

Mechanism of the Nitric Acid Oxidation of Olefins

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The nitric acid oxidation of olefins and of several related derivatives is described. In contrast to the oxidation of alcohols and ketones to carboxylic acids, the cleavage of olefins with nitric acid is specifically catalyzed by the vanadium ion. Several potential intermediates were examined for vanadium dependency. The formation of 2-nitrosocyclohexyl nitrate dimer and 2-ketocyclohexyl nitrate in the reaction of cyclohexene with a nitric acid solution of nitrogen tetroxide was demonstrated. An oxidation mechanism based on the addition of nitrogen tetroxide to olefins as nitrosonium nitrate followed by conversion to adipoin and cleavage with vanadic ion is proposed. The vanadium-catalyzed nitric acid oxidation of α -glycols and ketols to dibasic acids is shown to be an excellent preparative method.

Nitric acid has been useful for many years for oxidizing alcohols, ketones, and olefins to acids. In the oxidation of cyclohexanol and cyclohexanone to adipic acid, the mechanism has been fairly well worked out,¹ but, with olefins like cyclohexene, almost nothing has been published. The present paper² reports in detail our work and conclusions in this area and presents additional evidence for our proposed mechanism.²

Early in our study it became quite clear that the oxidation of olefins like cyclohexene and Δ^4 -tetrahydrophthalic acid to adipic acid and *meso*-1,2,3,4-butane-tetracarboxylic acid, respectively, went by an entirely different mechanism from the corresponding ketone or alcohol even though the end products were identical. The chief evidence supporting this conclusion is the discovery that olefin oxidation by nitric acid is specifically catalyzed by vanadium ion.^{2b} This remarkable catalysis can be observed at levels as low as 0.01 mole %. In the absence of vanadium, vigorous oxidation occurs but only lower dibasic acids, chiefly oxalic, are formed. Furthermore, 1 mole % levels of a large variety of elements comprising soluble salts of Mn, Cu, Cr, Se, Ti, Mo, W, Ru, Co, Zr, Ce, Fe, Ni, Ag, Hg, Ta, Nb, Pd, Pt, Pb, Bi, Sn, IO₄, As, Sb, Al, Os, and Ir gave only degradation products. This complete specificity is definitely not observed in the case of cyclohexanol and cyclohexanone^{1,3} where the use of vanadium and perhaps copper serve only to improve the yield a few per cent. This difference in mechanism is further substantiated by our failure to isolate any of the typical *ol*-one intermediates such as 6-nitro-6-hydroxyiminohexanoic acid or cyclohexanedione dimer hemihydrate (Table I, 16) as reported by Godt and Quinn and others.¹

Having established this clear difference we sought to determine what path the catalyzed olefin oxidation was taking both by isolating possible materials from early stages of the reaction and by testing logical candidates for vanadium dependency. An obvious route by way of cyclohexyl nitrate, which was easily obtained by addition of nitric acid⁴ to cyclohexene at room temperature,

could immediately be ruled out because this product was not oxidized under conditions which readily converted cyclohexene to adipic acid.⁵ In addition nitric acid in the absence of N₂O₄ but under vanadium catalysis reacted with cyclohexene at 5° in a different manner to give a brown oil. This crude material yielded only degradation products on further oxidation and therefore could not contain a key intermediate.

Other intermediates could be products formed by the essentially nonionic addition of nitrogen tetroxide to olefins. Thus, in an inert solvent (CCl₄, ether) nitrogen tetroxide adds to cyclohexene⁶ to give a mixture of 1,2-dinitrocyclohexane, 2-nitrocyclohexyl nitrate, 2-nitrocyclohexyl nitrite, and the dimer of 1-nitroso-2-nitrocyclohexane. Of these only the nitrate and nitrite esters were further oxidized to adipic acid, but since the yields were only 30–40% and since this result was not vanadium dependent they could not be intermediates.

The reaction was intercepted at what was presumably an early stage by keeping the temperature low (0–5°) and using a solution of nitrogen tetroxide in nitric acid. By these means, which would favor ionic addition, there was obtained without vanadium 2-nitrosocyclohexyl nitrate dimer^{7a} (II) and in the presence of vanadium 2-ketocyclohexyl nitrate (IV).^{7b} The dimer II was converted to IV by dilute nitric acid and both intermediates were convertible to adipic acid (VI) in high yields only in the presence of vanadium. A corresponding keto nitrate (15, Table I) of tetrahydrophthalic acid behaved in a similar manner.

The ketol nitrate IV has recently been prepared by other workers⁸ using nonionic solvents (*e.g.*, cyclohexane in place of nitric acid). In the latter method, however, cyclohexene was gradually added to a substantial excess of nitrogen tetroxide in cyclohexane. Under these conditions, even in nonpolar media, the concentration of nitrosonium nitrate would be considerably greater than in a reverse addition process. Also the effectiveness of an air stream^{9c} to obtain better efficiency may have been due to the inhibition of

(1) (a) H. C. Godt and J. F. Quinn, *J. Am. Chem. Soc.*, **78**, 1461 (1956); The n.m.r. spectra of cyclohexanedione dimer hemihydrate^{1b} is consistent with the structure given by these authors. (b) W. V. Van Asselt and D. W. Van Krevelen, *Rec. trav. chim.*, **82**, 51 (1963); **82**, 438 (1963). (c) Heinze, U. S. Department of Commerce, Office of Technical Services, Publication Board Report 73591, Washington, D. C., 1942, pp. 1043–1078.

(2) (a) This subject matter was first described in a preliminary communication by J. E. Franz and W. S. Knowles, *Chem. Ind. (London)*, 250 (1961). (b) A case which may bear some relation is the nitric acid oxidation of sugar to oxalic acid which is strongly catalyzed by vanadium: A. Neumann, L. Moeser, and E. Lindenbaum, *J. prakt. Chem.*, **75**, 146 (1907).

(3) A. F. Lindsay, *Chem. Eng. Sci. Suppl.*, **3**, 78 (1954).

(4) H. Toivonen, *Suomen Kemistilehti*, **29B**, 146 (1956); *Chem. Abstr.*, **51**, 14622d (1957).

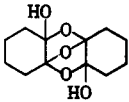
(5) C. H. Hamblet and D. B. Hanson, U. S. Patent 1,750,415 (1956).

(6) J. L. Riebsomer, *Chem. Rev.*, **35**, 157 (1945).

(7) (a) J. F. Herber, U. S. Patent 3,106,575 (1963); (b) J. E. Franz, U. S. Patent 3,080,414 (1963). Although we have no direct evidence we presume that the presence of vanadium promotes the conversion of II or some precursor of II to IV.

(8) (a) W. J. Arthur, U. S. Patent 3,095,442 (1963); (b) D. Zhuk, *et al.*, *Proc. Acad. Sci. USSR*, **136**, 41 (1961). (c) The referee suggests that the air stream probably acts not by inhibiting reaction of NO₂ radicals but by oxidation of N₂O₄, eliminating reactions of this oxide, or by the removal of water by formation of nitric acid.

TABLE I

No.	Compd. oxidized	Product	Yields, % (with V ⁺⁵)
1	Cyclohexene ^a	Adipic acid	58
2	<i>cis</i> - Δ^4 -Tetrahydrophthalic acid ^a	<i>meso</i> -Butane-1,2,3,4-tetracarboxylic acid	75
3	<i>trans</i> - Δ^4 -Tetrahydrophthalic acid ^a	<i>dl</i> -Butane-1,2,3,4-tetracarboxylic acid ^b	60
4	<i>cis</i> -1,2-Cyclohexanediol ^a	Adipic acid	92
5	<i>trans</i> -1,2-Cyclohexanediol ^a	Adipic acid	92
6	2-Hydroxycyclohexanone ^a (dimer or monomer)	Adipic acid	90
7	1,2-Cyclohexanedione	Glutaric acid	38
8	Adipic dialdehyde	Succinic acid	38
9	4,5-Dihydroxyhexahydrophthalic acid ^a	Butane-1,2,3,4-tetracarboxylic acid	90
10	Styrene	Benzoic acid	8
11	Styrenediol	Benzoic acid	95
12	2-Ketocyclohexyl nitrate ^a	Adipic acid	90
13	2-Nitrosocyclohexyl nitrate ^a (dimer)	Adipic acid	84
14	Cyclohexanedione monooxime	Adipic acid	39
15	4-Keto-5-nitrato-1,2-cyclohexanedicarboxylic acid ^a	Butane-1,2,3,4-tetracarboxylic acid	95
16		Adipic acid	89 ^d

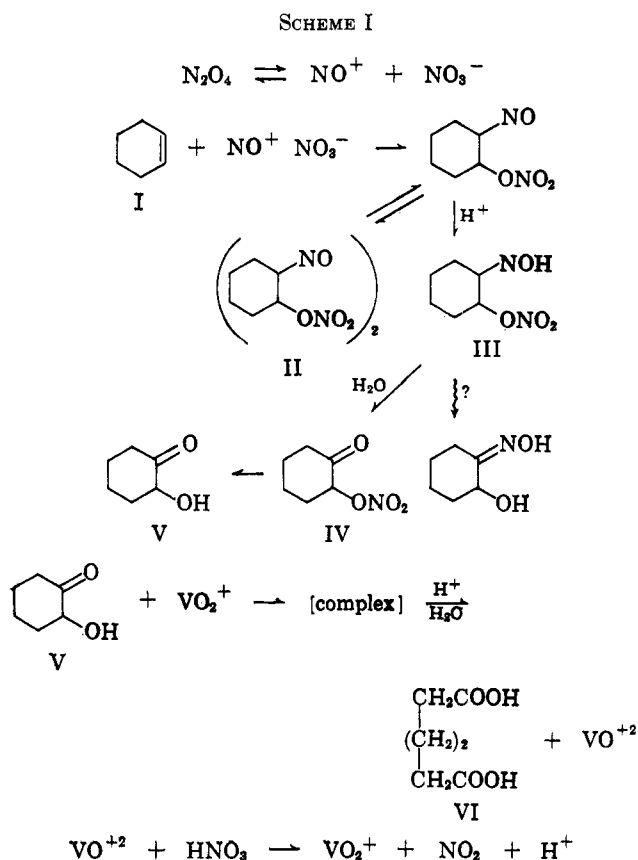
^a Only lower molecular weight oxidation products were obtained in the absence of V⁺⁵ (usually oxalic acid dihydrate). ^b B. Moldovskii and V. Babel, *Zh. Prikl. Khim.*, **36**, 1614 (1963). ^c See ref. 1a. ^d See ref. 1b.

competing free-radical reactions as is often the case (under some conditions, however, oxygen participates in the free-radical additions⁹). In ether and Skellysolve E we have found that simultaneous mixing of cyclohexene and nitrogen tetroxide yields the pseudonitrosite of Wieland and Blumich¹⁰ but none of the nitroso nitrate dimer obtained from nitric acid medium.

Table I lists possible precursors which were tested for vanadium dependency. The fact that both α -glycols and ketols are oxidized in high yields to dibasic acids without degradation shows not only that they could be possible intermediate but also that this vanadium-catalyzed oxidation is an excellent preparative method. Apparently, cyclohexanedione and its oxime (compounds 7 and 14) and adipic dialdehyde (8) cannot be intermediates because of low adipic acid yields. It is interesting to note that the Godt and Quinn dimer (16) clearly did show this vanadium dependency^{1b} making it a possible precursor, but all attempts to isolate this readily crystallizable product from our oxidations starting with olefin, adipoin, or adipoin dimer failed. It is remarkable that this compound, which is apparently a hydrated dimer of cyclohexane dione and which in many chemical reactions^{1a} behaves like the dione, acts so differently in the vanadium-catalyzed oxidation.

Adipoin oxime is a potential intermediate which has been described vaguely in the literature¹¹ several times. In our hands repeated attempts to prepare^{11b,c} this product in a pure state failed.

The evidence collected has enabled us to postulate a consistent and logical interpretation of the mechanism as illustrated in Scheme I. We propose that nitrogen tetroxide, initially formed by the first trace of oxidation, ionizes in nitric acid to nitrosonium nitrate and forms II by a noncatalyzed addition to cyclohexene (I) similar to the reported case¹² of isobutylene. In the presence of strong acid media II rearranges to III and



hydrolyzes^{12c} to IV. Further hydrolysis to adipoin may occur before the final step where V⁺⁵ cleaves the ring and forms adipic acid and V⁺⁴. The catalyst is then regenerated^{2,13} with strong nitric acid giving both nitrogen tetroxide as well as V⁺⁵ to complete the cycle.

(12) (a) E. Schoenbrunn and J. Gardner, *J. Am. Chem. Soc.*, **81**, 4905 (1959). (b) J. Gardiner and T. Steadman, German Patent 1,109,160 (1961). (c) The conversion of III to IV is not strictly a hydrolysis but probably a combined hydrolysis-oxidation reaction since hydroxylamine is not a reaction product.

(13) N. Tananaev, *Zh. Neorg. Khim.*, **1**, 27 (1956); *Chem. Abstr.*, **50** 10587 (1956).

(9) T. Stevens, *J. Am. Chem. Soc.*, **81**, 3593 (1959).

(10) H. Wieland and E. Blumich, *Ann.*, **424**, 75 (1921).

(11) (a) Belgian Patent 635,960 (1964); (b) F. Allison, *et al.*, *Helv. Chim. Acta*, **34**, 453 (1951); (c) W. Charlton, *et al.*, *J. Chem. Soc.*, 38 (1932).

Although we were unable to get a characterizable complex from vanadium and adipoin or any of the other likely intermediates, Waters¹⁴ showed that adipoin was readily oxidized to adipic acid by V⁺⁵ in acid solution. Presumably a cyclic chelate of vanadium is involved in this transformation. Since the oxidation goes rapidly without catalyst the vanadium evidently serves to increase the rate of the ring-cleavage reaction so that the formation of degradation products formed by successive nitration or nitrosation of positions adjacent to the carbonyl function is minimized.

In the preparation of adipic acid from cyclohexene a yield increase of 10 percentage points over the one-step oxidation was realized using a two-step method. The ketol nitrate was first prepared at low temperature and in the second step the crude mixture was then further oxidized with nitric acid in the presence of vanadium at 60°.

The vanadium-catalyzed oxidation of tetrahydrophthalic acid with nitric acid was studied in some detail. Although only 60–65% yields of *meso*-1,2,3,4-butanetetracarboxylic acid were obtained from the acid anhydride, the yield was improved to 75–78% when the free dibasic acid was used. In several experiments the off-gases obtained during the oxidation were analyzed for carbon dioxide and recoverable oxides of nitrogen (NO₂, N₂O₃, and NO). A carbon balance was obtained by analyzing the pot residues for carbon. It was thus found that 75% of the starting material was converted to the tetrabasic acid, 15% to carbon dioxide, and 10% to residues. About 35% of the nitric acid used was recoverable as N₂O₃ when the mole ratio of dicarboxylic acid to nitric acid was 1:5. Presumably, another 15 to 20% of the nitric acid would be recoverable from the mother liquors, whereas the remainder was converted into nitrogen and nitrous oxide.

The influence of temperature and concentration of nitric acid and catalyst in the oxidation were systematically studied. Above 65° the yields were lowered, whereas below 55° the reaction was too slow to be practical. For best results at least 5 moles of 70% nitric acid was required with a diminution in yield at lower concentrations. Passing oxygen or ozone through the reaction mixture during oxidation did not appear to exert any beneficial effect. A reverse order of addition, adding nitric acid to the dicarboxylic acid in acetic acid, gave poor results. In the absence of vanadium catalyst (0.01 mole %) tetracarboxylic acid yields were negligible, the major crystalline product being oxalic acid dihydrate. *meso*-1,2,3,4-Butanetetracarboxylic acid was found to be completely stable in nitric acid at 55–60° after 4 hr. of heating.

The nature of all of the side reactions which occur when Δ^4 -tetrahydrophthalic acid is oxidized with nitric acid are not known with certainty. One distinct possibility is that double-bond isomerization occurs prior to oxidation. The Δ^3 , Δ^2 , and Δ^1 isomers have been obtained¹⁵ by an acid-catalyzed isomerization of this type.

Experimental¹⁶

2-Ketocyclohexyl Nitrate (IV).—A mixture of 100 ml. of 70% nitric acid and 0.2 g. of ammonium metavanadate was placed in

a three-necked flask equipped with a gas inlet tube, agitator, dropping funnel, and thermometer. After cooling to 0° in an ice bath, 30 g. (0.32 mole) of nitrogen tetroxide and 33 g. (0.40 mole) of cyclohexene were added simultaneously with stirring during 4 hr. The temperature was maintained at 0–5° during the addition and at 0° for an additional hour thereafter. Water (150 ml.) was then added at such a rate that the temperature did not rise above 5° after which the ice bath was removed and the mixture was allowed to stir overnight. The reaction mixture was extracted with three 150-ml. portions of ether which were combined and washed with water, aqueous potassium bicarbonate, and finally water. After drying the solution over magnesium sulfate the solvent was carefully removed at room temperature under reduced pressure. The residual red oil (38.6 g.) crystallized to a yellow solid in a Dry Ice bath. After several recrystallizations from aqueous ethanol the white crystalline product melted at 31.5–32.5° and had a boiling point of 61° at 0.2 mm. The infrared spectrum in chloroform showed strong bands at 5.8, 6.1, 7.88, and 11.6 μ , for carbonyl and nitrate groups, respectively. By infrared analysis the crude red oil was shown to be 80% 2-ketocyclohexyl nitrate.

Anal. Calcd. for C₆H₉NO₄: C, 45.28; H, 5.71; N, 8.80. Found: C, 45.40; H, 5.82; N, 8.82.

2-Nitrosocyclohexyl Nitrate Dimer (II).—The reaction conditions were identical with those used in the preparation of IV except for the absence of the vanadium catalyst. After stirring overnight at room temperature, a white solid (4.35 g.) precipitated and was recovered by filtration. The product was purified by recrystallization from acetic acid: m.p. 148–149° dec. There was no adsorption in the 5–6- μ region of the infrared spectrum but strong nitrate bands appeared at 6.1 and 7.83 μ .

Anal. Calcd. for (C₆H₁₀N₂O₄)₂: C, 41.38; H, 5.79; N, 16.09. Found: C, 41.41; H, 5.90; N, 16.10.

In addition, the filtrate yielded 25.7 g. of red oil identical with that obtained in the preparation of 2-ketocyclohexyl nitrate.

Hydrolysis of Dimer II to IV.—A suspension of 3 g. of 2-nitrosocyclohexyl nitrate dimer in 50 ml. of 28% nitric acid dissolved after stirring for 24 hr. at room temperature. The solution was extracted with ether, washed with water, and dried over magnesium sulfate. After removal of solvent, 2.1 g. of red oil was recovered. The oil crystallized in a Dry Ice bath and melted at 31.6–32.6° when recrystallized from ethanol. The product was identical in all respects with the 2-ketocyclohexyl nitrate prepared in previous experiments.

4-Keto-5-nitrato-1,2-cyclohexanedicarboxylic Acid.—A mixture of 100 ml. of 70% nitric acid and 0.1 g. of NH₄VO₃ was placed in a four-necked flask equipped with a stirrer, condenser, gas inlet tube, solid addition conveyor, and a thermometer. The solid cyclohexanedicarboxylic acid (34.1 g.) was added uniformly with 17.2 g. of gaseous N₂O₄. The addition of the N₂O₄ took 3 hr. while the solid addition time was 5.5 hr. After the addition was complete the reaction was stirred at 0° for 1 hr.; 150 ml. of water was then added at such a rate that the temperature did not rise above 5°. The reaction mixture was allowed to warm to room temperature and stirred overnight. A white solid precipitated which weighed 8.53 g. (32%), m.p. 149–150° dec. The solid was recrystallized from ethyl acetate. The product had a tendency to hydrate and only after drying in a drying pistol was the anhydrous sample obtained, m.p. 145–146°. The infrared spectra showed a carbonyl peak at 5.77 μ , acid carbonyl at 5.85–5.9 μ , and nitrate at 6.12 and 7.77 μ .

Anal. Calcd. for C₈H₉NO₅: C, 38.87; H, 3.67; N, 5.67. Found: C, 39.27; H, 3.84; N, 5.34.

meso-Butanetetracarboxylic acid (12.3 g.) precipitated when the green filtrate was cooled to 0°, m.p. 190–191°.

4,5-Dihydroxyhexahydrophthalic Acid.—A mixture of 70 ml. (0.7 mole) of 30% aqueous hydrogen peroxide and 300 ml. (6.8 moles) of 85–90% formic acid was agitated and maintained at 40–45° as 85 g. (0.5 mole) of *cis*- Δ^4 -tetrahydrophthalic acid was added gradually. Stirring at 40–45° was continued an additional 2 hr. and the mixture was then allowed to remain at room temperature for 19 hr. After the solution was concentrated at reduced pressure, the glassy residue (112 g.) was dissolved in a solution of 60 g. (1.5 moles) of sodium hydroxide in 100 g. of water while maintaining the temperature below 50°. The resulting solution was allowed to remain at room temperature for 4 days and was then treated with 1.5 moles of concentrated hy-

(14) J. Littler, A. Mallet, and W. Waters, *J. Chem. Soc.*, 2761, 1767, 2772 (1960).

(15) R. Buckles and M. Deets, *J. Org. Chem.*, **23**, 485 (1958).

(16) All melting and boiling points are uncorrected. The infrared spectra were recorded on a Perkin-Elmer Model 137 Infracord.

drochloric acid. The solution was concentrated to dryness and the residue was extracted with methanol and then acetone. The methanol extract yielded 35 g. of tan solid melting at 168–172°, whereas 55 g. of nearly white solid, m.p. 176–178°; was obtained from the acetone. The latter material was further purified by recrystallization from methanol–benzene, m.p. 174–175°, neut. equiv. 108. (calcd. neut. equiv. 102). After recrystallizing from glacial acetic acid the product melted at 178° dec., neut. equiv. 102.

Anal. Calcd. for $C_8H_{12}O_6$: C, 47.05; H, 5.94; hydroxyl no., 16.7. Found: C, 47.20; H, 5.78; hydroxyl no., 18.5.

Nitric Acid Oxidations.—All oxidations were carried out by the gradual addition of 1.0 mole of the compound to be oxidized to 5.0 moles of 70% nitric acid containing 0.2 g. of ammonium metavanadate (when a catalyst was used). The temperature was maintained at 55–60° during addition and for an additional 2 hr. thereafter. After remaining overnight at room temperature the product was collected by filtration, washed with water, and recrystallized from a suitable solvent. The results are shown in Table I. The starting materials, *cis*-1,2-cyclohexanediol,¹⁷ *trans*-1,2-cyclohexanediol,¹⁸ adipic aldehyde,¹⁹ adipoin,²⁰ cyclohexyl nitrate,²¹ 1,2-cyclohexanedione,²² 1,2-cyclohexanedione dioxime,²² and 1,2-cyclohexanedione monoxime,²³ were prepared by methods described in the literature.

Two-Step Oxidation of Cyclohexene.—A mixture of 60 ml. of 70% nitric acid and 0.1 g. of NH_4VO_3 was placed in a three-necked flask equipped with a stirrer, condenser, ice-water-jacketed buret and dropping funnel, and a thermometer. The reaction mixture was cooled to 0° by means of an ice-salt-water bath and 37.5 g. (25.2 ml., 0.4 mole) of N_2O and 33 g. (0.4 mole) of cyclohexene were added simultaneously according to the time schedule in Table II.

TABLE II

Time, min.	Temp., °C.	N_2O_4 added, ml.	Cyclohexene remaining, ml.
0	0	0	43
25	2.5	9.1	37
55	4	18.1	27
90	1.5	21.7	17
105	2	25.3	13
170	2	...	0

The reaction was allowed to stir at 0° for 1.5 hr. The red intermediate was transferred to an ice-water-jacketed addition funnel and added to 24 ml. (0.4 mole) of 70% HNO_3 at 60°. The addition was regulated to maintain a temperature of 60–65°. During the addition which took 1.5 hr. a brown gas was evolved

(17) W. Rigby, *J. Chem. Soc.*, 1910 (1950).

(18) A. Roebuck and H. Adkins, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 217.

(19) J. English, *J. Am. Chem. Soc.*, **71**, 3310 (1949).

(20) (a) P. Bartlett, *ibid.*, **62**, 2933 (1940); (b) J. Sheehan, *et al.*, *ibid.*, **72**, 3376 (1950).

(21) N. Kornblum, *ibid.*, **74**, 3077 (1952).

(22) C. Hack, *et al.*, "Organic Syntheses," Coll. Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1963, p. 229.

(23) T. Geissman and M. Schlatter, *J. Org. Chem.*, **11**, 771 (1946).

and the reaction mixture turned green. After the addition the reaction was kept at 60° for 3 hr. after which it was allowed to cool to room temperature and subsequently packed in ice. The adipic acid precipitated out and was filtered and dried, yielding 37.3 g. The green filtrate was evaporated to one-half its volume and an additional 2.3 g. came out, making a total yield of 39.5 g. (68%). The melting point of the white solid was 150.5–152.5°.

Nitric Acid Oxidation of *cis*- Δ^4 -Tetrahydrophthalic Acid. **A. Carbon Balance and Off-Gas Analysis.**—Five typical runs were made purging the system with nitrogen and collecting the off-gases in two absorption flasks containing 200 ml. of 25% aqueous NaOH agitated with magnetic stirrers as follows: 70 g. (97% assay, 0.40 mole) of *cis*- Δ^4 -tetrahydrophthalic acid was added to 2.0 moles (125 ml.) of 70% nitric acid (or varied as in Table III) and 0.2 g. of ammonium metavanadate at 55–60° over 3 hr. and held at this temperature for an additional 2 hr. The mass was cooled to 5° and the product was filtered and washed with glacial acetic acid. The dry weight of the combined first and second crops was 73 g. (78% yield, m.p. 190–192°). In all cases the potentially recoverable nitric acid as NO_2^- came out about 35% of the acid charged. The carbon balance for a 1.00-mole run was obtained by adding up the carbon in the product, the 25 g. of residue (C, 42.0; H, 4.9; N, 5.4), and the CO_2 : moles of carbon/mole of reactant, 8.0; carbon in product, 6.0 moles; carbon in residue, 0.9 mole; carbon in CO_2 , 1.2 moles.

TABLE III

Run	70% HNO_3 , moles	CO_2 , moles	NO_2^- , moles	Recoverable HNO_3 , %	Yield of tetrabasic acid, %
1	2.30	0.44	0.79	34	72.5
2	1.90	0.44	0.64	34	75.5
3	1.49	0.42	0.54	36	66.5
4	1.95	0.49	0.68	35	75.3
5	2.00	0.48	0.70	35	75.0

B. Effect of Temperature.—The oxidations were conducted in the usual manner with 125 ml. of 70% nitric acid, 70 g. (97% assay, 0.40 mole) of Δ^4 -tetrahydrophthalic acid, and 0.2 g. of vanadium catalyst (see Table IV).

TABLE IV

Temp., °C.	Product, g.
90 ^a	30.0
85–80	59.8
80–60	64.6
60–55	70.0
50–45	68.0

^a Δ^4 -Tetrahydrophthalic anhydride used in place of the acid.

C. Effect of Nitric Acid (Moles).—Mixtures of various quantities of 70% nitric acid and 0.5 g. of vanadium catalyst were heated to 60° and 70 g. (0.40 mole) of Δ^4 -tetrahydrophthalic acid was added in the usual way. The yields are of pure dry butanetetra-carboxylic acid, m.p. 190–191°. Milliliters of HNO_3 (product in grams) follow: 150 (68.0); 125 (71.0); 100 (64.5); and 75 (49.5).