Oxidation of *tert*-Butylcyclohexane to Dibasic Acids with Ozone

A combination of two types of oxidants is more effective than either alone

D_{IBASIC} acids, particularly alkyl adipic acids, are important intermediates in making plasticizers and synthetic lubricants. Ozone has been used to oxidize hydrocarbons (3, 9, 10) and naphthene derivatives with an oxygen-containing gas (5). Long has reviewed reactions of ozone with saturated hydrocarbons (7). Durland and Adkins studied direct ozonization of cyclohexane (2), and obtained formic acid, adipic acid, and cyclohexanone in yields less than 10%. In general, ozonolysis of other naphthenes gave saturated alcohols, ketones, acids, unsaturated ketones, and unsaturated hydrocarbons in 20 to 35% yields.

When ozone is the only oxidizing agent, the yield of dibasic acids from naphthenes is small and products of low molecular weight are formed, indicating degradation of the initial intermediates. In oxidations with air or ozone carbonhydrogen bonds are attacked somewhat unselectively. These reactions proceed by a free radical mechanism, and all the carbon-hydrogen bonds in the intermediates are labile to attack by free radicals. To oxidize the intermediates to dibasic acids without degradation, the oxidant must attack the molecule selectively at the functional group. Oxidations that proceed through an ionic mechanism are selective.

Simultaneous use of a free radical and ionic oxidant was investigated. Ozone initiates free radical oxidation of hydrocarbons; dichromate oxidizes oxygenated compounds by an ionic mechanism (δ). By using these two oxidants together the initial intermediate is oxidized to stable dibasic acids by dichromate before further oxidation with ozone.

Experimental

Reagents. tert-Butylcyclohexane was prepared by hydrogenation of Phillips' pure grade tert-butylbenzene. Ozone was generated in a Welsbach T-23 ozonator at 115 volts and flow rate of 18.1×10^{-3} mole of oxygen per minute. Concentration of ozone entering and leaving the reactor was determined by passing a measured volume through a neutral potassium iodide solution, acidifving, and tirrating the iodine liberated.

fying, and titrating the iodine liberated. **Ozonizations.** The ozone bubbled into the reactants through a fritted disk in the bottom of a 500-ml. flask and left through a reflux condenser. The reactants were rapidly agitated by a sealed stirrer to ensure complete mixing of the two phases, and temperature was kept constant by immersing the flask in an ethylene glycol bath.

At the end of the run, the flask and condenser were rinsed with water and *n*-heptane, and the aqueous and organicphases separated.

Carbon dioxide was determined by adsorption in sodium hydroxide and titration of the unreacted caustic with hydrochloric acid, using phenolphthalein as indicator. Dibasic acids in the aqueous product were determined by precipitation of the insoluble silver salts after removal of dichromate and sulfate anions as the insoluble barium salts. Upon neutralization of the solution with sodium hydroxide, chromium hydroxide precipitated and was removed. This procedure gives total *tert*-butyladipic, adipic, glutaric, and succinic acids.

The carboxylic acids for three runs were analyzed by elution chromatography (7). Chromium interfered and was removed by reduction of dichromate with sulfur dioxide, followed by precipitation of chromium hydroxide. The latter was boiled with sodium sulfate to remove adsorbed salts of carboxylic acids.

Oxidation of Cyclohexyl Hydroperoxide. Cyclohexyl hydroperoxide was prepared in 58% purity by addition of cyclohexyl magnesium chloride to oxygen-saturated ether at -80° C. (11, 12). The product contained cyclohexanone as impurity. The crude hydroperoxide decomposed in the presence of 2N hydrochloric acid at room temperature into an unidentified aldehyde and additional cyclohexanone (2,4-dinitrophenylhydrazone, melting point 158-161° C.; known derivative, 161-163° C.).

The hydroperoxide was oxidized at 73° C. by a solution 1M in dichromate and 4M in sulfuric acid. The aciddichromate solution (100 ml.) was mixed with 2.5 grams of the 58% pure hydroperoxide and 50 ml. of benzene and refluxed 3 hours. The product gave a negative carbonyl test with an equal volume of 2N hydrochloric acid saturated with 2,4-dinitrophenylhydrazine. Thus, oxidation of the initial carbonyl decomposition products of the hydroperoxide to acids was complete. Cyclohexanone present as an impurity was also oxidized to acid. The aqueous product was analyzed for carboxylic acids by elution chromatography.

Oxidation of tert-Butyladipic Acid.

tert-Butyladipic acid was prepared by oxidation of 4-tert-butylcyclohexanol with 50% nitric acid (8). The alcohol was synthesized by hydrogenation of *p*-tertbutylphenol (Eastman Kodak Co.), with nickel on kieselguhr catalyst. The β -tert-butyladipic acid was oxidized by refluxing with acid-dichromate solution with stirring.

Results

Table I, A shows the advantage of using the two-component oxidation system at 47° to 50° C.

In run 162 (Table II), only water was added; in the other two runs, aciddichromate solution was added. Not only the yield of *tert*-butyladipic acid but the ratio of C_4-C_{10} dibasic acids to acids of lower molecular weight is increased by the inorganic oxidizing agent. The acid-dichromate solution decreases the number of individual compounds.

The consumption of ozone and dichromate was also investigated. The reaction had essentially ceased after 5 hours, because of total consumption of naphthene. Because of thermal decomposition, the ozone is consumed at a constant rate in the absence of naphthene; in its presence, rate of ozone consumption decreases with time. If a correction is made for thermal decomposition of ozone in run 163, 2.0 moles of ozone react per mole of naphthene in the charge.

The dichromate anion is partially reduced. For every mole of naphthene in the charge 1.43 and 1.30 moles of dichromate were reduced (runs 160 and 163). As the only difference was doubled reaction time for run 163, slow conversion of chromic cation to dichromate by ozone is indicated.

Experiments were made to elucidate the mechanism by which dichromate increases the dibasic acid yield. If dichromate selectively oxidizes an initial intermediate before this intermediate is degraded by further attack of ozone, treatment with dichromate after ozonization should not effect the same yield increase as ozonization in the presence of dichromate. This was the case. The product from run 164 was made 1*M* in dichromate and 4*M* in sulfuric acid, and the resulting mixture kept at 73° C. for 3 hours. A 27% loss of carboxylic acids resulted. Similar losses were ob-

tained on heating the products from runs 146 and 160, which contained residual dichromate. Thus, the acid-dichromate oxidizing agent causes some oxidative decarboxylation of carboxylic acids.

The initial intermediate formed in the ozonization reaction is probably a hydroperoxide. Peroxides have been identified in both ozonization of hydrocarbons (10) and air-oxidation of alkyl cyclohexanes (4). Thus, to test the

| Oxidation | Products | of | Cyclohexyl- |
|-----------|----------|------|-------------|
| | hydroper | bixc | e |

| Mole $\%$ of |
|--------------|
| Total Acid |
| 77,8 |
| 11.5 |
| 6.6 |
| 4.1 |
| |

mechanism further, oxidation of cyclohexyl hydroperoxide (58%) by aciddichromate solution was investigated.

In the presence of sulfuric acid alone, the hydroperoxide decomposes to cyclohexanone and an aldehyde. Thus, the dichromate oxidation was continued until these initial decomposition products were oxidized. Adipic acid was the main product, with smaller amounts of succinic and glutaric acids. Some of these acids originated by oxidation of impurities in the hydroperoxide, but the hydroperoxide is not degraded by acid-dichromate solution to carboxylic acids of low molecular weight.

The above mechanism also requires stable carboxylic acids in the presence of the acid-dichromate mixture and no

Stability of β -tert-Butyladipic Acid under Oxidative Conditions

| Run No. | β -tert- Butyl- adipic Acid, G. | Benzene, G. | 95% H₂SO4, G. | Na ₂ Cr ₂ O ₇ . 2H ₂ O, G. | Water, G. | Temp., °C. | Time, Hr. | Re- covery, % COOH |
|------------|---|----------------|---------------------|--|--------------|---------------|--------------|-----------------------------|
| 141 | 2.49 | 0 | 39 | 30 | 77 | 100 | 18 | 29 |
| 143 | 2.63 | 100 | 40 | 30 | 77 | 73 | 16.75 | 92 |

Table I. Two-Component System at 47° to 50° C. Has Distinct Advantages in Ozonization of tert-Butylcyclohexane

| | Run No. | Na2Cr2O7. 2H2O, G. | H₂O, G. | H ₂ SO ₄ , G. | Mole % COOH Based on TBC Charged (Ag ⁺ Method) | Mole % CO ₂ Based on TBC in Charge |
|---|----------------------------|--------------------------|---------------|--|---|---|
| | | A. Comparis | son of Cataly | rsts at 47-50° | C.a | |
| | 150 | 0 | 100 | 0 | 0 | |
| | 148 | 0 | 75 | 39 | 16 | • • |
| | 167 | 30 | 98 | 0 | 7 | |
| | 146 | 30 | 75 | 39 | 98 | |
| | | B. Comparis | son of Cataly | vsts at 63-70° | C. ^b | |
| | 162 | 0 | 75 | 0 | 33 | 4 |
| | 164 | 0 | 65 | 40 | 32 | 27 |
| | 166 | 32 | 96 | 0 | <1 | 27 |
| | 160 | 30 | 75 | 39 | 92 | 13 |
| | | C. Effect of | f Reaction T | ime at 63-6° | C. <i>°</i> | |
| | 160 (5 hr.) | 30 | 75 | 39 | 92 | 13 |
| • | 163 (10 hr.) | 30 | 75 | 39 | 110 | 17 |
| | | D. Effect of Oz | zone Concent | tration at 63– | 74° C. ^d | |
| | 158 (3.7% O ₂) | 30 | 75 | 39 | 72 | 20 |
| | 160 (5.6% O3) | 30 | 75 | 39 | 92 | 13 |
| | | | | | | |

^a TBC. 5.0-5.1 g.; ozone concn. 5.0-5.6%; reaction time 5-6 hr. ^b TBC. 5.0-5.1 g.; ozone concn. 5.6-6.0%; reaction time 4.75-5.25 hr. °TBC. 5.1 g.; ozone concn. 5.6-6.1%. ^d TBC. 5.0-5.1 g.; reaction time 5-5.25 hr.

Table II. Distribution of Carboxylic Acids in Ozonization Product Emphasizes Advantages of Two-Component Oxidation

| | Mole % Yiel | d Based on Naphth | nene Charged ^a |
|--|-----------------|----------------------|---------------------------|
| Acid | Run 162 | Run 160 | Run 163 |
| tert-Butyladipic | 4.3 | 15.6 | 18.3 |
| Adipic | 2.5 | 14.0 | 20.5 |
| Glutaric | 4.3 | 9.1 | 10.2 |
| Succinic | 5,5 | 9.5 | 10.9 |
| Unknown dibasic | 2.4 $(7)^{b}$ | 3.3 (3) | 9.8(1) |
| Total dibasic | 19 | 51 | 70 |
| Dibasic by silver ion method | 17 | 46 | 55 |
| Trimethylacetic | 3,8 | 3.4 | 5.0 |
| Acetic | 2.1 | 8.4 | |
| Formic | 3.1 | 4.7 | 2.4 |
| Malonic | 0.0 | 0.0 | 0.0 |
| Oxalic | 0.0 | 0.0 | 0.0 |
| Unknown polyfunctional monobasic | 1.6 (5) | 1.0 (1) | • • • |
| & For repetion conditions, see Table I | b Figure in ner | ontheses indicates n | umber of indivi |

For reaction conditions, see Table I. gure in parentheses indicates number of individua compounds.

attack on the carbon-hydrogen bonds of the naphthene.

At 100° C. tert-butyladipic acid undergoes oxidative decarboxylation in the presence of dichromate, but at 73° C. 89% tert-butyladipic acid was recovered, with small amounts of trimethylacetic, glutaric, and succinic acids, and a trace of oxalic. tert-Butylcyclohexane is not oxidized by acid-dichromate solutions at 108° C. The naphthene was refluxed with stirring in a solution 4Min sulfuric acid and 1M in sodium dichromate for 15.5 hours at this temperature. Pure naphthene was recovered almost quantitatively.

Conclusions

When tert-butylcyclohexane is oxidized with ozone, initial attack by ozone on different positions of the naphthene ring gives a mixture of dibasic acids. If the tertiary carbon-hydrogen bond reacts initially, further oxidation gives adipic or glutaric acid. To obtain tert-butyladipic acid, a secondary carbon-hydrogen bond must be initially oxidized. Although the tertiary hydrogen atom would be more reactive (4), there are ten times as many secondary hydrogen atoms as tertiary. Thus, tert-butyladipic acid is a major component.

A dibasic yield as high as 70% can be obtained by using dichromate with ozone. The ozone attacks a carbonhydrogen bond of the naphthene; the dichromate selectively oxidizes the initial intermediate to dibasic acids before the intermediate is randomly oxidized by ozone. Such two-component systems may have applications in oxidation of hydrocarbons other than naphthenes.

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