

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA, PHILADELPHIA, PENNSYLVANIA 19104]

## The Course of Ozonation of Ethers<sup>1</sup>

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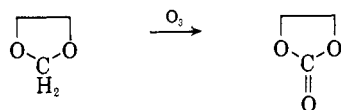
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When ozone in oxygen was passed through ethyl ethoxyacetate and *n*-propyl isopropyl ether, slightly more than 1 mole of ether was consumed per mole of ozone. The major reactions involve carbon-hydrogen bond cleavage, but considerable carbon-oxygen and even carbon-carbon bond cleavage is also observed. The products found are most reasonably explained by electrophilic attack of ozone on hydrogen rather than by a free-radical process.

### Introduction

This study was undertaken to provide additional information concerning the mechanism of the reaction between ozone and ethers, and to determine if this reaction could be a useful preparative or analytical tool. It was also anticipated that better understanding of the reactivity of ozone itself might result, since the initial attack of ozone in various systems is described as electrophilic, nucleophilic, or free radical.<sup>2</sup>

The first reaction of ozone with an organic substance, the reaction with diethyl ether, was reported by Schonbein<sup>3</sup> in 1855. Next von Babo<sup>4</sup> identified hydrogen peroxide, acetaldehyde, and acetic acid as products of this reaction. Highly explosive peroxides were isolated by both Berthelot<sup>5</sup> and Harries.<sup>6</sup> Fisher<sup>7</sup> showed that the main products from higher ethers were hydrogen peroxide and the ester corresponding to the ether; e.g., dibutyl ether gave butyl butyrate. Dallwigk<sup>8</sup> reported the infrared spectra of several ozonated ether solutions. Recently it was shown that cyclic ethers can be converted to lactones, and that cyclic formals can be converted to carbonate esters.<sup>9</sup>



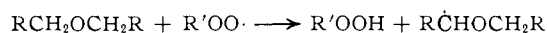
For the most part the reaction of ozone with ethers has been ignored since the work of Fisher,<sup>7</sup> perhaps because of the anticipation of dangerous mixtures. However, in this work no difficulties were encountered. The active oxygen compounds were kept in solution and not highly concentrated, but mildly treated to give stable products.

A recent interpretation<sup>2</sup> of the excellent experimental work of Fisher<sup>7</sup> suggested the radical intermediate



Since ozonations, including those in this present study, are usually carried out with 1 to 10% ozone in oxygen or air gas streams, and since this type of intermediate is believed to be involved in autoxidation of ethers,<sup>10</sup>

it would seem likely that oxygen would participate in the reaction if it proceeded through such an intermediate. The formation of such a radical through hydrogen abstraction by a process such as



will be affected by resonance and electrical factors similar to those affecting free-radical copolymerization.<sup>11</sup> Abstraction of hydrogen by a radical of high electron affinity, such as an oxygen radical or a chlorine atom, will be promoted by electron-releasing groups.<sup>12</sup> However, the differences in reactivity to the *t*-butoxy radical<sup>13</sup> and the chlorine atom<sup>12</sup> are relatively small, even for considerable changes at the carbon holding the hydrogen. One purpose of the present investigation was, therefore, to study the effect of structural changes at the ether group on ozone attack to see if this might provide information of significance in interpreting the mechanism of ozonation of ethers.

### Experimental

**Ozonation Techniques.**—The ozonator used in this research was a Welsbach Model T-23 laboratory ozonator.<sup>14</sup> The ozone concentration was always measured iodometrically before and after each experiment. For extremely small ozone dosages, an additional stainless steel needle valve and flow meter were employed.<sup>15</sup>

The ozonations were carried out in a semimicro gas-liquid reactor consisting of a round-bottomed 10-ml. flask, a gas outlet adapter, a gas-tight stirrer bearing, and a hollow rod gas inlet turbine bladed stirrer. The gas was introduced through the bearing into a hole in the agitator shaft, emerging in the liquid under the blades. A Dry Ice condenser was used to minimize the loss of volatile substances in the gas stream. The temperature was controlled by a water bath. All subsequent operations were carried out in the round-bottomed flask to avoid transfer losses.

**Gas-Liquid Chromatography.**—A Beckman Model GC-2 instrument was used for all the analyses. Helium was used as the carrier gas. The columns were: (i) a Beckman 70251, 12 ft.  $\times$  0.25 in., containing 11.2 g. of diethylene glycol succinate on 27.9 g. of Chromosorb W; (ii) a Beckman 92740 preparative-scale column, consisting of twelve 10 in. lengths of  $\frac{5}{8}$  in. nickel-plated brass tubing, containing 57 g. of diethylene glycol succinate on 143 g. of 60-80 mesh acid-washed Chromosorb W.

The g.l.c. fractions were collected using a Beckman 92730 Fraction Collector. Identification was made by comparison of the elution times of the fraction to the elution times of authentic samples and by collecting the fractions and comparing the infrared spectra of the fractions with the spectra of known compounds.

(11) T. Alfrey and C. C. Price, *J. Polymer Sci.*, **2**, 101 (1947); C. C. Price, *ibid.*, **3**, 772 (1948).

(12) C. C. Price and H. Morita, *J. Am. Chem. Soc.*, **75**, 3686 (1953).

(13) A. L. Williams, E. A. Oberright, and J. W. Brooks, *ibid.*, **78**, 1190 (1956).

(14) "Basic Manual of Applications and Laboratory Ozonation Techniques," The Welsbach Corp., Philadelphia, Pa.

(15) A. Maggiolo and A. Tumolo, *J. Am. Oil Chemists Soc.*, **38**, 279 (1961).

(1) Based on a dissertation submitted in June, 1963, by A. L. Tumolo in partial fulfillment of the requirements for the degree of Doctor of Philosophy. Part of this work was carried out in the laboratories of the Welsbach Corp.; their assistance is gratefully acknowledged.

(2) P. S. Bailey, *Chem. Rev.*, **58**, 925 (1958).

(3) C. F. Schonbein, *J. prakt. Chem.*, **66** [3], 273 (1855).

(4) L. von Babo, *Ann. Suppl.*, **2**, 265 (1862-1863); *Ann.*, **140**, 348 (1866).

(5) M. Berthelot, *Compt. rend.*, **92**, 895 (1881); *Ann. Chim. (Paris)*, [5] **27**, 229 (1882).

(6) C. Harries, *Ann.*, **343**, 311 (1905).

(7) F. G. Fisher, *ibid.*, **476**, 233 (1929).

(8) E. Dallwigk, *Arch. Sci. (Geneva)*, **6**, 421 (1953).

(9) A. Maggiolo, S. J. Niegowski, and A. L. Tumolo, Abstracts, 138th National Meeting of the American Chemical Society, Sept., 1960, p. 10P.

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Quantitatively the mixtures were determined by g.l.c. peak areas using the internal standard technique.<sup>16</sup>

**Ozonation of *n*-Propyl Isopropyl Ether.**—The ozonator controls were set at 90 v., 8 p.s.i.g. of oxygen, and a flow rate of 250 ml. per min. which produced 17.0 mg. (0.335 mmole) per min. of ozone.<sup>17,18</sup> *n*-Propyl isopropyl ether (4.794 g., 46.8 mmoles) was treated in the semimicro reactor at room temperature with the ozonized oxygen until 1.056 g. (22.0 mmoles) of ozone was introduced. It absorbed 1.017 g. (21.2 mmoles, 97%) of ozone. The reaction mixture weighed 5.079 g. Dry Ice traps after the reactor condensed a small amount of liquid composed mainly of starting material.

A few drops of the reaction mixture did not explode when it was put on a steel plate and struck repeatedly with a hammer, when it was dropped on a hot plate, or when it was held in a flame. It should be noted that our solution had at least 50% nonperoxidic material, and any attempts to concentrate the solution or increase the ozone dosage should be handled with all the caution normal for ether peroxides.

The test for hydrogen peroxide with titanium sulfate was positive and analysis showed 38% of theory of active oxygen. The yield is based on 1 mole of product per mole of ozone reacted, as are all other yields given.

To a 1.4896-g. aliquot portion, 0.1247 g. of hexane was added as an internal standard for the g.l.c. determination of the amount of *n*-propyl isopropyl ether that had reacted. The balance of the product was stirred overnight with 0.1 g. of 5% platinum on carbon which decomposed most of the active oxygen. The remaining active oxygen was removed by treatment with hydrogen at 1 m. of water pressure for 2.5 hr.

To the 2.588-g. aliquot portion of product remaining in the flask at this point, 0.258 g. of hexane was added as an internal standard for the g.l.c. analysis, which showed eleven peaks. The peaks accounted for 89% of the reaction mixture which is reasonable since water from decomposed hydrogen peroxide is present along with some acids and both are not eluted at the 70° column temperature used. Duplicate experiments were run and the results are given in Table I.

TABLE I  
RESULT OF OZONATION OF *n*-PROPYL ISOPROPYL ETHER

Peak	Compound	Known time, min.	Elution time, min.		Mole % per mole O <sub>3</sub>	
			Expt. 1	Expt. 2	Expt. 1	Expt. 2
1	Unidentified	..	3.4	3.4	(ca. 10)	
2	Hexane (standard)	4.4	4.5	4.5	..	..
3	Impurity in hexane	5.5	5.6	5.6	..	..
4	<i>n</i> -Propyl isopropyl ether	6.7	6.6	6.8	118	113 <sup>a</sup>
5	Acetaldehyde <sup>b,c</sup>	9.1	9.1	9.0	8.7	7.0
6	Propionaldehyde <sup>c</sup>	13.1	13.0	13.1	7.0	7.1
7	Isopropyl formate <sup>d</sup>	16.4	16.4	16.6	21	19
8	Isopropyl alcohol <sup>e</sup>	20.4	20.8	20.8	12	14
9	Isopropyl propionate	26.6	25.9	26.2	28.8	26.8
10	Propyl acetate	32.0	31.6	32.0	37.3	33.2
11	Propyl alcohol	35.9	36.3	36.8	17.6	16.6

<sup>a</sup> Calculated as moles consumed per mole of ozone reacted and determined on solution directly after ozonolysis. <sup>b</sup> Infrared spectrum not conclusive. <sup>c</sup> Yield based on area ratios only. <sup>d</sup> Yield corrected for acetone detected in spectrum and determined on another column as present to the extent of 8%. <sup>e</sup> Yield corrected for ethanol detected in spectrum.

**Ozonation of Ethyl Ethoxyacetate.**—The ozonator controls were set at 90 v., 8 p.s.i.g. of oxygen, and a flow of 250 ml. per min., producing an average of 21.4 mg. (0.446 mmole) per min. of ozone. Ethyl ethoxyacetate (5.780 g., 43.8 mmoles) was treated in the semimicro reactor at 30 ± 2° with ozonized oxygen until 2.14 g. (44.6 mmoles) of ozone was introduced. Only 0.691 g. (14.5 mmoles, 31%) was absorbed. The reaction mixture weighed 5.930 g. A few drops of the mixture did not explode when it was put on a steel plate and struck repeated

blows with a hammer, when it was dropped on a hot plate, or when it was held in a flame.

The mixture contained 33% of theory of active oxygen. To the 4.684 g. remaining, 1.207 g. of butyl butyrate was added as an internal standard for the g.l.c. determination of yields. The reaction mixture was treated with 0.1 g. of 5% platinum on carbon which decomposed most of the active oxygen. However, some peroxides persisted after 2.5 hr. After treating overnight with hydrogen at a pressure of about 1 m. of water, no peroxides could be detected by testing a small portion with acidified potassium iodide solution. The chromatogram showed nine components. Duplicate experiments were run and the results are given in Table II.

TABLE II  
RESULTS OF OZONATION OF ETHYL ETHOXYACETATE

Peak	Compound	Known time, min.	Elution time, min.		Mole % per mole O <sub>3</sub>	
			Expt. 1	Expt. 2	Expt. 1	Expt. 2
1-4	Unidentified	..	(2.3 to 3.5)		(ca. 2-10)	
5	Butyl butyrate (std.)	6.1	6.1	6.1	..	..
6	Ethyl ethoxyacetate	9.5	9.6	9.5	108	108 <sup>a</sup>
7	Ethyl glycolate	16.3	16.3	16.3	11	11
8	Diethyl oxalate <sup>b</sup>	19.5	19.5	19.5	5	7
9	Ethyl acetoxyacetate	21.7	21.6	21.7	55	55

<sup>a</sup> Calculated as moles consumed per mole of ozone reacted and determined on solution directly after ozonolysis. <sup>b</sup> Yield corrected for some ethyl formoxyacetate shown in infrared spectrum.

**Ozonation of Ethyl Acetate.**—Ethyl acetate was purified according to the method of Vogel<sup>19</sup>; 5.362 g. (60.9 mmoles) was treated with 2.21 g. (46.1 mmoles) of ozone by the procedures used for the ozonation of ethyl ethoxyacetate. Only 0.240 g. (5.0 mmoles, 11%) of ozone was absorbed. The product weighed 5.016 g. and contained 6% of theory of active oxygen. The product was reduced with 0.1 g. of 5% platinum on carbon and with hydrogen. Titration showed 4.2 mmoles of acid.

**Preparation of Di-*t*-butyl Ether.**—The method of Erickson and Ashton<sup>20</sup> was slightly modified. A solution of 46.5 g. (0.5 mole) of *t*-butyl chloride in 100 ml. of ether was mixed with 69.0 g. (0.25 mole) of silver carbonate. The mixture was placed in a flask with condenser and drying tube and shaken intermittently for 24 hr. The ether solution was decanted and the residue washed with ether. Distillation yielded 3.0 g. (23 mmoles, 9% of theory), b.p. 106-107°. It showed only one peak on g.l.c. column ii.

**Ozonation of Di-*t*-butyl Ether.**—In order to treat a small sample with a proportionally reduced amount of ozone it was necessary to reduce the rate of ozone introduced as described in the section on general ozonation techniques. The ozone production rate was 5.15 mg. (0.107 mmole) per min. The di-*t*-butyl ether (1.216 g., 9.34 mmoles) was found to absorb less than 3% of the ozone introduced.

## Discussion

The data indicate a remarkable activating effect for ozone attack on hydrogen atoms  $\alpha$  to an ether group. While *n*-propyl isopropyl ether absorbed 97% of the ozone fed, *t*-butyl ether with no  $\alpha$ -hydrogens consumed less than 3%. Furthermore, all the observed products can be accounted for by  $\alpha$ -attack. The sensitivity of the reaction to electron withdrawal is indicated by the fact that ethyl ethoxyacetate consumed only 30% of ozone introduced and ethyl acetate about 11%.

All these observations seem most logically accounted for by a transition state requiring electron donation to the site of ozone attack. An explanation based on radical attack would not account for a very small difference between secondary and tertiary hydrogen

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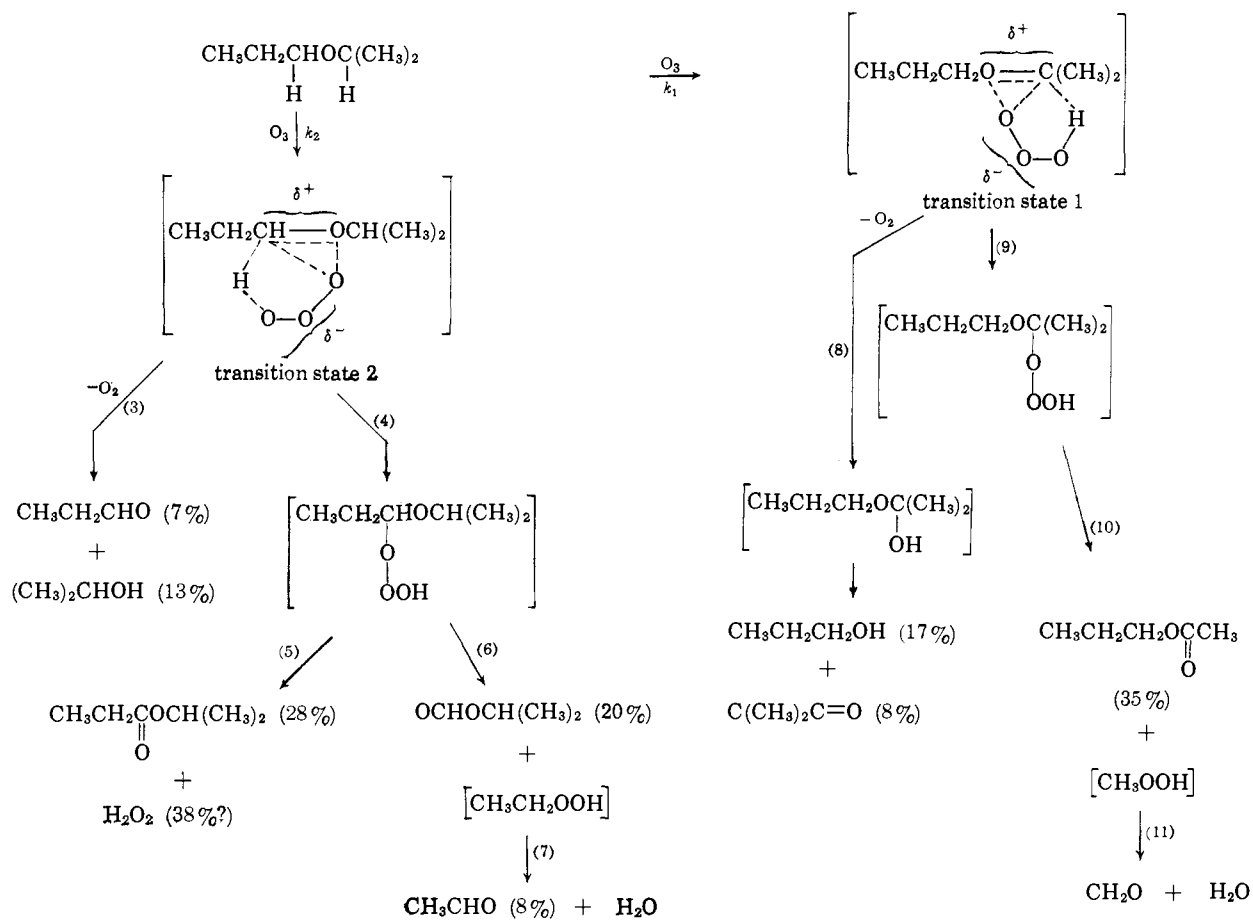
(17) V. R. Kokatnur and M. Jelling, *J. Am. Chem. Soc.*, **63**, 1432 (1941).

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(19) A. I. Vogel, "Practical Organic Chemistry," Longmans, Green and Co., New York, N. Y., 1956, p. 174.

(20) J. L. E. Erickson and W. H. Ashton, *J. Am. Chem. Soc.*, **63**, 1769 (1941).

SCHEME I



when  $\alpha$  to the ether, but a very substantial difference between secondary hydrogens  $\alpha$  and  $\beta$  to the ether.

On the basis of the facts now available, we would propose the course shown in Scheme I for the reaction, using *n*-propyl isopropyl ether as an example.

The importance of stabilization of a carbonium ion center by an  $\alpha$ -ether is well supported by the fact that under  $\text{S}_{\text{N}}1$  conditions chloromethyl alkyl ethers are many thousand times more susceptible to hydrolysis than is *n*-butyl chloride.<sup>21</sup>

Splitting of the intermediates with three consecutive oxygens would be expected since, except for ozone, the only known compounds with three consecutive oxygens are not stable in solution at room temperature.<sup>22,23</sup> The remaining transformations would be expected from known decompositions by ionic or radical mechanisms.

The material balance for the reaction was very satisfactory, since recovered ether indicated 1.15 moles of ether consumed per mole of ozone reacting and the products of reactions 3, 5, 6, 8, and 10 total a maximum of 1.13 moles. Since carbon free radicals react rapidly with oxygen, this stoichiometry argues against a major contribution from such intermediates involving reaction with oxygen, although some side reactions occurring by the radical route are not excluded.

(21) H. Bohme and K. Sell, *Ber.*, **81**, 123 (1948); H. Bohme, H. Fisher, and R. Frank, *Ann.*, **563**, 54 (1959); M. Murakami and S. Oae, *J. Chem. Soc. Japan*, **72**, 595 (1951).

(22) R. Criegee and G. Schroeder, *Ber.*, **93**, 689 (1960); P. S. Bailey, *Tetrahedron*, **18**, 388 (1962).

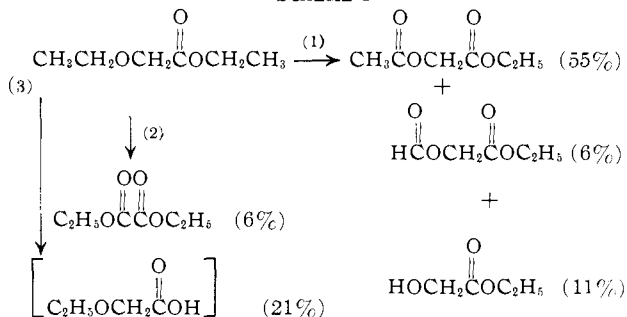
(23) The course outlined here for ozonation of ethers was presented at the Southwestern Regional Meeting, American Chemical Society, Houston, Texas, Dec. 5, 1963. At the same symposium, Dr. P. S. Bailey also proposed  $\text{RO}_2\text{H}$  type intermediates in the ozonation of aldehydes.

All the processes producing aldehyde or ketone as one of the products (3, 6, 8, and 10) show less of the carbonyl component. This could be due either to oxidation during the ozonation or reduction during the platinum treatment to decompose peroxides. The detection of 4% of ethanol could arise from the latter process. Failure to detect formaldehyde could be attributed to its volatility as well.

The relative attack at the two secondary hydrogens ( $k_2$ ) is somewhat greater than at the tertiary hydrogen ( $k_1$ ). From our data the ratio is  $k_1:k_2 = 52:61$ . Since there are two secondary hydrogens, this indicates that the tertiary hydrogen is actually 1.7 times as reactive as a secondary hydrogen.

The data suggest that elimination of oxygen before collapse of the intermediate transition state 2 occurs to about twice the extent it does for transition state 1. This can be rationalized as attributed to (a) some greater degree of stability of the tertiary carbonium center in transition state 1 as compared to the secondary carbonium center in transition state 2 and (b) some

SCHEME II



greater degree of steric hindrance to bond formation at the tertiary  $\alpha$ -carbon in transition state 1 as compared to the secondary  $\alpha$ -carbon in transition state 2.

The ozonation of ethyl ethoxyacetate is shown in Scheme II.

The acid indicated as arising from reaction 3 was measured by titration, but the identity of the acid as

ethoxyacetic acid was not established. However, cleavage of the ethyl ester group is a logical source for this acid, since ethyl acetate gave a very similar acid titer under similar ozonation conditions (4.2 *vs.* 2.9 mmoles).

A study of the reaction of polyethers with ozone is still in progress and will be reported shortly.

[CONTRIBUTION FROM CENTRAL RESEARCH DIVISION, AMERICAN CYANAMID COMPANY, STAMFORD, CONN.]

## The Nature of Electrogenative Hydrogenation

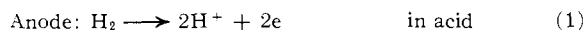
BY STANLEY H. LANGER<sup>1</sup> AND HENRY P. LANDI

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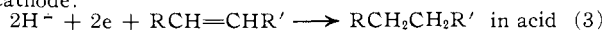
The electrogenerative hydrogenation process is characterized and its limitations are discussed. In this process, hydrogen and substrate are separated by an electrolyte acting as a barrier phase. Hydrogen ionizes at an anode and is transported through the electrolyte to a cathode. Generated electrons flow through an external circuit to the cathode where they combine with transported hydrogen ions and substrate to give hydrogenated product. Favorable thermodynamic factors drive the reaction and generate current. It is shown that hydrogen ion transport in the electrogenerative process is not caused by a simple hydrogen concentration cell effect. The hydrogenation reaction is found to be essentially stoichiometric for olefins with respect to reactants and current generated. Reactants should not be soluble in the barrier electrolyte phase. With platinum black electrode catalyst at room temperature, the electrogenerative hydrogenation process does not proceed readily with acetylene substrate. However, since reactants are separated, electrogenerative hydrogenation is advantageous when a chemical hydrogenation, such as reaction of hydrogen with cyclopropane, is inhibited because of adsorption of hydrogen on the catalyst surface.

In an earlier communication<sup>2</sup> we reported a new technique for electrochemical hydrogenation which was called *electrogenative hydrogenation*. With an acidic electrolyte acting as a barrier phase separating hydrogen and unsaturated hydrocarbon or other substrate, hydrogen gas is converted to hydrogen ions at an anode. The generated electrons flow through an external circuit to a cathode where they are consumed in reaction with substrate and transported hydrogen ions to give hydrogenated product. In base solution, electrode reactions are different (*vide infra*), but the net reaction is hydrogenation. Favorable thermodynamic factors drive the hydrogenation reaction. The purpose of this paper is to characterize the electrogenerative hydrogenation process and to indicate some of its limitations as well as advantages and applications.

Reactions in an aqueous electrolyte barrier phase may be represented as



Cathode:



### Experimental

A circuit diagram of ancillary apparatus used with an electrogenerative hydrogenation cell is shown in Fig. 1. The variable external resistor and cell internal resistance control the current drawn from the cell and, therefore, the potential at the hydrogenating electrode.

The platinum black-polytetrafluoroethylene electrodes were prepared as described previously<sup>3-5</sup> and generally were supported

on stainless steel or tantalum screen. Electrodes may also be made with platinum black and polyethylene. In the preparation of these electrodes, heavy catalyst loadings are not particularly desirable since they may interfere with gas diffusion to or from the electrodes and electrolyte.

Polarization is very slight at the hydrogen electrode (anode) with the currents used in this work, and practically all of the polarization observed<sup>2,4</sup> is at the hydrogenating electrode (cathode).

The internal construction of the electrogenerative hydrogenation cell used here is essentially the same as that described previously for hydrogen purification<sup>4</sup> and electrogenerative hydrogenation.<sup>2</sup> Electrode exposed area was 4.9 cm.<sup>2</sup>. All experiments were done at a temperature of 25°.

The experiments reported are typical and sampled from a number of similar experiments. The cell and associated apparatus which were found to be most useful are shown in Fig. 2. The plastic face plates were fitted with inlet and outlet stainless steel tubing so that cell operation could be studied under continuous flow conditions.

The face plates were fitted with additional outlets to hydrogen and hydrocarbon reservoirs so that inlet and outlet vents could be closed and the apparatus operated under static conditions while changes in gas volume were observed. Gas sample bulbs were incorporated in the apparatus on both sides of the cell as shown in Fig. 2 so that representative product samples could be obtained for mass spectral analyses.<sup>6</sup> A magnetic stirrer was incorporated in the gas circulation loop as shown to circulate the gas and to ensure thorough mixing of substrate with hydrogenated product. A buret and mixing chamber with provision for gas transfer were also included on the hydrogenating side of the cell to ensure that all substrate was exposed to the hydrogenating electrode. The gases were stored and manipulated over water.

Preparatory to each run, hydrogen was passed over both electrodes while the electrogenerative cell was shorted. A preliminary polarization curve was then run with hydrogen and olefin or other substrate. The indicated open circuit potential is the one achieved after about 0.5 hr. on open circuit after at least one previous polarization run. The change in potential then is less than 2 mv./5 min. This open circuit potential is reproducible to within 0.01-0.02 v. The polarization data represent steady-state conditions (with gases flowing) which are achieved after about 3 min. at specified current.

others, are commercially available from American Cyanamid Co., attn. A. B. Swift, Wayne, N. J.

(6) We thank Mr. A. Struck for these analyses.

(1) Correspondence should be addressed to the Department of Chemical Engineering, University of Wisconsin, Madison, Wis.

(2) S. H. Langer and H. P. Landi *J. Am. Chem. Soc.*, **85**, 3043 (1963).

(3) (a) G. V. Elmore and H. A. Tanner, *J. Electrochem. Soc.*, **108**, 69 (1961); (b) W. T. Grubb, Proc. 16th Ann. Power Sources Conf. (PSC Publications Committee, P. O. Box 891, Red Bank, N. J.), pp. 31-34.

(4) S. H. Langer and R. G. Haldeman, *Science*, **142**, 225 (1963).

(5) The 9 mg./cm.<sup>2</sup> platinum on tantalum screen electrodes, as well as