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3,256,323

PROCESS FOR OXIDIZING AROMATIC ETHERS TO AROMATIC ACIDS

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The present invention is directed to a method for producing aromatic acids by nitric acid oxidation. More particularly, the invention is concerned with the oxidation of a bifunctional aromatic ether with nitric acid to form the corresponding dibasic acid. In its more specific aspects the invention deals with oxidizing a bifunctional aromatic ether selected from the group consisting of dimethoxymethyl benzene, dimethoxymethyl toluene and dimethoxyxylene in a two-step method with nitric acid.

In the practice of the present invention bifunctional aromatic ethers are oxidized in two steps by first using low nitric acid strengths followed by high nitric acid strengths.

The present invention may be briefly described as a method for oxidizing a bifunctional aromatic ether selected from the group consisting of dimethoxymethyl benzene, dimethoxymethyl toluene and dimethoxymethyl xylene in two steps with aqueous nitric acid. The first step is carried out at relatively low acid strengths being within the range from about 20% to about 40% HNO₃ at a temperature within the range from about 60° to about 110° C. for a period of about 1 to about 4 hours. In the first step the bifunctional ether is oxidized to a mixture of the monobasic-aldehyde acid and dibasic acid, with the dibasic acid being only a small portion of the total mixture. The second step is the further oxidation of the acidic product formed in the first step with aqueous nitric acid of relatively high concentration within the range of about 60% to about 70% HNO₃ at a temperature within the range from about 70° to about 120° C. for a period of about 7 to about 9 hours whereby the dibasic acid corresponding to the bifunctional ether being oxidized is produced as the primary product.

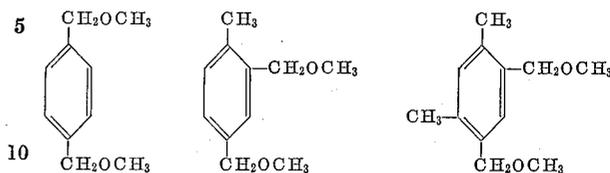
In the practice of the present invention the corresponding dibasic aromatic acid may be selectively made from the bifunctional aromatic ether of benzene, toluene or xylene by controlling the concentration of the nitric acid, the temperature under which the oxidation is conducted and the time in which the ether is oxidized by a selective two-step method.

Heretofore, dialkylbenzenes have been oxidized with nitric acid to produce the desired dibasic acids. In the nitric acid oxidation of dialkylbenzenes, however, high temperatures and pressures are required. It has been suggested that aromatics having such functional groups as aldehydes, ketones and alcohols be used as starting materials so that less severe conditions may be utilized. However, the use of aromatics having functional groups as feed materials in the oxidation with nitric acid has proved that while the initiation of the oxidation of the functional groups requires less severe conditions, and in this sense is easier, the oxidation cannot be easily controlled once oxidation starts and nitration of the aromatic may take place. Thus, to obtain the desired product, namely the dibasic acid from a bifunctional aromatic ether by merely selecting acid strength, temperature and time is a difficult oxidation. The present invention has overcome many of the problems, especially the close control required to produce the desired dibasic acids, by carrying out the oxidation of bifunctional aromatic ethers in an easy two-step process.

The bifunctional aromatic ethers employed in the practice of the present invention may suitably be bifunc-

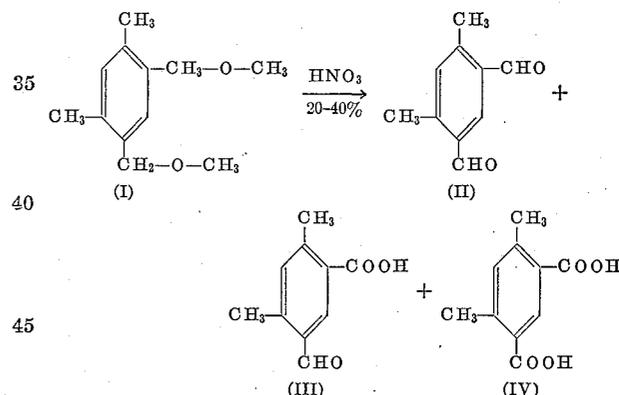
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tional benzene ethers, bifunctional toluene ethers and the bifunctional xylene ethers, such as exemplified by the following structural examples:



and the like

According to the present invention, the bifunctional aromatic ethers are oxidized with nitric acid in a two-step process. In the first step the nitric acid strength is within the range from about 20% to about 40% HNO₃. A preferred acid strength is about 30% to about 35% HNO₃. The oxidation usually begins at a temperature between 60° and 70° C., and the temperature is maintained within the range from about 60° to about 110° C. Preferably, the temperature is maintained between 70° and 106° C. The oxidation of the functional ether group is relatively easy and requires a period of about 1 to about 4 hours. It was found that the oxidation can be easily accomplished in a period of about 2 to about 3 hours. In the first step an acidic product is formed which consists essentially of the monobasic-aldehyde acid and the dibasic acid as well as the dialdehyde. The reaction of the first step is illustrated by the bifunctional xylene ether in the following structural equation:

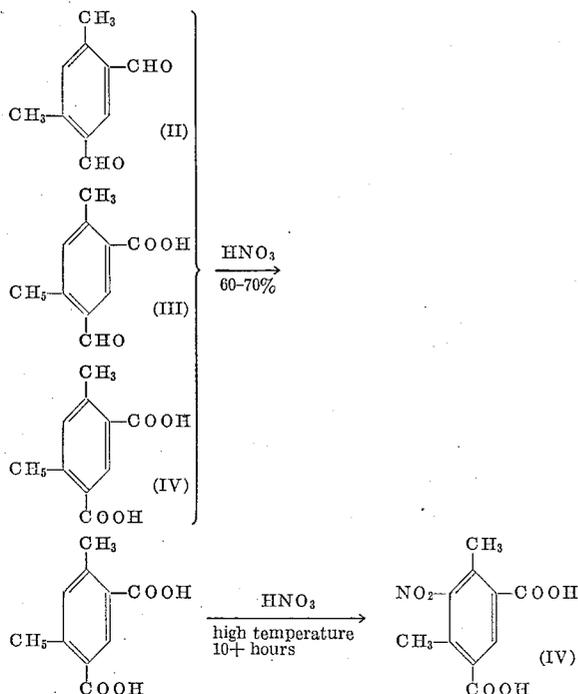


The acidic product is considered to be the mixture of the compounds illustrated by II, III and IV. This acidic product is further oxidized in a second step utilizing acid strengths within the range from about 60% to about 70% HNO₃. This acid mixture may be further oxidized at the higher acid strengths by merely changing the conditions in the same reaction vessel wherein the first step takes place or by separating the acidic product and placing it in a second reaction vessel. In the second step temperatures within the range from about 70° to about 120° C. are utilized. It is preferred that the temperature be maintained between about 75° and about 120° C. It is to be noted that some degree of control with regard to temperature and time must be maintained depending upon whether there are 0, 1 or 2 alkyl groups on the aromatic. The presence of alkyl groups tend to enhance nitration, and accordingly, the maximum temperature may necessarily be lower when alkyl groups are present than when there are no alkyl groups on the aromatic being oxidized. In the second oxidation step with nitric acid, the time required is about 7 to about 9 hours. The time of oxidation in the second step may run as little as 3 hours; however, only about 70 weight percent of the product is then

50
55
60
65
70

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the desired dibasic acid. The reaction of the second step may be illustrated by the following structural equations:



It is to be noted that the overoxidation of the dibasic acid results in the nitrated dibasic acid. While the nitrated acid is a valuable intermediate in the preparation of polymers and polymeric esters used in the formation of synthetic fibers, it is an undesired impurity when the dibasic acid is the desired product. Accordingly, while the reaction may be run to form the nitrated acid, the two-step process of the present invention enables high purity dibasic acid to be formed without the production of the nitrated acid.

The present invention will be illustrated by the following examples which are considered to be illustrative of the invention and are not to limit the scope thereof.

EXAMPLE I

1,4-bis(methoxymethyl) benzene is oxidized in a two-step process. The first step is illustrated by the two runs in Table I hereinafter:

Table I

	Run 1	Run 2
Materials charged, mols:		
1,4-bis(Methoxymethyl) benzene.....	0.2	0.2
Nitric acid.....	2.0	2.0
Operating conditions:		
Temp., ° C.....	70-105	70-105
Time, hrs.....	2.0	2.25
Nitric acid, wt. percent at start.....	30	30
Nitric acid, wt. percent at end.....	23	22
Acidic product:		
Wt., gms.....	29.3	30.5
M.P., ° C.....	270-340	200-360
Neut. equiv.....	169.6	119.6
Analysis, wt. percent:		
Terephthalic acid.....	22.3	32.6
4-carboxybenzaldehyde ¹	48.2	66.4
1,4-benzenedicarboxaldehyde ²	29.5	1.0



The acidic product which is a mixture of the dibasic acid, the monobasic-aldehyde acid, and dialdehyde as the analysis shows is recovered by cooling to 0° C. (ice water) and removing the nitric acid by decantation. The

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acidic product is washed with water before analysis to remove substantially all the nitric acid. In comparing the two runs it can be seen that the difference in time results in the oxidation of substantially all the dialdehyde; however, the dibasic acid is still only about one-third of the acidic product with the increased time.

A composite acidic product produced by runs similar to the above was formed and had the following composition.

Compound:	Wt. percent
Terephthalic acid.....	18.4
4-carboxybenzaldehyde.....	78.0
1,4-benzenedicarboxaldehyde.....	3.6

The second step of the oxidation is illustrated in Table II starting with the composite acidic product above.

Table II

Materials charged:			
Composite acidic product, gms.....	20.5	20.5	20.5
70% HNO (total) cc.....	184.7	169.4	254
Operating conditions:			
Temp., ° C.....	105-120	90-122	90-122
Time, hrs.....	3.0	4.5	8.0
Nitric acid at start, percent.....	70	70	70
Nitric acid at end, percent.....	63.7	68.5	68.9
Products:			
Wt., gms.....	20.33	21.5	21.8
M.P., ° C.....	300-375	370+	370+
Neut. equiv., gms.....	96.6	93.0	88.9
Analysis of products (NMR), wt. percent:			
Terephthalic acid.....	70	75.2	81.6
4-carboxybenzaldehyde.....	30	24.8	18.4
1,4-benzenedicarboxaldehyde.....	0	0	0

¹ 1.33 mols. ² 2.66 mols. ³ 3.99 mols.

Again the dibasic acid is recovered by cooling to 0° C. (ice water) whereby the dibasic acid precipitates and the nitric acid is decanted off. The dibasic acid is then washed with water until free of nitric acid.

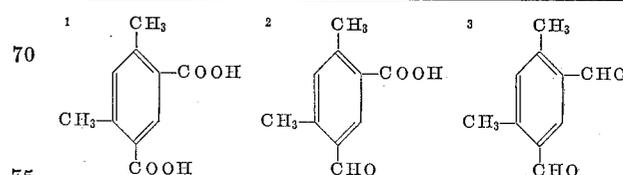
In a commercial operation two reaction vessels are used and the operation is substantially that as just described. The acidic product recovered from the first step, however, is not washed. The nitric acid from the second step is used to maintain the desired acid strength in the first step of the oxidation. Thus, maximum use is made of the nitric acid.

EXAMPLE II

4,6-dimethoxymethyl m-xylene is oxidized with 30% nitric acid. Three runs of the first step of the oxidation are illustrated in Table III.

Table III

	Run 1	Run 2	Run 3
Material charged:			
4,6-dimethoxymethyl m-xylene, mols.....	0.2	0.2	0.15
(38.8 g.).....	(38.8 g.)	(38.8 g.)	(29.1 g.)
Nitric acid, mols.....	2.0	2.0	1.5
Operating conditions:			
Temp., ° C.....	65-106	65-105	65-106
Time, hrs.....	2.5	2.5	2.5
Nitric acid at start, wt. percent.....	30	30	30
Nitric acid at end, wt. percent.....	22.0	21.5	21.2
Acidic product produced:			
Wt., gms.....	35.0	35.2	24.0
M.P., ° C.....	190-295	245-295	215-290
Composite of acidic product from all three runs:			
Wt., gms.....		94.2	
Neut. equiv.....		140.0	
Analysis, wt. percent:			
Dibasic acid ¹		38.0	
Aldehyde acid ²		60.0	
Dialdehyde ³		2.0	



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Two portions of the composite acidic product are further oxidized with 70% nitric acid. It is to be noted that the time and temperature must be controlled to prevent nitration of the 4,6-dimethylisophthalic acid. Thus, the ease of nitrating the alkyl aromatics is illustrated in Table IV.

Table IV

	Run 1	Run 2
Materials charged:		
Acidic product in Table III, gms.....	26.0	20.0
70% HNO ₃ (total) cc.....	¹ 134	² 178
Operating conditions:		
Temp., °C.....	75-93	75-120
Time, hrs.....	7.5	11.0
Nitric acid at start, percent.....	70	70
Nitric acid at end, percent.....	64.0	64.3
Product:		
Wt., gms.....	19.6	19.1
M.P., °C.....	280-285	295-305
Analysis of product (by NMR) wt. percent:		
4,6-dimethylisophthalic acid.....	93.50	0
Aldehyde acid.....	6.46	0
Dialdehyde.....	0	0
5-nitro-4,6-dimethylisophthalic acid.....	Trace	100

¹ 2.1 mols. ² 2.8 mols.

The foregoing examples illustrated the present invention wherein the two steps were physically separate. However, the two-step process may be accomplished in the same reaction vessel as illustrated hereinafter.

EXAMPLE III

2,4-dimethoxymethyl toluene (75 cc.) and 35% nitric

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acid (200 cc.) are charged to a flask equipped with a mechanical stirrer. This mixture is heated and stirred until reaction starts at 60° C. Thereafter the 35% nitric acid and the 2,4-dimethoxymethyl toluene are added simultaneously from two dropping funnels at a rate such that the reaction is maintained under control. Nitric acid and feed are added until about 0.2 of a mol of 2,4-dimethoxymethyl toluene and about 2.0 mols nitric acid have been added to the flask. Heating and stirring is continued and the temperature maintained to avoid a too rapid reaction rate. Addition of 70% nitric acid to the flask periodically maintains the nitric acid concentration near 35%. After about 3 hours of heating and stirring the mixture, the acid strength is brought up to about 70% nitric acid by removing some water and the addition of concentrated nitric acid to the flask. The temperature is then lowered to about 75° C. Seventy percent nitric acid is periodically added to maintain the nitric acid concentration near 70% and the reaction mixture is continuously heated and stirred for a further 7½ to 8 hours until the reaction is complete. Analysis of the product shows in excess of 85 weight percent of 4-methyl metaphthalic acid. The total reaction time is about 11 hours.

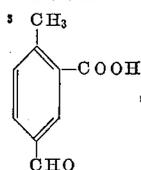
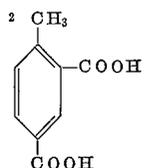
EXAMPLE IV

2,4-dimethoxymethyl toluene is oxidized with nitric acid as is illustrated in Table V below. At the start of the run, only 100 cc. of the diether and 200 cc. of 35% nitric acid are charged to the reactor.

Table V

Cumulative reaction time, hrs.	Sample	Temp., °C.	HNO ₃ added, mols	HNO ₃ strength, percent	Test for nitration of product	Neut. equiv.	Calc. from neut. equivs., wt. percent	
							Dibasic acid ²	Aldehyde acid ³
0	-----	82	-----	35.0	-----	-----	-----	-----
13	-----	90	4.00	5.5	-----	-----	-----	-----
5	A	90	4.263	21.2	Neg.....	129.8	32.05	67.95
7	B	85	6.722	40.6	Neg.....	110.0	59.73	40.27
10	C	85	-----	40.6	Neg.....	105.4	67.64	32.36
13	D	88	3.160	45.4	Neg.....	101.3	75.30	24.70
16.5	E	87	-----	45.2	Neg.....	99.2	79.47	20.53
19.0	F	92	-----	45.0	Neg.....	96.0	86.18	13.82
22.0	G	92	-----	44.4	Neg.....	94.2	90.14	9.86
25.5	H	93	4.00	43.7	Neg.....	92.6	93.80	6.20
32.5	I	105	2.424	42.3	Neg.....	91.7	95.81	4.19
33.0	J	105	-----	47.9	Neg.....	92.0	95.21	4.79
33.0			24.56					
Total			Total					

¹ At end of 2 hrs. the total feed, 2 mols has been added.



, mixture of two isomers.

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It can be concluded from this run that the second step of the oxidation to be effective must be carried out at acid strengths between about 60% and 70% HNO₃. It is further noted, however, that substantial reaction occurs with substantially no fortification of the acid. High acid even at the low acid strengths on the fresh feed and strengths (above 40%) cannot be used on fresh feed of the bifunctional aromatic ethers since the presence of the ether functional groups enhance nitration. Furthermore, the oxidation reaction using high acid strengths initially go out of control by producing excessive gases and rapidly increasing in temperature.

EXAMPLE V

4,6-dimethoxymethyl m-xylene (350 parts) is oxidized with 55-60% nitric acid (2,000 parts). The temperature is carefully maintained between 65° and 85° C. A yield of 300 parts representing 85% of theoretical and 95% pure dibasic acid is obtained containing 4-5% monobasic-aldehyde acid and a trace of the nitrated acid. The reaction requires in excess of 18 hours.

Example V illustrates the controlled operation required to obtain the dibasic acid in a one-step method. Furthermore, it is noted that such a method requires substantially more time than the two-step method of the present invention. Even though the temperature of the oxidation does not exceed 85° C. in the one-step operation, a trace of the nitrated acid is formed.

The foregoing examples are merely illustrative of the present invention and apply equally to the other isomer forms or to a mixture of the isomers.

The dibasic acids formed by the present invention have known utility and may suitably be employed in the preparation of alkyd resins and unsaturated linear polyesters.

The nature and objects of the present invention having been completely described and illustrated and the best mode having been set forth, what I wish to claim as new and useful and secure by Letters Patent is:

1. A method for oxidizing a bifunctional aromatic ether selected from the group consisting of dimethoxymethyl benzene, dimethoxymethyl toluene, and dimethoxymethyl xylene which comprises oxidizing said ether with nitric acid having a strength within the range from about 20% to about 40% HNO₃ at a temperature within the range from about 60° to about 110° C. for a period of about 1 to about 4 hours to form an acidic product, and oxidizing

said acidic product with nitric acid having a strength within the range from about 60% to about 70% HNO₃ at a temperature within the range from about 70° to about 120° C. for a period of about 7 to about 9 hours to produce substantially the corresponding dibasic acid.

2. A method in accordance with claim 1 wherein said bifunctional aromatic ether is dimethoxymethyl benzene.

3. A method in accordance with claim 1 wherein said bifunctional aromatic ether is dimethoxymethyl toluene.

4. A method in accordance with claim 1 wherein said bifunctional aromatic ether is dimethoxymethyl xylene.

5. A method for oxidizing dimethoxymethyl benzene to produce the corresponding dibasic acid which comprises oxidizing said dimethoxymethyl benzene with about 20% to about 30% nitric acid at a temperature within the range of about 70° to about 105° C. for a period of about 2 to about 3 hours to form an acidic product, and further oxidizing said acidic product with about 60% to about 70% nitric acid at a temperature within the range of about 90° to about 120° C. for a period of about 7 to about 9 hours whereby said dibasic acid is produced.

6. A method in accordance with claim 5 wherein said acidic product is cooled and the weak nitric acid is removed before oxidizing said acidic product.

7. A method for oxidizing dimethoxymethyl xylene to produce the corresponding dibasic acid which comprises oxidizing said dimethoxymethyl xylene with about 20% to about 30% nitric acid at a temperature within the range of about 65° to about 106° C. for a period of about 2 to about 3 hours to form an acidic product, and further oxidizing said acidic product with about 60% to about 70% nitric acid at a temperature within the range of about 75° to about 95° C. for a period of about 7 to about 9 hours whereby said dibasic acid is produced.

8. A method in accordance with claim 7 wherein said acidic product is cooled and the weak nitric acid is removed before oxidizing said acidic product.

References Cited by the Examiner

UNITED STATES PATENTS

2,497,889	2/1950	Hull	-----	260-523
3,068,280	12/1962	Katzschmann	-----	260-523

LORRAINE A. WEINBERGER, *Primary Examiner*.

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