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THE VAPOR PHASE HYDROLYSIS OF PHENYL CHLORIDE AND BROMIDE

BY LYMAN CHALKLEY, JR.[1]

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Introductory

Meyer and Bergius in their excellent work upon the hydrolysis of the phenyl halides[2] record an experiment in which water and phenyl chloride were heated under pressure to 300°. A trace of phenol was obtained. Except for this result there appears to be no mention in the literature of the possibility of effecting the hydrolysis of phenyl halides with water alone.

In the course of a search for new methods for the synthesis of phenol, the direct hydrolysis of phenyl chloride with water alone in the vapor phase was attempted and, rather surprisingly, found to be possible. In a preliminary experiment a few grams of chlorobenzene and water were passed at atmospheric pressure through a little silica gel heated to 500°. Phenol and acid were formed.

There was not available sufficient information in regard to the free energy changes involved to permit the calculation of the equilibrium at 500° in the reaction $C_6H_5Cl + H_2O = C_6H_5OH + HCl$. Yet before proceeding further it was desirable to know at least whether or not the equilibrium was such as to greatly favor the presence of phenyl chloride in the equilibrium mixture.

Therefore a preliminary attempt was made to reverse the original reaction. Hydrogen chloride and phenol were passed through silica gel heated to 500°. Phenol was recovered, and, except for a little discoloration, appeared to be pure. It crystallized at room temperature and was completely soluble in sodium hydroxide solution. No trace of phenyl chloride was found.

As these experiments indicated that the vapor-phase hydrolysis of phenyl chloride was, at least, an interesting possibility, the work reported in this paper was carried out.

This investigation was designed essentially as a first exploration of the field. After the work here reported was completed, a notice appeared of the filing of an English patent application[3] which seemed to indicate that the present line of experiment had already been anticipated in Germany; but since a detailed discussion of the German invention will probably not

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[1] Bakelite Corporation Fellow.

[2] Kurt Meyer and F. Bergius, *Ber.*, **47**, 3155–3160 (1914).

[3] I. G. Application No. 10206 of April 4, 1928, Convention date April 6, 1927. Illus. Official J., **2054**, 2149 (May 31, 1928).

be available for some years, the results of the present investigation are published with the idea that they may be of immediate interest.

My results indicate that at 300° and above chlorobenzene and bromobenzene can be hydrolyzed by water in the presence of a variety of catalysts. At temperatures around 500° the reaction is quite rapid. Phenol, the halogen acid and diphenyl ether appear to be the chief products. Silica gel, titania, thoria, zirconia, alumina and the blue oxide of tungsten were found to bring about the hydrolysis. The only catalyst that was tried which proved to be relatively inactive was a sample of kaolin. Titania and silica gel appear to be the most active.

Under the conditions of the experiments as they were carried out it proved easy to hydrolyze from 25 to 40% of the phenyl halide in one passage over the catalyst. The unhydrolyzed halide was recovered unchanged.

Experimental

Apparatus.—The apparatus used was the simplest that could be devised and consisted of a reservoir in which water and the phenyl halide were vaporized, a reaction tube which held the catalyst and was heated by a furnace and a receiver in which the products of the reaction were collected.

The reservoir was a 250-cc. distilling flask. In this were placed both the water and the phenyl halide, and the two were vaporized together, *i. e.*, the phenyl halide was steam distilled from the distilling flask. The vapor was passed through the catalyst held in a 1-meter pyrex tube having an inside diameter of about 2 cm. and heated by a 12-inch Hoskins' tube furnace. The lower end of the reaction tube was introduced directly into the mouth of a receiving flask in which the reaction products accumulated.

The side arm of the distilling flask reservoir was bent so that it would pass directly into the reaction tube when the latter was held in a vertical position. The gas-tight connection between the side arm of the distilling flask and the reaction tube was made with a rubber stopper. It was necessary to renew this stopper occasionally because of the disintegrating effect of the phenyl halides on the rubber.

Within the reaction tube the catalyst was supported on a spiral of pyrex glass rod, which was in turn held by a constriction in the reaction tube itself. A little pure shredded asbestos was usually placed on the glass spiral and the catalyst poured upon the asbestos. Fifty cc., the amount of silica gel used, filled 18 to 20 cm. of the tube. On top of the catalyst was placed sufficient shredded asbestos to fill the tube to above the region covered by the furnace. This asbestos filling was necessary to prevent drops of liquid which condensed in the side arm of the distilling flask from falling directly into the heated portion of the tube. The asbestos layer retained 1 to 3 g. of the reaction mixture.

The temperature of the furnace was determined and regulated by means of a thermocouple and a Brown control pyrometer. The thermocouple was placed in the furnace between the reaction tube and the furnace wall. Therefore, the temperature recorded was that of the furnace rather than that of the catalyst. However, with a not too rapid flow of gas the two temperatures do not differ greatly.

The reaction tube was connected with the receiving flask by means of a rubber stopper. A small glass tube which also passed through the rubber stopper provided an air vent. In a number of experiments this vent was connected with a wet test gas meter. In no case where the catalyst was heated to less than 700° was there any evidence of the evolution of gas. Of course, hydrogen halides would not show up on the dial of the gas meter, but in only one or two experiments was the reaction product saturated with halogen acid.

In the two experiments in which the catalyst was heated to above the melting point of pyrex, the glass reaction tube was replaced by a 3-ft. length of standard $^1/_4$-inch "Ambrac" pipe. This is a copper alloy containing approximately 75% of copper, 20% of nickel and 5% of zinc. The silica gel was supported in the Ambrac pipe on a spiral of copper wire.

Materials.—The first experiments were performed with Kahlbaum's chlorobenzene. In later work this was replaced by Eastman "practical" chlorobenzene. Both Kahlbaum's and the pure grade of Eastman bromobenzene were used and no difference was noticed in their behavior.

The silica gel employed as catalyst was 8- to 14-mesh material obtained from the Silica Gel Corporation. The other catalysts were prepared in the laboratory.

Preparation of Catalysts.—Zirconia was prepared by precipitation with ammonium hydroxide from a solution of 100 g. of zirconium nitrate (Kahlbaum) in 500 cc. of water. The precipitate was washed by decantation, collected on a filter and dried at 195°.

Aluminum hydroxide was precipitated with ammonia from a solution of 300 g. of aluminum nitrate in a liter of water. The product was collected on a filter, partially dried at 195° and dried further in the reaction tube.

Ammonium tungstate (75 g.) was dissolved in a solution of 25 g. of sodium hydroxide in 500 cc. of water. Tungsten oxide was precipitated from this solution by the addition of 100 cc. of hydrochloric acid. The precipitate was collected on a filter, dried overnight at 195°, then washed repeatedly with water and again dried at 195°. The yellow oxide so produced was reduced in the reaction tube to the blue oxide. In Expt. 9, listed below, the reduction was carried out with formic acid. In Expt. 10 the reduction was effected with alcohol.

The thoria catalyst was prepared as follows: 22.3 g. of thorium oxalate was dissolved in a solution of 50 g. of ammonium bicarbonate in 350 cc. of water and the solution was evaporated on 60 cc. (30 g.) of granulated pumice. The product was dried at 130° and the thorium salt decomposed to thoria by heating in the reaction tube.

To prepare the titanium catalyst 100 g. of anhydrous titanium tetrachloride was poured into one liter of water and the mixture made alkaline with ammonium hydroxide. The product when dried at 195° was an orange-colored powder.

Operation.—In the performance of the experiments the catalyst was first charged into the reaction tube. The quantity of silica gel used was always 50 cc. when the glass reaction tube was employed. Fifty cc. of the thoria catalyst on pumice was also used. With the other catalysts, however, the effective volumes varied; and, as they actually changed in the reaction tube, these volumes were not constant and were usually less than 50 cc.

Known quantities of water and of the phenyl halide under investigation were placed in the distilling flask along with some chips of unglazed porcelain. The distilling flask with its contents was then weighed and connected with the reaction tube.

When the reaction tube was heated to the temperature at which the experiment was to be run, the mixture of water and phenyl halide was slowly distilled by means of a gas flame. As the gas supply was quite irregular, the rate of distillation varied from one experiment to another, and constituted the least controlled factor in the experiments.

At the conclusion of an experiment the distilling flask was again weighed with its contents. The receiving flask with the reaction products was also weighed. The weights of the materials entering into the reaction, and the materials recovered never differed by more than 3 g. This difference was accounted for largely, if not completely, by the liquid held on the asbestos packing in the reaction tube.

The reaction product was separated into its two components, an aqueous layer and an oily layer. The weights and volumes of these layers were determined, and a portion of the aqueous layer was titrated with $N/10$ potassium hydroxide. From this titration the quantity of acid liberated in the hydrolysis was determined. The small amount of acid dissolved in the oily layer was neglected. That the acid formed was actually hydrochloric or hydrobromic was determined in several cases by the precipitation of the silver halide.

In a number of experiments the reaction product was distilled; but as no efficient micro-fractionating column was available, distillation did not provide a satisfactory method for the determination of phenol. However, distillation did demonstrate the presence of diphenyl ether. A quantitative determination of this substance was not attempted.

Phenol was determined by the following procedure. The oily layer of the reaction product (or its distillation products) was extracted with 20% sodium hydroxide solution, the extract combined with the aqueous layer of the reaction product, the whole neutralized with hydrochloric acid, filtered, treated with excess of bromine water and the precipitated tribromophenol bromide dried and weighed. This method is not altogether satisfactory but is sufficiently accurate for the work here considered.

That the product of the hydrolysis was actually phenol was shown by the reduction of some of the tribromophenol bromide with sodium acid sulfite and comparison of the melting points of the tribromophenol so formed and of a mixture of this tribromophenol with Kahlbaum's tribromophenol.

When Eastman "practical" chlorobenzene was used small quantities of a difficultly water-soluble phenol were formed. The presence of this little-soluble phenol was shown by the fact that when the alkaline extract of a hydrolysis product prepared from "practical" chlorobenzene was neutralized the solution became cloudy. This behavior suggests that chlorophenol may have been formed from small quantities of dichlorobenzene present in the "practical" chlorobenzene used. This phenomenon was not observed when the purest grade of chlorobenzene and bromobenzene was used.

Results

In Table I are shown in considerable detail the data from eight experiments in which silica gel was used as the catalyst. Kahlbaum's chlorobenzene was used in Expts. 1 and 2. Eastman bromobenzene was used in Expts. 3, 4 and 5. Eastman "practical" chlorobenzene was used in Expts. 6, 7 and 8.

In Expts. 1 to 6, inclusive, the temperature of the furnace was 500°. In Expt. 7 it was 550° and in Expt. 8 it was 600°.

The same silica gel was used in Expts. 1 and 2. A fresh sample was used for Expt. 3 and this sample was left in the tube and used also for Expts. 4 and 5. However, between Expts. 4 and 5 the reaction tube with the catalyst in it was heated to 600° for an hour while a stream of air was blown through. A fresh sample of catalyst was used for Expt. 6. This was retained in the reaction tube for Expts. 6, 7 and 8, but was heated to 600° in air after each experiment. The silica gel darkens with use but the heating in air burns off the coloring matter and restores the gel to its original light color. The results show that it also restores the catalytic activity.

In Table II are shown the results obtained with other catalysts, and with

TABLE I

DATA USING SILICA GEL

				Materials		Rate of flow of react. mixt.		Products			
No.	Duration, hrs.	Temp., °C.	Halide	Phenyl halide, g.	Water, g.	Phenyl halide, g./hr.	Water, g./hr.	Total, g.	Oil layer, g.	Water layer, g.	Water layer, cc.
1	2	500	Cl	75	32	37	16	104.5	74.5	30	30
2	0.5	500	Cl	23.4	10	46	16	31	23	8	8
3	2.5	500	Br	30	21	12	8.4	48	28.5	19.5	19
4	2.5	500	Br	34	22	13.6	8.8	53.5	30	23	20
5	0.5	500	Br	6		12		7.5	4		
6	17 min.	500	Cl	47	19	165	67	61.5	44	16	16
7	1.5	550	Cl	23	10	15.4	6.7	30	18.5	11	9
8	1.75	600	Cl	34	14	19.5	8	46	28.5	17	15

No.	Wt. diff. reactants and prods., g.	Water layer, N	Hydrolysis, %	Residue above 190° (uncorr.), g.	Phenol weighed as tribromophenol bromide g.	Phenol based on amt. of hydrolysis, %
1	2.5	2.34	10.5	0.5	4.45	68.5
2	2.5	1.8	7	..	..	..
3	3	2.66	26.5	1.5	2.7	57
4	0.5	1.44	13.3	..	..	..
5	..	4.05	43	..	0.246	21
6	4.5	1.02	3.3	..	..	..
7	3	8.63	38	..	3.85	53
8	2	7.7	38.2	1.5	5.25	49

silica gel at low and high temperatures. In this table the quantity of acid formed is given alone as being the most accurate index of hydrolysis (except when the metal tube was used). Fresh samples of catalyst were employed for each of the experiments 9 to 16, inclusive, and for 21. In the low-temperature experiments (16 to 20) there was practically no fouling of the catalyst and, therefore, fresh catalyst was not needed. As the silica gel used contained a trace of acid it was necessary to wash it with steam until the condensate was neutral before beginning the experiments. Between Expts. 21 and 22 the silica gel was heated in air to 845° for fifteen minutes.

Discussion

The experiments recorded in Table I show that phenyl chloride and phenyl bromide are readily hydrolyzed by steam when passed over silica gel at 500 to 600°. If Expts. 1, 2 and 6 are compared it will be seen that the amount of hydrolysis increases as the rate of flow of the reaction mixture over the silica gel is diminished. There is, therefore, no reason to believe that equilibrium in the hydrolysis of phenyl chloride was reached in the experiments. It is probable that the reaction mixture of phenyl chloride and steam of the composition used would undergo a greater hydrolysis than 10% at 500° if its contact with the catalyst were prolonged.

TABLE II

RESULTS WITH OTHER CATALYSTS

No.	Catalyst	Temp., °C.	Dur. of run, min.	Total wt. of prods., g.	Aq. layer, cc.	Acidity of aq. layer, $N/10$	Hydrolysis %
9	Blue tungsten oxide	500	30	Product alkaline from NH_3			
10	Blue tungsten oxide	500	30	28.5	7	1.88	0.73
11	ZrO_2	500	30	46	12	6.9	2.9
12	Al_2O_3	500	60	29	7.5	5.1	2.3
13	ThO_2	500	45	42.5	11	4.2	1.7
14	Kaolin	500	30	16	3	0.07	0.02
15	TiO_2	500	30	33.5	10	20.0	10.0
16[a]	SiO_2	260	30	5	..	0.05	..
17[b]	SiO_2	300	30	..	..	.04	..
18	SiO_2	350	30	13	..	1.11	..
19	SiO_2	400	30	16.5	..	4.45	..
20[c]	SiO_2	300	30	22.5	..	0.36	..
21	SiO_2	800	15	19	..	13.3	..
22	SiO_2	500	Short run indicated acid and phenol formed in quantity				

The formation of phenol was demonstrated in all experiments except No. 14.

[a] Faint trace of phenol. [b] Trace of phenol. [c] Phenol present.

At this same temperature, 500°, phenyl bromide hydrolyzes more completely than phenyl chloride under the conditions of the experiments. However, the phenyl bromide reaction mixture contained a higher molecular proportion of water than the phenyl chloride reaction mixture, and it was possible to pass the phenyl bromide over the catalyst at a slower rate.

At 550 and 600° phenyl chloride was found to hydrolyze to the extent of 38% under the conditions of the experiments.

In the last column of Table I are shown the yields of phenol obtained. The calculated yields of phenol corresponding to the halogen acid found are taken as 100%, and the figures given in the last column of Table I were computed on this basis. That is, for instance, the phenol found in Expt. 1 was 68.5% of 10.5% of the phenyl chloride used. The actual gross yield of phenol in Expt. 1 was about 7% of the phenyl chloride passed over the catalyst.

As already mentioned, the figures given for phenol yields are not very accurate, and that given for Expt. 5 is particularly questionable because of the small quantity of materials used in the reaction. However, it is safe to conclude that the chief reaction product is phenol but that the yield of phenol falls short of 100% of the phenyl halide hydrolyzed.

Under the conditions used a considerable amount of diphenyl ether is to be expected since Sabatier and Espil, working under conditions similar to those employed here, have shown that the system phenol–diphenyl ether–water comes to equilibrium when diphenyl ether constitutes about half, by weight, of the organic constituents.[4] Therefore, in calculating a net yield

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[4] Sabatier and Espil, *Bull. soc. chim.*, [4] **15**, 228 (1914).

from the hydrolysis, phenol and diphenyl ether should be considered together. There is not enough information to permit the calculation of such a net yield from these experiments, but it should be fairly good, at least.

Experiment 4 compared with Expt. 3 indicates a decrease in activity of the catalyst due to fouling. Experiment 5 indicates that the activity of the catalyst has been restored by the burning-off process.

The first results reported in Table II show that the hydrolysis of phenyl halides may be effected by a variety of hydration catalysts. As already pointed out, the various samples of catalyst were not used in the same state of subdivision and in the same amounts. As other factors also influence the activity of contact catalysts, the results obtained for the individual samples used cannot be rigidly compared. However, it appears that silica gel and titania are the most active; kaolin is the least active; and phenol was obtained from all of the experiments except the one in which kaolin was used.

Experiments 16 to 20 were carried out to learn something of the temperature range over which the hydrolysis took place. They show that at 300° both phenyl chloride and bromide hydrolyze at a measurable speed.

Conclusions

Phenyl chloride and phenyl bromide are readily hydrolyzed to the extent of at least 25 to 40% by passage of their vapor mixed with steam over silica gel at 500 to 550° and ordinary pressures.

The ability to catalyze the hydrolysis of the phenyl halides is not peculiar to silica gel but is possessed by a variety of hydration catalysts: silica gel, titania, alumina, thoria, zirconia and the blue oxide of tungsten. A sample of kaolin showed little activity.

Silica gel and titania appear to be the most active.

With silica gel as the catalyst the reaction proceeds at a measurable speed at 300° and above.

The products of the reaction are: the halogen acid, phenol, diphenyl ether and probably smaller quantities of other organic compounds. No pronounced halogenation of the phenol obtained in the primary reaction was noticed and no water-insoluble gases were evolved.

The activity of silica gel which has been fouled by use may be restored by heating the catalyst in air or oxygen. The activity of titania can be regenerated in the same way.

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