

421. *Mechanism of Elimination Reactions. Part XI. Kinetics of Olefin Elimination from tert.-Butyl and tert.-Amyl Bromides in Acidic and Alkaline Alcoholic Media.*

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Data are recorded to show the effect of homology on the rates of the constituent substitutions and eliminations which tertiary alkyl bromides undergo in bimolecular reactions with ethoxide ions, and also in unimolecular reactions in anhydrous ethyl alcohol. In this solvent the unimolecular reactions of tertiary alkyl bromides tend to predominate, and in the present experiments it was not found possible to isolate bimolecular processes; however, it was possible, by the use of considerable concentrations of ethoxide ions, to give them a dominating importance in the total reaction. *tert.*-Butyl and *tert.*-amyl bromides were studied, and the amylenes produced from the latter were analysed, in order to permit the division of the elimination rates and proportions into those parts which apply to the establishment of the double bond in the separate branches of the tertiary alkyl groups.

The bimolecular eliminations of these compounds in ethyl-alcoholic sodium ethoxide proceed considerably more rapidly than do the corresponding reactions of the simpler secondary and primary alkyl bromides; and they proceed too rapidly to permit the measurement of anything

more than limits to the rates of the accompanying bimolecular substitutions. Bimolecular elimination proceeds more rapidly in the *tert.*-amyl than in the *tert.*-butyl group, and rather more than the whole difference is represented by the increased rate of establishment of the double bond in the alkyl branch which becomes lengthened in the *tert.*-amyl group. This is interpreted in Part XVI.

The rate of the overall unimolecular reaction is greater for the *tert.*-amyl than for the *tert.*-butyl compound. The rate of unimolecular substitution is increased, but the proportion of such substitution is decreased, in the higher homologue. The rate, and the proportion, of unimolecular elimination are increased in the amyl compound. The increase of elimination rate is due to a large increase in the rate of establishment of the double bond in the alkyl branch which becomes lengthened, reinforced by smaller increases in the rate at which it enters the branches which remain similar in the two compounds. The increase in the proportion of elimination is the net result of a large increase in the proportion in which the double bond enters the lengthened alkyl branch, partly off-set by notable decreases in the proportions in which it enters the other alkyl branches. The theory of these relationships is given in Part XVI.

THIS paper carries into the field of tertiary alkyl halides our study of constitutional effects on the bi- and uni-molecular reactions of substitution and elimination which alkyl halides may undergo. The general effect of passing from the secondary to the tertiary alkyl series is that the unimolecular mechanisms of both substitution and elimination achieve a much greater relative importance. This is not primarily because the bimolecular reactions of the tertiary halides are slow : the bimolecular eliminations have been found to be faster in the tertiary series than in the secondary. The main cause of the shift of relative importance amongst the mechanisms is that the unimolecular reactions of both substitution and elimination are very much more rapid with tertiary alkyl halides than with secondary.

One effect of this is to remove the uncertainty, which prevailed through part of our study of the series of secondary halides, as to how much of an observed first-order substitution is unimolecular in mechanism and how much is a bimolecular solvolytic process. There is ample evidence that the observed first-order substitutions of tertiary alkyl halides are wholly unimolecular. It is equally definite that the first-order eliminations, which are probably entirely unimolecular even in the secondary alkyl series, are also wholly unimolecular in the tertiary series.

The principal complication which attends the study of the tertiary halides is that, in the hydroxylic solvents employed in this work, we can no longer kinetically isolate the bimolecular reactions from accompanying unimolecular processes. However, we have been able to give to the bimolecular eliminations a sufficient predominance in composite reactions to enable the bimolecular elimination rates to be measured with the requisite accuracy.

As with secondary, so also with tertiary, alkyl halides, different olefins can be formed in suitable cases by elimination along non-equivalent branches of the alkyl chain. The first-order and second-order elimination rates are then composite, and have to be split into the rates of the component simultaneous processes by means of data obtained for the purpose by analysis of the formed mixtures of isomeric olefins.

The tertiary alkyl halides thus studied were *tert.*-butyl and *tert.*-amyl bromides. The former can give but one olefin, *isobutylene*, whilst the latter gives mixtures of amylenes, *viz.*, trimethylethylene and 1-methyl-1-ethylethylene. Anhydrous ethyl alcohol, rather than an aqueous mixture, was employed as solvent, in order to keep the rates of the unimolecular reactions within manageable bounds, and to give as much assistance as possible to the bimolecular processes. Even then the latter could be made to dominate only by the use of considerable concentrations of sodium ethoxide. The temperature throughout the series of measurements was 25.0°.

For each alkyl halide a number of sets of measurements were made. From set to set the initially introduced sodium ethoxide was varied from none to a large excess, the reacting solutions being of three general types, *viz.*, weakly acidic, weakly alkaline, and strongly alkaline. Each set of experiments included at least two types of measurements, *viz.*, that of the total first-order rate-constant, and that of the proportion in which the total reaction produces olefin. The sets of experiments on *tert.*-amyl bromide included also analyses of the mixtures of isomeric olefins generated in each of the three types of solution mentioned above. From the results of these measurements it was possible to extract the required rate-constants.

The results of the measurements of total rates and olefin proportions are given in Table I. The following remarks are necessary in further explanation of the figures. The rates are expressed as first-order rate-constants, and this was always possible, whatever the dominant mechanism, because the concentrations were suitably chosen : the alkali was either absent, so that only unimolecular reactions took place, or it was so dilute that unimolecular reactions

predominated, or it was so concentrated that, although bimolecular reactions predominated, the alkali remained in substantially constant excess, giving rise to first-order reactions. In those olefin estimations which were made in the absence of initially added sodium ethoxide, the usual precautions were taken to avoid loss of formed olefin through acid-catalysed addition of the solvent: the olefin concentrations were measured at various times during the course of a run, and compared with the amounts of total reaction at corresponding times. At the concentrations employed, it was found that the first half-life of the reaction could safely be used for the olefin estimations. In the olefin measurements which were carried out with alkaline solutions, the initial concentration of sodium ethoxide was so adjusted that the mean alkalinity during the production of the measured olefin was the same as the mean alkalinity during the corresponding measurement of the total rate, to the degree of approximation warranted by the limits of accuracy of the olefin determinations. In these runs, the olefin concentration and the total reaction were measured at two times, one near the beginning and one towards the end of the reaction, and the proportion in which the reaction produces olefin was calculated from the differences.

TABLE I.

First-order rate-constants (k_1 in sec.^{-1}), and percentages of olefin formed, in the reactions of tertiary alkyl bromides in dry ethyl alcohol, and with ethyl-alcoholic sodium ethoxide in various concentrations, at 25.0° .

Total reaction rate.			Proportion of olefin.		
Initial [RBr].	Initial [NaOEt].	$10^6 k_1$.	Initial [RBr].	Initial [NaOEt].	% Olefin.
<i>tert.-Butyl bromide.</i>					
0.10350	0	0.451	0.02061	0	19.0 (mean)
0.01709	0.02386	0.522	{ 0.01710 0.01454	{ 0.0250 0.0272	{ 25.3 26.4
0.06397	0.0828	0.637	{ 0.07050 0.06980	{ 0.1013 0.1013	{ 44.4 47.7
0.03837	1.015	3.29	{ 0.09974 0.08324	{ 1.012 1.017	{ 90.0 92.6
0.03837	2.011	4.20	—	—	—
<i>tert.-Amyl bromide.</i>					
0.07278	0	1.09	0.03895	0	36.3
0.01593	0.02313	1.16	{ 0.01577 0.02519	{ 0.0267 0.0266	{ 45.9 46.7
0.06410	0.0848	1.57	{ 0.07380 0.09020	{ 0.1013 0.1013	{ 57.8 54.2
0.03885	1.015	6.24	{ 0.09260 0.08618	{ 1.012 1.014	{ 97.9 98.7
0.03430	2.011	7.02	—	—	—

An analysis of these results is contained in Table II. The method is as follows. Each first-order rate-constant, k_1 , for the total reaction is split into two component parts, the first-order rate-constants referring to substitution and to elimination, with the aid of the relevant olefin proportion. These first-order substitution and elimination constants are tabulated as $k(S_N1)$ and $k(E1)$, respectively, although these labels are partly misnomers. However, one notices that, for each alkyl halide, the figures for $k(S_N1)$ are independent of the alkali concentration to within the limits of precision set by the least accurate of the measurements, *viz.*, those of the olefin proportions. This shows that these constants are true unimolecular substitution constants, and are correctly labelled $k(S_N1)$. On the other hand, of the first-order elimination constants, tabulated as $k(E1)$, the majority clearly represent the rates of reactions of composite molecularity, and that is why, in the Table, most of these first-order constants are given in parenthesis. Each such constant has a part which is independent of the alkali and a part which depends on the concentration of alkali. Only for the experiments in initially neutral solutions do the first-order elimination constants represent true unimolecular constants, correctly labelled $k(E1)$. In the other cases, that part of the first-order rate which depends on the alkali is evidently due to a process of bimolecular elimination. It follows that, by dividing the increase in the first-order elimination constant, resulting from the addition of alkali, by the

mean concentration of alkali, one can arrive at the bimolecular elimination rate-constant $k(E2)$. The values of this constant, given in Table II, were obtained by first deriving constants thus, and then correcting them for the change in volume of the solvent between the temperature at which the solutions were prepared for the rate measurements and the temperature of the reactions themselves. The values of these bimolecular constants can be seen to fall notably at the highest concentrations (1N and 2N) of alkali, and this is undoubtedly a salt-effect. The bimolecular eliminations, as well as the bimolecular substitutions, by anionic reagents, of alkyl halides should exhibit substantial negative salt-effects, owing to the spreading of the anionic charge in the transition state of reaction (cf. Dostrovsky, Hughes, and Ingold, this vol., p. 1283). In fact, such salt-effects are known for the bimolecular substitutions and eliminations of primary and secondary alkyl bromides (Hughes, Ingold, Masterman, and MacNulty, *J.*, 1940, 899); and they are of just the same order of magnitude as the effects now found for the bimolecular eliminations of tertiary alkyl bromides.

TABLE II.

Analysis of kinetic data for the reactions of tertiary alkyl bromides in ethyl alcohol and with ethyl-alcoholic sodium ethoxide at 25.0°, showing the rate-constants [k_1 , $k(S_N1)$ and $k(E1)$ in sec.^{-1} , and $k(E2)$ in $\text{sec.}^{-1} \text{ g.-mol.}^{-1} \text{ l.}$] of the constituent reactions.¹

Mean [NaOEt].	$10^5 k_1$.	% Olefin.	$10^5 k(S_N1)$.	$10^5 k(E1)$.	$10^5 k(E2)$.
<i>tert.-Butyl bromide.</i>					
0	0.451	19.0	0.365	0.086	—
0.0153	0.522	25.9	0.387	(0.135)	~3.4 ²
0.0508	0.637	46.1	0.344	(0.293)	4.17
0.996	3.29	91.3	~0.29 ³	(3.00)	3.00
1.992	4.20	93.2 ⁴	~0.38 ³	(3.91)	1.97
<i>tert.-Amyl bromide.</i>					
0	1.09	36.3	0.695	0.395	—
0.0152	1.16	46.3	0.623	(0.537)	9.6
0.0527	1.57	56.0	0.690	(0.880)	9.44
0.996	6.24	98.3	—	(6.13)	5.90
1.994	7.02	98.6 ⁴	—	(6.92)	3.27

¹ The bimolecular substitution constant $k(S_N2)$ is too small to be extracted from the measurements, but the estimated errors in the olefin proportions allow the following upper limits to be deduced: for *tert.*-butyl bromide $k(S_N2) < 0.1 \times 10^{-6}$, and for *tert.*-amyl bromide $k(S_N2) < 0.2 \times 10^{-6} \text{ sec.}^{-1} \text{ g.-mol.}^{-1} \text{ l.}$

² Value rendered inaccurate by its dependence on the small difference between the two percentages 19.0 and 25.9% of olefin.

³ Values rendered uncertain by their dependence on the differences from 100 of the high olefin percentages 91.3 and 93.2%.

⁴ Calculated from the rate-constants and the other percentages of olefin for the same alkyl halide.

The determinations of the separate amylenes in the mixture of isomerides liberated from *tert.*-amyl bromide required quantities of olefin such that certain precautions had to be taken. In all cases the alkyl halide was initially 0.85—0.88M. If the experiment in acid solution had been conducted in the usual way, there would have been an equivalent generation of hydrogen bromide, which would have induced acid-catalysed solvent-addition to the olefins, and might have done so in such a way as to disturb the proportions. The method was therefore to add an indicator, and to prevent the solution from becoming more than weakly acid by the frequent addition of small amounts of alcoholic sodium ethoxide during the run. In the experiment in dilute alkaline solution, it was obviously inadmissible to add an equivalent of sodium ethoxide initially, and therefore, here again, an indicator was used, and small amounts of alcoholic sodium ethoxide were added at sufficiently frequent intervals to maintain the solution only very weakly alkaline. In the experiment in strongly alkaline solution an initially added excess of sodium ethoxide was used. In each case the olefins from the complete reaction were collected, freed from non-isomeric impurities, and analysed by the measurement of refractive index. The experimental results are in Table III.

By the use of the rate data in Table II, it is readily possible to extract from the result in Table III the proportions in which the isomeric olefins are produced by each of the two mechanisms of eliminations. These proportions, as well as the rate-constants of the four component reactions by which the two olefins are produced by the two mechanisms, are given in Table IV.

TABLE III.

Composition of amylenes obtained from *tert.*-amyl bromide by reaction in ethyl alcohol and with ethyl-alcoholic sodium ethoxide at 25°.0.

Expt. no.	[Am ^t Br] initial.	[NaOEt].		Me ₂ C:CHMe. %	MeEtC:CH ₂ . %
		Initial.	Mean.		
1	0.882	(None : solution weakly acid)		81.6	18.4
2	0.854	Very dilute	Very dilute	81.7	18.3
3	0.855	2.05	1.62	71.9	28.1

TABLE IV.

Compositions of amylenes produced by bi- and uni-molecular elimination from *tert.*-amyl bromide in ethyl alcohol at 25°. Rate-constants [k(E2) in sec.⁻¹ g.-mol.⁻¹ l.; k(E1) in sec.⁻¹] of the component processes of elimination.

Mechanism.	Percentages.			Rate-constants.*	
	Me ₂ C:CHMe.	MeEtC:CH ₂ .		Me ₂ C:CHMe.	MeEtC:CH ₂ .
E2	71.1	28.9	10 ⁶ k(E2)	6.72	2.72
E1	81.7	18.3	10 ⁶ k(E1)	0.323	0.072

* Ionic strengths in the neighbourhood 0.05.

We now collect corresponding results for *tert.*-butyl and *tert.*-amyl bromide, not only to show the effects of homology in these examples, but also to facilitate comparison with the analogous data for primary and secondary alkyl halides, given in the two preceding papers. In Table V the rate-constants for the bimolecular eliminations undergone by the two tertiary halides are given both in their collective form and with respect to elimination along each of the three branches of the tertiary alkyl chain. In Table VI the kinetic data for unimolecular substitution and elimination are similarly compared, with such particulars as are demanded by the circumstance that these reactions have two stages, both requiring consideration.

TABLE V.

Comparison of rate-constants [k(E2) in sec.⁻¹ g.-mol.⁻¹ l.] for bimolecular elimination from tertiary alkyl bromides in ethyl-alcoholic sodium ethoxide at 25°.

Alkyl halide.	10 ⁶ k(E2) ([NaOEt] ~0.05).		10 ⁶ k(E2) ([NaOEt] ~1.0).	
	Total.	Per branch.	Total.	Per branch.
$\begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \end{array} \text{CBr}$	4.17	$\begin{cases} 1.39 \\ 1.39 \\ 1.39 \end{cases}$	3.00	$\begin{cases} 1.00 \\ 1.00 \\ 1.00 \end{cases}$
$\begin{array}{c} \text{CH}_3 \cdot \text{CH}_2 \\ \text{CH}_3 \\ \text{CH}_3 \end{array} \text{CBr}$	9.44	$\begin{cases} 6.72 \\ 1.36 \\ 1.36 \end{cases}$	5.90	$\begin{cases} 4.20 \\ 0.85 \\ 0.85 \end{cases}$

We direct attention to the following points. The figures for the rates of bimolecular elimination from alkyl bromides (Table V) show that elimination proceeds more rapidly from the *tert.*-amyl than from the *tert.*-butyl group, and that the increase is due entirely to the increased rate of establishment of the olefinic double bond in that alkyl branch which becomes lengthened in the tertiary amyl group. As to the unimolecular reactions, the rate of the overall reaction is greater for the *tert.*-amyl compound than for the lower homologue. The rate of the unimolecular substitution is increased, but the proportion of unimolecular substitution is decreased, in the higher homologue. The rate of unimolecular elimination is also greater for *tert.*-amyl than for *tert.*-butyl bromide; and this result is due to a large increase in the rate of formation of the double bond in that alkyl branch which becomes lengthened in the tertiary amyl compound, reinforced by small increases in the rate at which it enters the alkyl branches

TABLE VI.

Comparison of rate constants [k_1 , $k(S_N1)$ and $k(E1)$ in sec^{-1}] and olefin proportions in unimolecular substitutions and eliminations of tertiary alkyl bromides in ethyl alcohol at 25° .

Alk in AlkBr.	$10^5 k_1$.	$10^5 k(S_N1)$.	$10^5 k(E1)$.		% Subn.	% Elimination.	
			Total.	Per branch.		Total.	Per branch.
$\begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{C} \\ \diagup \\ \text{CH}_3 \\ \text{CH}_3 \end{array}$	0.45	0.365	0.086	$\begin{cases} 0.029 \\ 0.029 \\ 0.029 \end{cases}$	81.0	19.0	$\begin{cases} 6.3 \\ 6.3 \\ 6.3 \end{cases}$
$\begin{array}{c} \text{CH}_2\text{-CH}_3 \\ \diagdown \\ \text{C} \\ \diagup \\ \text{CH}_3 \\ \text{CH}_3 \end{array}$	1.09	0.695	0.395	$\begin{cases} 0.323 \\ 0.036 \\ 0.036 \end{cases}$	63.7	36.3	$\begin{cases} 29.6 \\ 3.3 \\ 3.3 \end{cases}$

which remain similar in both compounds. The proportion of unimolecular elimination is likewise greater for *tert.*-amyl than for *tert.*-butyl bromide; but this is the net result of a big increase in the proportion in which the double bond enters the lengthened alkyl branch of the *tert.*-amyl group, partly off-set by marked decreases in the proportion in which it becomes established in these alkyl branches which remain similar in the two homologues. The theory of these relationships will be discussed in Part XVI.

EXPERIMENTAL.

Materials.—*tert.*-Butyl and *tert.*-amyl alcohols were converted into their bromides by shaking with concentrated aqueous hydrogen bromide at room temperature. After being dried with potassium carbonate, the products had the respective b. p.s $74^\circ/756$ mm. and $106^\circ/756$ mm.

Method of Kinetic Measurements.—In the experiments in initially neutral or dilute alkaline solution, the samples for analysis were withdrawn from the solution in bulk, which was contained in a stoppered measuring flask immersed in the thermostat. The acid or alkaline samples, usually 5 c.c., were run into 100 c.c. of well-cooled acetone or ethyl alcohol, and titrated with standard alkali or acid, lacmoid being used as indicator. Experiments in the more strongly alkaline media were conducted by the sealed-bulb method, and the determination of residual alkali was replaced by a determination of the liberated halide ion by Volhard's method. In the experiments in initially neutral solution, the "infinity" titres were obtained after dilution with water, in order to eliminate any error in these quantities arising from the slight reversibility of alcoholysis. In all cases first-order rate-constants were calculated from the expression $k_1 = (1/t)\log_e a/(a-x)$, where t is the time in seconds, a is the initial concentration of the alkyl bromide, and x is its concentration at time t .

Method for Olefin Proportions.—The extraction method was used (cf. the two immediately preceding papers.)

Method for Analysis of Amylene Mixtures.—Pure specimens of trimethylethylene and 1-methyl-1-ethylethylene were obtained, the first from a commercial sample by careful distillation through an efficient column, and the second from 2-methyl-*n*-butyl alcohol by way of the bromide. They had the refractive indices n_D^{20} 1.38774 and n_D^{20} 1.37774, respectively, in close agreement with the values reported by Sherrill and Walter (*J. Amer. Chem. Soc.*, 1936, **58**, 742); and the refractive indices of mixtures fitted a linear interpolation formula. The reaction mixtures from which the olefin was to be collected for analysis, were diluted with water; and the olefin was then isolated by distillation, washed with water, dried, and distilled. Its refractive index was measured, and its composition therefrom deduced.

Results of Measurements.—The principal numerical results are given in Tables I and III. The different types of measurement are illustrated by more detailed records contained in Tables VII—XII.

TABLE VII.

Illustrating determinations of first-order rate-constants (k_1 in sec^{-1}) of the reactions of tertiary alkyl bromides with initially neutral ethyl alcohol: *tert.*-butyl bromide.

(Solvent: EtOH. Temp. 25.0° . Initially $[\text{Bu}^t\text{Br}] = 0.1035\text{M}$. In the Table $[\text{Bu}^t\text{Br}]$ is expressed in c.c. of 0.03449N-alkali per 5 c.c. sample.)

t (min.).	$[\text{Bu}^t\text{Br}]$.	$10^5 k_1$.	t (min.).	$[\text{Bu}^t\text{Br}]$.	$10^5 k_1$.
0	15.01	—	1,859	9.09	4.49
104.4	14.59	4.52	2,070	8.59	4.49
274.0	13.95	4.50	3,057	6.42	4.63
428.3	13.40	4.41	4,706	4.15	4.55
598.9	12.83	4.37	5,874	2.90	4.66
1339	10.49	4.46	7,360	1.90	4.67
1376	10.34	4.51	10,080	1.05	4.40
1616	9.69	4.51			
				Mean	4.51

TABLE VIII.

Illustrating determinations of olefin proportions in reactions of tertiary alkyl bromides in initially neutral ethyl alcohol: tert.-amyl bromide.

(Solvent: EtOH. Temp. 25.0°. Initially $[Am^+Br] = 0.03895M$. Portions of 20 c.c. taken for estimation of acid and olefin. In the Table the acid is expressed in c.c. of 0.02513N-alkali, and the olefin is given by the bromine, measured in c.c. of 0.05128N-thiosulphate, which remains out of 10 c.c. of added standard bromine.)

<i>t</i> (min.).	Acid.		Bromine.		Olefin, %.
	Readings.	Mean.	Readings.	Mean.	
0	0.60, 0.60	0.60	12.85, 12.90, 12.88	12.87	—
295	5.40, 5.50	5.45	11.00, 11.00, 11.40	11.13	36.6
345	6.80, 6.80	6.80	10.70, 10.60, 10.65	10.65	36.5
510	8.55, 8.45	8.50	9.95, 9.85, 10.15	9.98	37.3
870	12.65, 12.65	12.65	8.45, 8.90, 8.60	8.65	35.8
1200	15.70, 15.80	15.75	7.65, 7.75, 7.60	7.66	35.1
					Mean 36.3

TABLE IX.

Illustrating determinations of first-order rate-constants (k_1 in sec.⁻¹) in reactions of tertiary alkyl bromides with dilute ethyl alcoholic sodium ethoxide: tert.-butyl bromide.

(Solvent: EtOH. Temp. 25°. Initially $[Bu^+Br] = 0.01709M$ and $[NaOEt] = 0.02386N$. In the Table $[Bu^+Br]$ is expressed in c.c. of 0.0211N-acid per 10 c.c. sample.)

<i>t</i> (min.).	$[Bu^+Br]$.	10^6k_1 .	<i>t</i> (min.).	$[Bu^+Br]$.	10^6k_1 .
0	8.10	—	1470	5.10	5.23
161.6	7.70	5.22	1871	4.45	5.33
276.2	7.43	5.21	2863	3.16	5.48
391.3	7.18	5.14	3300	2.75	5.45
506.5	6.95	5.04	4516	2.05	5.07
1296	5.38	5.26	6103	1.20	5.31
					Mean 5.22

TABLE X.

Illustrating determinations of first-order rate-constants (k_1 in sec.⁻¹) in reactions of tertiary alkyl bromides with concentrated alcoholic sodium ethoxide: tert.-butyl bromide.

(Solvent: EtOH. Temp. 25°. Initially $[Bu^+Br] = 0.03837M$ and $[NaOEt] = 1.015N$. In the Table $[Bu^+Br]$ is expressed in c.c. of 0.0234N-thiocyanate.)

<i>t</i> (min.).	$[Bu^+Br]$.	10^6k_1 .	<i>t</i> (min.).	$[Bu^+Br]$.	10^6k_1 .
0	8.20	—	268.0	4.95	3.14
51.5	7.39	3.36	344.5	4.20	3.24
80.6	6.97	3.36	404.6	3.80	3.16
120.0	6.44	3.35	484.3	3.00	3.46
159.6	6.00	3.26	523.5	2.90	3.31
228.0	5.20	3.33	577.4	2.65	3.26
					Mean 3.29

TABLE XI.

Illustrating determinations of olefin proportions in reactions of tertiary alkyl bromides with ethyl-alcoholic sodium ethoxide: tert.-butyl bromide (Expt. A).

(Solvent: EtOH. Temp. 25.0°. Initially $[Bu^+Br] = 0.09974M$ and $[NaOEt] = 1.0121N$. Portions of 20 c.c. used for estimations of bromide ion and olefin. In the Table the bromide ion is given by the silver, measured in c.c. of 0.07333N-thiocyanate, which remains out of 10 c.c. of added standard silver nitrate, and the olefin is given by the bromine, measured in c.c. of 0.09737N-thiosulphate, which survives out of 10 c.c. of added standard bromine.)

Initial readings.			Final readings.		
Silver.	Bromine.		Silver.	Bromine.	
29.80	47.15, 47.01, 47.15		2.55	10.95, 11.60, 11.00	
29.80	47.10, 47.20		2.65	11.20, 11.10, 11.05	
29.80 (mean)	47.20, 47.10		2.60	11.20, 11.25	
	47.13 (mean)		2.60 (mean)	11.16 (mean)	
Proportion of olefin = 87.8%.			Corrected for losses = 90.0%.		

TABLE XII.

Particulars of experiments on the composition of the mixture of amylenes obtained from tert.-amyl bromide by reaction in acidic or alkaline ethyl alcohol.

Initial Am ^t Br (g.).	Initial EtOH (c.c.).	[NaOEt].	Time at 25° (hrs.).	Yield, olefins (g.).	n_D^{20} .
200	1500	None : just acid	146	— ¹	1.38590
155	1200	Just alkaline	130	30	1.38591
155	1200	2.05N ²	12	70.5	1.38493

¹ Yield not measured.

² Initial value.

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