of R in the $S_2O_3^-$ — Br_2 reaction is 4, while that for the $S_4O_6^-$ — Br_2 reaction is $7/2 = 3 \cdot 5$. These two R values will then represent the limits which will be approached as the azide concentrations in the systems Br_2 — N_3^- — $S_2O_3^-$ and Br_2^- — N_3^- — S_4O^- approach zero. Fig. 3, 4 and 5 illustrate some of the results obtained. Fig. 3 and 5 relate to method (a) in which a mixture of NaN₃ and Na₂S₂O₃(Na₂S₄O₆) was run into bromine. In the experiments of these figures 5 ml. of a solution containing NaN, and Na₂S₄O₄(Na₂S₄O₄) of the concentrations indicated in the diagrams

NaN₃ and Na₂S₂O₃(Na₂S₄O₆) of the concentrations indicated in the diagrams were run into $37^{\circ}5$ ml. of a buffered solution in which $[\Sigma Br_2] = 0.025$ and [Br⁻] = 0.50. Fig. 4 relates to method (b); for these experiments S₂O₃⁻⁻ solution (0.01 M) or S₄O₆⁻⁻ solution (0.005 M) was run into a buffered solution containing 0.025 M Br + 0.50 M KBr + azide in concentrations given by the

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abscissa. Other experiments, details of which will not be given, have been made to determine the effect on R of varying [Br-], $[\varSigmaBr_2]$ and temperature. The whole of the results may be summarized as follows. The most striking feature of the determinations of R is the parallelism between the data for $S_2O_3^-$ and for $S_4O_6^-$. Under all comparable experimental conditions $Rs_2O_3^-$ and $Rs_4O_6^-$ at equivalent concentrations of inducing agent are nearly the same, $Rs_2O_3^-$ being slightly the greater, the difference between the two varying between or 5 under conditions when R is small to about 6 when R is large. Another feature of the results is the high values which R can attain ; the highest value measured is 113. The effect of increasing $[N_3]$ is to increase R. With method (a) the increase in R is inappreciable at low concentrations of azide, but an approximately linear increase begins at a concentration of azide near that of the bromine in the system. The effect of decreasing $[S_2O_3^-]$ is to increase R, and from Fig. 5 it would appear that as $[S_2O_3^-]$ approaches zero R increases without limit. A similar behaviour is found with $S_4O_6^-$. The effect of $[\varSigma R_{r_2}]$



on both $R_{S_2O_3^-}$ and $R_{S_4O_4^-}$ depends on the method employed in the determination. With method (a), R increases slightly with increasing $[\Sigma Br_2]$, the increase being the more pronounced the higher the concentration of azide. Using method (b), however, R diminishes with increasing $[\Sigma Br_2]$. The effect of bromide on $R_{S_2O_4^-}$ and $R_{S_2O_4^-}$ is nil when method (a) is used; with method (b), R increases with increasing $[Br^-]$. Finally R is only slightly temperature-dependent, as reducing the temperature from 18° to 0° only lowers R by about 10 %.

Reaction Mechanism

In the experiments described above, I mole $S_2O_3^{--}$ ($\frac{1}{2}$ mole S_4O^{--}) consumes 4 moles (3.5 moles) of Br₂; simultaneously $R_{S_2O_3^{--}} - 4$ ($R_{S_4O_3^{--}} - 3.5$) moles of Br₂ are consumed by reaction with N_3^{-} . The similarity under all conditions between the $R_{S_2O_3^{--}}$ and $R_{S_4O_3^{--}}$ values at equivalent concentrations shows that the mechanisms in the two reacting systems are in some way very closely associated; it is also clear, in view of the high R values which can be realized that chain mechanisms

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must be operative. The following mechanism will account qualitatively for the various effects that have been observed.

$S_2O_3^{} + Br_2 \longrightarrow S_2O_3Br^- + Br^-$			(1 <i>a</i>)
$S_4O_6^{} + Br_2 \longrightarrow 2S_2O_3Br^{}$.			(1 <i>b</i>)
$N_3^- + Br_2 \xrightarrow{\longrightarrow} N_3 Br + Br^-$.			(2)
$N_3Br + S_2O_8^{} \longrightarrow S_2O_3Br^- + N_8^-$			(3a)
$N_3Br + S_4O_6^- \longrightarrow S_2O_3N_3^- + S_2O_3Br^-$			(3b)
$S_2O_3Br^- + N_3^- \longrightarrow S_2O_3N_3^- + Br^-$	•	•	(4)
$S_2O_3N_3^- + N_3^- \longrightarrow S_2O_3^{} + 3N_2$.			(5)
$S_2O_3N_3^- + S_2O_3N_3^- \longrightarrow S_4O_6^{} + 3N_2$.		•	(6)
$S_2O_3N_3^- + S_2O_3Br^- \longrightarrow$) leading to formation	o n		
$S_2O_3Br^- + S_2O_3Br^- \longrightarrow \int of SO_4^{}$			(7)

All these reactions are postulated as being very fast; in addition it appears necessary to postulate that reactions (1a), (1b), (3a) and (3b) are in-trinsically faster than the direct reaction (2), and probably that they are also faster than all the other reactions. The intermediary catalysts suggested are $S_2O_3Br^-$ and $S_2O_3N_3^-$; reactions (1) or (3), (4) and (5) or (6) constitute the chain; reactions (7) are chain-breaking and lead to sulphate formation and cessation of reaction. The conditions of reaction are such that it is not possible to deal quantitatively with the kinetics of reaction on the basis of this or any mechanism, but qualitatively the above scheme accounts satisfactorily for the experimental results. The differences between the results obtained by methods (a) and (b) are accounted for in terms of formation of N_3Br by reaction (2). Though it is assumed that N_3Br can react with $S_2O_3^-$ or $S_4O_6^-$ by reaction (3), it is postulated that a reaction between N_3Br and $S_2O_3N_3^-$ analogous to reaction (5) either does not take place or is too slow to need consideration. In method either does not take place or is too slow to need consideration. In method (b), then, in which $S_2O_3^-(S_4O_6^-)$ is run into a mixture of Br_2 and NaN_3 , N_3Br formation has already taken place and if conditions are such that most of the ΣN_3 is present as N₃Br the value of R will not greatly exceed Host of the $\Sigma \Gamma_3$ is present as $\Gamma_3 \Sigma$ the value of Γ in Fig. 4, in which with increasing $[\Sigma N_3]$, R first remains nearly constant at 4 (3.5), until a concentration of $[\Sigma N_3]$ is reached which permits of significant concentrations of free N_3^- being present. It also accounts—by displacement of the equilibrium (2)—of the effects of concentrations of bromine and bromide on R using method (b). With method (a) it follows, on the basis that reactions (1) are faster than the formation of N_3Br by reaction (2), that free N_3^- will be available for reactions (4) and (5) to occur, and it is clear that R should increase with increasing $[\Sigma N_3^-]$ throughout the whole range of concentration of $[\Sigma N_3]$, as is found experimentally. It should be noted, however, that N_3Br formation does take place using method (a), as there is time between the addition of each drop for equilibrium (2) (a), as there is this between the autition of each drop in equilibrium (..., to establish itself, but since fresh N_3^- is continually being added, the chain length of the reaction is little affected. Thus using this method at low $[\Sigma Br_2]$ and high $[\Sigma N_3^-]$ it was found that when about 0.5 ml. out of a total of 5.0 ml. of the mixture of NaN₃ and Na₂S₂O₃(Na₂S₄O₆) had been run into the bromine solution the reaction mixture was practically colour-The value of R was still high, indicating that, as postulated by reactions (3*a*) and (3*b*), the complex N₃Br can maintain the concentration of catalyst. Thus the catalyst S₂O₃Br⁻ can be formed by reactions with S₂O₃⁻ or S₄O₆⁻ either from Br₂ or N₃Br, but for propagation of a chain the presence of free N₃ is necessary and the chain length increases with increases with increasing concentration of free N_s . In terms of the mechanism it can be seen if reactions (1*a*) and (1*b*)

In terms of the mechanism it can be seen if reactions (1a) and (1b) are of equal speed (and also reactions (3a) and (3b)) then under comparable conditions $R_{\mathbf{S}_{4}\mathbf{O}_{1}^{-}}$ should be greater than $R_{\mathbf{S}_{4}\mathbf{O}_{1}^{-}}$ by o.5.

Actually it is found that the difference is 0.5 when low R values are realized, e.g. at high $[S_2O_3^{-}]$ and low $[N_3^{-}]$, but the differences become the greater the higher the values which R attain. A simple way of accounting for this result would appear to be the assumption that reactions (1b) and (3b) are somewhat faster than reactions (1a) and (3a) respectively. This would result in a greater average concentration of catalyst being present when $S_4O_6^-$ is used than with $S_2O_3^-$, and, since the rate of formation of SO_4^- is according to (7) proportional to the square of the catalyst concentration while the rate of N₂ formation according to (5) and (6) is proportional to the catalyst concentration raised to a power between 1 and 2, $R_{s_20\overline{3}}$ - - 4 will be somewhat bigger than $R_{s_40\overline{s}}$ - - 3.5, and the difference will be the greater as the R's increase. Finally, the dependence of R on $[S_2O_3^{--}]$ (or $[S_4O_6^{--}]$) at constant $[\Sigma N_3^{--}]$ given by Fig. 5 is accounted for by the theory in a qualitative manner on the same basis, namely that the rates of the chain-breaking reactions increase with catalyst concentration and hence with concentration of added $S_2O_3^$ faster than do the rates of the reactions which yield nitrogen and continue the chain; hence R decreases with increase of concentration of $S_2O_3^-$ or $S_4O_6^-$. The theory can be applied to yield a quantitative relation between R and $[S_2O_3^-]$, but only if certain further assumptions be made. Thus, if it is postulated that (i) reactions (1) are extremely rapid, so that the $S_2O_3^-$ is almost completely converted into $S_2O_3Br^-$ before the remaining reactions take place to an appreciable extent, (ii) that the magnitude and the nature of the reaction zone around the drop is not dependent on the concentration of $S_2O_3^{--}$ in the drop; and (iii) that the ratio of $[S_2O_3Br^-]$ to $[S_2O_3N_3^-]$ in the reacting system is independent of the concentration of $S_2O_3^-$, it may be shown that, with constant $[\Sigma N_3^-]$,

$$R_{S_2O_3^{-}} - 4 \propto \frac{k + [S_2O_3^{-}]}{[S_2O_3^{-}]},$$

where k is a constant and $[S_2O_3^-]$ is the concentration of $S_2O_3^-$ in the solution which is being run into the remainder of the reaction mixture. This relation is in general agreement with the data of Fig. 5, both yielding plots of $I/(R_{S_2O_3^-} - 4)$ against $[S_2O_3^-]$ passing through the origin and concave to the $[S_2O_3^-]$ axis, but quantitatively the data cannot be well fitted into a relation of the above type. However, though assumption (iii) is probably justified, the others are open to much doubt, and it is not surprising that a simplified treatment will not reproduce the experimental results.

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