The Gas-phase Oxidation of Propylene-3-d_1

Seiichiro OBA[*1] and Wataru SAKAI

Department of Organic Synthesis, Faculty of Engineering, Kyushu University, Hakozaki, Fukuoka

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It has been reported by many workers that propylene oxide (PO) could be produced in a gas-phase oxidation of propylene with 15—30 vol% of oxygen.[1] Recently Kamiya investigated the reaction in detail and reported that the yield of PO based on the propylene consumed, was about 26%,[2] The results of similar reactions of propylene-acetaldehyde-oxygen mixtures have been reported by Imamura and Ota,[3] where the yield of PO seemed to be almost the same as that in Kamiya's experiments. Although the mechanism of PO formation has been proposed to be an intermolecular epoxidation of propylene with the hydroperoxy radical[4] or allyl hydroperoxide,[2] the present authors inferred that PO might be formed *via* the allyl radical and the allyl peroxy radical. In order to make it clear whether or not the allyl radical is involved in the reaction, they investigated the oxidation of propylene-3-d_1 catalyzed by ethyl iodide. If PO is produced *via* the allyl radical, the positions and the amount of deuterium in the resulting PO molecule should be different from those of the starting material.

Experimental

The Preparation of Deuterated Compounds. *Propylene-3-d_1* was synthesized from allyl chloride by

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[*1] Present address: Tokuyama Soda Co., Ltd., Tokuyama, Yamaguchi.

1) US. Pat. 2482284; 2530590; 2689253; 3132156.

2) Y. Kamiya, *Bull. Jap. Petro. Inst.*, **5**, 13 (1963).

3) J. Imamura and N. Ota, 18th Annual Meeting of Chem. Soc. of Japan, No. 20203.

4) W. E. Falconer and J. H. Knox, *Proc. Roy. Soc.*, **A250**, 493 (1959).

the method of N. R. C.[5] The isotopic purity of the resulting propylene-3-d_1 was above 97% as determined by specific gravimetry.

Propylene Oxide-3-d_1 was prepared by the perbenzoic acid epoxidation of the above-mentioned propylene-3-d_1 in a toluene solution at 20°C and was purified by gas chromatography (GC).

Apparatus and Procedure. The oxidation reactions were performed in a circulating-batch reactor. It consisted of a U-shaped Pyrex reactor (i.d. 13 mm), an aqueous sodium carbonate trap cooled with ice water, a soda-lime tube, a buffer tank, a pump, an ethyl iodide tube, and a mercury manometer. The reactor was heated in a salt bath controlled at 380±1°C.

Propylene and oxygen were added from time to time, so that the total pressure was restored to the initial state (1500—1600 mmHg), while the ratio of oxygen to propylene was kept to a scheduled value (0.20 in Run A and 0.25 in Run B).

The circulating gas was sampled at intervals of 5—10 min, and the composition was determined by GC. Ethyl iodide vapor was added as a radical-chain initiator by bubbling the circulating gas through the ethyl iodide layer cooled with ice water.

After the reaction had stopped, the PO in the aqueous trap was isolated and purified by extraction, distillation, and GC. In a preliminary experiment, the purity of PO thus obtained was 99.7%, the impurity was mainly acetaldehyde.

The resulting PO was analyzed by mass spectroscopy and by IR and NMR spectroscopies in a carbon tetrachloride solution. The mass spectrometric analyses were made with a Consolidated Elec. Co., model 21—103C, mass spectrometer. The IR spectra were measured with a Nippon Koken, model DS 301, doublebeam spectrophotometer. The NMR spectra were measured with a Varian A-60 analytical spectrometer, using TMS in chloroform as an external reference.

Analysis. Analyses of the reactant gases were made by GC with dinonyl phthalate and molecular sieve 13-X columns. The concentrations of PO, acetaldehyde, and formaldehyde were determined with a poly-ethylene glycol 6000 column.

Results and Discussion

The amounts of propylene-3-d_1 consumed and of the reaction products are summarized in Table 1, where the carbon distributions among the products, based on the reacted propylene, are also shown for the respective compounds.

The rest of the carbon balances could be found in a tarry substance in the reactor and in the carbon dioxide absorbed in the soda lime tube.

Besides these main products, small amounts of propionaldehyde, acetone, acrolein and allyl alcohol were detected. The formations of carbon monoxide and methane increased with the increase in the oxygen concentration.

The intermittent growths of the cool-flame reactions were noticed by means of an abrupt temperature increase (20—40°C). Therefore, it was seen that the reaction partly proceeded in a state corresponding to an induction period of a slow combustion.

TABLE 1. YIELDS AND CARBON DISTRIBUTIONS

Run	A		B	
	mmol	%	mmol	%
Propylene-3-d_1 consumed	45.8	—	50.2	—
Propylene oxide	3.8	8.2	2.6	5.2
Acetaldehyde	7.9	11.5	5.8	7.7
Formaldehyde	8.5	6.2	6.6	4.4
Methane	3.6	2.6	7.6	5.0
Carbon monoxide	32.4	23.6	38.3	25.4
Total	—	52.1	—	47.7

In a preliminary run with a low oxygen concentration (15%) and with a trap solution containing sodium bisulfite, the yield of PO was almost the same as that in the run without sodium bisulfite. Therefore, PO was not formed in the aqueous trap by the epoxidation of propylene with hydroperoxy compounds.

The IR spectrum of the resulting PO (Fig. 1) was in perfect agreement with that of the authentic propylene oxide-3-d_1. The NMR spectrum (Fig. 2A) was different from that of normal PO (Fig. 2B) at the methyl peaks. The strong doublet centered at 8.76 (τ-value) of normal PO is split further into a medium-strong quasi-quintet by substitution with deuterium for one of three hydrogens of the methyl group. The other peaks do not show any appreciable change. The relative integrated intensities of the signals were found to be as follows: a(quasi-quintet): b(quartet): c(quasitriplet): d(multiplet)=2.11: 0.96: 1.00; 0.93, which agreed well with the values of the authentic PO-3-d_1.

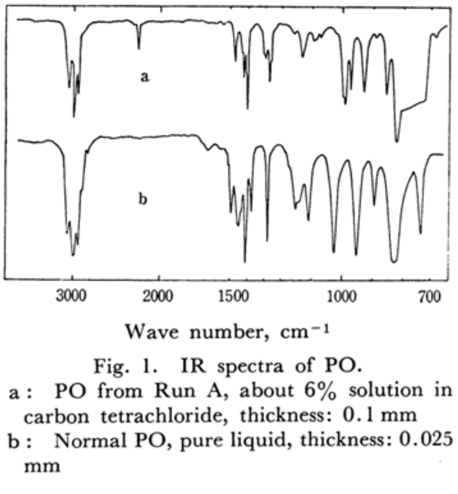

Fig. 1. IR spectra of PO.
a: PO from Run A, about 6% solution in carbon tetrachloride, thickness: 0.1 mm
b: Normal PO, pure liquid, thickness: 0.025 mm

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[5] Brit. Pat. 822617, National Research Council of Canada.

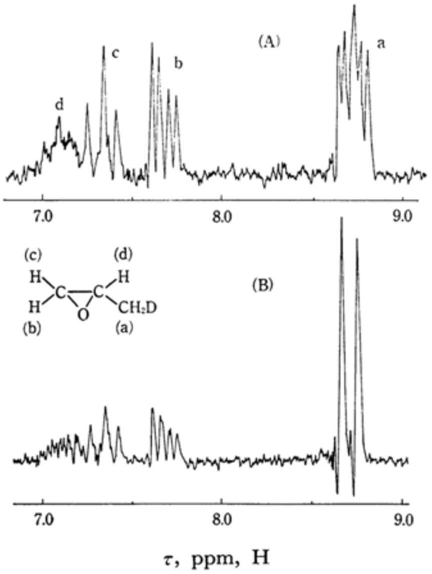


Fig. 2. NMR spectra of PO.
A: PO from Run A, about 6% solution in carbon tetrachloride
B: Normal PO, 8% solution

The data of mass spectroscopies of the respective PO are shown in Table 2 for their parent peaks (base peak: $m/e=29$).

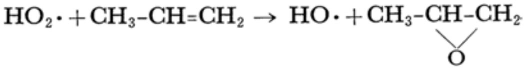
TABLE 2. PATTERN COEFFICIENT OF PO

m/e	Normal	Run A	Run B	PO-3-d_1
58	70.07	4.02	5.24	3.62
59	2.56	39.34	39.08	40.10

From these results, we concluded that most of PO must be formed without hydrogen abstraction from the methyl group.

There still remains the question what kind of species epoxidize propylene to PO. Cvetanovic reported⁶⁾ that PO was formed by the addition of an oxygen atom to propylene, accompanied by a comparable amount of propionaldehyde. White and his coworkers found that PO and propionaldehyde could be obtained in a similar oxidation at a high temperature⁷⁾ (625°C). Therefore, propionaldehyde is not unstable in this oxidation reaction. Since the formation of propionaldehyde was negligible in the present experiments, the oxygen-atom-addition reaction seemed to be unsuitable to account for the formation of PO in a gas-phase oxidation at a low temperature.

Therefore, it seems probable that PO is formed by an inter-molecular reaction between the peroxy radical and propylene:



$$HO_2\cdot + CH_3\text{-}CH\text{=}CH_2 \rightarrow HO\cdot + CH_3\text{-}\underset{\diagdown O \diagup}{CH\text{-}CH_2}$$

The hydroperoxy radical must be produced as a primary product in the gas-phase oxidation of propylene:

$$CH_2\text{=}CH\text{-}CH_3 + O_2 \rightarrow CH_2\text{=}CH\text{-}CH_2\cdot + HO_2\cdot$$

This radical is likely to be stable as compared with the alkyl peroxy radical, since the heat of reaction is consumed for the carbon-hydrogen bond rupture in the case of hydroperoxy-radical formation.

This inference seems to be supported by the observations that an enhanced rate of reaction was observed in the propane oxidation by the addition of propylene to propane,⁴⁾ and that a considerable amount of hydrogen peroxide can be produced in a propane oxidation.⁸⁾

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7) E. R. White, H. G. Davis and E. S. Hammack, *J. Am. Chem. Soc.*, **87**, 1175 (1965).

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