413. *The Measurement of Olefin Formation from Certain Alkyl Bromides: The Mechanisms of the Substitution and the Olefin Reactions with Alkyl Halides.*

By William Taylor.

Estimation of the proportion of olefin formed by the reaction of alcoholic sodium ethoxide with five alkyl bromides leads to two main results: (*a*) the proportion of olefin increases on passing from primary through secondary to tertiary bromides—an uncertainty which had existed about the last two is thus removed; and (*b*) two types of olefin mechanism are seen to operate, one in which the ethoxyl ion participates, and the other in which an un-ionised molecule reacts with the alkyl bromide.

Mechanisms for the substitution and the olefin reactions with alkyl halides and either anions or molecular reagents are discussed. In the latter case the mechanisms proposed are based largely on the present work and on that (this vol., pp. **1852**, **1853**) in which it has been shown that direct action takes place between the alkyl halide and the molecular reagent in both substitution and olefin reactions. These last two mechanisms are alternative to the ionisation mechanisms already proposed by Hughes and Ingold.

The ratio of olefin to substitution reactions, when an alkyl halide reacts with a base such as an alkali-metal hydroxide, alkoxide, or aryloxide, increases with: (i) increase in the strength of the base (see, *e.g.*, Segaller, J., 1913, **103**, 1430) or (ii) in its concentration (see, *e.g.*, Taylor, this vol., p. **343**), (iii) rise of temperature (see, *e.g.*, *idem, ibid.*), (iv) substitution of tertiary and secondary for primary halides (see, *e.g.*, Brussoff, *Z. physikal. Chem.*, 1900, **34**, 129; Segaller, *loc. cit.*; Hickinbottom, "Reactions of Organic Compounds," 1936, p. 366). Brussoff (*loc. cit.*) found that secondary gave more olefin than tertiary halides, whereas Segaller (*loc. cit.*) found that the latter gave olefin under conditions such that the former gave none.

Brussoff's method of olefin estimation, adopted also by Segaller, is not capable of high accuracy, and, accurate measurements being required for the elucidation of the mechanisms of the olefin and substitution reactions with alkyl halides, these have now been carried out at 25° and 55° with different proportions of sodium ethoxide in dry ethyl alcohol with the following bromides: primary, ethyl and β-phenylethyl; secondary, *iso*propyl and α-phenylethyl; tertiary, *tert.*-butyl. In addition, the proportions of olefin from the same bromides in the solvents ethyl alcohol, water, and carbon tetrachloride without any added sodium ethoxide, and from the bromides alone without any solvent or base, were, in some instances, also measured at the same temperatures and for the same periods of time as when alcoholic sodium ethoxide was used. The method of olefin estimation consisted of bromine addition in the well-washed carbon tetrachloride extract of the reaction liquid. It was essential to wash out all traces of alcohol from the extract. The results, showing the percentages of olefin formed, are in the table.

Table showing the effect of temperature, structure, solvent, and concentration of sodium ethoxide in alcohol on the percentage of olefin formation. The initial molar concentration of the bromide was always less than that of the base in order to avoid solvent effect, and at the higher concentrations of the base was always approximately 0·2. *The time, in hours, and the same throughout for any one bromide at any one temperature, is recorded in parentheses after the temperature.*

Medium.	Bromide.									
	Et.		Pr$^{\beta}$.		Bu$^{\gamma}$.		CH$_2$Ph·CH$_2$.		CH$_3$·CHPh.	
	25° (504).	55° (70).	25° (528).	55° (120).	25° (24).	55° (2).	25° (90).	55° (3).	25° (48).	55° (5).
Vapour	—	—	1·6	1·8	1·7	1·9	—	—	—	—
CCl_4	0	0	0	0	0	0	0	0	0	0
H_2O	—	—	—	—	1·8	2·3	—	—	—	—
H_2O + EtOH (1 : 1 by vol.)	—	—	3·5	3·6	4·6	4·8	—	—	—	—
EtOH	0	0	9·0	9·0	12·6‖	15·0‖	0	0	3·6	4·1
[NaOEt] = 0·05N. (approx.)	1·0	1·1	20·3	21·4	21·4	28·6	90·5	91·0	8·2	12·0
,, 0·10 ,,	—	—	—	—	33·5	37·4	90·6	91·8	11·1	15·2
,, 0·20 ,,	*	*	25·4§	27·6§	40·1	44·7	91·9†	92·5†	17·5‡	21·2‡
,, 0·40 ,,	—	—	—	—	49·0	53·2	92·2	92·8	21·9	28·3
,, 0·70 ,,	—	—	—	—	61·1	64·6	92·8	93·8	25·0	32·1
,, 1·2 ,,	—	—	—	—	65·0	68·5	93·3	94·4	25·5	32·7
,, 2·7 ,,	1·6	2·3	26·7	29·0	66·1	69·2	93·3	94·1	26·0	33·5

* Taylor (J., 1935, 1515) found 1·3.

† Taylor (this vol., p. 344) found 91·1 and 91·9 ± 1·2 respectively.

‡ Taylor (*ibid.*) found 19·3 and 20·7 ± 0·6 respectively.

§ Hughes, Ingold, and Shapiro (J., 1936, 235) found, with initial $[Pr^{\beta}Br] \sim 0·1$ and $[NaOH] \sim 0·85$ in " 80% " aqueous alcohol at 50°, 56·76% of olefin. A repetition of their method of estimation, however, revealed a distinct possibility of alcohol vapour having passed over into the standard bromine.

‖ Cooper, Hughes, and Ingold (this vol., p. 1280), employing the same method of olefin estimation as that used here, found, for the complete conversion of the bromide, 12·6% olefin in " 80% " aqueous ethyl alcohol at 25°. The olefin percentages given here when solvents alone were used are probably rather low for the reason given on p. 1967. They are, however, comparable among themselves.

(*a*) The results clearly show that, under the same conditions, with the series ethyl, *iso*propyl and *tert.*-butyl bromides, the proportion of olefin rises on passing from primary to *sec.*- and then to *tert.*-bromide. This removes any doubt as to the influence of structure on the proportion of olefin formation.

(*b*) Although β-phenylethyl bromide remains almost unchanged during 3 hours at 55° and yields no measurable olefin in dry ethyl alcohol alone, a very low concentration (*i.e.*, 0·05N.) of sodium ethoxide causes its complete reaction during this time and at this temperature, and produces *ca.* 90% of olefin. It is known (see, *e.g.*, Jones and Hughes, J., 1934, 1197) that sodium ethoxide in very dilute ethyl-alcoholic solution is a strong electrolyte, and hence it is probable that at this low concentration the ethoxyl ion is the agent responsible for this high proportion of olefin.

(*c*) As was to be expected (see p. 1962), the effects of increased temperature and of increased concentration of the sodium ethoxide are both to increase the proportion of olefin. The concentration effect is large for *iso*propyl, α-phenylethyl, and especially for *tert.*-butyl bromide, but small for the other two compounds. However, there is apparently an upper limit to the olefin proportion formed at any one temperature from any one bromide as the concentration of the base is increased. This limit is reached at different concentrations for the different bromides and at higher concentrations as one proceeds along the series Me, Pr^{β}, Bu^{γ}. There are two possible interpretations of this effect : (i) that it is due to increased ethoxyl-ion concentration and (ii) that the un-ionised molecule NaOEt is more efficient than the ion in olefin formation (or from the opposite viewpoint is less efficient in ether formation). The first is not probable, since the change in the proportion of olefin formation with *tert.*-butyl bromide on proceeding from ethyl alcohol alone—in which $[\mathrm{OEt}'] \sim 1 \times 10^{-9\cdot5}$—to a 0·05N-solution of the base could not possibly be thus explained. Hence the second explanation is probably correct, and indeed, certain considerations would make it appear that with all except β-phenylethyl bromide the ethoxyl ion plays little or no part in producing olefin. These considerations are that, for these four compounds only, the plot of olefin proportion formed during the same periods of time against concentration of base from zero to 2·7N., which is the approximate limit of solubility, is a smooth curve. This suggests that as the concentration of sodium ethoxide increases, it gradually assumes command over the total reaction at the expense of the less effective hydrogen compound HOEt until this command is complete. Hence the olefin proportion rises from the naturally low HOEt level to the relatively high NaOEt level.

(*d*) The effect of solvents alone in producing olefin from these compounds indicates that, although ethyl alcohol may have considerable effect, that of water is always very small, and that of carbon tetrachloride is nil. This is interpreted as showing that it is the basic nature of the solvent which is effective in producing olefin, since ethyl alcohol is a stronger base than water, whereas carbon tetrachloride has no basic properties.

(*e*) When small amounts—usually 0·2—0·3 g.—of *iso*propyl and *tert.*-butyl bromides were heated alone to 25° or 55° in hermetically sealed tubes of approximately 23 c.c. capacity, a very small proportion of olefin was formed. Since the liquids at 20° contained no olefin (direct test), it must have been formed in the vapour state. Brearley, Kistiakowsky, and Stauffer (*J. Amer. Chem. Soc.*, 1936, **58**, 43) have shown that the thermal decomposition of *tert.*-butyl chloride is a clean gaseous unimolecular decomposition (cf. Maass and Wright, *ibid.*, 1924, **46**, 2664 ; Maass and Sivertz, *ibid.*, 1925, **47**, 2883 ; Kharasch and Potts, *ibid.*, 1936, **58**, 57 ; Kistiakowsky and Stauffer, *ibid.*, 1937, **59**, 165 ; for discussion of the reverse reactions).

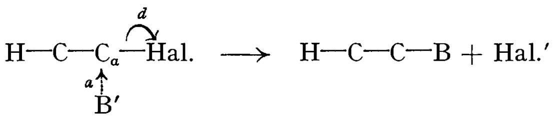
(*f*) Hence, it is seen that in forming olefin from these bromides under these conditions the ethoxyl ion, the un-ionised sodium ethoxide molecule, the solvent alcohol, and even the halide itself are all possible reagents.

Mechanisms of Substitution and Olefin Reactions.

Substitution and olefin reactions (with alkyl halides) of the types discussed above and in preceding papers (this vol., pp. 343, 992) may take place through the agency of anions or of un-ionised molecules.

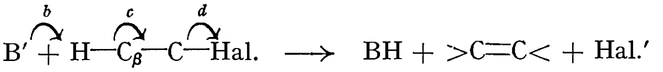
Reactions between Anions and Alkyl Halides.—Where anions only participate, both substitution (see, *e.g.*, Wislicenus, *Annalen*, 1882, **212**, 239) and olefin reactions (see, *e.g.*, Taylor, J., 1935, 1514) are kinetically of the second order and the mechanisms are commonly regarded as being bimolecular, *viz.*,

Substitution reaction (with anion)



$$\mathrm{H{-}C{-}}\underset{\substack{a\uparrow\\ \mathrm{B}'}}{\mathrm{C}_a}\overset{\overset{d}{\curvearrowright}}{-}\mathrm{Hal.} \longrightarrow \mathrm{H{-}C{-}C{-}B + Hal.'} \qquad (\mathrm{S_a})$$

Olefin reaction (with anion)

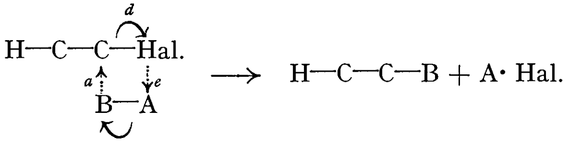


$$\overset{b}{\curvearrowright}\mathrm{B}' + \mathrm{H}-\overset{c}{\curvearrowright}\mathrm{C}_\beta-\overset{d}{\curvearrowright}\mathrm{C}-\mathrm{Hal.} \longrightarrow \mathrm{BH} + {>}\mathrm{C}{=}\mathrm{C}{<} + \mathrm{Hal.}' \qquad (\mathrm{O_a})$$

One important difference between these two types of reaction is that, although anions which are very feebly basic, *e.g.*, S_2O_3'' or $CH_3{\cdot}CO{\cdot}CH_2{\cdot}CO_2'$, cause the substitution to take place to the practical exclusion of the olefin reaction, the latter occurs the more readily the more strongly basic the anion; *e.g.*, OEt′ (alcoholic potash) is more effective in olefin formation than OH′ (aqueous potash) and both are more effective than the anions mentioned previously. Hence, it follows that, if the strength of a base be defined as its electron-donating power (the opposite viewpoint from proton affinity), then with an increase in this power the electron transfers *b* and *c* are facilitated relatively to *a*. This can only mean that β-hydrogen is more polarisable, *i.e.*, more readily has a positive charge induced on it, than α-carbon, and hence reacts the more readily the more strongly basic the anion. The relative reactivity of either centre will be increased, the more it becomes positively charged relatively to the other. Thus, the presence of a negative β-substituent such as Hal. or Ph confers a positive charge on β-hydrogen, so that, *e.g.*, in β-phenylethyl bromide and ethyl bromide, where the C_α–Hal. link is sensibly the same, olefin is formed in high proportion from the former but scarcely at all from the latter (see table). From the structures suggested by the author (*Rec. trav. chim.*, 1937, **56**, 898) for aliphatic compounds Alk.X, in which there is a supplementary binding of X (in the present case Hal.) by α-hydrogen in all but tertiary compounds, it follows that the positive charge on α-carbon decreases along the series Me, Et, Pr^β, Bu^γ, whereas, for the same halogen, that on β-hydrogen is much the same. Hence, the substitution mechanism will operate with decreasing efficiency in this order (see, *e.g.*, Wislicenus, *loc. cit.*) whilst the tendency to olefin formation will increase (this tendency will not necessarily be effective in producing olefin). The effect of substitution of I for Br or Br for Cl in an alkyl halide, owing to increased polarisability, will be to cause an increased induced positive charge on β-hydrogen relative to α-carbon by the approach of a strongly basic anion and hence increased olefin formation (see also J., 1935, 1514). Thus for the reaction between an alkyl halide and an anion the proportion of olefin formation will be determined by (1) the basic strength of the ion, (2) the relative sizes of the positive charges on α-carbon and β-hydrogen, and (3) the polarisability of the halogen.

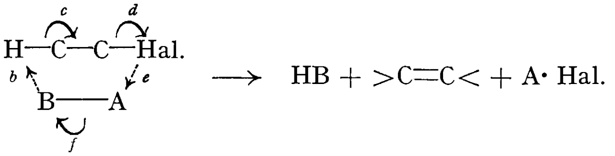
Reactions between Molecules and Alkyl Halides.—When a molecule reacts with an alkyl halide, even when this is tertiary, it has been shown (this vol., p. 1853) that the substitution reaction is kinetically of the second order and the mechanism is here assumed to be bimolecular. It is probable that the corresponding olefin reaction (see above) is similarly bimolecular. In these reactions the molecular reagent is capable of direct attack on all three reactive centres of the alkyl halide, *viz.*, α-carbon, β-hydrogen, and halogen, and the mechanisms proposed are:

Substitution reaction (with molecule)



$$\begin{array}{c}\mathrm{H-C-C}\overset{d}{\curvearrowright}\mathrm{Hal.}\\ a\uparrow\quad\downarrow e\\ \mathrm{B-A}\\ \curvearrowleft\end{array} \longrightarrow \mathrm{H-C-C-B} + \mathrm{A\cdot\ Hal.} \qquad (\mathrm{S_m})$$

Olefin reaction (with molecule)



$$\begin{array}{c}\mathrm{H-}\overset{c}{\curvearrowright}\mathrm{C-C}\overset{d}{\curvearrowright}\mathrm{Hal.}\\ b\nwarrow\qquad\swarrow e\\ \mathrm{B-\!\!-A}\\ \underset{f}{\curvearrowleft}\end{array} \longrightarrow \mathrm{HB} + {>}\mathrm{C}{=}\mathrm{C}{<} + \mathrm{A\cdot\ Hal.} \qquad (\mathrm{O_m})$$

The various electron shifts are regarded as taking place in small successive stages, and for each stage, simultaneously. In both of the corresponding ionic reactions, since the same electron transfer *d* must occur before the reaction is completed, it follows that, for any one anion and any one alkyl halide, substitution will be intrinsically preferred since the halogen is the adjoining atom to the α-carbon whilst it is three atoms removed from β-hydrogen. On the other hand, in the molecular mechanisms now proposed there is a direct attack on the halogen in both reactions, and hence, relatively to the ionic reactions, olefin formation will be preferred. This explains why, in the case of, *e.g.*, β-phenylethyl bromide (see table), the proportion of olefin increases with increasing concentration of sodium ethoxide, *i.e.*, with increasing concentration of the un-ionised base. From the above picture of the molecular mechanisms, it is clear that the alkyl halide and the molecule interact mutually, and that the former is as much a reagent as the molecule. Thus when the halogen of the alkyl halide is not partly bound by α-hydrogen (see above), as in *tert.*-butyl bromide, it is more free to react with A of AB, and therefore more readily induces dissociation of AB so that B acquires a greater power of electron donation and becomes a stronger base. Hence olefin formation results at the expense of substitution. It follows that olefin formation with any molecule such as NaOEt or HOEt will increase along the series of bromides Et, Pr^{β}, Bu^{γ}, since the bromine becomes increasingly reactive. This interprets the influence of structure on olefin formation (p. 1963). For a similar reason sodium ethoxide will be more effective than ethyl alcohol for olefin formation, since bromine in any one bromide will stimulate the dissociation of the former more readily than of the latter. Similarly, the alcohol will be more effective for olefin formation than water, since $\mathrm{OH}^{\delta-}$ is a weaker base than $\mathrm{OEt}^{\delta-}$. This interprets the effect of the constitution of the molecular reagent and of solvents on olefin formation (p. 1964). The ease of dissociation of AB, on which will depend the rate of reaction of the alkyl halide, will be determined, not only by the reactivity of the halogen, but also by the reactivities, *i.e.*, the sizes of the positive charges, of α-carbon and β-hydrogen. This is shown for α-carbon by the relative rates of reaction (mainly substitution) of these bromides with " 80% " aqueous ethyl alcohol—$\mathrm{Me} > \mathrm{Et} \sim \mathrm{Pr}^{\beta} \lll \mathrm{Bu}^{\gamma}$ (this vol., p. 992). The positive charge on α-carbon decreases along this series, and the effect of this is apparent from the relative rates of substitution under these conditions with Me and Et : for Pr^{β} and especially for Bu^{γ} this effect is masked by the reactivity of the bromine. The effect of a highly positive and therefore highly reactive β-hydrogen atom on the ease of dissociation of AB is shown by the high proportion of olefin formed when a strongly basic molecule such as NaOEt reacts with a halide in which there is a negative substituent such as Hal. or Ph on the β-carbon atom, *e.g.*, β-phenylethyl bromide. A weakly basic molecule such as HOEt or HOH will not readily be able to react with such a molecule since the bromine is not reactive enough in a primary halide to cause ready dissociation of HOEt. Secondary and especially tertiary halides, only, will have this power. In considering the possible effect of the substitution of I for Br or Br for Cl in an alkyl halide on the proportion of olefin formed by its reaction with a molecular reagent, two factors must be kept in mind : (1) the increased polarisability of halogen which, from what has been stated already, should lead to increased olefin-formation, and (2) the induced reactivities, *i.e.*, positive charges, on β-hydrogen and α-carbon by α-halogen, the ratio of which charges may be taken to decrease the smaller the effect inducing the charges—*i.e.*, decreasing along the series Cl, Br, I—and hence olefin formation will be decreased on this account. The results of Cooper, Hughes, and Ingold (this vol., p. 1280) and of Hughes and MacNulty (*ibid.*, p. 1283), showing that *tert.*-butyl and -amyl chlorides yield higher proportions of olefin than the corresponding bromides and iodides in " 80% " aqueous ethyl alcohol at 25°, are here interpreted as being due to the dominant effect of factor (2) when the base, as in this case—a mixture of ethyl alcohol and water—is not readily dissociated. When the molecular base is readily dissociated, as with sodium ethoxide, the effect of factor (1) will be dominant, as ordinary preparative methods of olefins, preferably from the iodides, indicate.

Mechanism ($\mathrm{S_m}$) would interpret the greater accelerating influence of added water on the rates of substitution of alkyl bromides in aqueous alcohol in the order Me, Et, Pr^{β}, Bu^{γ} (this vol., p. 992) as being due mainly to the greater reactivity of bromine in this order. The ionic products of ethyl alcohol and water being approximately 1×10^{-19} and 1×10^{-14}, respectively, it follows that the more reactive the halogen the more readily will water be dissociated in comparison with alcohol (or conversely, the more readily will the halide be dissociated by water). That α-carbon does exert a slight dissociating influence on the solvent molecules is possibly shown by the very small difference in the above accelerating effect of added water on methyl and ethyl bromides. The acceleration must be also partly ascribed to a true solvent effect (see this vol., p. 1853).

The accelerating effect of an ionic base on reaction rates in aqueous-alcoholic solutions of alkyl halides will, on the above mechanisms, be greatest where the halogen, owing to α-hydrogen bonding, has small reactivity, but β-hydrogen or α-carbon (or both) is highly reactive owing to its being positively charged. The least such effect will occur when the halogen is highly reactive and the positive charge on the α-carbon is negligible as in tertiary halides, for then the high concentration of the solvent, relatively to any *small* ionic concentration of added base, will determine the reaction rate (cf., however, the influence of undissociated base on the proportion of olefin formation—see table). This would explain the decrease in the accelerating effect of an ionic base in the halide series, Me, Et, Pr^{β}, Bu^{γ}.

The failure of acids to accelerate the hydrolysis of alkyl halides must be attributed to the instability of $BrH_2^{\cdot}$ relatively to $OH_3^{\cdot}$, as Bagster and Cooling (J., 1920, **117**, 693) showed by the electrolysis of hydrogen bromide in sulphur dioxide, *i.e.*, $HBr + H_2O \rightarrow H_3O^{\cdot} + Br'$, and not $HBr + H_2O \rightarrow H_2Br^{\cdot} + OH'$. This is so, since $AlkBr + OH_3^{\cdot} \rightarrow AlkOH + BrH_2^{\cdot}$ can be supposed to represent the reaction that would occur if acid catalysis could take place.

On the results (this vol., p. 1853) found for the hydrolysis of *tert.*-butyl bromide in acetone, *viz.*, that both this and the reverse reaction are kinetically of the second order and presumably are bimolecular, it is necessary to state that the "complex" in the mechanism (S_m) must be regarded as suffering "instantaneous" decomposition when formed in either direction; *i.e.*, the respective rates must depend on the respective probabilities of the formation of the complex from either pair of reagents. This disposes of the previous suggestion (this vol., p. 344) that the complex might be sufficiently stable to be capable of suffering a unimolecular decomposition.

EXPERIMENTAL.

The bromides were all materials of constant b. p. The requisite amount of the bromide was weighed into 10 c.c. of sodium ethoxide solution in ethyl alcohol dried as described previously (J., 1935, 1520), contained in a tube which was then hermetically sealed. This was protected by a stout closely-fitting outer tube,. and placed in a thermostat at the required temperature. When all the bromide had reacted, as was known from kinetic experiments for the higher concentrations of the sodium ethoxide solutions (>0·1N.), the tube was broken in a glass-stoppered bottle containing carbon tetrachloride (30 c.c.), and water (150 c.c.) was then added. The extent of decomposition was checked by titration with standard hydrochloric acid, phenolphthalein being the indicator. With the lower concentrations of sodium ethoxide and for the slower reactions at 25° this method gave the amount of bromide decomposed. When solvents only were used, the same time was allowed to elapse as that taken when alcoholic sodium ethoxide was employed; in these cases no attempt was made to check the extent of decomposition because of the known interaction of hydrogen bromide with ethyl alcohol. For this reason, although these results are comparable amongst themselves, they are not to be relied on as absolute values. The extraction and olefin estimation were carried out by the method previously described (this vol., p. 348), but using carbon tetrachloride (30, 10, 5, and 5 c.c.) washed with much water. In all cases except the styrene estimations, for which conditions already quoted were employed, the bromine addition was performed at room temperatures and during 2 hours.

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