# 444. *The Reaction between Ethylene and Bromine in Carbon Tetrachloride.*

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THE kinetics of the addition of bromine to ethylene in carbon tetrachloride solution in the dark was studied by Davis (*J. Amer. Chem. Soc.*, 1928, **50**, 2769), and his conclusions as to the nature of the addition process differed in several respects from those reached by the study of the addition of bromine to ethylenic compounds in which the double linkage is influenced by a carboxyl or carbethoxy-group (Williams and James, J., 1928, 343; Williams and Hanson, J., 1930, 1059). He found that the reaction is slow and of the bimolecular type, is strongly catalysed by water, is not influenced to any extent by added hydrogen bromide, and has a temperature coefficient less than unity. The addition of bromine to unsaturated acids and esters in a non-polar solvent has been shown to be essentially an autocatalytic reaction, strongly catalysed by added hydrogen bromide but only slightly by water, and invariably having a temperature coefficient exceeding unity. The expected effect of a carboxyl or carbethoxy-group on the double linkage is one of deactivation (Ingold and Ingold, J., 1931, 2354), and there is no apparent reason why the presence of the group should alter the whole nature of the reaction.

For this reason the dark reaction with ethylene in carbon tetrachloride solution was reinvestigated. The results differ in several important respects from those of Davis. By using dilute solutions and having the bromine always in excess, it has been possible to obtain concordant results, and these show definitely that the reaction is essentially an autocatalytic one, having an inhibition period of many minutes when the solutions are as dilute as is consistent with a fair degree of accuracy. With more concentrated solutions, the inhibition period disappears, but the second quarter of the reaction is still more rapid than the first. Since all the data presented in this communication were obtained by bromine analysis of samples withdrawn from the reaction mixture, the initial concentrations being obtained by extrapolation, the method could be used only when excess bromine was present.

It was found that the reaction was extremely sensitive to some catalyst, as stated by Davis (*loc. cit.*). In order to obtain concordant results, it was necessary to clean the glass reaction vessel in the same way each time and to use freshly made bromine and ethylene solutions. Even then, in a few cases, widely different velocities were obtained in duplicate runs. Davis suggests that this catalyst is water, and in order to test this hypothesis, the reaction was studied in a solvent which had a constant water content (about two-thirds saturated), through being in contact with a salt-hydrate pair such as $Na_2SO_4$–$Na_2SO_4,10H_2O$ (the method of Bury and Roberts, J., 1923, **123**, 2037). The reaction was considerably accelerated, but was still definitely autocatalytic. It was thus improbable that traces of water could cause the wide discrepancies between certain duplicate runs; and further, a fairly large concentration would be necessary to cause the rapid reaction that follows the inhibition period when the reactants are in dilute solution.

When the reaction proceeds in sunlight, it is extremely rapid and hydrogen bromide is visibly evolved. It can also be shown that traces of hydrogen bromide are produced when the reaction proceeds in the dark. As this substance is a most efficient catalyst for bromine addition to unsaturated acids and esters, it seemed likely that it is the catalyst in this reaction also. Davis, when studying its effect, forced the dry gas into tubes containing the reaction mixture. The solubility of the gas in carbon tetrachloride is very small and it is doubtful how much will dissolve under those conditions. A better test of its effect was to add a small volume of the saturated solution of it in the solvent to the reaction mixture during the inhibition period; when this was done, an extremely rapid reaction was observed, in which over 70% of the ethylene had reacted in 2 minutes (*i.e.*, the time taken to add the hydrogen bromide solution, shake, and withdraw a sample). In solution, therefore, the gas is an extremely active catalyst for the addition, and the autocatalysis is thus explained by preliminary substitution occurring before addition, as in the case of acids and esters.

In studying the temperature effect, the solvent of constant water content was used, since more concordant results could be obtained in this way. The velocities of addition were determined at 0° and at 18°, with the reactants present in approximately the same concentrations, and the velocity at 0° was found to be much greater than at 18°. This phenomenon has also been observed with the gaseous reaction (G. Williams, this vol., p. 1747).

The fact that autocatalysis is observed in the aqueous solvent makes it improbable that bromination occurs through the agency of a bromine hydrate as postulated by Davis (*loc. cit.*), while the strong catalytic effect of hydrogen bromide on all bromine additions shows that this substance plays a most important part in the addition process. Maass and Wright (*J. Amer. Chem. Soc.*, 1924, **46**, 2664) have shown by means of freezing-point curves that molecular attraction is exerted between ethylene and hydrogen bromide molecules at low temperatures, and the effect of hydrogen bromide in the addition reaction may be due to this attraction, the bromine reacting with the loose molecular compound so formed. This would also explain why the reaction has a " negative " temperature coefficient.

## EXPERIMENTAL.

*Materials.*—Br and $CCl_4$ were purified as described by Williams and James (*loc. cit.*). The $C_2H_4$ was prepared by the dehydration of abs. EtOH by $H_3PO_4$ ($d$ 1·75) and purified by passage through the following series of wash-bottles: (1) empty and in a freezing mixture at − 30°, (2) $H_2O$, (3) and (4) KOH aq., (5) and (6) conc. $H_2SO_4$, (7) a high tower containing $P_2O_5$. It was then bubbled under press. into the solvent, which was protected from atm. moisture. In this way it was possible to make a 0·03$M$-solution, but this lost $C_2H_4$ rather rapidly if left at atm. press. The solution was forced into the reaction vessel directly by a current of dry air.

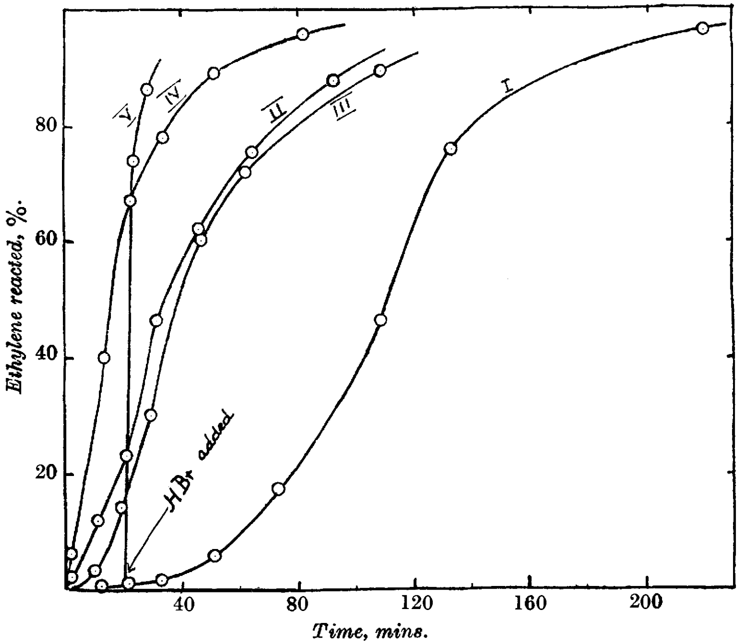
*Velocity Measurements.*—The reaction vessel was made of Pyrex glass, with all-glass joints, allowing for the rapid introduction and mixing of the reactants; samples for analysis could be forced out by dry, $CO_2$-free air into weighing bottles containing excess of KI aq., in which they were weighed. Since all the reacting solutions were dil., only a small approx. const. error was introduced by assuming the density of the solution to be the same as that of the solvent. These samples were then titrated against 0·02$N$-$Na_2S_2O_3$, back titration being against 0·01$N$-I.

The reaction vessel was cleaned with dil. NaOH aq., then with $CrO_3$ mixture, and was finally steamed out and dried. Approx. 200 c.c. of the $C_2H_4$ solution were syphoned into it, and it was placed in a thermostat at 18° (± 0·05°) in the dark. When it had attained the temp. of the bath, about 200 c.c. of a Br solution also at 18° were quickly added, the mixture was shaken vigorously, and a sample withdrawn for analysis. This withdrawal was generally about 2 min. after the addition of the Br, and the initial titre could be calc. with a fair degree of precision by extrapolation. The final titre was obtained by allowing the mixture to stand until two results gave the same value. This necessitated that the Br should be in excess in every determination.

HBr was added to the reacting solution in the form of a small vol. of a satd. solution in the solvent. This addition was done during the inhibition period, two samples having been withdrawn previously and analysed to show that the reaction was not proceeding with measurable speed. Owing to the fact that the vol. of the reacting mixture was not known accurately, the recorded concn. of the catalyst is only approx.

In previous work when $Na_2SO_4$–$Na_2SO_4,10H_2O$ was used to keep the $H_2O$ content of the solvent const., the rate of addition in the presence of solid salt was greater than in the filtered solution, presumably owing to the surface action of the salt. In this work, the wet solvent was kept in contact with the salt-pair until equil. had been attained, and the salt filtered off. The concn. of $H_2O$ in the solvent would then be approx. 0·0065*M*.

*Results.*—Since the type of reaction observed depends essentially on the concns. and is autocatalytic when no catalyst is initially present, no velocity consts. have been calc. When HBr is added in measurable amount, the reaction becomes too rapid for accurate measurement and its order cannot be found. The results are best represented graphically as in the figure. In the tabulated results, $x$ is the % of $C_2H_4$ that had reacted in time $t$ (mins.). Except for the series carried out at 0°, the temp. was 18°. The initial concn. of the $C_2H_4$ is given as $a$, and that of the Br as $b$. Out of a large number of experiments, only sufficient results are given in the following tables and in the figure to illustrate the factors that influence the addition process.



I.

$a = 0·00595$;
$b = 0·0217$.

| $t$. | $x$. |
|---|---|
| 12 | 0·9 |
| 23 | 1·2 |
| 33 | 1·5 |
| 51·5 | 5·8 |
| 73 | 17·4 |
| 109 | 46·4 |
| 133 | 75·8 |
| 220 | 96·1 |

II.

$a = 0·0136$;
$b = 0·0209$.

| $t$. | $x$. |
|---|---|
| 2 | 2·3 |
| 11 | 11·8 |
| 21 | 23·3 |
| 31·5 | 46·4 |
| 46 | 62·2 |
| 64 | 75·4 |
| 93 | 87·6 |

III.

$a = 0·0061$;
$b = 0·0176$.
Added $H_2O = 0·0065$.

| $t$. | $x$. |
|---|---|
| 2 | 0·5 |
| 10 | 3·4 |
| 19 | 14·1 |
| 29 | 30·1 |
| 47 | 60·2 |
| 62 | 71·9 |
| 109 | 89·3 |

IV, at 0°.

$a = 0{\cdot}0054$; $b = 0{\cdot}0187$.
Added $H_2O = 0{\cdot}0065$.

| $t$. | $x$. |
|---|---|
| 2 | 6·1 |
| 13 | 40·1 |
| 22 | 67·0 |
| 34 | 78·0 |
| 52 | 89·0 |
| 82 | 95·0 |

V.

$a = 0{\cdot}0053$; $b = 0{\cdot}0198$.
Added HBr = 0·005.

| $t$. | $x$. |
|---|---|
| 2·5 | 0 |
| 11 | 0 |
| 22 | HBr added |
| 23·5 | 73·6 |
| 28·5 | 86·3 |

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