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A STUDY OF THE RECOMBINATION REACTIONS OF FREE ATOMS BY THE THERMAL ANALYSIS OF BUDDE-EFFECT. II.

The Recombination of Bromine Atoms.

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The velocity-constants of recombination reactions of bromine atoms $Br+Br+M=Br_2+M$ (M: third molecules or atoms) have already been measured by several investigators.[1] The absolute values obtained by them, however, are different from one another by several times or more. It seems to be significant that the constants are measured by an entirely different method from those adopted by them.

In the previous papers[2] it was shown that the Budde-effect usually observed in halogens occurred also in hydrogen and that the recombination-constant of hydrogen atoms could be measured by applying the method of thermal analysis to the effect. In this investigation the analogous method was to be applied to the case of bromine. The matters, however, were not so simple in this case; it was unexpectedly found that the pressure change due to adsorption and desorption was superimposed on that due to the heat of recombination. Therefore, these two effects are first separately studied and then the recombination-constants in the gaseous phase are obtained.

Experimental.

Materials. Br_2: Brom "Kahlbaum" zur Analyse was first treated with KBr and then distilled three times in vacuum and finally stored with purified P_2O_5. O_2: oxygen which was obtained by electrolysis of KOH solution was passed successively through KOHconc., Pd-asbestos and a trap cooled with liquid air, and stored on P_2O_5. N_2: nitrogen was obtained from NaN_3 and stored on P_2O_5. Pure P_2O_5 (not including lower oxides) for bromine was prepared and used.

Apparatus: The apparatus used was similar to that in the previous papers and the details are omitted here. Light source was a low-pressure mercury lamp operated with 3–10amp. The light was passed successively through a lens, a shutter, a $CuSO_4$–NH_4OH filter and a lens. The reaction vessel was a cylindrical

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[1] H.J. Schumacher, *Chemische Gasreaktionen* (1938), p. 324.

[2] S. Shida, *Proc. Imp. Acad. Tokyo*, 17, 495 (1942); *Rev. Phys. Chem., Japan*, 16, 44 (1942).

form and made of the ordinary glass (D: 55mm, L: 70mm, volume 140cc). The pressure changes were recorded on bromide papers by means of an electric-capacity-differential-manometer and an electro-magnetic oscillograph. The sensitivity of the manometer was $1-3\times10^{-3}$ mmHg/mm. At the place exposed to bromine, any organic grease was not used at all, and sticky phosphoric acid was used with specially deviced taps. The surface exposed to bromine of the condenser was platinized.

Procedure. The increases in pressure on illumination and the decreases after shutting off the light were recorded and analysed. The period of illumination was $3\sim50$ sec. The total pressures of gas mixtures were 200, 300 and 400mmHg in the case of O_2–Br_2 mixtures (denoted by O_2–200, O_2–300 and O_2–400 respectively) and 440mmHg in the case of N_2–Br_2 mixture (denoted by N_2–440), including 20mmHg of Br_2 in every case.

Method of thermal analysis and heat of reaction. The equation of the thermal analysis of reaction velocity in a gaseous reaction originated by Professor S. Horiba is

$$K\frac{dx}{dt}=\frac{d(\Delta P)}{dt}+k(\Delta P) \qquad (1)$$

where x is the number of moles of the reacting substance in unit volume, t the time, ΔP the increase in pressure (mmHg) due to the heat of reaction, k the cooling-constant and K a constant which is calculated by $K=\frac{nRQ}{cV}$, where c is the heat capacity of unit volume and n the number of moles of the gas in the reaction vessel, R the gas-constant, Q the heat of reaction per mole, and V the volume. In the present case $x=[Br]$. This method was applied to the after-effect in the pressure curve after shutting off the light.

Let the energy of one Einstein light-quanta absorbed by bromine molecules be E and the heat of dissociation D. Then in the photo-stationary state during illumination the heat liberated is equal to that absorbed, and the heat of reaction $Q_L=E/2$. After shutting off the light, however, since the heat liberated is equal to that of recombination of surviving atoms, the heat of reaction $Q_D=D/2$, for the supply of the kinetic energy $(E-D)/2$ stops as soon as the light was shut off. Calculating E from the intensity distribution of mercury lines and the absorption-coefficient, the pressure and the depth of the layer of bromine, we take $Q_L=E/2=37$Kcal, while $Q_D=D/2=22.5$Kcal.

Experimental Results.

General form of pressure curves. In the previous experiments on hydrogen, the pressure curves showed simple forms of heating and cooling except the short periods immediately after the start of the exposure and the shutting off the light. In the present case, however, when the gas was illuminated the pressure increased and attained a maximum value. Then it began to decrease, finally becoming a slightly smaller stable value.[3] Similarly, when the light was shut off, the pressure decreased below the original value and attained a minimum value, and then it began to increase again and finally returned to the original value. When the period of illumination was short (3sec), this abnormality was very small, but as the period became long (10sec) it showed definitely the very phenomenon.

These circumstances are shown in Fig. 1 diagrammatically.

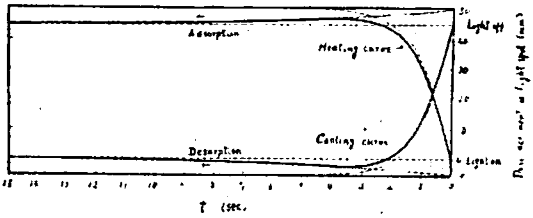

Fig. 1. General Form of the Budde-effect in Bromine.

A) Wall reaction.

Order of the process of adsorption and desorption. As will be discussed later, this abnormality seems to be caused by the adsorption of bromine atoms and by the desorption of bromine molecules. Now, the adsorption and desorption curves are extended to the moments of the exposure and of the shutting off the light respectively and let the deviation of the point on them at any moment from the level of the steady state be represented by Δp and that at $t=0$ by $\Delta p'_0$. The $\Delta p \sim t$ curves are shown in Fig. 2. In the same figure log Δp's are also plotted against t. In both cases of adsorption and desorption log Δp's fall on straight lines well, showing that these two curves are logarithmic ones. Calculating the constants by $k=2.3\,(\log \Delta p'_0 - \log \Delta p)/t$, we obtain $k=0.134$ from the adsorption curve and $k=0.148$ from the desorption curve, which almost coincide with each other.

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[3] Strictly speaking, this is not true so far as the exposure curve is concerned, for the pressure continued to decrease slowly even in the apparent stationary state.

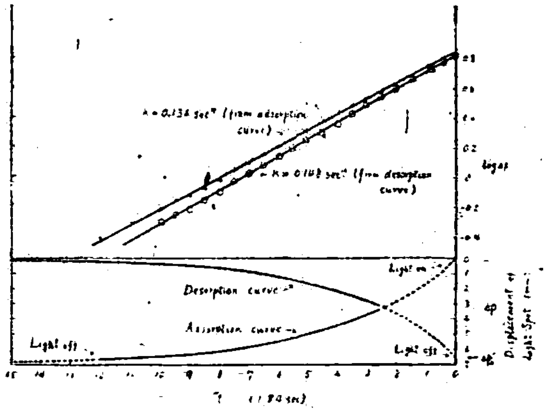

Fig. 2. Adsorption and Desorption Curves, O_2-400.

These results are interpreted as follows. The adsorption of bromine atoms proceeded at an almost constant velocity and the desorption of bromine molecules at a velocity proportional to the quantity of the adsorbed bromine. The constants of desorption obtained from the experiments on O_2–400 are given in Table 1. In all experiments almost the equal values are obtained irrespective of the period of illumination. $k=0.14\text{sec}^{-1}$ corresponds to a half-value-period of 4.8sec and a mean-life-period of 6.9sec.

Table 1. Desorption-constants.

Exp. No.	k (sec⁻¹)		Period of illumination (sec.)
	from desorption curves	from adsorption curves	
3	0.148	0.134	12
4	0.143	—	24
5	0.147	0.125	20
6	0.140	0.139	48
7	—	0.140	26
Av.	0.145	0.137	

Quantity of adsorbed bromine in equilibrium. In the example shown in Fig. 2 the light was shut off (at $t=12$) before the exposure curve attained its stationary state, *i.e.*, at a time when the equilibrium between adsorption and desorption was not yet established. The quantity of the adsorbed bromine in equilibrium, Δp_0, that is, the $\Delta p'_0$ which would be obtained if equilibrium was established, can be calculated from the equation $\log \Delta p_0/(\Delta p_0-\Delta p'_0)=kt/2.3$ where t is the period of illumination. Δp_0's are of the magnitude of 0.006–0.015mmHg under the present experimental conditions.

Taking the above example again to be $\Delta p_0 \doteqdot \Delta p'_0 = 7$mm (displacement of light spot) = 0.01mmHg and assuming 4×10^{-8}cm as a diameter of the bromine molecule, it follows that this quantity of bromine may occupy an area of 80cm^2 on the wall. Since the total area of the wall was about 150cm^2, it is inferred that about a half of the surface of the wall was covered with the adsorbed bromine.

Velocity of adsorption. As in equilibrium state the velocity of adsorption is equal to that of desorption, the former is given by $k(\Delta p_0)$. In the above example this amounts to $0.144 \times 0.01 = 0.0144$mmHg/sec. The velocity of the wall reaction, u_0, which is equal to the velocity of adsorption of bromine atoms is given by $u_0 = 2k(\Delta p_0)$.

Dependence of Δp_0 on the period of illumination. If the adsorption curve is really of the first order and has the same constant as that of the desorption curve, the quantity of the adsorbed bromine in equilibrium should be independent of the period of illumination. In fact, however, the former increased slowly with the latter; for instance, in the case of O_2–400 Δp_0 was 0.0076mmHg when the period of illumination was 12.3sec, while it increased to 0.0106mmHg when the period was doubled, 24.6sec.

B) Homogeneous reaction (Reaction velocity after shutting off the light).

As mentioned above the reaction velocity after shutting off the light was measured from the pressure curve by use of equation (1). An example of the analysis is given in Table 2. For convenience sake the displacement of light spot ΔG is used instead of Δp, and $v = \frac{d[Br]}{dt}$ expressed in mmHg/sec instead of mol/sec. cc.. As seen in the table the cooling-constant k increases linearly with ΔG; the values of k for $t = 0 \sim 9$ are determined by extrapolation from those for $t = 10 \sim 16$ when the after-effect vanishes. k's for t larger than 17 are constant, 0.91.[4]

The results obtained for O_2–300 under the same condition and for N_2–440 with different intensities of the light are given in the second lines in Tables 4, 5, 6, and 7. It is seen from the tables that the reactions of the free atoms continued for $0.3 \sim 0.5$ sec after the shutting off the light in every case.

C) Relations between wall reactions and homogeneous reactions.

In Table 3 the reaction velocities in a stationary state on the wall and in the homogeneous phase, which are obtained by the method described in **A)** and **B)**, respectively, are summarized with their ratios.

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[4] In general, the ΔP from which the cooling-constant begin to increase is about $\Delta P_0/2$ in every curve obtained with different gas mixture, pressures and light intensities, where ΔP_0 is the expansion in stationary state.

Table 2. O_2-300 No. 4 Sensitivity of manometer: 1.9×10^{-3} mmHg/mm.

t (0.0483 sec)	ΔG (mm)	$-\frac{d(\Delta G)}{dt}$ (mm/sec)	$\frac{1}{\Delta G}\frac{d(\Delta G)}{dt}$ (sec^{-1})	k (sec^{-1})	$k(\Delta G)$ (mm/sec)	$\frac{d(\Delta G)}{dt}+k(\Delta G)$ (mm/sec)	$v = \frac{d[Br]}{dt}$ (10^{-3}mmHg/sec)
0	35.2[5]	0	0	1.28	45.4	45.4	(v_0) 3.74
1	34.2	31.1	0.19	1.26	43.2	12.1	1.62
2	32.5	34.2	1.05	1.22	39.7	5.5	0.74
3	30.8	33.5	1.07	1.19	36.7	3.5	0.46
4	29.4	31.1	1.07	1.17	34.1	3.0	0.40
5	27.7	29.2	1.06	1.13	31.3	2.1	0.28
6	26.5	28.0	1.04	1.10	29.2	1.2	0.22
7	25.1	26.4	1.04	1.08	27.1	0.7	0.14
8	23.9	24.9	1.03	1.06	25.3	0.4	0.06
9	22.7	23.4	1.03	1.04	23.6	0.2	0.04
10	21.7	22.1	1.02	1.02	22.1	0	0

Table 3.

Exp. No.	Reaction velocity (10^{-3}mmHg/sec)			Ratio $\frac{v_0}{u_0}$
	Homogeneous v_0	Wall u_0	Total v_0+u_0	
O_2-200 No. 3	5.9	2.8	8.7	2.1
" No. 8	3.1	1.7	4.8	1.8
O_2-300 No. 4 and 5	3.7	2.0	5.7	1.9
N_2-440 No. 14	5.5	3.6	9.1	1.5
" No. 11	3.0	3.0	6.0	1.0

From the table it is seen that, first, the ratio (homogeneous reaction/wall reaction) increases with the total reaction velocity or the light intensity, secondly, N_2 is less effective than O_2 in suppressing the wall reaction and, thirdly, the difference of total pressure has no appreciable influence on the ratio.

D) Total reaction velocity and recombination-constants.

The total reaction velocity is the sum of those on the wall and in the homogeneous phase. If we assume that the velocity of the wall reaction is proportional to [Br] in the homogeneous phase and that of the homogeneous recombination to $[M][Br]^2$, the total reaction velocity after shutting off the light is expressed by

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[5] ΔG's are measured by taking the minimum point of the cooling curve as a base and contain the displacement of the opposite direction due to the adsorption-effect, which are, however, small when the period of illumination is short.

The ΔG's at small t's contain also slight increase in pressure due to the dissociation of bromine molecules and the corrections for it, which are only 0.2 mm even at t=0, have been made to the ΔG's at t=0, 1 and 2.

$$-\frac{d[Br]}{dt}=C[M][Br]^2+C_W[Br]^{6)} \qquad (2)$$

and

$$\begin{aligned} v&=C[M][Br]^2\\ v_0&=C[M][Br]_0^2\\ u_0&=C_W[Br]_0 \end{aligned} \qquad (3)$$

Integrating equation (2), we have

$$C_W=\frac{1}{t}\log\frac{[Br]_0\left\{C_W+C[M][Br]\right\}}{[Br]\left\{C_W+C[M][Br]_0\right\}}$$

Eliminating C, [Br] and $[Br]_0$ from (3) and (4), we get

$$C_W=\frac{1}{t}\log\frac{\sqrt{\frac{v_0}{v}}+\frac{v_0}{u_0}}{1+\frac{v_0}{u_0}} \qquad (5)$$

On the one hand from (3)

$$C=\frac{C_W^2}{[M]}\left(\frac{v_0}{u_0}\right)\frac{1}{u_0} \qquad (6)$$

Since v_0 and u_0 are obtained experimentally, we can calculate C_W from (5) and C from (6). The constants obtained are given in Tables 4, 5, 6 and 7.

Table 4. O_2-300 No. 4.

$v_0=3.74\times10^{-3}$mmHg/sec$=1.1\times10^{-10}$mol/sec. cc.

$u_0=2.02\times10^{-3}$mmHg/sec$=0.59\times10^{-10}$mol/sec. cc.

$\frac{v_0}{u_0}=1.9$; $[M]=1.76\times16^{-5}$mol/cc.

t (0.0483 sec)	v (10^{-3}mmHg/sec)	C_W (sec^{-1})	C ($10^{15}mol^{-2}.cc^2. sec^{-1}$)
0	3.74	—	—
1	1.62	3.48	10.9
2	0.74	3.76	12.8
3	0.46	3.40	10.5
4	0.40	2.79	7.0
5	0.28	2.73	6.8
6	0.22	2.86	7.4
7	0.13	3.16	8.7
		Av. 3.18	9.2

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6) In this calculation C_W's assumed to be a constant independent of the time, but strictly speaking this is not correct because convection decays with time. The apparent decrease of C_W and C with the lapse of time as seen in the tables is probably due to this fact. The error due to the assumption may be small when t is small.

Table 5. O_2-300 No. 5

Under the same condition as No. 4

t (0.0303 sec)	v (10^{-3}mmHg/sec)	C_W (sec^{-1})	C ($10^{15}mol^{-2}.cc^2. sec^{-1}$)
0	3.82	—	—
1	2.21	3.26	9.7
2	1.39	3.38	10.1
3	0.87	3.55	11.5
4	0.60	3.50	11.3
5	0.39	3.58	11.7
6	0.25	3.69	12.5
7	0.24	3.36	10.4
8	0.20	3.20	9.4
		Av. 3.44	11.0

Table 6. N_2-440 No. 11.

$v_0=2.95\times10^{-3}$mmHg/sec$=1.73\times10^{-10}$mol/sec. cc.
$u_0=2.96\times10^{-3}$mmHg/sec$=1.74\times10^{-10}$mol/sec. cc.
$v_0/u_0=1.0$; $[M]=2.65\times10^{-5}$mol/cc.

t (0.0525 sec)	v (10^{-3}mmHg/sec)	C_W (sec^{-1})	C ($10^{15}mol^{-2}.cc^2. sec^{-1}$)
0	2.95	—	—
1	1.18	4.4	4.1
2	0.52	5.1	5.3
3	0.28	4.8	4.7
4	0.20	4.3	3.83
5	0.14	4.0	3.3
6	0.10	3.7	2.8
		Av. 4.4	4.0

Table 7. N_2-440 No. 14.

$v_0=5.50\times10^{-3}$mmHg/sec 3.22×10^{-10}mol/sec. cc.
$u_0=3.6\times10^{-3}$mmHg/sec$=2.1\times10^{-10}$mol/sec. cc.
$v_0/u_0=1.5$: $[M]=2.65\times10^{-5}$mol/cc.

t (0.0764 sec)	v (10^{-3}mmHg/sec)	C_W (sec^{-1})	C ($10^{15}mol^{-2}$. cc. sec^{-1})
0	5.50	—	—
1	1.74	3.56	3.35
2	0.50	4.28	4.8
3	0.30	3.64	3.5
4	0.18	3.39	3.0
		Av. 3.7	3.7

Discussions of the Results.

What is the cause of the abnormality in the pressure curve? Ritchie and Smith[7] have already reported that the similar abnormality as that found here existed in the Budde-effect of Cl_2, and they ascribed it to the adsorption of Cl_3 molecules on the wall by convection. Rabinowitsch and his collaborators concluded that in their experimental conditions the convection did not complicate the experimental results on the dissociation of bromine molecules. However, Steiner and Hilferding[9] pointed out that the wall reaction, probably due to the convection, existed even at the total pressures of 300mmHg in the photochemical synthesis of HBr and emphasized the significance of the convection. In the present case the abnormality of the pressure curves and the dependence of cooling-constants on ΔP show the occurrence of the convection. It is obvious that the abnormality is neither of thermal nature nor due to the oxidation of bromine. The author concludes that it is due to the adsorption of some substance, probably bromine atoms, on the wall by the convection, because the arrival of the atoms by diffusion are quite improbable at the pressures used.

What is the desorbing substance? From the fact that the mean-life of the adsorbed substance was relatively long (about 7 sec) and that the desorption process was of the first order, it is inferred that the adsorbing substance was bromine molecules and that the rate-determining step was not the recombination of bromine atoms but the evaporation of bromine molecules.

The fact that the quantity of the adsorbed bromine in equilibrium increased with the period of illumination, as well as the fact that the exposure curve continued to fall slowly in the apparently stationary state, both indicating an apparent increase of the area of adsorbed surface, is due probably either to the occurrence of the multiple adsorption[10] or to the expansion of the adsorbed surface from the upper part of the wall of the reaction vessel to the lower part.

The recombination-constants obtained in this investigation are compared with those of other investigators[11] in Table 8. For the sake of reference the constants for A and H_2 as the third bodies are also listed. The author's value for O_2 agrees well with that obtained by Rabinowitsch, and for N_2 it is between of those obtained by Rabinowitsch and by Steiner.

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7) M. Ritchie and R.L. Smith, *J. Chem. Soc.*, 394 (1940).

8) E. Rabinowitsch, *Z. Phys. Chem.*, **B 33**, 275 (1936).

9) K. Hilferding and W. Steiner, *Z. Phys. Chem.*, **B 30**, 399 (1935).

10) The upper part of the wall where bromine atoms attained most easily is saturated at first, and thereafter excess atoms adsorb there making multiple layer.

11) As respect to the original literatures refer to 1).

Table 8. $C_M(10^{15}\text{mol}^{-2}.\ \text{cc}^2.\ \text{sec}^{-1})$: $-\frac{d[Br]}{dt}=C_M[M][Br]^2$

Authors		Steiner and Hilferding	Jost	Rabinowitsch and Lehmann	Smith, Ritchie and Ludlam	Ritchie	Present author
Methods		HBr-synthesis	HBr-synthesis	Decrease of absorption coeff. of Br_2	Magnitude of Budde-effect	HBr-synthesis	Thermal analysis of Budde-effect.
M	A_2	0.22		4.7	A	H_2	
	H_2	2.5	11.4	8.0	$\wedge$ H_2	$\wedge$ A	
	N_2	1.6		9.1	$\wedge$ N_2	$\wedge$ N_2	3.9
	O_2			11.5	$\wedge$ O_2	$\wedge$ O_2	10.0

From the recombination-constants obtained in this investigation by use of the ordinary method of calculation the ratio of the effective (recombining) collisions to the total number of collisions are calculated. It is shown that in one atmosphere in 1000 collisions 2.7 in the case of O_2 mixed and 1.1 in the case of N_2 mixed, are recombining ones. On the other hand, calculating the number of triple collisions $(Br+Br)+M$, assuming a collision period $\tau=1.5\times10^{-13}$ sec,[12] we know that one in 1000 double collisions is a trible one. It is concluded, therefore, that almost every triple collision is a recombining one.

Summary and Conclusions.

The pressure curves of the Budde-effect in bromine mixed with N_2 and O_2 have been recorded and analysed. The following conclusions are drawn from the results.

(1) The pressure curves are not simple heating and cooling curves, but involve a maximum and a minimum, which are interpreted as a result of the occurrence of adsorption.

(2) The desorption process is of the first order. The substance adsorbed is supposed to be the bromine molecule, the life-time of which is about 7 sec.

(3) Under the experimental conditions adopted, the wall reaction by convection occurs at a rate of the same order of magnitude as the homogeneous reaction.

(4) By the thermal analysis of the pressure curves after shutting off the light, the decay of the homogeneous recombination has been measured and the recombination-constants of bromine atoms obtained.

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[12] This value is obtained from the mean thermal velocity and a collision path, the latter of which is assumed to be approximately equal to the collision diameter of bromine atom.

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