

550. The Gattermann-Koch Reaction. Part II. Reaction Kinetics.

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A study of the reaction $C_6H_6 + CO \rightarrow C_6H_5 \cdot CHO$ has placed the catalytic halides in the following order of decreasing activity: $AlBr_3$, AlI_3 , $AlCl_3$, $FeCl_3$, while $TiCl_4$, $SnCl_4$, and $SbCl_5$ are practically inactive. The promoting action of Cu_2Cl_2 is shown to be relatively small. The synthesis with $AlBr_3$ is first order with respect to benzene, the effect of temperature on the yields being small up to 30° , above which there is a sharp fall in yield. The fall is shown to be due to decomposition of $C_6H_5 \cdot CHO$, the complicated time course of which suggests the presence of side reactions. The slowing effect of nitrobenzene as solvent, together with conductivity measurements, suggests that the HCO^+ ion is provided by $HCl + CO + AlBr_3 \rightleftharpoons HCO^+ + AlBr_3Cl^-$ and that the reaction velocity is determined by $HCO^+ + C_6H_6 \rightarrow C_6H_5 \cdot CHO + H^+$. The presence of Cu^+ ion may assist the supply of HCO^+ .

A tentative correlation is possible between the catalyst order and the order of the catalyst-benzaldehyde bond energies determined in Part I. Such a correlation finds an explanation in theoretical work by Ogg and Polanyi.

In this paper we examine the kinetics of the Gattermann-Koch reaction, and investigate the behaviour of a number of catalytic halides. Later we discuss the efficiency of the different catalysts in the light of the thermochemical data of Part I.

EXPERIMENTAL.

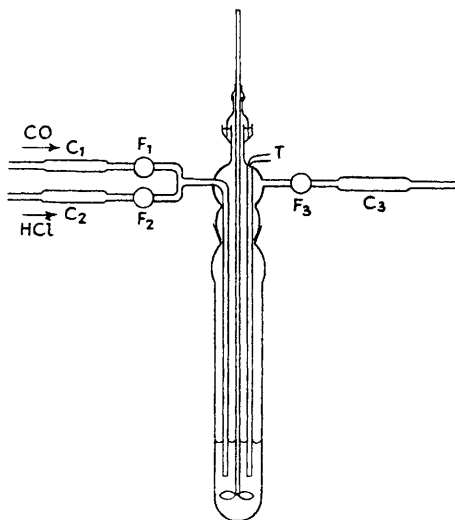
The reaction vessel is shown in Fig. 1. It consisted of a glass tube 30 cm. long by 5 cm. wide, and was closed by a ground-glass joint which carried inlet and outlet tubes, thermocouple pocket, and mercury-seal stirrer. The gases passed through calcium chloride tubes C_1 and C_2 , and capillary flow-meters F_1 and F_2 , before entering the vessel. The mixed gases left through flow-meter F_3 and calcium chloride tube C_3 . The flow-meters were calibrated, and from the difference in readings on inlet and outlet sides the amounts of gas absorbed in the reaction vessel could be calculated. The reaction vessel was immersed in a Dewar flask containing water, the temperature of which was manually controlled to $\pm 0.5^\circ$. The temperature of the reaction mixture was followed by a copper-constantan thermocouple and micro-ammeter.

The method of experiment was to fill the reaction vessel with 150 c.c. of benzene, and a weighed amount of catalyst (usually 0.1 g.-mole. reckoned as monomer). In cases where a promoter such as cuprous chloride was used, 0.02 g.-mole was added. The vessel was assembled, and first, hydrogen chloride was passed in at 30 c.c./min. for 30 minutes; next, nitrogen and hydrogen chloride were passed in at the rate at which it was intended subsequently to pass carbon monoxide and hydrogen chloride, usually 20 c.c./min. and 10 c.c./min., respectively. When total outflow equalled total inflow and the benzene was saturated, the nitrogen flow was switched over to carbon monoxide, and the flow carefully controlled by hand for the rest of the run. Control was possible to ± 1 c.c./min. and mean rates of flow are recorded in the tables. Using this technique it was possible to measure any absorption of carbon monoxide in the initial stages of the reaction.

After a given time, nitrogen was passed through to remove excess of hydrogen chloride and carbon monoxide, the reaction vessel was removed, and its contents were poured on 200 g. of ice. A few crystals of quinol were added to prevent oxidation of benzaldehyde, the solution neutralised with sodium carbonate, and steam-distilled until no further benzaldehyde could be detected in the distillate by the β -naphthol test (originally suggested to us by Dr. D. C. Pepper). 5 c.c. of the distillate were shaken with 5 c.c. of a 1% solution of β -naphthol in benzene, the benzene layer separated, and three drops of concentrated sulphuric acid added to it. After 5 minutes the colour of the ring developed in the bottom of the test tube gave a measure of the benzaldehyde concentration, *viz.*, 1 in 500, black; 1 in 5000, red; 1 in 50,000 orange; zero, yellow.

The benzaldehyde in the distillate was determined by a modification of Holloway and Krase's method (*Ind. Eng. Chem.*, 1933, 25, 497). The benzene was taken off over a 7-plate column, the distillate being shown by test to be free from benzaldehyde. Addition of 50 c.c. of alcohol then sufficed to make the residue homogeneous, after which it was made up to 250 c.c. or 500 c.c. with distilled water. 25 c.c. of this solution were added to excess of hydroxylamine hydrochloride, and the hydrochloric acid liberated titrated against $N/20$ -sodium hydroxide, with bromophenol-blue as an internal indicator. Blank titrations were made on the reagents used. The accuracy of the method was tested by adding known

FIG. 1.
Reaction vessel.



weights of benzaldehyde to the reaction vessel with benzene and catalysts, and carrying out an estimation: Run 0; benzaldehyde, added 1.03 g.; found 1.05 g. Run 16; benzaldehyde, added 1.03 g.; found 0.998 g.

In the runs with 75 c.c. of benzene and 75 c.c. of nitrobenzene, after ice-treatment and steam-distillation, the distillate contained benzene, nitrobenzene, benzaldehyde, and water. Experiment showed that practically all the benzaldehyde was in the non-aqueous layer, so this was separated and after further extraction of the aqueous layer with benzene the extracts were united and made up to 250 c.c. in a graduated flask. 25 C.c. were added to excess of hydroxylamine hydrochloride, and the liberated hydrochloric acid was titrated against *N*/20-sodium hydroxide, methyl-orange being used as it was not masked by the colour of the nitrobenzene. Because of the phase difference, the hydrogen chloride was not liberated immediately, but successive titrations showed the reaction to be complete in about 36 hours. The accuracy of the method was determined as $\pm 5\%$ on blank runs, and this sufficed for our purposes.

In addition, the velocity of decomposition of benzaldehyde by aluminium bromide was studied in benzene solution under conditions of concentration and temperature closely analogous to those resulting from the synthesis. The procedure was to deliver 1.05 g. of pure benzaldehyde from a calibrated pipette into a mixture of 13 g. of aluminium bromide and 75 c.c. of benzene. The components were then stirred in the reaction vessel for various times. The resulting solution was poured on ice, and steam-distilled, and the benzaldehyde extracted with benzene and titrated by the hydroxylamine hydrochloride method.

Materials.—Catalytic halides. See Part I. [For some experiments the aluminium bromide was freshly prepared by dropping bromine on heated aluminium and distilling the product. Free bromine was removed by pumping in a vacuum-desiccator (Winter and Cramer, *Ind. Eng. Chem.*, 1940, **32** 856).]

Benzene. "Thiophen-free" benzene was washed with concentrated sulphuric acid, then with water, dried (CaCl_2), and fractionated.

Carbon monoxide was taken from a cylinder supplied by I.C.I. Ltd. Hydrogen chloride was prepared by the action of sulphuric acid on ammonium chloride in a Kipp apparatus, and passed through a wash-bottle containing sulphuric acid.

Nitrobenzene. The B.D.H. product was dried (CaCl_2) and distilled.

TABLE I.
Synthesis of benzaldehyde.

Run.	Catalyst and wt. (g.).	Promoter and wt. (g.).	Time (hrs.).	Rate of CO (c.c./min.).	Rate of HCl	Temp.	Yield,	
							g.	%.
(a) 150 C.c. of benzene used.								
2	FeCl_3 16.2	—	6	22	10	15°	0.03	0.3
3	AlCl_3 13.4	—	6	21.5	12.0	13	0.03	0.3
4	AlCl_3 13.4	Cu_2Cl_2 1.98	6	21.5	13.5	16	0.05	0.5
5	AlI_3 40.8	—	6	22.0	10.0	23.5	1.92	18
6	SnCl_4 26.5	Cu_2Cl_2 1.81	6	21.0	10.0	16	0.02	0.2
7	SnCl_4 26.7	—	6	21.0	11.0	17	0.01	0.1
8	TiCl_4 19.8	—	6	21.0	10.5	16.5	0.02	0.15
9	SnCl_4 27.0	Cu_2Cl_2 1.95	6	21.0	10.0	20	0.02	0.15
12	FeCl_3 15.97	Cu_2Cl_2 1.98	6	19.5	9.0	19.0	0.06	0.6
14	SnCl_4 27.4	Cu_2Cl_2 1.98	6	19.0	9.0	16	0.02	0.1
15	SbCl_5 31.1	Cu_2Cl_2 2.04	6	19.5	9.5	21	0.02	0.2
17	TiCl_4 21.6	Cu_2Cl_2 1.93	6	20.0	8.5	19	0.02	0.2
18	AlCl_3 13.4	TiCl_4 2.41	6	20.0	9.5	18	0.01	0.1
19	AlCl_3 13.4	Cu_2Cl_2 1.94	6	20.0	9.5	18	0.31	3.0
20	AlI_3 40.8	—	6	20.0	7.0	25	1.84	17.0
22	AlI_3 41.5	—	6	20.0	—	22	0.06	0.5
23	AlBr_3 27.2	—	6	20.0	10	22	2.9	27
24	AlBr_3 26.6	—	4	19.5	10	20	2.1	19.7
25	AlBr_3 26.5	—	6	20	9.0	19.5	3.2	30.4
26	AlBr_3 26.2	—	2	19.5	9.5	20.5	1.1	10.6
27	AlBr_3 25.2	Cu_2Cl_2 1.94	6	20.0	8.5	21.5	3.5	35
29	AlBr_3 26.0	—	4	20.5	9.0	40.5	1.9	18.5
31	AlBr_3 26.9	—	4	20.0	7.5	30.5	2.5	23.3
32	AlBr_3 26.4	—	4	20.0	8.5	46.0	0.3	2.8
33	AlBr_3 27.2	—	4	20.0	9.0	9.5	2.2	20.5
34	AlBr_3 26.6	—	4	20.0	9.0	4.5	2.4	22.8
36	AlBr_3 26.7	—	4	20.0	9.0	15.0	2.2	20.3
37	AlBr_3 26.7	—	1	20.0	8.8	20.4	0.44	4.1
38	AlBr_3 26.7	—	0.5	20.0	10.0	20.4	0.23	2.1
39	AlBr_3 26.6	—	4	20.0	—	20.4	0.1	1.0
40	AlBr_3 26.3	—	4	20.0	—	20.4	0.1	1.2
41	AlBr_3 27.0	Cu_2Br_2 2.83	4	20.0	9.0	20.5	1.38	12.8
50	AlBr_3 23.9	—	6.5	20.0	1 c.c. H_2O	19.5	0.3	3.2
(b) 75 C.c. of benzene + 75 c.c. of nitrobenzene used.								
46	AlCl_3 13.9	—	6	20.5	9.5	21	0.07	0.6
47	AlCl_3 13.4	—	6	20.0	9.5	52	0.15	1.4
49	AlBr_3 26.2	—	4	20.5	9.0	19.5	0.2	1.9

Cuprous halides. These were prepared by passage of sulphur dioxide into a solution containing cupric sulphate and the appropriate sodium halide. The white precipitate was filtered off, washed with sulphurous acid solution, and dried in a vacuum-desiccator. Silver chloride and sulphate were prepared from silver nitrate and the appropriate sodium salt. B.D.H. mercurous chloride and mercuric chloride were used.

Benzaldehyde. The B.D.H. product was dried (CaCl_2) and distilled.

Results.—The results obtained are listed in Table I. The yield in the last column is calculated on the weight of catalyst used in the reaction. All runs in Table I (a) were made with 150 c.c. of benzene.

Decomposition of Benzaldehyde.—The rate of decomposition is only appreciable above 30° . The results are given in Table II.

TABLE II.

Decomposition of benzaldehyde on aluminium bromide.

Time (hrs.).	Temp.	$10^3/T$.	$\text{C}_6\text{H}_5\text{-CHO}$ remaining (g.).	Decompn., %.	Log decompn.
2	50°	—	0.864	17.8	—
4	50	3.10	0.440	58.1	1.76
6	50	—	0.204	80.5	—
8	50	—	0.141	88.2	—
4	35	3.25	0.90	14.3	1.16
4	20	3.42	1.06	—	—

Synthesis of Benzaldehyde.—It will be convenient to discuss the results with each catalyst separately.

Aluminium chloride. Run 3 was with commercial aluminium chloride and gave no observable carbon monoxide absorption and a negligible yield of benzaldehyde. Run 4 with 0.1 g.-mole of similar aluminium chloride and 0.02 g.-mole of cuprous chloride still gave a negligible yield, but summation of the flow-meter readings indicates a monoxide absorption of about 450 c.c., *i.e.*, 0.02 g.-mole, which suggests the formation of $\text{Cu}_2\text{Cl}_2 \cdot 2\text{CO}$. Run 19 with aluminium chloride freshly sublimed in hydrogen chloride and cuprous chloride as promoter gave a 3% yield of benzaldehyde, comparable with Hey's yield under similar conditions but at 45° (*J.*, 1935, 72). Titanic chloride has been reported as a promoter when a high pressure of carbon monoxide is used (B.P. 334,009) but Expt. 18 shows that it does not assist in the formation of benzaldehyde at atmospheric pressure.

Stannic chloride. Runs 6, 7, and 9 show that there was no yield of benzaldehyde and no absorption of carbon monoxide in the presence or absence of promoter. In run 14, 0.5 c.c. of water was added, but there was still no yield.

Titanic chloride. Runs 8 and 17 show that neither in the absence nor in the presence of promoter was there any yield of benzaldehyde or absorption of carbon monoxide.

Antimony pentachloride. Run 15, with cuprous chloride addition, gave no absorption and no yield. A small quantity of chlorobenzene was formed during the run.

Ferric chloride. By itself ferric chloride gave only a negligible yield, but in the presence of cuprous chloride there was 0.5% yield. No carbon monoxide absorption was observed in either case.

Aluminium iodide. Unfortunately, in runs 5 and 20, there was considerable decomposition of the aluminium iodide by the passage of hydrogen chloride, and the iodine evolved blocked the exit flow-meter, so the carbon monoxide absorption could not be measured. There was a yield of about 17.5% of benzaldehyde in these experiments. Run 22 was carried out with benzene saturated with hydrogen iodide, in the absence of hydrogen chloride, and there was only a very small yield. Although aluminium iodide is hardly ever mentioned as a Friedel-Crafts catalyst, a patent for its use in the Gattermann-Koch synthesis was taken out in 1899 (D.R.-P. 126,421).

Aluminium bromide. Run 25 was carried out with aluminium bromide freshly prepared by Winter and Cramer's method. The aluminium bromide was partly soluble in benzene, and passage of hydrogen chloride preliminary to the run resulted in a black oily complex (*cf.* Norris and Ingraham, *J. Amer. Chem. Soc.*, 1940, 62, 1298). No accurate measurements of carbon monoxide absorption could be made in this system since aluminium bromide or its decomposition products distilled into the exit flow-meter, in spite of intermediate traps of glass-wool and concentrated sulphuric acid. The yield in this particular run was 30.4%. Subsequently the effects of temperature, time, etc., were studied with amounts of aluminium bromide all from the same B.D.H. sample.

Runs 38, 37, 26, 24, and 23 give the time course of the synthesis at 20° . Fig. 2 shows that the reaction is of first order over the initial stage. If a is the initial number of moles of benzene, 1.69 in all cases, x the number of moles of benzaldehyde at time t , and $a-x$ the unchanged benzene, then for the reaction to be of first order in benzene

$$dx/dt = K(a-x) \text{ and } 2.303 \log_{10} a/(a-x) = Kt \quad \dots \quad (1)$$

The slope of the line in Fig. 2 gives $K = 4.9 \times 10^{-5} \text{ min.}^{-1}$. Holloway and Krase (*loc. cit.*), working in the absence of added hydrogen chloride, also found a first-order reaction with deviations in the later stages. This deviation is not due to the presence of a reversible reaction, since we found later that decomposition of benzaldehyde is negligible at this temperature. It is probably due rather to solubility effects. Unlike Holloway and Krase, we do not find an induction period; their induction period probably resulted from the need to build up a concentration of hydrogen chloride by the action of traces of moisture on the aluminium chloride. In our case the solution was saturated with hydrogen chloride before the experiment started.

Runs 34, 33, 36, 24, 31, 29, and 32 demonstrate the effect of temperature on the reaction velocity, as measured by percentage yield after 4 hours. They are plotted in Fig. 3. There is a strong decrease in yield with increase in temperature above 30° .

Runs 39 and 40 show the need for a continuous stream of hydrogen halide, a mere initial saturation being ineffective. In run 50 the use of wet benzene produced a 3% yield; presumably a continuous supply of hydrogen bromide resulted from the slow hydrolysis of the aluminium bromide.

Run 27 shows that cuprous chloride acts as a promoter, increasing the yield from 27 to 35%. Although later work has shown that the system $\text{AlCl}_3\text{-Cu}_2\text{Br}_2$ absorbs carbon monoxide, run 41 shows that cuprous bromide does not act as a promoter in the synthesis.

Nitrobenzene as Solvent.—Nitrobenzene forms a stable complex with aluminium chloride, the heat of formation as measured by us being about 8 kcal./mole of AlCl_3 . Since the heat of formation of the complex between aluminium chloride and benzaldehyde is 24.7 kcal., then neglecting entropy differences, we should expect the reaction $\text{C}_6\text{H}_5\cdot\text{NO}_2\cdot\text{AlCl}_3 + \text{C}_6\text{H}_5\cdot\text{CHO} \rightarrow \text{C}_6\text{H}_5\cdot\text{CHO}\cdot\text{AlCl}_3 + \text{C}_6\text{H}_5\cdot\text{NO}_2$ to go almost to completion. Since the nitrobenzene brings the aluminium chloride into solution, we might expect the use of nitrobenzene as solvent to increase the yield. Table I(b) shows that with aluminium chloride the yield is very small, and that with aluminium bromide yields are reduced by a factor of 10. The effect may arise from an activation energy for the complex displacement reaction above, or it may be due to an increase in dielectric constant of the bulk solvent (Eyring, Glasstone, and Laidler, "Theory of Rate Processes," New York, 1941, p. 442). Other cases are known where the use of nitrobenzene slows down a Friedel-Crafts reaction, and recently Fairbrother (*J.*, 1941, 293) has found that it decelerates the exchange of radioactive bromide between inorganic and organic halides.

FIG. 2.

Synthesis of benzaldehyde using AlBr_3 : first order with respect to benzene.

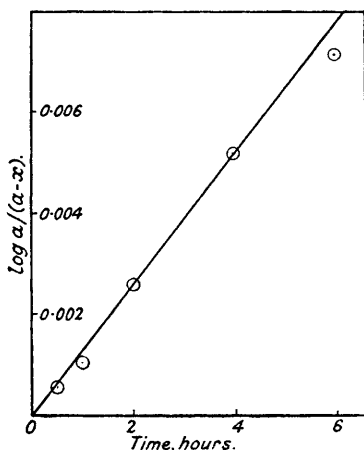
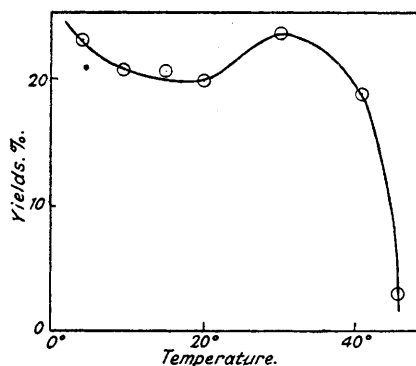


FIG. 3.

Percentage yield of benzaldehyde, based on AlBr_3 , with increasing temperature.



Promoter Action.—Gattermann and Koch (*Ber.*, 1897, **30**, 1622) suggested the use of cuprous chloride as promoter, since it was known to absorb carbon monoxide under certain conditions. We have endeavoured to define these conditions more precisely and to investigate the possibility of using other promoters. It is known that solutions of cuprous chloride in aqueous hydrochloric acid or ammonia will absorb carbon monoxide in the ratio $2\text{CO}\cdot\text{Cu}_2\text{Cl}_2$, but that dry cuprous chloride will not absorb it at atmospheric pressure. It has been shown in this paper that cuprous chloride in benzene in the presence of aluminium chloride will absorb carbon monoxide in the ratio $2\text{CO}\cdot\text{Cu}_2\text{Cl}_2$, and in run 27 it was shown that the system $\text{AlBr}_3\text{-Cu}_2\text{Cl}_2$ also absorbed carbon monoxide. In no other case was there any absorption of carbon monoxide, although such systems as $\text{SnCl}_4\text{-Cu}_2\text{Cl}_2$, $\text{TiCl}_4\text{-Cu}_2\text{Cl}_2$, $\text{FeCl}_3\text{-Cu}_2\text{Cl}_2$, $\text{SbCl}_5\text{-Cu}_2\text{Cl}_2$, and $\text{HCl-Cu}_2\text{Cl}_2$ were investigated, all in benzene solution. Because of their relationship to cuprous chloride, silver chloride and mercurous and mercuric chlorides were all investigated, but there was no absorption of carbon monoxide, either alone in benzene or with aluminium chloride in benzene. Silver sulphate absorbs carbon monoxide in concentrated sulphuric acid (Manhot and König, *Ber.*, 1927, **60**, 2183), but this is not the case in benzene with aluminium chloride. Runs 42 and 43 showed that $\text{Cu}_2\text{Br}_2\text{-AlCl}_3$ will absorb carbon monoxide, but $\text{Cu}_2\text{I}_2\text{-AlCl}_3$ will not do so. Although cuprous bromide is not usually quoted as an absorbent for carbon monoxide, it is known that in common with cuprous chloride it will absorb ethylene under pressure (Gilliland, Seebold, FitzHugh, and Morgan, *J. Amer. Chem. Soc.*, 1939, **61**, 1960). There is no reference to cuprous iodide absorbing either of these gases.

It seems very evident from these runs that carbon monoxide is absorbed only when the cuprous halide has formed a complex with the catalyst. Thus, carbon monoxide plus hydrogen chloride passed through aluminium chloride alone gave little change, but in the presence of cuprous chloride a brown complex was formed on the surface of the aluminium chloride which was partly soluble in benzene. When carbon monoxide plus hydrogen chloride was passed into aluminium bromide in benzene, a black oil was first formed at the bottom of the vessel, but in the course of the run the whole solution became black and apparently homogeneous. Cuprous chloride seemed to make no difference in this case, but both this salt and cuprous bromide are known to give complexes with aluminium bromide soluble in organic solvents (Plotnikov, *J. Gen. Chem. Russia*, 1933, **3**, 208). It is our theory that the complex $\text{Cu}^+[\text{AlCl}_4]^-$ precedes the absorption, and that then $\text{Cu}^+(\text{CO})$ is formed. This view finds some confirmation in conductance work described later.

The Decomposition of Benzaldehyde.—The decreased yields above 30° might be attributed to a true thermodynamic effect or to decomposition of benzaldehyde by a side reaction. Thus, Hey (*J.*, 1935, 72; 1938, 1847) and Schaarschmidt (*Ber.*, 1925, 58, 1914) found that benzaldehyde reacts with benzene in the presence of aluminium chloride at high temperatures to give anthracene and triphenylmethane. Similarly, they found that when carbon monoxide and hydrogen chloride are passed into boiling benzene with aluminium chloride or bromide, no benzaldehyde is obtained, but only anthracene and triphenylmethane.

Table II shows that the decomposition of benzaldehyde with aluminium bromide is only appreciable above 30°, and Fig. 4 shows percentage decomposition against time at 50°. These results do not fit a first- or second-order law, suggesting a complex decomposition. Hey (*loc. cit.*) suggests that the initial stage in anthracene formation is $C_6H_5 \cdot CHO \longrightarrow CO + C_6H_6$, but this would require first-order kinetics, so there may be further side reactions. Taking the decomposition in 4 hours as a rough measure of the velocity constant k , we have plotted an Arrhenius curve for the system (Fig. 5) which gives an activation energy of 11,000 cal.

Electrical Conductance.—Conductivity changes during the Gattermann-Koch reaction have been followed to investigate any ionic intermediaries, a method previously applied by Wertyporoch *et al.* (*Ber.*, 1931, 64, 1357) to other Friedel-Crafts systems.

FIG. 4.
Decomposition of benzaldehyde with
 $AlBr_3$ at 50°.

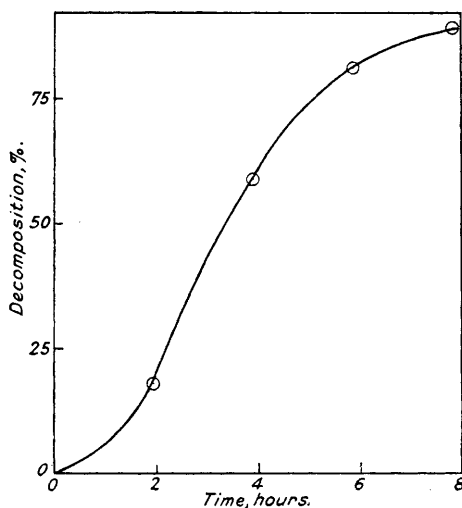
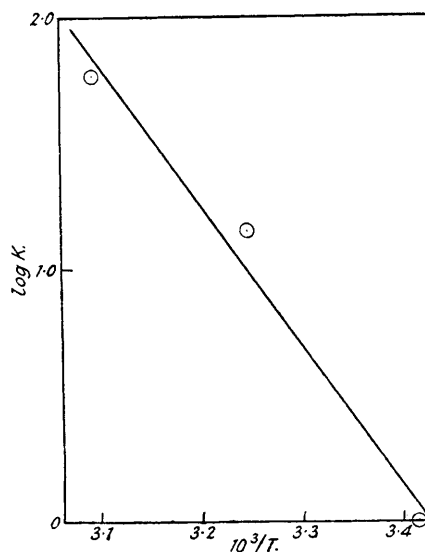


FIG. 5.
Arrhenius line for the decomposition of
benzaldehyde with $AlBr_3$.



A conductivity cell with smooth platinum electrodes, area 3.6 sq. cm., separation 1.6 cm., cell constant 0.2, was used with an A.C. bridge working over the range 10,000 Ω (accuracy 3%) to 10 M Ω (10%). The frequency used was 1000 cycles and the cell was kept at $25^\circ \pm 0.1^\circ$ in an oil-thermostat.

The specific conductivity κ of the benzene used in the cell was found to be 7×10^{-9} . Addition of aluminium bromide (20 g./150 c.c.) yielded a light-red solution with little change of conductivity, $\kappa = 8 \times 10^{-9}$. This agrees with Wertyporoch and Adamus (*Z. physikal. Chem.*, 1933, 168, 31), who give $\kappa \sim 10^{-9}$. When hydrogen chloride was passed into this solution the usual two layers were formed; the upper yellow layer had $\kappa = 5 \times 10^{-7}$ and the lower layer had $\kappa = 3 \times 10^{-3}$ (cf. Wertyporoch, $\kappa = 10^{-3}$). On passage of carbon monoxide (20 c.c./min.) and hydrogen chloride (10 c.c./min.) into the solution, it slowly became homogeneous and the resistance fell. A similar experiment with an aluminium bromide concentration of 6 g./150 c.c. is shown in Fig. 6. These results suggest that ions are formed, probably by $HCl + CO + AlBr_3 \rightleftharpoons HCO^+ + AlBr_3Cl^-$. However, a similar result was obtained with carbon monoxide in the absence of added hydrogen chloride, but a trace of hydrogen bromide was certainly present owing to hydrolysis.

In another run the reaction vessel contained 5.6 g. of aluminium bromide, 2.1 g. of cuprous chloride, and 150 c.c. of benzene. On stirring, this system gave a conducting solution, although not all the cuprous chloride dissolved; these results with previous transport measurements (Plotnikov, *Chim. et Ind.*, 1933, 30, 857) suggest to us the equilibrium $CuCl + AlBr_3 \rightleftharpoons Cu^+ + AlBr_3Cl^-$. On passage of hydrogen chloride, the conductivity was further increased, probably as the excess of aluminium bromide formed a complex with hydrogen chloride. When carbon monoxide and hydrogen chloride were passed in together, the conductivity was decreased, as in Fig. 7. This experiment is confirmed in Fig. 8, where different concentrations were used, *viz.*, 2.1 g. of cuprous chloride, 20 g. of aluminium bromide, and 150 c.c. of benzene. In this case all the cuprous chloride dissolved and the solution was more conducting. Hydrogen chloride produced a bigger increase in conductivity (because there was more aluminium bromide) and carbon monoxide a further decrease.

Following up the carbon monoxide effect, a decrease of conductivity was found when this gas *alone* was passed into an $\text{AlBr}_3\text{-Cu}_2\text{Cl}_2\text{-C}_6\text{H}_6$ mixture. A blank run showed that $\text{CO-HCl-C}_6\text{H}_6\text{-Cu}_2\text{Cl}_2$ was non-conducting.

These results suggest strongly that the ion CuCO^+ is formed which will have a smaller conductivity than Cu^+ on account of its increased size.

FIG. 6.

Passage of $\text{CO} + \text{HCl}$ into AlBr_3 in benzene.

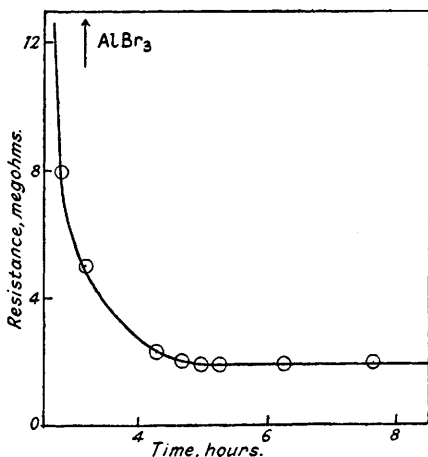


FIG. 8.

Passage of $\text{CO} + \text{HCl}$ into AlBr_3 (20 g.) + Cu_2Cl_2 (2.1 g.) in benzene.

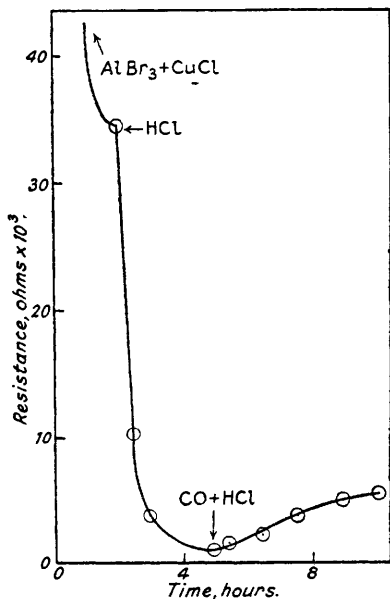


FIG. 7.

Passage of $\text{CO} + \text{HCl}$ into AlBr_3 (5.6 g.) + Cu_2Cl_2 (2.1 g.) in benzene.

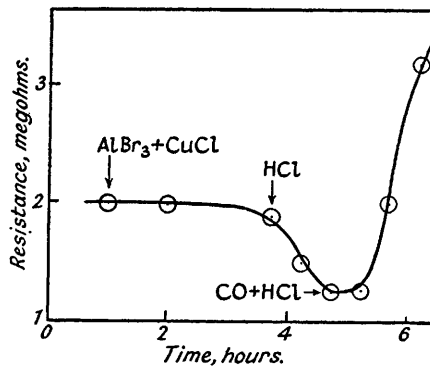
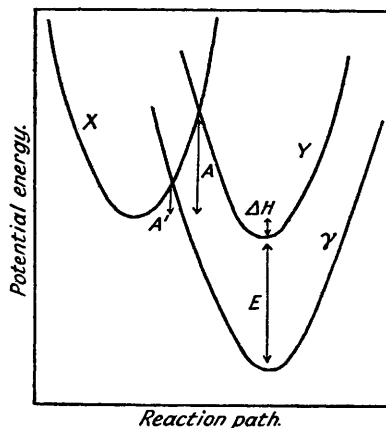


FIG. 9.

Potential-energy curves for benzaldehyde synthesis.



DISCUSSION.

Since the earliest papers it has been postulated that formyl chloride is the active species in the Gattermann-Koch reaction, but although there is evidence for its existence (Jovitschitsch and Losanitsch, *Ber.*, 1897, **30**, 135; Krauskopf and Rollefson, *J. Amer. Chem. Soc.*, 1934, **56**, 2542) it has never been isolated. Hopf and Nenitzescu (*Ber.*, 1936, **69**, 2244) describe the isolation

of a yellow-brown liquid of composition $\text{H}\cdot\text{COCl}\cdot\text{AlCl}_3\cdot\text{CuCl}$ which decomposes in water to give carbon monoxide and hydrogen chloride and is active in producing *p*-tolualdehyde from toluene.

The conductivity measurements clearly point to the formation of certain ions, and we postulate HCO^+ as the active one. In the aluminium bromide case, which we have studied in greatest detail, it is probably formed by the reaction $\text{HCl} + \text{CO} + \text{AlBr}_3 \rightleftharpoons \text{HCO}^+ + \text{AlBr}_3\text{Cl}^-$, followed by $\text{HCO}^+ + \text{C}_6\text{H}_6 \rightarrow \text{C}_6\text{H}_5\text{CHO} + \text{H}^+$ as the rate-determining step. This is of first order with respect to benzene, as found, and apparently has a small activation energy, for there is little change in yield from 4° to 30° ; the decrease in yield above this temperature has already been explained as being due to decomposition of benzaldehyde. The observed decrease in reaction velocity with increase of dielectric constant of solvent would be expected from this rate-determining step, as it involves the attack of an ion on a neutral molecule. This mechanism is in agreement with the work of Gattermann and Koch (*loc. cit.*), who obtained only *p*-tolualdehyde from toluene by this reaction—the *para*-position being active towards cationoid reagents.

Conductivity and absorption measurements suggest the following equilibrium in the presence of cuprous chloride: $\text{CO} + \text{CuCl} + \text{AlBr}_3 \rightleftharpoons \text{CuCO}^+ + \text{AlBr}_3\text{Cl}^-$. We do not need to stress that the effect of cuprous chloride cannot be to increase the thermodynamic activity of carbon monoxide; it is, however, possible that in the stationary state the reaction $\text{CuCO}^+ + \text{H}^+ \rightarrow \text{Cu}^+ + \text{HCO}^+$ gives a slightly higher concentration of HCO^+ than $\text{CO} + \text{H}^+ \rightarrow \text{HCO}^+$.

So far we have only considered the halide catalyst as an ionising agent, forming an anion and producing the cations Cu^+ , H^+ , and HCO^+ . We have ignored the interaction of halide and benzene, although it seems likely that the black oil formed between these two reactants in the presence of hydrogen chloride plays an important, although unknown rôle in Friedel-Crafts reactions.

It has been pointed out in Part I that the complex formed between the product benzaldehyde and the halide is important from the point of view of making the reaction thermodynamically favourable. This aspect is discussed on the basis of Table III, which lists the order of decreasing

TABLE III.

Yield of Ph·CHO (Table I).	<i>p</i> -C ₆ H ₄ MeAc (Dermer).	Review (Calloway).	— Δ <i>H</i> .	<i>E</i> .	Bond contraction (Skinner).
AlBr ₃	AlCl ₃	AlCl ₃	AlI ₃	AlI ₃	AlCl ₃
AlI ₃	FeCl ₃	FeCl ₃	AlBr ₃	AlBr ₃	AlBr ₃
AlCl ₃	SbCl ₅	ZnCl ₂	TiCl ₄	AlCl ₃	TiCl ₄
FeCl ₃	TiCl ₄	SnCl ₄	SnCl ₄	FeCl ₃	SnCl ₄
Inactive {	TiCl ₄	SnCl ₄	AlCl ₃	SbCl ₅	ZrCl ₄
	SnCl ₄	ZrCl ₄	SbCl ₅	TiCl ₄	SbCl ₃
	SbCl ₅	—	ZrCl ₄	SnCl ₄	—
	—	—	FeCl ₃	ZrCl ₄	
			SbCl ₃	SbCl ₃	

activity of Friedel-Crafts catalysts by various criteria. Col. 1 gives the order of activity we find for Gattermann-Koch reaction; col. 2 gives the results of Dermer and Billmeier (*J. Amer. Chem. Soc.*, 1942, **64**, 464) for the acetylation of toluene at 25° , the order being quite different at 110° . Col. 3 gives Calloway's order based on a survey of the literature (*Chem. Rev.*, 1935, **17**, 327). Cols. 4 and 5 give the halides in order of $-\Delta H$ for complex formation with benzaldehyde and *E*, the bond energy of the benzaldehyde complex, respectively, both of which are obtained in Part I. Finally, they are listed in order of their bond contractions, which Skinner (Manchester University Symposium on Friedel-Crafts Catalysis, 1945) suggests as a criterion of activity.

The placing of aluminium bromide before the iodide in col. 1 may, in part, be due to the greater solubility of the former and partial decomposition of the latter. Since the last three halides in this list are inactive, comparison is limited, but there is obviously better agreement between cols. 1 and 5 than between 1 and 4. There is also definite agreement between col. 2, where results are available for less active catalysts, and col. 5. There is a big discrepancy between cols. 1 and 6 in that aluminium bromide is much more active than the chloride.

It is seen from Tables VI and VII and the following text of Part I that for SnCl_4 , AlCl_3 , FeCl_3 , and SbCl_5 the yields of benzaldehyde at equilibrium conditions are in the order of the measured values of ΔH . The fact that the yields obtained experimentally are *not* in this order for these and other halides suggests that we are not dealing with equilibrium conditions but that

a rate process is involved. This is borne out by the calculation of yields in the case of aluminium chloride (cf. Table VII, where we show that at 25° the yield at equilibrium should be *at least* 90%). In practice, the highest yield obtainable in the time of experiment was 3%. Again, *p*-tolualdehyde is rapidly formed in 50% yield from toluene with aluminium chloride and cuprous chloride at 25°. Although the data necessary to make the calculation are not available, we should scarcely expect a large change in thermodynamic yield, but there are good grounds in electronic theory for expecting a more rapid reaction at the *para*-position. Thus, although complex formation is necessary to make the reaction thermodynamically favourable, the yield depends on the reaction velocity.

The above table shows a correlation between reaction velocity and bond energy which may be explained by treating the reaction in terms of intersection of two potential curves (Ogg and Polanyi, *Trans. Faraday Soc.*, 1935, **31**, 1375). In Fig. 9 curve *X* represents a potential curve of the initial state $C_6H_6 + CHO^+$ ($\longrightarrow C_6H_6 \cdot \overset{+}{C}HO$) and *Y* that of the final state ($C_6H_6 \cdot CHO^+ \longrightarrow H^+ + C_6H_5 \cdot CHO$). Reaction then occurs by transition at the crossing point from one curve to the other, *A* being the activation energy and ΔH the heat of reaction. When the product forms a complex with the halide of bond energy *E*, curve *Y* is displaced by this amount to *Y'*, thus lowering the activation energy from *A* to *A'* and increasing reaction velocity, which is proportional to $e^{-A/RT}$. Thus, halides with large *E* values lead to high reaction velocities, as is seen in Table III.

This view of catalytic action in the Gattermann–Koch reaction was first advanced by Eley (Ph.D. Thesis, Cambridge, 1940) and later independently by Polanyi (Manchester University Symposium on Friedel–Crafts Catalysis, 1945).

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