



The method here developed was first suggested by an investigation by Olson and Halford (*J. Amer. Chem. Soc.*, 1937, **59**, 2644), who, believing all solvolysis to be bimolecular, sought to establish their view in the example of the solvolysis of *tert.*-butyl chloride, by applying an activity rate equation to the solvent, as well as to the solute, in a kinetic test for bimolecularity. For solvolysis by mixtures of alcohol and water, their equation for the rate was

$$\text{Rate} = (k_a p_a + k_w p_w) p_{RX} \quad \dots \quad (1)$$

where the subscripts *a*, *w*, and *RX* denote respectively alcohol, water, and the alkyl halide, and the *p*'s represent partial vapour pressures. The symbols  $k_a$  and  $k_w$  denote kinetic constants, and Olson and Halford showed that, if these are determined by measurement of the rate of solvolysis at two extremes of solvent composition, then the equation satisfactorily expresses the rate of solvolysis at any intermediate solvent composition. On this evidence they concluded that the solvolytic reactions were indeed bimolecular. Then Bateman, Hughes, and Ingold pointed out (*J.*, 1938, 881) that the success of equation (1) as an interpolation formula for rates is not dependent on the assumed bimolecular mechanism, and that it could constitute an equally useful instrument for application to the rates of unimolecular reactions; but that an effective procedure for deriving conclusions relative to mechanism consisted in determining whether or not the same pair of constants,  $k_a$  and  $k_w$ , which are required to express rates of solvolysis by means of equation (1), would also correctly reproduce the proportions of the products when inserted in equation (2), namely,

$$\text{ROAlk}/(\text{ROAlk} + \text{ROH}) = k_a p_a / (k_a p_a + k_w p_w) \quad \dots \quad (2)$$

ROAlk and ROH are here the quantities of the ethereal and the alcoholic products, formed respectively from the solvent constituents Alk·OH and H<sub>2</sub>O by interaction with the alkyl halide RX. According to Olson and Halford's assumptions, the rate-derived constants should be applicable in equation (2), rates and products being determined in a single bimolecular reaction stage. The same pair of constants should, however, be in principle incapable of use for the calculation of both rates and product compositions if the mechanism is unimolecular, rates and products being in this case determined in different reaction stages. In the example of *tert.*-butyl chloride large discrepancies resulted when this test for bimolecularity was applied, consistently with the conclusion, previously reached on other grounds, that the solvolysis of this substance in aqueous media was unimolecular.

The mechanism of the aqueous solvolysis of *tert.*-butyl chloride has since then passed out of the stage of controversy, and we return to the subject only in order more completely to establish the general method of determining reaction mechanism; for Bateman, Hughes, and Ingold's work was incomplete in one respect: they certainly noted that, if the solvolytic reaction had been bimolecular, then, according to Olson and Halford's theory, equations (1) and (2) should have been consistently applicable, but they did not show that these equations are in fact consistently applicable in the case of a solvolysis which is admittedly bimolecular. A complementary experimental demonstration of this nature is evidently necessary for the establishment of the method.

It is already clear from earlier criteria that all the simpler primary alkyl halides undergo solvolysis in aqueous alcohol by the bimolecular mechanism (Hughes and Ingold, *J.*, 1935, 244; cf. Bateman, Cooper, Hughes, and Ingold, *J.*, 1940, 925). *n*-Butyl bromide was chosen for the present investigation, because it belongs to this class of halide, and because methyl *n*-butyl and ethyl *n*-butyl ethers could be estimated by the technique which Bateman, Hughes, and Ingold had developed for the corresponding *tert.*-butyl alkyl ethers.

The solvolysis of *n*-butyl bromide has been studied at 59.4° in methyl alcohol and in five mixtures of methyl alcohol and water; and also at 75.1° in ethyl alcohol and three mixtures of ethyl alcohol and water. In each case the first-order rate constant for solvolysis was determined, together with the "Henry's law constant" connecting the partial vapour pressure of *n*-butyl bromide with its concentration; the partial vapour pressures of the solvent constituents were already known from the work of Wrewsky (*Z. physikal. Chem.*, 1913, **81**, 17). In each case also the proportion was determined in which methyl *n*-butyl or ethyl *n*-butyl ether was formed. A very few units % of the *n*-butyl bromide became converted into Δ<sup>1</sup>-butene, and this proportion was estimated in a distributed selection of cases. The proportion of *n*-butyl alcohol being thence obtained by difference, all the data were available which were needed for the determination of mechanism.

As to the calculations, it is necessary to remark only that, since it is more convenient to deal with first-order rate constants than with instantaneous rates, the rate equation (1) is for practical purposes replaced by an equivalent specific rate equation, obtained by division throughout by the concentration of alkyl halide:

$$\text{Specific rate} = \frac{\text{Rate}}{[\text{RX}]} = k_1 = (k_a p_a + k_w p_w) \frac{p_{RX}}{[\text{RX}]} = (k_a p_a + k_w p_w) H_{RX} \quad \dots \quad (1')$$

Here  $H_{RX}$  is the "Henry's law constant" of the alkyl halide, defined for convenience as the partial vapour pressure divided by the molar concentration. All partial vapour pressures are expressed in mm. of mercury. The units of the kinetic constants  $k_a$  and  $k_w$  are (sec.<sup>-1</sup>) (g.-mol./l.) (mm. Hg.)<sup>-2</sup>. Specific rates are in sec.<sup>-1</sup>. For each series of solvents, the constants  $k_a$  and  $k_w$  were obtained from the measured specific rates of solvolysis at the extremes of the investigated range of solvent composition. The following values were found:

Methyl-alcoholic solvents at 59.4°	. . . . . $k_a = 1.32 \times 10^{-11}$ ; $k_w = 3.79 \times 10^{-11}$ .
Ethyl-alcoholic solvents at 75.1°	. . . . . $k_a = 2.10 \times 10^{-11}$ ; $k_w = 4.41 \times 10^{-11}$ .

It is shown in Table I that these constants enable the dependence of solvolysis rate on solvent composition to be calculated from equation (1') to within the accuracy of the observational data. (The main error, a few units

%, is contained in the "Henry's law constants," which were determined by aspiration. The first-order rate constants themselves are probably good to 1%.

TABLE I.

Rates of Solvolysis of *n*-Butyl Bromide in Aqueous Methyl-alcoholic Solvents at 59.4° and in Aqueous Ethyl-alcoholic Solvents at 75.1°, and Partial Vapour Pressures of the Reaction Components.

H <sub>2</sub> O in solvent.		Observed.					Calc.	H <sub>2</sub> O in solvent.		Observed.					Calc.
Wt. %.	Mols. %.	$p_a$ .	$p_w$ .	$H_{RX}$ .	$10^7 k_1$ .	$10^7 k_1$ .	Wt. %.	Mols. %.	$p_a$ .	$p_w$ .	$H_{RX}$ .	$10^7 k_1$ .	$10^7 k_1$ .		
Methyl-alcoholic solvents at 59.4°.															
0.0	0.0	609	0	47.2	3.8	*	20.0	30.8	439	58	155	13.9	12.5		
8.5	14.1	527	30	88.2	7.3	7.2	34.5	48.3	356	80	311	24.2	24.0		
16.7	26.3	461	52	147	11.6	11.9	45.8	60.1	302	92	486	36.4	*		
Ethyl-alcoholic solvents at 75.1°.															
0.0	0.0	665	0	55.3	7.8	*	33.3	56.2	393	227	323	56.7	58.6		
12.0	25.8	513	144	142	24.8	24.3	52.3	73.7	330	243	628	110.8	*		

\* The corresponding experimental values were used in order to calculate the constants  $k_a$  and  $k_w$ .

The kinetic constants, thus determined and tested, were next used in order to calculate product compositions for comparison with the compositions found analytically. The quantity calculated was the percentage extent to which the substitution reactions of *n*-butyl bromide proceed in the direction leading to methyl *n*-butyl or ethyl *n*-butyl ether: 100 ROAlk/(ROAlk + ROH). Any butylene formed merely represents so much *n*-butyl bromide diverted from the competing substitution processes. Reference to the experimental section, in which full analytical data are presented, will show that the actual amount of butylene produced is so small that it might have been neglected. However, for the sake of formal consistency we express the analytical results also in terms of the ratio 100ROAlk/(ROAlk + ROH). The comparison between the calculated and observed percentages of ether formed at the temperatures, and in the solvent mixtures, used for the kinetic investigation is shown in the left-hand section of Table II. In conformity with the presumption of a bimolecular mechanism, these values agree to within the error of the analytical determinations (a few units %).

In striking contrast stand the corresponding data obtained by Bateman, Hughes, and Ingold (*loc. cit.*) for *tert.*-butyl chloride, for which the formed proportion of ether was always 2—3 times larger than the proportion calculated. These figures are reproduced in the right-hand part of Table II. It would appear from the comparison that in the relation between solvent composition and product composition we have a very sharp criterion for mechanism.

TABLE II.

Illustrating determination of solvolytic mechanism by solvent variation.

(S <sub>N</sub> 2) <i>n</i> -Butyl bromide (this paper).					(S <sub>N</sub> 1) <i>tert.</i> -Butyl chloride (B., H., I., 1938).				
Solvent and temp.	Mols. % of H <sub>2</sub> O.	100ROAlk/(ROAlk + ROH).		Solvent and temp.	Mols. % of H <sub>2</sub> O.	100ROAlk/(ROAlk + ROH)			
		Calc.	Found.			Calc.	Found.		
MeOH-H <sub>2</sub> O mixtures at 59.4°	14.1	86	88	MeOH-H <sub>2</sub> O mixtures at 25.0°	16.4	43	83		
	26.3	75	74		28.4	29	68		
	30.8	72	72		40.0	17	49		
	48.3	61	61						
	60.1	53	51						
EtOH-H <sub>2</sub> O mixtures at 75.1°	25.8	63	63	EtOH-H <sub>2</sub> O mixtures at 25.0°	26.4	18	53		
	56.2	45	50		44.7	11	33		
	73.7	39	35		68.3	8	18		

However, it must not be forgotten that types of bimolecular reaction may exist for which Olson and Halford's rate equation does not represent so good an approximation as has here been illustrated,\* and also that it would

\* It has been noted before that equations (1) and (2) can only be approximate. According to the transition state theory, each of the terms  $k_a p_a p_{RX}$  and  $k_w p_w p_{RX}$  should be divided by the activity coefficient of the appropriate transition state. Bartlett has proposed an approximation in which these activity coefficients are taken as proportional to those of the corresponding solvent constituents, alcohol and water (*J. Amer. Chem. Soc.*, 1939, **61**, 1630). We have applied Bartlett's equations to our data and have obtained a similar general result, in particular, the same type of marked contrast between *n*-butyl bromide and *tert.*-butyl chloride. However, the agreement of Bartlett's formulæ with the experimental data for *n*-butyl bromide is definitely less exact than is that of Olson and Halford's formulæ, with respect both to the rates and to the product compositions. This led us to consider theoretically whether Bartlett's or Olson and Halford's approximation should be regarded as preferable. It is a difficult point on which to reach a definite conclusion, but we may note that both transition states contain hydrophilic quasi-ionic charges (due to the electron transfers), and both contain hydrophobic hydrocarbon radicals; also both contain a hydroxyl group associated with carbon and an extra proton. The combined effect of these features might be to render the activity coefficients somewhat insensitive to solvent composition, a circumstance which would favour Olson and Halford's approximation. In any case, since the common constitutional features mentioned are likely to be the most important determinants of the two activity coefficients, we might expect the latter to behave somewhat similarly, rather than the one behaving like the activity coefficient of water and the other like that of alcohol, as is assumed in Bartlett's approximation.

be possible for some particular unimolecular reaction to simulate accidentally the behaviour to be expected for a bimolecular process. For the one other unimolecular solvolysis for which the relevant investigation has been carried out, albeit incompletely, namely, the solvolysis of benzhydryl chloride, a very clear indication was obtained that a more complete study would have yielded results quite similar to those obtained by Bateman, Hughes, and Ingold for *tert.*-butyl chloride (Farinacci and Hammett, *J. Amer. Chem. Soc.*, 1937, **59**, 2544; Bateman, Hughes, and Ingold, *ibid.*, 1938, **60**, 3080).

## EXPERIMENTAL.

*Materials.*—*n*-Butyl bromide, dried and redistilled, had b. p. 100.5°/765 mm. Absolute methyl and ethyl alcohols were purified and fully dried by Lund and Bjerrum's method (*Ber.*, 1931, **64**, 210). Methyl *n*-butyl ether, prepared from *n*-butyl bromide and methyl-alcoholic sodium methoxide, had b. p. 71°/760 mm.; ethyl *n*-butyl ether, similarly obtained, had b. p. 92°/764 mm.

*Kinetic Measurements.*—Portions of 5 c.c. or 10 c.c. of the original solution of *n*-butyl bromide in the alcoholic or aqueous-alcoholic solvent were enclosed in sealed bulbs, which were immersed in the thermostat for the requisite times, and then cooled, cleaned, and broken under acetone, the liberated hydrobromic acid being finally titrated with sodium hydroxide. In the anhydrous and less aqueous solvents the first-order rate constants began to drift downward some time after the commencement of reaction, due to interaction of the liberated hydrogen bromide with the alcohol of the solvent. However, this disturbance did not enter early enough to interfere with the observation of satisfactory solvolytic rate constants. Table III shows the results of a typical run, and Table IV the summarised results of all the runs.

TABLE III.

*Solvolysis of n-butyl bromide: Kinetic run No. 16.*

[Solvent: Aqueous ethyl alcohol containing 88.0% by weight = 74.2 mols. % of ethyl alcohol. Temp. = 75.1°. *n*-Butyl bromide initially 0.0925M. Samples of 5.00 c.c. titrated with 0.0428N-sodium hydroxide.  $k_1 = (1/t) \ln a/(a-x)$  expressed in hr.<sup>-1</sup>.]

<i>t</i> (hrs.).	Titre (c.c.).	10 <sup>3</sup> <i>k</i> <sub>1</sub> .	<i>t</i> (hrs.).	Titre (c.c.).	10 <sup>3</sup> <i>k</i> <sub>1</sub> .	<i>t</i> (hrs.).	Titre (c.c.).	10 <sup>3</sup> <i>k</i> <sub>1</sub> .	<i>t</i> (hrs.).	Titre (c.c.).	10 <sup>3</sup> <i>k</i> <sub>1</sub> .
0.00	0.00	—	24.6	2.10	8.83	95.7	5.93	8.33	216.0	8.22	6.62
5.45	0.51	8.90	42.9	3.45	8.96	121.1	6.62	7.83	480.0	9.31	4.12
13.50	1.23	8.90	48.2	3.80	9.00	163.6	7.70	7.63	∞	10.80	—
19.10	1.70	8.97	64.7	4.75	8.95						

(The first seven values of *k*<sub>1</sub> lead to the mean 0.00893 hr.<sup>-1</sup>; the last five values show the incursion of the solvent reaction mentioned in the text.)

TABLE IV.

*Solvolysis of n-butyl bromide: Summarised results of kinetic experiments.*

[In all runs the *n*-butyl bromide was initially about 0.09M.]

Run No.	H <sub>2</sub> O in solvent.		No. of 10 <sup>3</sup> <i>k</i> <sub>1</sub> values averaged.	Range of 10 <sup>3</sup> <i>k</i> <sub>1</sub> values averaged.	10 <sup>3</sup> <i>k</i> <sub>1</sub> ( <i>k</i> <sub>1</sub> in hr. <sup>-1</sup> ).	
	Wt. %.	Mols. %.			Mean.	Mean.
Methyl-alcoholic solvents at 59.4°.						
1	0.0	0.0	10	1.34—1.39	1.37	} 1.37
2	"	"	4	1.35—1.39	1.37	
3	8.5	14.1	7	2.61—2.67	2.64	} 2.64
4	"	"	7	2.57—2.69	2.64	
5	16.7	26.3	7	4.10—4.27	4.16	} 4.16
6	"	"	5	4.11—4.19	4.15	
7	20.0	30.8	6	4.96—5.06	5.00	} 5.01
8	"	"	7	4.94—5.09	5.02	
9	34.5	48.3	10	8.74—8.95	8.82	} 8.83
10	"	"	6	8.79—8.92	8.84	
11	45.8	60.1	3	13.00—13.24	13.10	} 13.11
12	"	"	5	13.00—13.16	13.09	
13	"	"	10	13.00—13.20	13.13	
Ethyl-alcoholic solvents at 75.1°.						
14	0.0	0.0	6	2.78—2.84	2.80	} 2.80
15	"	"	4	2.80—2.82	2.81	
16	12.0	25.8	7	8.83—9.00	8.93	} 8.91
17	"	"	7	8.80—9.00	8.89	
18	33.3	56.2	11	19.5—21.3	20.5	} 20.4
19	"	"	5	19.8—20.6	20.3	
20	52.3	73.7	7	38.8—40.9	40.2	
21	"	"	5	38.9—40.5	39.7	} 39.9
22	"	"	7	39.0—40.4	39.9	

*Estimations of Methyl n-Butyl Ether and Ethyl n-Butyl Ether.*—The method was essentially the same as that employed by Bateman, Hughes, and Ingold (*loc. cit.*) in the case of the corresponding *tert.*-butyl ethers. The first step is to carry out an "isolation experiment," in which the reaction mixture is fractionated after dilution with water, and the ether isolated as described below; and the next is to proceed with a parallel "recovery experiment" on a synthetic solution corresponding in all respects to the completed reaction mixture, except for the omission of the trace of olefin. Isolation and recovery experiments were carried out for each of the eight aqueous-alcoholic media used in the kinetic runs. For all the aqueous methyl-alcoholic media the recovery of methyl *n*-butyl ether from synthetic solutions was 49 ± 1%;

and from all the aqueous ethyl-alcoholic media the recovery of ethyl *n*-butyl ether was 64—65%. Attempts to increase these figures failed, but repetitions showed that the figures themselves were reliably reproducible.

Original solutions for isolation experiments were each prepared from 1000 c.c. of the aqueous-alcoholic medium and 30.0 c.c. of *n*-butyl bromide. Each solvolysis was allowed to proceed until complete in a flask, immersed to the neck in the thermostat at the temperature of the corresponding kinetic run, and fitted with a reflux condenser stoppered at the top. A few drops of phenolphthalein were added, and the solution was kept only just on the acid side of the neutral point by periodic additions of a solution of sodium hydroxide in the particular aqueous-alcoholic medium employed in the experiment. This was to guard against further reaction by the initially formed solvolysis products. At the end of the period of heating, the solution was diluted with water to 1600 c.c., and fractionated with additions of water, and, in the later stages, of calcium chloride, just as in the former research, the precipitated ether being distilled from fused barium oxide and from potassium, and finally weighed and checked for purity by analysis. B. p.'s were correct and constant to  $\pm 0.4^\circ$  and analyses to  $\pm 0.3\%$ ; e.g., a weighed sample of methyl *n*-butyl ether had b. p. 70.6—71.4°/760 mm., and on analysis gave C, 68.12, 68.23; H, 13.57, 13.97 (Calc.: C, 68.18; H, 13.72%). Original solutions for the recovery experiments were made from 1100 c.c. of the aqueous-alcoholic medium (the excess of this over the amount used for the isolation experiment representing the volume of sodium hydroxide solution added during the course of the latter), 28 g. of sodium bromide, known weights, determined by the requirements of the corresponding isolation experiment, of *n*-butyl alcohol and of either methyl or ethyl *n*-butyl ether, and a few drops of phenolphthalein. The results are in Table V.

TABLE V.

Estimations of the methyl *n*-butyl ether and ethyl *n*-butyl ether formed by solvolysis of *n*-butyl bromide in aqueous methyl alcohol at 59.4° or aqueous ethyl alcohol at 75.1°.

(In all experiments the initial quantity of *n*-butyl bromide was 0.277 g.-mol.)

Solvent and temp.	H <sub>2</sub> O in solvent.		Isolated ether (g).	Mean recovery % (by expt.).	Ether formed.	
	Wt. %.	Mols. %.			Mols. %.	Mean.
MeOH + H <sub>2</sub> O at 59.4°	8.5	14.1	10.2	48	87	87
	16.7	26.3	{ 9.0 } { 8.7 }	50	{ 74 } { 71 }	73
	20.0	30.8	{ 8.4 } { 8.3 }	48	{ 72 } { 71 }	71
	34.5	48.3	{ 6.8 } { 7.2 }	48	{ 58 } { 62 }	60
	45.8	60.1	{ 6.0 } { 6.1 }	49	{ 50 } { 51 }	51
	EtOH + H <sub>2</sub> O at 75.1°	12.0	25.8	{ 11.0 } { 11.4 }	65	{ 60 } { 62 }
33.3		56.2	{ 8.9 } { 9.0 }	64	{ 49 } { 50 }	49
52.3		73.7	6.4	64	35	35

*Estimations of Olefin.*—It has been recognised in the course of previous work that, in solvolytic reactions which become acidic, any olefin formed may partly or wholly disappear again on account of an acid-catalysed addition to it of solvent molecules (Cooper, Hughes, and Ingold, J., 1937, 1280; Hughes and MacNulty, *ibid.*, p. 1283). Therefore, in order to determine the proportion in which an olefin is formed, it is in general necessary to follow the variations in its concentration from the commencement of reaction. For a certain time the amount of olefin present will bear a constant ratio to the amount of the original material destroyed: this constant value must represent the proportion in which the olefin is formed. At some stage, however, the ratio will begin to fall, even though the absolute amount of olefin present may for a time continue to rise; still later, the absolute amount will fall: the effects are successive consequences of the attack of solvent molecules on the first-formed olefin. If we are interested only in the formation of olefin, and not in its reactions, measurements may be stopped as soon as the above-mentioned ratio begins to depart from constancy.

These principles being employed, olefin production in the solvolysis of *n*-butyl bromide, in the solvents and at the temperatures employed for the kinetic runs, was estimated by the sealed-bulb method described in connexion with the kinetic measurements, with the exception that two bulbs were needed for each point on the record of olefin development, one for the alkalimetric estimation of the amount of *n*-butyl bromide destroyed, and the other for the estimation, by bromine addition, of the amount of olefin present. The latter measurement was made by cooling the bulb in a freezing mixture of solid carbon dioxide and alcohol, drying it, and breaking it under a mixture of carbon tetrachloride (60 c.c.) and ice-water. The mixture was shaken, and the carbon tetrachloride layer was first dried for 5 mins. with calcium chloride, and then treated with a solution of bromine in carbon tetrachloride nearly saturated with hydrogen bromide. After 5 mins. had been allowed for the interaction, the residual bromine was estimated by titration with thiosulphate after the addition of potassium iodide and water. The bromine solution was similarly standardised just before and just after the 5-min. interval allowed for the reaction. The results of a typical determination are recorded in Table VI, and a summary of all the values obtained is given in Table VII.

TABLE VI.

Olefin development in solvolysis of *n*-butyl bromide: Olefin run No. 5.

(Solvent: Aqueous ethyl alcohol containing 66.7% by weight = 43.8 mols. % of ethyl alcohol. Temp.: 75.1°. *n*-Butyl bromide initially 0.0927M. Samples of 5.00 c.c. titrated with 0.0428N-sodium hydroxide. Bromine uptake by samples of 5.00 c.c. measured by titration with 0.0455N-thiosulphate.)

Bu <sup>a</sup> Br destroyed (equiv. c.c. NaOH) .....	0.91	1.88	4.60	6.47
" " (% of initial Bu <sup>a</sup> Br) .....	8.4	17.4	42.5	59.9
C <sub>4</sub> H <sub>8</sub> present (equiv. c.c. Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> ) .....	0.03	0.06	0.15	0.14
" " (% of initial Bu <sup>a</sup> Br) .....	0.15	0.30	0.75	0.70
" " (% of Bu <sup>a</sup> Br destroyed) .....	1.8	1.7	1.8	1.2
" formed (% of Bu <sup>a</sup> Br destroyed) .....	1.8			—

TABLE VII.

Olefin formation in solvolysis of *n*-butyl bromide: Summarised results.(In all runs the *n*-butyl bromide was initially about 0.09M.)

Methyl-alcoholic solvents at 59.4°.				Ethyl-alcoholic solvents at 75.1°.			
Run No.	H <sub>2</sub> O in solvent.		Percentage in which Bu <sup>a</sup> Br is converted into C <sub>4</sub> H <sub>8</sub> .	Run No.	H <sub>2</sub> O in solvent.		Percentage in which Bu <sup>a</sup> Br is converted into C <sub>4</sub> H <sub>8</sub> .
	Wt. %.	Mols. %.			Wt. %.	Mols. %.	
1	8.5	14.1	1.7	4	12.0	25.8	2.7
—	16.7	26.3	(1.5) *	5	33.3	56.2	1.8
2	20.0	30.8	1.4	6	52.3	73.7	1.2
—	34.5	48.3	(1.1) *				
3	45.8	60.1	0.8				

\* Interpolated from the other results and used in the calculations in Table II.

It may be pointed out that the reason why we do not care what happens to the olefin, even though its reactions may lead to a *n*-butyl alkyl ether, is because in the estimation of these ethers we took the precaution of maintaining a nearly neutral solution in order (amongst other things) to block any route to the ethers other than that of direct solvolysis of the *n*-butyl bromide. Thus our estimates of ether, like that of olefin, and therefore like that of *n*-butyl alcohol by difference, represent what we require, namely, the quantities of these materials that are directly formed from *n*-butyl bromide, undisturbed by any interconversion of products subsequently to their formation. Since none of the reactions which interconvert the products consumes or produces hydron, they do not disturb the kinetic measurements.

*Partial-pressure Determinations.*—The partial pressures of *n*-butyl bromide in the solvents, and at the temperatures, employed for the kinetic measurements were determined by aspiration. The apparatus consisted essentially of a helical spiral, made from glass tubing 20 mm. in diameter, which was held on an upright axis in the thermostat, and was provided with an internally projecting capillary air inlet at the lower extremity, and with delivery arrangements at the upper. The helix was of such a length that when charged with 350 c.c. of the solution to be examined there was adequate free space at the upper end. It was necessary so to adjust the size of the capillary and the pitch of the helix that, on aspiration, a fairly copious procession of small bubbles was produced, which did not overtake one another on their way up the helix. Too high a pitch reduces the time available for the saturation of the bubbles; too low a pitch causes them to coalesce; the latter occurrence also resulted from too high a flow-rate, and too low a flow-rate gave opportunity for the composition of the solution to change by solvolysis during the course of the measurement. The upper end of the helix led successively to a small bulb and a U-tube, intended to catch splashes of liquid, and then to an inverted U-tube, the bend of which, projecting above the bath liquid, carried the delivery tube over the side of the thermostat to the male part of a ground joint. The part of this delivery tube which extended from the thermostat liquid to a point well past the top of the bend was provided with an electrical winding, by means of which it could be heated to about 100° during the course of a determination in order to prevent premature condensation. The only other part of this jointless all-glass unit which projected from the thermostat was the tube leading to the capillary inlet. This tube was connected at its upper end, through a ground joint, to the air-purifying train. By means of the ground joint at the delivery end of the helical unit, connection was made to a trap for the condensation of the aspirated vapour. Thence the gas line led through drying tubes to a calibrated aspirator, a branch being provided to accommodate a manometer.

The solution having attained the temperature of the thermostat, the condensation trap was replaced by a plain piece of tubing, and aspiration was started, in order to sweep out the delivery end of the apparatus and attain steady conditions. Then the trap, cooled in solid carbon dioxide and alcohol, was put into place, and about 50—150 c.c. of air, measured as to pressure and volume, were drawn through the apparatus. The trap was then detached, and fitted with a reflux condenser, and the condensate was boiled with a measured volume of standard alcoholic silver nitrate. The condensed *n*-butyl bromide was thus estimated by the disappearance of silver ion, as subsequently determined by titration with thiocyanate.

TABLE VIII.

Partial vapour pressures of 0.0927M-*n*-butyl bromide in aqueous methyl- and ethyl-alcoholic solutions.

Wt. % H <sub>2</sub> O.	Mols. % H <sub>2</sub> O.	<i>v</i> (c.c.).	<i>p</i> (mm.).	<i>v</i> <sub>RX</sub> (c.c.).	<i>p</i> <sub>RX</sub> (mm.).	Mean (mm.).	Wt. % H <sub>2</sub> O.	Mols. % H <sub>2</sub> O.	<i>v</i> (c.c.).	<i>p</i> (mm.).	<i>v</i> <sub>RX</sub> (c.c.).	<i>p</i> <sub>RX</sub> (mm.).	Mean (mm.).	
Methyl-alcoholic solvents at 59.4°.														
0.0	0.0	{	94	727	3.38	4.09	4.37	20.0	30.8	{	81	730	6.16	16.5
			93	734	3.42	4.42					101	730	5.62	12.3
			100	734	3.74	4.50					104	728	11.40	28.9
8.5	14.1	{	100	726	5.34	8.57	8.18	34.5	48.3	{	103	728	11.70	29.5
			73	726	3.52	7.79					80	728	8.51	28.1
			73	726	3.52	7.78					102	723	15.90	44.4
16.7	26.3	{	102	733	7.10	14.3	13.65	45.8	60.1	{	102	723	16.48	45.8
			100	733	7.09	14.6					101	730	15.80	45.5
			100	738	6.40	13.1					102	730	15.55	44.5
			98	738	6.02	12.6								
Ethyl-alcoholic solvents at 75.1°.														
0.0	0.0	{	187	716	21.65	5.08	5.13	33.3	56.2	{	125	733	43.70	29.2
			187	716	21.80	5.12					56	733	20.35	30.1
			140	724	13.82	5.12					55	732	20.40	30.3
			140	724	14.05	5.20					70	730	41.00	58.2
12.0	25.8	{	78	733	16.49	13.10	13.15	52.3	73.7	{	80	730	47.10	58.2
			82	733	17.20	13.20								
			100	717	28.10	13.15								

If a volume, *v* c.c., of dry air is saturated at *t*° and *p* mm. pressure, and if the condensate contains *w*<sub>a</sub>, *w*<sub>w</sub>, and *w*<sub>RX</sub> g. respectively of (methyl or ethyl) alcohol, water, and *n*-butyl bromide, the molecular weights of these substances being

$m_a$ ,  $m_w$ , and  $m_{RX}$  respectively, then the total volume after saturation will be  $(v + v_a + v_w + v_{RX})$  c.c., where  $v_a = 22400(t + 273) \times 760w_a/273pm_a$ ; analogous expressions hold for  $v_w$  and  $v_{RX}$ . The partial pressures of the constituent vapours will be  $p_a = pv_a/(v + v_a + v_w + v_{RX})$  mm., the formulæ for  $p_w$  and  $p_{RX}$  being similar. Eliminating  $v_a$  and  $v_w$  among these equations, we find  $p_{RX} = v_{RX}(p - p_a - p_w)/(v + v_{RX})$  mm. Here  $p$  and  $v$  are directly measured,  $v_{RX}$  follows from the measured  $w_{RX}$ , and  $p_a$  and  $p_w$  from Wrewsky's results.

In all experiments the initial concentration of *n*-butyl bromide was 0.0927M. Corrections for the diminution of concentration during the course of a measurement, either through solvolysis or through aspiration itself, were too small to be worth applying. The results are in Table VIII.

The corresponding "Henry's law constants" are obtained from the partial pressures by division by 0.0927, the molarity of the *n*-butyl bromide. These values, together with the partial pressures  $p_a$  and  $p_w$ , are listed in Table I.

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