ACTA CHEMICA SCANDINAVICA 7 (1953) 774–780

Preparation of Aromatic Carboxylic Acids by Side-Chain Oxidation with Dilute Nitric Acid at High Temperature and Pressure

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It is well known that aliphatic side-chains in aromatic compounds may be oxidized to carboxylic groups using nitric acid. Up to now this was generally performed by refluxing the organic compound with comparatively concentrated nitric acid. Very long reaction times were necessary using these older methods, the yields were low and large amounts of by-products were formed [1]. It has been claimed in an old German patent [2] that toluene can be oxidized to benzoic acid at 130—150° C under pressure but no figures were presented concerning pressure and yield. Later a series of alkylbenzenes have been oxidized in a similar way but the yields were low [3]. Recently it was claimed that terephthalic acid could be obtained in good yields when *p*-dialkyl benzenes were oxidized with nitric acid at 14 kg/cm^2. The reaction product was somewhat contaminated with toluic acid [4].

As nitric acid is an inexpensive oxidizing agent, research work was started in Bofors about ten years ago in order to find new ways of performing oxidations with nitric acid and to make them adaptable to full scale industrial manufacture. It was shown that a high temperature and a pressure as high as 30—50 kg/cm^2 gave fast and complete conversions and high yields of comparatively pure products [5]. In this way a considerable number of aromatic carboxylic acids have been prepared with good yield, *e.g.* benzoic acid, chloro- and nitrobenzoic acids, phthalic acids etc. This paper deals with some results, obtained by the oxidation of xylenes, cymenes, toluic aldehyde, ditolylsulfone and some chlorosubstituted aromatic hydrocarbons.

EXPERIMENTAL

For the experiments there was used a 2 500 ml autoclave made of stainless steel and fitted with stirrer, thermometer, pressure gauge, facilities for venting and two pressure chambers. The usual procedure was to charge the aromatic compound and the nitric acid, and then heat with stirring until the exothermic reaction started, generally around 170° C. The heating was then interrupted but nevertheless the pressure and temperature rose rapidly, thus indicating a violent oxidation reaction, and sometimes it was necessary to connect the autoclave with the pressure chambers in order to moderate the reaction. In certain experiments the pressure still rose, however, and then it was necessary to let out part of the gases formed. When the main part of the organic compound had been oxidized, which was when the pressure did not rise any more, the temperature was held at a certain level around 200° C for a certain time, and then the autoclave was emptied. The crude product was finally washed with water and dried.

This procedure was sometimes modified, so that only part of the components was charged at the beginning of the experiment and the remainder added later, when this first part had reacted. When this procedure was adapted, the pressure chambers were used for charging the autoclave using the autoclave's own pressure.

o-Xylene. Dilute nitric acid of 30 % concentration and *o*-xylene were charged in the autoclave. The nitric acid was used in a 30 % equivalent excess. The temperature was held at the level, indicated in Table 1, for 15 minutes, after the main reaction had been finished and the pressure also remained around the level indicated in the table during this period.

Table 1.

Temperature °C	Pressure kg/cm^2	Yield %	Eq. weight	Nitrogen (Dumas) %	HNO_3 in mother liquor %
168	39	69	87.0	0.5	9.7
183	43	57	83.9	0.4	11.2
187	49	69	84.6	0.3	6.7
189	49	70	83.9	0.4	8.6
191	50	71	83.8	0.3	6.5
194	52	69	83.2	0.3	7.9
172	39	74	87.7	0.7	9.1
172	42	80	88.4	0.6	9.7
183	50	66	84.7	0.3	9.6

As a further control to the purity, the crude products were analyzed by precipitating the K-salt of the phthalic acid in ethyl alcohol. This method, which is only approximate, indicated that the purity was between 94 and 97 % for all the samples.

The last three runs in the table were performed using the mother liquor from an earlier experiment under the same conditions.

As may be seen from the table, the best result was obtained when comparatively high temperatures and pressures were used.

The crude products in Table 1 crystallized from the mother liquors directly on cooling. The mother liquors from the filtration were evaporated and cooled, and then an additional quantity of crude product crystallized. This product had a comparatively high equivalent weight and a high nitrogen content. Consequently it was believed to contain a major part of mononitrotoluic acids, which are more soluble in water than is the phthalic acid. The weight of this crude product, crystallized from the mother liquor, was on an average about 20 % of the weight of the crude phthalic acid.

In a similar way *m-xylene* as well as mixtures of *m*-xylene and *p*-xylene have been oxidized. The results will be published later on.

p-Xylene. Using an equimolecular amount of nitric acid and charging all together the following results were obtained (Table 2).

Table 2.

Nitric acid conc. %	Temperature °C	Pressure kg/cm²	Yield %	Crude product Eq. weight	N(Dumas) %
15	169	40	84	90.6	0.7
15	172	37	79	91.2	0.7
25	165	37	86	93.1	0.5
25	174	38	85	91.0	0.5
25	196	40	83	86.3	0.5

In other series of experiments a certain surplus of nitric acid has proved to be preferable, in order to obtain a more complete oxidation. A rather high temperature, around 200° C, serves the same purpose. The crude product has been purified to pure terephthalic acid in a good yield. The purified as well as the crude products have been esterified with *n*-butyl alcohol to give pure terephthalic acid dibutyl ester in a good yield.

p-Cymene. The oxidation of *p*-cymene is still more violent than the oxidation of xylenes, and only small quantities could be oxidized, if the whole charge was put into the autoclave at the beginning of the experiment. If the *p*-cymene and the nitric acid were charged in portions, the capacity was, however, quite good. The experiments in Table 3 have been made using refined *p*-cymene with a specific gravity of 0.858. This quality, which was an ordinary refined *p*-cymene from a Swedish pulp mill, proved to have a purity of about 95 %, when carefully fractionated in a laboratory column (50 plates).

The values are representative of results obtained when *p*-cymene was oxidized with nitric acid using successive charging. It has, however, in other series of experiments, proved possible to obtain an 80–85 % yield using 15 % nitric acid.

In the same way a mixture of about 30 % *m*-cymene and about 70 % *p*-cymene was oxidized. The mixture was compared with a *p*-cymene of about 98 % purity. Using 30 % nitric acid in a 30 % excess at 200° C and 30 kg/cm², the mixture gave a 75 % yield, com-

Table 3.

Nitric acid conc. %	Nitric acid surplus %	Temp. °C	Pressure kg/cm²	Yield %	Crude reaction product Eq. weight	C %	H %	N %	Ash %
15	30	196	52	74	83.2	57.5	3.6	0.1	0.24
25	30	173	40	78	84.7	57.5	3.6	0.2	0.08
25	30	198	38	87	84.8	57.5	3.7	0.3	0.09
Calculated for terephthalic acid:					83.1	57.8	3.6		

pared with an 82 % yield from the pure *p*-cymene. The equivalent weights were about 85 for both products and the contents of nitroterephthalic acid, determined in a polarograph, were 2.5 and 1.8 % respectively.

p-Toluic aldehyde. *p*-Toluic aldehyde was made from toluene using the Friedel-Craft reaction and was identified by determination of density ($D_4^{20} = 1.024$) and refraction index ($n_D^{20} = 1.5453$). Aldehyde (40 g) and dilute nitric acid in 30 % excess, calculated for the oxidation to terephthalic acid, was charged, the autoclave was closed and the charge was heated while stirred. The heating was interrupted at about 180° C, when a vigorous reaction started, generating a rapidly rising pressure. The temperature rose to about 200° C and the pressure to 31—34 kg/cm². The pressure and temperature were held at that level for 15 minutes and the autoclave was then allowed to cool. The crude terephthalic acid was filtered, washed with water, dried and analyzed for equivalent weight and nitroterephthalic acid (polarographically). The result may be seen from Table 4.

Table 4.

Run No.	HNO_3 Conc. %	Temp. °C	Pressure kg/cm²	Crude terephthalic acid Yield	Eq. weight	Nitro-Compounds	Mother liquor HNO_3 %
1	15	200	31	79.5	83.1	1.6	6.2
2	15	206	31	83.5	83.6	0.9	5.9
3	30	203	33	84.2	84.5	2.9	10.7

The product from the experiments 2 and 3 were analyzed for C, H and N:

Run	C	H	N
2	57.7	3.6	0.2
3	57.8	3.6	0.3
Calculated:	57.8	3.6	

Another oxidation was made in which double the amount of aldehyde was charged and the corresponding amount of nitric acid added in two lots. When this first charge had reacted the rest of the nitric acid was charged under pressure. In that way a better capacity was obtained.

Ditolylsulfone. Ditolylsulfone, $CH_3 . C_6H_4 . SO_2 . C_6H_4 . CH_3$, is formed as a by-product of the sulfochlorination of toluene with chlorosulfonic acid. It is formed together with isomers, but the *p,p'*-compound is dominating.

For these experiments a starting material was used, which had been obtained as a by-product of the manufacture of toluene sulfonamides. It was leached several times with hot dilute sodium hydroxide to remove toluene sulfonamide and was then recrystallized from ethyl alcohol. After this treatment the material melted at 150—151° C and apparently consisted mainly of the *p,p'*-isomer.

The autoclave was charged with sulfone and nitric acid, the latter in 20 % excess over that required for the oxidation of two methyl groups to carboxylic groups. The autoclave was closed and the charge was heated while stirred. The heating was interrupted at about 180° C, when a vigorous reaction started, generating a rapidly rising pressure. The temperature rose to about 200° C and the pressure to 30—45 kg/cm². The temperature and pressure were held at that level for 15 minutes, and the autoclave was then allowed to cool. The crude product was filtered off, washed with water, dried and analyzed. The result may be seen from Table 5.

Table 5.

Sulfone g	HNO_3 conc. %	Temperature °C	Pressure kg/cm²	Crude product g	Yield %	Eq. weight	S %	N % Dumas
30	15	204	28	38	100	164.0	10.0	0.5
40	30	204	32	45	90	159.6	10.0	0.8
123	15	184	41.5	139	89	165.7	10.4	0.5
105	15	205	45	121	93	155.9	9.8	0.4

Calculated for $HOOC . C_6H_4 . SO_2 . C_6H_4 . COOH$: Eq. weight = 153; S = 10.5 %

o-Chlorotoluene. Using a nitric acid of 15 % concentration in a 10—30 % excess at 180—200° C and 25—40 kg/cm² a 75—80 % yield was obtained. The crude products had the equivalent weights 154.1—156.8 (calc. 156.5), melting points 138—139° C and chlorine contents 21.0—22.2 (calc. 22.7). The nitrogen content (Dumas) was found to be about 0.3 %. Using nitric acid of 30 % concentration in a 10 % excess at 200° C and 33 kg/cm² an 80 % yield of a crude product with the equivalent weight 155.8, melting point 138—139.5° C and chlorine content 20.4 % was obtained.

m-Chlorotoluene. The oxidation was performed with nitric acid of 15 % concentration in a 10 % surplus. When oxidizing at 200° C and 37 kg/cm² an 80 % yield of a crude product with the equivalent weight 157.1, melting point 144—148° C, chlorine content 24.0 %

and nitrogen content (Dumas) 0.7 % was obtained. When the reaction was performed at 183° C and 27 kg/cm^2 the yield was 72 % and the equivalent weight 159.8, melting point 138—142.5° C and chlorine content 22.4 %.

p-Chlorotoluene. The oxidations were performed with a nitric acid of 15 % and 30 % concentration respectively. The excess was 30 % in all experiments. The result from representative runs may be seen from Table 6.

Table 6.

HNO_3 conc. %	Temperature °C	Pressure kg/cm^2	Yield %	Eq. weight	Melting point °C	Cl %
15	180	28	87	156.1	242—242.5	22.4
15	200	39	88	156.1	242—242.5	20.4
30	180	31	89	155.5	242—242.5	21.4
30	200	33	91	156.6	242—243	21.3

The nitrogen content (Dumas) was around 0.5 %. The crude chlorobenzoic acids were purified by dissolving in alkali, removing the nitro compounds and precipitating after treatment with active carbon. Pure acids with accurate analytical data were obtained in 80—90 % yields.

3,4-Dichlorotoluene. Using nitric acid of 15 % concentration in a 30 % surplus at 18 kg/cm^2 and 190° C the yield was 76 % of a crude product with the following data: Equivalent weight 189.0 (calc. 190.9) chlorine 34.5 % (calc. 37.2), nitrogen (Dumas) 0.6 %. When the oxydation was performed using nitric acid of 30 % concentration in 30 % excess at 31 kg/cm^2 and 215° C, the yield was 86 % of a product with the following data: Eq.w. 192.0 Chlorine 36.8, nitrogen (Dumas) 0.5 %.

2-Chloro-4-nitrotoluene. The redistilled chloronitrotoluene (freezing point 62.4—62.6°C) was oxidized in the usual way and then the crude product was treated with caustic soda and reprecipitated in order to remove unconverted chloronitrotoluene. In a series of experiments it was found, that a big charge was possible because the reaction proceeded relatively calmly. Thus it was possible to charge as much as 300—400 g in the 2 500 ml autoclave without risking a too violent reaction. Table 7 shows some representative results, obtained with nitric acid of 30 % concentration in a 20 % excess. The acid was charged in two portions.

Table 7.

Temperature °C	Pressure kg/cm^2	Conversion %	Yield %	Melting point °C	Eq. weight
160—165	16	82	70	140—141	203.2
165—170	39	89	79	136—138	206.3
180	38	91	88	140—141	204.6
200	34	95	82	138—139	201.5

Experiments with nitric acid of 20 % concentration at 170—180° C and 25—35 kg/cm^2 gave a 72—76 % conversion and an 87—88 % yield of a product with a good analysis. Chlorine content analyses were in good accordance with the calculated values.

The author wishes to thank Dr. Allan Dahlén for his great interest in this work and for valuable discussions.

SUMMARY

Using dilute nitric acid at temperatures around 200° C and pressures around 30—50 kg/cm^2, *o*- and *p*-xylenes, *p*-cymene, *p*-toluic aldehyde, ditolylsulfone, 2-chloro-4-nitrotoluene and different chlorotoluenes were oxidized to the corresponding carboxylic acids in yields generally between 75 and 90 %. The crude acids were somewhat contaminated with nitrated products.

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Received February 5, 1953.