acid, acetic acid and water—the hydrolyzing mixture used by Whitmore and Fox. The mixture was poured into water and from the solid which separated the 1-naphthoic acid was extracted with dilute ammonia. After precipitation from its ammoniacal solution, the crude naphthoic acid was purified as described above. The yields obtained were from 20–25% of the calculated.

Summary

1. Contrary to a recent statement, 1-naphthoic nitrile is produced readily from 1-naphthylamine by the Sandmeyer reaction.

2. Very good yields of this nitrile can be obtained by a slight modification of the Korczynski method.

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THE CHEMICAL BEHAVIOR OF SOME BENZENOID HYDROCARBONS IN THE TESLA DISCHARGE

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Several years ago, during the course of a study of the Tesla luminescence spectra of benzene and some of its simple derivatives, some very interesting facts came to light in connection with the decomposition and behavior of these substances under the action of the Tesla discharge. Aside from the recent note of Harkins[3] and Gans on the decomposition of benzene, there appears to be no reliable literature on the subject of the chemical behavior of organic vapors in the electrical discharge; hence it has been thought worth while to record our experiences. It should perhaps be mentioned here that in our preliminary work several methods of excitation were tried. The results with the electrodeless discharge, later discarded because it failed to produce the desired spectra, have already been published[4] and are in agreement with the findings of Harkins and Gans.

The method finally selected was the Tesla discharge and is described in our previous paper.[5] However, it soon became evident that even with this discharge chemical changes were occurring in the vapors. This was indicated primarily by the formation on the discharge tube of shellac-like coatings similar to those formed in the electrodeless discharge, although no trace of the hydrogen lines, Swan bands, or ionized carbon lines appeared in the spectra obtained by this method. Moreover, further investigation

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[1] From a dissertation presented by J. B. Austin to the Graduate School of Yale University, June, 1928, in candidacy for the degree of Doctor of Philosophy.

[2] Commonwealth Fellow 1926–1928.

[3] Harkins and Gans, THIS JOURNAL, **52**, 2578 (1930).

[4] Austin, *ibid.*, **52**, 3026 (1930).

[5] Austin and Black, *Phys. Rev.*, **35**, 452 (1930).

revealed that crystalline solids were being condensed along with the unchanged vapor in the liquid-air trap. In some cases these crystallized by themselves in rings high up on the walls of the trap, in others they were found dissolved in the condensed liquid; in every case, however, the quantity obtained was very small.

For general convenience in description these products will be divided into two classes, those remaining in the discharge tube and those condensed by the liquid air.

Products Remaining in the Discharge Tube.—With every material investigated save one, cyclohexane, the walls of the discharge tube became coated with a thin film of a shellac-like substance ranging in color from a deep reddish-brown and black to buff. These coatings, which seemed to adhere to the walls when fresh, showed a tendency to crack and peel off on standing.

The conditions which appeared to produce the largest yields of these materials were slightly elevated temperatures (40–50°), comparatively high pressures (0.1 mm. to 1 mm.) and large electrode surface. Since the tube tended to heat up while in operation, no external heating appliances were employed. In order to take advantage of the other factors, a new tube was designed increasing the electrode surface (Fig. 1). This tube was essentially a glass Dewar flask with the inner space between the walls, ordinarily the vacuum space, serving as the reaction chamber. Two external electrodes were used, one formed by silvering the external surface of the inner wall and the other by wrapping lead foil around the outside wall. Unfortunately this design made it necessary to cut off the tube in order to remove the coatings on the inner wall, but with this tube greatly increased yields were obtained so that enough material for study was easily made.

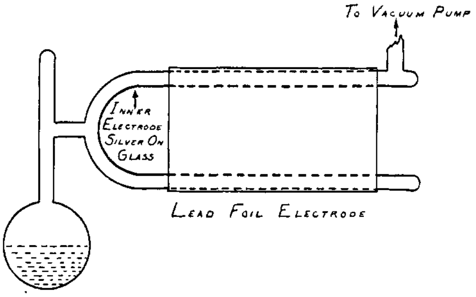

Fig. 1.—Apparatus for production of decomposition products.

An attempt to determine the properties of these materials showed them to be extraordinarily inert. They have no melting point but burn slowly with a luminous flame when heated to a sufficiently high temperature. They are insoluble in alcohol, acetone, ether, water, benzene, toluene, xylene, turpentine and ordinary acids and alkalies. Their densities as estimated by floating them in a series of alcohol–water mixtures are as follows: benzene product 0.94; toluene product 0.95; *p*-xylene 0.97. They appeared to have all the characteristics of highly polymerized or condensed aromatic molecules and seemed to have a number of properties in common with the products obtained by bombarding acetylene with high-speed cathode rays.[6]

Unlike the similar compounds described by Harkins and Gans they do not have the composition $(CH)_x$ but appear to contain some oxygen. The C and H analyses of several of them as determined by Professor J. B. Niederl are given in Table I.

TABLE I

ANALYSES

	C, %	H, %
Benzene product	73.38	4.77
Toluene product	79.16	5.90
p-Xylene product	77.14	6.52

These are average values for five determinations, the greatest deviation from the mean being 0.30%.

It will be seen that there remains to be accounted for from 15 to 20% of the weight of these compounds. Qualitative tests for nitrogen made with a method which under ordinary conditions detects nitrogen in a sample containing 0.1%. NH_4Cl gave completely negative results; hence it has been assumed that the remaining portion is oxygen, which is the only other element likely to be present under the circumstances.

The difference between our powders and those of Harkins and Gans is, however, easily accounted for since they took great precautions to dry their vapors and in our work at least a trace of water vapor was undoubtedly present. Indeed on making a careful study of our plates we find a faint band at about λ3064, which is the position of the strongest of the so-called "water vapor" bands. Furthermore, Urey and Lavin[7] have shown that an activated oxygen carrier, probably the OH molecule, will cause the formation of acetaldehyde in ethane under the action of an electrical discharge.

It would seem probable, therefore, that under our conditions the hydrocarbon is caused to react with the free OH radicals or ions in the vapor. The simplest empirical formula corresponding to the analysis of the powder from benzene is $(C_9H_7O_2)_x$. This formula must be regarded as an approximation to a type of compound which occurs in various polymerized forms since the product obtained is probably a complex of many related substances.

It will be shown in the section on crystalline products that diphenyl is formed from benzene vapor by the discharge. There is no reason to suppose that this coupling action ceases when two rings have been joined so that we should expect to find compounds composed of a great number of benzene rings coupled in various ways. If in addition we consider the presence of the water vapor ions, it is not difficult to imagine the formation

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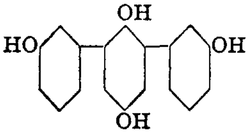
[6] McLennan, Perrin and Ireton, *Proc. Roy. Soc.* (London), **125A,** 246 (1929).

[7] Urey and Lavin, THIS JOURNAL, **51,** 3290 (1929).

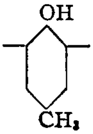
of phenolic compounds which would possess an even greater tendency to condense because of their phenolic character. This change is analogous to that observed in ethane by Urey and Lavin except that phenols are formed instead of aldehydes; this is not surprising since aldehyde formation in this case would involve the rupture of the ring.

Assuming that this coupling and phenol formation does take place, we are led to the possibility of some such compound as the following, whose formula would be $(C_9H_7O_2)_2$ (A). It should be emphasized here that we are suggesting not that this is the actual formula of the powder but that it may represent a unit in a larger complex.



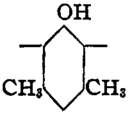
A

A study of the toluene and xylene powders lends some support to these views. The analysis of the product obtained from the former leads to the formula $(C_{21}H_{19}O_3)_x$. This may be explained by assuming a large molecule built up of (B) units, which would have the same general character as the molecule formulated for the benzene product.



B

The analysis of the xylene derivative leads to the approximate empirical formula $(C_{19}H_{19}O_3)_x$. This may be accounted for if we regard the molecular unit as (C) or C_8H_8O and if we consider the chain long enough to make the effect of the extra hydrogen atoms in the terminal rings negligible. The observed oxygen content, which is slightly above the proposed theoretical value, may be explained as arising from the presence of several phenol groups in some of the units.



C

It must be admitted that the lack of solubility in alkalies is not in accord with the phenolic character postulated, unless we assume a behavior similar to that observed in the monohydric phenols, where increasing molecular weight is accompanied by decreasing solubility. All of these remarks must await the accumulation of more data before they may be regarded as more than mere speculations; it is hoped, however, that they will provide a basis for discussion and will suggest new fields of endeavor and it is for these purposes that they are offered.

Crystalline Products

The evidence in the case of these compounds is much more conclusive than in the previous one. Since a general discussion is rather difficult until the data have been presented, the reactions of each vapor will be treated separately.

(a) **Benzene.**—After the condensate from the liquid-air trap was evaporated, the residue was examined, and was found to be a resinous matrix in which some small clear crystals were embedded. The identification of these crystals presented a number of difficulties, chief among which was the fact that so little material was available. The crystals were finally separated from the matrix by extraction with alcohol followed by partial evaporation of the resulting solution. They possessed the characteristic odor of diphenyl, their melting point was 69.5° in agreement with that of diphenyl and a mixture of these crystals with some diphenyl obtained from the Eastman Kodak Company showed an identical melting point. Moreover, the general optical properties of the unknown agreed with those of the Eastman sample. Both crystallized as flat monoclinic plates; both were strongly birefringent. Because of these conditions it was not deemed feasible to make an accurate determination of the refractive indices. However, the agreement of the general optical character added to the other evidence was regarded as sufficient proof that the unknown crystals were indeed diphenyl. It is interesting to note that these products are exactly the same as those obtained by Berthelot[8] in passing benzene vapor through a hot tube. No clue to the nature of the resinous material was obtained.

(b) **Toluene.**—With toluene several crystalline products were recovered. The first of these, which was found in a ring at the top of the trap, melted at 50.5°, which is in agreement with the melting point of dibenzyl. It was considered desirable to have some definite proof of the identity of this material, since it is in a sense the keystone of the series of compounds obtained with other substances. With the small amount of the unknown available, a determination of the optical properties seemed to be the most conclusive test.

In this case the refractive indices, which do not appear to have been previously recorded, were determined approximately. Since dibenzyl is soluble in the usual refractive index oils, a series of potassium iodide–mercury iodide solutions in a 50% glycerol–water mixture was used.

Dibenzyl crystallizes in monoclinic prisms which are strongly birefringent, making the exact determination of the indices rather difficult. The approximate values for the low and high indices are 1.53 and 1.74. The unknown crystals, in addition to having the crystalline form of dibenzyl, possessed approximately the correct indices. This was regarded as sufficient evidence to establish their identity.

When the liquid in the bottom of the liquid–air trap had been tapped off it was placed in an ice box for keeping. During the cooling some well-defined crystals appeared which were filtered off and dried. These were found to have the melting point (17.0°) of 2,2′-dimethyldiphenyl. No determination of the indices was made but in view of the formation of diphenyl from benzene it seems likely that the identification is correct.

A small amount of sirupy liquid was obtained on evaporating the remaining condensate from the trap. This liquid did not freeze at zero and had a high boiling point (above 200°). It was impossible to identify positively such a small amount of material but it is our belief that the liquid in question was a mixture of isomers of 2,2′-dimethyldiphenyl, several of which are high-boiling liquids.

(c) ***p*-Xylene.**—In this case a few crystals melting at 81° were found. This corresponds quite well with the melting point of di-*p*-tolylethane (82°); this reaction is analogous to the formation of dibenzyl from toluene and receives some confirmation from the known occurrence of that reaction. Here again a bit of sirupy liquid was obtained which, while unidentified, is believed to be a mixture of high-boiling liquid isomers.

(d) **Nitrobenzene.**—The accumulation of tar was so great that any attempt to separate crystals seemed futile.

(e) **Chlorobenzene.**—The chlorobenzene vapor decomposed to a very considerable extent under the discharge. A strong chlorine odor was observed when the system was opened and a strong benzene spectrum was obtained. Moreover, a few crystals of diphenyl were identified in the liquid-air trap.

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[8] Berthelot, *Compt. rend.*, **62**, 947 (1866).

(f) **Cyclohexane.**—No products were found. These reactions are summarized in Table II.

TABLE II

SUMMARY OF REACTIONS OBSERVED IN THE TESLA DISCHARGE

$2C_6H_6 = C_6H_5C_6H_5$
$2CH_3C_6H_5 = C_6H_5CH_2CH_2C_6H_5$
$2CH_3C_6H_5 = CH_3C_6H_4C_6H_4CH_3$
$2CH_3C_6H_4CH_3 = CH_3C_6H_4CH_2CH_2C_6H_4CH_3$
$4C_6H_5Cl = 2C_6H_6 + 2Cl_2 + C_6H_5C_6H_5$

Discussion

No discussion of these observations would be complete without a few speculations as to the mechanism of the reactions. Under the conditions of excitation several possibilities must be considered. Considering it axiomatic that reaction does not occur between normal unexcited molecules, we have a choice of the following: reaction between two ions, between an ion and a normal molecule, between two activated though un-ionized molecules, or between an activated and a normal molecule. Since products similar to our brown powders are produced by the electrodeless discharge and by the action of high-speed cathode rays, in which cases ionization seems to play a definite role, it would seem that we must look for reaction between ions in the present case. On the other hand, the conditions favoring increased yields, *i. e.*, higher temperatures and pressure, lead one to suppose that collisions must also be a factor. It is probable therefore that the process by which these substances are produced requires ionization of the vapor followed by a collision of the ions with other ions or normal molecules.

The authors wish to express their appreciation to Dr. E. T. Wherry for help and advice in the matter of the optical properties of the dibenzyl, to Dr. Elizabeth Gilman Roberts for help in the qualitative tests for nitrogen, to Professor J. B. Niederl for his analyses of the brown powders and to Mr. L. E. Faulhaber for help in preparing the manuscript.

Summary

The Tesla discharge in the vapors of benzene and its simple derivatives causes chemical action with the formation of two types of compounds; first, brown shellac-like compounds containing oxygen which are left in the discharge tube and appear to be condensed molecules of a phenolic type; second, relatively simple molecules which condense in well-defined crystals. In this latter class, diphenyl is produced from benzene and dibenzyl from toluene; isomers of these compounds are also formed. The low and high refractive indices of dibenzyl have been determined and are approximately 1.53 and 1.74.

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