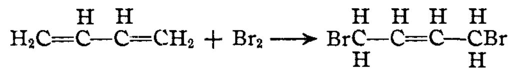
[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Action of Bromine on Butadiene

BY G. B. HEISIG AND JOHN L. WILSON

Eyring[1] and Eyring, Sherman and Kimball[2] applied quantum mechanics to reactions involving conjugate double bonds and made a study of addition of bromine to butadiene in the gas phase. They concluded that 1,4 addition would occur and that the reaction would be catalyzed by the walls of the container. In this paper, experimental data are presented to substantiate their conclusions.

The reaction was carried out in uncoated and paraffined glass spheres whose approximate volumes were 53, 275 and 512 cc. Runs were also made in the 275 and 512 cc. spheres packed with glass beads. The partial pressures of the bromine (b) and of the butadiene (a) in the experiments reported in this paper were equal as demanded by the equation



$$H_2C{=}\overset{H}{C}{-}\overset{H}{C}{=}CH_2 + Br_2 \longrightarrow Br\underset{H}{\overset{H}{C}}{-}\overset{H}{C}{=}\overset{H}{C}{-}\underset{H}{\overset{H}{C}}Br$$

In a previous communication[3] it was reported that the product formed was that expected, namely, 1,4-dibromobutene. This has been substantiated in subsequent runs. The velocity constants were calculated assuming that the reaction is bimolecular and that the reactants are weakly adsorbed,[4] using the formula

$$k = \frac{x}{at(a - x)}$$

in which a is the initial partial pressure of the bromine and butadiene and x is the decrease in the pressure at the time t. The constants in Table I were calculated using the initial pressure of bromine and butadiene. The initial time was taken at the completion of the mixing of the gases. The vapor pressure of the product was taken to be 12.7 mm. of α-bromonaphthalene (density 1.488) since there was this practically constant difference between the calculated and experimental drop in the pressure. The values of the velocity constant (k) for a reaction carried out in the small sphere increased, but finally became constant after approximately enough product had been formed to saturate the gas in the sphere with product. However, since enough product had been formed to saturate the gases in the medium and large spheres after the reaction had proceeded for only a minute, this trend is not obvious in these spheres. Typical data to show this are presented in Table I. Runs were then made in the small sphere using a larger partial pressure of the bromine and butadiene so that approximately the same number of molecules of product were formed over that required to saturate the gases and cover the surface of the sphere as were formed in the medium and large spheres. These data are given in columns 4, 5, 12 and 13 of Table I. Only the data for each run obtained after the gases in the spheres had been saturated with product were used in calculating the constants in Tables II–V. The time at which the gases were saturated with product was taken as the initial time. The drop in pressure in this region is twice the pressure of bromine or butadiene which has reacted, thus making it unnecessary to take into account the vapor pressure of the product. The pressures of the bromine and butadiene were calculated from the initial pressures of these gases present, total pressure drop, and the amount which had already reacted. Reaction constants were then calculated from the time that the partial pressure of the product became equal to its vapor pressure—12.7 mm. (α bromonaphthalene). Typical data for the different spheres and surfaces are presented in Tables II–IV.

The average values of the constants for these runs carried out in uncoated and paraffined spheres during which approximately the same number of molecules of product was formed over that required to saturate the gases in the reaction sphere and to cover the surface of the container with a unimolecular layer are given in Table V.

The products of these constants and the diameter of the spheres are also given. An examination of the data shows that the product (kd) is essentially the same for the small, medium and large reaction spheres whether uncoated or paraffined.

The constancy of these products when equivalent amounts of reactants are present is evidence that the reaction occurs largely on the surface of

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(1) Eyring, *Science*, **77**, 158–160 (1933).

(2) Eyring, Sherman and Kimball, *J. Chem. Phys.*, **1**, 586–592 (1933).

(3) Heisig, THIS JOURNAL, **55**, 1297 (1933).

(4) Taylor, "Treatise on Physical Chemistry," D. Van Nostrand Co., New York City, 1931, p. 1078.

TABLE I

$k \times 10^2$ FOR FIRST 90% OF REACTION

	Uncoated								Paraffined							
	Small				Medium		Large		Small				Medium		Large[c]	
	$a = b = 14.7$		$a = b = 23.9$		$a = b = 27$		$a = b = 29.4$		$a = b = 15.3$		$a = b = 23.7$		$a = b = 27.1$		$a = b = 29.5$	
t, min.	$-\Delta P$	k'	$-\Delta P$	k'	$-\Delta P$	k'	$-\Delta P$	k'	$-\Delta P$	k'	$-\Delta P$	k'	$-\Delta P$	k'	$-\Delta P$	k'
1	11.1	4.1	30.1	7.1	30.2	5.1	24.0[b]	2.1	0.0	...	22.4	4.0	4.4	0.33	13.4[d]	0.95
2	17.4	4.9	37.0	7.2	39.1	4.8	39.6[b]	3.4[f]	1.0	0.11	33.5	5.1	11.4	.49	33.2	2.1[f]
3	20.2	5.0	39.6	6.7	42.5	4.6	44.7[b]	3.5	1.4	.1	32.5	5.3	23.0	.91[f]	43.6	3.0
4	22.2	5.2	41.3	6.7	45.1	4.7	47.6[b]	3.4	2.0	.11	39.7	5.4	30.8	1.2	49.1	4.2
5	23.6	5.5	42.2	6.3	47.1[a]	4.6	49.9[b]	3.7	2.4	.13	40.8	5.2	36.0	1.5		
6	25.2[a]	6.3[f]	43.1	6.4	48.2[a]	4.7	51.7[b]	4.1	3.6	.14	42.0	5.5	40.2	1.8		
8	25.9[a]	5.0							4.8	.15	43.4[e]	5.1	43.8[a]	2.1		
10	26.4[a]	5.7							7.6	.21			46.7[a]	2.9		
12	26.9[a]	5.9							11.4	.32			48.7[a]	2.8		
14									15.4	.47						
18									21.2[a]	.78						
21									24.2[a]	1.1						
25									26[a]	1.4[f]						
45									28[a]	1.4						

[a] Add 0.5 min. to time. [b] Add 0.1 min. to time. [c] First 75% of reaction. [d] Add 0.05 min. to time. [e] Add 1 min. to time. [f] Line indicates that vapor pressure of product has been reached.

TABLE II

$k \times 10^2$ FOR REACTION AFTER GASES ARE SATURATED WITH PRODUCTS IN SMALL SIZED SPHERE

	Uncoated				Paraffined			
	Vol., 53.9 cc.		Diam. 4.6 cm.		Vol., 50.3		52 cc.	
	$a = b = 2$		$a = b = 8.8$		$a = b = 3.6$		$a = b = 11.8$	
t, min.	$-\Delta P$	k	$-\Delta P$	k	$-\Delta P$	k	$-\Delta P$	k
1	0.4	5.6	6.9	7.3			9.6	5.8
2	.6	4.4	9.5	6.7	0.5	1.0	13.6	5.8
3	.8	4.2	11.2	6.6			15.8	5.7
4	1.1	4.8	12.1	6.3			16.9	5.4
5			13.0	6.6	1.2	1.1	18.1	5.6
6	1.6	5.6	13.4	6.1			18.6	5.3
7			13.8	5.9				
8	1.8	5.1	14.2	6.0	1.4	0.84	19.5	5.0
10	2.0	5.0	14.9	6.3			20.2	5.0
12			15.3[a]	5.8				
14	2.4	5.4			2.3	.93		
16			15.8	5.9				
α	4.1		17.6		3.6		23.6	
Av. for	86%	4.7	90%	6.3	78%	.87	85.5%	5.5

[a] Add one minute to time.

the container. Further evidence for this conclusion is found in the large values of k when the reaction is carried out in the medium and large spheres filled with soft glass beads (Table VI). In this connection it should be noted that nearly 50% of the reaction took place before the first reading could be made.

The practically identical values of k for the paraffined and uncoated spheres were wholly unexpected in the light of the experiments of Norrish and co-workers,[5] but these results are reasonable, however, if the product which is formed is the actual surface on which the reaction takes place. Furthermore, if the product is somewhat more polar than glass, the increase in the values of k noted in Table I until the pressure has dropped sufficiently to saturate the gases and form a unimolecular layer on the surfaces of the spheres is accounted for. Also there should be a difference in the value of k in the runs carried out in the uncoated and paraffined spheres if insufficient product is formed to saturate the gases and form a unimolecular layer on the surface. This is clearly shown by the runs carried out in the small sphere using equivalent amounts of reactants in which insufficient product was formed to saturate the gases and to form a unimolecular layer on the surface, assuming the surface occupied by a mole-

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(5) Norrish, *J. Chem. Soc.*, **123**, 3006–3018 (1923); Norrish and Jones, *ibid.*, 55–62 (1926).

TABLE III

$k \times 10^2$ FOR REACTION AFTER GASES ARE SATURATED WITH PRODUCT IN MEDIUM SIZED SPHERE

	Uncoated Vol., 275.4 cc.; diam., 8.1 cm. $a = b = 13.2$		Paraffined Net vol., 274 cc. $a = b = 13.2$		Beads Net vol., 122.1 cc. $a = b = 5$	
t, min.	$-\Delta P$	k	$-\Delta P$	k	$-\Delta P$	k
1	8.9	4.5	6.1	2.8	6.3	34
2	12.3	3.5	10.5	2.5	8.3	42
3	14.9	3.3	14.0	2.9	8.6	41
4			16.2	3.0	8.8	37
5	18.7	3.7	17.8	3.1	8.9	32
6	19.5	3.6	19.1	3.3		
7	20.1	4.3	20.3	3.6	9.0	26
8	20.5	3.3	21.1	3.8	9.1	25
9	21.3	3.5	21.8	4.0		
10	21.4	3.3	22.3	4.1		
12	22.1	3.2	23.1	4.4	9.3	22
14	22.6	3.2				
16	23.1	3.3				
α	17.4		26.2		10.0	
Av. for	72%	3.5	81%	3.1	93%	37

TABLE IV

$k \times 10^2$ FOR REACTION AFTER GASES ARE SATURATED WITH PRODUCT IN LARGE SIZED SPHERE

	Uncoated Vol., 515 ± cc.; diam., 10 cm. $a = b = 14.2$		Paraffined Net vol., 513.4 cc. $a = b = 20.3$		Beads Net vol., 230.4 cc. $a = b = 8.2$	
t, min.	$-\Delta P$	k	$-\Delta P$	k	$-\Delta P$	k
1	9.4	3.5	13.8	2.5	8.0	12
2	13.2	3.1	21.8	2.9	12.1	17
3	15.8	2.9	25.4	3.0	13.9	17
4	18.0	3.1	28.2	2.8	14.8	28
5	19.3	3.0	29.9	2.8		
6	20.4	3.0	31.6	2.9	14.9	20
7	21.3	3.0	32.9	3.0		
8	22.0	3.0	33.9	3.1	15.1	18
9	22.7	3.1	34.8	3.3		
10	23.1	3.1	35.2	3.1	15.1	14
12	24.2	3.4	36.2	3.4		
14	24.7	3.4				
16	25.3	3.6				
α	28.4		40.5		16.1	
Av. for	95%	3.3	84%	2.8	97%	17

TABLE V

VALUES OF $kd \times 10^2$ FOR ALL RUNS IN WHICH REACTION OCCURRED ON SURFACE OF PRODUCT

	Uncoated						Paraffined					
Diameter	4.6 cm.		8.1 cm.		10.0 cm.		4.6 cm.		8.1 cm.		10.0 cm.	
a/b	k	kd	k	kd	k	kd	k	kd	k	kd	k	kd
1	6.3	29	3.8	30	3	30	5.5	25.3	3.8	30	2.9	29

cule of product is 10^{-16} sq. cm., the value of k for the reaction in the uncoated sphere is 4.5 and that for the paraffined sphere was 0.87. The data for the reaction occurring in the small paraffined sphere using 15.3 mm. of reactants show clearly that the reaction starts very slowly at a paraffin surface, but the rate increases as more product is formed and becomes constant when the surface has become coated with product.

The kinetics of the reaction which takes place when an excess of butadiene is used are more complicated and are being further investigated.

Norrish and his co-workers[5] have shown that the reaction between chlorine or bromine and ethylene is a surface reaction and that the rate depends on the nature of the surface of the vessel. The comparative surface activities are: glass, stearic acid, paraffin. An inspection of the data of the reaction of chlorine and ethylene shows that sufficient product (ethylene chloride) is formed to saturate the gases and lay down a unimolecular layer on the walls of the reaction vessel when about 30% of the bromine has reacted. The data in experiments 10 and 11 in which the reaction is carried out on a glass surface show that 30% of the bromine has reacted between the second and fourth seconds (first and second readings) of experiment 10 and between the start of the reaction and the second second (start and first reading) in experiment 11. It seems questionable then, whether the surface of the reaction vessel is glass after the reaction has proceeded past this stage. Insufficient data are given to make a similar calculation for the reaction between bromine and ethylene. Stewart and Edlund[6] concluded that the reaction between bromine and ethylene was bimolecular and occurred at the surface. They did not consider the reaction beyond the point at which the vapor pressure of ethylene dibromide was reached. G. Anderson[7] concluded that simple addition of bromine to the double bond of ethylene occurs at 16° except in the presence of an excess of bromine or in the presence of water. The reaction takes place on the surface of the container. In his experiments the runs were not carried beyond the point at which the vapor pressure of the product was reached.

Experimental

The method used was to fill a sphere of known volume with a known mixture of nitrogen and bromine. A portion of the mixture was removed by opening to an evacuated bulb of known volume. Then sufficient butadiene measured in a Ramsay buret to give a ratio of butadiene to

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[6] Stewart and Edlund, THIS JOURNAL, 45, 1014 (1923).

[7] G. Anderson, *J. Chem. Soc.*, 1747–1758 (1932).

bromine of not less than one, was mixed with sufficient nitrogen in the Ramsay so that the number of moles of mixture was equal to the number of moles of nitrogen–bromine mixture removed from the reaction sphere. The butadiene–nitrogen mixture was then introduced into the reaction sphere. The sphere, illuminated by an automobile spotlight, and the tubing for introducing the nitrogen–butadiene and bromine mixtures were immersed in a thermostat maintained at 25 ± 0.01° by a vacuum tube relay circuit.[8] The drop in the pressure was measured by means of a differential manometer filled with α-bromonaphthalene.

Bromine.—The bromine used in the first set of experiments was a part of that used by Reyerson and Cameron[9] in their experiments on the sorption of bromine by silica gel and charcoal. It had been purified by the method of A. Scott.[10] That used in the second set of experiments was the ordinary C. P. bromine purified by the method of Baxter and Grover.[11] Both samples were carefully dried by distilling the liquid from and passing the gas through resublimed phosphorus pentoxide prepared from the ordinary C. P. product by the method of Finch and Peto.[12] The subliming chamber (7.6 cm. iron pipe) was placed in a large gas muffle furnace[13] and maintained at a bright red heat. There were no lower oxides of phosphorus present. The dried bromine was then fractionated in a closed system under its own vapor pressure and the middle fraction was used. The stopcocks were lubricated with the metaphosphoric acid prepared according to Stephens.[14] The bromine (30 cc.) was stored in a saturator (I) having one 200-cc. sphere connected in series with 3 smaller bulbs. The mercury sealed stopcocks (5 and 6) were lubricated with the metaphosphoric acid lubricant. The containers were so arranged in a cluster that they could be completely immersed in an automatic low temperature thermostat controlled by a thermionic relay panel described by Cameron.[15] The bath (alcohol) was maintained at −38.1 ±0.05° while nitrogen from a tank was passed at the rate of about 40 cc. a minute. The vapor pressure of bromine at −38.1° was 3.6 mm. and 6.4 mm. at −32.2°.

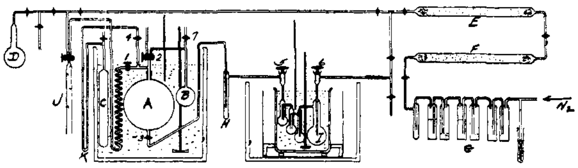

Fig. 1.

Nitrogen.—The nitrogen was purified by passing through 3 double wash bottles (G) containing a 40% potassium hydroxide solution to remove any carbon dioxide, dried by passing through a long tube filled with calcium chloride (F), and then through a tube (E) filled with resublimed phosphorus pentoxide on glass wool.

Butadiene.—The butadiene was prepared by the action of zinc dust on 1,2,3,4-tetrabromobutane prepared according to Heisig.[16] It was stored in a sphere from which appropriate amounts could be removed and measured in the Ramsay buret (J) as the occasion demanded. The pressure in the Ramsay buret was obtained by measuring the difference in the levels of mercury in the leveling bulb and in the buret with a cathetometer or later by measuring the difference in levels of mercury in a closed manometer and in the buret. The closed manometer was an integral part of the buret.

Procedure

The procedure for making a run was to evacuate the reaction sphere (A), evacuating bulb (B), the tubing leading to the Ramsay and to the bromine saturators with an efficient oil pump. The stopcock (1) leading to the Ramsay and (2) to the evacuating bulb were then closed, nitrogen was admitted into the saturator and then the reaction sphere was filled with the bromine–nitrogen mixture. When the reaction sphere was filled, the stopcock (2) was turned to allow the bromine–nitrogen mixture to pass into the air. The reaction sphere was flushed for at least thirty minutes. At the start of the flushing process, the stopcock (4) leading to the manometer (K) was opened and the tube leading to the manometer was filled with the bromine–nitrogen mixture by increasing and decreasing the pressure in the manometer bulb (C).

When the flushing process was complete, the stopcocks (6, 5, 3, 2) were successively closed and a part of the bromine and nitrogen removed from the reaction sphere by opening stopcock (2) to the evacuated sphere (B). After closing the stopcock to the evacuated sphere air was admitted to B through (7). The butadiene–nitrogen mixture was then run into the reaction sphere, stopcock (1) closed, and stopcock (4) leading to the manometer opened. About twenty to thirty seconds were required for introducing the hydrocarbon mixture. Readings were taken every half minute at first and then at greater intervals as the reaction proceeded until no appreciable change in pressure was noted.

If the product was not wanted, it was pumped off, or the reaction sphere and connections were removed and carefully cleaned by washing with ether, alcohol and water. A paraffin–vaseline lubricant was used to lubricate the stopcocks and ground glass joint leading to the reaction sphere.

Coated Spheres.—The reaction spheres were coated with paraffin by pouring about 10 g. of hot paraffin into the sphere and evacuating with an oil pump while the paraffin solidified in the sphere which was being rotated during the cooling. The tubes leading to the reaction sphere and to the manometer were flushed with molten paraffin. Since the density of the solid paraffin was known to be 0.82, the net volume of the reaction sphere could be calculated.

Packed Spheres.—The medium and large spheres were filled with flattened glass beads such as are used for a necklace. The average dimensions were 2.6 × 3.8 mm. The diameter of the hole was about 0.8 mm. These beads were of uncertain origin and were cleaned with cleaning solution and very thoroughly washed. The density of the beads was found to be 2.79, thus making it possible to determine the actual volume in the sphere.

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(8) Heisig and Gernes, *Ind. Eng. Chem., Anal. Ed.*, **6**, 155 (1934).

(9) Reyerson and Cameron, *J. Phys. Chem.*, in press.

(10) A. Scott, *J. Chem. Soc.*, **103**, 847 (1912).

(11) Baxter and Grover, THIS JOURNAL, **37**, 1027 (1915).

(12) Finch and Peto, *J. Chem. Soc.*, **121**, 692 (1922).

(13) Through the courtesy of the Division of Chemical Engineering.

(14) Stephens, THIS JOURNAL, **52**, 635 (1930).

(15) Cameron, Ph.D. Thesis, University of Minnesota, 1932.

(16) Heisig, THIS JOURNAL, **55**, 2304 (1933).

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Summary

The reaction between equivalent amounts of butadiene and bromine has been studied in small, medium and large spheres on "glass" and paraffined surfaces.

The rate of the reaction increases until the vapor pressure of the 1,4-dibromobutane formed is reached and the walls are covered by a unimolecular layer and then becomes constant.

The constancy of the product (*kd*) of the velocity constants (*k*) for a dimolecular reaction (calculated from the time that sufficient 1,4-dibromobutene is formed to saturate the gases and form a unimolecular layer on the surface, "glass" or paraffin) and the diameters of the spheres is evidence for a surface reaction.

The identity of the product (*kd*) of the velocity constants and the diameters of the "glass" and paraffined spheres indicates that the reaction must occur on a surface of reaction product rather than the wall itself and this is further proved by the small value of the velocity constant in the paraffined spheres in which an insufficient amount of reaction product is formed to coat the surface.

The large values of the velocity constants for the reaction in the packed spheres is further evidence for the reaction occurring at the surface.

The question is raised as to whether the reaction surface is actually glass in Norrish's studies of the reaction between ethylene and chlorine.

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[CONTRIBUTION NO. 189, DEPARTMENT OF CHEMISTRY, KANSAS STATE COLLEGE]

Relation of Surface Tension to other Physical Properties of Liquid Mixtures

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Although attention has been called to the antibatic relation of surface tension to vapor pressure[1] and to compressibility[2] no attempt has been made to establish which of these two relations takes precedence in systems of completely miscible liquids where deviations from the ideal occur in surface tension, compressibility, or vapor pressure data. Obviously a serious difficulty arises in selecting systems which may demonstrate the unobscured relation of two properties to each other without any possible correlation with the third. Such investigations are made further difficult because of the scarcity of compressibility data. A simple apparatus has been designed for the purpose of measuring compressibility directly under pressures of two to three atmospheres. Compressibility measured under such low pressures was felt to be better suited for comparison with surface tension under atmospheric conditions than the high pressure data obtainable in some instances.

Fortunately a system was found which exhibited wide deviation from the normal in one of these properties but followed close to the ideal in the other two. Methanol–chloroform mixtures show wide deviation from the normal in respect to their vapor pressure data, as might be expected from the fact they form a minimum boiling mixture. Surface tension and compressibility data, however, were nearly ideal, indicating that this correlation has unquestionably greater significance in this system of liquids than the relation of vapor pressure to either compressibility or surface tension. This system was found to be strictly ideal with respect to density and index of refraction also, but it was radically abnormal with respect to fluidity.

Experimental Procedure

A technical grade of chloroform was extracted with concentrated sulfuric acid until the washings were no longer discolored. The chloroform was then refluxed for a short time over quicklime and distilled through an efficient fractionating column. The middle fraction, boiling within a 0.3° range covering the accepted boiling point given by the "International Critical Tables," was reserved and immediately made up into the mixtures with methanol.

A C. P. grade of methanol was taken through the standard procedure of preparing absolute alcohol and frac-

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[1] Worley, *J. Chem. Soc.*, **105**, 273 (1914).

[2] Freundlich, "Colloid and Capillary Chemistry," translated from third German edition, 1922, E. P. Dutton Co., New York, p. 78.