THE INTERACTION OF SOME AROMATIC HYDROCARBONS, ALCOHOLS, AND ALDEHYDES WITH NITROGEN PEROXIDE

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As a part of an extensive investigation of the chemical behavior of nitrogen peroxide towards organic compounds we have been led to study, as a result of contradictory statements in the literature, the action of this gas on certain hydrocarbons, alcohols and aldehydes of the aromatic series. It is well known that nitrogen peroxide can react under specific conditions either as a nitrating or an oxidizing reagent, but an exhaustive review of the literature reveals a record from which one cannot draw definite conclusions with respect to the specific behavior of the simplest representative of these three classes of compounds towards this reagent. As a result of our research our attention has been directed particularly to the oxidizing properties of nitrogen peroxide and in the study of the types of compounds discussed in this paper we have detected very little evidence of the utility of nitrogen peroxide as a practical nitrating agent.

Aromatic Hydrocarbons

Leeds[2] reported the formation of oxalic acid, nitrobenzene and picric acid by the continued action of nitrogen peroxide on benzene. Friedburg[3] later investigated the reaction in carbon disulfide solution and identified both mono- and dinitrobenzene. Frankland and Farmer[4] state, however, that this peroxide has no action on benzene and their observation was confirmed recently by Kast and Günther.[5] Finally, we have recorded in the patent literature applications of the use of nitrogen peroxide for nitration of hydrocarbons of the benzene series.[6] The latest investigator to study this reaction is Wieland,[7] who reports the formation at 80° of nitrobenzene, trinitrobenzene, picric acid and other water-soluble nitrogen compounds. At ordinary temperature there was no reaction, and Wieland advances the hypothesis that the reaction at 80° takes place

[1] Constructed from a Dissertation presented by L. W. Bass to the Faculty of the Graduate School of Yale University in June, 1923, in Candidacy for the degree of Doctor of Philosophy.

[2] Leeds, THIS JOURNAL, 2, 277 (1880).

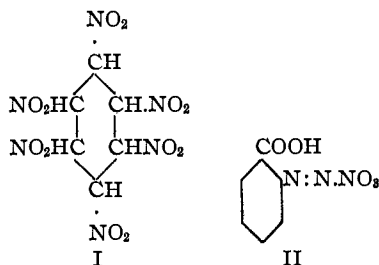[3] (a) Friedburg, *ibid.*, 4, 252 (1882). (b) Friedburg and Mandel, *ibid.*, 12, 7 (1890).

[4] Frankland and Farmer, *J. Chem. Soc.*, 79, 1356 (1901).

[5] Kast and Günther, *Z. ges Schiess- und Sprengstoffw.*, 14, 81, 103 (1919).

[6] Ger. pat., 207,170; "Friedländer," 9, 107; Ger. pat., 214,045; "Friedländer," 9, 142, *Ber.*, 46, 586 (1913).

[7] Wieland, *Ber.*, 54, 1776 (1921).

through addition with formation of hexanitrocyclohexane (I) as the primary product of reaction.

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\begin{array}{c}
NO_2 \\
\cdot \\
CH \\
NO_2HC \quad CH.NO_2 \\
NO_2HC \quad CHNO_2 \\
CH \\
\cdot \\
NO_2 \\
I
\end{array}
\qquad
\begin{array}{c}
COOH \\
N:N.NO_3 \\
\\
II
\end{array}
$$

We have reinvestigated this reaction at ordinary temperature and have obtained results in accord with the observation of Friedburg.[3] We allowed our reagents to interact in sealed ampules and operated both in the dark and under exposure to sunlight for months, but in no experiment were we able to identify any nitration products except the mono- and dinitro-derivatives, and the yields of these were very small.

In the case of the hydrocarbon toluene we also met with contradictory statements. Leeds[2] states that this hydrocarbon and nitrogen peroxide react on long standing (5 months) with formation of several products among which he claims to have identified oxalic acid, dihydroxybenzoic acid, o-nitrotoluene, benzoic acid and dinitrocresol. Here again Frankland and Farmer[4] and Kast and Günther[5] state that this hydrocarbon dissolves in nitrogen peroxide without reaction. It was our experience, when we allowed these reagents to interact in sealed ampules out of contact with air, that the peroxide interacted as an oxidizing agent and benzoic acid was the only product formed. When the reaction was conducted in sunlight or the light of a quartz-mercury arc we obtained evidence of the formation of a small amount of nitrotoluene.

When the nitro hydrocarbons are dissolved in nitrogen peroxide we find very little evidence of reaction at ordinary temperature.[4,5,7] In our research we studied the behavior of the three isomeric nitrotoluenes, but in no case did we observe any further nitration when they were exposed to the action of nitrogen peroxide for several days. They were all characterized by their stability, the methyl group resisting oxidation at ordinary temperature.

Of the higher aromatic hydrocarbons anthracene is apparently the only one to receive attention. By allowing this hydrocarbon to interact with nitrogen peroxide in benzene solution we have observed only changes involving oxidation with formation of anthraquinone. This confirms the observations of Leeds,[2] and Frankland and Farmer.[4]

Aromatic Alcohols

So far as the writers are aware the only aromatic alcohols which have been studied with regard to behavior towards nitrogen peroxide are benzyl

alcohol and the corresponding o- and p-nitro derivatives. Cohen[8] states that all three compounds are oxidized quantitatively in chloroform solution by nitrogen peroxide to their corresponding aldehydes. The mechanism of the reaction is explained by the intermediate formation of nitrosites.[9]

In the light of the fact that toluene is oxidized to benzoic acid by nitrogen peroxide it was difficult for us to understand how the oxidation of benzyl alcohol by nitrogen peroxide could stop at the aldehyde stage. It seemed probable that benzoic acid would be the final product of the reaction. On repeating this work we subjected benzyl alcohol to oxidation and obtained a yield of aldehyde corresponding to less than 45% of that calculated. All of the alcohol had been destroyed by the action of nitrogen peroxide and the quantity unaccounted for as aldehyde was shown to have been converted into benzoic acid. In fact, the aldehyde and acid were produced in approximately equivalent quantities. The acid represents the second stage of oxidation, and it is reasonable to assume that an excess of the oxidizing agent would finally destroy all aldehyde formed.

Aromatic Aldehydes

The results obtained by Cohen[8] would lead one to conclude that aromatic aldehydes are extremely stable in the presence of nitrogen peroxide. This is not a result that one would predict, and on repeating the work with benzaldehyde, and the isomeric m- and p-nitrobenzaldehyde we find that the aldehyde group in every case is finally converted into the carboxyl group. In other words, these aldehydes are converted by the action of nitrogen peroxide into their corresponding acids. The same result was obtained when we conducted the reactions in chloroform,[8] or allowed the oxide to act on the respective aldehydes under the influence of sunlight or in the dark.

Especially interesting was the behavior of o-nitrobenzaldehyde towards nitrogen peroxide. The reaction in chloroform solution resulted in the formation of two characteristic products: first, the simple oxidation product o-nitrobenzoic acid which was easily identified, and second, a diazo derivative of benzoic acid. The structure of this latter compound has not been definitely established but, from the experimental data which have been obtained, it seemed probable that it is identical with the diazonium salt (II) previously described by Griess.[10] A more thorough investigation of this reaction is to be carried out for the purpose of establishing the constitution of this compound and for determining the mechanism of its formation.

[8] Cohen and Calvert, J. Chem. Soc., 71, 1050 (1897). Cohen and Harrison, ibid., 71, 1057 (1897).

[9] Ref. 3b, p. 50. Ref. 4. Schlenk, Mair and Bornhardt, Ber., 44, 1169 (1911). Tassilly and Leroide, Bull. soc. chim., [4] 7, 622 (1910).

[10] Griess, Ber., 9, 1653 (1876).

Experimental Part

Experiments were conducted in the absence of light and also under conditions of long exposure to sunlight or to the light of a mercury-arc lamp. Many experiments were carried out but we will record only the results of one trial which is representative of a given series. The effect of catalysts other than light on the course of our reactions was not investigated.

Benzene.—1. Twelve g. of benzene and 3.0 g. of liquid nitrogen peroxide, in a sealed ampule, were allowed to stand in a dark closet for 3 months. The only apparent change was the formation of minute colorless crystals in quantity too small for identification. The green reaction mixture on distillation gave 9.0 g. of benzene and about 0.3 g. of a yellow oil which was identified as nitrobenzene. There was practically no pressure when the ampule was opened, indicating no appreciable oxidation. We obtained no evidence of the formation of dinitrobenzene or picric acid.

2. Ten g. of benzene and 2.5 g. of nitrogen peroxide, in a sealed ampule, were exposed to direct sunlight over a period of 3 months. The color of the reaction mixture changed gradually from deep green to reddish-orange. Here again we observed the formation of a minute quantity of characteristic crystals as in the previous experiment. On distillation the reaction mixture yielded 6.0 g. of benzene, 2.1 g. of nitrobenzene, and 0.9 g. of m-dinitrobenzene (m. p., 90°). In other words, the light had stimulated the change, operating to produce nitration products. We did not observe the formation of picric acid.

Toluene.—1. Twelve g. of toluene and 2.5 g. of nitrogen peroxide, in a sealed ampule, were allowed to stand in a dark closet for 3 months. At the end of this time the color of nitrogen peroxide had disappeared, the liquid had become yellow and a very small quantity of a yellow solid had deposited. The reaction mixture returned to us 7.6 g. of unaltered toluene and 4.1 g. of a crystalline substance which was identified as benzoic acid. There was no evidence of the formation of a nitro derivative.

2. Anhydrous nitrogen peroxide gas in excess was passed over 50 g. of dry toluene in a transparent quartz tube. During this operation, which was continued for 4 hours, the tube was illuminated by means of a quartz-mercury arc, and the temperature of the toluene did not rise above 55°. On distillation we obtained a small quantity of a low-boiling liquid, which decomposed on standing at ordinary temperature with slow evolution of nitrogen peroxide and unaltered toluene.

3. The experiment described above was repeated with the same quantity of toluene but with the substitution of a water-cooled quartz reaction tube. The duration of the illumination was increased to 6 hours. On distillation the reaction mixture yielded 13.0 g. of the unstable low-boiling liquid (40–80°), 32.0 g. of toluene, and 2.5 g. of a crystalline solid which consisted almost entirely of benzoic acid.

The low-boiling liquid (40–80°) on redistillation showed no definite boiling point, but gradually decomposed with the formation of pure toluene and liberation of nitrogen peroxide in large quantity. This product appears to be an unstable addition product of the peroxide and toluene. In this case, therefore, the nitrogen peroxide acted as an oxidizing reagent and practically no nitration took place.

o-, m- and *p*-**Nitrotoluenes.**—Our method of operating was the same with the three isomers. Nitrogen peroxide in excess was passed in the form of gas through a solution of 10 g. of the respective nitrotoluene in 30 cc. of dry benzene. This treatment was continued for 6 hours and the mixture then allowed to stand in a sealed flask for 3 days. The excess of peroxide and benzene was then removed by distillation, the highly colored residue dissolved in ether and the solution washed with a small volume of 5%

sodium hydroxide solution. In the experiment with o-nitrotoluene we recovered 9.6 g. of this nitro compound, and from the alkaline solution only 0.06 g. of crystalline material was obtained. This possessed all the properties of o-nitrobenzoic acid. In the experiments with m- and p-nitrotoluenes similar results were obtained, and from the alkali wash liquors we obtained only very small quantities of the corresponding acids, amounting to 0.06 g. and 0.16 g., respectively.

Anthracene.—A solution of 1.0 g. of anthracene and 0.5 g. of nitrogen peroxide in 60.0 g. of benzene was sealed in an ampule and preserved in a dark closet for 3 months. Within 5 days the color of the peroxide had disappeared completely and the green solution had become deep red. On opening the ampule there was no pressure, and after heating the liquid to remove benzene we obtained a dark colored residue consisting of a mixture of unaltered anthracene and anthraquinone; 0.2 g. of pure anthraquinone was obtained by sublimation. A second ampule containing the same proportions of reagents was sealed and exposed to light on the roof of the laboratory for 3 months. Practically the same result was obtained as in the first experiment, the yield of sublimed anthraquinone being 0.2 g.

Benzyl Alcohol.—Five g. of benzyl alcohol, 5.0 g. of nitrogen peroxide and 30.0 g. of chloroform were sealed in an ampule and the mixture was allowed to react for 4 days. The ampule was then opened and the chloroform washed with 5% sodium hydroxide solution. From the chloroform we succeeded in isolating a quantity of pure benzaldehyde-phenylhydrazone (m. p., 155°) corresponding to 1.04 g. of aldehyde. The alkaline solution was acidified with hydrochloric acid when benzoic acid was precipitated at once and melted sharply at 121°. We recovered 1.01 g. of this acid. Practically the same yields of aldehyde and acid were obtained in a duplicate experiment.

Benzaldehyde 1.—Ten g. of benzaldehyde and 4.0 g. of nitrogen peroxide, in a sealed ampule, were allowed to stand in a dark closet for 3 months. Colorless crystals began to deposit during the first day, and the reaction appeared to be complete in 3 weeks. On removal from the ampule, the crystalline solid, which had a slight odor of benzaldehyde, was identified as benzoic acid, melting at 120°. In a duplicate experiment in which we exposed molecular proportions of the reagents ($2C_6H_5CHO$ and N_2O_4) to sunlight for three months we obtained a yield of benzoic acid corresponding to 75% of that calculated. The remainder of the aldehyde had been transformed into a resinous product.

In a third experiment we used 10 g. of benzaldehyde and allowed the reaction to proceed for only four days. After working up the reaction products as described above we recovered nearly 50% of the aldehyde, and separated 4.1 g. of benzoic acid, melting at 120°.

m- and p-Nitrobenzaldehydes.—Both aldehydes (2 g.) were dissolved in chloroform (30 g.) with 2.5 g. of nitrogen peroxide and the mixture sealed in ampules. After standing for 14 days the reaction mixtures were examined for unaltered aldehyde and oxidation products. In the case of the *meta* isomer we recovered 0.98 g. of aldehyde melting at 57–58° and separated 0.95 g. of pure m-nitrobenzoic acid melting at 140–141°. In the experiment with the *para* isomer we recovered 0.93 g. of p-benzaldehyde and separated 0.96 g. of p-nitrobenzoic acid (m. p., 235–236°). In other words, the two aldehydes oxidized with equal ease.

o-Nitrobenzaldehyde.—A solution of 2.0 g. of o-nitrobenzaldehyde and 3.0 g. of nitrogen peroxide in 30.0 g. of dry chloroform was sealed in an ampule and allowed to stand for 14 days. The reaction mixture was then poured out and a quantity of tabular yellow crystals, which had deposited on the walls of the tube, was removed and dried in the atmosphere (see below).

The excess of nitrogen peroxide was removed from the chloroform solution by distillation at room temperature under diminished pressure. The colorless liquid residue

was then dried over sodium sulfate and after removal of the chloroform by distillation the residue was extracted with 5% aqueous sodium hydroxide. The total residue yielded after purification 1.03 g. of unaltered aldehyde melting at 45° and 0.3 g. of o-nitrobenzoic acid (m. p., 148°).

The tabular, yellow crystals which deposited on the walls of the ampule weighed 0.55 g. This product was found to be exceedingly unstable and decomposed with explosive violence when heated to 99–103°. It could also be exploded when rubbed violently on an anvil. It was insoluble in most of the common organic solvents but dissolved easily in water giving an acid solution. While the compound can be preserved unaltered for months when kept dry, solution in water stimulates a slow decomposition with evolution of nitrogen. This compound exhibited all the properties of a diazonium salt and coupled with β-naphthol to form a characteristic red dye. After decomposition by warming with water the property of coupling with naphthol was completely destroyed. A solution of the compound in cold water gave no coloration when treated with a drop of ferric chloride, while the same solution after boiling gave a characteristic purple color which was discharged by alkali. The substance formed by heating with water behaved in every respect like salicylic acid. The properties of the compound and its characteristic behavior towards specific reagents indicate a diazonium compound to which we assign provisionally the constitution II. We shall continue the study of this compound and also the mechanism of the reaction leading to its formation.

Summary

1. The aromatic hydrocarbons, benzene and toluene, show little tendency to interact with nitrogen peroxide at ordinary temperature. On long exposure to the action of the peroxide it is possible to detect evidence of nitration and oxidation. Anthracene is oxidized slowly by nitrogen peroxide to anthraquinone.

2. Benzyl alcohol is oxidized by nitrogen peroxide at ordinary temperature to benzoic acid.

3. The aromatic aldehydes, benzaldehyde and the three isomeric nitro derivatives, are all transformed into their corresponding acids by the action of nitrogen peroxide.

4. o-Nitrobenzaldehyde interacts with nitrogen peroxide to give in small amount a substance possessing the properties of a diazonium salt.

5. In none of the reactions which we have studied have we been able to detect any pronounced catalytic effects by conducting the reaction in sunlight.

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