238. *The Kinetics of the Reaction between Carbonyl Sulphide and Water.*

By H. W. THOMPSON, C. F. KEARTON, and S. A. LAMB.

THE development of the theory of activation and the application of the kinetic theory to the calculation of collision frequencies have led to a satisfactory understanding of the mechanism of chemical change in the gaseous phase. Attempts have recently been made to apply similar considerations to reactions in solution by estimating the Arrhenius energy of activation from the observed temperature coefficient of the reaction velocity, and then taking the product of a calculated collision frequency and the necessary activation factor, in order to find the degree of agreement with the measured reaction rate.

Bimolecular reactions in solution appear to fall into two classes (Moelwyn-Hughes, *Chem. Rev.*, 1932, **10**, 241). On the one hand, there are processes the rate of which is given by the simple formula $z.e^{-E/RT}$, z being the collision frequency and E the energy of activation; on the other, there are many reactions the measured rate of which is considerably lower than the calculated value (Thompson and Blandon, J., 1933, 1237). A comparison of rates and energies of activation of the same " abnormally slow " reaction when occurring in different solvents suggests that the slowness does not arise as a result of solvent deactivation, and there are other experiments which confirm this view. It appears that the difference in rate in the different solvents is due to catalytic activity of these. One generalisation is that reactions between neutral molecules are usually slow, and those between a neutral molecule and an ion are " normal." Hinshelwood has suggested that the presence of an ionic atmosphere may remove some type of selection principle similar to those found in spectroscopy (J., 1933, 1357).

Bimolecular reactions in solution are of two types: (i) those between two solutes in an inert solvent, and (ii) those in which the solute reacts with the solvent. Calculation of the collision frequencies in reactions of the latter type is difficult, but can be made on certain assumptions, and almost all the examples studied show a satisfactory agreement with the hypothesis of activation (Moelwyn-Hughes, J., 1932, 95). Scarcely any examples have been reported in which the same reaction has been examined, on the one hand, as a solute–solute process, and on the other, as a solute–solvent reaction. The most satisfactory case of this is the reaction between acetic anhydride and ethyl alcohol, which has been studied in alcoholic solution and also in hexane and carbon tetrachloride. This reaction has also been examined in the gas phase, in which it is " abnormally slow " just as in the inert solvents (Moelwyn-Hughes and Hinshelwood, J., 1932, 230; Moelwyn-Hughes and Rolfe, *ibid.*, p. 241).

There is one solute–solvent reaction which has appeared to be in disagreement with theory, *viz.*, that between carbonyl sulphide and water. The discrepancy has been attributed to inexplicable catalytic influences of hydroxyl ions present. In the work now to be described this reaction has been re-examined (*a*) as a solute–solvent reaction, (*b*) as a bimolecular reaction in ethyl alcohol, and (*c*) in the gas phase.

EXPERIMENTAL.

Carbonyl sulphide was prepared by adding saturated ammonium thiocyanate solution to well-cooled sulphuric acid (Moser, " Die Reindarstellung der Gase "), hydrogen sulphide and cyanide, carbon dioxide and disulphide, and sulphur dioxide being removed by absorbents. The final product was passed through concentrated sulphuric acid and collected in a liquid-air trap, whence it could be distilled off as required.

Two different experimental methods were used for the investigations in the liquid phase. The first was as described by Buchböck (*Z. physikal. Chem.*, 1897, **23**, 123) and involved the expulsion by mercury of known amounts of solution at intervals from a completely filled reaction vessel submerged in a thermostat. In the second method, measured volumes of solution were sealed in small glass tubes and allowed to remain in the thermostat for different periods, after which the contents were analysed. Both methods gave essentially the same results, but the reaction in ethyl alcohol could not be studied by the former method owing to some interaction with the mercury.

The reaction was followed by the rate of formation of hydrogen sulphide. Measured volumes of solution were transferred into ice-cooled iodine solution, and excess iodine back-titrated with sodium thiosulphate.

To obtain a solution of carbonyl sulphide, distilled water, freshly boiled out in a vacuum, was transferred in an atmosphere of nitrogen to a wash-bottle and placed in the thermostat for some time. Carbonyl sulphide was then passed through it, the unabsorbed gas passing through a 10 cm. column of mercury. The initial concentrations were determined as by Buchböck, who decomposed the carbonyl sulphide rapidly in alkaline solution and estimated the hydrogen sulphide formed. In order to avoid errors due to the oxidation of the alkali sulphide, an alkaline solution of zinc sulphate was used, zinc sulphide being precipitated equivalent to the hydrogen sulphide present. Excess acid was added to neutralise the alkali, and the hydrogen sulphide liberated from the zinc sulphide determined as above.

The pure dry ethyl alcohol was prepared by the method of Segaller (J., 1913, **103**, 106) and Wiig (*J. Physical Chem.*, 1928, **32**, 961). The commercial product was refluxed for 6 hours over caustic potash and freshly-prepared silver oxide to remove any aldehyde, then refluxed successively over lime and calcium for 6 hours, and finally distilled directly into the vessel in which the solution was to be made.

The reaction in the gas phase was followed by heating known amounts of water and carbonyl sulphide together in sealed soda-glass tubes of *ca.* 60 c.c. capacity at a constant temperature for definite periods, the hydrogen sulphide produced then being estimated, by opening the chilled tubes under excess iodine, washing them out, and titrating the excess iodine. Weighed amounts of water were obtained by partly filling thin-walled glass capillaries; these were introduced into the reaction vessels, which were drawn off, sealed to a suitable filling apparatus, evacuated, filled with carbonyl sulphide to the desired pressure, and finally sealed off. A small amount of carbonyl sulphide was always decomposed in the sealing process. Series of these tubes were prepared, each containing different amounts of the reactants, and the capillaries were broken by shaking. The tubes were then submerged in the heating bath. The volumes of the tubes were subsequently determined by filling with water.

1. *The Reaction in Aqueous Solution.*—In water, carbonyl sulphide is hydrolysed thus: $COS + H_2O = CO_2 + H_2S$. Buchböck found that at 15—40° the reaction closely followed a unimolecular law. The velocity constant was given by $\log_e k = -11{,}737/T + 45{\cdot}66$, which corresponds to an energy of activation of 23,240 cals. We have found velocity constants and a temperature coefficient agreeing essentially with those of Buchböck. Typical results are given in the following tables. The velocity constants are calculated from the expression $k = 2{\cdot}303/t \,.\, \log_{10} a/(a - x)$, in g.-mols./l./sec. In the tables, x is the number of c.c. of thiosulphate equivalent to the iodine used, c the concentration of carbonyl sulphide, and t the time in minutes.

(1) Temp. 30·0°.
$c = 0{\cdot}0157$; $a = 69{\cdot}6$.

t.	x.	$k \times 10^5$.
0	0	—
39	6·2	3·98
80	11·9	3·97
203	27·1	4·03
281	34·2	4·00
393	42·0	3·92
525	49·6	3·96
614	53·6	3·99
1491	67·6	3·97
1848	68·8	4·00
∞	69·6	—
	Mean	3·98

(2) Temp. 47·4°.
$c = 0{\cdot}00556$; $a = 30{\cdot}4$.

t.	x.	$k \times 10^5$.
0	0	—
12	5·9	29·6
25	10·9	29·6
37	14·95	31·3
54	19·25	30·5
75	22·9	31·1
98	25·25	30·1
129	27·65	30·9
172	29·2	31·3
∞	30·4	—
	Mean	30·6

(3) Temp. 36·4°.
$c = 0{\cdot}01293$; $a = 48{\cdot}1$.

t.	x.	$k \times 10^5$.
0	0	—
29	7·0	9·04
59	13·1	8·98
97	19·65	9·02
135	24·8	8·94
179	29·6	8·87
268	36·5	8·84
359	41·1	8·95
∞	48·1	—
	Mean	8·95

(4) Temp. 41·9°.
$c = 0{\cdot}00379$; $a = 15{\cdot}5$.

t.	x.	$k \times 10^5$.
0	0	—
25	3·35	16·2
47	5·8	16·6
69	7·75	16·7
94	9·3	16·2
123	10·9	16·5
186	13·1	16·7
287	14·65	16·8
∞	15·5	—
	Mean	16·6

(5) Temp. 25·0°.
$c = 0{\cdot}00597$; $a = 25{\cdot}4$.

0	0	—
110	3·25	2·07
234	6·4	2·07
380	9·6	2·08
599	13·5	2·11
1200	19·5	2·04
1428	21·1	2·09
1692	22·9	2·27
3037	24·7	1·97
4140	25·2	2·07
∞	25·4	—
	Mean	2·09

(6) Temp. 15·5°.
$c = 0{\cdot}0376$; $a = 228{\cdot}7$.

0	0	—
141	11·0	0·58
377	28·5	0·59
1170	76·0	0·57
1420	87·4	0·56
1669	99·4	0·56
2612	134·4	0·56
3100	149·9	0·57
4150	174·0	0·57
∞	228·7	—
	Mean	0·57

The mean velocity constants at the different temperatures are summarised in Table I. The temperature range is rather greater than that used by Buchböck. The plot of $\log_{10} k$ against $1/T$ shows that the results can be represented by $k = 1{\cdot}06 \times 10^{12} \times e^{-22,170/RT}$.

TABLE I.

T, Abs.	$10^3/T$.	$k \times 10^5$.	$\log_{10} k$.	T, Abs.	$10^3/T$.	$k \times 10^5$.	$\log_{10} k$.	T, Abs.	$10^3/T$.	$k \times 10^5$.	$\log_{10} k$.
288·5°	3·466	0·57	$\bar{6}$·7559	303·3°	3·297	4·18	$\bar{5}$·6212	313·8°	3·187	14·3	$\bar{4}$·1553
298·0	3·356	2·09	$\bar{5}$·3201	308·1	3·246	7·41	$\bar{5}$·8698	314·9	3·176	16·4	$\bar{4}$·2148
302·8	3·302	3·84	$\bar{5}$·5843	309·1	3·235	8·49	$\bar{5}$·9289	320·2	3·123	30·4	$\bar{4}$·4829
303·0	3·300	3·98	$\bar{5}$·5999	309·4	3·232	8·88	$\bar{5}$·9484	320·4	3·121	30·5	$\bar{4}$·4843

The influence of hydrochloric and acetic acids at different concentrations upon the reaction velocity is shown by the following results at 35·1° :

	Hydrochloric acid.				Acetic acid.			
Normality	0	0·99	1·99	3·97	0	0·98	1·97	3·92
$k \times 10^5$	7·41	5·32	3·69	1·51	7·41	6·96	6·42	5·04

2. *The Reaction in Alcohol.*—The velocity constant k in Table II is calculated from the equation $k = 2{\cdot}303/t(a - b) \,.\, \log_{10} b/(a - x)/a(b - x)$, in g.-mols./l./sec. Where the initial concentrations a and b are approximately equal, however, the more amenable expression $k = x/at(a - x)$ is employed. A satisfactory bimolecular constant is obtained.

TABLE II.

(1) Temp. 75·0°.
$a = 0{\cdot}10$; $b = 0{\cdot}018$.

$t \times 10^{-3}$ (secs.).	$100x$.	$100(a-x)$.	$100(b-x)$.	$k \times 10^5$.
43·5	0·45	9·55	1·35	6·77
75·3	0·675	9·325	1·125	6·55
134·7	0·98	9·015	0·815	6·23
221·4	1·34	8·66	0·46	6·71
303·6	1·555	8·445	0·245	7·32
418·5	1·65	8·35	0·15	6·71
∞	1·8	—	—	—
			Mean	6·72

(2) Temp. 60°.
$a = 0{\cdot}1802$; $b = 0{\cdot}0675$.

$t \times 10^{-3}$ (secs.).	$100x$.	$10(a-x)$.	$100(b-x)$.	$k \times 10^5$.
52·8	1·24	1·68	5·51	2·21
91·5	1·925	1·61	4·825	2·16
142·5	2·825	1·52	3·925	2·31
224·7	3·385	1·46	3·365	1·92
360·0	4·75	1·33	2·00	2·24
420·0	5·0	1·30	1·75	2·16
657·3	5·525	1·25	1·125	1·92
660·0	5·75	1·23	1·00	2·05
∞	—	—	—	—
			Mean	2·12

The mean values at three temperatures are given below :

T, Abs.	$10^3/T$.	$k \times 10^5$.	$\log_{10} k$.	T, Abs.	$10^3/T$.	$k \times 10^5$.	$\log_{10} k$.	T, Abs.	$10^3/T$.	$k \times 10^5$.	$\log_{10} k$.
348°	2·874	6·42	5·8075	341°	2·933	3·99	5·6010	333°	3·003	2·44	5·3874

These data give a satisfactory linear plot of $\log_{10} k$ against $1/T$, from which the energy of activation is 14,930 cals. Although this value may be somewhat inaccurate, it is certain that the energy of activation in alcohol is considerably lower than in aqueous solution. This surprising result makes it desirable to examine the possible sources of error. The only one which must be seriously considered is that the alcohol was insufficiently dried, causing an inaccurate velocity constant. In our opinion this does not apply, in view both of the experimental method used to guard against the difficulty, and of the uniformity of the results.

In the course of the experiments it was discovered that carbonyl sulphide reacts extremely slowly with dry alcohol. Although this reaction is not recorded in the literature, the two substances are known to react in the presence of caustic potash : $COS + KOH + C_2H_5{\cdot}OH = H_2O + SK{\cdot}CO_2C_2H_5$. For a variety of reasons the reaction involved here is probably $COS + C_2H_5{\cdot}OH = CO_2 + C_2H_5{\cdot}SH$. The products gave the following tests : (i) The smell of the solution was like that of ethyl mercaptan; (ii) alcoholic mercuric chloride gave a white precipitate; (iii) after removal of hydrogen sulphide by evaporation, copper sulphate solution gave no precipitate, although with Bender's salt $SK{\cdot}CO_2C_2H_5$ it is said to give a white precipitate.

The rate of this reaction between carbonyl sulphide and alcohol was relatively so slow as not to disturb that between carbonyl sulphide and water in alcoholic solution.

3. *The Reaction in the Gas Phase.*—In these experiments there is a possibility that some carbonyl sulphide might dissolve in the liquid water and a slight reaction occur during the 1 minute's heating period. At the lowest temperature employed, however (180°), no interaction could be detected.

The results of the measurements in unpacked soda-glass vessels (cylinders, 12 cm. × 2·4 cm. diameter) are summarised below. The constants are calculated from the appropriate expression used in Section 2.

TABLE III.

(1) Temp. 277°.

[COS].	[H_2O].	COS changed, %.	*t*, mins.	$k \times 10^3$.
0·01923	0·0215	12·8	46·5	2·5
0·01799	0·0311	22·0	61·5	2·3
0·0199	0·0399	42·2	121·0	2·4
0·01013	0·0168	40·2	145·0	4·8
0·01819	0·0114	26·4	198·0	2·9
			Mean	3·0

(2) Temp. 300°.

[COS].	[H_2O].	COS changed, %.	*t*, mins.	$k \times 10^3$.
0·0201	0·0283	18·9	26·0	5·9
0·0151	0·0651	50·4	37·5	5·5
0·0187	0·0496	52·85	51·5	5·5
0·01714	0·0192	55·6	93·5	10·9
0·0191	0·0270	36·4	121·0	2·7
			Mean	6·1

(3) Temp. 344·5°.

[COS].	[H_2O].	COS changed, %.	*t*, mins.	$k \times 10^3$.
0·0119	0·0210	80·5	36·0	5·2
0·01295	0·0119	48·0	45·5	2·9
0·0124	0·0179	75·3	54·5	3·7
0·01147	0·0084	45·0	61	3·1
0·00876	0·0148	70·2	80·5	2·3
			Mean	3·4

(4) Temp. 382°.

[COS].	[H_2O].	COS changed, %.	*t*, mins.	$k \times 10^3$.
0·0230	0·0298	77·6	16·5	87
0·0166	0·0098	32·95	17·5	58·5
0·0172	0·0262	85·96	21·5	97
0·0190	0·0227	86·52	23·5	137
0·0150	0·0221	84·53	36·0	120
			Mean	100

(5) Temp. 244°.

[COS].	[H_2O].	COS changed, %.	*t*, mins.	$k \times 10^3$.
0·0208	0·0524	6·0	57	0·35
0·0214	0·0176	4·12	101	0·41
0·01095	0·0326	15·0	166	0·48
0·0274	0·0063	4·5	185·5	0·75
0·0123	0·0398	70·0	459	0·87
			Mean	0·57

(6) Temp. 295°.

[COS].	[H_2O].	COS changed, %.	*t*, mins.	$k \times 10^3$.
0·0160	0·054	33·6	149	3·7
0·0154	0·0223	25·0	60	3·9
0·0174	0·0184	6·1	37	1·8
0·0142	0·0069	38·6	207·5	7·5
			Mean	4·2

The constants in the above tables are not satisfactory, for the variation about the mean is sometimes considerable, but when it is remembered that the measurements are made over a temperature range of about 140°, with an alteration in the reaction rate of *ca.* 22-fold, the discrepancy is not so great. The bimolecular velocity constants are sensitive to small errors in *a* and *b*, and traces of water due to incomplete or uneven drying of the vessels may lead to serious errors. The plot of $\log_{10} k$ against $1/T$ (from the following data) is nearly a straight line, giving a value of the Arrhenius energy of activation of 25,720 cals.

T, Abs.	$10^3/T$.	*k*.	$\log_{10} k$.	*T*, Abs.	$10^3/T$.	*k*.	$\log_{10} k$.
517°	1·934	0·00057	$\bar{4}\cdot7559$	573°	1·745	0·0061	$\bar{3}\cdot7853$
550	1·818	0·003	$\bar{3}\cdot4771$	617·5	1·620	0·034	$\bar{2}\cdot5315$
568	1·761	0·0042	$\bar{3}\cdot6232$	655	1·527	0·10	$\bar{1}\cdot0000$

The irregularities just mentioned might be taken as implying the presence of a predominantly heterogeneous process. The reaction was therefore studied at 335° in both packed and unpacked vessels. The acceleration in a packed vessel, though definite, was not considerable. For a 5-fold increase in surface/volume ratio, these results imply the presence of *ca.* 15% heterogeneous reaction. In a vessel packed with powdered glass the acceleration was rather more marked.

Unpacked vessel.

[COS].	[H_2O].	COS changed, %.	*t*, mins.	$k \times 10^2$.
0·014	0·0213	74	60	2·6
0·021	0·011	79	50	3·2
0·016	0·052	81	30	2·0
			Mean	2·6

Packed vessel.

[COS].	[H_2O].	COS changed, %.	*t*, mins.	$k \times 10^2$.
0·0152	0·0306	87	41	3·96
0·0180	0·023	72	30	4·80
			Mean	4·4

DISCUSSION.

The experiments on the aqueous hydrolysis indicate an expression for the velocity constant $k = 1\cdot06 \times 10^{12} \times e^{-22.710/RT}$. If, however, in the calculation of E allowance is made for the variation of solvent viscosity with temperature, *i.e.*, $k = \text{const.} \times \eta \,.\, e^{-E'/RT}$, then $E' = 26{,}260$ cals. and $k = 5 \times 10^{16}\, \eta e^{-26{,}260/RT}$. The collision frequencies calculated by two independent methods (cf. Moelwyn-Hughes, *op. cit.*) are $1\cdot79 \times 10^{16}\, \eta$ and $2\cdot35 \times 10^{15}\, \eta$, against the experimental value of $5 \times 10^{16}\, \eta$. Buchböck's data give $k = 1\cdot74 \times 10^{17}\, \eta e^{-27.010/RT}$. It seems, therefore, that the disparity between calculated and observed reaction velocity is not as marked as has been supposed, but the measured rate is still in excess of that predicted. The approximate nature of the expressions for the collision frequencies may account for some divergence, but, on the other hand, the effect of acids suggests that catalytic influences of ions are involved.

The measured velocity constant of the bimolecular reaction in ethyl alcohol is considerably lower than that which would be expected for a reaction occurring at the temperatures involved with the measured energy of activation of 15,000 cals. The molecular diameters of carbonyl sulphide and water being taken as 5×10^{-8} and 1×10^{-8} cm. respectively, $k^{60°}_{\text{calc.}} = 16$ and $k^{75°}_{\text{calc.}} = 42$, the observed values being $2{\cdot}4 \times 10^{-5}$ and $6{\cdot}4 \times 10^{-5}$. For a water diameter of 10^{-7} cm. the discrepancy is diminished by about 5-fold. An error of several thousand calories in the determined value of E—though very improbable—would still leave a considerable discrepancy between the calculated and the measured constants.

If it is assumed as a first approximation that the gaseous process measured is not seriously affected by a concurrent heterogeneous process, similar calculations show that the calculated exceeds the observed rate by some powers of ten. For instance, if $E = 25{,}500$ and $\sigma_{\text{water}} = 5 \times 10^{-8}$ cm., at 295° the ratio $k_{\text{calc.}}/k_{\text{obs.}} = 2{\cdot}4 \times 10^4$. If the measured energy of activation is lower than that of the true gas reaction, the discrepancy will be smaller; it is, however, unlikely that E will be greater than about 30,000 cals. and at the same time the true rate of the homogeneous process will have to be lower than the rate measured.

It thus appears that (1) the rate of aqueous hydrolysis of carbonyl sulphide is somewhat higher than would be " calculated "; (2) in alcoholic solution the interaction of carbonyl sulphide and water is bimolecular, E is much lower than in the aqueous hydrolysis, and the rate is " abnormally " low; (3) in the gas phase E is higher and the rate is still " abnormally slow "; (4) ionic species appear to have catalytic influence upon the reaction. These results suggest that, in general, the reaction between the two substances is " slow " and only becomes " normal " when an ionic atmosphere is present.

The hydroxyl ion appears to be particularly able to facilitate some process essential to the reaction. If in the gas phase and in alcohol the bimolecular process is $COS + H_2O \longrightarrow CO_2 + H_2S$, whereas in aqueous solution there is superposed the concurrent reaction $COS + H_2O + OH' \longrightarrow HCO_3' + H_2S$, then in aqueous solution

$$\text{rate} = k_1\,[COS][H_2O] + k_2\,[COS][H_2O][OH']$$

and if the first term is much less than the second

$$k_2 = -\frac{d\,[COS]}{dt} \cdot \frac{1}{[COS][H_2O][OH']} = \frac{k_1}{[OH']}$$

Then in the absence of added acids, approximately, $k_2 = k_1/\sqrt{K_w}$ so that $d \log k_2/dT = d \log k_1/dT - \frac{1}{2}d \log K_w/dT$ and therefore $E_2 = E_1 - \frac{1}{2}Q$ where Q is the heat of ionisation of water, *viz.*, 13,700 cals. The observed values of E_1 and E_2 are 22,700 and 14,900 cals.

On the other hand, there are reasons for believing that the hydroxyl ion may not be unique as a catalyst, and there may here be an example of " basic catalysis." Attempts to study the reaction in buffer solutions have so far proved fruitless owing to deposition of sulphur and other experimental difficulties.

SUMMARY.

The kinetics of the reaction between carbonyl sulphide and water occurring (*a*) in aqueous solution, (*b*) in alcohol, and (*c*) in the gas phase, have been examined. In the gas phase and in alcohol the bimolecular reaction observed is some powers of ten slower than would be calculated from theory by assuming the observed energy of activation. In aqueous solution, the measured rate is slightly greater than that calculated. The reaction is catalysed by many substances and ions, of which the hydroxyl ion is perhaps the most effective. In aqueous solution there may be an example of " basic catalysis."

THE OLD CHEMISTRY DEPARTMENT,
THE UNIVERSITY MUSEUM, OXFORD.

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