# **248.** Mechanism of Substitution at a Saturated Carbon Atom. Part VII. Hydrolysis of isoPropyl Halides.

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The determinations of the rate constants and of B and E in the Arrhenius equation,  $k = Be^{-E/RT}$ , for the substitution and elimination reactions which have been shown to occur simultaneously in the alkaline hydrolysis of *iso* propyl bromide are here extended to include the chloride and the iodide. The simultaneous reactions are a "bimolecular" substitution, *e.g.*,

 $OH^- + Pr^{\beta}Br \longrightarrow Pr^{\beta}OH + Br^-$ 

a " unimolecular " substitution, e.g.,

$$\begin{cases} \Pr^{\beta} Br \xrightarrow{slow} \Pr^{\beta+} + Br^{-} \\ \Pr^{\beta+} + OH^{-} \xrightarrow{fast} \Pr^{\beta} OH \end{cases}$$

and a "bimolecular" elimination, e.g.,

 $OH^- + Pr^{\beta}Br \longrightarrow C_3H_6 + H_2O + Br^-$ 

For all the reactions there is a much larger velocity difference between chloride and bromide than between bromide and iodide : the observed spacing is referred to a joint dependence of the rate on both C-Hal. bond-strength and halogen polarisability. The bimolecular substitution is much slower for the *iso*propyl than for the ethyl halides in agreement with views advanced in earlier papers. The dependence of the chief velocity differences on the separate parameters of the Arrhenius equation is discussed.

MUCH has been written in previous parts of this series on the interest attaching to such sequences as Alk = Me, Et,  $Pr^{\beta}$ ,  $Bu^{\gamma}$  in relation to the mechanism and kinetics of nucleophilic substitutions of the form

$$Y + Alk \longrightarrow Y - Alk + X$$

Experimental studies have been contributed for this and other alkyl series in cases in which the substituting agent Y takes forms such as OH, OEt, OPh, OAc. Hal. whilst the displaced group X is  $NR_3$ ,  $SR_2$  or Hal. This paper continues the study of the homologous alkyl series, and belongs to the group of investigations for which the substituting agent is OH.

OH or OEt and the displaced group a halogen atom.

It has been shown that, for the first two members of the alkyl series, Alk = Me, Et, the substitution of the halogen by OH or OEt is a bimolecular process, whilst for the last member  $Alk = Bu^{\gamma}$  substitution by OH is unimolecular in aqueous solvents. In Part VI (J., 1936, 225) it was proved in the example of *iso* propyl bromide that when  $Alk = Pr^{\beta}$ the bimolecular and unimolecular reactions have comparable velocities, and are present together under conditions convenient for measurement. We now extend the investigation to isopropyl chloride and iodide, so that we can compare the rates of the constituent reactions for the three isopropyl halides. As with isopropyl bromide so with the chloride and iodide there is an accompanying elimination of olefin, and this is bimolecular. The separate rate constants of the olefin eliminations having been evaluated, we can compare these also for the three halides. The results also permit comparisons between the bimolecular rates for the isopropyl halides and the total (bimolecular) rates for the ethyl halides, and, account being taken of the work described in Part VIII (following paper), between the unimolecular rates for the *iso*propyl halides and the total (unimolecular) rates for the *tert*.-butyl halides. Measurements have been made at different temperatures : the temperature coefficients of the several reactions can thus be compared, and their dependence on the nature of the alkyl group and of the halogen atom can be deduced.

We shall as usual designate the bimolecular substitution and elimination  $S_N 2$  and E2 respectively, and the unimolecular substitution  $S_N 1$ . The method employed in the evaluation of the separate rate constants was similar to that described in Part VI (*loc. cit.*). The first-order reaction was isolated by the use of low concentrations of hydroxide ions (neutral or acidic solutions), while the olefin elimination and the total reaction were measured in fairly concentrated alkaline solutions. The solvents used, "60%" and "80%" aqueous ethyl alcohol, are denoted by A and B respectively in Table I, which records the velocity coefficients at  $80.0^{\circ}$  for the three *iso* propyl halides. The units of *k* are l./g.-mol.-sec. or sec.<sup>-1</sup> as the case may be. The right-hand column contains results by Grant and Hinshelwood (J., 1933, 258) for the total bimolecular reaction,  $S_N 2 + E2$ , of the corresponding ethyl halides in 100% ethyl alcohol (C).

TABLE I.

Velocity Coefficients (10<sup>4</sup>k) of Hydrolysis \* of Ethyl and isoPropyl Halides at 80°.

	S	<sub>N</sub> 2.	E	2.	S	<sub>N</sub> 1.	$S_N 2 +$	E2.
Solvent.	Ã.	B.	Ã.	B.	Á.	B.	Ċ.	_
$Halide \begin{cases} \Pr^{\beta} Cl & \dots \\ \Pr^{\beta} Br & \dots \\ \Pr^{\beta} I & \dots \\ \end{cases}$	3.56 8.18	$\begin{array}{c} 0.136 \\ 4.97 \\ \end{array}$	$5.01 \\ 23.14$	$     \begin{array}{c}       0.189 \\       7.805 \\      \end{array} $	$0.836\\1.16$	$0.00889 \\ 0.289 \\$	EtCl EtBr EtI	$7.73 \\ 226 \\ 460$

\* Alcoholysis also takes place but this does not affect any of the deductions drawn in this paper (cf. Part VI and the experimental section).

Two points stand out clearly in this comparison. The first is that, despite the difference of solvent and the fact that Grant and Hinshelwood record only the collective constants for the total reactions of the ethyl halides, the bimolecular substitution is much slower for the *iso*propyl halides than for the ethyl halides. This has been discussed in some detail in relation to the bromides in Part VI, and all that need be added is that the relation is general for the three halides, and can be explained on the lines already considered.

The second point is that for all these reactions there is a much larger velocity difference between chloride and bromide than between bromide and iodide. This was also a feature of the early results of Conrad and Bruckner (Z. physikal. Chem., 1889, 4, 631) relating to the action of sodium ethoxide on alkyl halides in alcoholic solution (RBr/RCl = ca. 60 and RI/RBr = ca. 2 for a number of alkyl groups), and a similar irregular sequence was recorded recently by Bergmann, Polanyi, and Szabo (*Trans. Faraday Soc.*, 1936, 32, 843) for the reaction of sodium iodide with the  $\beta$ -n-hexyl halides in acetone solution (Br/Cl = 620, I/Br = 19). This raises some very complicated questions, but we may point out that, whereas the C—Hal. bond strengths and stretching force-constants vary in a fairly regular manner in the series Cl, Br, I, the polarisabilities of these atoms vary irregularly, the large separation being between bromine and iodine. Bond strengths and stretching force-constants relate to dissociation into neutral atoms or radicals in the absence of a solvent, and hence it is only reactions taking place without electron transference in the gaseous phase that would be expected, *a priori*, to be represented by nearly equally spaced velocity ratios, on the basis of the variation in bond strengths and force-constants. Reactions in solution of the type under discussion will be profoundly influenced by polarisation, polarisability and solvation factors, and it is not surprising that there does not appear to be any obvious relationship between bond strengths or force-constants and velocity in these reactions. The dependence of the energy required for electron transference on halogen polarisability might conceivably produce the observed spacing of the rates.

It remains for us to examine the behaviour of the Arrhenius critical energy in relation to these measurements. The value of the parameters B and E in the equation  $k = Be^{-E/RT}$  are recorded in Table II; E is in kilo-cals. and B in l./g.-mol.-sec. or sec.<sup>-1</sup>, according as the reaction is bimolecular or unimolecular.

TABLE II.

Arrhenius Parameters B and E for Hydrolysis of Ethyl and isoPropyl Halides.

				Е.				
	S	<sub>1</sub> 2.	E	2.	SN	1.	S	$_{N}2 + E2.$
		·		L	<u> </u>	~	L. L.	
Solvent.	А.	В.	А.	В.	А.	в.		С.
$(Pr^{\beta}C)$	-	23.0		24.8		$23 \cdot 2$	EtCl	23.0
Halide Pr <sup>β</sup> Br	20.8	21.7	$22 \cdot 1$	22.6	22.7	$23 \cdot 2$	EtBr	21.0
[Pr <sup>β</sup> Ι	20.7		$\overline{22}\cdot\overline{2}$		$23 \cdot 8$		EtI	21.0
				$10^{-9}B.$				
$\int Pr^{\beta}Cl$		2.6		48		0.21	EtCl	149
Halide Pr <sup>β</sup> Br	2.7	14	<b>25</b>	83	$9 \cdot 0$	6.5	EtBr	241
$\Pr^{\beta}$ I	$4 \cdot 9$		141		<b>62</b>		EtI	508

We confine discussion here to the bimolecular reactions, because the following paper contains a further experimental study of unimolecular reactions of the type  $S_N 1$ .

It has been emphasised in previous papers that no simple significance can be attached to the allocation of small velocity differences between the parameters of the Arrhenius equation. However, for reactions  $S_N 2$  and E2 of the *iso*propyl halides, and for the total reaction  $S_N 2 + E2$  of the ethyl halides, the fairly large rate differences between the chlorides and the bromides appear chiefly as differences in the critical energies (cf. Grant and Hinshelwood, *loc. cit.*). Between bromides and iodides there is no difference of any account in the *E* values or, of course, in the *B* factors, since the velocities themselves are insufficiently separated. On the other hand, as far as the comparisons can be made (for it is to be noted that the solvents are different), the velocity difference between the bimolecular substitution ( $S_N 2$ ) for the *iso*propyl halides and the total reaction (largely  $S_N 2$ ) for the ethyl halides appears mainly as a difference in *B* for the three halides examined. It was noted in Part VI that the temperature coefficient of E2 was greater than that of  $S_N 2$  in the case of *iso*propyl bromide, and we now see that this is also true of the chloride and the iodide.

#### EXPERIMENTAL.

*Materials.*—The *iso*propyl chloride was dried over phosphoric oxide and fractionated from a little anhydrous sodium carbonate, the fraction, b. p.  $36 \cdot 5^{\circ}/760$  mm., being used for the measurements. The *iso*propyl iodide was shaken with mercury to remove iodine, dried over phosphoric oxide, and fractionated twice, b. p.  $89 \cdot 5^{\circ}/760$  mm. It was kept in a brown bottle in the dark, and no further coloration took place. The "60%" aqueous alcohol was made by mixing 6 l. of lime-dried alcohol with 4 l. of water, and the "80%" aqueous alcohol by mixing 8 l. of the alcohol with 2 l. of water.

Velocity Measurements.—The thermostats at 50°, 70°, and 90° could be set to within 0.05°. The one kept at  $109.6^{\circ}$  was subject to larger fluctuations over short periods of time, but the average temperature over 15-min. intervals was sensibly constant. The initial concentration of the isopropyl halides was determined by introducing an accurately weighed quantity into the appropriate medium (initially neutral or strongly alkaline) and making up to a standard volume; where possible this was checked by observation of the asymptotic value of the halide-ion concentration after long intervals. For each run a number of small, thin-walled, glass tubes, each containing 5-c.c. portions of the reaction mixture, were sealed, and heated in the thermostat, and at successive intervals of time a tube was removed, quickly cooled, and opened. The contents were estimated either by the change in the acidity of the solution, or by a modified silver nitrate titration. In the former method, the tubes were broken under about 100 c.c. of absolute alcohol and the acid was titrated with, e.g., 0.02N-sodium hydroxide, lacmoid being used as indicator. The latter method is suitable for hydrolysis in the presence of excess of alkali. In the case of *iso*propyl chloride the method was as follows : a tube is broken under ether, and the alkali neutralised with aqueous sulphuric acid; nitric acid, excess of standard silver nitrate solution, and the indicator (ferric alum) are added, and the excess of silver ions is estimated by titration with standard ammonium thiocyanate. The ether plays a dual rôle—it extracts the unreacted *iso* propyl chloride, and thus minimises further hydrolysis and reaction with silver nitrate, and it improves the end-point by coagulating the silver chloride formed. In the case of *iso*propyl iodide the method had to be modified, as direct titration with silver nitrate, even in the presence of ether, led to a reaction with the unchanged halide. The method adopted was as follows: the tube was broken under carbon tetrachloride, which dissolves the organic iodide; the inorganic iodide was then extracted twice with water, and the aqueous layer was neutralised with aqueous sulphuric acid and titrated with silver nitrate, eosin being used as indicator.

The propylene was estimated as described in Part VI (loc. cit.).

Estimation of isoPropyl Ethyl Ether.—Large-scale experiments were carried out on the hydrolysis of the chloride only. After completion of the reaction, the product was carefully fractionated, and the first fraction, b. p. below  $70^{\circ}/760$  mm., was refluxed with sodium to remove water and alcohol. The ether was distilled into a cooled, tared receiver, and weighed. In acidic solution it was estimated that *iso*propyl ethyl ether was formed to the extent of about 30 mols.%, and in alkaline solution to the extent of 5 mols. %, of which 1% was due to  $S_{\rm N}1$ .

The First-order Reactions.—isoPropyl chloride. In a preliminary run it was observed that the acid titre increased to a maximum and then decreased (Table III). A maximum corresponding to incomplete reaction might, of course, have been due to a reversible hydrolysis:  $Pr^{\beta}Cl + H_2O \implies Pr^{\beta}OH + HCl$ , but the subsequent decrease was obviously due to another cause. It was traced to a reaction between the hydrochloric acid and the ethyl alcohol medium [Table IV (a)], and it was shown that the analogous reaction with the *iso*propyl alcohol formed in the hydrolysis must be inappreciable in comparison [Table IV (b)]. In order to determine the first-order rate constant, we therefore had to resort to the "initial velocity" method. Initially neutral solutions were used, and the reaction was followed to the extent of about 30% by

#### TABLE III.

Demonstrating the decrease in the concentration of HCl in the hydrolysis of *iso*propyl chloride in "80%" aqueous ethyl alcohol. Temp. 109.65°. Initially  $[Pr^{\beta}Cl] \sim N/5$  and [HCl] = 0. [HCl] expressed as equivalent c.c. of 1.475N/10-NaOH per 5 c.c. of solution.

t (hrs.)	 . <b>1.00</b>	$2 \cdot 00$	6.00	10.00	25.70	80.00	100.00
[HCl]	 3.25	$6 \cdot 20$	16.25	$22 \cdot 45$	32.70	30.80	$29 \cdot 90$

# TABLE IV.

Demonstrating the reaction between hydrochloric acid and (a) "80%" aqueous ethyl alcohol, (b) "80%" aqueous ethyl alcohol + *iso*propyl alcohol. Temp. 109.65°. Initially [HCl] ~ N/10. [HCl] expressed as equivalent c.c. of N/20-NH<sub>4</sub>CNS per 5 c.c. of solution. X = [HCl] reacted (in the same units).

	(a) [Prβ	OH] = 0.	(b) [Pr <sup><math>\beta</math></sup> OH] ~ N/5.			
t (hrs.).	[HCl].	Χ.	[HCl]	Χ.		
0.00	30.80		30.30			
3.50	26.80	4.00	26.25	4.05		
10.00	20.65	10.12	20.05	10.25		
20.00	13.60	17.20	10.25	17.20		

determination of the increase in acidity. The unimolecular constant was not very seriously affected by the secondary reaction over the initial range (Table V), and the true value was found by a graphical extrapolation to zero time of the results of at least two separate runs. Measurements were made at 90.0° and 109.65°. The first-order constants may be taken as  $k_{90.0°}$  (hr.<sup>-1</sup>) = 0.00798 and  $k_{109.65°}$  (hr.<sup>-1</sup>) = 0.0416.

### TABLE V.

Illustrative record of two out of a number of experiments to determine the unimolecular rate constants of the hydrolysis of *iso*propyl chloride in "80%" aqueous alcohol at two temperatures. Initially [Pr<sup>β</sup>Cl] ~ N/5. Samples of 5 c.c. titrated. [Pr<sup>β</sup>Cl] expressed as equivalent c.c. of  $1\cdot475N/100$ -NaOH.  $k_1 = \text{first-order rate constant in hours}^{-1}$ , calculated from the formula  $k_1 = (1/t) \cdot \log_e\{a/(a - x)\}$ , where a is the initial concentration of *iso*propyl chloride and x the decrease in concentration.

Te	mp. 90·0	۰.	Te	mp. 90•0	°.	Ter	np. 109∙6	$5^{\circ}$ .	Ten	ıp. 109∙6	5°.
<i>t</i> (hrs.).	$[Pr^{\beta}C1].$	$10^{3}k_{1}$ .	<i>t</i> (hrs.).	$[\Pr^{\beta}C1].$	$10^{3}k_{1}$ .	t (hrs.).	[Pr <sup>β</sup> Cl].	$10^{2}h_{1}$ .	t (hrs.).	$[Pr^{\beta}Cl].$	$10^{2}k_{1}$ .
`0∙0ó	73.95		16.10	65.40	7.62	0.00	73.50		3.10	$64 \cdot 90$	4.03
$4 \cdot 00$	71.65	7.88	$21 \cdot 17$	63.05	7.52	0.20	72.00	$4 \cdot 14$	4.55	61.05	4.07
7.00	70.05	7.74	27.00	60.00	7.74	0.75	71.40	3.87	6.00	57.70	4.03
10.00	68.50	7.74	42.50	54.25	7.28	1.00	70.70	3.89	8.01	54.35	3.77
12.25	67.45	7.62				1.51	$69 \cdot 10$	4.09	10.00	51.50	3.54
						2.00	67.75	4.07			

iso *Propyl iodide*.—In "80%" aqueous ethyl alcohol appreciable quantities of iodine were formed after 5—10% of reaction had taken place. This may result either from the oxidation of the hydriodic acid produced in the hydrolysis, or from a non-hydrolytic decomposition of the alkyl iodide. Determinations of the amounts of free iodine formed when N/10-solutions in "80%" aqueous ethyl alcohol of (a) hydriodic acid and (b) isopropyl iodide were left under identical conditions showed that by far the greater amount results from direct decomposition of the *iso*propyl iodide. Special precautions to exclude the access of light and air, such as passing a stream of nitrogen through the solution before sealing the tubes, and enclosing them in black bags, effected a decrease in the iodine content; but the application of the initial velocity method to the results met with little success, even after applying a correction for the iodine (estimated by titration with thiosulphate). In "60%" aqueous ethyl alcohol, however, the hydrolytic reaction was greatly facilitated at the expense of the decomposition; and it was possible to follow 50% of the reaction satisfactorily by determination of the increase in acidity, the iodine formation being unimportant to that point. Light and oxygen were again excluded as far as possible, and under these conditions a good unimolecular constant was obtained (Table VI). Measurements were made at 50.0° and 69.9°.

#### TABLE VI.

Demon	strating	the firs	t-order r	ate con	stant o	of the h	ydrolys	is of $i$	sopro	pyl io	dide in	. ** 60	%"	aque	eous
alcohol. 🕻	Гетр. 5	0∙0°.	Initially	$[Pr^{\beta}I]$	~ N	/10. Sa	mples	of 5	c.c. 1	titrate	ed. [F	PrβI]	exp	ressec	i as
equivalent	c.c. of	1.475N	7/100-Na/	OH. /	$e_1 = fi$	rst-orde	r const	tant i	n hoi	urs <sup>-1</sup> ,	calcul	ated	in t	he u	sual
way.															

t (hrs.).	$[\Pr^{\beta}I].$	$10^{2}k_{1}$ .	t (hrs.).	$[\Pr^{\beta}I].$	$10^{2}k_{1}$ .
0.00	33.83		23.00	22.68	$1.7\overline{4}$
3.50	31.80	1.77	26.60	21.08	1.78
7.00	$29 \cdot 92$	1.76	30.00	19.73	1.80
$9 \cdot 10$	28.73	1.79	34.65	18.18	1.79
11.95	27.28	1.80	47.20	14.78	1.76
				Average	1.77

Another run at 50.0° gave  $k_1 = 0.0178$ , and two runs at 69.9° gave  $k_1 = 0.152$  and 0.153.

The Total Second-order Reaction.—The hydrolysis of the chloride and the iodide may be discussed together in this connection as the treatment was the same in both cases with the exception of the experimental methods of analysis already discussed. The method of calculation is the same as that described in Part VI. It is necessary to calculate the second-order constant, given the first, from observations of the total reaction. A bimolecular "constant"  $K_2$  is calculated from the formula  $K_2 = \frac{1}{t(b-a)} \cdot \log_e \frac{b}{a} \frac{(a-x)}{(b-x)}$ , where a and b are the initial concentration after time t; the true bimolecular constant  $k_2$  is then obtained by applying a correction for the simultaneous unimolecular reaction (constant =  $k_1$ ). The relationship is  $k_2 = K_2 - k_1/(b-x)$ 

simultaneous unimolecular reaction (constant =  $k_1$ ). The relationship is  $k_2 = K_2 - k_1/(b - x) + t(dK_2/dt)$  and, as long as most of the reaction is of the second order, the last term can often be neglected. Table VII contains an illustrative record of two out of a number of experiments to

determine the bimolecular constant, together with the average constants obtained in this set of measurements.

## TABLE VII.

Illustrating determination of bimolecular rate constants. "Corr.  $k_1$ " signifies the correction to be applied to  $K_2$  in order to deduce the true second-order constant  $k_2$ .  $K_2$  and  $k_2$  are in l./g.-mol.-hour and  $k_1$  is in hours<sup>-1</sup>.

				(a)	180 <i>Pv0</i> f	oyi chlorid	e.				
Solv $0.2N$ .	/ent '' 80 [NaOH]	%" aque and [Pr <sup>β</sup>	ous eth Cl] exp	yl alcohol. ressed in c.	Temp c. of N/	o. 70∙0°. 20-NH.CI	Initiall NS per a	y [NaOH 5 c.c. of s	$[] \sim 0.3$	8N and [Pr/	<sup>3</sup> CI] ~
t (hrs.)	. [Pr <sup>β</sup> Cl].	[NaOH].	$10^2 K_2$ .	' Corr. k <sub>1</sub> .'	$10^{2}k_{2}$ .	t (hrs.).	Pr <sup>β</sup> Cl].	[NaOH].	$10^{2}K_{2}$ .	" Corr. k <sub>1</sub> ."	$10^{2}k_{2}$ .
0.00	20.55	83.00				17.10	11.50	73.95	$4 \cdot 42$	0.0012	4.25
3.00	18.35	80.80	4.69	0.0016	4.53	$23 \cdot 25$	9.50	71.95	4.41	0.0018	4.23
7.00	15.95	78.40	4.57	0.0016	$4 \cdot 41$	26.00	8.65	71.10	$4 \cdot 46$	0.0018	4.28
11.40	13.85	76.25	4.48	0.0016	4.32	37.00	6.70	69.15	4.13	0.0018	3.95
16.00	12.15	74.60	4.28	0.0017	4.11	50.10	$4 \cdot 40$	66.85	4.31	0.0018	4.13
										Average	4.25

Another run at  $70.0^{\circ}$  gave  $k_2 = 0.0429$ , and two runs at  $90.0^{\circ}$  gave  $k_2 = 0.299$  and 0.301.

(b) isoPropyl iodide.

Solvent " 60%" aqueous alcohol. Temp. 69·85°. Initially [NaOH] ~ 0·8N and [Pr<sup> $\beta$ </sup>I] ~ 0·1N. [NaOH] and [Pr<sup> $\beta$ </sup>I] expressed in c.c. of N/40-AgNO<sub>3</sub> per 5 c.c. of solution.

t (mins.).	$[\Pr^{\beta}I].$	[NaOH].	$K_2$ .	" Corr. k <sub>1</sub> ."	' k <sub>2</sub> .	t (mins.).	$[\Pr^{\beta}I].$	[NaOH].	K2.	" Corr. k <sub>1</sub> ."	$k_2$ .
0.00	18.05	157.65				11.50	9.10	148.70	4.69	0.50	4.49
1.50	16.45	156.05	4.73	0.19	4.54	16.00	7.05	146.65	4.67	0.21	4.46
3.50	14.65	154.25	4.59	0.50	4.39	$22 \cdot 50$	4.80	$144 \cdot 40$	4.73	0.21	4.52
6.00	12.55	$152 \cdot 15$	4.69	0.20	4.49	30.00	3.10	142.70	4.77	0.21	4.56
8.50	10.90	150.50	4.63	0.50	4.43					Average	$4 \cdot 49$
A (1)	,	00 050	,	4.40	1 /		00	1 0.00	0 1	0.000	

Another run at 69.85° gave  $k_2 = 4.48$ , and two runs at 50.0° gave  $k_2 = 0.630$  and 0.626.

The Separate Second-order Reactions.—In order to find the ratio in which the second-order constant  $k_2$  should be split up between the second-order substitution and the elimination, it is necessary to estimate the amount of olefin formed, and also to calculate the proportion  $x_1/(x_1 + x_2)$  of the total reaction  $x = x_1 + x_2$  which has proceeded through the unimolecular route. The formula used for the calculation (cf. Part VI) is

$$x_1/(x_1 + x_2) = x_1/x = k_1/\{k_1 + k_2(b - \frac{1}{2}x)\}$$

The results are in Table VIII. Col. 1 records the temperature; col. 2 gives the observed percentage of olefin formed in the completed reaction, each figure representing the mean of at least four determinations. Col. 3 gives the calculated percentage of products formed by the unimolecular substitution; and col. 4 the figures obtained, by difference, for the products formed by the bimolecular substitution. The last two columns contain the factors which, when multiplied into the total second-order rate constants (Table VII), will give the rate constants for the two separate bimolecular reactions.

#### TABLE VIII.

				$S_N 2$	$\mathbf{E2}$
Temp.	E2 (%) (obs.).	$S_N1$ (%) (calc.).	$S_N 2$ (%) (diff.).	$\overline{S_N2 + E2}$	$\overline{S_N2 + E2}$
(a) isoPr	opyl chloride in '' 80	0% '' aqueous ethy [NaOH] ~	l alcohol. Initial $\sim 0.8N$ .	$[\Pr^{\beta} Cl] \sim 0.2l$	V. Initial
70.0	54.90	3.90	41.20	0.429	0.571
90.0	58.40	3.60	38.00	0.394	0.606
(b) isoPro	opyl iodide in '' 60%	'' aqueous ethyl : [NaOH] ~	alcohol. Initial [P $\sim 0.8N$ .	$\mathrm{Pr}^{\beta}\mathrm{I}] \sim 0.1N.$	Initial
50.0	67.20	3.70	$29 \cdot 1$	0.302	0.698
69.85	70.30	3.30	26.4	0.273	0.727

Summary of Rate Constants.—Table IX summarises all the rate constants determined in this investigation. Table IX (a) gives the mean values of the unimolecular rate constants,  $k_1$  (reaction  $S_N l$ ), in hours<sup>-1</sup> for the temperatures investigated. Table IX (b) and (c) contain the rate constants of the bimolecular substitution (reaction  $S_N 2$ ) and the bimolecular elimination (reaction E2) respectively, obtained by decomposing the total bimolecular rate constants of Table VII in accordance with the factors given in Table VIII. The units are l./g.-mol.-hour.

		Table	E IX.			
(a) React	ion S <sub>N</sub> 1.	(b) React	(c) Reac	(c) Reaction E2.		
Temp.	k <sub>1</sub> .	Temp.	k2.	Temp.	k2.	
	A. isoProp	yl chloride in '' 8	0%" aqueous eth	yl alcohol.		
90·0°	0.00798	70·0°	0.0183	70·0°	0.0244	
109.65	0.0416	90.0	0.118	90.0	0.182	
	B. isoProp	pyl iodide in '' 60	% '' aqueous ethy	l alcohol.		
50.0	0.0178	50.0	0.190	50.0	0.438	
69.85	0.153	69.85	1.225	69.85	3.265	

The Arrhenius parameters of the several reactions are given in the introduction.

Our thanks are due to the Chemical Society for a grant.

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[Received, April 24th, 1937.]