565. *Acid–Base Catalysis in Non-aqueous Solvents. Part XIII.* The Depolymerisation of Paraldehyde in Ethereal Solutions of Proton Acids and Lewis Acids.*

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Kinetic measurements have been made on the depolymerisation of paraldehyde in ether at 0°, catalysed by hydrogen chloride, hydrogen bromide, and a number of metallic halides. The reaction is throughout of the second order with respect to the catalyst, and there are no essential differences between proton acids and Lewis acids, though the latter include the most effective catalysts. No co-catalyst is needed.

The term *acid* is commonly taken to mean a species (molecule or ion) which has a tendency to lose a proton, but the same word is now sometimes used to denote molecules or ions which have a tendency to accept an electron-pair (*e.g.*, BF_3, Ag^+, etc.). Opinions differ as to whether it is desirable to use the word acid in this second sense (cf. Bell, *Quart. Reviews*, 1947, **1**, 113), but these questions of nomenclature are of little significance, and it is of much greater importance to obtain experimental evidence of the behaviour of the two classes of reagent. In this paper we shall refer to them as *proton acids* and *Lewis acids* respectively.

G. N. Lewis's extended use of the word acid was based partly on certain experimental similarities, including the power of both classes of acid to catalyse a variety of reactions. While this is true in a general sense, there are few instances in which catalysis by both proton acids and Lewis acids has been established for one and the same reaction, and no investigations in which a quantitative comparison has been made between the catalytic powers of acids of both classes. Quantitative measurements with Lewis acids are difficult to carry out, since the reaction velocity is often greatly affected by the presence of small quantities of impurities, which may act either as inhibitors or as co-catalysts. There are in fact a number of reactions in which Lewis acids exert a catalytic effect only when a small quantity of proton acid is present (cf., *e.g.*, Plesch, Polanyi, and Skinner, *J.*, 1947, 257; Plesch, *J.*, 1950, 543; Evans and Meadows, *J. Polymer Sci.*, 1949, **4**, 359; Norrish and Russell, *Trans. Faraday Soc.*, 1952, **48**, 91). In these circumstances the action of the

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catalyst depends upon the transfer of a proton from the proton acid with the co-operation of the Lewis acid, *e.g.*, $BF_3 + H_2O + S \longrightarrow [BF_3OH]^- + SH^+$, where S is the substrate.

The depolymerisation of paraldehyde has proved to be a suitable reaction for comparing the catalytic effect of acids of both classes. It has previously been shown (Bell, Lidwell, and Vaughan-Jackson, *J.*, 1936, 1792) that the depolymerisation is catalysed by carboxylic acids and hydrogen chloride in anisole, benzene, and nitrobenzene solution, the reaction being strictly of the first order with respect to paraldehyde and approximately of the second order with respect to the catalyst (apparent order 1·6—2·5). Acid catalysis has also been demonstrated in the depolymerisation of paraldehyde vapour, taking place on the surface of the reaction vessel (Bell and Burnett, *Trans. Faraday Soc.*, 1937, **33**, 355). Preliminary tests showed that Lewis acids also were very effective catalysts in solution, though in anisole and chlorobenzene the reactions were too fast for quantitative study, being greatly inhibited by traces of moisture. Satisfactory results were, however, obtained by working at 0° in diethyl ether, where the basic properties of the solvent are sufficient to reduce the electrophilic powers of the Lewis acids by co-ordination.

EXPERIMENTAL

Preparation of Materials.—The solvent used was carefully purified from alcohol and acetaldehyde, since the former was found to retard the reactions greatly and the latter is the product of depolymerisation. Commercial solvent ether was shaken with fifteen successive portions of water, dried ($CaCl_2$), and kept over sodium for at least 4 days. The ether was then distilled through a column, 8″ high, packed with pellets of sodium hydroxide. Whenever possible the solvent was distilled directly into the reaction vessel at this stage. For some experiments "AnalaR" ether was distilled through the sodium hydroxide column: the kinetic results were the same with both ether preparations. Paraldehyde was purified by fractional distillation, only the middle fraction being retained.

The catalysts were employed in the form of concentrated solutions in ether. "AnalaR" ferric chloride was twice sublimed in a current of dry air and dropped into dried ether, a slight cloud of oxide being removed by decantation. The concentration of the solution was determined by reduction with stannous chloride and titration with dichromate. Aluminium chloride solution was similarly prepared from the re-sublimed solid, and the solution analysed gravimetrically by precipitation with oxine. Ferric bromide could not be purified by sublimation, on account of decomposition, and commercial samples of this compound were found to have an unexpectedly low catalytic activity. Ethereal solutions were therefore prepared by the following method. Pure iron wire was allowed to react for a fortnight at room temperature with an excess of "AnalaR" bromine. The excess of bromine was removed by a current of dry air, and dry ether distilled into the same vessel. The solution was decanted from a small residue and analysed colorimetrically by means of the thiocyanate complex (cf. Allport, "Colorimetric Analysis," Chapman and Hall, p. 53). Stannic chloride (Kahlbaum) was redistilled in a current of dry air. Solutions more concentrated than about 0·04M could not be prepared because of the formation of a sparingly soluble addition compound with the ether. Their concentrations were estimated by hydrolysis and titration with sodium hydroxide. Titanium tetrachloride was redistilled twice in a current of dry air, and the ethereal solution analysed gravimetrically by precipitation of the titanium with oxine. Boron trichloride was redistilled twice, and the ethereal solution analysed by hydrolysis and titration with sodium hydroxide (methyl-red). Fused sticks of zinc chloride were scraped and dropped into dry ether. The solution was decanted from a small residue of zinc hydroxide, and its concentration determined gravimetrically by precipitation with oxine. Hydrogen bromide was prepared by dropping bromine on to a mixture of red phosphorus and water and was passed successively through moist red phosphorus, anhydrous calcium bromide, and phosphoric oxide before absorption in dry ether. Hydrogen chloride was prepared from sulphuric acid and sodium chloride and dried with calcium chloride and phosphoric oxide.

Measurement of Reaction Velocity.—The reactions were carried out in vessels of the type previously described (Bell and Levinge, *Proc. Roy. Soc.*, *A*, 1935, **151**, 211) immersed in melting ice. During any additions or withdrawals a current of air dried by passage through calcium chloride and solid sodium hydroxide was passed through the open space at the top of the reaction vessel. This precaution was necessary, since small quantities of moisture could greatly retard the reaction, or even stop it altogether, especially when very effective catalysts were being used in low concentrations. In starting a reaction dry ether and catalyst solution were successively added to the weighed vessel, and the whole was brought to 0°, after which approx. 0·1 g. of paraldehyde was added from a calibrated pipette. Samples of about 0·7 g. were withdrawn at intervals and run into 25 c.c. of 0·1M-sodium hydrogen sulphite solution. The amount of acetaldehyde formed was then determined volumetrically by the method described by Bell, Lidwell, and Vaughan-Jackson (*loc. cit.*). Tests showed that none of the catalysts used interfered with the determination of acetaldehyde. In presence of stannic chloride fading end-points were at first obtained, but this was prevented by allowing the aldehyde–bisulphite mixture to stand for 5 minutes with the excess of iodine before adding sodium hydrogen carbonate. It is probable that some of the stannic chloride is reduced to the stannous condition by the bisulphite, and that the stannous ion is reoxidised only slowly by the iodine.

RESULTS

The reactions were always initially of the first order, and remained so until at least one-third of the paraldehyde had been converted into acetaldehyde. In the later stages of the reaction the velocity fell off more rapidly than was demanded by a first-order law, and with most catalysts the depolymerisation stopped when 60—70% of the theoretical amount of acetaldehyde had been formed. This value refers to an initial paraldehyde concentration of about 0·05M : the extent of conversion was greater with more dilute solutions, but it was not noticeably dependent upon the catalyst concentration. This suggests that the equilibrium conversion of paraldehyde into acetaldehyde is incomplete under our conditions, and this view is supported by the quantitative data given in the Table.

Equilibrium in presence of 0·03M-*aluminium chloride.*

Initial [paraldehyde]	Depolymerisation, %	K = [acetaldehyde]^3/[paraldehyde]
0·0146	86·5	0·028
0·0160	85·1	0·029
0·0233	73·3	0·022
0·0270	76·3	0·037
0·0336	67·2	0·028
0·0356	66·0	0·029
0·0392	60·7	0·024
0·0482	60·4	0·035
		Mean K = 0·029

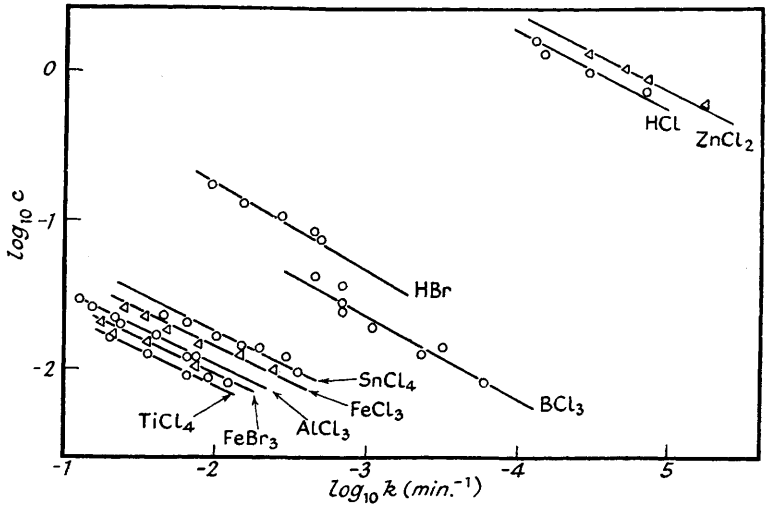
The constancy of K is as good as could be expected, since in this range an error of 1% in measuring the percentage depolymerisation produces an error of 10% in K. Further support comes from some experiments with 0·02M-ferric chloride as catalyst in which equilibrium was approached from both ends in two separate experiments, giving $K = 0·026$ and 0·035 respectively. These equilibrium constants at 0° accord reasonably with the finding by Bell, Lidwell, and Vaughan-Jackson (*loc. cit.*) that a 1% solution in benzene at 20° depolymerises to the extent of 80% (corresponding to $K = 0·27$) : the polymerisation of the pure liquid is exothermic to the extent of 12·6 kcal. per mole of paraldehyde.

The setting up of an equilibrium does not give a complete explanation of the behaviour of the latter part of the reaction. If the reaction mixtures were kept for a long time the aldehyde concentration decreased again slowly, probably because of its conversion into another type of polymer, such as metaldehyde. Moreover, with hydrogen bromide and zinc chloride as catalysts (and probably also with boron trichloride and hydrogen chloride) the reaction did not stop at 60—70% conversion but went to 90% or further. These catalysts had to be used in high concentrations to obtain convenient reaction rates, and it is likely that they stabilise the acetaldehyde by co-ordination, thus displacing the equilibrium. It is clear, however, that none of these complications will affect the early part of the reaction, and the velocity constants in the Figure were obtained from a logarithmic plot of the first 30—50%; the first-order velocity constants are in units of $\log_{10}$ min.$^{-1}$ and the catalyst concentrations in moles/1000 g. With titanium tetrachloride the logarithmic plots fell off very steeply, and the constants given for this catalyst are obtained from initial slopes.

DISCUSSION

The data obtained (cf. Figure) are not of high accuracy or reproducibility, but are sufficient to establish a number of general points about the reaction. The Lewis acids appear to be able to act as catalysts without the co-operation of a proton acid, since none of the latter is present in the solution, and the addition of small quantities of water has a retarding effect. The experiments with hydrogen bromide and chloride show that no appreciable catalysis would be caused by small quantities of these substances formed by hydrolysis. The order of the reaction with respect to catalyst is always close to two, and the lines in the Figure are drawn with a slope of exactly two. Similar behaviour was found in previous work with proton acids in other solvents (Bell, Lidwell, and Vaughan-Jackson, *loc. cit.*). This second-order dependence on catalyst concentration suggests that the paraldehyde molecule has to be attacked by two catalyst molecules before depolymerisation takes place. Even in the absence of catalyst three acetaldehyde molecules can be formed by an electronic displacement, and the rôle of the acid catalyst will be to facilitate the formation of the carbon–oxygen double bond by its electrophilic action. If two carbonyl groups are formed this automatically leads to the formation of the third and the break-down of the whole molecule, and it is therefore reasonable that two catalyst molecules should be required. It may be noted that the removal of only one acetaldehyde molecule from the paraldehyde ring leaves behind an unstable species (either a di-radical or the ion $\overset{-}{O}\cdot CHMe\cdot O\cdot \overset{+}{C}HMe$), and it is more probable that the depolymerisation takes place in a single step.

Depolymerisation of paraldehyde in ether (c = *catalyst concn.*)



The Figure shows that even a very strong proton acid such as hydrogen bromide is inferior as a catalyst to almost all the Lewis acids. The latter lie fairly close together in their catalytic effects, with the exception of zinc chloride, which is a very weak catalyst. There is already ample evidence that the relative catalytic effects of Lewis acids vary considerably from one reaction to another, even the order of effectiveness being frequently changed (cf., *e.g.*, Dermer and Billmeier, *J. Amer. Chem. Soc.*, 1942, **64**, 465). This behaviour is probably connected with steric effects, and appears in equilibria as well as in kinetics, thus making it impossible to arrange Lewis acids in any unique order of strengths (Lewis, *J. Franklin Inst.*, 1938, **226**, 293).

The Figure shows that hydrogen bromide is about 100 times as efficient a catalyst as hydrogen chloride, the catalytic efficiency being taken as inversely proportional to the concentration needed to produce a given velocity. Similarly, Bell and Burnett (*Trans. Faraday Soc.*, 1939, **35**, 324) found hydrogen bromide to be about 300 times as effective as hydrogen chloride in the depolymerisation of trioxymethylene in decalin solution. It is generally agreed that hydrogen bromide is the stronger acid of the two, but there is little quantitative information as to their acid strengths. Kolthoff (*J. Amer. Chem. Soc.*, 1934, **56**, 1007) measured the conductivities of 0·005M-solutions in glacial acetic acid and found these to be in the ratio HCl : HBr = 9 : 160, indicating a ratio of dissociation constants of about 1 : 300. Calculation from thermodynamic data shows that in the gas phase the dissociation $HX \longrightarrow H^+ + X^-$ requires about 10 kcal./mole more for HCl than for HBr (Bell and Burnett, *loc. cit.*, 1939), but the difference will be less in solution, since the solvation energy of Cl^- will be greater than that of Br^-.

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