CIX.—*The Reaction Between Sodium Benzylthiosulphate and Iodine.*

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IN 1909 Price and Twiss (T., **95**, 1489) showed that alkylthiosulphates react with iodine in aqueous solution, with the formation of disulphides, the reaction being analogous to that between alkylselenosulphates and iodine, which has been found to take place quantitatively (Price and Jones, T., 1909, **95**, 1729) according to the equation

In the note it was stated that, in all probability, the reaction is direct, and does not consist in a primary hydrolysis of the alkylthiosulphate by water and oxidation of the resulting mercaptan; it was hoped that measurements of velocity would throw light on the mechanism of the reaction.

The present authors have now carried out an extended series of measurements on the velocity of reaction between sodium benzylthiosulphate and iodine in aqueous solution at 25°, the results of which are given in this paper. The measurements are not as complete as we could desire, but as the joint work could not be continued, they have had to be brought to a conclusion. Although incomplete, the results obtained are of interest, and are now published, since it is doubtful when the reaction could be further investigated.

An aqueous solution of pure sodium benzylthiosulphate remains

neutral for weeks at the ordinary temperature, so that hydrolysis does not appear to take place, under these conditions, according to the equation

Also, catalysis by acids takes place extremely slowly at temperatures up to 100° , unless the acid is concentrated. For example, 50 c.c. each of *N*/10-hydrochloric acid and *N*/10-sodium benzylthiosulphate were mixed, and the solution maintained at 100° for four hours. Five c.c. of the original solution were equivalent to 17.70 c.c. of a solution of sodium hydroxide, and the titre had only increased to 18.00 c.c. after the four hours. Again, measurements of the electrical conductivity of such solutions at 25° showed that reaction took place extremely slowly.

The reaction between sodium benzylthiosulphate and iodine (in potassium iodide solution) takes place fairly rapidly at 25° , so that it is obvious that there is no primary hydrolysis by the water, succeeded by oxidation of the resulting products with iodine.

Before proceeding to measurements of velocities, it was necessary to prove that the reaction is quantitative, in accordance with the equation

To known weights of sodium benzylthiosulphate were added a known excess of *N*/10-iodine solution; after keeping for a week, the excess of iodine was determined. It was found that the molar ratio of sodium benzylthiosulphate to iodine necessary for oxidation was respectively 1.94: 1 and 1.92: 1 in the two experiments, so that the reaction is quantitative.* At the same time, these experiments indicated that there might be considerable difficulty in obtaining accurate measurements of velocity, owing to adsorption of the iodine by the benzyl disulphide, which precipitates out as it is formed. It was conceivable that, owing to this adsorption, there might be a considerable difference in the results when the reaction mixture was kept still and when it was well shaken. The following curve, which gives the results obtained in five different experiments, shows, however, that the results are remarkably concordant,† and apparently independent of the method of treatment of the reaction mixture.

The reaction mixture was prepared by mixing, at the ordinary temperature, 50 c.c. each of solutions of sodium benzylthiosulphate

* We are indebted to Dr. Twiss for carrying out these experiments.

† In most cases the results of different experiments agreed even better than those for which the details are given here.

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and iodine of such strengths that the resulting solution was 0.0125-*M*, 0.05-*M*, and 0.025-*M* with respect to iodine, potassium iodide, and sodium benzylthiosulphate respectively. Ten c.c. of the reaction mixture were then transferred, by means of a pipette, either into small test-tubes of Jena glass or into small tubes constricted ready for sealing. The test-tubes were closed with paraffined corks, the constricted tubes sealed at the blow-pipe, and the various tubes immersed in a thermostat at definite times. Some of the tubes were kept still, and some kept revolving continuously by an appropriate arrangement, whereby the contents were well shaken. At

definite intervals of time the whole of the contents of each tube was titrated with 0.01*N*-thiosulphate solution.

Although the results are satisfactory, it is possible for considerable errors to occur, at times, in the individual titrations; consequently, for each particular set of concentrations used, a number of different measurements of velocity were made, and a smoothed curve drawn through the plotted results. From these smoothed curves the figures in the following tables were obtained. Moreover, instead of making up the reaction mixtures as indicated above, it was found better previously to heat the individual solutions at 25°, and make up each small tube of the reaction mixture separately, by adding, by means of a pipette, the required amount

of the solutions (and water if necessary). The tubes were of such a size that the reaction mixture nearly filled them; in some cases test-tubes of Jena glass were used, in other cases weighing tubes with tightly fitting stoppers. In all cases the tubes were shaken in the thermostat.

According to the equation already given, the reaction should be of the second order with respect to sodium benzylthiosulphate, and of the first order with respect to the iodine. This was tested by carrying out measurements with either of the components in excess.

Iodine in Excess.—In these experiments, in order to determine the extent to which the reaction had proceeded, it was found advisable to run the reaction mixture into a known excess of standard thiosulphate solution, and determine the excess of the thiosulphate by titration with standard iodine solution, the procedure thus differing from that described above, and holding for all other sets of experiments.

The results are given in the following tables, where t is the time in minutes, measured from the moment at which the reaction mixture was made up, x the extent to which the reaction has proceeded, expressed in terms of c.c. of 0.01*N*-thiosulphate, k_1 and k_2 are the velocity-constants calculated according to reactions of the first and second order respectively, reckoning from the time of the first titration; c represents the original quantity of sodium benzylthiosulphate in each tube, expressed in c.c. of 0.01*N*-thiosulphate. The concentrations given at the head of each table are expressed in mols. per litre; for example, 0.4KI represents a solution which is 0.4-molar with respect to potassium iodide in the reaction mixture. NaBz represents sodium benzylthiosulphate. In each case the figures given represent the mean values of four different sets of experiments.

I. 0.4KI, 0.05I₂, 0.01NaBz. $c=20$.

t	20	30	40	50	60	70	80	90	100
x	0.53	0.78	1.02	1.25	1.50	1.72	1.94	2.15	2.35
$k_1 \times 10^6$	—	562	553	546	555	548	544	539	533
$k_2 \times 10^6$	—	67	66	66	67	67	67	66	66
Mean..... $k_1 \times 10^6 = 547$.					Mean..... $k_2 \times 10^6 = 67$.				

II. 0.4KI, 0.05I₂, 0.005NaBz. $c=10$.

t	60	80	100	120	140	160	180
x	0.80	1.03	1.23	1.44	1.64	1.83	2.00
$k_1 \times 10^6$	—	(550)	520	522	520	516	506
$k_2 \times 10^6$	—	139	133	135	136	137	137
Mean..... $k_1 \times 10^6 = 517$.				Mean..... $k_2 \times 10^6 = 136$.			

III. 0.2KI , 0.025I_2 , 0.005NaBz . $c=10$.

t	50	70	90	110	130	150
x	0.81	1.08	1.33	1.59	1.85	2.09
$k_1 \times 10^6$	—	648	633	642	652	651
$k_2 \times 10^6$	—	164	163	168	174	176
Mean..... $k_1 \times 10^6=645$.	Mean..... $k_2 \times 10^6=169$.					

It would be difficult to decide the order of the reaction with respect to sodium benzylthiosulphate from a comparison of the values obtained for k_1 and k_2 , since, although those of k_2 remain very constant throughout the experiment, those of k_1 are also fairly constant. The matter is readily decided, however, by appeal to the ordinary methods used in such cases. Since in experiments I and II the concentration of the iodine is the same, and it is in large excess, the ratio of the values obtained for the velocity-constants in these two experiments should be 1. For k_1 the ratio is $547:517=1.06$, whereas for k_2 it is $67:136=0.49$, thus indicating that the reaction is of the first order with respect to the sodium benzylthiosulphate. The same result is obtained if use is made of the equation $n=1+\log t_1/t_2/\log c_1/c_2$, where n is the order of the reaction, t_1 and t_2 are the times necessary for the reaction to proceed a definite fraction of its course in two different experiments, and c_1 and c_2 are the concentrations of the sodium benzylthiosulphate in the two experiments. In the above experiments, I and II, the reaction is complete to the extent of 10 per cent. in 83 and 77.5 minutes respectively, from which it follows that $n=0.901$, that is, the reaction is unimolecular with respect to the sodium benzylthiosulphate.

At first sight it would seem as if the result obtained in III contradicts the above conclusions. The concentration of the iodine in these experiments is only half of what it is in II, that of the sodium benzylthiosulphate remaining the same, and therefore the value of the velocity-constant should be one-half of what it is in II, in accordance with the equation $dx/dt=kB(A-x)$, where A is the concentration of the sodium benzylthiosulphate and B the concentration of the iodine, which is present in excess. The value of k_1 calculated is therefore equal to kB , and will depend on the value of B . The ratio of the velocity-constants in II and III should therefore be 2; it is actually $517:645=0.80$, there thus being no agreement. It will be shown later, however, that the velocity of reaction depends, not on the total concentration of iodine in the solution, but on the concentration of the free iodine. In II and III the concentrations of the free iodine are respectively 0.000196 and 0.000195 mols. per litre at 25° , that is, they are the same, and therefore the ratio of the velocity-constants should be equal to 1,

the actual ratio being 0.80. Considering the complicated nature of the reaction, this may be considered as satisfactory.

Sodium Benzylthiosulphate in Excess.—The results are given in the following tables. k_1 represents the velocity-constants calculated according to a reaction of the first order; the meaning of K' will be explained later. c represents the original quantity of iodine present in each tube, expressed in c.c. of 0.01*N*-thiosulphate.

IV. 0.04KI, 0.005I₂, 0.1NaBz. $c = 20$.

t	5	7.5	10	12.5	15	17.5	20
x	4.70	5.80	6.85	7.90	8.82	9.68	10.43
$k_1 \times 10^4$	—	130	140	135	136	137	136
$K' \times 10^5$	—	120	124	128	133	135	134
Mean..... $k_1 \times 10^4 = 136$.				Mean..... $K' \times 10^5 = 129$.			

V. 0.04KI, 0.005I₂, 0.05NaBz. $c = 20$.

t	5	10	15	20	25	30
x	2.75	4.20	5.58	6.80	8.02	9.20
$k_1 \times 10^4$	—	76	78	77	79	81
$K' \times 10^5$	—	69	71	71	73	77
Mean..... $k_1 \times 10^4 = 78$.			Mean..... $K' \times 10^5 = 72$.			

VI. 0.02KI, 0.0025I₂, 0.05NaBz. $c = 10$.

t	5	7.5	10	12	14	15	17.5	20
x	2.60	3.47	4.21	4.70	5.17	5.37	5.85	6.30
$k_1 \times 10^4$	—	217	213	207	206	204	201	201
$K' \times 10^5$	—	106	106	103	104	103	103	104
Mean..... $k_1 \times 10^4 = 207$.				Mean..... $K' \times 10^5 = 104$.				

In the above tables, IV, V, and VI, the figures given are the mean of five, two, and two experiments respectively.

The values of k_1 are fairly constant in each experiment. If the reaction is of the first order with respect to the total iodine, the ratio of the velocity-constants in experiments IV and V should be 2, since the concentration of the sodium benzylthiosulphate in IV is twice what it is in V; the actual ratio is $136:78=1.7$. The ratio of the velocity-constants in experiments V and VI, in which the concentration of the sodium benzylthiosulphate is the same, should be 1; the actual ratio is $78:207=0.37$, which altogether disagrees with the theoretical ratio. It follows, therefore, that the reaction is not of the first order with respect to the total iodine.

The possibility remains that it is the free iodine which enters into reaction with the sodium benzylthiosulphate, and not the iodine present as tri-iodide ion. This was tested by the following experiments in 52 per cent. alcoholic solution. The values of $A - x$ in the following table represent the titre, expressed in c.c. of 0.01*N*-thiosulphate solution, of 10 c.c. of a solution of the composi-

tion 0.05KI, 0.0125I₂, 0.025NaBz; those of $A - x'$, the titre of 10 c.c. of a solution of the composition 0.0125I₂, 0.025NaBz. t is the time which has elapsed since the solutions were mixed.

t	16	51	171	301	532
$A - x$	23.66	23.36	21.65	19.61	15.69
t	16	22	32	47	75
$A - x'$	12.50	11.96	11.42	10.80	9.80
					8.33

The reaction thus proceeds enormously faster in the absence of potassium iodide, the value of the iodine titre falling to one-half in sixteen minutes; moreover, it begins to slow down very quickly after a time, owing to the fact that free iodine is removed from the solution by the hydriodic acid formed during the course of the reaction. These experiments show, at the same time, that the reaction proceeds much more slowly in aqueous-alcoholic solution in the presence of potassium iodide than it does in aqueous solution.

Assuming that the reaction is unimolecular with respect to both the sodium benzylthiosulphate and the free iodine, the velocity-equation may be written:

$$dx/dt = k(A - 2x)\phi,$$

where A is the initial molar concentration of the sodium benzylthiosulphate, ϕ is the molecular concentration of the free iodine at the time t , and x is the number of molecules of iodine which has disappeared at the time t . The diminution in concentration of the sodium benzylthiosulphate is then $A - 2x$, since, according to the reaction equation, $2x$ mols. of sodium benzylthiosulphate disappear for each x molecules of iodine.

Let B represent the total molecular concentration of iodine and C the total molecular concentration of potassium iodide at the commencement of the reaction.

If sodium benzylthiosulphate is present in large excess, the velocity equation may be written:

$$dx/dt = kA\phi = K\phi,$$

where $K = kA$.

At the time t ,

$$C = [\text{KI}] + [\text{KI}_3] \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$\text{The total iodine} = B - x = \phi + [\text{KI}_3] + [\text{HI}_3] \quad . \quad . \quad . \quad . \quad . \quad (2)$$

since hydriodic acid is formed during the reaction.

The total concentration of hydriodic acid is:

$$2x = [\text{HI}] + [\text{HI}_3] \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$\text{Also} \quad [\text{KI}]\phi / [\text{KI}_3] = k' = [\text{HI}]\phi / [\text{HI}_3] \quad . \quad . \quad . \quad . \quad . \quad (4)$$

From (1) and (2) by subtraction,

$$C - B + x = [\text{KI}] - \phi - [\text{HI}_3] \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Addition of (3) and (5) gives

$$C - B + 3x = [\text{KI}] + [\text{HI}] - \phi \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Also from (4) and (2)

$$\begin{aligned} [\text{KI}] + [\text{HI}] &= k'([\text{KI}_3] + [\text{HI}_3]) / \phi, \\ &= k'(B - x - \phi) / \phi. \end{aligned}$$

Substitution in (6) then gives:

$$\begin{aligned} C - B + 3x &= k'(B - x - \phi) / \phi - \phi, \\ \therefore k' / \phi &= (\phi + C - B + 3x) / (B - x - \phi), \\ &= \omega, \text{ where } k' / \phi = \omega, \end{aligned}$$

$$\therefore x(\omega + 3) - B\omega + C - B = -\phi(\omega + 1) = -k' - k' / \omega \quad (7)$$

This equation, on differentiation, gives:

$$(\omega + 3)dx/dt = (B - x + k' / \omega^2)d\omega/dt,$$

that is,

$$K(\omega + 3)k' / \omega = (B - x + k' / \omega^2)d\omega/dt,$$

since $dx/dt = K\phi = Kk' / \omega$.

$$\therefore \frac{(B - x)\omega^2 + k'}{\omega(\omega + 3)} \cdot \frac{d\omega}{dt} = Kk'.$$

On integration, this equation gives:

$$R \log_e(\omega + 3) + (k' / 3) \log_e \omega + 3R / (\omega + 3) - 3B = Kk't + \text{const.} \quad (8)$$

where $R = 2B + C + 2k' / 3$.

The integration-constant is evaluated as follows:

When $t = t_0$, $x = x_0$,

$\therefore$ from (7)

$$x_0(\omega + 3) - B\omega + C - B = -k' - k' / \omega.$$

$$\therefore \omega = (P + 3x_0 + Q) / 2(B - x_0),$$

where $P = C - B + k'$ and $Q = \sqrt{(P + 3x_0)^2 + 4(B - x_0)k'}$.

Substituting this value of ω in (8), and subtracting the resulting equation from (8), we get, finally,

$$\begin{aligned} 2 \cdot 3026R \log(\omega + 3) - 2 \cdot 3026R \log(S + 3) + 2 \cdot 3026(k' / 3) \log \omega - \\ 2 \cdot 3026(k' / 3) \log S + 3R / (\omega + 3) - 3R / (S + 3) = Kk'(t - t_0), \end{aligned}$$

where $S = (P + 3x_0 + Q) / 2(B - x_0)$.

The values of K' ($= Kk'$) given in tables IV, V, and VI are calculated from this equation, k' being taken as having the value 0.00138 at 25° (compare Bray and MacKay, *J. Amer. Chem. Soc.*, 1910, **32**, 914; Washburn and Strachan, *ibid.*, 1913, **35**, 681). x is expressed in cc. of 0.01N-thiosulphate. The values of K' are calculated in terms of molecules per litre.

In IV and VI the results are very satisfactory, but in V there is a gradual rise in the values of the constant.

The ratio of the values of K' in IV and V should still be 2, the experimental ratio being 129:72=1.8. The ratio in experiments V and VI is 72:104=0.7, as compared with the theoretical ratio 1. This agreement may be taken as satisfactory when the complicated nature of the reaction is taken into account.

It should be mentioned that the equation $dx/dt = k(A - 2x)\phi$ leads to the ordinary unimolecular equation when the total concentration of the iodine is large compared with that of the sodium benzylthiosulphate, so that the results obtained with iodine in excess do not need further discussion.

Sodium Benzylthiosulphate in Equivalent Molecular Proportions—The equation representing the velocity of reaction is again

$$\begin{aligned} dx/dt &= k(A - 2x)\phi \\ &= 2k(B - x)\phi \\ &= K(B - x)\phi, \end{aligned}$$

where A and B have the same signification as before.

In the same way, as was deduced above, it follows that

$$(\omega + 3)dx/dt = (B - x + k'/\omega^2)d\omega/dt,$$

that is,

$$K(\omega + 3)(B - x)\phi = (B - x + k'/\omega^2)d\omega/dt.$$

Now k'/ω^2 is very small, and can be neglected,* in comparison with $B - x$.

$$\therefore (B - x)d\omega/dt = K(B - x)(\omega + 3)\frac{k}{\omega},$$

$$\therefore \frac{\omega d\omega}{\omega + 3} = Kk'dt,$$

$$\therefore \omega - 3 \log_e(\omega + 3) = Kk't + \text{const.}$$

As before, when $t = t_0$, $x = x_0$, and $\omega = (P + 3x_0 + Q)/2(B - x_0)$, where P and Q have the same meaning as before.

Elimination of the constant term then leads to the equation:

$$\omega - 6.9078 \log(\omega + 3) - S + 6.9078 \log(S + 3) = Kk'(t - t_0),$$

where S has the same meaning as before.

The results of various experiments are given in the following tables. k_1 represents constants of the first order, and will be referred to later.

VII. 0.2KI, 0.025I₂, 0.05NaBz. $c = 100$.

t	30	60	90	120	150	180	210	240
x	4.80	8.30	12.00	15.40	18.70	21.50	24.20	26.40
$Kk' \times 10^4$...	—	97	105	108	111	111	112	111
$k_1 \times 10^5$	—	54	57	57	57	56	55	53

VIII. 0.0533KI, 0.0066I₂, 0.0133NaBz. $c = 20$.

t	30	40	46	50	56	60	70	80	90
x	2.00	2.68	3.06	3.30	3.63	3.84	4.44	5.00	5.40
$Kk' \times 10^4$...	—	302	312	315	317	313	328	338	331
$k_1 \times 10^5$	—	92	102	112	120	126	133	138	135

* The equation was, in the first case, integrated without neglecting k'/ω^2 . The calculated values of the constants were the same as those obtained when k'/ω^2 is neglected.

IX. 0.04KI, 0.005I₂, 0.01NaBz. $c = 20$.

t	30	60	90	120	150	180	210	240
x	2.30	4.30	6.05	7.70	9.10	10.30	11.40	12.30
$Kk' \times 10^4$...	—	373	401	445	482	518	563	599
$k_1 \times 10^3$	—	174	172	176	175	174	174	172

X. 0.05KI, 0.0125I₂, 0.025NaBz. $c = 25$.

t	15	20	25	30	35	40	45	50	55	60
x	3.70	4.57	5.40	6.15	6.90	7.60	8.33	8.93	9.53	10.13
$Kk' \times 10^4$...	—	360	373	377	390	400	419	425	436	450
$k_1 \times 10^3$	—	362	361	350	353	351	355	350	347	347

The figures given in the above tables are the mean results from three, eight, three, and six experiments respectively.

The values of Kk' are constant in VII, fairly constant in VIII, and increase continuously in IX and X. In VII, VIII, and IX the ratio of the concentration of the potassium iodide to the iodine is always the same, and it will be noticed that the more dilute the solutions are the greater is the tendency of the values of Kk' to increase during the experiment. This increase is especially noticeable in IX, where the reaction was followed over 60 per cent. of its course, whereas in VII and VIII it was allowed to proceed only to the extent of about 25 per cent. The constants also rise continuously in X, where the ratio of the concentrations of the potassium iodide to iodine is only half what it is in the other three experiments; the reaction was followed over 40 per cent. of its course.

Comparison of the values of Kk' in the various experiments also shows that instead of being the same, as they should be, theoretically, they become greater with greater dilution of the solutions used. This may be another example of what has been found to be the case in other reactions (compare Segaller, T., 1913, **103**, 1154, for the literature), or it may, more probably, be due to the velocity equation not taking into account all the factors that influence the course of the reaction. During the reaction acid is liberated, but this has no catalytic effect, as was proved by experiments in which sulphuric acid was added to the reaction mixture. It seems more probable that the disturbing influence causing the constants to rise during the reaction is the precipitation of benzyl disulphide during the course of the reaction. The precipitated disulphide adsorbs iodine, and it is conceivable that the reaction in the adsorbed system may proceed more quickly than in the non-adsorbed. Attempts were made to test this supposition, but the experiments had to be discontinued, for reasons stated at the commencement of this paper, before a satisfactory conclusion could be reached. To obtain comparable results, the benzyl disulphide

should be added to the reaction mixture in approximately the same state of division as that which it has when it is precipitated during the course of the reaction. This can only be done satisfactorily by adding an alcoholic solution of the disulphide to the reaction mixture; alcohol is thereby added to the medium, and, as has already been mentioned, the velocity in aqueous-alcoholic solutions is very much smaller than in aqueous solutions. In one experiment which was tried there was a slight acceleration at the commencement of the reaction, even in the presence of alcohol, but it was not very marked.

If finely powdered, dry benzyl disulphide is added to the reaction mixture, its surface is in quite a different condition from that of the disulphide, as it precipitates during the course of the reaction, so that absolutely trustworthy results cannot be obtained. In the following experiment the benzyl disulphide was precipitated from alcoholic solution by pouring into water, collected, washed, and dried, before being added to the reaction mixture. A blank experiment was made at the same time, the measurements being carried out at room temperature.

0.08KI, 0.01I₂, 0.02NaBz.

The reaction mixture was run into a known excess of thio-sulphate solution, the excess then being titrated with standard iodine solution, the number of c.c. used being given by x ; x' is the titre for the same solution in the presence of benzyl disulphide, 1 gram of which was added to 20 c.c. of the reaction mixture:

t	60	120	180
x	4.27	6.50	9.10
x'	5.05	7.00	10.90

The results seem to indicate that there is an acceleration due to the benzyl disulphide, but we should not like to bind ourselves to that conclusion without further experiment.

The fact that the constants have different values in the different experiments may also be accounted for on the assumption that it is the anion only of the sodium benzylthiosulphate which enters into reaction with the iodine. In the velocity equation deduced, no account has been taken of the dissociation of the various compounds present in solution; indeed, the reaction mixture is so complex that it would be a somewhat difficult proposition to do so, and would entail an extended series of experiments the utility of which would be somewhat doubtful. The consideration of this effect is complicated by the fact that sodium benzylthiosulphate was, unfortunately, used in the experiments instead of the potassium salt. However, potassium iodide is always present in considerable excess in the reaction mixture, even if the (unwarrantable) assumption is

made that the sodium benzylthiosulphate is completely transformed into the potassium salt in the solution. This excess of potassium iodide would tend to suppress the dissociation of the potassium benzylthiosulphate, the dissociation being suppressed to the greatest extent in the more concentrated solution, especially when one takes into account the fact that the amount of the potassium iodide varied with that of the sodium benzylthiosulphate, and was not kept constant in the various solutions. The concentration of the benzylthiosulphate anion would thus be relatively greater in the dilute than in the concentrated solutions, and the variation of the constants would thus be explained. This would account for the fact that in X, where the concentration of the potassium iodide is only twice that of the sodium benzylthiosulphate, the constants are greater than in VIII, where the ratio of these concentrations is 4, although the latter solution is more dilute with respect to sodium benzylthiosulphate. Similar reasoning would explain why the value of k_1 in III is greater than in II, although the concentration of the sodium benzylthiosulphate is the same in the two solutions.

Mechanism of the Reaction.—In the tables VII—X, the values of k_1 calculated according to a reaction of the first order are given, and it will be noticed that they are fairly constant in each experiment; in fact, the more the values of Kk' rise, the more constant become the values of k_1 . It might at first sight be supposed that the reaction is really one of the first order, one of the components undergoing some change at a definite rate, the product then being acted on by the other component with great velocity. However, the experiments with either component in excess invalidate this conclusion, and show that the reaction is really bimolecular. That such satisfactory results were obtained with either of the components in excess, as compared with those when the components were present in equivalent molecular proportions, is only another instance of the fact that disturbing factors are eliminated to a great extent by this method of experiment.

Since the reaction is bimolecular, it is probable that the first stage in the reaction, and the one of which the velocity is measured, is the combination of a molecule of iodine with a molecule of sodium benzylthiosulphate, union taking place at the unsaturated sulphur atom, in accordance with the equation:

This kind of reaction is comparable with that which is known to occur between organic sulphides and chlorine, bromine or iodine (compare Fromm and Raiziss, *Annalen*, 1910, **374**, 90; Fromm, *ibid.*, 1913, **396**, 75). The compound thus produced is then decomposed very quickly, with the formation of benzyl disulphide, sodium

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hydrogen sulphate, and hydriodic acid. It is possible to formulate a scheme showing in what way this reaction could take place, but experimental evidence being wanting, there does not seem to be much value in doing so.

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