Autoxidation of Isobutyraldehyde

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The liquid phase autoxidation of isobutyraldehyde to peroxyisobutyric acid was investigated with ozone as an initiator. The selectivity of the peroxyacid increases with decrease in the amount of aldehyde converted per unit volume of reacting fluid, increase in the ozone feed rate, and decrease in temperature. A few percent of water in solvents increases the selectivity, although too much water brings about a reverse effect. Isopropyl alcohol, acetone, isopropyl formate, propane, propylene, carbon dioxide, and carbon monoxide are observed as by-products besides isobutyric acid. Purified peroxyisobutyric acid (97.2 wt%) was obtained by fractionally distilling the autoxidation product and some of its physical properties were determined. The utility of the peroxyacid as an epoxidizing agent is described.

Isobutyraldehyde is available as a by-product of the *n*-butyraldehyde production by the hydroformylation of propylene. However, little is known about its autoxidation to peroxyisobutyric acid.[1] This paper reports on the autoxidation of isobutyraldehyde in the liquid phase with ozone as an initiator.

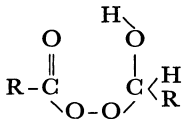
Results and Discussion

Variations of the Selectivity of Peroxyisobutyric Acid (II) with Reaction Conditions. The influence of reaction conditions was investigated with a stirred flow reactor using ethyl acetate saturated with water at room temperature as a solvent. The autoxidation of isobutyraldehyde (I) involves the following two stages:

$$\underset{\text{I}}{{}^{i}\text{PrCHO}} + O_2 \rightarrow \underset{\text{II}}{{}^{i}\text{PrCO}_3\text{H}}\ (\text{Rate, } R) \qquad (1)$$

$${}^{i}\text{PrCHO} + {}^{i}\text{PrCO}_3\text{H} \rightarrow \underset{\text{IV}}{2\,{}^{i}\text{PrCO}_2\text{H}} \qquad (2)$$

Formation of intermediate addition product (III) is known in the reactions of aliphatic saturated aldehydes with peroxyacids.[2-5]



III

The amount of intermediate peroxide III (R=^{i}Pr) was estimated by NMR to be less than 0.05 mol/l. Thus, peroxyisobutyric acid (II) could be approximately estimated by iodometric titration, III being neglected. Isobutyric acid (IV) and unchanged I were determined by glpc after II had been reduced with dimethyl sulfide. The results are shown in Table 1, where

$$\text{Conversion of I} = \frac{\text{I converted (mol)}}{\text{I fed (mol)}} \times 100,$$

$$\text{Selectivity of II} = \frac{\text{II produced (mol)}}{\text{I converted (mol)}} \times 100$$

The variations of the selectivity of II with reaction conditions (conversion, feed concentration of I, ozone feed rate, and temperature) are summarized as follows: the selectivity increases with decreasing conversion of I (Runs 3, 2; 6, 5, 4; 14, 13), decreasing feed concentration of I (Runs 5, 2, 1), increasing ozone feed rate (Runs 9, 12, 3), and decreasing reaction temperature (Runs 14, 1).

White and Bailey[6] suggested that ozone attacks an aromatic aldehyde to form a transient intermediate peroxide, which decomposes to give radicals and initiates autoxidation.

$$\text{RCHO} + O_3 \rightarrow \text{X} \qquad (3)$$

$$\text{X} \rightarrow n\text{R}' \cdot \qquad (4)$$

Assuming that the initiation of the autoxidation of I occurs according to the above mechanism and the rate of reaction (3) is rapid enough to be represented by the feed rate of ozone (r),[7] we obtain

$$r_i = nr \qquad (5)$$

where r_i is the rate of initiation. The general mechanism for autoxidation is

$$\text{R}' \cdot + \text{RCHO} \rightarrow \text{R}'\text{H} + \text{R}\dot{\text{C}}{=}\text{O} \qquad (6)$$

$$\text{R}\dot{\text{C}}{=}\text{O} + O_2 \rightarrow \text{R-C}(=\text{O})\text{-O-O}\cdot \qquad (7)$$

$$\text{R-C}(=\text{O})\text{-O-O}\cdot + \text{RCHO} \xrightarrow{k_p} \text{R-C}(=\text{O})\text{-OOH} + \text{R}\dot{\text{C}}{=}\text{O} \qquad (8)$$

$$2\,\text{R-C}(=\text{O})\text{-O-O}\cdot \xrightarrow{k_t} \text{Non-radical products} \qquad (9)$$

and the steady-state approximation leads to

$$\left[\text{R-C}(=\text{O})\text{-O-O}\cdot\right] = \left(\frac{nr}{k_t}\right)^{1/2} \qquad (10)$$

Thus, the rate of the formation of II would be

$$\text{d[II]/d}t = R - k_2[\text{I}][\text{II}], \qquad (11)$$

$$R = k_p\left[\text{R-C}(=\text{O})\text{-O-O}\cdot\right][\text{I}]$$

$$= k_p\left(\frac{nr}{k_t}\right)^{1/2}[\text{I}] = k_1 r^{1/2}[\text{I}] \qquad (12)$$

where the rate of reaction (2) is assumed to obey second-order kinetics (rate constant, k_2).

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Table 1. Autoxidation of I in ethyl acetate saturated with water[a)]

Run no.	Feed I mol/l	Feed I mol/hr	Feed O_2 mol/hr	Feed $O_3\times10^5$ mol/l·s[b)]	Residence time s	Temp. °C	Product mol/l I	Product mol/l II	Product mol/l IV	Conv. of I %	Select. of II %
1	1.00	0.177	0.81	4.41	1630	10	0.35	0.59	0.02	65	91
2	2.00	0.306	1.21	6.32	1550	10	0.66	1.12	0.04	67	84
3	2.00	0.218	1.21	5.14	2670	10	0.45	1.26	0.19	78	81
4	3.00	0.585	1.21	4.90	1570	10	1.25	1.38	0.40	58	79
5	3.00	0.342	0.49	4.93	2240	10	0.95	1.40	0.40	68	68
6	3.00	0.333	1.21	4.96	2720	10	0.82	1.49	0.40	73	68
7	2.02	0.398	0.64	0.37	6010	10	0.58	1.12	0.14	71	78
8	2.03	0.410	0.51	0.94	5870	10	0.51	1.11	0.13	74	73
9	2.10	0.412	0.42	1.25	5400	10	0.47	1.20	0.19	78	74
10	2.00	0.104	0.49	1.58	5370	10	0.43	1.22	0.13	79	78
11	2.01	0.396	0.64	1.78	5650	10	0.38	1.22	0.20	81	75
12	2.00	0.122	0.49	2.01	4920	10	0.44	1.20	0.10	78	77
13	1.00	0.500	1.01	3.78	482	40	0.47	0.43	0.09	53	81
14	1.00	0.260	0.42	4.58	831	40	0.37	0.49	0.10	63	78
15	2.00	0.900	1.22	5.76	768	40	0.91	0.56	0.40	55	51

a) Autoxidation with a stirred flow reactor. b) Moles per unit volume of reacting fluid per unit time.

In the stirred flow reactor, the material balance for I or II at steady-state affords

$$F[\mathrm{I}]_0 = \{R+k_2[\mathrm{I}][\mathrm{II}]\}V + F[\mathrm{I}],$$

$$[\mathrm{I}]_0 - [\mathrm{I}] = \tau\{R+k_2[\mathrm{I}][\mathrm{II}]\} \quad (13)$$

$$0 = \{-R+k_2[\mathrm{I}][\mathrm{II}]\}V + F[\mathrm{II}],$$

$$[\mathrm{II}] = \tau\{R-k_2[\mathrm{I}][\mathrm{II}]\} \quad (14)$$

where $[\mathrm{I}]_0$ is the feed concentration of I, [I] and [II] are the concentrations of I and II in the product, respectively, F is the volumetric flow rate, and τ is the residence time. From Eqs. (13) and (14), we obtain

$$R = \frac{1}{2\tau}\{[\mathrm{I}]_0-[\mathrm{I}]+[\mathrm{II}]\} \quad (15)$$

$$k_2 = \frac{1}{2\tau[\mathrm{I}][\mathrm{II}]}\{[\mathrm{I}]_0-[\mathrm{I}]-[\mathrm{II}]\} \quad (16)$$

R values were estimated from Eq. (15) using the data listed in Table 1. Figures 1 and 2 show the log R *vs.* log[I]

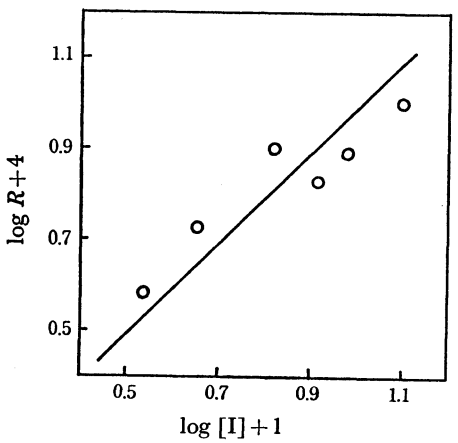

Fig. 1. Plot of log R *vs.* log [I]. r, $(4-6)\times10^{-5}$ mol/l·s; 10 °C.

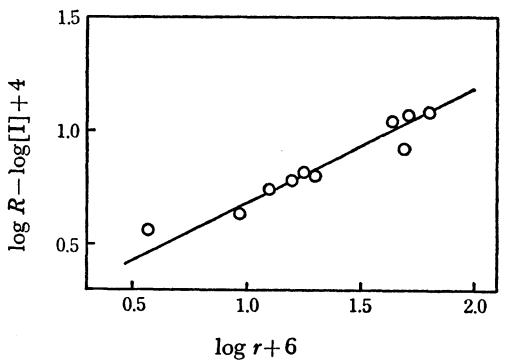

Fig. 2. Plot of log R−log [I] *vs.* log r. 10 °C.

Table 2. Rate data of the autoxidation of I in ethyl acetate saturated with water

Run no.	Temp. °C	$R\times10^4$ mol/l·s	$k_1\times10$ [l/mol·s]$^{1/2}$	$k_2\times10^4$ l/mol·s
1	10	3.8	1.6	0.9
2	10	7.9	1.5	1.0
3	10	5.3	1.6	1.0
4	10	10.0	1.1	0.7
5	10	7.7	1.2	1.1
6	10	6.7	1.2	1.0
7	10	2.1	1.9	0.4
8	10	2.2	1.4	0.6
9	10	2.6	1.6	0.7
10	10	2.6	1.5	0.6
11	10	2.5	1.6	0.8
12	10	2.8	1.4	0.7
			Av. 1.5	Av. 0.8
13	40	10.0	3.5	5.1
14	40	6.7	2.7	4.7
15	40	10.7	1.5	6.8
			Av. 2.6	Av. 5.5

(at approximately equal r) and the $\{\log R - \log[I]\}$ *vs.* $\log r$ relationships, respectively. Our data approximately satisfy Eq. (12). Constants k_1 and k_2 were evaluated from Eqs. (12) and (16), respectively, and are listed in Table 2.

Division of Eq. (14) by Eq. (13) and introduction of Eq. (12) give

$$\frac{[II]}{[I]_0-[I]} = \frac{\kappa-[II]}{\kappa+[II]} \tag{17}$$

where

$$\kappa = k_1 r^{1/2}/k_2 \tag{18}$$

Equation (17) expresses the dependence of the amount of II formed on that of I converted at various κ values. Figure 3 illustrates the [II] *vs.* $\{[I]_0-[I]\}$ curves calculated from Eq. (17) using κ values of 12 and 3. At the ozone feed rate of $(4—6)\times10^{-5}$ mol/l·s, the observed values of [II] and $\{[I]_0-[I]\}$ are also plotted in Fig. 3, in which the κ values are approximately 12 and 3 at 10° and 40 °C, respectively. The selectivity of II, defined as $[II]/\{[I]_0-[I]\}$, increases with decreasing $\{[I]_0-[I]\}$ at a constant κ, and with increasing κ at a constant $\{[I]_0-[I]\}$. Since a decrease in the conversion or the feed concentration of I leads to a decrease in $\{[I]_0-[I]\}$ and a lower reaction temperature or a higher feed rate of ozone leads to a larger κ value, all these effects result in an increase in the selectivity of II.

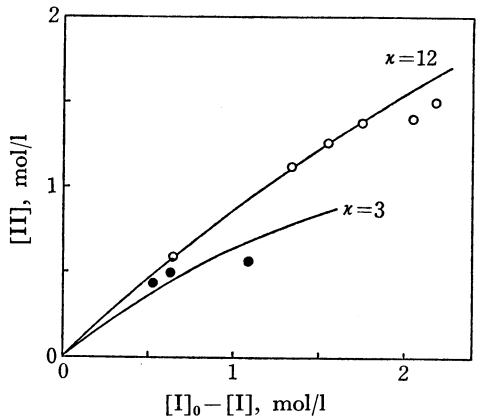

Fig. 3. [II] as a function of $[I]_0-[I]$.
Solid line, calculated from Eq. (17); ○, observed at 10 °C (r, $(4-6)\times10^{-5}$ mol/l·s); ●, observed at 40 °C (r, $(4-6)\times10^{-5}$ mol/l·s).

The values of k_1 and k_2 lack somewhat in constancy. This might be due to the difficulty of analysis and/or an over-simplification of the reaction kinetics. However, the above semi-quantitative treatment explains the results in spite of the complexity of the reaction.

Effect of Water. The effect of water was investigated by batchwise autoxidation. Figure 4 shows the yield of II as a function of water content in the solvent. A few percent of water in acetone increases the yield, although too much water brings about a reverse effect. The autoxidation in ethyl acetate saturated with water at room temperature[8] under similar reaction conditions as above gives II in about a 10% higher yield than that in anhydrous ethyl acetate.

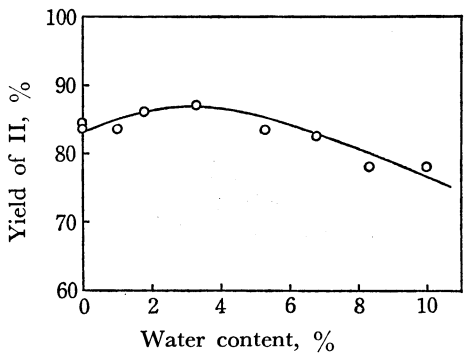

Fig. 4. Effect of water content in solvent on the yield of II.
Batch reactions at 40 °C; solvent, acetone; $[I]_0$, 1.00 mol/l; volume of reacting fluid, 200 ml; O_2, 0.52 l/min; O_3/O_2, 0.22 mmol/l; reaction time, 1.5 hr.

By-products. Besides IV, isopropyl alcohol and acetone were observed in 1—3% yields as by-products. They were identified through appropriate crystalline derivatives. When the autoxidation product was left to stand at 80—90 °C, their amounts of (particularly isopropyl alcohol) increased markedly. A possible pathway for the formation of these by-products is as follows:

$$II \rightarrow {}^{i}Pr\text{-}C(=O)(O\cdot) + \cdot OH \tag{19}$$

$${}^{i}Pr\text{-}C(=O)(O\cdot) \rightarrow {}^{i}Pr\cdot + CO_2 \tag{20}$$

$${}^{i}Pr\cdot + II \rightarrow {}^{i}Pr\text{-}OH + {}^{i}Pr\text{-}C(=O)(O\cdot) \tag{21}$$

$${}^{i}Pr\cdot + O_2 \rightarrow {}^{i}Pr\text{-}O\text{-}O\cdot \tag{22}$$

$${}^{i}Pr\text{-}O\text{-}O\cdot \rightarrow Me_2C{=}O + \cdot OH \tag{23}$$

A peak, the retention time of which agreed with that of isopropyl formate, was detected by glpc. This peak appeared in a comparable amount with that of isopropyl alcohol or acetone in the autoxidation in anhydrous ethyl acetate, but only in a trace amount in ethyl acetate saturated with water. On adding I to the autoxidation product, the intensity of this peak increased. Apparently, this was derived from the Baeyer-Villiger reaction of II with I.[9]

$$I + II \begin{cases} \xrightarrow{2\,IV} \\ \xrightarrow{IV} {}^{i}Pr\text{-}O\text{-}C(=O)\text{-}H \end{cases} \tag{24}$$

Isopropyl alcohol observed in the autoxidation in ethyl acetate saturated with water may have been partly derived from the hydrolysis of the formate. Carbon dioxide, carbon monoxide, propane, and propylene were detected by glpc in the exit gas. The formation of these by-products could be explained by Eqs. (20), (25), and (26).

$${}^{i}Pr\text{-}\dot{C}{=}O \rightarrow {}^{i}Pr\cdot + CO \tag{25}$$

$$2\,{}^{i}Pr\cdot \rightarrow CH_3CH_2CH_3 + CH_3CH{=}CH_2 \tag{26}$$

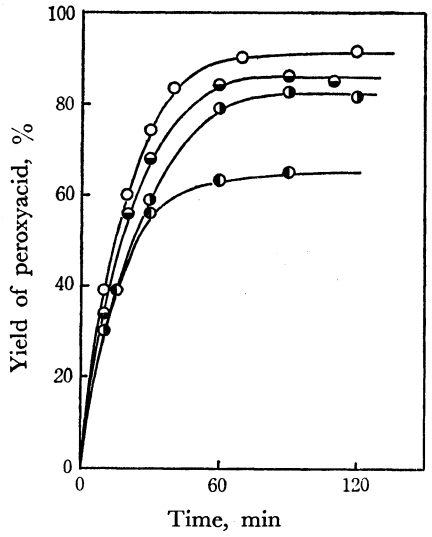

Fig. 5. Autoxidation of aldehydes.
Batch reactions at 40 °C; $[RCHO]_0$, 1.00 mol/l; solvent, ethyl acetate saturated with water (anhydrous ethyl acetate in the case of acetaldehyde); volume of reacting fluid, 200 ml; O_2, 0.52 l/min; O_3/O_2, 0.22 mmol/l; ○, isobutyraldehyde; ◒, *n*-butyraldehyde; ◑, propionaldehyde; ◐, acetaldehyde.

Comparison with Other Aldehydes. The autoxidation of I was compared with that of acetaldehyde,[10] propionaldehyde, and *n*-butyraldehyde. I gives peroxyacid in the highest yield (Fig. 5). This might be a reflection of the electron-donating nature of ^{i}Pr group, which would facilitate reaction (8), in view of preference for the attack of peroxy radicals on carbon-hydrogen bonds with the highest electron density.[11]

The solution of II, thus obtained, can be stored satisfactorily by addition of a small amount of stabilizer such as the sodium salt of a partially esterified polyphosphate.[12]

Epoxidation. The solution of II obtained by batchwise autoxidation was used for the epoxidation of cyclohexene. The rate constants are shown in Table 3 together with those by Frostick *et al.*,[13] who used peroxyacetic acid solution obtained by pyrolyzing α-hydroxyethyl peroxyacetate. Peroxyacid II can be used effectively as an epoxidizing agent.

Physical Properties of Peroxyisobutyric Acid (II). By fractional distillation under reduced pressure II was isolated from the autoxidation product. The purity was determined to be 97.2 wt% by iodometric titration. Some of the physical properties are listed in Table 4.

Table 3. Epoxidation of cyclohexene

Peroxyacid	Solvent	Temp. °C	$k\times10^6$ l/mol·s	$\Delta H^{\ddagger}$ kcal/mol	$-\Delta S^{\ddagger}$ e.u.
Peroxyisobutyric acid	EtOAc[a]	10	102	15.0	23.6
		25	412		
		40	1420		
Peroxyacetic acid[b]	EtOAc	0	20.2		
		15	104	16.9	16.2
		20	172		
		25	283		

a) Saturated with water. b) Ref. 13.

Table 4. Physical properties of II[a]

Bp	41.0 °C/30 mmHg (116—117 °C/760 mmHg)[b]
Mp	−30—−28 °C
d_4^{25}	1.049
Latent heat of vaporization	10.7 kcal/mol (13—65 mmHg)

a) 97.2 wt%. b) By extrapolation.

Experimental

All boiling points and melting points are uncorrected. NMR spectra were taken with a Varian A-60A spectrometer. Ozone was generated with a Nihon-Ozone 0-3-2 generator. Gas-liquid partition chromatographic data were obtained with a Hitachi K-23 gas chromatograph using helium as a carrier gas. Aldehydes were distilled under nitrogen just before use.

Autoxidation. Batch reactions were carried out in an all-glass cylindrical reactor having an external jacket as well as an internal coil for heat exchange. Oxygen containing ozone entered the reactor through a glass frit in the bottom and was vented through a Dry Ice condenser.

Continuous reactions were carried out in a glass vessel thermostatically controlled at a specified temperature. Under stirring, a solution of isobutyraldehyde was fed to the reactor into which oxygen containing ozone was dispersed through a glass frit in the bottom. The gas stream was vented through a Dry Ice condenser. Samples of the product stream, which overflowed, were chilled at once in a Dry Ice-acetone mixture and immediately subjected to analysis.

Analysis. α-Hydroxyisobutyl Peroxyisobutyrate (III, R=^{i}Pr): NMR spectrum was taken at −46 °C. Peroxide III (R=^{i}Pr) was estimated by comparing the peak area of $-O\diagdown\atop-O\diagup$C$\langle^{H}$ proton (δ, 4.94) with that of the aromatic protons of mesitylene (δ, 6.75) as an internal standard.

Peroxyisobutyric Acid (II): A 1 ml sample was introduced into a flask containing 2 g of potassium iodide, 45 ml of water, 5 ml of acetic acid, 10 ml of chloroform, and a few pieces of Dry Ice. The liberated iodine was titrated with 0.1 M aqueous sodium thiosulfate solution to a colorless end-point.

Isobutyraldehyde (I) and Isobutyric Acid (IV): Dimethyl sulfide, 1 ml, was added dropwise to a 5 ml sample in a Dry Ice-acetone bath. The mixture was allowed to stand in an ice box for 15 min and analyzed by glpc on a Porapack Q column at 170 °C using benzene as an internal standard. Free IV in the reaction mixture was determined by subtracting II from the total IV found by glpc. Preliminary experiments showed that the reaction of dimethyl sulfide with II to yield dimethyl sulfoxide and IV was quantitative under the above conditions.

Identification of By-products. Glpc analysis (PEG 6000 column, 60 °C) of the autoxidation product, obtained by the ozone-initiated batchwise reaction in anhydrous ethyl acetate ($[I]_0$, 1.0 mol/l; 40 °C), showed three by-product peaks, x_1, x_2, and x_3. The retention times of x_1 and x_3 agreed with those of acetone and isopropyl alcohol, respectively. On decomposing the peroxyacid by heating the autoxidation product at 80—90 °C for 29 hr or by adding a small amount of cobaltic acetylacetonate and heating the mixture at 80—

90 °C for 30 min, the amounts of x_1 and x_3 (particularly x_3) increased markedly, while that of x_2 remained almost unaltered.

The retention time of x_2 agreed with that of isopropyl formate. When 80 ml of the autoxidation product was left to stand for 6.3 hr at 40 °C with 10 ml of I, the amount of x_2 increased by a factor of 4.5.

The autoxidation product, obtained with cobaltic acetylacetonate as an initiator ($[I]_0$, 1.0 mol/l; $[Co(acac)_3]$, 1.0×10^{-5} mol/l; 40 °C), decomposed spontaneously on being left to stand at room temperature. This was fractionally distilled with a 30 cm packed column (271 g).

Fraction	Head temp., °C	Wt., g
1	69.0—70.4	10.6
2	70.4—76.0	45.9
3	76.0—78.0	197.0

Acetone 2,4-dinitrophenylhydrazone (mp 122.5—123.5 °C) and isopropyl 3,5-dinitrobenzoate (mp 110—114 °C) were obtained from fractions 1 and 2, respectively. Mixture melting points with the authentic samples showed no depression.

Kinetic Measurements. To a solution of cyclohexene (210 ml), thermostated at a specified temperature, was added a solution of II (40 ml) stabilized by addition of a small amount of the sodium salt of a partially esterified polyphosphate. Ethyl acetate saturated with water at room temperature was used as a solvent. The initial concentrations of cyclohexene and II were $(2.93—5.85) \times 10^{-1}$ and 1.31×10^{-1} mol/l, respectively. The reaction mixture was constantly agitated and the progress of the reaction was determined by analysis of II. The solution of II used in these measurements was prepared by the ozone-initiated batchwise autoxidation of I ($[I]_0$, 1.0 mol/l; 40 °C).

Isolation of Peroxyisobutyric Acid (II). A solution of I in anhydrous ethyl acetate (250 ml, 3.0 mol/l) was autoxidized at 5—16 °C (batchwise; O_2, 72 l/hr; O_3/O_2, 0.29 mmol/l). 2.3 molar solution of II was obtained after 70 min. A portion of this solution was distilled at 150 mmHg to remove most of the solvent, then at 30 mmHg to obtain crude II. This was purified by fractional distillation with a 30 cm packed column; bp 41 °C/30 mmHg. An all-glass apparatus was used, and a small amount of the sodium salt of a partially esterified polyphosphate was added before each distillation. Purified II, the purity of which was determined to be 97.2 wt% by iodometric titration, was stored in a Dry Ice box.

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7) Only a very small proportion of ozone was observed in the exit gas as long as I remained. As an example, in a batch autoxidation of I ($[I]_0$, 1.0 mol/l; volume of reacting fluid, 200 ml; O_2, 0.93 l/min; O_3/O_2, 0.564 mmol/l; 40 °C), the total ozone vented was less than 5% of the one introduced in 70 min until the reaction was virtually completed.

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