Summary

The dehydration of 1-butanol and 2-butanol over aluminum oxide at 300–350° gave butenes which were converted to the bromides. By means of fractional distillation at 50 mm. the three component dibromobutanes were separated from one another but not in a pure state. The approximate compositions of the butene mixtures were 68% 1-butene, 12% 2-butene, b. p. 0.3° and 20% 2-butene, b. p. 3.0° from 1-butanol and 26, 26 and 48%, respectively, from 2-butanol.

The butene mixture obtained from 2-bromobutane was partially separated by fractional distillation. It contained 15–20% of 1-butene, the balance consisting of a mixture of the isomeric 2-butenes.

When hydrogen bromide in glacial acetic acid reacted with 1-butene, the product was practically pure 2-bromobutane.

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THE REACTION RATES OF POTASSIUM IODIDE WITH 1,2- AND 2,3-DIBROMOBUTANE. THE ANALYSIS OF MIXTURES OF THE NORMAL BUTENES[1]

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The butenes are the simplest unsaturated hydrocarbons which exist in isomeric as well as stereoisomeric forms, *viz.*, 1-butene, *cis*-2-butene, *trans*-2-butene and isobutene. The variety of isomeric changes which they might conceivably undergo in passing from one form to another would include: (1) stereoisomeric change, for example, *cis*- to *trans*-2-butene, or *vice versa;* (2) shifting of the double bond, 1-butene or 2-butene, or *vice versa;* and (3) shifting of a methyl group, isobutene to 1- or 2-butene, or *vice versa.* A study of the transformations of these comparatively simple olefins would presumably be of value in the study of the higher olefins.

Before undertaking an investigation on the effect of subjecting the isomeric butenes to different treatments, it was first necessary to develop a satisfactory method of analyzing mixtures containing any combination of these four hydrocarbons. For this purpose the analysis of mixtures of the three normal butenes, *viz.*, 1-butene, *cis*-2-butene and *trans*-2-butene

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would serve the purpose since isobutene can apparently be removed by absorption methods.[4] Moreover, the dibromide of this hydrocarbon has a boiling point some 10° lower than any of the others and in the proposed method it could be separated out by fractional distillation. Fortunately this hydrocarbon would not be present in many of the mixtures, especially those being studied at first, and for that reason also the analysis of the normal butenes serves our purpose.

Besides the fractional distillation of the corresponding dibromides, no method for analyzing mixtures of the three normal butenes has appeared in the literature.

The Analytical Method

The method herein developed depends upon the fact that each of the three normal butenes is quantitatively converted into a pure dibromide on treatment with bromine, and each of these dibromides has a different second-order reaction rate with potassium iodide in methanol at 75° to form potassium bromide, free iodine and an unsaturated hydrocarbon, thus: $C_4H_8Br_2 + 2KI \longrightarrow C_4H_8 + 2KBr + I_2$. Since these rates are not symbatic with the boiling points of the dibromides, while the physical properties of density and refractive index are, a combination of rate with one of these properties suffices for the analysis of any mixture of these three dibromides, and therefore of the three normal butenes. For this purpose the densities proved to be more useful than the refractive indices, since they differ by larger amounts.

In Table I are shown the boiling points of the three normal butenes[5] and the boiling points, densities, refractive indices and reaction rate constants of the corresponding dibromides. The rates with which these dibromides react with potassium iodide are proportional to the first power of both the dibromide and potassium iodide concentrations and are therefore second-

TABLE I

PHYSICAL CONSTANTS

Hydrocarbon			Corresponding dibromide						
					Density *in vacuo*		Refractive index		Second-order rate with KI
Name	B. p., °C. (corr.)	Mm.	Name	B. p. at 50.0 mm., °C.	d_4^{25}	d_4^{20}	n_D^{25}	n_D^{20}	
1-Butene	−6.7 to −6.5	748	1,2-dibromobutane	80.5–80.7	1.7870	1.7951	1.5125	1.5150	0.0765
Cis-2-butene	+2.95 to +3.05	746	Racemic 2,3-dibromobutane	75.6–75.8	1.7836	1.7916	1.5125?	1.5147	0.0297
Trans-2-butene	+0.3 to +0.4	744	Meso-2,3-dibromobutane	72.7–72.9	1.7747	1.7829	1.5092	1.5116	0.0544

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[4] (a) Michael and Brunel, *Am. Chem. J.*, **41**, 135 (1909); (b) Konowaloff, ***Ber.***, **13**, 2395 (1882); *cf.* Butlerow, *ibid.*, **9**, 77 (1878); (c) Davis, THIS JOURNAL, **50**, 2780 (1928); (d) Davis and Schuler, *ibid.*, **52**, 721 (1930).

[5] (a) Lucas and Dillon, *ibid.*, **50**, 1460 (1928); (b) Young, Dillon and Lucas, *ibid.*, **51**, 2528 (1929).

order. The discussion of the order of the reaction is taken up later on in this paper.

The rate with which iodine is formed when a mixture of the three dibromobutanes reacts with potassium iodide is given by Equation 1

$$\frac{\mathrm{d}c}{\mathrm{d}t} = k_{2a}(C_a)(C_{KI}) + k_{2b}(C_b)(C_{KI}) + k_{2c}(C_c)(C_{KI}) \qquad (1)$$

in which C_a, C_b and C_c are the molal concentrations of the three dibromobutanes, A, B, C and k_{2a}, k_{2b}, k_{2c} are the respective second-order reaction constants of the pure components with potassium iodide. This expression is the summation of the three individual rates typified by Equation 2

$$\frac{\mathrm{d}c}{\mathrm{d}t} = k_{2a}(C_a)(C_{KI}) \qquad (2)$$

and is true if the reaction rates are additive. Integration of (1) would give an expression by means of which the progress of the reaction could be followed for any mixture at any time, *t*, by a determination of the amount of iodine formed. However, the awkwardness of this integration makes it desirable to use instead a simpler expression by means of which an approximation to the real rate can be obtained. Equation 1 may be written in another form (Equation 3)

$$\frac{\mathrm{d}c}{\mathrm{d}t} = (k_{2a}x + k_{2b}y + k_{2c}z)C_{KI}\ C \qquad (3)$$

where x, y and z are the respective molal fractions of A, B and C and ΣC is the total concentration of the dibromides. Setting

$$K_2 = k_{2a}x + k_{2b}y + k_{2c}z \qquad (4)$$

Equation (3) becomes

$$\frac{\mathrm{d}c}{\mathrm{d}t} = K_2 C_{KI}\ \Sigma C \qquad (5)$$

In Equation 5 K_2 occupies formally the position of a second-order reaction rate constant; it is, however, not constant, because each dibromide disappears at a different rate due to the fact that k_{2a}, k_{2b} and k_{2c} have different values, with the consequence that the molal fractions change with time. The rate of change of the molal fractions will depend upon the individual constants k_{2a}, k_{2b} and k_{2c} and will be small when these are of the same order of magnitude. Since this is true in the present case, the mole fractions and hence the value of K_2 will not undergo much change during a not too great interval of time. Accordingly, for experiments in which the reaction is not allowed to proceed too far, Equation 5 may be integrated under the assumption of constancy of K_2, and the value of K_2 taken as that corresponding to the initial molal fractions. K_2 is designated as a "pseudo" second-order reaction rate constant since it is not a true constant.

Assuming that the density of a mixture of the three dibromides may be obtained additively, their relationship may be expressed by Equation 6

$$D = d_a x + d_b y + d_c z \qquad (6)$$

in which D is the density of the mixture, while d_a, d_b and d_c are the densities of the respective components, A, B and C. Combining 4 and 6 with the additional Equation 7

$$x + y + z = 1 \qquad (7)$$

the following solutions for the unknowns are obtained by means of determinants

$$x = \frac{-k_{2b}(d_c - D) + k_{2c}(d_b - D) - K_2(d_b - d_c)}{\Delta} \qquad (8)$$

$$y = \frac{k_{2a}(d_c - D) - k_{2c}(d_a - D) + K_2(d_a - d_c)}{\Delta} \qquad (9)$$

$$z = \frac{-k_{2a}(d_b - D) + k_{2b}(d_a - D) - K_2(d_a - d_b)}{\Delta} \qquad (10)$$

where $\Delta = k_{2b}(d_a - d_c) - k_{2c}(d_a - d_b) - k_{2a}(d_b - d_c) = 0.0005004$.

The assumption that the density of the mixture is an additive function of the individual densities, d_a, d_b and d_c, and that its specific reaction rate constant, K_2, is also an additive function of the individual constants k_{2a}, k_{2b} and k_{2c} would appear to be warranted in view of the fact that halogen compounds of this type are non-polar, non-associated liquids, mixtures of which would presumably deviate but little from ideal solutions.[6]

This method of calculating compositions, besides involving the above assumptions, requires that Equations 4, 6 and 7 should be independent of one another or, in other words, the proportionality constants should not be related in the following way

$$k_{2a} : k_{2b} : k_{2c} = d_a : d_b : d_c$$

Moreover, greater accuracy is realized by the fact that these constants are not symbatically related, that is, the higher-boiling 2,3-dibromide has a higher density but a lower reaction rate than the lower-boiling 2,3-isomer, while the 1,2-dibromide has the highest boiling point, density and reaction rate.

The deviations of approximately 1% in the rate constants of the pure compounds and the error involved in the calculations of the pseudo constant, K_2, determine the maximum error, which appears to be approximately 4% (see Tables VII and IX).

The Reaction Rates

Of the many compounds with which the dibromides react, for example, potassium iodide, sodium thiosulfate, sodium phenolate, potassium cyanide, silver nitrate, ammonia and substituted ammonias, the reactions with the first two only were studied. In all cases except with potassium iodide the amount of material reacted would be obtained from the difference between two much larger quantities while in this case the extent of the reaction can be determined directly and with less error from the amount of iodine formed.

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[6] A mixture of ethylene bromide and propylene bromide is an ideal solution. Zawidzki, *Z. physik. Chem.*, **35**, 129 (1900).

The reaction with sodium thiosulfate was carried out in sealed tubes at 100°, preliminary experiments having shown that the rate was too slow at lower temperatures.[7] The reaction as carried out under these conditions is subject to two sources of error: the final titration of the excess of unused thiosulfate varies on the one hand with the gaseous volume above the reacting solution in the sealed tubes and on the other hand with the length of time the unopened reaction tubes stand after removal from the thermostat. Perhaps these errors are not significant at lower temperatures and therefore need not be considered, but they are interfering factors when the reaction is carried out at a temperature of 100°. A fairly satisfactory second-order constant was obtained in the reaction of thiosulfate with pure 1,2- and a mixed 2,3-dibromobutane, but because of the difficulty involved this method was not as suitable as the reaction with potassium iodide.

The reaction rates of alkyl chlorides with potassium iodide in absolute acetone have been studied by Conant and Kirner[8] and Conant and Hussey,[9] who found that the reactivities of the alkyl chlorides decrease in the order, primary, secondary and tertiary. The reaction rates of many dibromo-substituted compounds with potassium iodide have been investigated by Biilmann[10] and by van Duin.[11] Biilmann worked in dilute sulfuric acid solution and van Duin in both 70% ethanol and 70% ethanol acidified with hydrochloric acid. The reaction proceeds differently with the two classes of compounds, an alkyl chloride forming an alkyl iodide and potassium chloride, a dibromide forming an unsaturated compound, iodine and potassium bromide. Van Duin[11b] observed a difference in the reactivities of stereoisomeric dibromides, mesodibromosuccinic acid having a much higher rate than the racemic form. The three dibromobutanes (Table I) would thus be expected to differ in their rates, since the 1,2-dibromide contains a primary bromine atom, more reactive than a secondary, and the isomeric 2,3-dibromides exist as meso and racemic forms.

There are several mechanisms by which the reaction of potassium iodide with these dibromides may proceed, as shown by Equations 11 to 13 inclusive.

$$C_4H_8Br_2 + KI \longrightarrow C_4H_8BrI + KBr \qquad (11a)$$

$$C_4H_8BrI + KI \longrightarrow C_4H_8I_2 + KBr \qquad (11b)$$

$$C_4H_8I_2 \longrightarrow C_4H_8 + I_2 \qquad (11c)$$

$$C_4H_8Br_2 + KI = C_4H_8BrI + KBr \qquad (12a)$$

$$C_4H_8BrI + KI = C_4H_8 + I_2 + KBr \qquad (12b)$$

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[7] Slator [*J. Chem. Soc.*, **85**, 1286 (1904); **87**, 481 (1905)] studied the reaction of sodium thiosulfate with ethylene halides at temperatures ranging from 25 to 60°.

[8] Conant and Kirner, THIS JOURNAL, **46**, 232 (1924).

[9] Conant and Hussey, *ibid.*, **47**, 476 (1925).

[10] Biilmann, *Rec. trav. chim.*, **36**, 319 (1916).

[11] (a) Van Duin, *ibid.*, **43**, 341 (1924); (b) van Duin, *ibid.*, **45**, 345 (1926); (c) Kruyt and van Duin, *ibid.*, **40**, 258 (1921).

$$C_4H_8Br_2 + 2KI = C_4H_8I_2 + KBr \tag{13a}$$
$$C_4H_8I_2 = C_4H_8 + I_2 \tag{13b}$$

In addition to the steps enumerated above, each process may, and probably does, involve to some extent the reaction of iodine with potassium iodide as given in Equation 14

$$I_2 + KI = KI_3 \tag{14}$$

In general, the rate will be second order if expressed by (11) and (12), and third order if by (13), provided the reactions of the different steps proceed with markedly different rates. In (11) and (12) the slow reaction may be either (a) or (b), and in (13) it must be (a), since Slator[12] found that diiodides and iodobromides in the presence of iodide ion dissociate quite rapidly even at temperatures of 25 and 35°. It is not possible to establish the extent to which iodine and potassium iodide react according to Equation (14) since in methanol part of the iodine is probably combined with the solvent. Moreover, even though KI_3 is formed, its effect upon the reaction rate can be made negligible by keeping the ratio of potassium iodide to iodine large.

In the experimental work the concentrations of both the reactants were varied. The rate was found to be second order, and to be proportional to the first power of the concentration of both the potassium iodide and dibromobutane. The reaction may then be represented by (11) or (12), but not by (13). This is in accordance with the observations of Biilmann, who studied the behavior of dibromopropionic acid with potassium iodide, but is not in agreement with those of van Duin, who concluded that this reaction and other similar ones were third order, according to Equation 13.

The specific second-order rate constant of a pure dibromide, k_2 (Equation 15), is derived from the differential form (Equation 16).

$$k_2 = \frac{2.303}{t(a - 2b)} \log_{10} \left(\frac{b(a/b - 2\phi)}{a(1 - \phi)}\right) \tag{15}$$
$$dc/dt = k_2(C_{KI})(C_{C_4H_8Br_2}) \tag{16}$$

The third-order constant, k_3 (Equation 17), given for comparison in Tables II, III and IV, is derived from the differential form (Equation 18).

$$k_3 = \frac{1}{t(a - 2b)^2} \left[2.303 \log_{10} \left(\frac{b(a/b - 2\phi)}{a(1 - \phi)} - \frac{2\phi(a - 2b)}{a(a/b - 2\phi)}\right)\right] \tag{17}$$
$$dc/dt = k_3(C_{KI})^2(C_4H_8Br_2) \tag{18}$$

In these equations t is time in hours, a is initial concentration of potassium iodide in moles per liter at 20°, b is initial concentration of dibromobutane in moles per liter at 20° and ϕ is fraction of the total dibromobutane which had reacted at the time, t. The values of k_2 and k_3 are thus expressed in hours and moles per liter at 20°, rather than in hours and moles per liter at 75°. This is done because the solutions are made up at 20° and the concentrations (a) and (b) would each differ at the two temperatures by a factor which is proportional to approximately the cubical coefficient of ex-

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[12] Slator, *J. Chem. Soc.*, **85**, 1697 (1904).

pansion of methanol. Since the ratio of two concentrations occurs in each of the variable terms involving ϕ, the values of k_2 in moles per liter at 20° and of k_2 in moles per liter at 75° are each constant in themselves and differ from each other by this factor. Likewise the values of k_3 at the two temperatures are each constant in themselves but differ from each other by the square of this factor.

The pseudo second-order reaction constant, K_2, of mixtures is also calculated according to Equation 15.

Description of the Method

Materials.—The potassium iodide, "P. W. R. Analytical," was ground in an agate mortar to a powder, dried at 100° for twenty-four hours and kept in a desiccator until used. The sodium thiosulfate solution, 0.02 *N*, was made by dissolving "P. W. R. Analytical" material in distilled water and was allowed to stand some time before use. It was stored in the dark and standardized at frequent intervals against standard potassium dichromate.

The three dibromobutanes used for the reaction rate measurements were those prepared from pure 1-butene,[5a] *cis*-2-butene and *trans*-2-butene.[5b] The dibromides were fractionally distilled at 50 mm., the products boiling completely within a temperature range of 0.2° (Table I), indicating that each was a pure substance and not a mixture of isomers.

The synthetic methanol used as the solvent was purified by refluxing with sodium hydroxide and distilling from the solid. Water was subsequently added in order to bring the strength to 99.00%. It was not considered feasible to work with absolute methanol since the specific reaction rates are markedly affected by the addition of water to methanol, being much greater at a dilution of 75% than at 99%. Thus the accidental addition of traces of water to absolute methanol might produce greater effects than a slight variation in the composition at 99.00%.

The methanol as prepared usually contained a slight amount of impurity which reacted slowly with iodine at 75°. It was therefore necessary to determine the correction for this impurity by adding to the solvent definite amounts of iodine and potassium iodide equivalent to those encountered in the actual rate measurements and measuring the iodine decrease against time. These corrections, which for three different samples of methanol amounted to 0.00, 1.10 and 1.27 ml. of 0.02 *N* sodium thiosulfate per 20 ml. of solvent, were added to the titration values as determined in the different rate measurements.

Apparatus.—The reaction tubes were made by drawing out very thin glass test-tubes, previously cleaned and dried, to form a constriction near the end. They had capacities slightly greater than 20 ml. A thermostat suitable for carrying on reactions in the dark was maintained at 74.93 ± 0.03°.

Procedure.—Each solution containing the reactants was made up to exactly 250 ml. at 20.0°, thoroughly mixed and pipetted into 8 or 10 reaction tubes with a 20-ml. pipet (exact volume, 19.94 ml.). Great care was exercised in keeping the solutions at exactly 20° while being made to volume and while being pipetted, since methanol has a large coefficient of expansion. The tubes were then sealed and placed in the thermostat, care being taken to avoid a large temperature drop by increasing the voltage of the continuous heater just before inserting the tubes. Tubes which were allowed to stand at room temperature for several hours showed no signs of reaction. The time could be considered from the time of immersion. At various intervals tubes were removed from the thermostat, quickly cooled in ice water and broken into a 600-ml. beaker containing 75 ml. of distilled water, 2 g. of potassium iodide and about three-fourths of the amount of sodium thiosulfate solution required for the titration. Thiosulfate was then added until the end-point as indicated with starch was reached. Reaction rate constants were then calculated from the titration values and are shown in the tables.

The densities of the dibromobutanes were determined with a 10-ml. pycnometer. The values have been calculated to vacuum[13] by applying the equation: $d_4^t = \frac{w_l}{w_w}(d_w - \sigma_2) + \sigma_3$. Here $\sigma_2 = \sigma_3 = 0.0012$ and the temperature of w_l and w_w are the same. Densities of the pure compounds are shown in Table I and of mixtures in Table VIII.

Results

In the tables which list the reaction rates, the following notations are used: KI is initial concentration of potassium iodide in moles/liter at 20° (given by "*a*" in the rate expressions, Equations 15 and 17), $C_4H_8Br_2$ is initial concentration of dibromobutane in moles/liter at 20° (given by "*b*" in the rate expressions), *t* is time in hours, ϕ is fraction of dibromide used up at time *t*, and k_2 and k_3 are second-order and third-order specific reaction constants.

In the experiments represented by Tables II, III and IV, essentially the same dibromide concentration was used throughout and essentially two different concentrations of potassium iodide, the ratio between these last two being approximately 1.5 to 1. In each table the second-order constants calculated for the two potassium iodide concentrations are in satisfactory agreement, whereas the third-order constants are not. This shows that the rates are proportional to the first power and not the second power of the potassium iodide concentration. Since previous work on other dibromides by investigators[10,11] had shown the rate to be proportional to the first power of the dibromide concentrations, and since preliminary work on the three dibromobutanes confirmed this observation, as was to be expected, evidence for this conclusion is not given here.

TABLE II

REACTION RATE OF 1,2-DIBROMOBUTANE WITH POTASSIUM IODIDE IN 99.0% METHANOL AT 74.93°

KI, 0.2298 *M*; $C_4H_8Br_2$, 0.03428 *M*				KI, 0.1470 *M*; $C_4H_8Br_2$, 0.03397 *M*			
Time	ϕ	k_2	k_3	Time	ϕ	k_2	k_3
12.50	0.1940	0.0774	0.347	12.50	0.1302	0.0784	0.552
15.50	.2334	.0775	.351	15.50	.1585	.0787	.556
19.25	.2794	.0775	.354	19.00	.1879	.0779	.555
23.75	.3307	.0778	.358	23.75	.2303	.0793	.572
27.25	.3647	.0771	.357	27.25	.2516	.0771	.559
37.50	.4587	.0772	.365	37.50	.3279	.0785	.583
40.75	.4835	.0769	.365	40.75	.3505	.0790	.591
	Average	.0773	.357		Average	.0784	.567

Percentage variation from the mean: $k_2 = 0.6\%$, $k_3 = 22.8\%$.

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[13] Reilly, Rae and Wheeler, "Physico-Chemical Methods," D. Van Nostrand Co., New York, **1925**, p. 322.

TABLE III

REACTION RATE OF RACEMIC 2,3-DIBROMOBUTANE WITH POTASSIUM IODIDE IN 99.0% METHANOL AT 74.93°

KI, 0.2327 *M*; $C_4H_8Br_2$, 0.02612 *M*

Time	ϕ	k_2	k_3
11.00	0.0721	0.0296	0.128
15.42	.0994	.0295	.128
21.50	.1343	.0293	.127
31.75	.1928	.0297	.130
35.50	.2114	.0295	.129
41.67	.2454	.0299	.132
45.50	.2638	.0299	.132
54.75	.3074	.0300	.134
	Average	.0294	.130

KI, 0.1498 *M*; $C_4H_8Br_2$, 0.02785 *M*

Time	ϕ	k_2	k_3
11.00	0.0500	0.0313	0.212
15.42	.0683	.0309	.209
21.33	.0903	.0301	.204
31.75	.1318	.0304	.208
35.50	.1462	.0305	.210
41.67	.1693	.0306	.212
	Average	.0306	.209

Percentage variation from the mean: $k_2 = 2.0\%$, $k_3 = 23.5\%$.

TABLE IV

REACTION RATE OF MESO-2,3-DIBROMOBUTANE WITH POTASSIUM IODIDE IN 99.0% METHANOL AT 74.93°

KI, 0.2217 *M*; $C_4H_8Br_2$, 0.03287 *M*

Time	ϕ	k_2	k_3
11.50	0.1262	0.0541	0.249
14.50	.1552	.0539	.249
17.50	.1837	.0539	.250
21.00	.2173	.0545	.254
27.75	.2759	.0549	.259
36.50	.3416	.0547	.261
39.50	.3627	.0547	.261
43.17	.3853	.0543	.261
	Average	.0544	.256

KI, 0.1461 *M*; $C_4H_8Br_2$, 0.02629 *M*

Time	ϕ	k_2	k_3
11.50	0.0848	0.0539	0.375
14.50	.1063	.0542	.378
17.50	.1259	.0540	.379
21.00	.1515	.0551	.389
27.75	.1952	.0557	.396
36.50	.2440	.0551	.396
	Average	.0545	.386

Percentage variation from the mean: $k_2 = 0.1\%$, $k_3 = 20.2\%$.

In determining the dependence of the specific reaction constant on the concentration of potassium iodide it was necessary to decrease this concentration to somewhat lower values than those ordinarily employed in the rate measurements. Thus under these conditions the ratio of the concentration of potassium iodide to dibromide was small compared to the usual values. With a ratio above 6.0, the values of the specific reaction constants were independent of this ratio in so far as investigated (that is, up to 12.0), but below 6.0 the specific reaction constants were found to increase slightly. This effect although quite small is very definite since it invariably occurred when the ratio was low; for example, the values for a given sample of dibromide were 0.0364 and 0.0365 when the ratios were 9.44 and 8.32, respectively, but 0.0381 when the ratio was 4.29.

Table V shows the iodine correction for one sample of methanol. Because of the low rate it was not possible to apply this correction before twenty hours; consequently in the rate determinations of the dibromides, readings taken under twenty hours are in error. Table VI shows that this iodine correction does not affect the second order rate constant.

TABLE V

REACTION OF METHANOL WITH IODINE

Time in hours	0.00	11.42	21.17	36.33
0.02 N I_2 reacted, ml.	0.00	1.23	1.27	1.27

TABLE VI

EFFECT OF IODINE CORRECTION UPON REACTION RATE

Methanol	1	2	3	4
Iodine correction	0.00	0.45	1.10	1.27
Second-order constant	0.0761	0.0769	0.0773	0.0766

The specific second-order reaction rates of the pure dibromides are summarized in Table VII.

TABLE VII

REACTION RATES OF PURE DIBROMOBUTANES WITH POTASSIUM IODIDE IN 99.0% METHANOL AT 74.93°

Mean values from different runs at slightly varying concentrations

Material	Run	No. of exptl. detns. of k_2	k_2	Mean k_2	Deviation from the mean, %
1,2-Dibromobutane, a	23	5	0.0773		+1.05
b	32	7	.0761	0.0765	−0.52
b	34	6	.0766		+ .13
a	45	8	.0761		− .52
Racemic 2,3-dibromobutane	27	6	.0297	.0297	+ .17
	42	6	.0296		− .17
Meso-2,3-dibromobutane	21	6	.0544		.00
	22	5	.0545		+ .18
	38	6	.0541	.0544	− .55
	39	8	.0540		− .73
	41	6	.0550		+1.10

The two samples, a and b, were prepared from different samples of 1-butene.

The satisfactory agreement in the case of the two samples of the 1,2-dibromide shows that the experimental conditions can be duplicated. This is likewise demonstrated by the fact that two of the authors (R. T. Dillon and W. G. Young) obtained for each of the three compounds constants which are essentially identical.

When the method was applied to different mixtures of the dibromobutanes satisfactory pseudo second-order constants were obtained as shown in Table VIII.

The compositions of these mixtures are given in Table IX. Duplicate runs were made on Mixtures B and D, the less satisfactory result in each case being shown in Table VIII.

In Table IX these observed values of the pseudo constant K_2 are compared with the values calculated from the known constants of the com-

TABLE VIII

REACTION RATES OF DIBROMOBUTANE MIXTURES WITH POTASSIUM IODIDE IN METHANOL AT 74.93°

Mixture	A			B	
KI concn.	0.02283 molal			0.1484 molal	
$C_4H_8Br_2$ concn.	0.02054 molal			0.01734 molal	
Time	ϕ	k_2	Time	ϕ	k_2
32.00	0.3280	0.0562	16.25	0.1429	0.0652
33.00	.3382	.0566	19.50	.1683	.0650
34.92	.3548	.0568	22.50	.1914	.0652
36.42	.3655	.0567	25.83	.2169	.0651
38.17	.3765	.0554	28.75	.2377	.0656
40.33	.3931	.0564	34.00	.3074	.0660
	Average	0.0566			0.0653

Mixture	C			D	
KI concn.	0.2291 molal			0.2284 molal	
$C_4H_8Br_2$ concn.	0.0254 molal			0.02621 molal	
Time	ϕ	k_2	Time	ϕ	k_2
18.00	0.2052	0.0571	24.72	0.2216	0.0457
20.50	.2311	.0576	28.28	.2536	.0468
23.50	.2619	.0583	31.50	.2767	.0467
26.50	.2903	.0584	41.75	.3463	.0467
29.50	.3175	.0587	44.00	.3588	.0463
39.75	.3953	.0585	46.50	.3739	.0463
41.75	.4105	.0582	48.25	.3825	.0460
43.75	.4233	.0579	50.16	.3928	.0459
46.00	.4389	.0558?	53.42	.4116	.0459
47.75	.4494	.0578			
	Average	0.0583			0.0462

ponents. In all cases the observed values are low, a result which is not surprising since K_2 should presumably decrease as the molal fraction ratio of the pure dibromobutanes changes. The percentage of the 1,2-dibromobutane is in all cases low, the maximum deviation being about 4%.

TABLE IX

REACTION RATES, DENSITIES AND CALCULATED COMPOSITIONS OF DIBROMOBUTANE MIXTURES

	Component			Dibromobutane mixture					
			d_4^{25}	% composition by		"Pseudo" constant K_2		Density in vacuo, d_4^{25}	
Mixture	Substance	k_2	in vacuo	Wt.	Anal.	Calcd.	Obs.	Calcd.	Obs.
A	1,2-Dibromobutane, pure	0.0765	1.7870	45.06	42.0				
	2,3-Dibromobutane, mixed	.0365	1.7816	35.81	39.6	0.0590	0.0566	1.7827	1.7826
	2,3-Dibromobutane, pure	.0544	1.7747	19.13	18.4				
B	1,2-Dibromobutane, pure	.0765	1.7870	79.38	77.4, 76.1	.0668	.0659		
	2,3-Dibromobutane, pure	.0297	1.7836	20.62	22.6, 23.9		.0653		
C	1,2-Dibromobutane, pure	.0765	1.7870	58.57	54.6	.0599	.0583		
	2,3-Dibromobutane, mixed	.0364	....	41.43	45.4				
D	1,2-Dibromobutane, pure	.0765	1.7870	26.53	23.2, 24.4	.0470	.0457		
	2,3-Dibromobutane, mixed	.0364	....	73.47	76.8, 75.6		.0462		
E	1,2-Dibromobutane, pure	.0765	1.7870	57.53	55.9			1.7828	1.7829
	2,3-Dibromobutane, mixed	....	1.7777	42.47	44.1				

In order to conserve the limited supply of the pure 2,3-dibromobutanes, mixtures of these two isomers resulting from fractional distillation were generally used in place of the pure compounds.

Rate measurements with the pure dibromobutanes were made at 59.72°. From the results at the two temperatures the heats of activation, Q, and the temperature coefficients were calculated by means of the Arrhenius equation. The values are given in Table X.

TABLE X

TEMPERATURE COEFFICIENTS AND HEATS OF ACTIVATION

Dibromobutane	k_2		Heats of activation, cal.	Temp. coeff. for 10°	
	59.72°	74.93°		$\frac{69.72^\circ}{59.72^\circ}$	$\frac{74.93^\circ}{64.93^\circ}$
1,2-	0.0147	0.0765	24,900	3.01	2.91
2,3-meso-	.00896	.0544	27,300	3.33	3.22
2,3-racemic	.00462	.0297	28,100	3.46	3.34

Summary

The specific reaction rates of 1,2-dibromobutane and of racemic and meso-2,3-dibromobutane with potassium iodide in methanol have been measured at 60 and at 75°. They are second-order reactions. The heats of activation and temperature coefficients have been calculated.

The reaction rates of mixtures of these dibromides have likewise been measured at 75°. Calculation of the composition of binary mixtures from the reaction rates and of a ternary mixture from the reaction rate and density gave results in satisfactory agreement with the known compositions. The maximum deviation was 4%.

Mixtures of the three normal butenes may be analyzed by first converting them to the corresponding dibromides and determining for these the reaction rates and densities.

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THE COMPOSITION OF BUTENE MIXTURES RESULTING FROM THE CATALYTIC DECOMPOSITION OF THE NORMAL BUTYL ALCOHOLS

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Introduction

Within recent years considerable interest has been attached to the decomposition of the normal butyl alcohols, partly because of its importance as a source of butenes and partly because of its bearing upon the theory of catalysis. These decompositions would be of particular value if they should yield, under the proper conditions, pure butenes, rather than mixtures of these hydrocarbons.

The catalytic decomposition of 1-butanol was first accomplished by Le

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