419. *Mechanism of Elimination Reactions. Part IX. Kinetics of Olefin Elimination from* n-*Propyl,* n-*Butyl,* n-*Amyl, and* iso*Butyl Bromides in Alkaline Alcoholic Media.*

By M. L. DHAR, E. D. HUGHES, C. K. INGOLD, and S. MASTERMAN.

Data are recorded illustrating certain constitutional effects on the rates of the constituent substitutions and eliminations which primary alkyl bromides undergo in bimolecular reactions with ethoxide ions in ethyl alcohol. The constitutional effects studied are the lengthening of a normal chain, the successive introduction of β-linked methyl substituents, and the effect of a β-phenyl substituent.

As regards bimolecular elimination rates, the effect of increasing the normal chain-length from ethyl to *n*-propyl is to produce a marked acceleration, whilst further increase of chain-length is accompanied by a gradual decrease in the elimination rate. Successive β-linked methyl substituents continue to increase the bimolecular elimination rate, and a β-phenyl substituent increases it greatly. The significance of these results is considered in Part XVI. The changes in the bimolecular substitution rate are by no means parallel. They are in accord with a previous discussion (Dostrovsky, Hughes, and Ingold) of aliphatic substitution in terms of polar and steric influences.

THIS paper and those which follow are concerned with the study of constitutional effects on elimination reactions. We shall deal in this and the next two papers with olefin elimination from alkyl halides, and after that take up the case of olefin formation from sulphonium salts.

Our attack upon the constitutional problem concerning olefin formation from alkyl halides was actually commenced in Part V (Hughes, Ingold, Masterman, and MacNulty, *J.*, 1940, 899). It was there pointed out that such a study cannot be conducted except in association with a kinetic analysis, the lack of which renders the extensive previous literature on olefin elimination practically useless for the purpose in view. The need arises partly from the fact that nucleophilic substitutions and eliminations commonly occur together, and have usually been measured together without discrimination. It also arises from the circumstance that substitution and elimination may each occur by either or both of two mechanisms, so that, without kinetic control, a comparison between two substances may be rendered meaningless because different mechanisms, or different mixtures of mechanisms, are, or might be, in operation in the cases compared.

In general, then, we have four component reactions, which are in principle distinguishable by a combined study of the kinetics and products of the overall reaction. The component reactions are those which we label S_N2, S_N1, $E2$, and $E1$. Our programme is to ascertain the rates of these constituent processes, or of as many of them as have measurable rates under the conditions chosen, for the reactions of a series of alkyl compounds so selected as to display the effects of progressive changes in the structure of the alkyl group.

This task was begun in Part V, which records the results of a comparative study of the reactions of ethyl, *iso*propyl, and *tert.*-butyl bromides, as well as of 2-phenylethyl and 1-phenylethyl bromides, with sodium ethoxide in dry ethyl alcohol. We have now similarly investigated a series of primary alkyl bromides, of which ethyl bromide may be regarded as the parent. The examples have been chosen in order to illustrate three types of progressive structural change, as follows. (Series 1) The series ethyl, *n*-propyl, *n*-butyl, *n*-amyl exemplifies the effects due to the progressive lengthening of a chain. (Series 2) The series ethyl, *n*-propyl, *iso*butyl illustrates the effect of successively introduced β-linked methyl substituents, and includes all the primary groups of the series from which olefins can be formed without rearrangement (the *neo*pentyl group gives olefin with rearrangement). (Series 3) The series ethyl, *n*-propyl, 2-phenylethyl is of interest in connexion with the relative magnitude of effects attributable to any hyperconjugation or conjugation of the terminal part of the radical, H, Me, Ph.

The reactions of all these compounds were conducted in ethyl-alcoholic sodium ethoxide. The common temperature was 55·0°, the same as in Part V. The initial concentration of sodium ethoxide was always about 0·1N, the alkyl halide being in deficit, so that the solutions remained alkaline. The total salt concentration was thus uniformly about 0·1M. Under these conditions kinetic complications are at a minimum, since the first-order reactions, S_N1 and $E1$, do not arise in any of the examples treated. We find in each case two second-order reactions S_N2 and $E2$, which maintain a constant ratio to each other. Our procedure is therefore to measure the rate-constant k_2 of the total second-order reaction ($S_N2 + E2$), and then split it into its components, $k(S_N2)$ and $k(E2)$, on the basis of a measurement of the proportion in which olefin is produced. Because under the alkaline conditions, olefin, when once formed, does not enter into reaction with the solvent, such a measurement can suitably and conveniently be made towards the end of reaction.

TABLE I.

Second-order rate-constants (k_2 *in* $sec.^{-1}$ $g.$-$mol.^{-1}$ $l.$), *and percentages of olefin formed, in the reactions of primary alkyl bromides with sodium ethoxide in anhydrous ethyl alcohol at* 55·0° (*concentrations* ~0·1M).

Alkyl bromide.	10^5k_2.		% Olefin.	
	Individual values.	Mean.	Individual values.	Mean.
n-Propyl	59·9, 60·1	60·0	8·7, 9·0	8·9
n-Butyl	43·9, 43·5, 44·3	43·9	9·3, 10·4	9·8
n-Amyl	39·6, 38·9	39·2	8·5, 9·3	8·9
*iso*Butyl	14·3, 14·3, 14·3, 14·1	14·3	58·2, 58·6, 61·0, 60·4	59·5

Table I contains the new measurements of the total bimolecular rate constants, and of the proportions in which olefin is formed, in the reactions of the alkyl bromides. In Table II these data, as well as corresponding data, taken from the record in Part V, for two other primary alkyl bromides, are analysed in terms of the rate constants of the individual bimolecular reactions of substitution and elimination, S_N2 and $E2$.

TABLE II.

Analysis of the kinetic data for the reactions of primary alkyl bromides with sodium ethoxide in ethyl alcohol at 55°, *showing the variation of the rates of bimolecular substitution and bimolecular elimination with progressive changes in the structure of the alkyl group.*

Series.	Alkyl bromide.	10^5k_2.	% Olefin.	$10^5k(S_N2)$.	$10^5k(E2)$.
1	$CH_3{\cdot}CH_2Br$	174	0·9	172	1·6
	$CH_3{\cdot}CH_2{\cdot}CH_2Br$	60·0	8·9	54·7	5·3
	$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2Br$	43·9	9·8	39·6	4·3
	$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2Br$	39·2	8·9	35·7	3·5
2	$CH_3{\cdot}CH_2Br$	174	0·9	172	1·6
	$CH_3{\cdot}CH_2{\cdot}CH_2Br$	60·0	8·9	54·7	5·3
	$(CH_3)_2CH{\cdot}CH_2Br$	14·3	59·5	5·8	8·5
3	$CH_3{\cdot}CH_2Br$	174	0·9	172	1·6
	$CH_3{\cdot}CH_2{\cdot}CH_2Br$	60·0	8·9	54·7	5·3
	$C_6H_5{\cdot}CH_2{\cdot}CH_2Br$	593	94·6	32	561

The figures in Table II are arranged in such a way as to show the variation of the different rates, and of the olefin proportions, in the three structural series which the available data allow us to illustrate. We need not now comment on the substitution rates, since the stronger variations have recently been theoretically discussed in terms of the polar and steric effects exhibited by alkyl groups in bimolecular reactions (Dostrovsky, Hughes, and Ingold, *J.*, 1946, 173). As to the elimination rates we shall here restrict ourselves to pointing out the empirical relations; which are that a progressive increase in the chain-length of the alkyl group is accompanied at first by a marked increase, and then by a gradual decrease, in the bimolecular elimination rate; that successive β-linked methyl substituents in the alkyl group considerably increase the rate; and that a β-phenyl substituent greatly increases the rate. A theoretical discussion of these relationships is included in Part XVI.

EXPERIMENTAL.

Materials.—Commercial *n*-propyl, *n*-butyl, and *n*-amyl bromides were dried with anhydrous potassium carbonate and with calcium chloride and fractionated. The fractions having the respective b. p.s 70·8°/755 mm., 101·5°/767 mm., and 127·7°/754 mm. were taken for the measurements now reported. The available sample of *iso*butyl bromide was found to contain *tert.*-butyl bromide as an impurity. This was destroyed by shaking the material for 3 hours at 20° with dilute aqueous sodium hydroxide containing acetone. After addition of excess of water, the unchanged bromide was recovered, dried, and fractionated. It had b. p. 91·5°/760 mm. The alcohol used as solvent was prepared by drying commercial absolute alcohol by the method of Lund and Bjerrum (*Ber.*, 1931, **64**, 210).

Method of Kinetic Measurements.—Portions, usually 5·0 c.c., of the reaction mixture, taken from a standard measuring flask, were enclosed in the cold in sealed tubes, which were placed in the thermostat (55·0° ± 0·05°) for known times, and then broken each under 100 c.c. of cold anhydrous ethyl alcohol in order to stop the reaction. The surviving alkali was then titrated with standard hydrochloric acid, with the use of lacmoid as indicator. Second-order rate constants were calculated from the formula $k_2 = \{1/t(a - b)\}\log_e \{b(a - x)/a(b - x)\}$, where t is the time in seconds, a and b are the initial concentrations of alkali and alkyl bromide, and x is the concentration of alkali destroyed in time t. The constants thus obtained were corrected for the change in volume of the solvent between the temperature at which the solutions were made up and the temperature of the thermostat.

Methods for Olefin Estimations.—Propylene was estimated by the aspiration method (Hughes, Ingold, and Shapiro, *J.*, 1936, 230), and all other olefins by the extraction method (Hughes, Ingold, Masterman, and MacNulty, *J.*, 1940, 901). Experiments by the latter method were always conducted in the following way. About 14 samples of the original solution in sealed bulbs were simultaneously placed in the thermostat, and about half of them were removed and chilled after two minutes, this moment being regarded as the time of commencement of the reaction to be investigated. Two of the removed tubes were used for the estimation of free alkali as described above, and the others were employed for the estimation of any olefin which might have been formed during the period in which the temperature was being raised to that of the thermostat. The other tubes were removed from the thermostat and chilled after a time sufficient to allow the decomposition to proceed nearly to completion. Again two tubes were used to estimate surviving alkali, and the others in order to estimate the olefin present. The amount of total reaction, and the amount of olefin formed, between the two times, could then be deduced, and hence the production of olefin could be calculated as a fraction of the total reaction.

Results of Measurements.—These are summarised in Table I. As illustrations, an individual measurement of the total bimolecular rate-constant, k_2, for *n*-butyl bromide is recorded in Table III, and an individual measurement of the proportion in which butylene is produced from *n*-butyl bromide is given in Table IV.

TABLE III.

Illustrating determinations of total second-order rate-constants (k_2 *in* $sec.^{-1}$ $g.-mol.^{-1}$ *l.*) : n-*butyl bromide* (*Expt. C*).

(Solvent : EtOH. Temp. : 55·0°. Initially [BuBr] = 0·08762M and [NaOEt] = 0·1038N. In the Table, [BuBr] and [NaOEt] are each expressed in c.c. of 0·03107N-acid per 5 c.c. sample.)

t (min.).	[NaOEt].	[BuBr].	10^4k_2.
0	16·70	14·10	—
25	15·81	13·21	4·36
60	14·70	12·10	4·35
97	13·73	11·13	4·35
125	13·05	10·45	4·24
180	11·94	9·34	4·42
235	11·10	8·50	4·28
295	10·33	7·73	4·20
355	9·55	6·95	4·31
445	8·83	6·23	4·16
508	8·46	5·86	4·01
560	8·05	5·45	4·06
767	6·92	4·32	4·07
895	6·30	3·70	4·17
1110	5·60	3·00	4·22
1243	5·35	2·75	4·11
1328	5·20	2·60	4·06
1387	5·08	2·48	4·06
1958	4·22	1·62	4·14
" ∞ "	2·60	0·00	—

(Mean k_2, $4·19 \times 10^{-4}$; corrected for solvent expansion, $4·43 \times 10^{-4}$ $sec.^{-1}$ $g.-mol.^{-1}$ l.)

TABLE IV.

Illustrating determinations of olefin proportions by the extraction method : n-*butyl bromide* (*Expt. B*).

(Solvent : EtOH. Temp. : 55·0°. Initially [BuBr] = 0·08139M and [NaOEt] = 0·1008N. Portions of 20 c.c. were used for estimation of alkali and olefin. In the Table the alkali in each sample is expressed in c.c. of 0·06244N-acid, whilst the olefin is given by the amount of bromine, measured in c.c. of 0·1972N-thiosulphate, which survives out of 5·0 c.c. of added standard bromine.)

Initial readings.		Final readings.	
Alkali.	Bromine.	Alkali.	Bromine.
32·32	20·80, 20·65, 20·77	6·22	19·05, 18·80, 19·15
32·25	20·68, 20·68	6·20	19·27, 18·90, 18·84
32·28 (mean)	20·72 (mean)	6·21 (mean)	19·00 (mean)

(Alkali consumed : 24·07 c.c. Olefin formed : 1·72 c.c. Olefin = 10·4%.)

Products.—Since *iso*butyl bromide is known to undergo transformation to *tert.*-butyl bromide at elevated temperatures, it was considered desirable to show that no such change could have occurred under the conditions of the alkaline alcoholysis to which the kinetic measurements apply. *iso*Butyl bromide was therefore boiled for 40 hours with dilute sodium hydroxide, and the alcohol thereby formed was isolated. It was identified as *iso*butyl alcohol by conversion into the *p*-nitrobenzoate, m. p. 70—71°, and a determination of the mixed melting point of the latter with an authentic specimen.

In order to confirm the individuality of the *iso*butylene produced by the hydrolysis of *iso*butyl bromide, the olefin, generated from 50 g. of *iso*butyl bromide and 500 c.c. of 2N-ethyl-alcoholic sodium ethoxide, was led through a series of condensers and traps designed to retain alcohol, and was collected at −80° and distilled. It was then carefully combined with bromine in methylene chloride solution. The dibromide on distillation showed the characteristics of an almost pure substance, and had the b. p., 60—61°/35 mm., and refractive index $n_D^{20°}$ 1·5102, of the dibromide of *iso*butylene.

SIR WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES,
UNIVERSITY COLLEGE, LONDON, W.C.1.

[*Received, January* 15*th*, 1948.]