251. *Mechanism of Substitution at a Saturated Carbon Atom. Part X. Hydrolysis of β-*n*-Octyl Bromide.*

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The substitution and elimination reactions which occur simultaneously in the alkaline hydrolysis of β-*n*-octyl bromide are quite analogous to those relating to *iso*propyl halides (this vol., p. 1177). They have been analysed kinetically and given separate rate constants. A comparison with similar data for the hydrolysis of *iso*propyl bromide shows the effect on each of the constituent reactions of increasing the chain-length in a secondary halide. The rates of the unimolecular substitution and the bimolecular elimination are lower for the higher homologue, while the rate of the bimolecular substitution remains practically unchanged. An interpretation of these results is advanced. The data are utilised in the following paper on the stereo-orientation of substitutions in β-*n*-octyl bromide.

The experiments recorded in this paper were carried out with a three-fold object. First, it having been shown that the hydrolysis of *iso*propyl halides in aqueous-alkaline media involves simultaneous unimolecular and bimolecular mechanisms, and that a change from this simple secondary alkyl system to the simplest primary and tertiary systems caused the disappearance of one mechanism or the other, it was desired to ascertain the effect on these constituent processes of passing to a higher homologue whilst maintaining the secondary character of the alkyl group. Secondly, the Walden inversion is being contemporaneously studied in these laboratories by the method of correlating the configurational effect of a substitution with its kinetics; and in this work β-*n*-octyl bromide has been chosen as a representative secondary halogeno-paraffin on account of the ease with which it can be obtained in optically active forms; therefore, of the secondary halides which we might have used in the pursuit of our first objective, we selected β-*n*-octyl bromide, so that our results would assist the parallel investigation. Thirdly, we desired to clear the ground for a prospective investigation into the mechanism of certain related elimination reactions, which we felt would be most profitably studied in the higher members of the alkyl series. Having summarised our results, we shall confine discussion to the first of these three aspects; their application in relation to the second is elucidated in the following paper, and their extension along the lines of the third is partly described in one of the last of the accompanying papers (this vol., p. 1277).

The solvent was " 60% " aqueous ethyl alcohol, one of the two solvents used for the *iso*propyl halides. The temperature was 80·0°, and when the measurements at this temperature were complete it was decided not to extend them to other temperatures, because the rates of the constituent reactions of β-*n*-octyl bromide were not sufficiently different from the corresponding rates for *iso*propyl bromide to justify an attempted analysis on the basis of the Arrhenius equation.

As with *iso*propyl bromide, so also with β-*n*-octyl bromide, we obtained a total reaction of mixed order in the presence of moderate concentrations of alkali. The first-order reaction was isolated by the use of neutral or acid solutions and consisted essentially in substitution. The rate of the first-order reaction having been measured, it was possible to show that the remaining part of the total reaction which takes place in alkaline solution was of the second order. This second-order reaction, however, consisted partly of olefin elimination; and by suitable measurements of the octylene formed, it was possible to divide the total second-order rate between substitution and elimination.

The rate constants are shown, together with those for *iso*propyl bromide, in Table I. The first-order constant for *iso*propyl bromide was specially determined because, for a reason of experimental expediency, the " 60% " ethyl alcohol solvent was made up in a different manner from that used in the previous work, and must have been of slightly different composition. The unimolecular hydrolysis of alkyl halides is very sensitive to changes in the composition of an aqueous medium, and in this case we found a rate constant about 8%* lower than we should have calculated from the results of the former work. The tabulated values for the bimolecular rate constants of *iso*propyl bromide are, however, calculated from the data obtained in the previous investigation, since such second-order rates are much less sensitive to small changes in the composition of the medium. The first-order constants are in sec.$^{-1}$, and the second-order constants in l./g.-mol.-sec.

TABLE I.

Rate constants of the constituent reactions of the hydrolysis of *iso*propyl bromide and β-*n*-octyl bromide in " 60% " aqueous ethyl alcohol at 80·0°.

	$10^4k_1(S_N1)$.	$10^4k_2(S_N2)$.	$10^4k_2(E2)$.
*iso*Propyl bromide	0·908	3·56	5·01
β-*n*-Octyl bromide	0·519	3·55	4·40

Notwithstanding the kinetic analysis described, all the rate constants given in this table are composite. It is shown in another paper (p. 1277) that a small proportion of the reaction measured as S_N1 is due to olefin formation. More notable in the present connexion is the fact that a large proportion of the unimolecular substitution, S_N1, consists in ethoxylation accompanying the hydroxylation. We have not, however, attempted to determine the proportion of these products, because it is our view that the rate-determining process of all

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* This corresponds to a difference of *ca.* 0·5% in the composition of the aqueous media.

of them is one and the same, *viz.*, the electrolytic dissociation of the alkyl halide. This is what the total first-order rate constant measures, so the figures recorded in the table under " S_N1 " are quite the proper quantities to compare.

We note that the unimolecular rate for β-*n*-octyl bromide is the smaller, although the inductive effect of the additional *n*-amyl chain would have been expected to make it the larger. There is here a choice of explanations. " Steric hindrance " due to the extra chain could reduce the rate, *e.g.*, by diminishing solvation in the transition state, but it is possible that we have under observation an example of the effect postulated by Baker and Nathan (J., 1935, 1844) in which the electrons forming the C—H bonds of a methyl group participate in a tautomeric displacement which diminishes as the hydrogen atoms are replaced ($\overset{\curvearrowright}{\text{H—CH}_2}\text{—CHMe}\overset{\curvearrowright}{\text{—Br}}$ more easily ionised than $C_5H_{11}\cdot CH_2\cdot CHMe\cdot Br$).

The bimolecular substitutions (S_N2) are also composite inasmuch as ethoxylation accompanies hydroxylation. It is difficult to determine accurately the proportion of each reaction, but experiments on the isolation of ethyl β-*n*-octyl ether from the products of hydrolysis of *d*-β-*n*-octyl bromide under conditions similar to those employed in our kinetic measurements (following paper) set a lower limit (*ca.* 20% of the total bimolecular substitution) to the ethoxylation. Since each reaction takes place in one stage, and through a distinct transition state, our rate constants represent the sums of those relating to the independent reactions.

The table shows that the rate constant for the bimolecular substitution (S_N2) is the same for β-*n*-octyl bromide as for *iso*propyl bromide. This occasions no surprise, as the effect of the additional alkyl chain is expected to be much smaller for bimolecular than for unimolecular substitution (cf. Hughes, Ingold, and Shapiro, J., 1936, 225).

The bimolecular elimination (E2) must again be composite, since the removal of a proton from the alkyl halide molecule may be assisted by a hydroxide ion or by an ethoxide ion in the aqueous-alcoholic solvent. There is, however, no way of distinguishing between these reactions. The table shows that the rate of olefin formation is lower for β-*n*-octyl than for *iso*propyl bromide. This could be explained on purely statistical grounds, for in the former only five β-hydrogen atoms are available for elimination as against six in the latter. The replacement of a β-hydrogen atom by an alkyl group must, however, introduce polar factors, which also contribute towards the result; but these are difficult to assess at present owing to lack of knowledge regarding the mutual influence of the β-hydrogen atoms. We may point out that the observed effect is in harmony with Hofmann's rule for olefin elimination (cf. Hanhart and Ingold, J., 1927, 997).

EXPERIMENTAL.

β-*n*-Octyl bromide was prepared by passing dry hydrogen bromide into β-*n*-octyl alcohol at 100°. The aqueous layer was removed at intervals, and the organic layer was again saturated with hydrogen bromide until the separation into layers ceased. The bromide was shaken with concentrated sulphuric acid to remove any unchanged alcohol, separated, dried in ethereal solution over anhydrous sodium carbonate, and distilled; b. p. 79°/17 mm., yield *ca.* 75%.

Rate Measurements.—We were handicapped in the selection of a suitable solvent by the insolubility of β-*n*-octyl bromide in water and of alkali hydroxides in non-hydroxylic media. Experiments in various mixtures of water with inert solvents such as acetone were frustrated either by a separation into two layers when the alkali was introduced in requisite amount or by the insolubility of the β-*n*-octyl bromide. We finally had to resort to aqueous ethyl-alcoholic media; and the mixture which gave the least proportion of β-*n*-octyl ether while still maintaining a homogeneous state at 80° contained 60% by volume of alcohol. Even in this medium the bromide is sparingly soluble at room temperature, and the reaction mixture had to be made up in a special way. Portions of 5 c.c. of a homogeneous solution of the halide (*ca.* *N*/10) in 80% aqueous ethyl alcohol (obtained by mixing 8 l. of lime-dried alcohol with 2 l. of water) were introduced into a number of thin-walled, glass tubes; 5 c.c. of 40% aqueous ethyl alcohol (4 l. of alcohol with 6 l. of water) were added to each, and the tubes were sealed, placed in the thermostat, kept at 80·00° ± 0·02° for known times, and then broken under 100 c.c. of absolute alcohol. In the experiments in alkaline solution the 5 c.c. of 40% aqueous ethyl alcohol were replaced by an equal volume of *ca.* 2*N*-potassium hydroxide in 40% alcohol. The reactions were followed by estimating bromide ion in the neutralised or faintly acid solution by titration with 0·025*N*-silver nitrate in the presence of eosin. Similar experiments were carried out with *iso*propyl bromide in initially neutral solution.

Estimation of Olefin.—The sealed tube was broken under carbon tetrachloride (150 c.c.), and the organic layer was washed with dilute sulphuric acid and water; 10 c.c. of a solution of bromine in carbon tetrachloride were added, the mixture was left for 30 minutes, and the remaining bromine estimated by titration with standard thiosulphate after addition of potassium iodide. A blank experiment was run in the same way with 10 c.c. of the medium, and the result of this experiment was taken as the bromine equivalent when no olefin was present.

Reaction Products.—The isolation of the reaction products under conditions similar to those obtaining in our kinetic measurements is described in Part XI (following paper). Octylene, β-*n*-octyl alcohol, and ethyl β-*n*-octyl ether were isolated both in acid and in alkaline hydrolysis. A quantitative separation is impracticable, but the yield of olefin from the alkaline hydrolysis (47 mols. %) is in satisfactory agreement with our estimations, and the isolation of ethyl β-*n*-octyl ether gives a minimum figure (7 mols. %) for the ethoxylation.

The First-order Reaction.—The results of a typical kinetic experiment are recorded in Table II; k_1 is the first-order rate constant calculated from the formula $k_1 = (1/t) \cdot \log_e\{a/(a - x)\}$, where a is the initial concentration of β-*n*-octyl bromide and x the decrease in concentration; a was determined by measuring the asymptotic value of x after long intervals.

Table II.

Initially, [β-*n*-$C_8H_{17}Br$] ~ $N/20$ and [NaOH] = 0. [β-*n*-$C_8H_{17}Br$] expressed in c.c. of 0·025*N*-$AgNO_3$ per 10 c.c. of reaction mixture; k_1 is in hours^{-1}.

t (hrs.)	0·00	0·65	1·00	1·71	2·40	3·90	5·40	6·90	8·65
[β-*n*-$C_8H_{17}Br$]	20·55	18·30	16·90	14·90	13·20	9·90	7·60	5·60	4·00
10^3k_1	—	178	195	188	184	187	184	188	189

The Total Second-order Reaction.—The method of calculating the second-order constant from observations of the total reaction is the same as that described for the *iso*propyl halides (J., 1936, 225; this vol., p. 1177). In Table III, k_2 is the bimolecular " constant " calculated from the formula

$$K_2 = \frac{1}{t(b - a)} \cdot \log_e\frac{b(a - x)}{a(b - x)}$$

where a and b are the initial concentrations of β-*n*-octyl bromide and sodium hydroxide respectively, and x is the decrease in concentration after time t. " Corr. k_1 " = $k_1(b - x)$ signifies the correction (due to the simultaneous unimolecular reaction, rate constant = k_1) which must 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.

Table III.

Initially, [β-*n*-$C_8H_{17}Br$] ~ 0·05*N* and [NaOH] = 0·8*N*. [β-*n*-$C_8H_{17}Br$] and [NaOH] expressed in c.c. of 0·025*N*-$AgNO_3$ per 10 c.c. of solution.

t (hrs.).	[β-*n*-$C_8H_{17}Br$].	[NaOH].	K_2.	" Corr. k_1."	k_2.
0·00	20·75	321·00	—	—	—
0·050	18·45	318·60	2·96	0·23	2·73
0·100	16·20	316·45	3·12	0·24	2·88
0·133	15·00	315·25	3·07	0·24	2·83
0·160	13·80	314·05	3·09	0·24	2·85
0·200	12·70	312·95	3·11	0·24	2·87
0·250	11·20	311·45	3·13	0·24	2·89
0·300	9·90	310·15	3·14	0·24	2·90
0·367	8·50	308·75	3·10	0·24	2·86
0·483	6·45	306·70	3·10	0·24	2·86
0·633	4·70	304·95	3·02	0·25	2·77
0·750	3·40	303·65	3·32	0·25	3·06
				Average	2·86

The Separate Second-order Reactions.—In the following table, col. 1 gives the percentage of olefin formed by the second-order process [obtained by applying a correction (0·7%) to the total olefin estimation to account for the small amount which is produced by the simultaneous first-order process]; col. 2 gives the percentage of products formed by the total first-order reaction calculated from the relationship given in Part VI, and col. 3 gives the figures, obtained by difference, for the products formed by the bimolecular substitutions. Cols. 4 and 5 contain the factors which, when multiplied into the total second-order rate constant (Table III), give the rate constants (recorded in cols. 6 and 7 in l./g.-mol.-hour) for the two separate bimolecular reactions.

E2 (%).	S_N1 + E1 (%).	S_N2 (%).	$\frac{S_N2}{S_N2 + E2}$.	$\frac{E2}{S_N2 + E2}$.	$k_2(S_N2)$.	$k_2(E2)$.
51·1	7·2	41·7	0·448	0·552	1·28	1·58

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