226. *Influence of Substituents on the Additive Reactivity of Ethylene Derivatives. Part II. Effects of Catalysts on the Relative Rates of Addition of Bromine.*

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The object of these researches is to determine, first, the effect of a single group, R, on the rate of reaction of $R \cdot CH:CH_2$ towards addenda, and secondly, the rules under which such effects are compounded when several R's are simultaneously attached to the group C:C. When the electronic classification (nucleophilic or electrophilic) of the reagent is known, the influence on reaction rate should be capable of correlation with the modes of electron displacement characteristic of R.

Part I (Ingold and Ingold, J., 1931, 2354) commenced a study, which this paper continues, of the reactivity of ethylene derivatives towards the unambiguously electrophilic reagent, bromine. It was shown that the effect of substituents, R, could not in general be deduced by analogy with other reactions (tautomerism, aromatic substitution, etc.), because the polarisation and polarisability of a group contribute with different relative weights for every reaction, and it is impossible to tell in advance how these factors should be weighted in the addition reaction with bromine. It was also shown that the intrinsic effects of R's when present singly could not in general be deduced by an analysis of results for compounds in which several R's are present together : two activating groups could jointly deactivate, and *vice versa*. Theory defines the scope of these ambiguities, and it happens that most known results are affected by them. Therefore the authors of Part I sought to establish the fundamental relationships concerning group influence in the bromine addition reaction by choice of the proper examples, which, however, are not convenient for the purpose of detailed kinetic measurement. Accordingly, recourse was had to the com-

petitive method, which can be applied to these rapid reactions and is also useful in eliminating many difficultly controllable catalytic influences. Provided that side reactions be absent, the method is valid in proportion as this elimination is perfect; but there are conceivable types of catalysis for which it would be perceptibly imperfect, and the difficulty is to know whether any of these types are present. In Part I the conditions of validity were stated, but it could not be proved that ethylene and its simple derivatives fulfilled them : the position was simply that nothing was known to the contrary. The object of this paper is to consolidate the conclusions of Part I by means of a special investigation of this question.

The addition of bromine to ethylene and its simple derivatives is carried out in the dark, and in methylene chloride as inert solvent. (There is no known gaseous addition of bromine to olefins.) The competitive method consists in introducing the bromine into a solution of two olefins (with certain restrictions as to proportions and method of mixing), and calculating the ratio of the rates from the proportions of the products of the completed reaction. The formula for this calculation is obtained from the differential equation, $dy/dx = k_y(y_o - y)/k_x(x_o - x)$, where x and y are concentrations of the olefins and the zero suffix refers to zero time.* The formula holds provided only (1) that no serious proportion of any olefin is consumed in side reactions, (2) that the addition is of first order with respect to olefin, (3) that the addition is governed by *not more than one independent* catalyst or group of catalysts. Conditions (1) and (2) are known to be fulfilled (Plotnikow, *Z. physikal. Chem.*, 1905, **53**, 605; Herz and Mylius, *Ber.*, 1906, **39**, 3816; Hofmann and Kirmreuther, *Ber.*, 1909, **42**, 4481; Sudborough and Thomas, *J.*, 1910, **97**, 715, 2450; Brüner and Fischler, *Z. Elektrochem.*, 1914, **20**, 64; Davis, *J. Amer. Chem. Soc.*, 1928, **50**, 2769; Williams and James, *J.*, 1928, 343; Part I, *loc. cit.*; James and Robinson, *J.*, 1933, 1453); condition (3) is the difficult one to guarantee.

We were led to return to this question by Williams's discovery (*J.*, 1932, 2911) that the reaction between ethylene and bromine in carbon tetrachloride in the dark is autocatalytic; it has a definite period of induction. Williams showed that hydrogen bromide, traces of which are produced in the course of addition, is a very powerful catalyst.

There can be no doubt that this observation is of general importance for the addition of bromine to olefins in non-hydroxylic solvents. Reviewing Plotnikow's experiments on the reaction between bromine and ethylene in ether at or near $-100°$, we find good bimolecular velocity constants for most of the individual experiments; but the constants varied from one experiment to another, and in one case a low but rising constant was obtained. We assume that the controlling factor was the hydrogen bromide in commercial bromine, and that in the last-mentioned experiment the bromine was more nearly pure than usual. James and Robinson obtained good bimolecular constants for the addition of bromine to the cinnamic acids in carbon tetrachloride provided that sufficient hydrogen bromide was added initially. Brüner and Fischler realised bimolecular kinetics for the reaction between bromine and ethyl cinnamate in solution by the use of other initially added catalysts, iodine monobromide and antimony tribromide. We have verified that the phenomena observed by Williams for ethylene in carbon tetrachloride also occur in ethylene chloride, although the periods of induction are somewhat shorter in this solvent.

The importance of autocatalysis in relation to the fulfilment of condition (3) is this : During the induction stage the question of fulfilment obviously does not arise; and during the final, rapid stage condition (3) must be satisfied, because the instantaneous rate constants of simultaneous autocatalytic reactions (all other cases are trivial) must eventually diverge; it is whilst the speed is passing through the smaller of the values associated with an appreciable amount of total reaction that we cannot be sure of the fulfilment of condition (3).

A method of avoiding this uncertainty is, of course, to add sufficient hydrogen bromide initially to mask the autocatalytic reaction : condition (3) is then satisfied.

We have determined the approximate rate of the autocatalytic reaction of ethylene and

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* The solution of this equation is wrongly stated in Part I, but the results were calculated with the correct solution, as can be verified from the figures given.

bromine in methylene chloride, and also the approximate catalytic activity of hydrogen bromide. These data give the order of the amount of initially added hydrogen bromide necessary for the masking of the autocatalytic reaction. The corresponding rate is too great for accurate measurement by the direct method, but is well within the range of the competitive process, which begins to fail only at speeds comparable with the speed at which two liquids can be mixed.

We have re-investigated two of the comparisons described in Part I, *i.e.*, (*a*) the competition between *as.*-dimethylethylene and ethylene, and (*b*) that between styrene and ethylene. Table I contains the proportions in which the bromides were formed in the presence of initial quantities of hydrogen bromide ranging from nil to much more than was required to mask the autocatalytic reaction. For each set of experiments the results are practically the same, and they are identical with those recorded in Part I to within the limits of experimental accuracy. This seems to mean that condition (3) is in fact fulfilled throughout the *whole* of the autocatalytic process, although we could not have expected it *a priori*. It is possible also, however, that the accuracy of the results of Part I was further safeguarded through failure to remove the last traces of hydrogen bromide from the bromine; for the method of purification then used was less rigorous than that which we have employed. We have also carried out a competition not described in Part I, *viz.*, (*c*) that between trimethylethylene and propylene. Preliminary experiments had shown that quinoline is a powerful catalyst for the addition of bromine to olefins, small traces destroying the period of induction in the reaction with ethylene. Since the presence of sufficient quinoline automatically ensures the absence of any hydrogen bromide, catalysis by quinoline can evidently be made to satisfy condition (3). The competition between trimethylethylene and propylene was therefore carried out first in the presence of initially added hydrogen bromide, and secondly in the presence of quinoline; the results were identical to within the limits of analytical accuracy (Table I). In all these experiments the two olefins in competition were initially present in approximately equal proportion; a correction for the slight departures from equality has been applied to the observed compositions of the products in order to obtain comparable figures for record in Table I. The numerical particulars from which these figures are derived are set out in Table II.

TABLE I.

Olefins.	Initial mol. concn. of X.	Mol. proportion (X = 1) of catalyst.		Proportion of YBr$_2$ (corr.). This paper.		
		HBr.	C$_9$H$_7$N.	Mols. %.	Mean.	Part I.
(*a*) { Y = CMe$_2$:CH$_2$ X = CH$_2$:CH$_2$ }	0·32 0·18	— 0·0027	— —	83·4 } 82·5 }	83·0 ± 0·5	81·8 ± 3·6
(*b*) { Y = CHPh:CH$_2$ X = CH$_2$:CH$_2$ }	0·30 0·12 0·31 0·27	— 0·0032 0·0038 0·0078	— — — —	73·5 76·0 72·8 74·7 }	74·2 ± 1·1	73·5 ± 1·5
(*c*) { Y = CMe$_2$:CHMe X = CH$_2$:CHMe }	0·32 0·34	0·0019 —	— 0·0038	88·7 } 90·7 }	89·7 ± 1·0	—

The new experiments were carried out in methylene chloride at − 78°, whilst in Part I the solvent was the same but the temperature was − 35°. It would appear from the comparison in Table I that the ratio of the velocities of addition is not a sensitive function of temperature.

It is noteworthy that all the known catalysts for the addition of bromine to olefins in solution—iodine monobromide, antimony tribromide, hydrogen bromide, and quinoline—are themselves capable of forming dibromides.

EXPERIMENTAL.

Materials.—Ethylene, prepared according to Weber and Walton (*J. Physical Chem.*, 1930, **34**, 2693), was purified by passage through 10% aqueous potassium hydroxide, and concentrated sulphuric acid, dried with phosphoric oxide, liquefied, and fractionally distilled, with neglect of head and tail fractions. *as.*-Dimethylethylene, prepared as described by Davis (*loc. cit.*), was dried as gas by means of copper sulphate, liquefied, and carefully fractionated (b. p. 65°).

Commercial trimethylethylene and styrene were dried and freshly fractionated before each experiment. A.R. Bromine was dried by shaking with sulphuric acid for several hours, distilled, fractionally frozen four times, out-gassed in a high vacuum at − 78° several times (the product being melted and resolidified between each evacuation), and distilled over freshly fused potassium bromide in a strongly baked-out all-glass still, with neglect of considerable head and tail fractions. Commercial methylene chloride was dried with phosphoric oxide and distilled.

Dark Reaction between Ethylene and Bromine in Methylene Chloride.—Solutions of the reagents in methylene chloride, brought to 18° in dark brown bottles, which had been cleaned with alkali and chromic acid and well steamed, were mixed; and samples were withdrawn and delivered into potassium iodide solution with a darkened pipette. The consumption of bromine was followed by thiosulphate titration. The concentration of the original bromine solution was similarly determined, and that of the original ethylene solution was obtained from the asymptotic consumption of bromine, which was always employed in excess. Examples are given below of an autocatalytic reaction and of one deliberately catalysed by the addition of hydrogen bromide.

	Autocatalytic reaction (18°).

Concn. of C_2H_4 = 0·0101M.
  „ Br_2 = 0·100M.
Initial concn. of HBr = zero.

Time, mins.	C_2H_4 reacted, %.
0·7	0·0
4·0	0·0
11·0	19·2
30·0	46·8

Catalysis by added hydrogen bromide (18°).

Concn. of C_2H_4 = 0·0275M.
  „ Br_2 = 0·0351M.

Time, mins.	C_2H_4 reacted, %.
0·7	0·0
2·0	0·0
[4·0; HBr added = 0·00010M]	
5·0	37·3
7·0	58·8
10·0	74·5
30·0	98·0

Competition of Olefins for Bromine in Methylene Chloride.—The apparatus, general procedure, and detailed methods were exactly as described in Part I, except that refractometric analysis of the dibromides was used where possible to check ultimate analysis, and that where necessary the mixtures of dibromides were completely distilled in a vacuum with liquid air as refrigerant in order to avoid loss. In the experiments with trimethylethylene, refractometric analysis only was employed, ultimate analysis being unsuitable. The linearity of refractive index with respect to molar composition was experimentally confirmed for each of the mixtures of dibromides analysed in this way. The results are in Table II (X = C_2H_4 or C_3H_6 as given in Table I).

TABLE II.

Y.	Initial mol. concn. of X.	Mol. proportion (X = 1) of			Compn. of dibromides, mols. % of YBr_2.
		Y.	Br_2.	Catalyst.	
$CMe_2{:}CH_2$	0·320	0·980	0·365	—	83·1
„	0·183	1·110	0·374	0·0027 *	84·0
$CHPh{:}CH_2$	0·304	1·015	0·420	—	73·9
„	0·115	1·027	0·415	0·0032 *	76·5
„	0·308	0·973	0·380	0·0038 *	72·3
„	0·265	0·962	0·390	0·0078 *	74·1
$CMe_2{:}CHMe$	0·318	1·055	0·303	0·0019 *	89·2
„	0·339	0·960	0·420	0·0038 †	90·3

* Hydrogen bromide.   † Quinoline.