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# Low-Temperature Infrared Studies of the Styrene–Ozone Reaction. Formation of an Unusual Ozonide

**I. C. Hisatsune, Kiyonori Shinoda,[†] and Julian Heicklen***

*Contribution from the Department of Chemistry and Center for Air Environment Studies, The Pennsylvania State University, University Park, Pennsylvania 16802.*

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**Abstract:** Styrene was reacted with $O_3$ at low temperatures and infrared spectra of the system were recorded. On warming the system from −196 °C, only a single product was formed at about −110 °C. This ozonide was relatively stable and did not decay until about −55 °C; it even appeared to persist at room temperature. The decomposition of the ozonide produced $C_6H_5CHO$ as the sole detectable aldehyde product. In the presence of $CH_3OH$, it decayed rapidly even at −100 °C. The behavior of this ozonide is different from that of styrene secondary ozonide reported by earlier workers. The data suggest that it is the primary ozonide.

## Introduction

We have examined the low-temperature reaction of ozone with styrene to see if the first product is the primary ozonide or the $\pi$ complex, or both. Previous work in our laboratory[1] showed that $C_2H_4$ reacted with $O_3$ to produce the primary ozonide, but not the $\pi$ complex, whereas toluene reacted with $O_3$ to produce the $\pi$ complex, but not the primary ozonide. Furthermore, this earlier work showed that generally alkyl-substituted ethylenes gave both products.

Bailey and his co-workers[2-4] had examined the low-temperature ozonation of mesitylene, 1-mesityl-1-phenylethane, 1-mesityl-1-phenylethylene, and 1-methoxy-1,2,2-trimesitylethylene and found that only the $\pi$ complexes were formed, which decomposed when warmed to give epoxides. Hence, one might expect that styrene may also give a $\pi$ complex. However, this may not follow necessarily since work in our laboratory[5] on chlorinated ethylenes showed that the multisubstituted compounds gave only $\pi$ complexes, but that the monosubstituted compound, $C_2H_3Cl$, gave a primary ozonide as well.

The reaction of $O_3$ with styrene has been studied previously. Briner and his collaborators[6,7] reacted $O_3$ with styrene in $CCl_4$ solution and measured the infrared and Raman spectra of the reacted mixture (presumably at room temperature, though this is not stated). The reaction mixture showed new infrared bands at 1708, 1213, 1065–1055, and 936 $cm^{-1}$ which were assigned to an ozonide (presumably the secondary ozonide).

Keaveney et al.[8] reacted styrene with $O_3$ at −65 to −75 °C in the presence of $CH_3OH$ and measured the reaction products, which consisted of $C_6H_5CHO$, $CH_2O$, and two peroxides. All four compounds were produced in about equal amounts, and it was concluded that $O_3$ could cleave the double bond to produce either aldehyde and zwitterion with equal likelihood. This result is surprising since their study of the $O_3$ reaction with propenylbenzene and 2-methylpropenylbenzene gave almost entirely the aromatic aldehyde and the appropriate hydroperoxide. These styrene–$O_3$ results may be questionable since $O_3$ is known to react with $CH_3OH$ to produce $CH_2O$,[9] at least under some conditions. Furthermore, Fliszar[10] found that the styrene reaction with $O_3$ in $CCl_4$ solution at 25 °C gave initially much more $C_6H_5CHO$ than $CH_2O$, and that only as the reaction progressed did the $CH_2O$ yield equal the $C_6H_5CHO$ yield. He also studied the reaction at 15–35 °C in $CCl_4$ solution containing $CH_3OH$ and found only $C_6H_5CHO$ and hydroperoxide as products. Thus, Fliszar concluded that only the cleavage to give $C_6H_5CHO + CH_2O_2$ was important. Therefore, another reason for us to reexamine the low-temperature styrene–$O_3$ reaction was to see which products are formed.

## Experimental Section

Styrene was reacted with ozone directly on the liquid nitrogen cooled infrared window of a low-temperature cell. The infrared spectra of the samples were recorded as the cell was warmed to a given temperature and then recooled to −196 °C. The experimental details are given in earlier papers.[1,5] Reagent grade styrene was used after being degassed under vacuum and distilled.

## Results

When $O_3$ was mixed with styrene at −196 °C, sometimes a greenish yellow color was initially seen, but it disappeared immediately on warming. This coloration was not always seen and no unaccounted infrared bands were present. Possibly this color belongs to a very unstable $\pi$ complex which is reversibly formed at temperatures slightly above −196 °C. With further warming no additional infrared bands were seen until a temperature of −100 ± 10 °C was reached. Then the styrene bands diminished and a single new product was formed whose spectrum resembled those of ozonides observed in our laboratory.[1,5] According to its spectrum, this ozonide appeared to be stable until the temperature was raised to about −55 °C, when it started to decay and new bands belonging to $C_6H_5CHO$ and probably a peroxidic polymer began to appear. No $C_6H_5CHO$ was ever detected during the formation of the initial ozonide. The decomposition of the ozonide was relatively slow, and the stronger of its infrared bands were often still detectable even when the cell approached room temperature or when the sample was pumped off the window and then recondensed again.

The low-temperature ozonolysis of styrene in the presence of $CH_3OH$ was also examined. No reaction was evident until the temperature reached near −110 °C, when the styrene bands began to disappear. However, no ozonide was formed. Instead, as the styrene decayed, infrared bands due to $C_6H_5CHO$, $CO_2$, and $HC(O)OCH_3$ grew. Thus, either $CH_3OH$ reacted very rapidly with the ozonide or it destroyed a precursor of the ozonide. To distinguish these possibilities, $CH_3OH$ was added to a sample in which the ozonide had already formed and the ozone had been depleted. [The latter condition was necessary since $CH_3OH$ was found to react with $O_3$ at 25 °C to give $CO_2$ and $HC(O)OCH_3$.] On warming this sample, the ozonide decayed rapidly even at about −100 °C and $C_6H_5CHO$, $CO_2$, and $HC(O)OCH_3$ were again produced.

Finally, the room temperature ozonolysis of styrene was examined in a gas cell. The vapor-phase spectrum showed, in addition to bands of styrene, characteristic peaks due to $C_6H_5CHO$, $CO_2$, and HCOOH. Some noncondensable gas, presumably oxygen, was also present in the cell.

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[†] Toyama Technical College, Hongo, Toyama-shi, 930-11, Japan.

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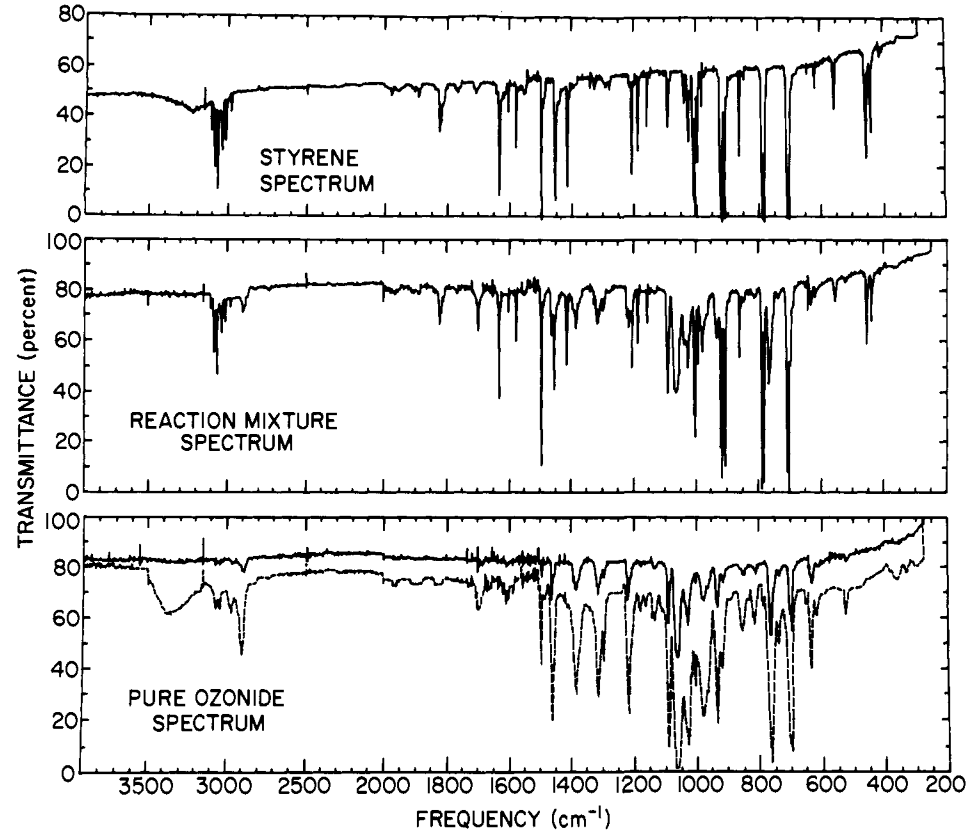

**Figure 1.** Infrared spectra of styrene and reaction products of the styrene-$O_3$ reaction: top, pure styrene at −180 °C; center, a styrene-$O_3$ mixture warmed to −55 °C in which some ozonide bands have appeared; bottom, two samples of pure ozonide made by warming styrene-$O_3$ mixtures to −40 °C, pumping away the unreacted styrene and $O_3$, and recooling to −180 °C.

**Table I.** Infrared Bands of a Styrene Ozonide at −180 °C

| obsd frequencies, $cm^{-1}$ | possible assignments |
|---|---|
| 3055 vw | aromatic CH stretch |
| 3025 vw | aromatic CH stretch |
| 2958 vw | ozonide CH stretch |
| 2888 m | ozonide CH stretch |
| 1960 vw | combination |
| 1900 vw | combination |
| 1820 vw | combination |
| 1695 vw | combination |
| 1600 vw | aromatic ring stretch |
| 1490 w | aromatic ring stretch |
| 1458 m | aromatic ring stretch |
| 1380 m | $CH_2$ deformation |
| 1310 m | CH bend |
| 1290 w | aromatic CH bend |
| 1212 m | $CH_2$ rock |
| 1173 vw | aromatic CH bend |
| 1156 vw | aromatic CH bend |
| 1128 w | ozonide ring stretch |
| 1085 m | aromatic CH bend |
| 1060 vs | ozonide ring stretch |
| 1022 s | ozonide ring stretch |
| 975 s | ozonide ring stretch |
| 930 m | ozonide ring stretch |
| 846 w | aromatic ring bend |
| 808 w | ozonide ring bend |
| 752 s | aromatic CH bend |
| 732 w | combination |
| 690 s | aromatic ring bend |
| 630 w | aromatic ring bend |
| 610 vw | aromatic ring bend |
| 520 vw | aromatic CH bend |
| 360 vw | ozonide ring bend |

Infrared spectra of styrene, the styrene-$O_3$ reaction mixture, and the initially formed ozonide are shown in Figure 1. The absorption bands of solid styrene (upper spectrum) are all very sharp, but those of the ozonide are relatively broad. In the middle spectrum, showing a partially reacted system, the broad peak at 1060 $cm^{-1}$ is due to the strongest ozonide peak. The lower two spectra of the ozonide itself were obtained by pumping on the samples as they were warmed to −40 °C, by which temperature the unreacted styrene is effectively removed. However, some decomposition of the ozonide is unavoidable in this process, and the weak peak at 1700 $cm^{-1}$ in the spectrum of the thicker sample (dotted curve, lower spectrum) is due to the strongest band of $C_6H_5CHO$.

The peak frequencies of our solid ozonide recorded at −180 °C are listed in Table I. The bands at 1212, 1060, and 930 $cm^{-1}$ present here must correspond to the three of the four ozonide peaks observed by Briner and co-workers,[6,7] but the 1708-$cm^{-1}$ peak reported by these investigators is undoubtedly due to the carbonyl band of $C_6H_5CHO$. Thus, our initial reaction product is an ozonide, but its assignment to either a primary ozonide (1,2,3-trioxolane) or a secondary ozonide (1,2,4-trioxolane) requires further analysis of the available data.

Since the spectrum of our initial reaction product resembles those of other primary ozonides,[1] particularly the spectrum of a vinyl chloride primary ozonide,[5] our product may be a styrene primary ozonide. Then, its failure to change into a secondary ozonide is not unexpected since the reactivity of $C_6H_5CHO$ with its complementary zwitterion may be low under our experimental conditions. Earlier, we noted that primary ozonides of tetramethylethylene[1] and vinyl chloride[5] also failed to yield their secondary ozonides, evidently owing to low reactivities of acetone and formyl chloride with their respective associated zwitterions. However, if our initial product is a primary ozonide, then it has a remarkable thermal stability. The most stable primary ozonides observed in our earlier studies were those of tetramethylethylene[1] and vinyl chloride,[5] whose decomposition rates became appreciable at about −90 and −70 °C, respectively. Although these temperatures are not very different from the decomposition temperature of −55 °C for our styrene ozonide, neither of the previous primary ozonides survived warming to room temperature. It may be that the weak spectrum we observed in our residual samples at room temperature is due to a secondary ozonide whose intense bands are indistinguishable from those of the primary ozonide, but that does not seem very likely.

If, on the other hand, our ozonide is a styrene secondary ozonide, this assignment raises some experimental difficulties. First, styrene ozonide becomes the only secondary ozonide for which we have failed to detect by low-temperature infrared spectroscopy the associated primary ozonide. Second, $C_6H_5CHO$ should be a precursor to the secondary ozonide, and it should have been readily observed under our experimental conditions. Finally, the thermal stability of our ozonide is very different from that of a styrene secondary ozonide prepared by Criegee and Korber.[11] These authors found their ozonide to be stable up to 50 °C in a neat state or in solutions of benzene, $CCl_4$, or $CHCl_3$. In several other solvents, their ozonide was unstable and decomposed by a first-order kinetics giving $C_6H_5CHO$ as the exclusive aldehyde. The decomposition half-life was the shortest in $CH_3OH$ solvent, being about 22 min at 50 °C. In isopropyl alcohol the half-life was 113 h at the same temperature. Compared to these results, our ozonide decomposition became appreciable at −100 °C in the presence of $CH_3OH$ and at about −55 °C by itself. On the basis of these data, we prefer to suggest that our ozonide may be a styrene primary ozonide. A tentative assignment of the infrared spectrum, where the oxolane ring modes have been distinguished from those characteristic of the styrene,[12] is presented in Table I.

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# Lipophilic [2.2.2] Cryptands as Phase-Transfer Catalysts. Activation and Nucleophilicity of Anions in Aqueous–Organic Two-Phase Systems and in Organic Solvents of Low Polarity

**Dario Landini,*[1a] Angelamaria Maia,[1a] Fernando Montanari,*[1a] and Pietro Tundo[1b]**

*Contribution from the Centro C.N.R. and Istituto di Chimica Industriale dell'Universita',*
*20133 Milano, Italy, and the Istituto di Chimica Organica dell'Universita',*
*10125 Torino, Italy.*

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**Abstract:** Kinetics of nucleophilic substitutions by a homogeneous series of anions in *n*-octyl methanesulfonate, catalyzed by lipophilic cryptand [2.2.2, $C_{14}$] **1**, have been measured in a chlorobenzene-water two-phase system. Cryptand **1** behaves as a phase-transfer catalyst, and reactions follow a mechanism identical with that found for quaternary salts $Q^+Y^-$. The observed pseudo-first-order rate constants are linearly related to the concentration of cryptate $[K^+\subset(2.2.2,\ C_{14})]Y^-$ in the organic phase. They can be simulated in a homogeneous PhCl solution by adding the amount of water associated with the cryptate and with the substrate in the PhCl-$H_2O$ two-phase system, the reactivity scale being $N_3^- > CN^- > Br^- \sim I^- > Cl^- > SCN^-$. The hydration state of anions in $[K^+\subset(2.2.2,\ C_{14})]Y^-$ is the same as that found for $Q^+Y^-$. In anhydrous PhCl reaction rates increase up to 15-fold and the reactivity scale ($CN^- > N_3^- > Cl^- > Br^- > I^- > SCN^-$) becomes identical with the well-known sequence in dipolar aprotic solvents. Lipophilic cryptates exist as monomeric species in low-polarity solvents. In these conditions they probably represent the best approach to a model of solvent-separated ion pair. Owing to the low polar interaction and the absence of association, the reactivity shown by the unsolvated anion is probably the maximum obtainable in solution.

The mechanism of liquid to liquid phase-transfer catalysis (PTC) by lipophilic onium salts is well established.[2-6] In addition to onium salts, several systems capable of forming inclusion complexes with metal cations have been used as phase-transfer catalysts: crown ethers,[7] cryptands,[8] and polypode ligands.[9] Common properties for all these catalysts are a high lipophilic character, which allows transfer of anions from the aqueous phase to organic media of low polarity, and a topology imposing a large separation between the anion and the cationic center;[10] thus the weak solvation and the slight interaction between the opposite ions lead to strong anion activation.

However, these similarities do not mean that the reaction mechanism demonstrated for quaternary salts also applies to all other cases. Other mechanisms cannot a priori be excluded, expecially the possibility that reactions occur at the water-organic solvent interface.

Azamacrobicyclic polyethers (cryptands) are particularly attractive for anion activation, since they form stable cation inclusion complexes (cryptates) in which a spheroidal ligand

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