heated on a steam-bath with 300 ml. of 1.7% NaOH for one hour. The pure acid, precipitated with HCl, melted at 335° and had a neutral equivalent of 180.

Bis-(*p*-carbomethoxyphenyl)-phenylphosphine Oxide.—The crude acid such as described above (37 g.) was esterified as for the methyl analog. Several crystallizations of the product from benzene–petroleum ether yielded 18 g. of pure ester, m.p. 165–166°.

Anal. Calcd. for $C_{22}H_{19}O_5P$: C, 67.00; H, 4.86; P, 7.86. Found: C, 67.00; H, 5.11; P, 7.80.

Tris-(*p*-carboxyphenyl)-phosphine Oxide.—Tri-*p*-tolylphosphine (15 g.) was oxidized in pyridine solution with potassium permanganate and 10 g. of a white, powdery acid was obtained, m.p. 323–330°. Michaelis[2] reported a melting point of 247°.

Anal. Calcd. for $C_{21}H_{15}O_7P$: neut. equiv., 136.8. Found: neut. equiv., 136.0.

Tris-(*p*-carbomethoxyphenyl)-phosphine Oxide.—The above acid (8 g.) was esterified in methanol with sulfuric acid as the catalyst. The crude product was crystallized by cooling the solution to Dry Ice temperature and melted at 106–112°. Recrystallization from benzene–petroleum ether yielded 6 g. of ester, m.p. 123–125°.

Anal. Calcd. for $C_{24}H_{21}O_7P$: C, 63.8; H, 4.68; sapn. equiv., 150.8. Found: C, 63.4; H, 4.90; sapn. equiv., 153.4.

Phenyldi-*p*-tolylphosphine Sulfide.—This compound was prepared from phenyldichlorophosphine sulfide in a manner analogous to that used for the oxide. The major portion of the by-product bitolyl was separated by solution in low boiling petroleum ether. The phenyldi-*p*-tolylphosphine sulfide was purified by repeated crystallization from acetone. It formed clusters of glassy prisms, melting at 153.5–154°; yield 62%.

Anal. Calcd. for $C_{20}H_{19}PS$: C, 74.53; H, 5.94; P, 9.61; S, 9.96. Found: C, 74.46; H, 5.99; P, 9.21; S, 10.00.

When this compound was oxidized with potassium permanganate, as in preceding experiments, the sulfur was replaced by oxygen and bis-(*p*-carboxyphenyl)-phenylphosphine oxide was obtained.

Stability of Phosphine Oxides.—Phosphine oxides possess great thermal and chemical stability. They withstand strong oxidizing or reducing treatments, normal hydrolytic reactions, and nitrations. They may be distilled at high temperatures under reduced pressure without sign of decomposition. However, when a small sample (0.7 g.) of ethyldi-*p*-tolyphosphine oxide was heated with water at 245° for two hours, in a sealed tube, the aqueous washings from the tube were distinctly more acid than cold washings of a similar quantity of phosphine oxide. The contents of the tube possessed a phosphine-like odor.

WILMINGTON, DELAWARE

[CONTRIBUTION FROM THE WALKER LABORATORY, DEPARTMENT OF CHEMISTRY, RENSSELAER POLYTECHNIC INSTITUTE, AND THE DEPARTMENT OF CHEMISTRY, UNIVERSITY COLLEGE, LONDON]

The Direct Cyanogenation of Benzene

BY GEORGE J. JANZ

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The reaction of cyanogen with benzene in the gas phase at atmospheric pressure and 740° is reported. When cyanogen is used in excess, biphenyl and para-cyanogen formation reactions are suppressed. Benzonitrile is the primary product formed (42% yields) although even at short contact times, dinitriles are obtained (8% yields). The reaction of cyanogen with benzonitrile under similar conditions gives only dinitriles as the product. The dinitrile product is found to be a mixture of 1,4- and 1,3-isomers only, and the 1,4-dinitrile isomer (terephthalonitrile) is formed in larger amounts. Thermodynamic calculations for reactions of interest with reference to the direct cyanogenation of benzene are reported.

The only reference to a reaction of cyanogen with benzene is a report by Merz and Weith[1] that when the reactants were passed through a hot tube (glowing faintly red) benzonitrile and terephthalonitrile were formed in small amounts, as well as biphenyl. This communication reports on a reinvestigation of this reaction which may be considered as a direct cyanogenation of an aromatic compound. The interest lay primarily in establishing the conditions of temperature and ratio of reactants favorable for this reaction, and in the nature and composition of the products obtained.

Experimental

Apparatus and Chemicals.—The reaction vessel was a silica tube (outside diameter, 1.3 cm.). This was mounted in a vertical position in the furnace which had been constructed with a 2.5 cm. diameter steel pipe suitably insulated and wound with nichrome resistance wire. Temperatures were measured with a chromel–alumel thermocouple. The benzene and cyanogen, metered into the system at controlled rates, were mixed in a preheater before passing into the reaction zone. A receiver cooled with an ice-water mixture was connected to the exit of the reactor to trap the liquid products. A series of traps at −80° were used to condense the more volatile products.

The cyanogen was prepared by the reaction of aqueous sodium cyanide with copper sulfate. A modification of the apparatus of Hahn and Leopold[2] was used for the cyanogen generator and the cyanogen was stored in small steel cylinders after it had been dried and redistilled.[3] The benzene was the thiophene free grade from Eastman Kodak Co. Organic Chemicals. All experiments were at atmospheric pressure.

Benzene and Cyanogen.—The reaction was first attempted at 500° using an equimolar ratio of reactants and flow rates to give a 20-second contact time. Only traces of benzonitrile were found in the product. At about 640°, similar reaction times, the yields of benzonitrile were still quite small, but at about 750°, the yields were considerably greater. A short reaction time was chosen to minimize side reactions. Using the reactants in equimolar ratio at these temperatures, it was found that biphenyl was also formed. This side reaction was suppressed when cyanogen was used in excess. At 745° and 2–3 seconds contact time, using a twofold excess of cyanogen in the feed, the yield of benzonitrile was as high as 42%, calculated on the benzene conversion per pass. Even at these short reaction times, some phthalonitriles (1 to 5%) were also obtained in the reaction product. The benzene conversion per pass calculated from the input and the benzene recovered unreacted, was about 46%. With silica chips packing in the reactor, the yields were lower, probably indicating that side reactions are being promoted by this packing. As well as silica, tests were made using steel chips, a cobalt oxide on alumina, and pumice chips. With the exception of the latter, in each case side reactions (*e.g.*, polymerization of cyanogen, decomposition) were promoted rather than the direct cyanogenation reaction. The pumice did not appreciably affect the rate or course of reaction and may thus be of interest as a catalyst support in evaluating the activity of various catalysts in this reaction.

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(1) V. Merz and W. Weith, *Ber.*, **10**, 753 (1877).

(2) G. Hahn and W. Leopold, *ibid.*, **68**, 1974 (1935).

(3) G. J. Janz, R. G. Ascah and A. G. Keenan, *Can. J. Research*, **B25**, 272 (1947).

Benzonitrile and Cyanogen.—Because of the dinitriles present in the reaction products above even at short reaction times, the direct reaction of benzonitrile and cyanogen was also carried out. At 720° and a 2-second reaction time, with a 1.5 molar excess of cyanogen in the feed, the benzonitrile conversion per pass was 14%, and the yield of phthalonitriles was 26%. Under similar conditions, but at an 18-second reaction time, the benzonitrile conversion was 20%, and the yield of phthalonitriles was 63%.

Separation and Identification of Products.—The reaction mixture was distilled at atmospheric pressure to recover unreacted benzene. Distillation at reduced pressure next gave a fraction boiling in the range of 68° (10 mm. pressure). This fraction distilled at 190–192° at atmospheric pressure (benzonitrile, lit. 190.7°). Hydrolysis of this product gave benzoic acid (m.p. 120°, lit. 121°, mixed m.p. 120–121°). The identification was confirmed by the identity of the X-ray powder diffractions of the authentic benzoic acid and the unknown. The material remaining in the pot was solid at room temperature. From this the phthalonitriles were obtained by boiling with decolorizing carbon in glacial acetic acid and recrystallization. A carbon, hydrogen and nitrogen analysis on the dinitrile fraction established that this fraction had the composition $C_6H_4(CN)_2$ (*Anal.* Found: C, 74.80; H, 3.29; N, 21.43. Calcd.: C, 75.01; H, 3.11; N, 21.88). Hydrolysis of this fraction to the dibasic acid, and comparison of the X-ray powder diffraction pattern for terephthalic acid showed this to be a mixture. The method described by Smith[4] was used to separate the mixture of dibasic acids by their barium salts. In this manner barium terephthalate was recovered. The X-ray diffraction powder pattern of this was identical to that for the terephthalic acid. The dibasic acid recovered from the other barium salt was esterified and identified as the dimethyl ester of isophthalic acid (dimethyl ester, m.p. found 63.5–64.8°, lit. 68°. *Anal.* Found: C, 61.73; H, 5.21. Calcd.: C, 61.85; H, 5.16).

Chemical means of separation to establish quantitatively relative amounts of the terephthalo- and isophthalonitriles in the product seemed inadequate. A method of analysis of these mixtures by ultraviolet absorption was set up using isopropyl alcohol as solvent. Terephthalonitrile had two absorption maxima, at 2820 and 2900 Å., with extinction coefficients 96 and 93, respectively, at a concentration of 0.0164%. Isophthalonitrile also had two absorption maxima, at 2800 and 2880 Å., with extinction coefficients of 27 and 25.5, respectively, at a concentration of 0.0516%. Standard absorption curves were obtained, and the method of analysis was tested using mixtures of known composition. For a terephthalonitrile content of 70.7%, the ultraviolet analysis showed 73.7%. This was judged to be of sufficient accuracy for the method. The dinitrile mixtures were thus analyzed, and the results obtained were:

Run	Composition of dinitrile product, % Terephthalonitrile	Isophthalonitrile
1	84.6	15.4
A	80.0	20.0
B	65.6	34.4

The dinitrile fraction in run I was a product of the direct reaction of benzene with cyanogen, and runs A and B, by the reaction of benzonitrile with cyanogen.

Discussion

Data on the behavior of both benzene and cyanogen toward heat are available and of interest with reference to these direct cyanogenation reactions. The thermal dissociation of cyanogen into free radicals has been the subject of several investigations.[5,6,7] The heat of dissociation for this reaction is most probably 120–130 kcal. White measured the equilibrium constant for the reaction at 1227° and, by thermodynamic calculation, predicted that the formation of free cyano radicals first becomes appreciable at about 400°. By use of these data for cyanogen, the degree of dissociation at 750° is found to be 10^{-11}. This corresponds to a concentration of free cyano radicals of about 10^5 radicals per cc. The pyrolysis of benzene at moderately high temperatures with formation of biphenyl is well known and undoubtedly proceeds by a free radical mechanism. The optimum temperature for biphenyl formation was reported as 750° by Zanetti and Egloff.[8]

$$(CN)_2 \rightleftarrows (2CN)$$

A high degree of thermal stability might be expected for both the cyano and phenyl free radicals[9] since a double bond cannot be formed by decomposition of either of these radicals. Pyrolysis leading to degradation of these reactants should not be too serious therefore, even at moderately high temperatures.

In the present work, it was found that the dinitriles formed in the direct cyanogenation reactions consisted of a mixture of the para and meta isomers in each case. One would have expected a mixture of para and ortho isomers rather than the above if the direct cyanogenation proceeds by nuclear substitution as the cyano-group is para–ortho directing. The results thus are in accord with the concepts of a free radical mechanism rather than a nucleophilic substitution type mechanism.

The interesting features in the work described lie in the fact that very little biphenyl or para-cyanogen were obtained under the conditions used. The temperature range of 750° has been reported as the optimum for biphenyl formation from benzene and is also one at which cyanogen is appreciably dissociated into free radicals. It was found that if benzene was used in excess, or in equimolar ratio to cyanogen, some biphenyl was always obtained in the product. However, with an excess of cyanogen no biphenyl was present in the reaction product. This must mean that the reactions to form benzonitrile are much faster than either the addition of the cyano-free radical to cyanogen or addition of the phenyl radical to benzene, reactions which would lead to para-cyanogen and biphenyl formation.

The free energy changes for both benzonitrile formation and biphenyl formation can be calculated at 750°, *i.e.*

$$C_6H_6(g) + (CN)_2(g) \rightleftarrows C_6H_5CN(g) + HCN(g) \quad (1)$$

$$2C_6H_6(g) \rightleftarrows (C_6H_5)_2(g) + H_2[g] \quad (2)$$

In the direct cyanogenation reaction, the thermodynamic data for all the compounds with the exception of benzonitrile are well established. The data for benzonitrile were estimated using the method of group increments[10,11] with toluene as the parent compound. The free energy change for this reaction at 750° is thus −18.4 ± 1.0 kcal. In the case of the formation of biphenyl, this equilibrium has been directly measured by Vveden-

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[4] M. E. Smith, This Journal, **43**, 1920 (1921).

[5] G. B. Kistiakowsky and H. Gershinowitz, *J. Chem. Phys.*, **1**, 432 (1933).

[6] J. U. White, *ibid.*, **8**, 459 (1940).

[7] N. C. Robertson and R. N. Pease, *ibid.*, **10**, 490 (1942).

[8] J. E. Zanetti and G. Egloff, *Ind. Eng. Chem.*, **9**, 350 (1917).

[9] M. Szwarc, *Far. Soc. Discussions*, **10**, 143 (1951).

[10] J. W. Anderson, G. H. Beyer and K. N. Watson, *Nat. Petrol. News*, **36**, R476 (1944).

[11] J. G. M. Bremmer and G. D. Thomas, *Trans. Far. Soc.*, **43**, 779 (1947).

skii and Frost[12] up to 920°. At 750°, accordingly, the free energy change for biphenyl formation from benzene is +4.3 kcal. Using the free energy change as criterion of the feasibility of a reaction, it is seen that thermodynamically the direct cyanogenation of benzene is much more favorable than the formation of biphenyl. On thermodynamic grounds, the direct cyanogenation reaction is predicted as capable of proceeding very far in the direction of benzonitrile, and the conditions for undertaking a catalyst search to promote the rate to a more favorable degree are thus good.

Acknowledgment.—The author wishes to express his appreciation to Dr. A. W. Patterson for the analyses of the dinitrile mixtures by ultraviolet absorption, and Canadian Industries Limited, Montreal, Canada, for kind permission to publish these results.

TROY, N. Y.

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[12] A. A. Vvedenskii and A. V. Frost, *J. Gen. Chem. U. S. S. R.*, **2**, 542 (1932).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CANADIAN SERVICES COLLEGE, ROYAL ROADS]

A Kinetic Study of the Alkaline Scission of 4-Hydroxy-3-methoxy-β-nitrostyrene

BY ROSS STEWART

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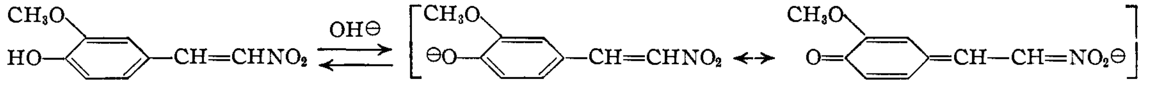
Kinetic and spectral evidence are presented to show that in basic solution the colored anion of 4-hydroxy-3-methoxy-β-nitrostyrene reacts with hydroxyl ion to produce an intermediate which, in turn, decomposes to give vanillin and nitromethane.

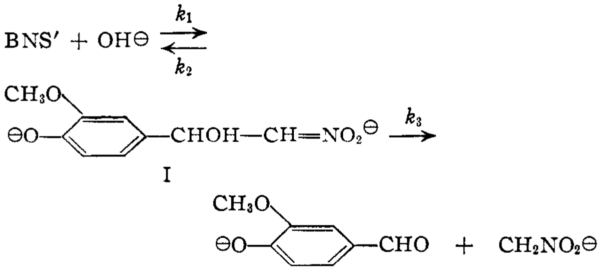
The compound 4-hydroxy-3-methoxy-β-nitrostyrene (BNS) has been recently examined as an acid-base indicator.[1] In acid solution it is yellow but in basic solution it possesses an intense red color which fades on standing to give a colorless solution. The structure of the red species is presumably the resonance hybrid BNS′. This research was undertaken to establish the mechanism of the fading in color of this ion.

To test this postulate the rate of fading of BNS′ was studied under various conditions. If the first step is correct, the Brönsted–Debye–Hückel relation should hold since a reaction between two ions is postulated. The reaction should also be first order with respect to both BNS′ and hydroxyl ion. The intense red color of BNS′ permits this reaction to be followed colorimetrically. Both colorimetric and spectrophotometric methods were used in this study.



BNS BNS′

In a study of *p*-hydroxy-β-nitrostyrene and related substances, Hahn and Stiehl[2] concluded that the colored species had the structure $O=C_6H_4=CH-CH=NO_2Na$, which faded to give $NaOC_6H_4$-$CHOHCH=NO_2Na$ and, finally, *p*-hydroxybenzaldehyde. Proof for this mechanism was not advanced. A somewhat similar mechanism is postulated here involving a nucleophilic attack by hydroxyl ion at the α-carbon atom of the side chain of the hybrid anion, BNS′, to give I. This substance could then decompose to give vanillin and nitromethane, which would exist as the anions II and III if the solution were sufficiently basic.



I

II III

Experimental

Materials.—BNS was prepared and purified as previously described.[1a] Vanillin (Eastman Kodak Co.) was recrystallized from water. Nitromethane (Matheson Co.) and all solvents required were distilled before use. Distilled water was boiled just before use. A standard solution of BNS containing 80 mg. of BNS per 50 ml. of absolute ethanol was made up before each series of kinetic runs and before all the spectral determinations.

Apparatus.—A Beckman model DU quartz spectrophotometer was used to obtain the absorption curves. This instrument equipped with thermospacers was also used for many of the rate measurements, the balance being obtained with the Fisher electrophotometer (model 7-089).

Rate Measurements.—The reaction vessels used were 100-ml. volumetric flasks immersed in a constant temperature bath at 25 ± 0.04°. At zero time one ml. of the standard solution of BNS in ethanol was pipetted into the reaction vessel which had been made up to 99 ml. with the required amount of carbonate-free sodium hydroxide, sodium chloride and distilled water. When the electrophotometer was used to follow the drop in concentration of BNS′ a certain volume of solution was withdrawn from the flask at regular intervals and the transmission of these samples measured. In some cases this procedure was also followed with the spectrophotometer. In others, the Beckman quartz cells were kept at constant temperature by means of thermospacers, and a series of transmission readings was obtained on the same sample. Good agreement between the three methods was obtained. A series of runs in which the one ml. of ethanol used as solvent for the BNS was replaced by methanol, dioxane, and pyridine showed the effect of the ethanol to be negligible. The only change in the rate was found when commercial dioxane was used. One ml. in 100 ml. had the effect of doubling the rate of fad-

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[1] (a) R. Stewart and R. H. Clark, *Can. J. Research*, **B26**, 7 (1948); (b) M. G. S. Rao, C. Srikantia and M. S. Iyengar, *J. Chem. Soc.*, 556 (1925).

[2] G. Hahn and K. Stiehl, *Ber.*, **71B**, 2154 (1938).