Oxidation of Cyclohexane to Adipic Acid with Nitrogen Dioxide

WILLIAM F. HOOT[1] AND KENNETH A. KOBE
University of Texas, Austin, Tex.

Cyclohexane was directly oxidized to adipic acid with nitrogen dioxide. Solutions of nitrogen dioxide in cyclohexane were allowed to react at temperatures from 50° to 90° C.; the yield of adipic acid was 98% at 50° C. after a reaction time of 43 hours. At the higher reaction temperatures, lower yields of adipic acid resulted although the reaction rate of nitrogen dioxide increased. The reaction rate of nitrogen dioxide for a cyclohexane solution which initially contains 6.6 weight % NO_2 is expressed by

$$\log_{10} k = 16.72 - \frac{5840}{T}$$

where k = reaction rate constant, hours^{-1} and T = absolute temperature, ° K. This reaction rate constant expresses rate of reaction of nitrogen dioxide in the expression $-\log_{10} C = k\theta - 1.51$, where C = moles of NO_2 per mole of cyclohexane and θ = reaction time, hours.

ADIPIC acid is a commercially important dibasic acid which is used as an intermediate in the production of nylon. Processes for the manufacture of adipic acid utilize a number of steps:

1. Benzene → phenol → cyclohexanol → adipic acid
2. Cyclohexane → cyclohexanol → cyclohexanone → adipic acid
3. Cyclohexane → adipic acid

Process 3, the direct oxidation of cyclohexane with nitrogen dioxide, was studied in an effort to find a more economical method for the synthesis of adipic acid.

Prior literature is meager on the reaction between cyclohexane and nitrogen dioxide. Schorigin and Topchiev (9) nitrated cyclohexane in the vapor phase and presence of ultraviolet light without formation of adipic acid. Doumani and coworkers (4, 5) reported the observation that adipic acid separates from a nitrogen dioxide–cyclohexane solution on prolonged standing. Cyclohexyl nitrite was observed to decompose slowly to adipic acid (7).

The main reaction between cyclohexane and nitrogen dioxide to adipic acid is believed to be

Cyclohexane + 5 NO_2 (Nitrogen dioxide) ↓↑ 5/2 N_2O_4 (Nitrogen Tetraoxide) → Adipic Acid + 5 NO (Nitric Oxide) + H_2O (1)
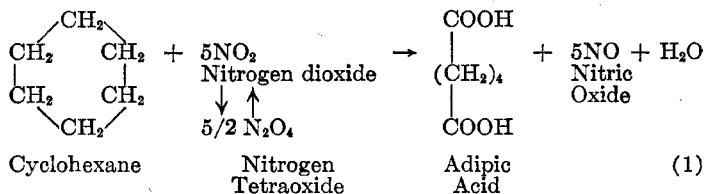
Experimental

Nitrogen dioxide was prepared by the reactions

$$2NaNO_2 + 2HNO_3 \rightarrow 2NaNO_3 + H_2O + NO + NO_2 \quad (2)$$

$$2NO + O_2 \rightarrow 2NO_2 \quad (3)$$

Concentrated nitric acid was added dropwise to aqueous sodium nitrite solution in the presence of sodium nitrite crystals while

[1] Present address, Pan American Refining Corp., Texas City, Tex.

oxygen was fed continuously through the apparatus to oxidize the nitric oxide. The product gases were dried by passage through Drierite and condensed in traps immersed in solid carbon dioxide. This impure mixture was purified by redistillation into a current of oxygen, dried by passage through phosphorus pentoxide, and frozen in traps immersed in solid carbon dioxide. The resulting nitrogen dioxide crystals were colorless (if slowly frozen) or snow white (if rapidly frozen).

The properties of the cyclohexane were: density at 25° C., 0.7737 gram per ml.; refractive index, n_D^{25}, 1.4233; and normal boiling point, 80.7° C. These properties are almost identical with the properties of pure cyclohexane as reported by the National Bureau of Standards. Purity of the cyclohexane was 99.45 mole % as determined by the freezing point method.

Mixtures of cyclohexane and nitrogen dioxide were prepared by pouring the liquid nitrogen dioxide into a known weight of chilled cyclohexane and determining the total weight. Nitrogen dioxide was completely soluble in cyclohexane up to the highest concentration used (61 weight % of nitrogen dioxide).

Reaction tubes of approximately 160-ml. capacity were made from glass tubing (28 mm. o.d.); one end was closed to a test tube end, and the other was joined with a 10 mm.-o.d. tube. The cold nitrogen dioxide–cyclohexane solution was poured into chilled reaction tubes through a thistle tube; these reaction tubes were then sealed by pulling out the glass tubing.

The samples were immersed in a water bath maintained at a preselected temperature. At timed intervals, individual samples were removed and immersed in crushed ice to arrest the reaction. The time lag in heating was less than one minute in reaching the bath temperature or in cooling the sample to 5° C. After chilling, the samples were extracted with distilled water to dissolve the adipic acid crystals and the unreacted nitrogen dioxide, which reacts with water according to the equation

$$2NO_2 + H_2O \longrightarrow HNO_2 + HNO_3$$

The reaction tube was rinsed four times with distilled water, and the washings were used to extract the cyclohexane layer. The cyclohexane layer and combined water extracts were then weighed. Aliquot portions were used for analyses.
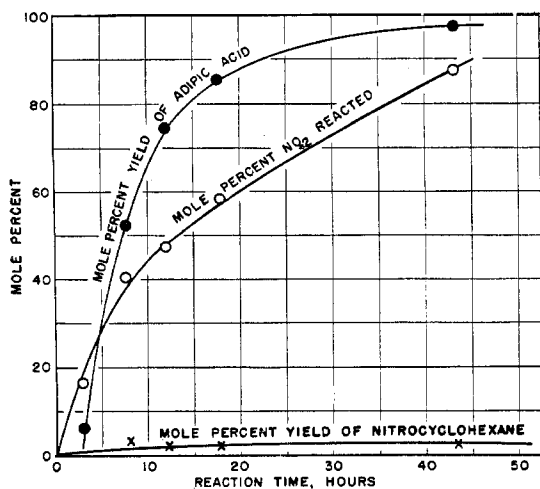
Figure 1. Oxidation of cyclohexane with NO₂ at 50° C.

Charge: 0.130 mole NO₂ per mole cyclohexane
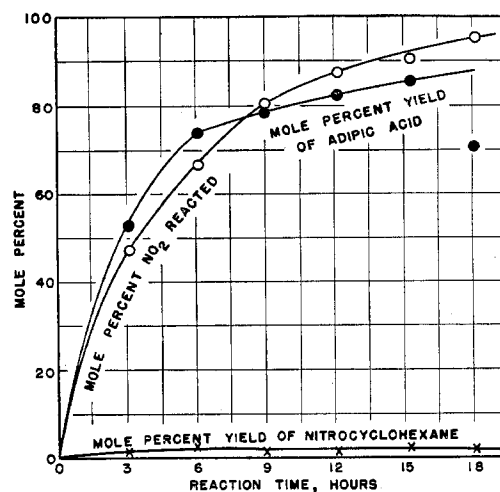
Figure 2. Oxidation of cyclohexane with NO₂ at 60° C.

Charge: 0.128 mole NO₂ per mole cyclohexane
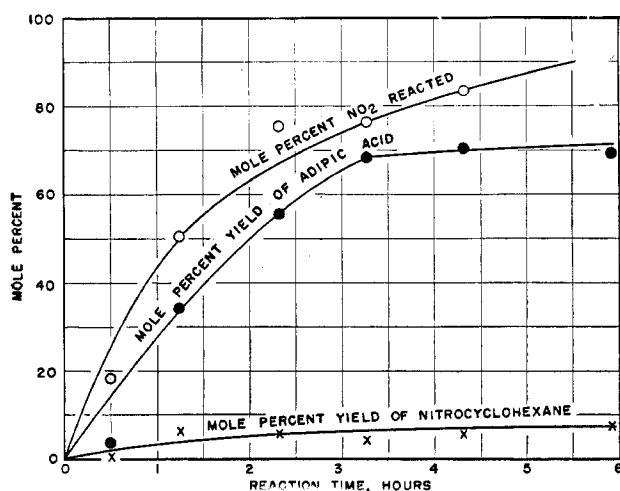
Figure 3. Oxidation of cyclohexane with NO₂ at 70° C.

Charge: 0.128 mole of NO₂ per mole of cyclohexane
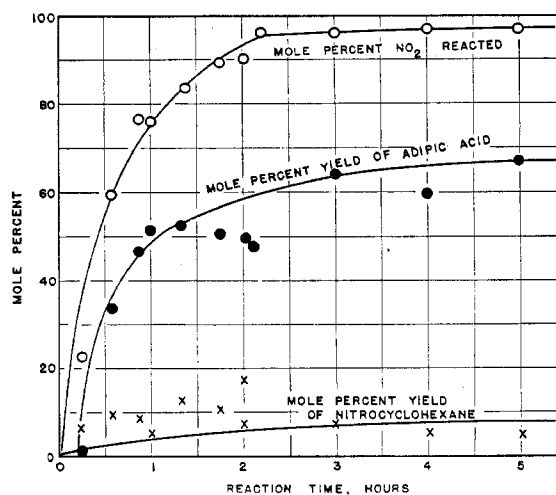
Figure 4. Oxidation of cyclohexane with NO₂ at 80° C.

Charge: 0.128 mole of NO₂ per mole of cyclohexane

Analytical Procedure for Dibasic Acids

Dibasic acids were determined as the disilver salt. For any probable dibasic acids from the oxidation of cyclohexane, only the disilver salts are formed, and they are relatively insoluble and without water of hydration.

A 25-ml. aliquot of the water layer was titrated with decinormal sodium hydroxide to the phenolphthalein end point to determine the total acidity. The dibasic acids were precipitated from this practically neutral solution after addition of 10 ml. of an aqueous silver nitrate solution containing 20 weight % of silver nitrate. The precipitate was filtered through a sintered glass (fine porosity) crucible. Ethyl alcohol (95%) was used to transfer and wash the precipitate. The crucibles were then dried for one hour at 110° C., cooled, and weighed. The dibasic acids were calculated and reported as adipic acid as follows:

$$\text{Millimoles of adipic acid} = \frac{\text{Weight of silver adipate}}{359.88} \times 1000$$

Reacted nitrogen dioxide was calculated as follows:

Reacted NO_2 = NO_2 charged − unreacted NO_2
Unreacted NO_2 = (H^+ equivalents from total acidity) −
2 (moles of adipic acid)

This analytical procedure was checked using samples of pure adipic acid. The molecular weight was calculated from twice the equivalent weight (from the total acidity); this mole weight was compared to a mole weight of 146.14 for adipic acid. The analytical results are shown in Table I.

Table I. Check of Analytical Method Using Pure Adipic Acid

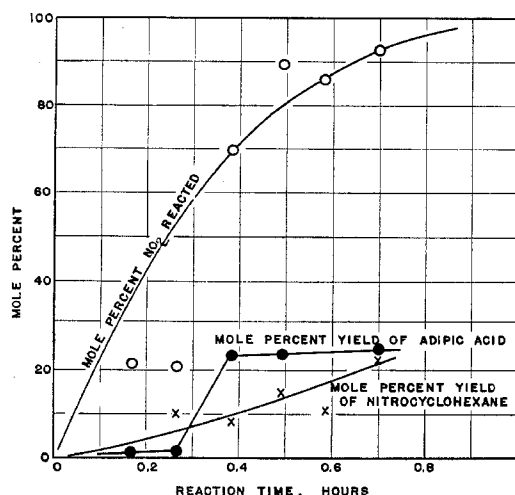| Sample of Adipic Acid, Grams	Molecular Weight from Acidity	Silver Adipate Precipitated, Grams	Adipic Acid Found, Grams	Deviation, %
0.0432	147.1	0.1121	0.0455	+5.3
0.1113	146.6	0.2790	0.1133	+1.8
0.1993	146.8	0.4952	0.2011	+0.9
0.2858	146.4	0.7116	0.2899	+1.4
0.3113	145.9	0.7711	0.3131	+0.6
0.3553	146.2	0.8860	0.3597	+1.2

Figure 5. Oxidation of cyclohexane with NO₂ at 90° C.

Charge: 0.133 mole of NO₂ per mole of cyclohexane

Single Crystallization of Adipic Acid from Dibasic Acids

Adipic acid was isolated and recovered from an aliquot portion by being dissolved in distilled water and recrystallized. The crystals were filtered from the mother liquor, dried at 120° C., and weighed.

Melting points of the crystals were 150° to 152° C. The melting points of these crystals mixed with pure adipic acid were 151° to 153° C. Calculation of the molecular weight from the neutralization equivalent was further proof of adipic acid. The recovery of adipic acid was calculated from the weight of the crystals recovered and the weight of dibasic acids originally present. The adipic acid left in the mother liquor was estimated from the volume of mother liquor, the temperature of the solution, and the solubility of adipic acid in water. Attané and Doumani (1) have reported the solubility of adipic acid in water.

Estimation of Nitrocompounds

Higher boiling nitrocompounds were determined as the residue after the slow evaporation of aliquot portions of the water layer and cyclohexane layer. This residue was corrected for the weight of dibasic acids present.
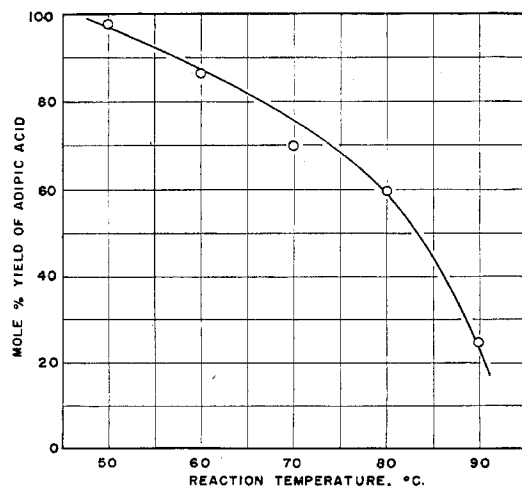

Figure 6. Effect of reaction temperature on ultimate yield of adipic acid

The presence of nitrite was identified by a characteristic nitrite reaction (6), but a positive color test for di- and trinitrocompounds (2) was not obtained. With sodium hydroxide, the unknown became orange and when acidified with hydrochloric acid became green (this is an indication for a pseudo nitrole). The test for a secondary nitroparaffin was negative. Neither did the solution give the transformation by zinc and glacial acetic acid to cyclohexanone nor the reduction with zinc and hydrochloric acid to cyclohexylamine—both of these are reactions of nitrocyclohexane (8). Nitrocyclohexane also yields cyclohexanone by treatment with sodium hydroxide to form the sodium salt and subsequent acidification (3). This test was negative for the unknown. The refractive index, n_D^{20}, was 1.479 for the unknown.

Although the nitrocompound was not identified, the yield is reported as nitrocyclohexane.

Calculation of Product Yield

Based on reaction 1, the mole % yield of adipic acid based on nitrogen dioxide was defined as

$$\frac{\text{Moles of adipic acid formed}}{\text{Moles of NO}_2 \text{ reacted}} \ (5) \ (100)$$

Data and Results of Investigation

Preliminary work to find approximate reaction rates and suitable concentrations consisted of 12 runs varying in concentration from 0.5 to 16% by weight of nitrogen dioxide in cyclohexane at 40° and 60° C. These products were used to identify the reaction products and develop an analytical scheme.

With a fixed initial concentration of nitrogen dioxide in cyclohexane of 6.6% by weight (0.13 mole of NO₂ per mole of cyclohexane), the reaction rates and yields of dibasic acids reported as adipic acid were determined at temperatures between 50° and 90° C. The results, which are shown in Figures 1 through 5, show the yield of adipic acid as a function of reaction time. The mole percentage of nitrogen dioxide reacted and the yield of nitrocyclohexane are also shown in Figures 1 through 5.

In Figure 1 the yield of adipic acid is 98 mole % using a reaction temperature of 50° C. However, the reaction rate is slow—i.e., only 88% of the nitrogen dioxide was reacted after 43 hours. The yield of nitrocyclohexane was constant at 3 mole %. Notice in Figures 2 through 5, how higher reaction temperatures decrease the yields of dibasic acids and also decrease the reaction time.

At a reaction temperature of 60° C. (Figure 2), the yield of adipic acid was 86 mole % after 15 hours, and 91% of the nitrogen dioxide was reacted. The yield of nitrocyclohexane was 2%.

At 70° C. (Figure 3), the yield of adipic acid was 69% at a reaction time of 3.3 hours where the total nitrogen dioxide reacted was 77%. The yield of nitrocyclohexane was 4%.

Figure 4 shows the reaction at 80° C.; the yield of adipic acid was 64% at a reaction time of 3 hours where the total nitrogen dioxide reacted was 96%.

The reaction at 90° C. is shown in Figure 5. After a reaction time of 0.58 hour the yield of dibasic acid was 25% and 86% of the nitrogen dioxide had reacted.

The ultimate yield of adipic acid as a function of reaction temperature is shown in Figure 6.

Figure 6 was constructed from the final yields shown in Figures 1 through 5. These results show that the yield of adipic acid decreases with higher reaction temperature.

In order to determine the amount of dibasic acids shown as adipic acid, pure adipic acid was recrystallized from individual samples which were selected for the longest reaction time at a given temperature. The yields of recrystallized adipic acid (m.p., 150–152° C.) are shown in Figure 7.

The results in Figure 7 show that the ultimate yield of pure adipic acid decreases with increasing reaction temperature. At a reaction temperature of 90° C., no adipic acid was recovered from the dibasic acid products.
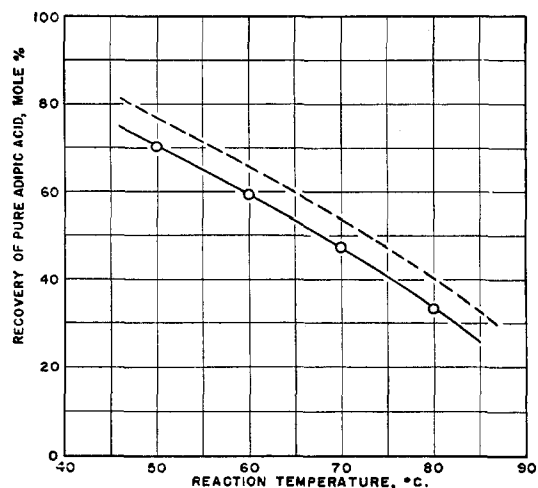
Figure 7. Ultimate yield of adipic acid by recrystallization of dibasic acids

Solid line represents recovery of adipic acid crystals (m.p., 150–152° C.); broken line includes adipic acid estimated to be in mother liquor

In order to determine the kinetics of the reaction between cyclohexane and nitrogen dioxide, the mole ratios of reactants were varied. Six samples were charged with concentrations of about 10, 20, 30, 40, 50, and 74 mole % of nitrogen dioxide at a reaction temperature of 70° C. Forty minutes after the samples were put in the water bath, the most concentrated mixture detonated violently. This explosion completely demolished the experimental apparatus. In view of the unexpected explosion, it was decided to present the data of this investigation at this time.

Reaction Rate between Cyclohexane and Nitrogen Dioxide

This reaction is assumed to be pseudo-unimolecular since the cyclohexane was present in large excess. The logarithm of the concentration of unreacted nitrogen dioxide was plotted versus the reaction time. This correlation of the data agreed nearly perfectly with the theory. These reaction rate constants are then the product of a higher order reaction constant and the concentration of cyclohexane. In order to show the influence of temperature, these reaction rate constants were plotted as the logarithm of reaction rate versus the reciprocal of the absolute temperature. This resulted in a straight line. From these results, the energy of activation was found to be +26,700 calories per mole of nitrogen dioxide. The expression for the reaction rate constant as a function of temperature is

$$\log_{10} k = 16.72 - \frac{5840}{T}$$

where k = reaction rate constant, hours^{-1}, and T = absolute temperature, ° K.

This reaction rate constant, k, expresses the rate of reaction in the form

$$-\log_{10} C = k\theta - 1.51$$

where C = moles of NO_2 per mole of cyclohexane, and θ = reaction time, hours.

In using these equations, note that they apply only to mixtures that initially contain 0.13 mole of nitrogen dioxide per mole of cyclohexane.

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Mononitration of o- and p-Nitrotoluene

KENNETH A. KOBE, CHARLES G. SKINNER, AND HERSHEL B. PRINDLE

University of Texas, Austin, Tex.

DINITROTOLUENES . . .

first published information on how process variables affect yield in the second step of TNT production

The yield of dinitrotoluenes from both o- and p-nitrotoluene has been determined as a function of the process variables—amount and concentration of sulfuric acid, temperature, time, and distribution of sulfuric acid between the mixed acid and the nitrator. Both isomers give essentially quantitative yields of 2,4-dinitrotoluene under the indicated optimum conditions.

FOR the past several years a study has been conducted in these laboratories in an effort to define more fully the nitration characteristics of aromatic compounds—i.e., benzene, toluene, the xylenes, cumene, and p-cymene (5, 7, 8, 9, 10).

Since 2,4,6-trinitrotoluene is, and has been since World War I, the single most important high explosive, a thorough study of its preparation is important. However, there are few published data in the experimental journals concerning the production characteristics of the intermediates. This is probably due to the fact that nearly all the research has been conducted in operating plants. There are available, however, some recipes (which are more or less typical of all aromatic nitration reactions)