

determined and the atomic parachor for germanium calculated. Good agreement with the value predicted by Sugden was observed. The anomaly obtained in the case of germanium tetraethoxyl is explained by the difference in structure.

ITHACA, NEW YORK

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 299, AND FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH]

THE REACTION RATE OF POTASSIUM IODIDE WITH DIBROMIDES OF THE ETHYLENE BROMIDE TYPE

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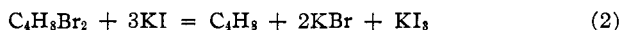
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Introduction

In a method for analyzing mixtures of the three normal butenes it was necessary¹ to utilize the specific reaction rate constants of the corresponding dibromobutanes with potassium iodide in methanol at 75°. The stoichiometric equation involved was expressed by equation (1)



Kinetically the reaction was readily followed by the titration of the iodine. It was pointed out in this article that the equation could equally well, and more probably should, have been expressed as follows



which differs from the first form only by equation (3)



In an aqueous solution this reaction of iodine with potassium iodide takes place completely; but in an alcoholic solution this is perhaps questionable and for this reason the first form of the dibromide reaction was used in the previous paper. In this article, however, are given calculations made from the experimental data of van Duin² which show that equation (3) is evidently complete even in alcoholic solutions and, therefore, that one mole of dibromide³ reacts with three moles of potassium iodide according to equation (2). Hence this stoichiometric equation should be the basis for the differential equations expressing the velocity of the reaction.

However, the use of either equation would not alter the result previously found, namely, that kinetically the reaction is one of the second order, the rate being proportional to the first power of the concentrations of both

¹ Dillon, Young and Lucas. *THIS JOURNAL*, **52**, 1953 (1930).

² Van Duin, *Rec. trav. chim.*, **43**, 341 (1924).

³ The term "dibromide" as used herein is understood to mean only ethylene bromide and its homologs, or their substituted derivatives.

the dibromobutane and the potassium iodide.⁴ This is in accord with the results of Biilmann,⁵ who found that the reaction of 2,3-dibromopropanoic acid with potassium iodide in dilute sulfuric acid at 25° was also of the second order. In addition it may be mentioned that Slator⁶ has found that the reactions of ethylene bromoiodide and ethylene iodide with potassium iodide are very rapid. From this it follows that the comparatively slow reaction of ethylene bromide, presumably involving either one or both of the preceding compounds as an intermediate product, would not be of the third order, but of the first or second. On the other hand, van Duin^{2,7} discusses the work of Biilmann and Slator, rejects their conclusions and reports that the reaction of dibromides⁸ with potassium or sodium iodide is of the third order.

For this reason, it was deemed desirable to extend somewhat the investigations previously described. The work was aided financially by a grant made to Professor A. A. Noyes by the Carnegie Institution of Washington. The author is indebted to Professor Howard J. Lucas for his valuable criticisms and suggestions.

Experimental

The procedure and technique used in the rate measurements are as described in the previous work.¹ To this description the following further details should be added. The purified ethylene and propylene bromide boiled, respectively, at 130.3–130.5° and 140.0° at 743–744 mm. The small corrections for the disappearance of iodine due to its reaction with impurities remaining in the purified alcohol solvents were made with greater accuracy for the experiments involving short intervals of time. For the preparation of the reaction mixtures the dried potassium iodide was weighed into the volumetric flask and the salt completely dissolved by shaking with almost the required volume of solvent. The solution was brought to a temperature of 20° in a thermostat, the required amount of dibromide was added from a weighing pipet and the solution quickly made up to the exact volume. The solution was next pipetted into the reaction tubes. They were then sealed, placed in a light-tight thermostat which was regulated to within $\pm 0.03^\circ$ of the desired temperature, removed at appropriate intervals and analyzed by titration with 0.02

⁴ Since the potassium iodide concentration is seven to twelve times that of the dibromide, calculation of the second order constant according to either stoichiometric equation leads to substantially the same numerical value of the constant. (See Table IV.)

⁵ Biilmann, *Rec. trav. chim.*, **36**, 319 (1917).

⁶ Slator, *J. Chem. Soc.*, **85**, 1697 (1904).

⁷ Van Duin, *Rec. trav. chim.*, **45**, 345 (1926).

⁸ Van Duin tested the order only with ethylene bromide but his conclusions were generalized for all dibromides.

N thiosulfate. The second and third order specific reaction rate constants were calculated from the analytical data by means of the usual integrated expressions for k_2 and k_3 .⁹ They are, on the basis of equation (2)

$$k_2 = \frac{2.303}{t(a-3b)} \log_{10} \frac{b(a/b-3\varphi)}{a(1-\varphi)} \quad (4)$$

$$k_3 = \frac{1}{t(a-3b)^2} \left[-\frac{3\varphi(a-3b)}{a(a/b-3\varphi)} + 2.303 \log_{10} \frac{b(a/b-3\varphi)}{a(1-\varphi)} \right] \quad (5)$$

where t is the time in hours, a and b are the initial concentrations of potassium iodide and dibromide, respectively, in moles per liter at 20° and φ is the fraction of the dibromide which had reacted at the time t . The values of k_2 and k_3 are thus expressed in (hours)⁻¹ (moles/liter)⁻¹ and (hours)⁻¹ (moles/liter)⁻², respectively.

The times involved in the rate measurements were always taken from the time of immersion of the tubes in the thermostat. The reactions were in all cases so slow at 20° that the interval between the addition of the dibromide and the insertion of the tubes into the thermostat, namely, twenty to thirty minutes, was entirely negligible. The concentration of the dibromides was kept essentially constant throughout the work since the rate is undoubtedly proportional to the first power of this value.^{1,2,6} Measurements were made with at least two different initial concentrations of the potassium iodide in order to determine the dependence of the reaction rate upon the concentration of this reactant.

Results and Discussion

Influence of Iodine upon the Rate of Reaction.—This influence is shown in Table I. Thus, when either second or third order constants are calculated on the basis of the stoichiometric equation (1) the presence of some initial iodine in the reaction mixture leads to lower values of the constants than in the absence of this initial iodine (*e. g.*, 2.68 and 0.648 as against 3.04 and 0.727 without the iodine). As may be seen, these values differ by approximately 10% which corresponds with the decrease in iodide ion concentration brought about by the introduction of iodine into the reaction mixture in experiment B. However, when second order constants are calculated on the basis of equation (2) in which the formation of triiodide ion is taken into account, the values are practically identical (*e. g.*, 0.742 and 0.734). It is perhaps needless to say that in these last calculations a correction is necessary for the effect of this initial iodine upon the concentration of the iodide ion. The results indicate that equation (2) is the correct stoichiometric form to use in the calculation of the specific rate constants for this reaction.

⁹ The expression for k_3 in the preceding article¹ (equation 17) is incorrectly printed, the logarithm applying only to the first term within the brackets.

TABLE I
INFLUENCE OF TRIIODIDE FORMATION ON THE REACTION RATE OF $p\text{-NaSO}_3\text{C}_6\text{H}_4\text{CHBr-CHBrCOONa}$ WITH POTASSIUM IODIDE^a

KI, 0.25 M Dibromide, 0.025 M	Time, min.	k_2^b	Constants $\times 10^3$ k_3^c	k_2^d
A. Without initial iodine	931	3.03	0.742	0.749
	1721	3.06	.741	.752
	2586	3.08	.718	.739
	3856	2.99	.705	.727
	Average	3.04	.727	.742
B. With initial iodine ($\cong 0.1$ initial KI)	932	2.75	0.675	0.757
	1724	2.71	.659	.745
	2587	2.68	.644	.735
	3858	2.58	.613	.705
	Average	2.68	0.648	0.734
Difference between A and B, %		12.6	11.5	1.1

^a These experimental data were taken from the work of van Duin (Ref. 2).

^b On the basis of equation (1):

$$k_3 = \frac{1}{l(a-2b)^2} \left[-\frac{2\phi(a-2b)}{a(a/b-2\phi)} + 2.303 \log_{10} \frac{b(a/b-2\phi)}{a(1-\phi)} \right]$$

The values were calculated and reported by van Duin.

^c On the basis of equation (1)

$$k_2 = \frac{1}{l(a-2b)} \log_{10} \frac{b(a/b-2\phi)}{a(1-\phi)}$$

^d On the basis of equation (2): k_2 from equation (4).

Order and Temperature Coefficients of the Reaction Rates.—The detailed data relating to the reaction rate measurements of ethylene bromide with potassium iodide in methanol at 30.00, 59.72 and 74.93° are given in Table II. Table III gives the data for propylene bromide at 59.72 and 74.93°. The values of k_2 and k_3 were calculated from equations (4) and (5), respectively. The same terms and units are used in these tables

TABLE II
REACTION RATE CONSTANTS OF ETHYLENE BROMIDE WITH POTASSIUM IODIDE IN 99% METHANOL
Temp. 30.00°

KI, 0.2152 M C ₂ H ₄ Br ₂ , 0.02450 M				KI, 0.1469 M C ₂ H ₄ Br ₂ , 0.02529 M			
Time	ϕ	k_2	k_3	Time	ϕ	k_2	k_3
91.4	0.1757	0.0101	0.0484	90.7	0.1191	0.0099	0.0702
100.8	.1925	.0102	.0490	100.0	.1318	.0103	.0711
115.3	.2154	.0101	.0490	114.5	.1485	.0100	.0712
126.2	.2340	.0102	.0496	125.4	.1610	.0100	.0715
136.9	.2498	.0102	.0497	136.2	.1750	.0101	.0728
151.5	.2719	.0102	.0500	150.8	.1911	.0101	.0731
174.4	.3061	.0103	.0508	173.7	.2163	.0102	.0740
Average		0.0102	0.0495	Average		0.0101	0.0720

TABLE II (Concluded)

Temp. 59.72°				Temp. 59.72°			
Time	ϕ	k_2	k_3	Time	ϕ	k_2	k_3
8.25	0.3985	0.299	1.46	8.25	0.2863	0.292	2.10
11.25	.4914	.299	1.49	11.25	.3630	.296	2.19
13.25	.5420	.297	1.50	13.25	.4099	.299	2.26
15.25	.5909	.299	1.54	15.50	.4572	.302	2.33
17.25	.6332	.301	1.57	17.25	.4890	.303	2.37
20.25	.6823	.298	1.57	20.25	.5396	.305	2.46
23.25	.7268	.298	1.61	23.25	.5795	.302	2.49
Average		0.299	1.53	Average		0.300	2.32

Temp. 74.93°			
Time	ϕ	k_2	k_3
1.00	0.2347	1.29	...
1.25	.2884	1.32	...
1.67	.3661	1.35	...
3.00	.5564	1.39	...
Average		1.34	

TABLE III

REACTION RATE CONSTANTS OF PROPYLENE BROMIDE WITH POTASSIUM IODIDE IN 99% METHANOL

Temp. 59.72°				Temp. 59.72°			
Time	ϕ	k_2	k_3	Time	ϕ	k_2	k_3
17.50	0.04365	0.0118	0.0540	21.00	0.04331	0.0116	0.0641
22.08	.05381	.0116	.0531	25.00	.05110	.0115	.0640
25.50	.06175	.0116	.0530	30.83	.06150	.0114	.0630
31.00	.07306	.0113	.0520	35.83	.06648	.0106	.0590
41.75	.09432	.0110	.0505	45.25	.08337	.0107	.0595
46.32	.1031	.0109	.0502	51.00	.09117	.0105	.0582
51.58	.1133	.0108	.0499	57.00	.1018	.0104	.0587
56.58	.1228	.0107	.0497	66.00	.1286	.0117	.0658
66.00	.1441	.0110	.0509	Average		0.0111	0.0615
Average		0.0113	0.0515				

Temp. 59.72°				Temp. 74.93°			
Time	ϕ	k_2	k_3	Time	ϕ	k_2	k_3
21.00	0.03651	0.0118	0.0788	17.87	0.1952	0.0580	..
25.00	.04143	.0114	.0773	20.50	.2179	.0575	..
30.83	.04861	.0109	.0742	26.08	.2688	.0581	..
35.83	.05537	.0108	.0736	31.00	.3105	.0586	..
45.25	.06911	.0108	.0736	42.05	.3907	.0585	..
51.00	.07670	.0107	.0731	56.75	4.800	.0584	..
57.00	.08511	.0107	.0734	Average		0.0582	
66.00	.1017	.0111	.0769				
Average		0.0110	0.0751				

as indicated previously for these two equations except that the concentrations of potassium iodide and dibromide are indicated by KI and $C_2H_4Br_2$ (or $C_3H_5Br_2$) instead of by a and b . As is evident, there is good agreement among the second order values both in individual experiments and in ones with different initial iodide concentrations, whereas the third order values show wide deviations.

Since the preceding section indicates that equation (2) is the correct one for these reactions in alcoholic solutions, this same method of calculation has been applied to the data previously published on the dibromobutanes.¹ The values of the reaction constants for all of the compounds investigated are summarized in Table IV. The table includes rate measurements of the reaction carried out in aqueous methanol and ethanol solutions in order to determine possible effects arising from the addition

TABLE IV
SUMMARY OF REACTION RATE CONSTANTS

Temp., °C.	Dibromide (~0.022 M)	KI concn. (M)	Solvent wt. per cent. of methanol	Specific reaction rate constants		
				k_2	k_3	
30.00	CH_2BrCH_2Br	0.2152	99.2	0.0102	0.0495	
		.1469	99.2	.0101	.0720	
		.2207	63.0	.0154		
		.1496	63.0	.0157		
59.72	CH_2BrCH_2Br	.2237	99.0	.299	1.53	
		.1531	99.0	.300	2.32	
		.2240	72.0	.402		
		.1516	72.0	.411		
	$CH_3CHBrCH_2Br$.2208	99.0	.0113	0.0515	
		.1827	99.0	.0111	.0615	
		.1491	99.0	.0110	.0751	
		.2194	72.0	.0166		
		.1524	72.0	.0169		
		.2225	68.3 ^a	.0261		
	$CH_3CH_2CHBrCH_2Br$.1519	68.3 ^a	.0260		
		.2281	99.0	.0148 (0.0147) ^b		
		.2287	99.0	.00902 (.00896) ^b		
		.2281	99.0	.00465 (.00462) ^b		
74.93	CH_2BrCH_2Br	.2157	99.0	1.34		
		.2170	99.0	.0582		
	$CH_3CHBrCH_2Br$.2298	99.0	.0800 (.0773) ^b	0.357 ^c	
		.2296	99.0	.0787		
	$CH_3CH_2CHBrCH_2Br$.1470	99.0	.0811 (.0784) ^b	.567 ^c	
		.2217	99.0	.0562 (.0544) ^b	.256 ^c	
	$CH_3CHBrCHBrCH_3$	(meso)	.1461	99.0	.0564 (.0545) ^b	.386 ^c
		(racemic)	.2327	99.0	.0301 (.0294) ^b	.130 ^c
		(racemic)	.2273	99.0	.0301	
		(racemic)	.1498	99.0	.0310 (.0306) ^b	.209 ^c

^a Wt. per cent. ethanol. ^b Previously reported value (Ref. 1); see footnote c, Table I. ^c Previously reported value (Ref. 1); see footnote b, Table I.

of water to the methanol solvent and from the substitution of ethanol for methanol. It is evident that at least as far as non-ionic dibromides are concerned there is no doubt that the reaction is of the second order.

Two interesting comparisons can be drawn from the values of k_2 collected in Table IV. They are, first, at a given temperature the rates of reaction for all of the dibromides investigated are of the same order of magnitude, with the exception of ethylene bromide, which reacts much faster than the others, and, second, for a given compound the reaction rate is greater in the mixed solvent which has the higher molal fraction of water.

In Table V are given the values of the heats of activation Q , and the temperature coefficients for 10° , calculated according to the Arrhenius equation from the rate constants at 59.72° and 74.93° . It is interesting that the temperature coefficients of 1,2-dibromopropane and 1,2-dibromobutane are practically identical, a result not unexpected in view of their similarity in structure.

TABLE V

HEATS OF ACTIVATION AND TEMPERATURE COEFFICIENTS FOR REACTIONS OF DIBROMIDES WITH POTASSIUM IODIDE IN 99% METHANOL

Dibromide	k_2		Heat of activation, cal.	Temperature coefficient for 10°	
	59.72°	74.93°		59.72°	74.93°
$\text{CH}_2\text{BrCH}_2\text{Br}$	0.300	1.34	22700	2.73	2.64
$\text{CH}_3\text{CHBrCH}_2\text{Br}$.0111	0.0582	25100	3.02	2.92
$\text{CH}_3\text{CH}_2\text{CHBrCH}_2\text{Br}$.0148	.0800	25500	3.09	2.98
$\text{CH}_3\text{CHBrCHBrCH}_3$ (meso)	.00902	.0563	27700	3.39	3.27
$\text{CH}_3\text{CHBrCHBrCH}_3$ (racemic)	.00465	.0304	28400	3.50	3.37

Recalculation of van Duin's Results.—The third order specific rate constants reported by van Duin^{2,7} are not the same for different initial concentrations of potassium iodide. It may be readily seen from the results that second order constants would be in much better agreement. It suffices to say that the values which have been recalculated, while they do not agree as well as those given in Table IV, obviously indicate that van Duin was in error when he assumed that the rates were of the third order.

Influence of Ionic Strength upon the Reaction Rates.—The Brönsted theory¹⁰ of the velocity of ionic reactions is well known and has been applied extensively. The effect of the ionic strength upon the classical second order specific rate constant is indicated by the relation $k_2 = k_0 10^{2.5\nu} \sqrt{\mu}$ which holds strictly only in dilute solution. However, even

¹⁰ Brönsted, *Z. physik. Chem.*, **102**, 169 (1922); "Theory of the Velocity of Ionic Reactions" in the Columbia University Lectures, "Contemporary Developments in Chemistry," Columbia University Press, March, 1927; see also, Brönsted and Livingston, *THIS JOURNAL*, **49**, 435 (1927).

in the relatively concentrated solutions in which the rate measurements of the reaction between dibromides and iodide ion have all been made, the effects predicted by the Brönsted expression may be qualitatively demonstrated. Van Duin measured the rates of reaction of potassium and sodium iodide with dibromides capable of undergoing ionization and found an increase in the specific reaction rate with an increase in concentration of iodide ion or on the addition of various salts to the reaction mixture. Incidentally, the result was not ascribed to the Brönsted effect. The reaction of potassium and sodium iodide with a non-ionizable dibromide, namely, ethylene bromide, has been carried out in this work and in this case the rate was found to decrease only slightly on the addition of salts. Thus, in the case where both reactants are ionic and are of the same sign, the reaction rate increases with ionic strength, but where one of the reactants is electrically neutral, the ionic strength is without effect on the rates. The results are summarized in Table VI

In addition it should be pointed out that the rates of reaction of dibromo acids with potassium iodide as reported in Table VI are not affected by altering the ionic strength of the solutions by changing the concentration of either the potassium iodide or the added hydrochloric acid. This is logical since the amount of hydrochloric acid present in these reactions should be sufficient to depress completely the dissociation of these weak organic acids so that in their reactions with iodide ion they conform to the case where one of the reactants is electrically neutral. It is not surprising, however, that the specific rate constant of 2,3-dibromopropanoic

TABLE VI
INFLUENCE OF IONIC STRENGTH ON THE REACTION RATES OF DIBROMIDES WITH
POTASSIUM IODIDE

	Molal concn.			μ	$k_2 \times 10^3$
	KI	Added substance	Added substance		
	1.0	1.07	1.10
A. Ionized dibromide, ^a <i>p</i> -NaSO ₃ C ₂ H ₄ -	2.0	2.07	1.49
CHBrCHBrCOONa, 0.025 M	1.0	1.0	KBr	2.07	1.54
	1.0	1.0	KCl	2.07	1.57
	1.0	0.5	CaCl ₂	2.57	1.73
B. Un-ionized dibromide, ^b CH ₂ Br-	0.22	0.22	80.0
CH ₂ Br, 0.022 M	.22	0.11	KCl	.33	77.9
	.22	.22	KBr	.44	72.5
C. Undissociated dibromo acid, ^c	.5	.125	HCl	.63	0.343
CH ₂ BrCHBrCOOH, 0.025 M	1.0	.125	HCl	1.13	.317
	2.0	.250	HCl	2.25	.364
	2.0	.500	HCl	2.50	.354

^a These results were calculated from the data of van Duin (Ref. 2). Similar results may be calculated from his data for CH₂BrCHBrCOONa. ^b These results were obtained in this work: temp. 40°; solvent, 60% ethanol. ^c Also, recalculated from data of van Duin (Ref. 2). Other acids gave the same results

acid under the various conditions tabulated (Table VI) differs from the rate¹¹ when there is no free hydrochloric acid present. In this last instance partial dissociation of the organic acid undoubtedly occurs.

Summary

The reaction rates of potassium iodide with ethylene bromide and propylene bromide in methanol have been measured at 30, 60 and 75° and found to be of the second order. From the influence of iodine upon the rate it has been shown that in alcoholic solutions one mole of dibromide reacts with three moles of potassium iodide.

Previously reported second order constants for the reaction of the butylene bromides have been recalculated on this basis. From these rate constants, the heats of activation and temperature coefficients for ethylene bromide, propylene bromide and the three normal butylene bromides have been calculated.

Recalculation of van Duin's results show that the reactions of probably all dibromides with potassium iodide are second order and not third order as he claimed.

An increase in the ionic strength of the reaction medium by the addition of neutral salts slightly decreases the reaction rate of the non-ionic dibromides with iodide ion. On the other hand, under these conditions the reaction rate is appreciably increased in the case of ionized dibromides as the Brönsted theory demands.

¹¹ Ref. 2, p. 351: $k_3 = 0.123 \times 10^{-3}$, $k_2 = 0.246 \times 10^{-3}$.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

THE PHOTOCHEMICAL REACTION BETWEEN QUININE AND DICHROMIC ACID. I. QUANTUM YIELDS

BY GEORGE S. FORBES, LAWRENCE J. HEIDT AND CHARLES G. BOISSONAS¹

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Earlier studies of this reaction^{2,3,4} left unsolved a number of problems such as the relation of quantum yield to wave length, the consequences of light absorption by dichromic acid, and the details of the secondary processes. Bodenstein⁵ and later Kistiakowsky⁶ published critical discussions of these papers. Morton⁷ has recently proposed a reaction mechanism in

¹ International Research Fellow, 1927-1928.

² Goldberg, *Z. physik. Chem.*, **41**, 1 (1902); *Z. Wiss. Phot.*, **4**, 56 (1906).

³ Luther and Forbes, *THIS JOURNAL*, **31**, 770 (1909).

⁴ Forbes, Woodhouse and Dean, *ibid.*, **45**, 1891 (1923).

⁵ Bodenstein, *Z. physik. Chem.*, **85**, 329 (1913).

⁶ Kistiakowsky, "Photochemical Processes," The Chemical Catalog Co., Inc., New York, 1928, pp. 39-41.

⁷ Morton, *J. Phys. Chem.*, **33**, 1135 (1929).