per second for gases and possibly not more than 2 feet per second for liquids. With K as large as 10, this would only amount to 16.5 and 0.6 foot of fluid, if the fluid were a gas or a liquid, respectively. If the gas were air at ordinary conditions, the above loss would correspond to only 0.25 inch of water.

The value of K for a resistance, such as a perforated plate or grid work of baffles, depends upon the ratio of the combined area of the distributed openings to the total flow area. If the openings are considered as submerged orifices of discharge coefficient C and combined area A_0, the relationship between K and the area ratio can be estimated for large K values by:

$$CA_0 \sqrt{\frac{2g}{w}(p_1 - p_2)} = AV_{av}$$

and

$$K\frac{V^2_{av}}{2g} = \sqrt{\frac{p_1 - p_2}{w}}$$

Thus

$$K = \left(\frac{A}{A_0}\right)^2 \frac{1}{C^2}$$

A value of $K = 10$, if C is assumed to be 0.6, corresponds to

$$\frac{A}{A_0} = \sqrt{10 \times \overline{0.6}^2} = 1.9$$

In other words, for $K = 10$, the combined area of the uniformly distributed openings should comprise approximately half the total cross-sectional area. It is assumed, of course, that the flow through the openings is in the turbulent region.

Obviously, in the choice of the kind of resistance it is essential to consider the possibility of fouling. The reason is not so much that the energy loss might become excessive, but rather that uneven build-up or coating on the resistance might actually aggravate rather than correct an already maldistribution. In some applications fouling will occur eventually, regardless of the resistance design, but it is often feasible to provide means of cleaning the resistance by brushing, rapping, or fluid jet lancing.

In each of the two methods described, it must be realized that the downstream station designated by subscript 2 is immediately after the transition in method 1 and immediately following the resistance in method 2. Thus, station 2 is not situated far enough downstream for wall friction to have produced any important influence on the velocity profile. In this regard, however, a downstream distance equal to several channel widths is usually required to establish the normal distribution due to wall friction.

In the preceding derivations it is tacitly assumed that the flow is rectilinear and parallel to the channel axis. Actually, for a very irregular distribution and particularly for one that is extremely asymmetrical, there will be some cross flow and mixing of the fluid before reaching and while passing through the transition or resistance. This will cast some doubt on the accuracy of Equation 1 and can conceivably alter the effective value of K over portions of the otherwise uniform resistance. Attention is also called to the fact that the distribution ahead of either the transition or the resistance will be influenced somewhat by the presence of these structures themselves. But even under drastic conditions the equations should, at least, serve as fair approximations.

NOMENCLATURE

p = static pressure in fluid, lb./sq. ft.
V = velocity of flow, ft./sec.
V'_{2av} = downstream velocity corresponding to V_{1av} (Equation 4), ft./sec.
δ = velocity ratio defined by Equation 5, dimensionless
A = cross-sectional area of flow, sq. ft.
da = differential cross-sectional area of flow, sq. ft.
g = acceleration due to gravity, ft./sec./sec.
w = weight density of fluid, lb./cu. ft.
K = energy-loss coefficient due to resistance, dimensionless
α = kinetic energy coefficient (Equation 17), dimensionless

Subscripts
1, 2 = upstream and downstream conditions, respectively
av, *max* = average and maximum values

Benzoic Acid from Phosgene and Benzene

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IN CONNECTION with the insect and rodent control program of the armed forces during the war, several esters of benzoic acid, particularly benzyl benzoate, were found to be valuable as miticides. Consequently, an ambitious production schedule for benzyl benzoate was planned. This program was of such proportion that production methods for starting materials such as benzyl chloride and benzoic acid which did not depend upon toluene as the basic chemical had to be investigated.

In this connection the Chemical Warfare Service undertook an exploratory laboratory study of the aluminum chloride–catalyzed reaction between benzene and phosgene with the view of obtaining benzoic acid. A specific advantage of the process lies in the fact that chlorine-free benzoic acid is necessarily formed:

$$C_6H_6 + COCl_2.AlCl_3 \longrightarrow C_6H_5COCl.AlCl_3 + HCl \text{ (gaseous)}$$

$$C_6H_5COCl.AlCl_3 + 8H_2O \longrightarrow C_6H_5COOH + Al(H_2O)_6^{+++} + H_3O^+ + 4Cl^-$$

Although there are several references in the early published chemical literature on the liquid-phase reaction between phosgene and benzene in the presence of aluminum chloride (*2*), it remained for Wilson and Fuller (*3*) to point out the feasibility of this process for the production of benzoic acid. Wilson and Fuller discovered that, when benzene is added slowly to a cold mixture of phosgene, carbon disulfide, and aluminum chloride, the major reaction product formed is benzoyl chloride along with a smaller amount of benzophenone. Under the reaction conditions employed, the benzoyl chloride formed was hydrolyzed and subsequently isolated as benzoic acid.

The data of Wilson and Fuller indicate that carbon disulfide is an essential diluent in the reaction mixture. In the absence of carbon disulfide, these authors report a very low yield of benzoic acid, the major product being benzophenone. The process employing carbon disulfide as reaction solvent was later patented by Norris and Fuller (*1*), who also claimed that hydrocarbons, free of olefins, may be substituted for carbon disulfide.

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The preparation of benzoic acid through the aluminum chloride–catalyzed reaction between benzene and an excess of liquid phosgene was found to be superior to the previously known reaction between these reagents in such inert reaction solvents as carbon disulfide. The yields of benzoic acid, in the process here described, are dependent upon the reaction time and the molar ratios of aluminum chloride to benzene and phosgene to benzene, respectively. For a molar relation of phosgene to benzene to aluminum chloride equal to 3 to 1 to 1, a maximum yield of benzoic acid of 55–58% of theory, based on benzene, is obtained after a reaction period of 16–18 hours at 3–8° C. The by-product of the reaction is benzophenone. An increase of the aluminum chloride–benzene molar ratio above unity accelerates the reaction but does not increase the over-all yield of benzoic acid. A decrease of the phosgene–benzene molar ratio below 3 to 1 reduces the yield of benzoic acid and increases the yield of benzophenone. The reaction between phosgene and benzene produces a grade of benzoic acid which is free of nuclear chlorine.

That carbon disulfide, or some other inert diluent, had to be present in the reaction mixture was explained by Wilson, Fuller, and Norris in the following way: A slow addition of benzene to a cold mixture of carbon disulfide, aluminum chloride, and phosgene formed predominantly the  $C_6H_5-\underset{\underset{O}{\parallel}}{C}-Cl.AlCl_3$ complex which was insoluble in carbon disulfide. Thus, carbon disulfide served to remove the desired complex from the reaction medium as an insoluble solid, so that the complex, once formed, was denied the opportunity of reacting with more benzene to form the undesired benzophenone.

The present authors checked the work of Wilson and Fuller and found, in addition to the undesirability of introducing carbon disulfide into the reaction mixture, that the presence of this diluent contaminates the benzoic acid product with a small amount of a sulfur-containing impurity of highly obnoxious odor. When hexane was tried in place of carbon disulfide, no benzoic acid was obtained.

It was found that these difficulties could easily be obviated by conducting the reaction in an excess of liquid phosgene and omitting carbon disulfide or any other foreign diluent from the reaction mixture. In general, the results obtained by this method are more reproducible and, what is more important, the elimination of carbon disulfide leads to purer products. Yields for both procedures are of the same order of magnitude.

GENERAL PROCEDURE

A desired quantity of phosgene (ranging from 1.0 to 6.0 moles) was condensed in a tared 500-ml., three-neck, round-bottom flask by immersing the flask in an ice water bath. After the proper amount of liquid phosgene had been weighed into the flask, the flask was equipped with a mercury-seal stirrer, a thermometer, a dropping funnel, and a gas escape tube terminating in a calcium chloride trap. After being mounted the reactor flask was immersed in a 4-pint Dewar flask which was charged with an ice water mixture. The temperature of the phosgene was thus maintained at 3–8° C. A desired quantity of aluminum chloride, depending upon the run made (Table I), was added to the liquid phosgene with stirring. After addition of all the aluminum chloride, benzene was allowed to drop into the reaction medium at a slow rate, indicated in more detail in Table I. The entire reaction mixture was then stirred at 3–8° C. for a previously determined length of time.

At the end of the reaction period, the contents of the reaction flask were poured onto about 1 to 1.5 liters of cracked ice. This step served to hydrolyze the aluminum chloride complex and thus liberate benzoyl chloride. In those runs where an excess of aluminum chloride was used with respect to benzene (i.e., a mole ratio of aluminum chloride to benzene greater than 1), it was observed that the hydrolysis went directly to benzoic acid and left but little unhydrolyzed benzoyl chloride.

After the hydrolyzed reaction product had reached room temperature and all of the excess phosgene had either been decomposed or evaporated off, the organic layer was separated and the aqueous layer was extracted twice using about 75-ml. of diethyl ether in each extraction.

The combined organic product–extract layers were poured into 750 to 1000 ml. of approximately 7–8% aqueous sodium hydroxide and warmed. The ether was expelled, and any residual benzoyl chloride was transformed into sodium benzoate. After cooling, the solution was filtered free of benzophenone. To the filtrate a quantity of concentrated hydrochloric acid sufficient to precipitate all of the benzoic acid was added with stir-

TABLE I. DATA ON REACTION OF PHOSGENE WITH BENZENE

Expt. No.	$COCl_2$, Moles	$AlCl_3$, Moles	C_6H_6, Moles	Addition of C_6H_6		Reaction after Adding C_6H_6		Yield of Benzoic Acid			Benzophenone Formed		Benzene Accounted For in Products	
				Time, min.	Temp., ° C.	Time, hr.	Temp., ° C.	Grams	Mole	% of theory	Grams	Mole	Mole	% of total
1	2.0	0.5	0.5	10	4–5	2	4–5	9.5	0.080	15.6	..	...	...	..
2	2.0	0.5	0.5	10	4–5	4	4–6	20.0	0.164	32.8	..	...	..	..
3	2.0	0.5	0.5	10	3–6	8	5–6	25.6	0.210	41.9	..	...	...	..
4	2.0	0.5	0.5	15	4–9	10	4–6	22.4	0.183	36.7[a]	..	...	...	..
5	2.0	0.5	0.5	10	3–7	12.5	3–5	29.2	0.239	47.8	..	...	...	..
6	2.0	0.5	0.5	15	4–8	16	3–5	26.5	0.217	43.4[b]	..	...	...	..
7	2.0	0.5	0.5	15	3–8	20	4–6	32.9	0.269	53.9	12.5	0.069	0.338	67.6
8	2.0	0.5	0.5	20	4–5	20	5–6	30.4	0.249	49.8[b]	16.4	0.090	0.339	67.8
9	3.0	0.5	0.5	55	4–5	20	5–6	34.6	0.283	56.7	..	...	...	..
10	2.0	0.5	0.5	15	3–4	24	4–6	34.8	0.285	57.0	..	...	...	..
11	2.0	0.75	0.5	20	4–5	2	4–5	18.0	0.147	29.5	10.9	0.060	0.207	41.4
12	2.0	0.75	0.5	32	4–5	6.5	4–5	32.3	0.264	52.9	15.6	0.086	0.350	70.0
13	2.0	0.75	0.5	25	4–5	18	4–7	35.5	0.291	58.1	19.9	0.109	0.400	80.0
14	2.0	1.0	0.5	32	4–5	2	4–5	25.6	0.210	41.9	12.3	0.068	0.278	55.6
15	2.0	1.0	0.5	20	4–5	6.25	4–6	35.1	0.287	57.5	14.6	0.080	0.367	73.4
16	2.0	1.0	0.5	30	4–6	18	4–8	35.3	0.289	57.8	21.3	0.117	0.406	81.2
17	1.5	0.75	0.5	20	4–5	6	4–6	35.1	0.287	57.5	18.5	0.102	0.389	77.8
18	1.0	0.75	0.5	27	4–5	6	4–6	29.5	0.242	48.3	23.9	0.131	0.373	74.6
19	1.5	1.0	1.0	47	4–8	6	4–6	51.3	0.420	42.0	43.8	0.240	0.660	66.0
20	1.5	1.5	1.0	31	5–6	6	5–7	46.2	0.378	38.7	49.3	0.271	0.649	64.9
21	1.0	1.0	1.0	28	4–5	6	5–8	41.8	0.342	34.2	52.5	0.288	0.630	63.0

[a] Slight loss due to alternate method of separation.
[b] Small mechanical losses during handling of product.

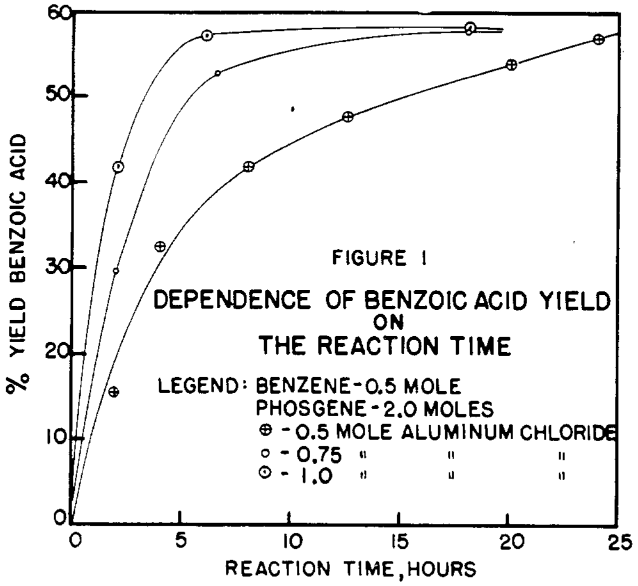

FIGURE 1

DEPENDENCE OF BENZOIC ACID YIELD ON THE REACTION TIME

ring. The precipitated acid-brine mixture was cooled to about 5–10° C., and subsequently the benzoic acid was filtered off with suction and dried in air. When dry its weight was determined.

In the procedure described, the initial crude reaction product was separated immediately from the aqueous layer containing dissolved aluminum chloride. A more troublesome procedure for the isolation of benzoic acid, leading, however, to slightly lower yields as compared with the procedure just described, took advantage of the amphoteric property of hydrated aluminum salts. After the crude reaction mixture was poured onto ice and the hydrated reaction mixture had reached room temperature, sufficient 40–50% aqueous sodium hydroxide solution was added to convert all the aluminum to the soluble aluminate, and sufficient (an excess) to convert benzoic acid and benzoyl chloride to sodium benzoate. The solution was filtered free of benzophenone and the filtrate was acidified as before with concentrated hydrochloric acid. At this point sodium aluminate was again transformed into gelatinous aluminum hydroxide together with the precipitation of free benzoic acid from sodium benzoate. An excess of hydrochloric acid again dissolved the aluminum hydroxide as its chloride, and left benzoic acid ready for suction filtration as before. The necessity of using many more times the quantities of sodium hydroxide and hydrochloric acid as compared with the first procedure made this latter method less desirable. Another disadvantage was the likelihood of obtaining solid sodium chloride, particularly if insufficient quantities of water were employed, and thus necessitating purification of the crude benzoic acid obtained. In the runs of Table I the first procedure for the isolation of benzoic acid was followed throughout, except in run 4 where the latter method was employed.

Although no attempts were made in this investigation to recover unused excess phosgene, it is believed that this can be accomplished with the aid of proper refrigeration equipment.

The results of twenty-one runs, together with specific reaction conditions in each, are compiled in Table I.

ANALYSIS OF DATA

The data in Table I reveal the fact that the reaction between phosgene and benzene is dependent upon three main factors: reaction time, molar ratio of aluminum chloride to benzene, and molar ratio of phosgene to benzene.

For a molar ratio of aluminum chloride to benzene of 1 to 1, the reaction occurs at a slow rate, reaching the 50% conversion point only after 16 to 18 hours:

Expt. No.[a]	Reaction Time, Hours	Yield of Benzoic Acid, %	Expt. No.[a]	Reaction Time, Hours	Yield of Benzoic Acid, %
1	2	15.6	5	12.5	47.8
2	4	32.8	7	20	53.9
3	8	41.9	10	24	57.0

[a] Reagents used: 0.5 mole benzene, 0.5 mole aluminum chloride, 2.0 moles phosgene.

If the molar ratio of aluminum chloride to benzene is increased to a value greater than unity, the rate of reaction is markedly enhanced (Figure 1). There is, however, no increase in over-all yield. The following results also show that the yield of benzophenone increases slightly as the aluminum chloride–benzene ratio is raised:

Expt. No.[a]	$AlCl_3$, Moles	Reaction Time, Hours	Yield of Benzoic Acid		Yield of Benzophenone, Grams
			Grams	%	
1	0.5	2	9.5	15.6	..
3	0.5	8	25.6	41.9	..
7	0.5	20	32.9	53.9	12.5
11	0.75	2	18.0	29.5	10.9
12	0.75	6.5	32.3	52.9	15.6
13	0.75	18	35.5	58.1	19.9
14	1.0	2	25.6	41.9	12.3
15	1.0	6.25	35.1	57.5	14.6
16	1.0	18	35.3	57.8	21.3

[a] Reagents used: 0.5 mole benzene, 2.0 moles phosgene.

From the standpoint of economics, as little phosgene as practicable should be used in this reaction. The effect of varying molar ratios of benzene to phosgene on the yield of benzoic acid follow:

Expt. No.[a]	$AlCl_3$, Mole	$COCl_2$, Moles	Yield of Benzoic Acid		Yield of Benzophenone, Grams
			Grams	%	
21	0.5	0.5	20.9	34.2	26.3
19	0.5	0.75	25.7	42.0	21.9
20	0.75	0.75	23.1	38.7	24.7
18	0.75	1.0	29.5	48.3	23.9
17	0.75	1.5	35.1	57.5	18.5
12	0.75	2.0	32.3	52.9	15.6

[a] 0.5 mole of benzene used in each experiment. The reaction period was 6 hours except in experiment 12, where it was 6.5 hours.

The data indicate that the amount of benzophenone increases as the molar ratio of aluminum chloride to benzene is increased. Experiment 17 shows that the molar ratio of phosgene to benzene should not be less than 3 to 1. Experiment 9 (Table I) shows that increasing the amount of phosgene from 2 to 3 moles per 0.5 mole of aluminum chloride and benzene each has but little effect on the total yield of benzoic acid produced; that is, the yield of acid is not increased above the 57% value which appears to be easily attainable under more economic conditions (experiments 13 and 17, Table I).

The combined effects of aluminum chloride and phosgene concentrations as given in the two preceding tables point to the conclusions that molar ratios of phosgene to aluminum chloride to benzene of 3 to 1.5 to 1 are probably best suited for this process. These ratios give the maximum obtainable yield of benzoic acid in a reasonably short time.

The reaction between phosgene and benzene produces a grade of benzoic acid which is highly pure and free of chlorine, with a minimum effort in purification. The products described in this report were entirely free of chlorine (less than 0.01%) after one recrystallization from water.

Attempts to use catalysts other than aluminum chloride were without success. The reaction has not yet been studied in pilot plant equipment.

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