175. *Mechanism of Elimination Reactions. Part V. Kinetics of Olefin Elimination from Ethyl,* iso*Propyl,* tert.*-Butyl and α- and β-Phenylethyl Bromides in Acidic and in Alkaline Alcoholic Solution. Effects due to, and Factors influencing, the Two Mechanisms of Elimination.*

By EDWARD D. HUGHES, CHRISTOPHER K. INGOLD, STANDISH MASTERMAN, and BASIL J. MCNULTY.

Notwithstanding a criticism by W. Taylor (1937), the work of Hughes, Ingold, and Shapiro (1938) on the proportions and kinetics of olefin elimination from *iso*propyl bromide is found to be correct. On the other hand, Taylor's results for the proportions of olefin formed in a range of examples are incorrect. Taylor's work has been partly revised; one reason why it could not be completely revised is that some of the reactions whose products are allegedly estimated do not proceed at all at the temperatures stated.

We have supplemented our work on the proportions of olefin formed from alkyl bromides by a study of the corresponding reaction kinetics, according to the pattern set by Hughes, Ingold, and Shapiro's investigation. In close analogy with previous experience relating to the Walden inversion (1937), it has been found that an investigation of the kinetics of the reactions associated with olefin elimination is definitely required in order to reveal what is happening; but that once this is known, the apparently inconsistent observations of the older literature fall into place, and it is possible for the first time to make widespread, and rationally based, predictions as to the effect of chemical constitution and physical condition on the phenomenon. In close analogy with previous experience relating to substitution (1935), the key throughout is duality of mechanism. A discussion is given of the effect of the structure of the alkyl halide, the constitution of the reagent, the nature of the solvent, and the concentration; a previous discussion of the remaining variable, temperature, is referred to. We also outline, and carry through the first stage in the execution of, an experimental programme designed to give quantitative significance to the theory by the provision of important rate constants of the constituent mechanisms (E1 and E2). This is done for ethyl, *iso*propyl, *tert.*-butyl and α- and β-phenylethyl halides.

SINCE the earlier Parts of this series appeared (1937) Taylor has published a number of papers which (the method of private approach having failed) it is regrettably necessary to controvert, not only as to the inferences, but also with respect to many of the recorded observations. The points are dealt with as they arise in the first six of this running group of papers, the remaining ten being concerned with a more normal extension of our study of substitution. As it will be necessary to discuss a large number of Taylor's papers, including all which have appeared in the last two years,* it is convenient to number them: (1) J., 1935, 1514; (2) J., 1937, 343; (3) *ibid.*, p. 992; (4) *ibid.*, p. 1852; (5) *ibid.*, p. 1853; (6) *ibid.*, p. 1962; (7) *Rec. Trav. chim.*, 1937, **56**, 898; (8) J., 1938, 840; (9) *J. Amer. Chem. Soc.*, 1938, **60**, 2094; (10) J., 1939, 478; (11) [Added 23.3.40] *ibid.*, p. 1872.

In sections (1) and (2) below we shall refer to experimental data on the proportions of olefin eliminated during the hydrolysis or alcoholysis of some alkyl halides. In section (3) we shall discuss the variation of this proportion with constitution, concentration and other factors.

(1) *A Criticism.*

In paper (6) Taylor reported estimations of the proportions of olefin formed from a number of alkyl halides, including *iso*propyl and *tert.*-butyl bromide; this was done at two temperatures, and in several " media," *viz.*, the vapour, carbon tetrachloride, water, aqueous ethyl alcohol, and dry ethyl alcohol under various conditions of alkalinity. The extensive series of results given would be valuable if it were trustworthy. In one case, however, as Taylor himself noticed, the figure given could be checked against a value already published by Hughes, Ingold, and Shapiro (J., 1936, 225) for *iso*propyl bromide; and there was not even qualitative agreement. The last-named authors had found 56·8% of propylene in the product of the reaction of *iso*propyl bromide with alkaline 80% aqueous alcohol at 50°; a change to a drier alcoholic solvent, or to a higher temperature should (and does) raise this figure (*idem, ibid.*); but, for the alcoholysis of the same bromide in alkaline, anhydrous ethyl alcohol at 55°, Taylor recorded 27·6% of propylene. (We shall see later that the correct value is 75% for these conditions.) He dealt with the discrepancy as follows: " Hughes, Ingold, and Shapiro found, . . . in 80% alcohol at 50°, 56·8% of olefin. A repetition of their method of estimation, however, revealed a distinct possibility of alcohol vapour having passed over into the standard bromine " (used to estimate the olefin).

In view of this implied criticism we re-examined Hughes, Ingold, and Shapiro's method, which consists in aspirating the gaseous olefin, after trapping alcohol vapour, into a solution of bromine, the standardisation of which is substantially a similar " blank " experiment without the olefin. A careful further study showed the method to be essentially reliable, the results tending to be a little low if in error at all, although with due precaution and some experience they can be made accurate to 1—2% for percentages in the neighbour-

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* [Added 23.3.40.] The present papers were for the most part written in the spring and summer of 1939, and the manuscripts have not been changed except by a limited number of dated additions. The latter have been written from the Edward Davies Chemical Laboratories, Aberystwyth, where for some months past three of the authors (L. C. B., E. D. H., and C. K. I.) have been receiving kind hospitality from Professor T. Campbell James, whom it is desired to thank.

hood of 60. We find the particular result on which Taylor sought to throw doubt to be accurate, certainly to within this limit.

Having failed to elucidate the discrepancy thus, we next examined Taylor's procedure, which consists in extracting the olefin with carbon tetrachloride, washing the extract thoroughly with water to remove all traces of alcohol (this he states to be essential), and then measuring the uptake of bromine. Using this method, we were able to imitate Taylor's values qualitatively. But quantitatively the results were quite unreproducible, and it is obvious to us, that if Taylor had repeated his measurements he could not have failed to realise that something was amiss. What is wrong is that in the process of washing away " all traces " of alcohol most of the gaseous olefin escapes. The method is a possible one for non-volatile olefins, but certainly not for gaseous olefins.

Now the method of estimating olefins formed in reactions by extraction with carbon tetrachloride or chloroform has been developed by us since 1933 (Hughes and Ingold, J., 1933, 523, and six subsequent papers), but we have always found it necessary to take precautions indicated by the nature of the olefin under analysis. An olefin like styrene can be estimated practically without precautions; but this is not so for the lightest olefins, not only because of their volatility, but also because the partition ratios are insufficiently favourable to permit indiscriminate washing of the solvent extract with water. In view of Taylor's failure with the method it seems desirable to specify the main points of a moderately accurate technique for volatile olefins. They are (cf. also p. 910) : (1) Use of an adequate quantity (very much more than Taylor's) of chloroform; (2) working below 0°; (3) omission of all washings with water, except that the introduction and subsequent removal (once) of a small quantity of aqueous acid is necessary to secure the destruction of alkali; (4) removal of unseparated water and a good deal of dissolved alcohol by means of calcium chloride; (5) introduction into the bromine solution of hydrogen bromide, which strongly and selectively catalyses the addition of bromine to the olefin (the hydrogen bromide does not itself add appreciably under these conditions), and renders the simultaneous attack of bromine on any imported alcohol small and readily estimated by " blank " experiment; (6) incorporation of the " principle of the blank experiment " into the standardisation process. Even with precautions 1—5, losses of olefin are not entirely avoided; but we have reduced them (except for ethylene) to small proportions, and standardised them rather precisely. Thus the most important part of the " blank " procedure is the determination of these losses by application of the complete method to artificially prepared solutions of the olefins. Carried out in this way, the extraction method is comparable in accuracy with the aspiration method for *iso*butylene, and almost so for propylene, though its application to ethylene is not satisfactory.

As no reliance could be placed on Taylor's table of values, we have done what we can to revise it, since its revision contributes to a more general research on olefin elimination the main part of which will be published later. We have, however, extended our revision only over a distributed sample of conditions relating to Taylor's main solvent, dry ethyl alcohol, and the higher of his two temperatures, 55°; for it would have taken long to produce so many data as he recorded by any reliable method known to us.* The discrepancy already considered is typical for the halides mentioned. Other reasons for not extending the revision are given on p. 910.

(2) *Methods and Results.*

In order to be able to give a clear picture of the whole phenomenon of the varying proportions in which olefins are formed during the hydrolysis and alcoholysis of different alkyl halides under different conditions, we found it necessary also to make a study of the reaction kinetics over the ranges of conditions used in the experiments on olefin production. As we increase the concentration of alkali for one particular alkyl halide, the kinetics pass over from first order to second, because the alkali enters directly into the second-order

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* It happens that in a research with quite a different object from this, Dhar and one of us have recently been measuring the elimination of olefin during the hydrolysis of *tert.*-butyl bromide in dry ethyl alcohol at 25°; this is the second of Taylor's two temperatures. The results, carefully checked, reveal discrepancies with Taylor's values of just the same kind as those disclosed in this paper.

reaction but not into the rate-determining stage of the first. It is important to know when this change happens. As might have been expected from the smaller ionising power of alcohol than of water, and from the probably greater nucleophilic activity of ethoxide than of hydroxide ions, the change tends to occur earlier in anhydrous alcohol than in the aqueous alcoholic solvents which we have employed previously.

The older literature of olefin formation from alkyl halides is prolific but entirely empirical, and the results are at first sight confusing. Indeed the situation reminded us strongly of that in which we found the Walden inversion when we commenced to study that subject. Guided by this experience, we considered the best hope of rationalisation to be the procedure indicated in the previous paragraph. Of the four chief variables, *viz.*, halide structure, reagent, solvent, and concentration [temperature is less important, and was discussed by Hughes, Ingold, and Shapiro (*loc. cit.*)], we deal experimentally with only two, *viz.*, halide structure and concentration, and our treatment of halide structure is far from complete. We hope in due course to apply the same method over a representative range of all the main variables. However, we discuss them all at the present time, since our previous work, together with that now communicated, already makes clear the type of result we must expect in this wider field, and removes much of the apparent inconsistency of the older literature.

The experimental results are in Table I. The large figures are those of main significance, the small ones being of the nature of experimental detail, included to avoid duplicating the record in the experimental section of the paper. For the olefin estimations, the aspiration method was used for ethyl and *iso*propyl bromides; our form of the extraction method was used throughout; the agreement was satisfactory, even for ethyl bromide. We do not think that any of the olefin figures are likely to be in error by more than 2%, and those given for ethyl bromide are probably correct to within 0·3%. The reason why the aspiration and extraction methods gave the same result for ethylene (usually to within 0·2%), although the extraction method is in principle unsatisfactory, is that so little ethylene is formed that a proportionately considerable error has only a small absolute value. Naturally we used more than the normal amount of alkyl halide in order to increase the absolute quantity of ethylene to be measured, and, because of its low solubility, employed more than the normal amount of chloroform for extraction. In one case, that of *iso*propyl bromide in acid solution, we are able to give the result for olefins only in qualitative form, because the reaction is so slow : we know that after 20% of reaction no measurable quantity of olefin had been produced; although if we could have completed the reaction the propylene might have been measurable.

With regard to the kinetic data, a good deal of the necessary explanation is in the " key " at the top, or in notes incorporated in the body of the Table; the following remarks are supplementary. The unmeasured first-order rates for ethyl and β-phenylethyl bromide are probably of the same order of magnitude as the measured first-order rate for *iso*propyl bromide. Where a second-order rate is measured in dilute and in concentrated alkali, we find a reduced value in concentrated alkali : this is due to " salt effects," *i.e.*, to deviations from the concentration form of the mass-law in strong solutions. As we had to maintain a constant temperature throughout, some of the rates were very small, others inconveniently great. Slow first-order rates in acid solution are measured by the method of initial velocities, because in the later stages of reaction analysis is disturbed by interaction of the liberated hydrogen bromide with the solvent. The second-order reactions in concentrated alkali are very rapid, and the recorded constants can be regarded only as rough approximations. Kinetic experiments in which first- and second-order reactions are present together in comparable proportions are illustrated in the experimental section, but no constants are recorded in the Table, because of the great errors that attend an *a priori* mathematical analysis of such experiments. If the concentration mass-law were strictly true, *i.e.*, if rate constants applied unchanged over large changes of alkali concentration, we could exactly calculate the proportions of the constituent reactions; but owing to the incursion of salt effects in the more concentrated alkaline solutions, this is not possible, and the best estimates that we can make (cf. p. 912) of these proportions are necessarily rather rough (cf. notes in the Table). The above applies, in particular, to α-phenylethyl bromide. For *iso*propyl bromide we can give accurate values for the second-order rate constants in dilute alkali, because, although the first-order reaction is simultaneously present, its proportion is small and we know its rate constant. On the other hand, for *tert.*-butyl bromide we cannot similarly give accurate values for the first-order rates in dilute alkali, because, although the proportion of the simultaneous second-order reaction is also small, its determined rate constant is subject to a salt effect which cannot be precisely estimated.

No attempt has been made to analyse the proportions of olefin into parts for which the first- and second-order reactions are separately responsible : the figures tabulated are plain experimental values. In convenient cases, *e.g.*, the acid hydrolyses of *tert.*-butyl and α-phenylethyl bromide, the development of olefin was followed during the run; this ensures that no error shall arise through the incursion of olefin hydration (Hughes and MacNulty, J., 1937, 1283). The same could not easily be done (nor was it necessary) for the rapid reactions in alkaline solution, for which the olefin proportions were obtained by analysis of the product of the completed reaction. For the reactions of mixed order the olefin proportion would have varied through the run, and the analysis of the variation would have presented the same difficulties as those of the corresponding kinetic analysis. For these reactions the olefin values were obtained for (and apply only to) the completed reaction. The figures for styrene are in fair agreement with Taylor's values.

TABLE I.

First- and Second-order Rate Constants for, and Percentages of Olefin formed in, Reactions of Alkyl Bromides in Dry Ethyl Alcohol at 54·9° ± 0·05°.

Key : PEB = phenylethyl bromide; k_1 = first-order rate constant in sec.$^{-1}$; k_2 = second-order rate constant in sec.$^{-1}$g.-mol.$^{-1}$ l.; $[NaOEt]_{appx.}$ = approximate value of [NaOEt] adopted for convenience in tabulation; $[NaOEt]_0$ = accurate initial NaOEt in rate experiments; $[NaOEt]_m$ = accurate mean of initial and final [NaOEt] in olefin experiments. The horizontal lines indicate the approximate range of supersession of the first-order by the second-order reaction, and vice versa. As to " mixed order " reactions see p. 902.

Conditions		Acid	Dil. alkali			Conc. alkali			
$[NaOEt]_{appx.}$		None	0·02	0·05	0·1	1·0	1·5	2·0	2·5N
EtBr	10^5k_1	small							
	10^4k_2		—	19·7	17·4	—	—	11·9	—
	C_2H_4, %	—	0·9	—	—	0·8	1·0	1·3	—
	$[NaOEt]_0$	—	—	0·0478	0·0962	—	—	1·82	—
	$[NaOEt]_m$	—	0·0265	—	—	1·23	1·55	2·23	—
$Pr^{\beta}Br$	10^5k_1	0·0173							
	10^4k_2		—	2·01 *	2·12 *	—	—	0·97	—
	C_3H_6, %	small †	—	71·4	—	—	78	—	80
	$[NaOEt]_0$	—	—	0·0491	0·0972	—	—	1·98	—
	$[NaOEt]_m$	—	—	0·0445	—	—	1·61	—	2·48

* Corrected for the few units % of first-order reaction simultaneously present.
† Not more than a very few units % (see text).

Conditions		Acid	0·02	0·05	0·1	1·0	1·5	2·0	2·5N
$Bu^{\gamma}Br$	10^5k_1	19·8	23·3 *	24·2 *	mixed order				
	10^4k_2					—	—	*ca.* 5·0	—
	C_4H_8, %	27·9	32·7	—	—	86	—	93	97
	$[NaOEt]_0$	—	0·0224	0·0482	—	—	—	1·89	—
	$[NaOEt]_m$	—	0·0150	—	—	0·98	—	1·91	2·54

* Values too high because they are not corrected for the few units % of second-order reaction simultaneously present (see text).

Conditions		Acid	0·02	0·05	0·1	1·0	1·5	2·0	2·5N
α-PEB	10^5k_1	19·2	—	* mixed order	† mixed order				
	10^4k_2					—	*ca.* 15	—	*ca.* 16
	C_8H_8, %	*ca.* 0·0	—	8·6	17·3	—	33·8	—	34·1
	$[NaOEt]_0$	—	—	0·0718	0·136	—	1·53	—	2·45
	$[NaOEt]_m$	—	—	0·0473	0·106	—	1·48	—	2·40

* About ¼ of the completed reaction is second-order.
† About ½ of the completed reaction is second-order.

Conditions		Acid	0·02	0·05	0·1	1·0	1·5	2·0	2·5N
β-PEB	10^5k_1	small							
	10^4k_2		—	65·8	59·3	—	—	—	—
	C_8H_8, %	—	95·5	—	94·6	—	—	—	93
	$[NaOEt]_0$	—	—	0·0428	0·118	—	—	—	—
	$[NaOEt]_m$	—	0·0234	—	0·080	—	—	—	2·04

(3) *Discussion.*

The first reasonably accurate and complete kinetic analysis of hydrolysis or alcoholysis with olefin elimination in a simple alkyl halide was Hughes, Ingold, and Shapiro's study of *iso*propyl bromide (*loc. cit.*); extensions were subsequently made to *iso*propyl chloride and iodide, *β*-*n*-octyl chloride and bromide, *tert.*-butyl chloride, bromide and iodide, and the three corresponding *tert.*-amyl halides (Hughes and Shapiro, J., 1937, 1177, 1192; Hughes, Ingold, and Shapiro, *ibid.*, p. 1277; Cooper, Hughes, and Ingold, *ibid.*, p. 1280; Hughes and MacNulty, *loc. cit.*). The general outcome may be summarised as follows: In the first place there is a second-order reaction, which consists of two simultaneous and independent reactions, substitution and elimination (S_N2 and E2), in certain proportions; and superposed on these, there is a first-order reaction, consisting also of simultaneous substitution and elimination (S_N1 and E1), but in quite different proportions. In a particular case it may be possible to simplify this covering statement for a specified range of conditions, if it happens that within this range at least one of the four constituent reactions is slow in comparison with the others.

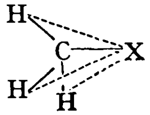
Now Taylor noticed a further discrepancy in the previous literature. Both Brussoff (*Z. physikal. Chem.*, 1900, **34**, 129) and Segaller (J., 1913, **103**, 1430) had studied the proportions in which olefins are eliminated from alkyl halides in alkaline solutions; and whilst Brussoff had found the order prim. < sec. > tert., Segaller's results had indicated sec. < tert. Taylor's (incorrect) results for *iso*propyl and *tert.*-butyl bromide gave the order sec. < tert. His comment was that " Brussoff's method of olefin estimation . . . is not capable of high accuracy," and that his own " accurate measurements " remove " any doubt as to the influence of structure on the proportions of olefin formation."

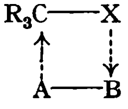
Our results indicate, on the contrary, that most of the earlier work on olefin formation may be correct, at least approximately. Thus in the particular example on which Taylor challenged our values, he was (though apparently unaware of it) in conflict with previous investigators additional to Brussoff and ourselves. Nef (*Annalen*, 1899, **309**, 126; 1901, **318**, 1) obtained 74% of propylene from the action of ethyl-alcoholic sodium ethoxide on *iso*propyl bromide; and Nef's similar value, 75%, for ethyl-alcoholic potassium hydroxide was approximately confirmed by Bell and Clark (*Trans. Roy. Soc. Canada*, 1935, [3], **29**, 61), who, using this reagent in a very concentrated form, 4·5N, obtained the value 83%. We show that, with sodium ethoxide, values ranging from 71—80% are obtained, depending on the concentration, 0·05—2·5N, of this reagent.

Concerning Brussoff's and Segaller's opposite sequences for secondary and tertiary halides, a glance at Table I (or at Fig. 1, explained later) will show that both may be correct if the conditions are appropriate. For *iso*propyl and *tert.*-butyl bromides in reaction with alcoholic sodium ethoxide, Brussoff's inequality applies to the more dilute alkaline solutions and Segaller's to the more concentrated (though other factors are involved in the actual reasons why these investigators obtained their sequences, as will appear later). Thus the only previous indefensible conclusion concerning the secondary-tertiary sequence is that of Taylor's quoted. Actually the result depends on the changes of reaction order, which were unknown to Brussoff and Segaller, though a knowledge of such changes was available to Taylor (cf. J., 1937, 343).

We shall not discuss Taylor's theory of the effect of alkali concentration on the relative proportions of substitution and olefin elimination, because the theory is incorrectly founded and neglects the essential changes of kinetic type. We also think it unnecessary to go into detail concerning his theory of the effect of structural changes, since this involves an appeal (paper 7) to formulæ of type I and relies (paper 6) on an assumed reaction-form II (two-point attack by adjacent atoms on adjacent atoms), which does not satisfactorily accommodate the Walden inversion (cf. paper 7) known to be general amongst the substitutions contemplated (Cowdrey, Hughes, Ingold, Masterman, and Scott, J., 1937, 1252). Instead, we shall state our own view.

(I.)





(II.)

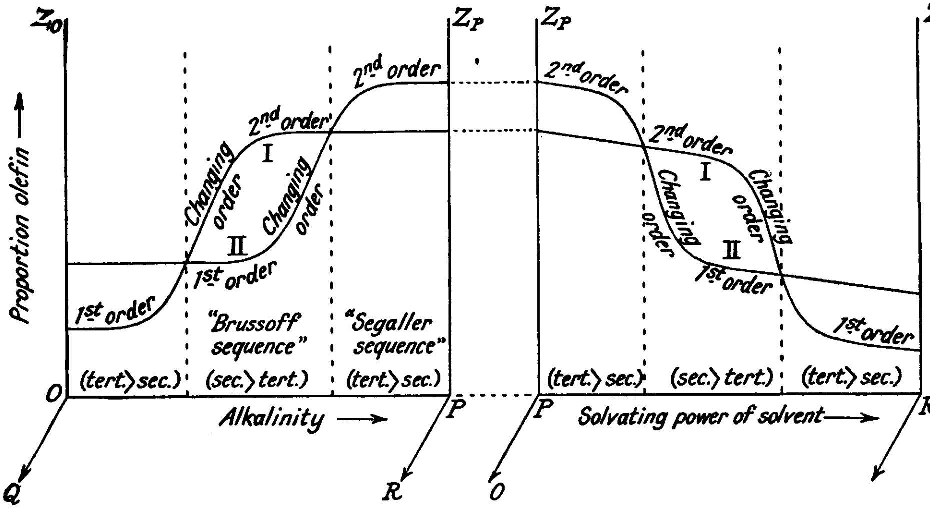
The connexion between olefin proportion and kinetic type can be followed from Table I, in which the horizontal lines guide the eye to the regions where kinetic change occurs. The data for *tert.*-butyl and α-phenylethyl bromides show the general relationship most completely, and the five sets of results collectively make it perfectly clear: so long as the kinetic order * remains single (first order only or second only) the olefin percentages remain almost constant; but when the order is changing the olefin percentage is simultaneously shifting from its old characteristic value to its new. One characteristic value represents the ratio $E1/(S_N1 + E1)$, and the other the ratio $E2/(S_N2 + E2)$.

The central point of our theory of the connexion with structure has already been given by Hughes and Ingold (J., 1935, 244; cf. Gleave, Hughes, and Ingold, *ibid.*, p. 236), who showed (in advance of the observations) that we should expect the change from first to second order with increasing alkalinity to occur at successively later stages in the series primary, secondary, tertiary, for aliphatic halides, and that for one kind of halide (*e.g.*, secondary) it should occur later when a phenyl substituent occupies the α-position of the alkyl group.

Schematic Representation of the Connexion between Olefin Proportion, Alkyl Halide Structure, Alkalinity and the Solvent Composition.

(All scales arbitrary.)

FIG. 1. FIG. 2.



[As regards the position of the change of reaction order, curve II applies to an alkyl group which has more, or more strongly, electron-releasing α-substituents than the alkyl group of curve I.]

The interaction of the relationships indicated in the two preceding paragraphs is schematically illustrated in Fig. 1, in which curve I might represent an *iso*propyl, and curve II a *tert.*-butyl halide, in reaction with sodium ethoxide. We see two intersections, and therefore that, in a sufficient p_H range, there may be a double inversion as between Brussoff's and Segaller's types of sequence. If we shift one curve vertically, or alter its vertical span, there could be fewer intersections (one or none), as might be illustrated by comparing ethyl and *iso*propyl, or β- and α-phenylethyl halides.

In Fig. 1 the solvent is supposed to be kept constant, the alkalinity alone being varied. But quite analogous considerations apply for variation of the solvent with the alkalinity kept constant. We know that in alkaline solution the importance of the first-order reaction relatively to the second diminishes along the series tertiary, secondary, primary; and also that the effect of a more highly solvating solvent is to retard the second-order reaction and accelerate the first (Hughes and Ingold, *loc. cit.*). Therefore, if at a fixed alkalinity which leads to second-order reactions in a particular solvent, we change to more strongly solvating

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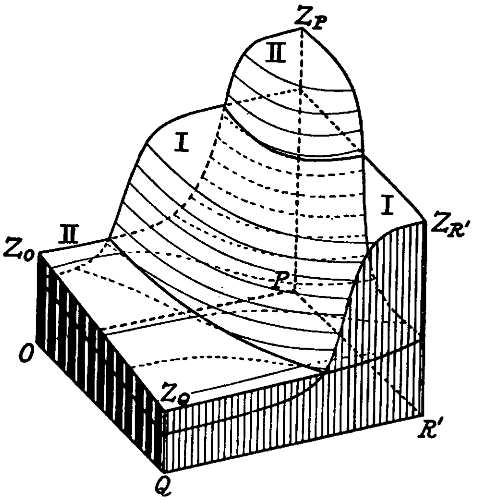
* Reference here and in the sequel is to the order of the measured, total reaction. This order will change when the order of *either* of the constituent processes (substitution and elimination) is changing.

solvents in a progressive manner, the first reaction to drop from second order to first will be that of the tertiary halide, the next that of the secondary, and the last that of the primary halide. Thus, if we make a plot of olefin proportions against solvent variation, we must obtain curves of the type shown in Fig. 2, with up to two intersections, and therefore the possibility of a double inversion as between the " Brussoff " and " Segaller " types of sequence in a sufficiently extended range of solvents. The main qualitative difference from the curves of Fig. 1 is that the new curves will not be horizontal when the reaction order is single on account of the solvent effect on the separate rate-ratios $E2/(S_N2 + E2)$ and $E1/(S_N1 + E1)$. The directions of the deviations shown in Fig. 2 are taken from Hughes, Ingold, and Shapiro's study of the variation of the former ratio for *iso*propyl bromide, and Hughes and MacNulty's investigation of the variation of the latter for *tert.*-amyl chloride, in alcohol–water mixtures (*loc. cit.*).* Actually the solvent-range, pure alcohol to pure water, is sufficient to illustrate only the first two of the three sections into which Fig. 2 is divided by ordinates drawn at the intersections.

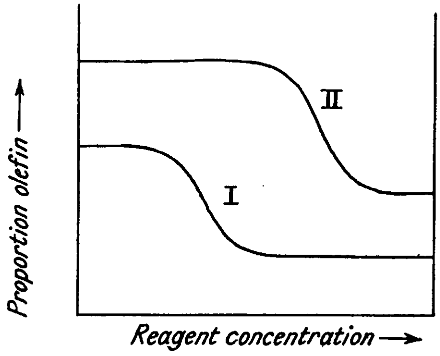
FIG. 3.



Relief corresponding to Figs. 1 *and* 2.

FIG. 4.

Schematic Representation of Connexion between Olefin Proportion and the Concentration of a Weakly Basic Reagent (*Scales Arbitrary*).



(For significance of I and II, see note under Figs. 1 and 2.)

For the purpose of considering alkalinity and solvent effects together it is convenient to sketch out the three-dimensional relief of which Figs. 1 and 2 are mutually perpendicular sections (with PZ_P in common). As much of the relief as is necessary to understand the behaviour of alcohol–water mixtures is shown in Fig. 3.

On this basis we can review the previously published literature more coherently than heretofore. The sequence which Taylor associated with the name of Segaller (to whose work reference is made later) was first obtained by Nef (*locc. cit.*). He used rather concentrated alkali and drier alcoholic solvents than most other investigators, often absolute alcoholic sodium ethoxide. Thus he was working near the PZ_P ordinate, and we can therefore understand his sequence prim. < sec. < tert. On the other hand Brussoff (*loc. cit.*), and probably also Bell and Clark (*loc. cit.*), were working in the middle region of Fig. 2, apparently a little to the right of the first intersection : the solvent in " concentrated alcoholic potash " would have to be regarded as wet ($2KOH = H_2O$) even if the reagent were made from dry alcohol and freshly fused potassium hydroxide; in practice extra water is always introduced with the alkali; and furthermore Brussoff states that he used wet alcohol. Therefore it is natural that these investigators should obtain the sequence prim. < sec. > tert. French and his collaborators (*J. Amer. Chem. Soc.*, 1934, **56**, 1346; 1935, **57**,

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* Variation in the same sense has been found in unpublished investigations by Cooper and Hughes on the hydrolysis (with elimination) of *tert.*-butyl bromide in acidic ethyl alcohol–water mixtures at 25° and in acidic acetone–water mixtures at 50°.

1574, 1576) used only water as solvent (two liquid phases being present), and a range of alkalinity corresponding to the right-hand section of the face $QR'Z_{R'}Z_Q$ of Fig. 3. Thus they obtained the order sec. > tert., and observed a rising proportion of olefin with increasing alkalinity in the case of the secondary compound. Woodburn and Whitmore (*ibid.*, 1934, **56**, 1394) also used water, but with a wide p_H range; however, they studied only tertiary halides. Their results are confirmatory as far as they go, though the method of experiment introduces disturbances (cf. Hughes and MacNulty, *loc. cit.*, p. 1288).

One other major factor has to be considered, *viz.*, the reagent. The above applies without modification only to strongly basic reagents, such as the hydroxide and ethoxide ions. For many alkyl halides these reagents give considerable proportions of olefin in the second-order reaction, and in the illustrative curves we have shown these proportions as higher than those characterising the corresponding first-order decompositions. Now in the second-order elimination the attack of the reagent is on hydrogen whilst in the second-order substitution it is on carbon, and therefore the olefin proportion for the second-order reaction will depend on the relative nucleophilic activities of the reagent towards hydrogen and towards carbon. But we know that these two properties do not run exactly parallel; that activity towards hydrogen is on the whole more sensitive to progressive constitutional change than activity towards carbon. To take an extreme case, the bromide ion has practically no nucleophilic activity for hydrogen (basicity), but retains a moderate activity for carbon (halogen exchange reactions). Therefore as we pass through a basicity series, such as OH^-, OPh^-, OAc^-, Br^-, we would expect the second-order olefin proportion to fall practically to zero, and at a certain intermediate stage (which cannot theoretically be specified) to fall below the proportion characteristic of the first-order reaction. The results of Segaller (*loc. cit.*), who used phenoxide ions in absolute alcohol, can be explained if we may infer that the anticipated inversion of the proportions characteristic of the two reaction orders has already occurred with the phenoxide ion. For, if we redraw Fig. 1, setting the right-hand levels below the left-hand levels, but keeping the right-hand levels in order amongst themselves (the change of reagent is unlikely to affect this), then both the intersections disappear (Fig. 4), and one sees that the sequence, tert. > sec., applies throughout the concentration range. If this is true for phenoxide ions, it surely will be for acetate ions; and thus we can explain why Mereshkowsky (*Annalen*, 1923, **431**, 231), using acetate ions, duplicated Segaller's finding.

We omit from this review detailed treatment of the formation of olefins from alkyl halides in the presence of silver salts, because the central point is very simple: the decomposition under these conditions is a heterogeneous analogue of the unimolecular homogeneous reaction, as has already been shown in connexion with the Walden inversion (Cowdrey, Hughes, Ingold, Masterman, and Scott, *loc. cit.*). We also omit the subject of olefin formation by the reaction of alkyl halides with amines, because the discussion, which would be necessary, of the factors influencing the formation and the decomposition of ammonium salts would inevitably be lengthy, being a double application of principles analogous to those already illustrated.

On the basis of the collation scheme given (into which our previous work fits perfectly) there is nothing of significance in the literature that cannot be understood. Also we are for the first time able rationally to choose the best condition for obtaining a desired result.

One can appreciate how, in the absence of such a scheme, the apparent inconsistencies of the literature have led to misconceptions. These have been repeatedly copied in papers and books, and persist in modern text-books of Organic Chemistry. As it is very desirable that these errors (which are not even mutually consistent) should be corrected in future editions of such books, we mention the most important (omitting references, which, however, all relate to the last 4 years): (1) That ethyl bromide and alcoholic potassium hydroxide give mainly ethylene (they give about 1%). (2) That the aqueous hydrolysis of halides to alcohols is greatly accelerated by alkalis (true only for primary and some secondary halides). (3) That the main substitution products given by alcoholic potassium hydroxide are alcohols. (4) That alcoholic potassium hydroxide does not give substitution products (Nef disproved both these statements 40 years ago by *isolating* 50—60% of alkyl ethyl ethers from the reaction products of several primary halides with alcoholic potassium hydroxide). (5) That aqueous potassium hydroxide does not give olefins. (6) That tendency to olefin production amongst alkyl halides is to be represented without qualification by the sequence prim. < sec. < tert. (disproved by Brussoff in 1900). (7) That tendency to olefin elimination from the same alkyl group follows the series chloride < bromide < iodide (generally true only for bimolecular reactions; whilst for unimolecular reactions the proportions of olefin are in first approximation the same, the small observed differences tending on the whole in the opposite direction).

We have seen that the representation of the whole field of phenomena depends on our being able to construct curves such as those shown in Fig. 1. Disregarding salt effects, one can completely construct such curves if one knows the four rates S_N1, S_N2, E1, E2. Now it would be a prohibitively lengthy task to determine all these rate constants individually, at close spacing, and over a wide range of all the possible variables; but we have shown in many papers since 1933 how, in the case of the first two rates, S_N1 and S_N2, theory can aid us by enabling qualitative inferences to be made from a strictly limited number of suitable observations. We know in fair detail how the rates S_N1 and S_N2 must vary with constitutional, reagent and solvent changes, so that series can be often filled in when only a few members have been studied. Thus our object now must be to bring the other two rates, E1 and E2, into a like position, the experimental task being to produce a relatively small number of suitable observations, the usefulness of which theory can extend.

One item of this programme can be contributed now, by pointing to the effect of α-substitution in the alkyl group on the rates of the constituent reactions. Table II contains the data. It illustrates the necessity for such kinetic analysis (commenced by Shapiro and two of us in 1936) as a preliminary to the rational solution of the problem of elimination reactions. It also illustrates the uselessness of the previous literature for this purpose. For instance, if we were to compare total bimolecular rates for ethyl and *tert.*-butyl halides under strongly alkaline conditions, we should be comparing an almost pure substitution with an almost pure elimination; whilst, if we were to compare rates regardless of kinetic order (as has often been done) for the same two halides but under conditions of dilute alkalinity, we should be comparing a bimolecular substitution with a mixture of unimolecular substitution and unimolecular elimination.

TABLE II.

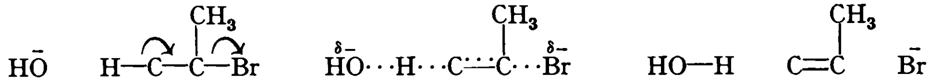
Rates of the Four Reactions constituting the Hydrolysis of Alkyl Bromides in Dry Ethyl Alcohol at 55°.

Key: See Table I, p. 903. Values relating to concentrated alkaline solutions (N and over) are given in parentheses.

Bromide.	$S_N1(10^5k_1)$.	$S_N2(10^4k_2)$.		$E1(10^5k_1)$.	$E2(10^4k_2)$.	
Ethyl	—	20	(12)	—	0·20	(0·12)
*iso*Propyl	≯0·017	0·50	(0·21)	≯0·001	1·5	(0·75)
tert.-Butyl	14	—	(≯0·2)	5·5	—	(∼5)
α-Phenylethyl	19	—	(∼10)	≯0·5	—	(∼5)
β-Phenylethyl	—	∼3	(—)	—	60	(—)

The values for reactions S_N1 and S_N2 are included in the table for the sake of completeness: they merely confirm what was previously known and explained (Hughes, Ingold, and Patel, J., 1933, 530), *viz.*, that an α-alphyl substituent speeds the former reaction and in general retards the latter, whilst an α-phenyl substituent also accelerates the former reaction but has little effect on the latter. However, the figures for reactions E1 and E2 bring out a new set of relationships which can be summarised in the statement that an α-alphyl substituent, and, more effectively, an α-phenyl substituent, speed both reactions, especially E1.

The explanation of the large effects on reaction E1 is simple: they are mainly due to facilitation of the rate-controlling ionisation, just as for reaction S_N1. The smaller accelerating effect of α-alphyl substituents on reaction E2 is connected, in our view, with the circumstance that alphyl groups always release electrons to unsaturated (double or triple bonded or aromatic) carbon. Baker and Nathan's interpretation of this, on the basis of an assumed quasi-conjugation involving CH-bond electrons, $\mathrm{H{-}\overset{\curvearrowright}{C}{-}\overset{\curvearrowright}{C}{=}C}$ (J., 1935, 1844), is considered partly true (this vol., p. 949), and we shall use the theory illustratively, because it represents the most conservative extension of our ordinary conceptions of mesomeric stabilisation, though the theory's emphasis on the part played by alkyl hydrogen is unnecessary for our purpose. Anything analogous to conjugation always stabilises a system. Considering, first, the initial and the final state of reaction E2, one can see that the energy level of the latter will be depressed more than that of the former by the " conjugated " α-alphyl substituent :



Initial state Transition state Final state

But if this is true, the energy level of the transition state must also be lowered more than that of the initial state, because in the transition state some unsaturation has already developed between the α- and β-carbon atoms. Therefore facilitation of the reaction is to be expected. Obviously a properly conjugated α-phenyl substituent should exhibit the effects considerably more powerfully than an α-methyl substituent. As we shall be dealing with the effect of β-substituents on the rates of reactions E1 and E2 in a later paper, we reserve comment on the data for β-phenylethyl bromide.

As stated, our point of view concerning the influence of alkyl groups on unsaturated systems is much more general than is expressed in the above illustration. The basic reason why exchange degeneracy and all other forms of resonance stabilise a system is that they allow greater liberty of motion to the electrons, and thus reduce the electronic zero-point energy in accordance with the uncertainty principle. Thus when two atoms of identical nuclear charge, one atom saturated and the other unsaturated, are linked, as in toluene, the electrons always tend to concentrate in the direction of the unsaturated atom, because this means that, on the average, more electrons have freer motions, and that, by their obtaining freer motions, the system will be stabilised. This is not mesomerism, not even Baker and Nathan's form of it; but it can be considered to involve resonance (cf. *Nature*, 1938, **141**, 314).* The applications are wide-spread, but we give just two illustrations, one in the field of physical properties and the other in that of chemical reactions. First, the theory explains why unsymmetrical unsaturated hydrocarbons have dipole moments whilst saturated hydrocarbons do not; the theory definitely requires a dipole moment in *tert.*-butylbenzene qualitatively similar to that in toluene, and in the direction which has been established for toluene. Secondly, it accounts for Linstead's general result (cf. *Ann. Reports*, 1927, **24**, 111) that, in the tautomerism of unsaturated acids and ketones, the introduction of an alkyl group at either end of the " three-carbon system " shifts the equilibrium in the direction which places the unsaturation next to the alkyl group; equilibrium depends, of course, directly on the energy difference between the interconvertible systems.†

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* We use the term " resonance " in the general (and original) sense of Heisenberg, and reserve the term " mesomerism " for the narrower phenomenon, *viz.*, that extension of valency theory which many authors call " resonance," and Pauling, with greater precision, calls " resonance among several valence bond structures." Of course, the use in this sense of the unqualified term " resonance " is not incorrect; it is merely not specific.

† In a general review of the theory of organic reactions, it was stated : " It has been empirically observed that alkyl groups behave as if they repel electrons when attached to unsaturated [carbon] centres, and it is probable that this relationship between saturated and unsaturated hydrocarbon radicals in combination is quite general. The theory of these effects is at present obscure " (Ingold, *Chem. Rev.*, 1934, **15**, 239). This confession of ignorance is now unnecessary : the above explanation of the effect as a form of resonance completes the theory of 1934. Furthermore, a contemporaneous paper on the special theory of aromatic free radicals concluded with the remark : " The feeble stabilising action [on such radicals] of alkyl groups is not really intelligible on any present theory, but seems to suggest the existence of factors of resonance dependent on inductive electron displacement " (Ingold, *Trans. Faraday Soc.*, 1934, **30**, 52). This reserved statement also can now be superseded. The

The effect of passing to more highly solvating solvents on the absolute rate of reactions E1 and E2 has already been illustrated in the papers of Hughes, Ingold, and Shapiro, and of Hughes and MacNulty (*loc. cit.*) : the rate E1 rises rapidly, and the rate E2 falls slowly. Both results are in conformity with the solvent theory of Hughes and Ingold (*loc. cit.*), which can be applied to elimination just as easily as to substitution. The effect on reaction E1 is essentially due to the solvent influence on the rate-controlling ionisation, in the transition state of which new charges are created. In reaction E2, on the other hand, a pre-existing charge is distributed in the transition state; wherefore solvation must reduce the energy of this state more than it reduces that of the initial state : thus it impedes reaction. Effects due to charge distribution in the transition state are always smaller than those due to the creation or destruction of charges.

Supplementary Note.—We must explain why we did not further extend the revision of Taylor's data on this subject. The main reason is that in none of the other examples of major interest could we carry out satisfactory experiments. For instance, Taylor records proportions of olefin eliminated from alkyl halides in the gas phase at 25° and 55°. Now Brearly, Kistiakowsky, and Stauffer (*J. Amer. Chem. Soc.*, 1936, **58**, 43) have studied this decomposition for *tert.*-butyl and *tert.*-amyl chlorides, but at much higher temperatures, and it is clear from their results that similar experiments started many years ago at either of Taylor's temperatures would not yet have produced a detectable quantity of olefin. An extension of this work in the gas phase is now being made by Hughes and Wassermann, whose results emphasise the difficulty : and this is not an isolated example. With regard to Taylor's experiments on olefin production from the polyhalogeno-ethanes (paper 1), it is fortunate that a careful prior investigation of the same subject had (apparently unknown to Taylor) been published by Olivier and Weber (*Rec. Trav. chim.*, 1934, **53**, 1087). A discussion of their results would be too long for inclusion here, but we may say that they are in full agreement with our own experiments and interpretation.

EXPERIMENTAL.

Careful attention was paid to the purification of the halides and the purification and complete drying of the ethyl alcohol.

Kinetic Measurements.—In most experiments the method of sealed bulbs was used, portions of the reaction solution taken from the standard measuring flask being sealed up, with cooling where necessary, heated in the thermostat, and then broken under a cold solvent to stop the reaction. For titration with acid the bulb was broken under absolute alcohol, for titration with alkali under acetone, and for Volhard estimation under aqueous nitric acid covered with a large layer of ether, which was used to extract the organic material. Lacmoid was used as indicator for the acid–alkali titrations. Corrections for thermal expansion between the temperatures of the standard flask and the thermostat were applied to second-order rate constants.

Olefin Estimations : Aspiration Method.—Owing to the length of this process, it was used only for the analysis of the products of completed reaction, not in the intermediate stages of a run. Usually the whole of the reacted solution was taken for this purpose, an equal amount of the original reaction medium being employed for the blank estimation. The method is described by Hughes, Ingold, and Shapiro (*loc. cit.*), except for the improvement (which is not so important as in the extraction method) of adding hydrogen bromide to the chloroformic bromine solution.

Olefin Estimations : Extraction Method.—At certain stages of reaction, or in some cases after its conclusion, two bulbs were simultaneously removed from the thermostat, one for the estimation of the extent of reaction as described in the paragraph headed " Kinetic Measurements," and the other for olefin analysis by the extraction method. The latter was cooled to −80°, and

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stabilising effect is indeed a " factor of resonance," and the involved electron displacement is that which *was* classified as " inductive " before its cause was understood; we now recognise, however, that it has not the simple electrostatic origin of the inductive effect proper, but is a peculiar manifestation of resonance, which becomes especially noticeable in the absence of any considerable electrostatic effect. More specifically, alkyl groups enhance radical stability by admitting additional electron density to that part of the molecule where (owing particularly now to the free radical centre) the spatial freedom of the electrons is greater, and their velocities (and energies) consequently smaller. Thus the more specialised theory of free radicals is also now completed. This matter is topical in that Dr. S. T. Bowden (private communication) has recently obtained new evidence concerning the stabilising influence of alkyl groups on triarylmethyl radicals.

introduced into a vessel, containing chloroform (200 c.c.) and a considerable excess of dilute sulphuric acid (25 c.c.), which was closed and cooled until the aqueous layer was partly frozen. At this stage the bulb was broken by shaking, and the chloroform layer, as well as a further well-cooled chloroform extract of the aqueous layer, was run on to pure calcium chloride in a closed flask, shaken with this reagent, and then allowed to react for 30 minutes with a chloroform solution of bromine containing hydrogen bromide. The reaction was initially very rapid, and the quantity of bromine used was so adjusted that the excess during most of the 30-minute period (*i.e.*, after the initial rapid absorption) was small. At the end of the period the excess of bromine was estimated in the usual manner. The precaution of minimising the excess of bromine is particularly important in order to avoid error due to bromine substitution in the estimation of *iso*butylene and styrene. A pair of bulbs were similarly treated after only a few minutes in the thermostat with corresponding precautions as to minimisation of the excess of bromine. These " initial " estimations controlled total reaction, and the development of olefin, during the warming-up period, and gave a good time-zero, identical for the measurement of total reaction and of olefin. Volatility errors remained, and these were estimated, after the method had been well standardised, by making solutions in chloroform, such that they would subsequently be comparable in concentration with those which had been estimated, of prepared or commercial samples of ethylene, propylene, or *iso*butylene, estimating the olefin in one portion directly, and in another after running into a mixture of ethyl alcohol (20 c.c.), chloroform (200 c.c.) and dilute sulphuric acid (25 c.c.), and putting the whole through the process described above. The volatility losses were fairly uniform for each olefin, and the values obtained were used to correct the original analytical figures. For *iso*butylene the losses were 6%, for propylene 16%, and for ethylene about 55% of the quantities required to be estimated. The reason why our results for ethylene agreed sufficiently well with those obtained by the aspiration method, in spite of the enormous volatility correction, is mentioned earlier.

Results.—These are summarised in Table I, except for those reactions of mixed order for which no constants can be quoted. In this section we illustrate these and some other experiments which involve some special difficulty or complexity.

The following is an example of a run which was so rapid in relation to the time required for manipulation that the results had to be smoothed graphically before constants could be calculated: Reaction of α-phenylethyl bromide in strongly alkaline solution: $[\text{bromide}]_{t=0} =$ 0·03248M, $[\text{NaOEt}]_{t=0} = 2{\cdot}447$N, $[\text{bromide}]_t$ expressed in c.c. of 0·1015N-thiocyanate per 10 c.c. sample (k_2 in sec.$^{-1}$g.-mol.$^{-1}$ l.):

t (mins.)	0·0	1·0	2·0	3·0	4·0	5·0	6·0	7·0	8·0	9·0	15	30
[Bromide] (obs.)	3·20	2·20	1·85	—	1·50	—	—	0·66	—	—	0·10	0·02
[Bromide] (graph)	3·20	2·26	1·88	1·58	1·28	1·02	0·90	0·35	0·51	0·40	—	0·00
10^5k_2	—	18·4	16·3	15·9	15·9	14·7	15·8	16·0	16·1	15·8	—	—

The result for 10^5k_2 is quoted in Table I as " *ca.* 16," because it is certainly not as accurate as the above figures make it appear. (Other results obtained by the smoothing method are similarly indicated in Table I.) The olefin was estimated by the extraction method in the product of the completed reaction, the " initial " reading being replaced in this case by a blank experiment with the medium on account of the rapidity of the reaction. Expressing bromine and olefin in equivalent c.c. of 0·05066N-thiosulphate, the results were as follows: Residual bromine (initial), 24·2, 24·3, 23·7. Residual bromine (final), 6·5, 6·7, 6·8, 6·8, 6·6 c.c. Olefin, 17·6, 17·4, 17·3, 17·3, 17·5. Mean, 17·4 c.c. = 34·1%.

We found it difficult to be certain whether any olefin is formed in the acid alcoholysis of α-phenylethyl bromide and therefore record the figures. [Bromide] is expressed in equivalent c.c. of 0·0500N-alkali per 10 c.c. sample. $[\text{Bromide}]_{t=0}$ was obtained by weighing, and not from an " infinity " titration, since in long experiments the hydrogen bromide becomes involved in reaction with the medium. Bromine and [olefin] are in equivalent c.c. of 0·05066N-thiosulphate (k_1 is in sec.$^{-1}$):

t (mins.)	0·0	11·0	18·0	28	40	56	76	100	∞
[Bromide]	15·89	14·01	12·89	11·55	10·10	8·29	6·82	5·35	0·00
10^5k_1	—	19·1	19·4	19·1	18·9	19·4	18·4	18·2	—
Br_2	9·93, 9·87 9,82, 9·90	—	—	—	9·60, 9·77 9·71	—	9·58 9·72	—	9·85, 9·65 9·70
Mean Br_2	9·88	—	—	—	9·69	—	9·65	—	9·73
[Olefin]	0·00	—	—	—	0·19	—	0·23	—	0·15

The final olefin value, if real, corresponds to 0·5%.

Cooper, Hughes, and Ingold showed (J., 1937, 1280) that *iso*butylene undergoes addition reactions in acidic aqueous alcohol, so that, in order to obtain the proportion formed from a *tert.*-butyl halide, it is necessary to trace the development of olefin from the beginning and discard the results when the apparent proportion begins to fall. It appears that a similar phenomenon occurs with anhydrous alcohol. The procedure is illustrated in the following run with *tert.*-butyl bromide. Each olefin figure is a mean of three concordant estimations which are omitted in order to condense the table. The solution being initially neutral, $[\mathrm{Bu^{\gamma}Br}]_{t=0}$ was obtained by weighing, and not from an " infinity " titre, because in prolonged runs the hydrogen bromide interacts with the solvent. $[\mathrm{Bu^{\gamma}Br}]$ is expressed in c.c. of 0·0482N-alkali per 10 c.c. sample (k_1 is in sec.$^{-1}$) :

t (mins.)	0	1	5	10	12	19	32	47	79
[Bromide]	10·09	9·98	9·52	—	8·70	8·09	6·90	5·75	—
10^5k_1	—	(1·80)	1·93	—	2·06	1·94	1·98	1·99	—
% Olefin	—	—	—	28·7	—	27·0	—	22·6	18·7

The last two readings represent the beginning of the portion of the run which is to be disregarded.

We were afraid that in the estimation of ethylene by the aspiration method this olefin might fail to be completely absorbed in the bromine solution, because of the greater volatility and lower reactivity of this olefin than of its homologues. We therefore added a third bromine trap to the arrangement described by Hughes, Ingold, and Shapiro. That this precaution is adequate is shown in the following example of an ethylene estimation. The ethylene formed during reaction in a solution (220 c.c.) initially 0·820M with respect to ethyl bromide and 2·60N with respect to sodium ethoxide was caught, after alcohol vapour had been trapped in a strongly cooled empty bulb, in three bromine solutions whose initial and final volumes and concentrations, as measured by titration of 5 c.c. samples with 0·0879N-thiosulphate, were as shown below. Bromine vapour carried from the traps was caught in potassium iodide and titrated.

	Initial vol.	Final vol.	Initial titre.	Final titre.	KI titre.	Loss of $\mathrm{Br_2}$.
Br-trap (1)	25·0 c.c.	23·5 c.c.	11·59 c.c.	3·36 c.c.	5·88 c.c.	49·5 c.c.
Br-trap (2)	25·0	25·5	11·59	9·13		
Br-trap (3)	35·0	35·0	11·59	11·02		

The loss of bromine corresponds to 0·00217 g.-mol. of ethylene. A Volhard titration on the residual alcoholic solution gave bromide ion equivalent to 0·749N, *i.e.*, 0·166 g.-mol.; wherefore the proportion of ethylene is 1·3%.

For mixed-order reactions containing a small proportion of a first-order component of known rate constant, Hughes, Ingold, and Shapiro's method of calculation can be used to find the second-order constant; but this procedure is not possible in the reverse case if the constant of the minor second-order reaction can only be obtained directly from experiments subject to salt effects; and it is not accurate if the two reactions are present in comparable proportions. Owing to these difficulties two rate runs of the last kind, applying to α-phenylethyl bromide, for which also the determined second-order constants are subject to a salt effect, are given in detail :

(1) $[\text{Bromide}]_{t=0} = 0{\cdot}0489\text{M}$, $[\text{NaOEt}]_{t=0} = 0{\cdot}07185\text{N}$. [Bromide] is expressed in equivalent c.c. of 0·0500N-acid per 10 c.c. sample.

t (mins.)	0·0	7·0	16·0	24	33	44	55	68	90	120
[Bromide]	9·78	8·21	6·69	5·60	4·86	4·02	3·12	2·50	1·64	1·00

(2) $[\text{Bromide}]_{t=0} = 0{\cdot}0614\text{M}$, $[\text{NaOEt}]_{t=0} = 0{\cdot}1364\text{N}$. [Bromide] is expressed in equivalent c.c. of 0·05995N-acid per 10 c.c. sample.

t (mins.)	0·0	5·0	11·0	16·0	23	32	42	55	75	110
[Bromide]	22·75	21·00	19·65	18·30	17·10	16·05	15·10	14·20	13·15	12·38

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