Oxidation of Toluene with Dilute Nitric Acid at High Temperature and Pressure

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It was shown already by Fittig¹ that benzoic acid was formed by boiling toluene with nitric acid. Konowalow² used dilute acid at 125—130° C and Sachsse³ carried out the oxidation at 120—150° C. Coblenz and Walker⁴ maintained toluene in contact with nitric acid of about 40 % strength at about 100° C for several days and Seydel⁵ carried out the reaction at 110° C and 5 kg/cm² in the presence of catalysts. Askenasy, Elöd and Trogus⁶ studied this reaction at high temperatures under oxygen pressure and obtained a 65—70 % yield of benzoic acid. The yields are otherwise poor in spite of long reaction times and very much by-products are formed.

This paper summarizes some results, obtained during research work performed in order to find new ways of oxidizing aromatic hydrocarbons and make this process adaptable to industrial manufacture⁷.

The oxidation of toluene with dilute nitric acid is a rather slow process at ordinary pressure, and temperatures around 100° C. The reaction is, however, very fast at higher temperatures and pressures. It was shown that temperatures around 200° C and pressures around 30—50 kg/cm² should be used in order to obtain a good yield of a comparatively pure product. Under such conditions, the conversion is complete in a few minutes and the process may be run with a very good capacity. The concentration of the nitric acid is preferably kept within the limits 10—50 %. The reaction is difficult to start if the concentration is lower than 10 %, and it might be difficult to control if the concentration is higher than 50 %. Even at concentrations of 10—50 % certain steps must, however, be taken in order to control the reaction. A suitable charging of the reaction vessel by adding the nitric acid or both the reactants continuously is necessary. If the acid is added continuously to the organic compound during the course of the reaction, a low concentration of the nitric acid in the reaction mixture will obviously be maintained all the time, even if a comparatively concentrated acid is added. Under these circumstances no excess of acid can arise in the reaction mixture until possibly when the last portion of acid is added. The process has also been developed to a continuous one by charging acid and toluene with high pressure pumps

and continuously discharging *via* a regulating device in timed relation to the addition of new starting material. In order to control the reaction, it is necessary to let out the gases formed, continuously or intermittently, if the pressure should show a tendency to rise too high.

A very important problem connected with this process is to restrict the formation of nitrated by-products. The nitration rate increases with increasing concentration of nitric acid in the reaction mixture. It is, however, possible to charge comparatively concentrated acid if this is made continuously as described above, keeping the concentration in the reaction mixture at a low level and avoiding excess of acid. The nitric acid supplied should be consumed by the oxidation reaction as rapidly as possible. Both temperature and pressure must be kept at a high level, because this means an increase in the rapidity of the oxidation reaction, which is much more important than the increase in the rapidity of the nitration. An increase in pressure especially was shown to depress the amount of nitrated by-products in the crude benzoic acid. When oxidizing toluene along these lines, it was possible to obtain a yield of 85–90 % of a crude benzoic acid, containing about 10 % of nitrobenzoic acids and about 1 % of picric acid. When the nitric acid is in this way consumed very quickly and is present in less than the equivalent amount and at low concentration during the main part of the reaction period, the corrosive action is very much reduced.

The nitrobenzoic acid mixtures were found to contain mainly the *p*-isomer. The acids could be separated by fractional distillation of the crude acid mixture or of the esters. The nitro compounds could also be removed quantitatively by reduction with sulfur dioxide in alkaline solution ¹⁰.

There are, however, further compounds formed as by-products and intermediate products in this process. From crude benzoic acid made in a pilot plant by continuous oxidation of toluene with 33 % nitric acid at 200° C and 30 kg/cm² there were isolated about 0.5 % of mononitro toluenes, primarily the *o*-isomer and about 0.1 % of benzaldehyde. It has also been possible to isolate phenylnitromethane from the crude acid. This compound was prepared by Konowalow ² by reacting toluene with nitric acid at 100–105° C for 24 hours. It is also known that by heating at 225° C this compound is decomposed, giving benzaldehyde, water and nitrogen oxides. Actually, when the above crude benzoic acid was heated at 230° C for 2 hours, benzaldehyde distilled in a yield of approximately 1 % of the weight of the acid and some nitrogen dioxide was formed. It was also found that phenylnitromethane could be oxidized to benzoic acid in good yield, using dilute nitric acid at high temperature and pressure.

Askenasy, Elöd and Trogus ⁶ considered phenylnitromethane to be an intermediate step in the oxidation of toluene to benzoic acid with nitric acid although they did not isolate this compound from their reaction products. As phenylnitromethane has now been isolated from the reaction product and has been oxidized to benzoic acid, it seems likely that it is an intermediate in this process. The *o*- and *p*-nitrobenzoic acids are doubtless formed by oxidation of the corresponding mononitrotoluenes, which are formed primarily at the beginning of the experiments when the nitric acid concentration is comparatively high. *p*-Nitrotoluene gives an almost quantitative yield in such condi-

tions, whereas *o*-nitrotoluene is oxidized to a mixture of *o*-nitrobenzoic acid, and picric acid⁷. *o*-Nitrotoluene is oxidized comparatively slowly and it is formed in larger amount than the *p*-isomer when toluene is nitrated. This explains the fact that mainly *o*-nitrotoluene was found in the crude benzoic acid and very little of the *p*-isomer. Some *m*-nitrobenzoic acid is, of course, also formed by oxidation of *m*-nitrotoluene. This nitrotoluene is, however, formed in very small amounts and most of the *m*-nitrobenzoic acid present has evidently been formed by nitration of benzoic acid with dilute nitric acid.

Ethyl benzene was also oxidized in the same way, giving crude benzoic acid in 75–80 % yield at 170–190° C and 30–40 kg/cm. Finally *isopropylbenzene* was oxidized to crude benzoic acid.

EXPERIMENTAL

Apparatus and experimental procedure. The oxidations were performed in a stainless steel autoclave according to a general procedure reported in a previous paper⁸. The yields reported above do not include small quantities of benzoic acid, dissolved in the mother liquor and washing water. Most of the experiments were batch-wise but benzoic acid was also made continuously in the following way: The autoclave was charged with a small quantity of toluene, about 10 % of the autoclave volume, together with the equivalent amount of nitric acid. This first charge was then heated under stirring until the reaction started. Then more of the components were charged. When the autoclave had been filled to the discharge level, a discharge pipe was opened and the same quantity of reaction product was automatically discharged per time unit as was supplied in the form of starting materials.

Picric acid. This contaminant was determined by precipitation with copper sulphate solution in ammonia or colorimetrically at smaller concentrations. The picric acid could be removed from the crude benzoic acid by leaching with water.

Nitrobenzoic acids. These compounds were determined polarographically in aniline solution on samples free from picric acid or with correction for picric acid according to a method developed in this laboratory⁹. Different methods for separation of the nitrobenzoic acids from the benzoic acid have been investigated. Sublimation and crystallisation from different solvents did not give complete separation, nor did reduction with iron and hydrochloric acid. Reduction with SO₂ in alkaline solution was, however, found to be a very efficient method for removing the nitrobenzoic acids completely¹⁰. Another way to remove the nitrobenzoic acids, which also made it possible to isolate them, was fractionation under vacuum. When a crude acid, containing 15 % of nitrobenzoic acid, was distilled in a short laboratory column at 100 mm Hg, there was obtained an 80 % yield of distillate in the form of white benzoic acid with less than 0.01 % of nitrobenzoic acid and a distillation residue, of mainly *p*-nitrobenzoic acid. (Melting point 235–236° C, equ.w. 165.7.) When such distillations were made on a technical scale, however, the residue contained a little more benzoic acid. Attempts were made to isolate the nitrobenzoic acids from such a residue by crystallization from ethyl alcohol and by esterification. From the mixture of ethyl esters the *p*-isomer could be isolated in a rather pure form by fractionation.

Benzaldehyde and nitrotoluenes. By the vacuum fractionation of 450 kg of crude benzoic acid, made in a pilot plant by continuous oxidation of toluene with 33 % nitric acid at 30 kg/cm² and 200° C, there were obtained 60 kg as a first fraction. This fraction was redistilled and gave 14.6 kg of a fraction, boiling up to 185° C at 100 mm Hg. The temperature then remained constant and only benzoic acid distilled. The product, boiling up to 185° C was oily and had a red to brown color. One kg was redistilled in a laboratory column with 3 plates at 10–12 mm Hg and five fractions were cut. They were analysed for benzaldehyde with sodium bisulphite and iodine. In addition to this the benzaldehyde was precipitated with phenylhydrazine and identified by the melting point as benzaldehydphenylhydrazone after two crystallisations from ethyl alcohol. The nitrotoluenes in fraction 2 were determined as amines after reduction of the corresponding

fraction with Zn and HCl. The amines were fractionated and *o*- and *p*-toluidines were identified through their boiling points and the melting points of their hydrochlorides. Fraction 3 was redistilled after removing acid compounds with alkali and then investigated in a polarograph. The boiling point and the polarographic data indicated, that *o*-nitrotoluene was the main product. Table 1 shows the result of this distillation:

Table 1.

Fraction No.	Boiling point, °C, at 11 mm Hg	Percent by weight	Composition
1	60–68	3	Mainly benzaldehyde
2	68–96	7	Benzaldehyde 10 %, <i>o</i> -nitrotoluene about 70 %, <i>p</i> -nitrotoluene about 10 %
3	96–131	11	Mainly <i>o</i> -nitrotoluene
4	131–135	25	Benzoic acid, somewhat contaminated with nitrotoluenes
5	135	45	Benzoic acid (m.p. 122.5–123.5 Eq.wt. 122.7)
Residue		2	
Losses		7	

Phenylnitromethane. The above mentioned crude benzoic acid, made continuously in a pilot plant, was extracted with toluene, the toluene was evaporated and the residue was dissolved in diethyl ether and treated with saturated sodium bicarbonate to remove strong acids and then with saturated Na_2CO_3 and 2 *N* NaOH. The solution in NaOH was acidified, and the oily product which then separated was distilled at 21 mm Hg. The main part of the oil boiled at 108–118° C and had the following data:

$n_D^{20} = 1.5323$, $D_4^{20} = 1.1587$ (Phenylnitromethane boiling point at 4 mm Hg 118–119° C, $n_D^{20} = 1.5323$, $D_4^{20} = 1.1598$). The oil was investigated polarographically, which also indicated that it mainly consisted of phenylnitromethane.

According to a procedure described by Black and Babers¹¹ phenylnitromethane was made in a fairly good yield by reacting benzyl cyanide with methyl nitrate to phenylnitroacetonitrile, converting this to phenylnitroacetic acid with sodium hydroxide and treating the said acid with concentrated hydrochloric acid. The phenylnitromethane boiled at 97–99° C (5 mm Hg) and had $n_D^{20} 1.5327$ and $D_4^{20} 1.1607$. It was oxidized with 15 % HNO_3 in a 20 % equivalent excess at 180–200° C and 20–25 kg/cm² according to the general procedure described above. From 34 grams of phenylnitromethane there was formed 28 grams of a product with the following analyses: Eq.wt. 132, N (Dumas) 2.36 %. This was dissolved in ammonia and purified by reduction with SO_2 . After precipitating and washing there was obtained a white product with the following analyses: Eq.wt. 121.0, melting point 123° C, nitrobenzoic acid about 2 % (polarographically). Investigation in ultra-violet spectrophotometer showed that the product was mainly benzoic acid.

Oxidation of toluene. Continuous oxidation of toluene to benzoic acid was carried out with 15 % nitric acid at 175–190°. In one case the reaction was run with a toluene excess of 30 %, 3.5 % nitric acid being discharged and the final product containing 11 % nitrobenzoic acid as by-product. The corrosive effect on the autoclave, which was made of stainless steel (45 % Cr, 5 % Ni), was only 0.2–0.3 g/m²/h. If the same reaction was carried out with a nitric acid excess of 60 %, the concentration of the discharged nitric acid amounted to 10 %, the content of nitrobenzoic acid in the crude reaction product was 21 % and the corrosive effect was greater than in the preceding example. Yields of more than 80 % have been obtained in such oxidation experiments.

Oxidation of ethyl benzene. Ethyl benzene ($D_4^{20} = 0.867$, $n_D^{20} = 1.4944$) was oxidized with a 30 % surplus of nitric acid. The result may be seen from Table 2.

Table 2.

Nitric acid concentration %	Temperature °C	Pressure kg/cm ²	Crude product			
			Yield %	Eq.wt.	Melting point °C	Nitrobenzoic acid %
15	166	21	62	131.6	116—117	12
15	156	36	69	123.9	119—120	7
15	168	41	80	123.7	118—119	6
15	168	42	80	128.4	115—116	11
15	191	40	69	122.2	118.5—119.5	7
30	150	32	79	129.1	115—117	11
30	162	36	74	125.9	115—117	10

The products were identified in ultra-violet spectrophotometer as mainly benzoic acid.

Oxidation of isopropyl benzene. This oxidation was made with nitric acid of 15 % concentration in a 20 % excess at 185—195 °C and 35 kg/cm². From 60 g of the hydrocarbon there was obtained 45 g of a compound with equiv. weight 127 and N (Dumas) 1.20 %. This was purified by reduction with SO₂ and a 75 % yield was obtained of a white product, which was identified in ultra-violet spectrophotometer as mainly benzoic acid.

SUMMARY

Toluene was oxidized with dilute nitric acid at 30—50 kg/cm² and 170—200 °C to give crude benzoic acid in a yield of more than 80 %. The optimal conditions for this oxidation were studied. Nitrobenzoic acids, mainly the *p*-isomer, were formed as by-products together with small amounts of picric acid. Furthermore it was possible to isolate benzaldehyde, nitrotoluenes and phenylnitromethane in crude benzoic acid from continuous oxidation. Phenylnitromethane was oxidized to benzoic acid with dilute nitric acid at 170—200 °C under pressure.

Ethyl benzene and isopropyl benzene were oxidized in the same way as toluene giving crude benzoic acid in good yields.

The author wishes to thank Dr. Allan Dahlén for his helpful interest during this work and for valuable suggestions. Part of the analytical work was done by Folke Sahlin, Gustaf Brandt and Marita Renström.

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Received February 25, 1954.

Acta Chem. Scand. **8** (1954) No. 5