Synthesis of Some Organic Compounds by Electric Discharge. I-V.

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(Received December 26, 1950)

Introduction

Most of the studies on the organic reactions in the electric discharge have been very qualitative in nature. For example, even the synthesis of simple organic compounds by non-disruptive electric discharge has not yet been succeeded from both the practical and the theoretical point of view. The reason for this is that the variables to obtain a desired compound are not systematically examined and also that the identification of the reaction product is not made accurately.

During these five years, the authors have found some interesting reactions occurring in silent discharge, which had not yet been reported in the literature. These reactions are summarized as follows.

(1) Formation of phenol from benzene and air.

(2) Formation of benzyl alcohol, benzaldehyde, benzoic acid and cresols from toluene and air.

(3) Formation of cyclohexanol and cyclohexanone from cyclohexane and air.

(4) Formation of aniline and other basic compounds from benzene and ammonia.

The authors have then undertaken the present study in order to establish a new practical method of the synthesis of these compounds. The study also seeks to establish the fundamental chemistry of these synthetic reactions in the discharge and at the same time to present some mechanisms and theory of these reactions.

Synthesis of Phenol from Benzene.(1) (II, III)

When a mixture of benzene and air was discharged in an ozonizer under suitable conditions, phenol was obtained in yields as high as 30% of the total reaction product. The apparatus was a simple one as is shown in Fig. 1.

Air was bubbled into benzene reservoir at a definite temperature in order to obtain a mixture of benzene and air of constant composition. The content of benzene gas in air could be varied by changing the temperature of the reservoir and the rate of flow of air. The mixed gas was then flowed into the operated ozonizer at constant velocity. The exit gas was passed through 2 N sodium hydroxide solution and then cooled through a trap to 5° to condense almost of the unconverted benzene together with the reaction product which was not absorbed in the alkali solution. A part of the unconverted benzene and gaseous reaction products, if existed, were allowed to exhaust. During the reaction, solid brown deposit was formed on the glass wall of the ozonizer. This deposit, after the reaction, was dissolved by washing the wall with an alkali solution and the latter was added to the above sodium hydroxide solution in which the phenolic substances formed was contained.

Separation of phenol and other acidic reaction products from the sodium hydroxide solution was carried out according to the following scheme.

Phenolic substances thus obtained boiled at 76-78° at 11 mm.Hg and was thought to consist of pure phenol. It was purified by repeating the distillation. The final product

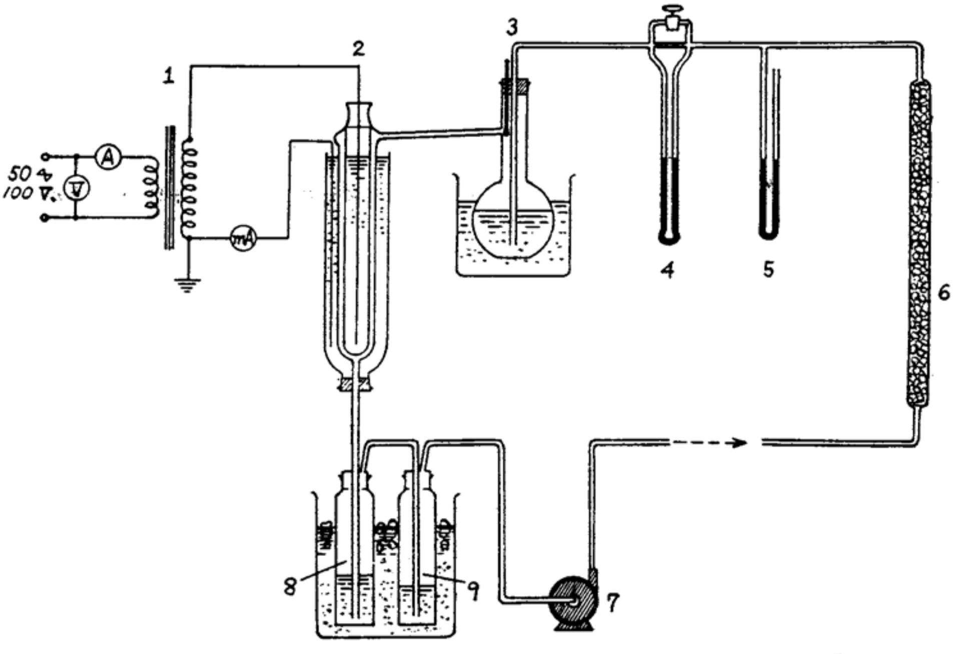

Fig. 1.—1, Transformer; 2, discharge tube; 3, benzene reservoir; 4, flowmeter; 5, manometer; 6, $CaCl_2$ tube; 7, blower; 8, NaOH solution; 9, trap.

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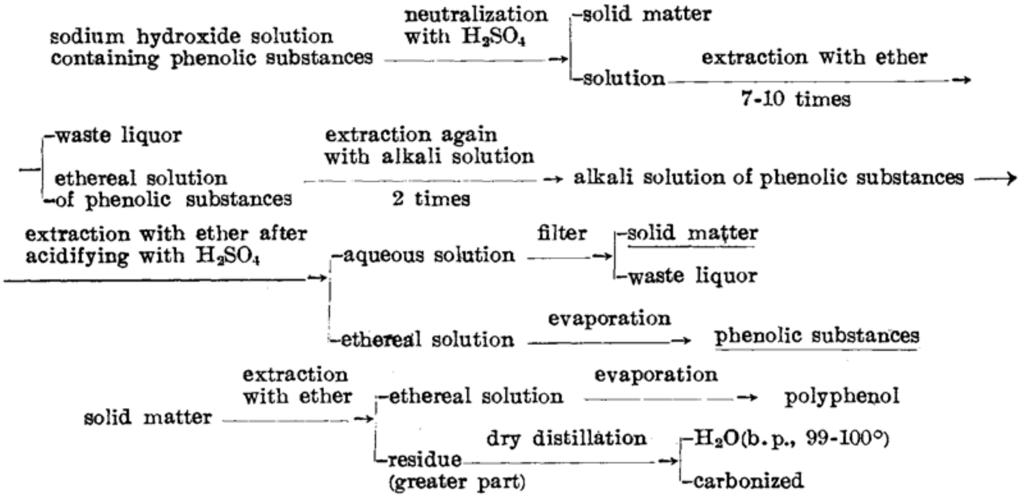
(1) A part of the research was already published in Japanese in *Jour. Chem. Soc. Japan*, **71**, 518 (1950).



boiled at 177-178° at atmospheric pressure and crystallized at room temperature.

Conditions of experiments and results obtained are shown in Table 1.

Table 1

	Run 1	Run 2	Run 3
Electrical factor			
Cycle	50	50	50
Volt (secondary), kV.	15	15	15
Current (″), mA.	1.25	1.25	1.25
Temp. of ozonizer, °C.	50	50	50
Composition of gas used, Vol.%			
C_6H_6	5.0	6.5	7.5
Air	95.0	93.5	92.5
Temp. of gas, °C,	30	20	20
Gas pressure, mm.	750	750	750
Rate of flow, l./hr.	120	120	30
Time, hr.	56	17	15.5
C_6H_6 used, kg.	1.0	0.5	0.13
Reaction products			
Phenol, g.	2.5	1.3	1.2
Other products, g.	6.0	3.0	3.7
Conversion efficiency, %			
(grams of liquid and solid reaction products/grams of C_6H_6 used) × 100	0.85	0.86	3.8
% of phenol in total reaction product	30	30	25

Magnitude of the tube: all glass (pyrex) ozonizer. Effective length, 22 cm.; space gap, 0.25 cm.; diameter, 4 cm.

Formation of gaseous decomposition products of benzene has not been able to recognize exactly.

As is clear from the table, under the conditions described above, 0.85-3.8% of benzene used could be converted to phenol and other reaction products by running it with air one time in the ozonizer (effective length, 22 cm.). The quantity of phenol in the reaction product was reached to about 30% and the electrical energy consumed was about 150-250 kwhr./1 kg. phenol.

In these experiments, solid brown deposit was always formed on the glass wall and it is the main reason for the decrease of the conversion of benzene to phenol. Later, it was found that when the glass wall of the discharge tube was covered with liquid layer of benzene, the formation of solid deposit was reduced to to a very small quantity and the reaction product consisted mainly of phenol. In this case, the mixed gas of benzene and air, before flowing into the ozonizer, was cooled by the methods shown in Fig. 2, so a part of benzene was condensed and it was run down on the glass wall of the ozonizer, where the silent

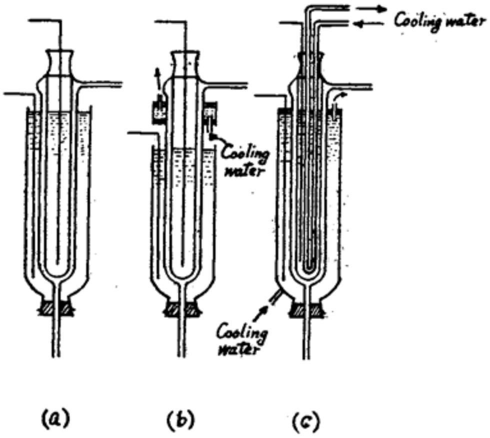


Fig. 2.—(a), air cooling; (b) and (c), water cooling.

discharge occurred. Other procedures were almost the same as the case described above. Results obtained are shown in Table 2.

In this case, the electrical energy consumed was about the same as in the case of Table 1.

Table 2

Discharge tube	Run 1	Run 2	Run 3
	(same as Table 1)		
Electrical factor			
Cycle	50	50	50
Volt (secondary), kV.	15	15	15
Current (″), mA.	1.3	1.3	1.3
Rate of flow of air, l./hr.	25	50	50
Temp. of gas, °C.	45	64	60
Gas pressure, mm.	755	765	755
Temp. of ozonizer, °C.	58	58	20
Method of cooling of the mixed gas	Fig. 2, (a)	Fig. 2, (b)	Fig. 3, (c)
Rate of ruuning of liquid C_6H_6, cc./hr.	120	550	550
Time, hr.	60	30	32
C_6H_6 used, kg.	6.3	14.5	15.5
Reaction product			
Phenol, g.	3.8	1.7	1.6
Other products, g.	2.0	0.7	0.4
Conversion efficiency (same as Table 1), %	0.1	0.017	0.013
% of phenol in total reaction product	66	71	80

Table 3

	Run 1	Run 2	Run 3	Run 4
Magnitude of the tube (all glass (pyrex) ozonizer)				
Effective length, cm.	24	25	50	70
Space gas, cm.	0.25	0.25	0.25	0.25
Diameter (outer), cm.	4.0	3.5	3.5	3.5
Electrical factor				
Cycle	50	50	50	50
Volt(secondary), kV.	15	15	15	15
Primary kwhr.	1.32	1.36	2.24	2.85
Temp. of ozonizer, °C.	40	40	40	40
Composition of gas used, Vol. %				
$C_6H_5CH_3$	1.8	2.1	2.1	2.2
Air	98.2	97.9	97.9	97.8
Temp. of gas, °C.	17	18	18	18
Gas pressure, mm.	765	725	725	725
Rate of flow, l./hr.	60	60	60	60
Time, hr.	110	80	80	62
$C_6H_5CH_3$ used, g.	510	420	418	332
Total reaction product, g.	17.9	14.1	27.1	28.5
Conversion efficiency, %				
(grams of total reaction product/ grams of $C_6H_5CH_3$ used) × 100	3.5	3.4	6.5	8.6

The Oxidation of Toluene. (IV)

By using the same silent discharge apparatus described in Fig. 1, results were obtained which are summarized in Table 3. In this case, the variation of the conversion efficiency due to the effective length of the ozonizer was examined.

Analysis of the Reaction Product :—The reaction product was caught in the trap containing 5 *N* sodium hydroxide solution and some toluene which was cooled to 4-5°.

The total product was separated into the neutral part (dissolved in unconverted toluene) and the acidic prat (dissolved in 5 *N* sodium hydroxide solution). The neutral part, after driving off the unconverted toluene by distillation, was subjected to fractional distillation under reduced pressure. It was thus separated into four fractions which had the properties shown in Table 4 and were identified as benzaldehyde (Fraction 1) and benzylalcohol (Fraction 2) respectively. Recovery of acidic compounds from the alkali solution was carried out as usual and the crude product thus obtained was also subjected to fractional distillation under reduced pressure into four fractions. Fraction 2 and 3 had the properties noted in Table 4 and were identified as *o*-cresol and benzoic acid respectively.

Table 4

Neutral Part		Acidic Part	
Fraction (B. p., °C.)	Properties	Fraction (B. p., °C.)	Properties
1. $(50\text{-}55)_5$	B.p., 179-181°C. $n_D^{20}=1.545$ benzalphenylhydrazone M. p., 156°C.	1. $(20\text{-}35)_{35}$	odor like to CH_3COOH
2. $(70\text{-}75)_5$	B.p., 200-205°C. $n_D^{20}=1.540$	2. $(60\text{-}65)_5$	B. p., 187-191°C. $n_D^{20}=1.543$ color reaction with $FeCl_3$, +
3. $(100\text{-}120)_5$	$n_D^{20}=1.567$	3. $(100\text{-}110)_5$	M.p., 121°C. sublime
4. Residue		4. Residue	

Table 5

	Run 1	Run 2	Run 3	Run 4
(1) Benzyl alcohol, g.	5.2	3.7	7.2	8.7
(2) Benzaldehyde, g.	3.3	1.8	3.7	6.7
(3) Benzoic acid, g.	0.3	0.5	0.7	0.8
(4) *o*-Cresol, g.	4.8	4.0	6.8	4.0
(1)+(2)+(3)+(4)/ Total reaction product × 100, %	76	71	68	71
(1)+(2)+(3)+(4)/ kwhr. g.	10.3	7.4	8.2	7.1

The yield of the main reaction product is shown in Table 5.

Mean percentage of each compounds in the reaction product was as follows: (1) Identitified products: benzylalcohol 26-30%, benzaldehyde 13-20, benzoic acid 2-4%, *o*-cresol 25-28%; (2) unidentified products: solid deposit on the wall 9-10%, fraction 3 of the neutral part 4-5%, fraction 1 of the acidic part 1-4%, distillation residue 11-17%.

In the ozonizer, toluene was found to be oxidized more easily than benzene. It was converted to the extent of 3.5-8.6% to give benzylalcohol, benzaldehyde, benzoic acid and cresols as main products, by running it only one time in the ozonizer. (Effective length, 25-75 cm.). Solid brown deposit formation on the glass wall was very small in this case.

Oxidation of side chain (1) and nucleus (2) of toluene are the main reactions. The ratio of the two reactions (1)/(2) was about 1.6-1.9 in the above experiment. But it may somewhat vary according to the voltage applied, the effective length of the tube and the rate of the flow of gas.

Oxidation of Cyclohexane. (V)

By the oxidation in an ozonizer, cyclohexane gave a mixture of cyclohexanol and cyclohexanone with a fair conversion efficiency. Methods of experiments were almost the same as the above two cases. The results are summarized in Table 6.

Table 6

	Run 1	Run 2	Run 3
Magnitude of the tube (all glass (pyrex) ozonizer)			
Effective length, cm.	75	75	75
Space gap, cm.	0.25	0.25	0.25
Diameter (outer), cm.	3.5	3.5	3.5
Electrical factor			
Cycle	50	50	50
Volt (secondary), kV.	20	25	20
Primary kwhr.	1.7	2.4	1.35
Temp. of ozouizer, °C.	45-55	55-60	45-50
Composition of gas used, Vol. %			
Cyclohexane	7.7	6.9	6.0
Air	92.3	31.1	94.0
Temp. of gas, °C.	20-22	17-19	15-19
Gas pressure. mm.	740	740	740
Rate of flow, l./hr.	21.7	21.5	50.5
Time, hr.	50	50	40
Cyclohexane used, g.	314	282	456
Total product, g.	80.2	122	80.5
Cyclohexanol, g.	44.1 (55%)	54.1 (44%)	50.3 (63%)
Cyclohexanone, g.	14.7 (18%)	30.4 (25%)	17.7 (22%)
Adipic acid, g.	5.0 (6%)	6.1 (26%)	2.3 (13%)
Distillation residue, g.	16.4 (20%)	31.4 (25%)	10.2 (13%)
Conversion efficiency, %	25.5	43.3	17.7

In this case, the gas flowing out the ozonizer was cooled through a trap containing some cyclohexane to 5-10° to condense the total reaction product together with unconverted cyclohexane. The crude product, after driving off the unconvertd cyclohexane by distillation, was subjectd to fractional distillation into four fractions which had the properties shown in Table 7.

Table 7

Fraction (B.p., °C.)	Properties		Note
1. $(42\text{-}50)_{3-4}$	B.p., 155-158°C., $n_D^{20}=1.4507$,	Cyclohexanone semicarbazone M. p., 166-167°C.	Chclohexanone
2. $(50\text{-}60)_3$	B. p., 158-163°C.,	Cyclohexanol phenylurethane M. p., 80°C.	Cyclohexanol
3. $(153\text{-}180)_2$	M. p., 148-150°C.		Adipic acid
4. Residue			

The oxidation of cyclohexane in the ozonizer was found to proceed very fast as compared with the case of aromatic hydrocarbons. The conversion efficiency reached to about 18-43% by running it one time in the ozonizer (effective length, 75 cm.). The reaction product consisted mainly of cyclohexanol and cyclohexanone and their content in the product were 44-63% and 18-25% respectively.

The results of these three researches offer a possibillity of the use of silent discharge for the industrial preparation of (1) phenol from benzene, (2) benzylalcohol, benzaldehyde and cresols from toluene, and (3) cyclohexanol and cyclohexanone from cyclohexane respectively.

Synthesis of Aniline from Benzene and Ammonia.(2) (I)

Benzene has also been studied in an ozonizer in the presence of ammonia in order to obtain aniline according to the following reaction.

$$C_6H_6+NH_3=C_6H_5NH_2+H_2 \quad \Delta F=+9900 \text{ cal.}$$

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(2) Already publised in Japanese in *Jour. Chem. Soc. Japan*, **71**, 343 (1950). So this description is an abstract of the result.

An example of the experimental conditions and results obtained are summarized in Table 8.

Table 8

Magnitude of the tube: all glass ozonizer; effective length, 30 cm.; space gap, 0.26 cm. Conditions: cycle, 50; volt (secondary), 13 kV.; current (secondary), 2.5 mA.; temp. of ozonizer, 30°C.; temp. of trap, −5°C.; gas pressure, 730 mm.; rate of flow, C_6H_6 8.2 l./hr. NH_3 34 l./hr.; composition of mixed gas, C_6H_6/(total gas) × 100 = 20; time, 63 hr. Results; C_6H_6 used, 1.8 kg.; NH_3 used, 1.6 kg.; liquid products subjected to fractional distillation, 14.08 g.

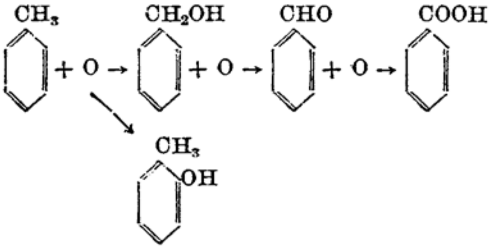
Fraction (B. p.,°C.)	Yield, g.	n_D^{20}	Properties	Note
81-85	7.46			Unconverted benzene (mainly)
85-100	0.23		Crystallized by absorbing CO_2 in air. Picrate and chloroplatinate were formed.	Aliphatic amine or diamine
100-115	0.12			
$(67\text{-}76)_{15}$	1.08	1.5410 $d_4^{20}=$ 1.000	B.p.,175-182°C. M. p., of acetanillide, 113°C.	Aniline
$(91\text{-}92)_{15}$	0.14	1.5420	A crystal (M.p. 63°C.) was isolated	*m*-phenylenediamine
$(111\text{-}114)_{15}$	0.28	1.5440		
$(121\text{-}134)_{13}$	0.19	1.5390		
Residue	0.75			
Loss	3.83			Unconverted benzene

Summary

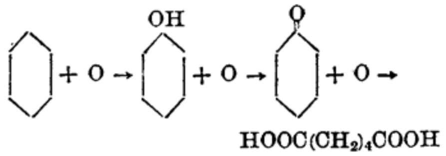
(1) By running a gas mixture of aromatic and hydroaromatic hydrocarbons and air in an ozonizer, following reactions were found to occur mainly.

(a) C_6H_6 $C_6H_6 + O \rightarrow C_6H_5OH$

(b) $C_6H_5CH_3$



(c) C_6H_{12}



(2) Conversion efficiency at one run under suitable conditions was found to be (a) 0.86-3.8% (effective length of ozonizer, 22 cm.), (b) 3.5-8.6% (effective length of ozonizer, 25-75 cm.), and (c) 18-43% (effective length of ozonizer, 75 cm.), respectively. The yield of each compound produced (grams of each compound produced/grams of total reaction product × 100) was as follows: (a), phenol 25-30%; (b), benzylalcohol 26-30%, benzaldehyde 13-20%, benzoic acid 2-4%, *o*-cresol 25-28%; and (c), cyclohexanol 44-63%, cyclohexanone 18-25%.

(3) In the case of the oxidation of benzene, the yield of phenol could be increased to above 60% of the total reaction product by the special method.

(4) Aniline and other basic compounds were obtained by the reaction of benzene and ammonia in an ozonizer.

In conclusion, one of the authors (K. Sugino) wishes to express his hearty thanks to Prof. M. Suzuki of Tokyo Municipal University for his sincere friendship which facilitated this research. The authors also extend their thanks to Dr. K. Odo, Lecturer of Tokyo Institute of Technology and Mr. K. Shirai, Assistant of the same Institute, for their valuable collaboration on the analytical work. Thanks are also due to their collaborators, H. Yamada, M. Hattori and H. Yamakawa, who gave earnest assistance in the investigations. The cost of this research has been defrayed from the Grant in Aid for Fundamental Scientific Research of the Ministry of Education and from the funds of the Nippon Carbide Industries Inc. to which thanks are due.

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