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GAS PHASE REACTIONS OF PHENYL RADICALS[1]

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In this note, some observations on the reactions of phenyl radicals in the gas phase at elevated temperatures are described. The work was done in conjunction with a study of the oxidation and pyrolysis of benzene (3). It is shown that dimerization of phenyl radicals probably does not occur to a great extent at 450° C. or higher, but that the radicals readily form substitution products with several aromatic hydrocarbons.

Jaquiss and Szwarc (2) showed that the primary products of the pyrolysis of benzil are phenyl radicals and carbon monoxide. This diketone was, therefore, used as a source of phenyl radicals in the present investigation. Benzil, which was a B.D.H. reagent, was pyrolyzed in sealed Pyrex tubes of diameter 2.5 cm., volume 40 ml., for 40 minutes at 450 to 500° C., both alone and in the presence of benzene, carbon dioxide, anthracene + carbon dioxide, and naphthacene + carbon dioxide. The liquid and solid products were quantitatively analyzed by chromatography on alumina, the developing being done with petroleum ether (b.p. 40–60° C.). Representative gas samples were analyzed by chromatography on a charcoal column after the procedure of Ray (4).

RESULTS

Only a few representative experiments will be described:

(1) 300 mm. of benzil, 450° C. Most of the benzil decomposed to a tarry material which contained no detectable diphenyl.

(2) 300 mm. of benzil + 5 atm. of benzene, 450° C. About 80% of the benzil decomposed. The brown product contained 0.8 M. of diphenyl per mole of benzil decomposed.

(3) 300 mm. of benzil + 20 atm. of benzene, 450° C. The sole non-gaseous product other than a trace of benzaldehyde was diphenyl, 1.2 M. per mole of benzil decomposed. At 500° C., 1.6 M. of diphenyl per mole of benzil decomposed was obtained. Hydrogen was also a product, but only 0.3 M. per mole of benzil decomposed was found. A complete series of runs at 440° C. showed that the mole fraction of benzil decomposed (0.5) was virtually independent of the pressure of benzene over a benzene pressure range of 0 to 30 atm. The pyrolysis of benzene alone at 500° C. yielded about 2% as much diphenyl as in the benzil runs. Benzaldehyde was a trace product at the two temperatures. A

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blank run on 300 mm. of benzaldehyde + 15 atm. of benzene showed that the aldehyde was stable.

(4) 300 mm. of benzil + 20 atm. of carbon dioxide, 450° C. The product was a tar which contained negligible diphenyl.

In view of the recent use of polynuclear aromatic hydrocarbons as radical traps (5), it was considered of interest to study the effect of anthracene and naphthacene on the gas phase reactions of phenyl radicals. In the following experiments, the reactants were diluted with a high pressure of carbon dioxide to maintain the conditions of total pressure comparable with those obtained in the benzene runs at high pressure.

(5) 300 mm. of benzil + 300 mm. of naphthacene + 16 atm. of carbon dioxide, 480° C. The benzil all decomposed. Products found were 5-phenylnaphthacene (0.3 M. per mole of benzil decomposed) and 5,12-phenylenenaphthacene. The compounds, after partial resolution from unidentified hard material on the chromatography column, were identified by their ultraviolet absorption spectra in benzene (1). A careful search in the products revealed no trace of benzene or diphenyl.

(6) 300 mm. of benzil + 300 mm. of anthracene + 16 atm. of carbon dioxide, 480° C. The column was not capable of completely resolving the products, but the absorption spectra of several fractions revealed the presence of a substantial amount of 9-phenylanthracene. A little yellow compound may have been either 9,12-diphenylanthracene or 1,9-phenyleneanthracene.

Neither anthracene nor naphthacene alone decomposed under the conditions of pyrolysis.

The gaseous products from the side reactions of phenyl radicals were methane, C_2 hydrocarbons, and possibly hydrogen. The principal decomposition product of phenyl was, however, brown tar. In the above experiments, no trace of higher polyphenyls, such as terphenyl, was found under any conditions.

DISCUSSION

The following conclusions can be drawn: The absence of appreciable diphenyl in the products of the pyrolysis of benzil in the presence of carbon dioxide suggests that the dimerization of phenyl radicals is not a major source of diphenyl under the run conditions. The detection of considerable phenyl-substituted polynuclear hydrocarbons in those runs where anthracene or naphthacene were present shows that phenyl radicals can take part in the following reaction:

$$C_6H_5 + ArH = C_6H_5Ar + H, \quad ArH = \text{aromatic hydrocarbon.}$$

The absence of benzene in the products shows that phenylation is not a two-stage process,

$$C_6H_5 + ArH = C_6H_5ArH,$$

$$C_6H_5ArH + C_6H_5 = C_6H_6 + C_6H_5ArH.$$

The yields of diphenyl in excess of the moles of benzil decomposed show that phenyl radicals also react with benzene. By analogy with the reaction with polynuclear hydrocarbons, the following reaction is envisaged,

$$C_6H_5 + C_6H_6 = C_{12}H_{10} + H. \qquad [1]$$

Hydrogen arises from

$$H + C_6H_6 = C_6H_5 + H_2. \qquad [2]$$

This sequence requires that the moles of hydrogen be at least equal to the moles of diphenyl in excess of the moles of benzil decomposed. The hydrogen yield is actually considerably less than this, and hence, if reaction [1] occurs, there must be some fate of the hydrogen atom which does not result in the formation of one molecule of hydrogen per atom of hydrogen reacted. Benzaldehyde may arise from a reaction such as

$$H + C_6H_5COCOC_6H_5 = C_6H_5CHO + C_6H_5 + CO. \qquad [3]$$

If reaction [1] were the only fate of the phenyl radical in the presence of excess benzene, and if reaction [3] occurred as often as the straight benzil pyrolysis reaction, the yield of diphenyl would be at least 1.5 times the benzil decomposed. Since benzaldehyde is formed only in traces, [3] is not a major process; this means that the yield of diphenyl should actually be in excess of that figure. But, except at 500° C. and very high benzene pressures, this is not the case, and hence the phenyl radical must undergo reaction other than [1]. Another possible fate of phenyl is reaction with benzil itself. But, the mole fraction of benzil decomposed is virtually independent of the pressure of benzene, although the fate of phenyl depends so markedly on the pressure of benzene. This suggests that a reaction between phenyl and benzil does not compete with a reaction between phenyl and benzene. The only alternative fates of phenyl which appear to satisfy these conditions are thermal decomposition and reaction with hydrogen atoms. The complete scheme then becomes:

$$C_6H_5COCOC_6H_5 = 2C_6H_5 + 2CO,$$

$$C_6H_5 + C_6H_6 = C_{12}H_{10} + H, \qquad [1]$$

$$C_6H_5 + H = C_6H_6, \qquad [4]$$

$$C_6H_5 = \text{inactive products (tar, } CH_4\text{, etc.),} \qquad [5]$$

$$H + C_6H_6 = C_6H_5 + H_2, \qquad [2]$$

$$H + C_6H_5COCOC_6H_5 = C_6H_5CHO + C_6H_5 + CO. \qquad [3]$$

Reaction [5] accounts for the tarry products in the absence, or presence of small amounts only, of benzene. Reaction [2] will become increasingly important as the temperature is raised, so that the yield of diphenyl will increase, as is, in fact, the case.

At temperatures where [5] and [2] are negligible, this scheme, omitting [3], results in 1 M. of diphenyl per mole of benzil decomposed; under conditions where [2] occurs, the yield of diphenyl is in excess of 1 M. per mole of benzil decomposed, and a chain process involving [1] and [2] will occur. At temperatures much above 500° C., benzene itself decomposes to phenyl radicals complicating the reaction. A chain process involving [1] and [2] is probably the source of diphenyl in the pyrolysis of benzene (3). Reaction [5] will decrease the over-all diphenyl yield.

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