CCCXXIII.—*Influence of Substituents on the Additive Reactivity of Ethylene Derivatives. Part I. Preliminary Observations on the Addition of Bromine in Solution.*

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SINCE the original formulation of an orientation theory of conjugative additions (Burton and Ingold, J., 1928, 1894; compare J., 1929, 2012; Ingold, *Chem. and Ind.*, 1928, **47**, 269) our knowledge of the subject has been enriched by so considerable a body of observations, the results of which were or could have been foreseen by means of the theory, that its main outlines may be accepted as established. On the other hand, there are many important questions connected with addition which the theory is not yet in a sufficiently developed state to answer, mainly owing to lack of knowledge concerning the relative effects of different substituents on the reactivity towards addenda of an attached unsaturated linking. The position is to this extent comparable with that in which the electronic theories of tautomerism and of aromatic substitution found themselves in 1927, and analogy with the subsequent development of these topics suggests that a further advance in the theory of addition will require certain basic data concerning the effect of substituents on additive reactivity.

It might be thought that analogy with these subjects, tautomerism and substitution, the theoretical aspects of which are at present more advanced, would furnish the necessary information without the need for special experiments; and to a limited extent this is true. We can be sure, for instance, that the majority of those groups which activate anionotropic systems and promote aromatic hydrogen-replacement by the ordinary substituting agents will increase the additivity of an ethylene towards reagents such as halogens, hydrogen halides, and nitrogen peroxide the more active ions of which are positive, and will decrease reactivity to such addenda as hydrogen, hydrogen cyanide, nitromethane, and ethyl malonate whose more active ions are negative; and, similarly, that most of those substituents which facilitate prototropy and aromatic halogen-replacement by basic reagents will de-activate the ethylene nucleus towards the former group of reagents and activate it towards the latter. There are, however, strongly restrictive limits to the validity of such superficial reasoning; for the fundamental theory of the polarisation and polarisability of molecules shows that a series of substituents arranged according to their behaviour in connexion with any one of the three groups of phenomena here compared (tautomerism, substitution, and addition) cannot in general be applied to either of the others. The reason for this is that whilst the inductive effect (I) of a group is mainly a time-invariable property of the group, depending only to a relatively small extent on the environment and on the reaction, the time-variable electromeric effect (T) depends not only on the group but also, and equally essentially, on the reaction. Hence it is only in the rather few cases into which the T-effect cannot enter that groups may be expected to maintain a substantially identical inter-relationship with regard to their effects on the three types of reaction considered. An example will illustrate the matter.

The Me-substituent (effect $+ I$ only *) facilitates anionotropic change (Burton and Ingold, *loc. cit.*); it also increases the rate of aromatic nuclear nitration (Ingold and Shaw, J., 1927, 2918; Ingold, Lapworth, Rothstein, and Ward, this vol., p. 1959); both effects are simple in origin and correspond with the permanent electron-repulsion of the group. On the other hand, the Cl-substituent (effect $- I + T$) strongly promotes anionotropic change (*e.g.*, in p-$Cl{\cdot}C_6H_4{\cdot}CHX{\cdot}CH{:}CH_2$, where X is a mobile group such as ·OH; Burton and Ingold, *loc. cit.*) but depresses reactivity in aromatic nitration (*e.g.*, the p-nitration of $Cl{\cdot}C_6H_5$; Ingold and Shaw, *loc. cit.*); the first effect corresponds to electron-release and the second to electron-attraction. The difference is clearly traceable to the difference of the electrical mechanisms of the two reactions. On the one hand, anionotropic change involves the complete ionic dissociation of X as X⊖ (Burton, J., 1928, 1650), and hence the electron-demand at the seat of reaction is maximal; its measure is the *integral* positive charge which is left behind when X dissociates; the electron-release symbolised by $+ T$ is a polarisability effect, and increases in proportion to the electron-demand; accordingly, in this reaction, the electrometric electron-release at the moment of reaction is also maximal, and is strong enough to outweigh the prior handicap created by the contrary permanent polarisation, $- I$, of chlorine; hence the total effect, $- I + T$, corresponds to reaction-facilitation. On the other hand, in aromatic nitration, the electron-displacements transmitted through the nucleus are required only for the orientation of the reagent (that is, its molecular union by *fractional* electrovalencies), the subsequent process of substitution proceeding by local electrical interchange without the need for more extensive electron displacements in the aromatic nucleus (Ingold and Ingold, J., 1926, 1313); the electron-demand made on the

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* As the modes of action of the inductive and direct effects do not require to be distinguished in these examples, the customary simplification of including both under the designation of the former is adopted.

orienting substituent is therefore comparatively small, and the consequent electromeric effect of the group correspondingly so; hence, although the + *T*-effect is a significant factor in the nitration of chlorobenzene, as is shown by its *op*-orientation, it is, nevertheless, insufficiently powerful to overcome the de-activating influence of the permanent polarisation, — *I*, of the chlorine atom, and the total effect, — *I* + *T*, in this case represents reaction-inhibition.

Generalising from this example, it will be evident that the influence of any given group exhibiting the + *T*-effect on different reactions requiring electron-accession must depend on the electron-requirements of the several reactions; and that, accordingly, a comparison of the effects of such a group on such reactions would enable these reactions to be placed in order with regard to the intensities of their electron-demand. An analogous statement applies to groups exhibiting the — *T*-effect in relation to reactions requiring electron-recession.

The above-mentioned difficulty about the theoretical interpretation of additive reactions may therefore be expressed by stating that, because, aside from *ad hoc* data, it is not possible accurately to gauge the electrical requirements of additions in comparison with those of other reactions, it is also not possible theoretically to deduce a complete sequence representing group-effects on additions by interpolation from known group-series relating to other reactions. *A priori* considerations do indeed give some assistance, but only of a general character. When $\overset{\curvearrowleft}{X}{—}Y$ adds to $R{—}C_{\alpha}\overset{\curvearrowright}{=}C_{\beta}$, the process being initiated by the orientation of $(\delta +)Y$ to $(\delta -)C_{\beta}$ (additions of Br_2, HBr, etc.),* the electron-demand made on R might have any value between a very small one and that which corresponds to the development of a free integral charge on C_{α}; the actual value in a given case will depend on that degree of electrostriction between X and C_{α} which is necessary to determine the consolidation of the initial union between Y and C_{β}, or, in other words, on the degree to which the second stage of addition " backs up " and overlaps the first.† This,

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* Addition initiated by the attack of $(\delta -)$Hal. would also be theoretically possible, provided that the intrinsically small reactivity of negative halogen could be overcome by the attachment of a sufficiently powerful electron-sink to the olefinic residue; it is not yet known whether any of the available groups (·CHO, ·COR, $\cdot NO_2$) are in fact competent to cause this anticipated reversal of normal reactivity; the practical criterion which would reveal such an occurrence would be that the rate of addition would pass through a minimum as the efficacy of the electron-sink was progressively increased.

† Somewhat analogously, in the subdivision of the first stage (addition of $H\ominus$) in the reduction of unsaturated substances by metals dissolving in aqueous or alcoholic media, Burton and Ingold (J., 1929, 2022) assume that the degree of electrostriction of protons (or of metallic kations) necessary to determine

in turn, depends, *inter alia*, on the degree of prior polarisation of X—Y, and the case of maximal electron-demand will arise in the addition of previously formed and dissociated ions. In this extreme case the influence of substituents should correspond with their effect in anionotropy. There is abundant evidence, however, that in the additions of halogens and hydrogen halides the polarised molecule is the reagent,* and the electron-demand created by these additions must therefore be comparatively small. Accordingly, in studying the effect of substituents on such additions we may expect to find closer analogies with aromatic substitution than with anionotropy—a conclusion which has been confirmed experimentally. Analogous general anticipations are, of course, possible for additions initiated by anionic attack (additions of HCN, HSPh, etc.). Of the two illustrations here cited, the former exemplifies the addition of preformed ions and the latter is probably (at least in certain cases) a reaction of the molecule; the difference should create predictable differences in the effects of substituents.

It seems hardly possible at present to carry the theory of group-influence beyond the stage represented by the very general conclusions illustrated, which accordingly must form the point of departure of investigations designed to yield greater precision of view.

This first contribution deals with the addition of bromine to substituted ethylenes in an inert solvent. The effect of substituents on the reactivity of unsaturated compounds towards bromine has been the subject of a number of previous observations, but it is impossible to correlate much of the data owing to the incursion of uncontrolled catalytic and photochemical influences. Bauer, however, has provided several qualitative comparisons (*Ber.*, 1904, **37**, 3317; 1907, **40**, 918), and the results recorded by Reiche, van Wyck, and Waele (*Helv. Chim. Acta*, 1921, **4**, 242) may be taken as roughly comparable amongst themselves. The former worker concluded

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the actual transference of electrons from the metal to the unsaturated substance will depend, *inter alia*, on the electron-pressure of the metal. This, indeed, is inherent in the known facts regarding the hydrion potentials necessary to determine reduction of a given unsaturated substance with different metals.

* The recognition of the molecular character of addenda is often taken for granted in order to simplify the expression of conclusions about which " ion " (*i.e.*, structural, combined ion, not free ion) of an addendum initiates attack. This applies, for instance, to the discussion on p. 2354, and to some earlier remarks (*Ann. Reports*, 1928, **45**, 147) dealing with the modes of addition of hydrogen bromide and thiophenol to styrene. Analogously, in the subdivision of the first stage (addition of H$\ominus$) of reduction (preceding footnote) the statement (Burton and Ingold) that the kationic component becomes " reversibly attached " to the organic molecule envisages attachment by all degrees of electrostriction.

that alkyl, phenyl, bromine, carboxy-, and cyano-substituents de-activate the ethenoid nucleus, whereas the latter investigators obtained small and ambiguous effects for alkyl groups, but supported Bauer's deduction regarding the de-activating influence of phenyl and carboxyl substituents. Reference should also be made to the dynamical investigations of Herz and Mylius (*Ber.*, 1906, **39**, 3816), Hofmann and Kirmreuther (*Ber.*, 1909, **42**, 4481), Sudborough and Thomas (J., 1910, **97**, 715, 2450), Williams and James (J., 1928, 343), and Davis (*J. Amer. Chem. Soc.*, 1928, **50**, 2769); and, in addition to such special observations, general preparative experience is also a possible source of qualitative information of the kind required. The common difficulty, however, about the interpretation of all such recorded results * is that, in the available comparisons, *two* or more groups are simultaneously attached to an ethenoid centre; and it can be foreseen on theoretical grounds, what is also demonstrable in fact, namely, that the influences of the separate groups may not compound simply but may interact in a way which invalidates analysis. For example, resultant de-activation can arise either from two de-activating groups, or from one de-activating and one activating group, or even from two activating groups; so that the observation of de-activation due to two substituents does not necessarily show that either would act in this sense if present singly. Even pairs of identical groups are not (except in certain special cases) free from the possibility of inverted mutual action. Two illustrations, both involving very well-known results, will typify the situation. First, the difficulty which attends the addition of bromine to tetrabromoethylene might be regarded as confirming Bauer's and Reiche, van Wyck, and Waele's deduction that the bromine substituent *per se* de-activates the ethylenic linking; it will be shown later, however, that this inference cannot justly be derived either from the fact mentioned above or from any of those adduced in the investigations cited; it will appear, nevertheless, that the conclusion itself is correct. Secondly, the difficulty attending the addition of bromine to tetraphenylethylene might be considered an apt demonstration of the inference derived both by Bauer and by Reiche, van Wyck, and Waele, namely, that the phenyl group *per se* de-activates the ethenoid nucleus; it will be shown, however, that this deduction is also a *non sequitur*, all the arguments which have led to it having contained the same fallacy; it will appear, furthermore, that, despite the unanimity of previous opinion, the conclusion itself requires inversion. It may be added that, according to our results and those of Davis (and consistently with theory), the methyl substituent

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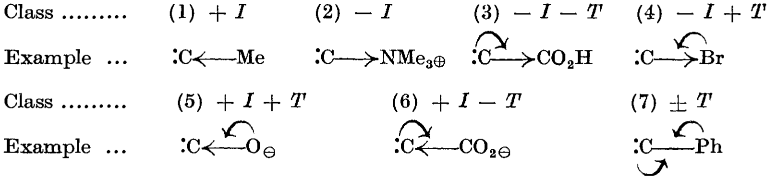
* Except Davis's (see later), which were not available when these experiments were commenced.

activates the ethenoid centre, contrary or equivocal previous conclusions being similarly traceable to the complex mutual actions of the accumulated substituents.

In the experiments described hereunder we have avoided these difficulties by a suitable choice of examples, and have minimised the danger of disturbances due to difficultly controllable catalytic and photochemical influences by employing the competitive method. Ethylene itself as the standard, together with the substituted ethylene under investigation, were allowed to compete in the same solution for a limited quantity of bromine; the proportions of the bromides were determined and the speed of addition of the substituted ethylene relatively to that of ethylene itself was deduced therefrom. Alternatively, an ethylene derivative which had already been compared with ethylene in this way was used as a subsidiary standard for competition with a second ethylene derivative the reaction-rate of which was too diverse from that of ethylene itself to permit of satisfactory comparison by the direct method. The velocities thus calculated, which are relative to that of ethylene as unity, may be termed "reduced velocities," and further consideration to the principles underlying their derivation is given later (p. 2365).

At this preliminary stage of the enquiry no attempt has been made to press the method to the limits of possible accuracy, although this may later become desirable in certain special cases. The present object is rather to obtain a general survey of the phenomena, and, indeed, further work in the same direction must necessarily precede the selection of profitable examples for the establishment of standard values.

The classes of substituents for which distinctive effects on speeds of addition are expected to arise either when the substituent considered is the only one attached to the ethylenic centre, or when it is present in conjunction with other like or unlike groups, may be symbolised as follows.*



Class	(1) $+I$	(2) $-I$	(3) $-I-T$	(4) $-I+T$
Example ...	$\colon C \leftarrow Me$	$\colon C \rightarrow NMe_3^{\oplus}$	$\colon C \rightarrow CO_2H$	$\colon C \rightarrow Br$
Class	(5) $+I+T$	(6) $+I-T$	(7) $\pm T$	
Example ...	$\colon C \leftarrow O^{\ominus}$	$\colon C \leftarrow CO_2^{\ominus}$	$\colon C - Ph$	

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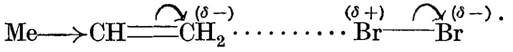
* In a fuller classification, case (7) would be sub-divided according to the sign of the inductive effect associated with the ambiguous electromeric mechanism. Substituted aryl groups could be found to illustrate the subdivision.

For obvious reasons all these classes are not equally important in connexion with bromine-addition, and only some are illustrated in the sequel.

The electrical theory relating to the methyl substituent (class 1) is simple in its essentials : the group repels electrons ($+I$) and should therefore facilitate the addition of a reagent such as bromine the reactive ion of which is positive ; and the attack should be oriented mainly at the ethenoid carbon atom more remote from the substituent :



$$\mathrm{Me}\longrightarrow\mathrm{CH}\overset{\curvearrowright}{=\!=}\overset{(\delta-)}{\mathrm{CH}_2}\cdots\cdots\cdots\overset{(\delta+)}{\mathrm{Br}}\overset{\curvearrowright}{-\!-}\overset{(\delta-)}{\mathrm{Br}}\,.$$

Moreover the methyl group belongs to the limited category of substituents (classes 1 and 2) which, owing to the absence of any mechanism for electromeric change, cannot of themselves give rise to an inverted mutual effect; accordingly, the accumulation of methyl groups should (in the absence of substituents outside the named category) produce a progressive increase in the speed of addition.

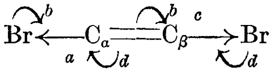
The observational data, which may be symbolised as follows (r.v. = reduced velocity), are in accord with these expectations : $H_2C{:}CH_2$ (r.v. = 1·0) $Me_2C{:}CH_2$ (r.v. = 5·5) $Me_2C{:}CMe_2$ (r.v. = 14·0). They also emphasise a point which is implicit in the preceding statement of the theory, namely, that it is not dissymetric substitution and the consequent electrical dissymmetry of the double linking which constitutes the primary facilitating influence of substitution; for the electron-displacements of the addition process must be substantially confined to the ethenoid centre and hence it is the polarisability of the corresponding electrons, not their state of polarisation, which is the important factor; the polarisability will obviously be greater the more the positive nuclear field is overlaid by the electron-screen which the electron-repelling methyl groups create. Thus the tetramethyl compound, although it is structurally and electrically symmetrical, reacts more rapidly than the unsymmetrical dimethyl compound, the double linking of which must be definitely polar.

We have not yet made quantitative measurements on any example belonging to class 2 ($-I$), but, with suitable inversions, the theory follows closely along the lines illustrated for class 1. The strong de-activating effect of the group $\cdot NR_3^+$ is qualitatively indicated by Ingold and Rothstein's inability to prepare dibromides of unsaturated salts of the type $\{R_3N\cdot CH_2\cdot CH{:}CH\cdot NR_3\}^{\cdot\cdot}X'_2$ (this vol., p. 1666).

Some possible abnormalities associated with class 3 have already been mentioned (p. 2356, footnote), but these cannot apply to the carboxyl group, the $-T$-effect of which is weak, although other complexities might enter were this group present along with others capable of electromeric effects. However, the uniform sign of the polar components ($-I-T$) allows unequivocal theoretical prediction to this extent, namely, that the carboxyl group, either alone, or in the presence of a substituent of class 1 or 2, should invariably de-activate. This has been illustrated by a comparison of acrylic acid with ethylene (Found: r.v. for acrylic acid $< 0{\cdot}03$) and of crotonic acid with propylene (Found: speed-ratio $= 0{\cdot}13 : 1$).

Substituents of class 4 ($-I+T$) present a more complex problem, for, to take the Br-group as example, it cannot be decided *a priori* whether the activating $+T$-process will fail to compensate, or will over-compensate, the de-activating $-I$-effect. Comparison of vinyl bromide with ethylene has, however, shown that the bromine substituent definitely deactivates (r.v. $< 0{\cdot}04$), this behaviour resembling that which is observed in aromatic substitution (Ingold and Shaw, *loc. cit.*) but contrasting with that which obtains in anionotropy.* The closer analogy between halogen-additions and aromatic substitution than between halogen-additions and anionotropy was expected (p. 2357) from a consideration of the conditions controlling the excitation of electromeric effects.

From this result it can be deduced unequivocally that any dibromoethylene, and *a fortiori* tetrabromoethylene, will exhibit a strong passivity; thus, considering attack at C_β in the following system,



we know that processes *a* and *b* together lead to deactivation (observation on vinyl bromide), that the state of polarisation *c* will intensify this result, and that the polarisability *d* will not function; and similar conclusions follow for attack at C_α, in which polarisability *d* is effective but *b* is not stimulated. On the other hand, this argument from the simpler case to the more complex cannot be reversed; for, the de-activating influence *c* being always present in C_β-attack, an observed de-activation in the system formulated would yield no conclusion as to the direction, either of the joint effects *a* and *b* in the absence of *c*, or of *c* and *d* in absence of *a*; in other words, the observation would be incapable of an analysis leading to the

* This statement goes slightly beyond the established facts inasmuch as the halogen for which an activating effect in anionotropy was observed was chlorine; but, having regard to the known polar relations of the halogens, this result indirectly shows that bromine and iodine (not necessarily fluorine) would act similarly. In the same way, the observed de-activating effect due to bromine on the addition reaction now studied shows indirectly that fluorine and chlorine (not necessarily iodine) would act analogously.

intrinsic effect of a single bromine atom. This type of difficulty applies to all the arguments on the basis of which intrinsic de-activation has previously been assumed for bromine, and thus our observation seems to be the first substantial demonstration of this point.

The phenyl group (class 7) has interest of a closely related character. Like bromine, it exhibits duplex polar action, but with this difference, namely, that *both* the component effects are polarisabilities ($\pm T$). The difficulty, illustrated for bromine, of comparing on an *a priori* basis polar effects of unlike kinds therefore does not arise in the case of phenyl, and, owing to this simplification, theory is able to furnish an unequivocal indication regarding the influence of the group ; of the two electromeric effects it is the one symbolised $+T$ which the electron-demanding reaction should stimulate, wherefore the intrinsic behaviour of phenyl should be that of an activator. This conclusion is contrary to expressed opinion, but an examination of the relative rates of the addition of bromine to styrene and to ethylene has, nevertheless, confirmed it (Found : r.v. for styrene = 3·24).

The well-known passivity of tetraphenylethylene, and of certain other stilbene derivatives, towards bromine (compare p. 2358) does not, of course, establish intrinsic de-activation by a phenyl group. Indeed, these observations, in conjunction with ours on styrene, show that the inverted mutual action of like groups, anticipated as possible for substituents with duplex polarity, actually occurs in the case of the phenyl group. The detailed explanation which would be appropriate to tetraphenylethylene, for example, is that any activating negative charge which might be conferred on C_β owing to the exhibition of the $+T$-effect by an α-phenyl substituent would at once excite the $-T$-effect in a β-phenyl substituent and thus would become absorbed into an aromatic nucleus; similar statements relate to activation of C_α. In short, if the ethenoid system succeeds in robbing Peter it cannot escape paying Paul, and the circumstance that electro-chemical theory thus naturally accommodates the known facts of the matter does not dispose of the necessity for taking steric hindrance into consideration if results emerge which indicate its intervention.

EXPERIMENTAL.

Search for a suitable solvent resulted in the choice of methylene chloride for the following reasons : (1) this being a non-ionising substance, the second stage of the reaction is not diverted by the stoicheiometric intervention of a solvent molecule (as, *e.g.*, in the formation of bromoethoxy-compounds by means of alcoholic bromine) ; (2) being a polar solvent, methylene chloride is an effective catalyst, wherefore adventitious catalysis by polar impurities, etc., is expected to be relatively less important, and results are more uniformly reproducible, than in a non-polar solvent such as carbon tetrachloride (see later, and compare Sudborough and Thomas, *loc. cit.*, and Davis, *loc. cit.*); (3) ethylene was found to be sufficiently soluble in methylene chloride to permit experiments at convenient concentrations; (4) methylene chloride could be quantitatively separated from the bromides by fractional distillation under conditions indicated later.

The temperature throughout the experiments was — 35°, and was maintained by means of liquid ammonia. The commonly experienced difficulty of keeping liquid ammonia at its b. p. in Dewar vessels, due to the tendency of that liquid towards semi-adiabatic evaporation, was overcome by designing the bromination bulb to fit the orifice of the Dewar vessel moderately closely and by packing the small gap between them with cotton wool. The reasons for the use of a relatively low temperature were (*a*) to permit the dissolution of a larger amount of ethylene and (*b*) to reduce the speeds of the reactions (see next paragraph).

With the solvent and temperature stated, experiments with initial concentrations of ethylene up to 0·25*M* were readily feasible, and this value was uniformly adopted as the initial concentration, both of the experimental substance and of the standard. Enough bromine to combine with one half of one of the unsaturated compounds was slowly added, with rapid mechanical stirring, in the form of a 0·5*M*-solution in the same solvent at the same temperature. It is an essential condition of the experiments (see later) that local excess of bromine should not persist during the progress of any considerable amount of reaction in a restricted region. So far as could be told by visual observation, the stirrer produced a uniform distribution of each drop of the added bromine solution in 1—2 seconds. In the case of tetramethylethylene, the addition-reaction of which was the most rapid of those investigated, some minutes were required to effect substantial completion of the process in methylene chloride at — 35° when the concentrations of the reactants were of the order of 0·1—0·2*M*. It follows that the condition mentioned is fulfilled, especially as in the competitive experiments the bromine was added to keep pace with decolorisation and its concentration was therefore at all times very low.

The bromination bulb had the following sealed-in connexions :—(1) a mercury-sealed, all-glass, spiral-ribbon stirrer of steep pitch. (2) A reagent funnel with cock, and a fine jet delivering just within the crown of the bromination-bulb and near the stirrer. (3) A gas-inlet, with tap and drying tubes, leading from a gas-burette nearly to the bottom of the bulb. (4) A similar gas-inlet, with similar fittings, leading from a second gas-burette. (5) A gas-outlet, with tap and drying-tubes, leading from the top of the bulb to the first gas-burette. (6). A similar gas-outlet leading to the second gas-burette. (7) A gas-inlet with tap, for distilling in liquefied gases. (8) A vent with tap and drying tube. (9) A liquid outlet-tube through which the liquid contents of the bulb could be ejected by gas-pressure whilst the bulb remained in position in its cooling-bath. No rubber was used except in connexion with the gas burettes.

The use of the apparatus requires little description. The methylene chloride was introduced through(2), and, when it had been cooled, ethylene was passed from one gas-burette, through the solvent, to the other, and then back again until the requisite volume had been absorbed. The second unsaturated substance was distilled in through (7), or introduced in solution through (2), according to its volatility. The bromine solution was added through (2), and the product was removed through (9) by applying a pressure of nitrogen to the vent tube.

The analytical procedure depended on the complete separation of the bromination products from large volumes of the solvent, and the method of distillation used was standardised with $0{\cdot}125M$-solutions of ethylene dibromide (24 g. per litre) in methylene chloride. This is approximately the molar concentration of the mixed bromides isolated from the competition experiments, and ethylene dibromide, being the most volatile, provides the most severe test. The separation was effected in two stages. In the first a Dufton still-head, 1·3 metres long, was used, which was furnished with a wooden air-jacket with suitable holes to give regulated convection, and a standard rate of distillation was maintained. This process removed all but a few c.c. of solvent, and this amount, together with the small quantity required to wash the ethylene dibromide into the second (small) still, was removed through a Dufton column 5 cm. long, the inner portion of which was constructed so that it could be pushed down the neck of the flask into the space between the bulb and the side-arm. After this distillation had been completed, the column was withdrawn and a small thermometer was inserted until its bulb was at the base of the neck of the flask; the liquid was then boiled so gently that its vapour condensed up to a steady level about 1 cm. above the bulb, and, if the b. p. was that of ethylene dibromide, the separation was deemed complete, and the product was weighed. Its purity was afterwards tested by distillation and analysis. In the final series of seven tests the error (always loss) on 1 l. (1380 g.) of solution had the mean value 0·26 g., that is, 0·02% of the whole or 1·1% of the bromide (the worst individual error was exactly twice this), and the products gave correct b. p.'s and analyses. This error is within the limits of reproducibility of the competition experiments (see later).

The compositions of the isolated mixtures of bromides were determined either by ultimate analysis, or by the estimation of a characteristic group, or by quantitative separation, according to the properties of the individual substances. The presumed analytical error varied from case to case, but was in the neighbourhood of 1—3%.

The premises on which the speed-ratio is calculated from the yields and analytical results are as follows. Denoting by x_0 and y_0 the initial concentrations of the unsaturated compounds X and Y, and by x and y their concentrations after a time t from the commencement of reaction, the instantaneous speeds of the two reactions are assumed to be expressible by the equations

$$\dot{x} = k_x(x_0 - x)[\mathrm{Br}]_t^m \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$\dot{y} = k_y(y_0 - y)[\mathrm{Br}]_t^m \quad . \quad . \quad . \quad . \quad . \quad (2)$$

whence, by division, we obtain

$$dy/dx = k_y(y_0 - y)/k_x(x_0 - x) \quad . \quad . \quad . \quad (3)$$

These equations imply that the addition of bromine to each unsaturated substance is of the *first* order with respect to that compound. It is usually considered that such reactions are also of the first order with respect to bromine, but that is not assumed: any order, m, would permit the derivation of equation (3), provided that m is the *same* for the two similar reactions. Again, the non-appearance of factors involving the concentration of a catalyst does not imply the supposition that the reactions are uncatalysed: we might have added the factor $[\mathrm{Cat}]_t^n$ to each of equations (1) and (2) without affecting (3). It is, however, assumed that the speeds are dominated essentially by *one* catalyst, although the active mass of this may either be constant (as was intended in selecting a polar solvent), or may vary in any erratic manner with time, provided only that in the latter case both reactions are of the same order, n, with respect to such a catalyst. Similarly, since equation (3) does not involve the bromine-concentration, this also may vary in any unknown and irregular manner (as, indeed, it did in the hand-regulated addition of this reagent) without affecting the validity of equation (3). It is, of course, implicit in the equations that there is no side reaction: none was observed in any of the experiments recorded.*

The integrated form of equation (3) is

$$k_y/k_x = (\log y_0 - \log y)/(\log x_0 - \log x) \quad . \quad . \quad . \quad . \quad (4)$$

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* Except (doubtfully) a very small amount of polymerisation of acrylic acid.

and its form imposes a further important condition of validity, namely, that at no time must either x or y, which have to be determined as their differences from x_0 and y_0 by means of the analytical data, become very small, because then the value of the corresponding logarithms would become so sensitive to the precise values of the quantities themselves, which would be obtained as small differences of larger quantities, as to render the calculated k-ratio very inaccurate. Hence it is necessary to use a definite deficit of bromine so that neither unsaturated compound can ever be even nearly used up. Our practice was to maintain an excess of at least 100% of each unsaturated substance. Furthermore, equation (4) implies that x and y are at all times uniform throughout the mass of solution taken for analysis; for if this were not so, a volume-integration, as well as a time-integration, would be necessary to express the true relation between the k's and the bulk-concentrations. Hence the bromine was added gradually, distributed rapidly, and its concentration was kept so low that any uncontrolled inequality in distribution could not sensibly affect the space-distribution of the unsaturated substances, having regard to the large reserves of these materials which were present. The molecular composition of the bromides directly measured the ratio $(y_0 - y)/(x_0 - x)$, and either the yield of bromides or the consumption of bromine measured the sum $(y_0 - y) + (x_0 - x)$. Hence these experimental quantities permitted the numerical solution of equation (4).

The methylene chloride was dried by calcium chloride and phosphoric oxide and distilled, head and tail fractions being discarded. The bromine was dried by sulphuric acid and twice distilled in an all-glass apparatus, large head and tail fractions being neglected in each distillation.

The results are summarised in the following table, which is succeeded by some particulars intended to supplement the above general description of the experimental method. One mol. of each unsaturated substance, and 0·5 mol. of bromine, were used throughout. The headings of the table require no explanation, except that in col. 4 the mean deviations from the means are added to the analytical data in order to indicate the degree of consistency of the measurements.

Expt. Nos.	Y.	X.	Composition bromides (mols. % YBr_2).	$\frac{k_y}{k_x}$.	R.v. of Y.
1—4	$CMe_2{:}CH_2$	$CH_2{:}CH_2$	81·8 ± 3·6	5·5	5·5
5	$CMe_2{:}CMe_2$	$CH_2{:}CH_2$	91·2	(13·6)	(13·6)
6—8	$CMe_2{:}CMe_2$	$CMe_2{:}CH_2$	69·2 ± 1·1	2·54	14·0
9—10	$CH_2{:}CH{\cdot}CO_2H$	$CH_2{:}CH_2$	1·6 ± 1·6	<0·03	<0·03
11—13	$CHMe{:}CH{\cdot}CO_2H$	$CHMe{:}CH_2$	13·9 ± 1·4	0·13	—
14—15	$CHBr{:}CH_2$	$CH_2{:}CH_2$	0·0 ± 2·5	<0·03	<0·03
17—19	$CHPh{:}CH_2$	$CH_2{:}CH_2$	73·5 ± 1·5	3·24	3·24

(Expts. 1—4.) *as*-Dimethylethylene was prepared from *iso*butyltrimethylammonium hydroxide, washed with acid and water, and dried in the form of gas with phosphoric oxide, liquefied, and redistilled. The compositions of the mixed bromides were determined by ultimate analysis.

(Expts. 5—8.) Tetramethylethylene was prepared by reduction of its dibromide (obtained from pinacol), dried, and fractionated. Expt. 5 showed that the proportion of tetramethylethylene dibromide formed simultaneously with ethylene dibromide was too high to permit the expectation of trustworthy values of the reduced velocity for tetramethylethylene, and, accordingly, the examination of this hydrocarbon was continued (Expts. 6—8) by the indirect method in which *as*-dimethylethylene was used as the subsidiary standard. The compositions of the bromides were obtained by partial separation of the crystalline tetramethylethylene dibromide and by ultimate analysis of the unseparated portion.

(Expts. 9—10.) Freshly prepared and purified acrylic acid was used, but traces of its polymeride appeared to accompany the traces of bromo-acid which resulted from the experiment. The ethylene bromide and acrylic acid were isolated together by distillation and the acrylic acid was estimated by titration with alkali; the substances were also separated by extraction with methylene chloride in the presence of alkali.

(Expts. 11—13.) Crotonic acid was prepared from crotonaldehyde by Delépine and Bonnet's method (*Compt. rend.*, 1909, **149**, 39). The ethylene dibromide, crotonic acid, and dibromobutyric acid, which remained after removal of the solvent, were partly separated by distillation, and, as those fractions which contained the whole of the ethylene bromide and the whole of the bromo-acid also contained some crotonic acid, the proportion of this acid in the fractions was estimated by titration and analysis.

(Expts. 14—15.) Freshly distilled vinyl bromide was used, and no polymerisation during the experiment was detected. No evidence of the presence of tribromoethane in the addition product could be detected qualitatively by distillation, and ultimate analysis showed the product to consist substantially of ethylene bromide.

(Expts. 17—19.) Freshly distilled styrene was used; no polymerisation or bromine-substitution was detected. The styrene bromide was separated quantitatively by distillation (m. p. and mixed m. p. 70—73°). The ethylene bromide and styrene were separated and weighed together, and the latter was estimated by conversion into its bromide, which was found to be practically pure (m. p. as above) on recovery after the ethylene bromide had been pumped off from the warmed mixture.

It seems noteworthy that the reproducibility of these experiments by the method of competition is of the same order generally as the presumed errors in the analyses of the bromides, and also varies from case to case in much the same way. It follows that, contrary to our original expectation, the consistency of the experiments *may* be limited mainly by our analytical errors, and the possibility is worth exploration in attempted future refinement. The other most likely source of inconsistency is the non-fulfilment of the assumption that one catalyst (which, according to intention, is the polar solvent) controls the rates.

We have to thank Dr. H. G. Smith for valuable assistance in connexion with these experiments, which were carried out in 1927—28 in the University of Leeds.

UNIVERSITY COLLEGE, LONDON. [*Received, August 5th,* 1931.]