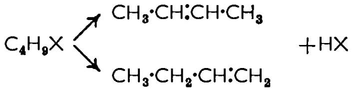
538. *Gas-phase Eliminations. Part II.** *The Pyrolysis of s-Butyl Chloride, and the Direction of Eliminations from s-Butyl Compounds.*†

By Allan Maccoll and R. H. Stone.

The pyrolysis of s-butyl chloride has been shown to be a homogeneous unimolecular process at 330—390°, producing hydrogen chloride and a mixture of isomeric butenes. The Arrhenius parameters (log *A* 13·62; *E* 49·6 kcal./mole) are compared with recorded values for other secondary halides, verifying a common mechanism for all. Vapour-phase chromatography has been used to determine the composition of the mixture of butenes produced by unimolecular elimination from s-butyl chloride, bromide, iodide, and acetate. Catalysis of the transformation but-1-ene $\rightleftharpoons$ but-2-ene by hydrogen halides and by iodine has been observed. The results are discussed in the light of current theories of reactivity.

In investigating factors influencing the direction of elimination, it is desirable to work with a series of compounds for which the mechanism of elimination has been established. Such a series, the simplest of its type, involving β-methylation, is provided by the s-butyl compounds, elimination from which is homogeneous and unimolecular and follows the stoicheiometric scheme:



$$C_4H_9X \begin{array}{l} \nearrow CH_3{\cdot}CH{:}CH{\cdot}CH_3 \\ \searrow CH_3{\cdot}CH_2{\cdot}CH{:}CH_2 \end{array} + HX$$

with X = Cl, Br, I, or OAc. Vapour-phase chromatography affords a simple technique for separating the three olefinic products, but-1-ene and *cis*- and *trans*-but-2-ene. Two extreme types of elimination have long been recognized,[1] Saytzeff, leading to the most highly alkylated ethylene, and Hoffman, leading to the least alkylated ethylene. The former is characteristic of the *E*1 reaction of alkyl halides, and the latter of the *E*2 reaction of alkylsulphonium salts, in ionising solvents. The present investigation takes on a special interest in view of the analogy that has been proposed [2] between gas-phase eliminations and reactions in polar solvents. After recording the kinetics of the pyrolysis of s-butyl chloride, this paper describes the direction of elimination from s-butyl halides and s-butyl acetate.

The Pyrolysis of s-Butyl Chloride.—The reaction was studied by a static method in a reaction vessel seasoned with the products of the decomposition of allyl bromide, by measuring the rate of pressure increase.[3] That the stoicheiometry is well represented by the equation, $C_4H_9Cl \longrightarrow C_4H_8 + HCl$, follows from two pieces of evidence. First, no permanent gases or hydrocarbons other than the butenes were observed in the products. And, secondly, the ratio of final (p_f) to initial (p_0) pressure approached the theoretical value of 2, the mean value being 1·93 (Table 1). In view of this and of the clean nature of the elimination for other alkyl chlorides,[4,5] it was not deemed necessary further to check the stoicheiometry.

That the reaction is of the first order follows from the linearity of the plots of log $(2p_0 - p_t)$ against t, and from the lack of dependence of the first-order rate coefficients

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* Part I, Maccoll, *J.*, 1958, 3398.

† For a preliminary account see Kekulé Symposium on Theoretical Organic Chemistry, Butterworths, London, 1959.

[1] Ingold, " Structure and Mechanism in Organic Chemistry," Bell, London, 1953.

[2] Maccoll and Thomas, *Nature*, 1955, **176**, 392.

[3] Maccoll, *J.*, 1955, 965.

[4] Barton and Howlett, *J.*, 1949, 155; Barton, Head, and Williams, *J.*, 1951, 2039; Howlett, *J.*, 1952, 4487; Barton and Onyon, *Trans. Faraday Soc.*, 1949, **45**, 725; Brearley, Kistiakowsky, and Stauffer, *J. Amer. Chem. Soc.*, 1936, **58**, 43; Swinbourne, *Austral. J. Chem.*, 1958, **11**, 314.

[5] Barton and Head, *Trans. Faraday Soc.*, 1950, **46**, 114.

on initial pressure (Table 2). Results at various temperatures confirmed this conclusion and so first-order constants were calculated for all the runs. The temperature-dependence of the rate constants in the range 330—390° is shown in Table 3. These values lead to the Arrhenius equation

TABLE 1.

Temp. (c)	391·3°	372·3°	356·2°	332·6°	329·8°
p_0 (mm.)	280	254	132	187	340
p_t/p_0	1·93	1·92	1·89	1·94	1·97

TABLE 2. *Rate coefficients, at* 356·8° C.

p_0 (mm.)	155·0	335·0	408·0	490·0
10^5k_1 (sec.$^{-1}$)	27·6	28·5	28·5	27·2

$$k_1\ (\text{sec.}^{-1}) = 4{\cdot}14 \times 10^{13} \exp(-49{,}600/\boldsymbol{R}T)$$

which fitted the experimental results very well.

TABLE 3. *Temperature dependence.*

Temp.	391·3°	372·3°	363·6°	360·2°	356·8°	342·6°	329·8°
10^5k_1 (sec.$^{-1}$)	191	63·5	39·7	29·4	28·0	10·2	3·87
No. of runs	6	8	6	5	4	4	3

In determining the mechanism of the reaction, it remained to verify its homogeneity and to test for a chain mechanism by the use of an inhibitor. To check the homogeneity, runs were carried out in a reaction vessel packed with glass tubing to give a surface–volume ratio increased by a factor of 6. The results (Table 4) show a 20% increase in the mean rate constant ($25{\cdot}2 \times 10^{-5}$ sec.$^{-1}$). In view of the large increase in surface–volume ratio, it may be concluded that the reaction is homogeneous. The inhibitor chosen was cyclohexene, which has been proved [6] to be very efficient in inhibition studies in the bromide series. Table 5 shows the effect of different ratios of inhibitor to substrate partial pressures (p_i/p_0). The mean value for the runs in the presence of varying partial pressures of cyclohexene is $14{\cdot}6 \times 10^{-5}$ sec.$^{-1}$ which is close to the value $14{\cdot}7 \times 10^{-5}$ sec.$^{-1}$, observed for the substrate alone. Chain mechanisms thus appear to play little part in the decomposition.

TABLE 4. *Reaction at higher surface–volume ratio, at* 354·2°.

p_0 (mm.)	149	169	165	173	250	290
10^5k_1 (sec.$^{-1}$)	29·1	24·6	26·6	22·6	22·1	26·4

TABLE 5. *Effect of inhibitor, at* 350°.

p_i/p_0	0·17	0·60	0·66	0·83	1·05
p_0 (mm.)	237	195	191	181	185
10^5k_1 (sec.$^{-1}$)	14·8	14·4	14·5	14·7	14·7

It may be concluded that s-butyl chloride decomposes by a homogeneous, unimolecular reaction into a mixture of butenes and hydrogen chloride. This is in line with the behaviour of other alkyl chlorides studied by Barton, Howlett, and their co-workers. The Arrhenius parameters for a series of i-propyl and s-butyl halides are shown in Table 6, together with the relative rates for the series chloride, bromide, and iodide and for i-propyl/s-butyl, the temperature being chosen in each case such that the smaller rate constant has the value of 10^{-4} sec.$^{-1}$. Comparisons of the ratios given confirm a common mechanism for all the compounds.

An interesting point arises as to the effect of β-methylation, which may either be a

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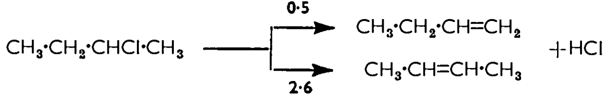
[6] Maccoll and Thomas, *J.*, 1957, 5033.

first-order effect on the β-carbon–hydrogen bond, or a second-order effect on the α-carbon–chlorine bond. If the former is true, the increase in rate in going from i-propyl to s-butyl chloride should be due entirely to elimination towards the centre of the molecule, resulting in but-2-ene. Thus, at 361°, if i-propyl chloride is assigned a rate of 1, that of s-butyl chloride is 3·1. This would imply:

TABLE 6. *Some relative pyrolysis rates.*

	Chloride [5]		Bromide [7]		Iodide [8]	
	Pr^i	Bu^i	Pr^i	Bu^i	Pr^i	Bu^i
log A	13·40	13·62	13·62	13·53	14·49	14·90
E (kcal. mole^{-1})	50·5	49·6	47·8	46·5	48·0	47·9
k_{Pr^iX}/k_{Pr^iCl} (360·8°)	1		13·5		89	
k_{Bu^iX}/k_{Bu^iCl} (343·4°)	1		11·5		85	
k_{Bu^iX}/k_{Pr^iX}	3·1 (360·8°)		3·5 (319·1°)		2·8 (294·0°)	



$$CH_3{\cdot}CH_2{\cdot}CHCl{\cdot}CH_3 \begin{cases} \xrightarrow{0\cdot5} CH_3{\cdot}CH_2{\cdot}CH{=}CH_2 \\ \xrightarrow[2\cdot6]{} CH_3{\cdot}CH{=}CH{\cdot}CH_3 \end{cases} + HCl$$

and the ratio of but-1-ene to but-2-ene should be 1 : 5·2, giving 84% of but-2-ene. Analysis of the product mixture gives 60% of but-2-ene (see below). The effect of the β-methyl group thus appears to be predominantly a second-order effect on the carbon–chlorine bond. The effect is analysed in a different fashion in Table 7, which shows that the added methyl group not only increases the rate of elimination in the branch to which it is added, but also in the branch which is unchanged. This type of behaviour has earlier been noted by Ingold [1] for t-butyl and t-pentyl halides undergoing elimination by the $E1$ mechanism in a polar solvent. Further evidence of the second-order nature of the effect of β-methylation comes from work by Wong [9] on the series Me_2CClR, with R = Me, Et, Pr^i, and Bu^t. The rate of elimination progressively increases with β-methylation, despite the fact that in the last compound elimination is of necessity entirely in the shorter branch.

TABLE 7. *Directions of reaction, at* 361°.

Rate per branch	Chloride used	Rate per branch
0·5	$CH_3{\cdot}CHCl{\cdot}CH_3$	0·5
1·83	$CH_3{\cdot}CH_2{\cdot}CHCl{\cdot}CH_3$	1·24

Direction of Elimination from s-Butyl Compounds.—When an equilibrium exists between the products of a given reaction, the reaction may be determined by (*a*) thermodynamic or (*b*) kinetic considerations. In the former case the equilibrium proportions of the products would be expected; in the latter, proportions away from the equilibrium ones, followed by a slow approach to equilibrium. For this reason, it is important to show, in the case where kinetic control is suspected, that the half-life of isomerisation is very much greater than the half-life of the elimination. The equilibrium proportions of the various isomeric butenes, computed from the data in the literature,[10] are shown in Table 8, over the relevant temperature range.

TABLE 8. *Composition of products.*

Temp.	276·8°	331·8°	356·8°	381·8°	406·8°	431·8°
But-1-ene (%)	12·6	13·6	14·9	16·0	17·3	18·3
trans-But-2-ene (%)	55·2	54·1	52·8	52·0	50·8	49·7
cis-But-2-ene (%)	32·2	32·2	32·2	32·1	32·0	31·8

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[7] Maccoll and Thomas, *J.*, 1955, 979, 2445.

[8] Holmes and Maccoll, *Proc. Chem. Soc.*, 1957, 175; Holmes, Ph.D. Thesis, London, 1957.

[9] Wong, Ph.D. Thesis, London, 1958.

[10] " Selected Values of the Physical and Thermodynamic Properties of Hydrocarbons," Carnegie Press, Pittsburgh, 1953.

In order to verify that the rate of isomerisation was slow, a number of experiments were carried out with the pure butenes. The following observations were made at 342·8°. (1) In a clean vessel, the *cis–trans*-equilibrium was readily attained, but no isomerisation from but-1-ene to but-2-ene or *vice versa* could be observed during 1 hour. (2) In a carbon-coated vessel, *cis–trans*-isomerisation was even more rapidly attained than in a clean vessel, but no but-1-ene was formed from but-2-ene in 4 hr. However, about 2% of but-2-ene was formed from but-1-ene in the time. (3) The approach to equilibrium between but-2-ene and but-1-ene was markedly catalysed by hydrogen chloride, hydrogen bromide, and iodine.

In the investigation of catalysis by hydrogen halide and iodine, the catalyst was produced by decomposing the appropriate i-propyl compound in the presence of but-1-ene. The amount of hydrogen halide or iodine produced could be estimated from the area of the propene peak on gas–liquid chromatography. The results, shown in Table 9, clearly indicate catalysis by the hydrogen halides and by iodine, the catalytic efficiency being in the order iodine > hydrogen bromide > hydrogen chloride. However, it may be inferred that the rates are slow compared with the rate of decomposition of the secondary butyl halide, at the temperatures used for the investigation of the products. When acetic acid was used as catalyst, no isomerisation of but-1-ene was observed.

TABLE 9. *Effect of catalysts.*

	Catalyst: hydrogen chloride. Temp. 342·8°.				
Reaction time (hr.)	4	4	18	16	
Mol. ratio,* acid : butene	0	0·30	0·75	2·00	
Isomerisation (%)	2	2	33	70	
	Catalyst: hydrogen bromide. Temp. 342·8°.				
Reaction time (hr.)	2	1·5	18		
Mol. ratio,* acid : butene	0·5	2·0	2·0		
Isomerisation (%)	16	70	82 (equil.)		
	Catalyst: iodine. Temp. 353·8°				
Reaction time (hr.)	1	1	1	0·67	0·50
Mol. ratio,* acid : butene	0·9	1·1	1·3	1·4	3·7
Isomerisation (%)	69	75	79	63	69

* Obtained at the moment of sampling.

TABLE 10. *Product analyses*

	s-Butyl chloride.							
Temp.	291·3°	372·3°	363·6°	360·2°	356·8°	342·6°	329·8°	
But-1-ene (%)	41·7	30·2	40·5	38·1	42·9	37·3	41·2	
cis-But-2-ene (%) *	37·5	36·4	38·9	40·6	35·6	38·5	36·7	
	s-Butyl bromide.							
Temp.	387·6°	382°	357·8° †	345·8°	350° †	349·8°	344·2°	
But-1-ene (%)	27·6	25·0	22·7	23·7	24·0	24·8	26·2	
cis-But-2-ene (%) *	33·9	38·6	41·3	37·9	40·0	35·4	36·6	
Temp.	341·1°	341·1° †	333·3°	322·2°	320·4°	309·4° †	289·1°	289·1° †
But-1-ene (%)	23·2	22·6	22·0	21·3	23·2	24·0	19·6	18·4
cis-But-2-ene (%) *	36·3	39·0	39·9	36·9	38·2	40·5	39·4	41·2
	s-Butyl iodide.			s-Butyl acetate.				
Temp.	312·6°	297·7°	273·9°	339°	321°	318°	316·8°	
But-1-ene (%)	17·5	15·5	17·3	53·4	54·1	54·0	53·6	
cis-But-2-ene (%) *	37·0	37·3	37·4	35·9	36·3	33·7	37·5	

* *cis*-Butene is cited as a percentage of the total but-2-ene.

† These runs were done with cyclohexene as an inhibitor (Kale, Maccoll, and Thomas, *J.*, 1958, 2016).

In analyses of the products, the reaction time used was approximately the half-life. The results are shown in Table 10.

In order to reduce the catalysis by hydrogen halides, some experiments were carried out in the presence of ammonia. It was expected that the ammonia would condense as the ammonium halide, in the cool dead-space, thus at least partially removing hydrogen halide from the system. The results for s-butyl chloride and bromide are shown in Table 11. Comparison of Tables 10 and 11 suggests that catalysis by hydrogen halide has little effect in the case of s-butyl chloride, but an appreciable effect in the case of s-butyl bromide. From the reported values, it is suggested that the best values for the percentage of but-1-ene produced by gas-phase elimination from the appropriate s-butyl compound are as shown in Table 12. While the figures for the acetate[11] and chloride are considered to be a reliable representation of the products produced at the instant of reaction, it is possible that the bromide figure is somewhat low because of subsequent catalysed rearrangement; the iodide figure is almost certainly low.

TABLE 11. *Pyrolyses in presence of ammonia.*

	s-Butyl chloride (temp. 354°)			s-Butyl bromide (temp. 342·60)		
Init. press. of halide (mm.)	109	110	107	109·5	110·5	108·0
Press of ammonia (mm.)	188·5	100	50·7	157·2	104	52·5
But-1-ene (%)	41·7	42·0	40·9	36·2	34·3	32·5

The logarithm of the percentage of trans-*but-2-ene in the total but-2-ene as a function of* T^{-1}. *Chlorides* •, *bromides* ○, *iodides* ◑, *acetates* ●. *The full line gives the equilibrium values; the broken lines represent* ±5% *of these.*

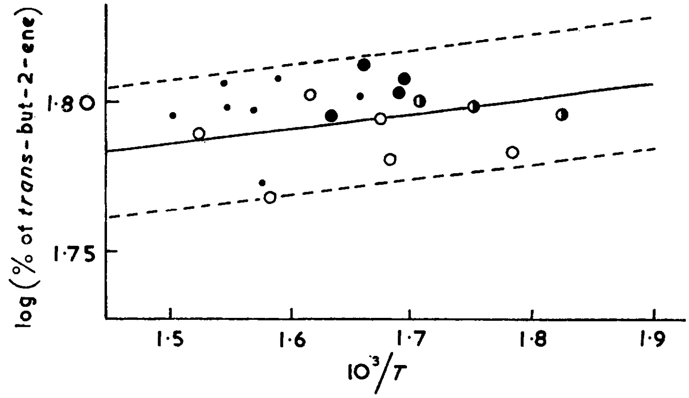

TABLE 12. *Best values for pyrolysis.*

Compound	Acetate	Chloride	Bromide	Iodide
But-1-ene (%)	54	40	34	17

It can be concluded from the figures in Table 10 for the amount of *cis*-but-2-ene that, under the conditions of the present experiments (carbon-coated vessels and the presence of hydrogen halide or iodide), the *cis–trans*-equilibrium is rapidly attained. This is shown in the Figure where the log of the percentage of *trans*-but-2-ene is plotted against T^{-1}. The full line represents the equilibrium value, and the broken lines ±5% deviations. All the experimental points lie within these limits. That this is also true for the acetate

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[11] Cf. Froemsdorf, Collins, Hammond, and DePuy, *J. Amer. Chem. Soc.*, 1959, **81**, 643; Haag and Pines, *J. Org. Chem.*, 1959, **24**, 877.

suggests that the carbonaceous surface is the more important factor in establishing the equilibrium. It is worthy of note that if planarity or near-planarity is required in the transition state for elimination then the *trans*-form will be favoured. But, as has been seen earlier (Table 8), this is also the form that is favoured by thermodynamic stability.

EXPERIMENTAL

s-Butyl chloride was prepared by shaking a commercial sample with hydrochloric acid, then with 5% sodium hydrogen carbonate solution and with water, drying ($CaCl_2$), and distillation through a 1-m. column packed with glass helices. The physical constants were: b. p. 68·1°/750 mm., n_D^{25} 1·3944 (lit.,[12] 68·25°/760 mm., 1·3946). s-Butyl bromide, treated in the same fashion as the chloride, with substitution of hydrobromic acid for hydrochloric acid, had b. p. 91·1°/756 mm., n_D^{25} 1·4341 (lit.,[13] 91·2°/750 mm., 1·4342). A newly obtained commercial sample of s-butyl iodide was left over silver powder for several days and then distilled from silver powder, through a short column; it had (" lit." below denotes ref. 12) b. p. 119·5°/737 mm., n_D^{25} 1·4971 (lit., 120·0°/760 mm., 1·4975). The isopropyl halides, used only in the isomerisation experiments, after purification had the physical constants: chloride, b. p. 39·0°/766 mm., n_D^{25} 1·3750 (lit., 38·4°/760 mm., n_D^{25} 1·3755); bromide, b. p. 59·5°/765 mm., n_D^{25} 1·4224 (lit., 59·35°/760 mm., 1·4228); iodide, b. p. 89·7°/761 mm., n_D^{25} 1·4959 (lit., 89·45°/760 mm., 1·4970). A commercial sample of cyclohexene was shaken with sodium hydrogen sulphite solution, dried ($CaCl_2$), and distilled in an atmosphere of nitrogen; it had b. p. 83·0°/760 mm., n_D^{25} 1·4435 (lit., 82·8°/760 mm., 1·4437).

The apparatus and techniques used for the kinetic investigation were essentially the same as those described earlier.[3]

The gas-chromatographic column was 20 ft. long, packed with a 2 : 3 w/w mixture of ethyl acetoacetate and Celite 545. The column was cooled to 4°; nitrogen was used as the carrier gas; and detection was by means of a katharometer and recorder. The apparatus was calibrated with pure butenes, obtained from the Chemical Research Laboratory, and checked by analysis of an equimolar mixture of butenes. The mean of the results of eight determinations gave but-1-ene 32·8, *trans*-but-2-ene 33·4, and *cis*-but-2-ene 33·6%. The analysis was based on area measurements (peak height × 0·5 peak width), and it was concluded that no corrections for differences in thermal conductivity were necessary.

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[12] Timmermans, " Physico-Chemical Constants of Pure Organic Compounds," Elsevier, Amsterdam, 1950.

[13] Heston, Hennelly, and Smyth, *J. Amer. Chem. Soc.*, 1950 **72**, 2072.