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Photolysis of Ozonides in the Gas Phase

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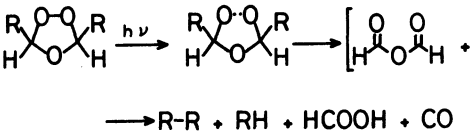
Synopsis. Photolysis of four kinds of simple ozonides (ethene, propene, 2-butene, and isobutene ozonides) in the gas phase were carried out. The contribution of the double-β-scission mechanism was 4—13%. The main reaction path is proposed to be intramolecular hydrogen abstraction followed by radical forming unimolecular decomposition.

Ozonides are oxidants possibly present in photochemical smog since they are known to be formed in the gas-phase ozoneolefin reactions.[1,2] While photolytic decomposition is thought to be one of the degradation paths of ozonides in the atmosphere, photolysis of ozonide in gas phase has never been reported yet. Photolysis of ozonides in the liquid phase was suggested to proceed *via* a double-β-scission after the cleavage of oxygen-oxygen bond as follows.[3]


(1)

Formic anhydride, however, has never been detected. In the present study, gas-phase photolysis of ozonides in near UV region was studied and the reaction mechanism is discussed.

Experimental

Ethene, propene, 2-butene, and isobutene ozonides (hereafter referred to as EO, PO, BO, and IO, respectively) were prepared by the reaction of ozone with ethene, propene, *cis*-2-butene, and isobutene, respectively, in isobutane at −78 °C. They were treated with K_2CO_3[4] and further purified with trap-to-trap distillation. UV spectrum of EO was obtained by use of Cary 17D spectrometer.

The photochemical reactor was an 11 L cylindrical quartz vessel (120 mm i.d., 1000 mm long) equipped with multireflection mirrors for long-path (40 m) Fourier transform infrared spectroscopy (LP-FTIR). Six Sun lamps (Toshiba FL 20 SE, $260 \leq \lambda \leq 400$ nm, $\lambda_{max} = 310$ nm) surrounded the reactor coaxially. Ozonides (15—20 mTorr) (1 Torr = 133.32 Pa) were photolyzed in 1 atm of N_2 at 30 ± 2 °C. Photolysis of BO without any buffer gas was also carried out. The irradiation time was 30 min, 1 h, 2 h, and 2 h for EO, PO, BO, and IO respectively. The concentrations of reactants and products were monitored by means of the LP-FTIR. The spectra were obtained with every 128 scans (scanning time was about 5 min) at a resolution of 1 cm^{-1}.

Results and Discussion

Products and their yields in the photolyses of ozonides are shown in Table 1. Formic anhydride which had been postulated as an intermediate in the liquid phase photolysis was detected for the first time as a product by means of gas-phase IR spectroscopy.

Table 1. Molar percent yield of products in the photolysis of ozonides

	EO[a)]	PO[b)]	BO[c)]	IO[c)]
[Ozonide]$_0$/mTorr	16.66	18.77	18.47	19.83
$-\Delta$[ozonide]/mTorr	5.39	10.93	8.64	9.61
CO	69.8	43.5	40.4	49.6
CO_2	31.6	16.2	22.4	46.0
HCHO	44.8	19.8	—	19.2
HCOOH	54.0	21.3	6.4	18.8
CH_4	—	6.0	14.4	1.2
CH_3OH	—	6.6	10.4	14.4
CH_3CHO	—	13.5	24.4	—
CH_3COOH	—	9.2	18.8	8.2
C_2H_6	—	—	9.6	—
HCOOCHO	5.8	6.2	9.4	—
$CH_3COOCHO$	—	3.6	6.5	12.3
$CH_3COOCOCH_3$	—	—	2.4	—
CH_3COCH_3	—	—	—	30.0
CH_3COOCH_3	—	—	—	3.5
CH_2CO	—	1.2	1.0	—

a) Yields were obtained after 30 min irradiation. b) Yields were obtained after 1 h irradiation. c) Yields were obtained after 2 h irradiation.

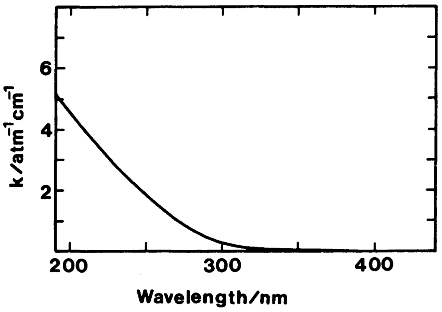
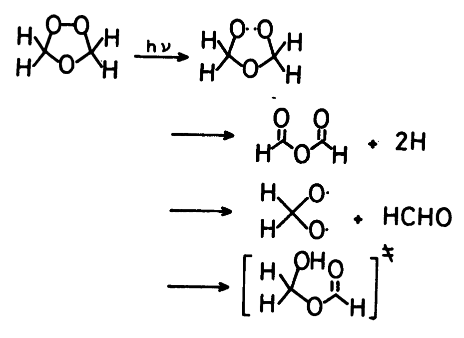


Fig. 1. Gas-phase UV spectrum of ethene ozonide.

EO has a UV absorption (Fig. 1) due to peroxidic O–O bond suggesting that the primary process of the photolysis of ozonides proceeds *via* the O–O bond rupture in an analogous way to peroxides.[5] Initial splitting of the O–O bond would be followed by unimolecular fragmentation or intramolecular hydrogen abstraction of the intermediate biradical, *e.g.*,


(2a)
(2b)
(2c)

Energy diagram of this reaction sequence in the case

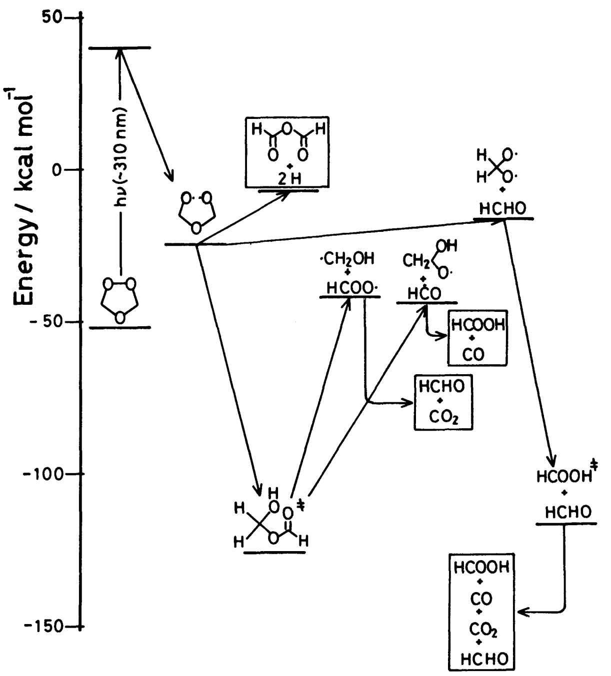


Fig. 2. Energy diagram of the photolysis of ethene ozonide.

of EO is schematically shown in Fig. 2. Heats of formation of the compounds shown in Fig. 2 are estimated by the method of Benson[6] except for OCH_2OCH_2O which is assumed to be ≈27 kcal mol^{-1} above ozonide on the basis of activation energy of thermal decomposition reported by Hull *et al.*[4] Reaction 2a is the double-β-scission process, which was suggested[3] to be the main reaction path in the liquid-phase photolysis of ozonides. The detection of formic anhydride in the photolysis of EO, PO, and BO established the participation of the double-β-scission also in the gas-phase photolysis of ozonides. Besides formic anhydride, acetic formic anhydride ($CH_3COOCHO$) was observed in the photolysis of PO, BO, and IO, and acetic anhydride ($CH_3COOCOCH_3$) was produced in the photolysis of BO. These facts indicate that not only alkyl groups but hydrogen atoms can also be released by the double-β-scission. This can account for the production of glutaric anhydride in the photolysis of cyclopentene ozonide in the liquid phase.[3]

Since further fragmentation of acid anhydride cannot occur on energetic basis (see Fig. 2), the contribution of the double-β-scission in the photolysis of ozonides under 1 atm of N_2 can be estimated based on the yields of the anhydrides to be 5.8, 9.8, 18.3, and 12.3% for EO, PO, BO, and IO, respectively. Thus, the contribution of double-β-scission increases as the number of CH_3 substituent group in the ozonides increases. Detection of CH_2CO and CH_3OH in the photolysis of PO and BO, and that of CH_3COOCH_3 in the photolysis of IO suggest the occurrence of the reaction of the type of Eq. 2b. This reaction involves C–O bond cleavage after O–O bond rupture and results in the production of aldehydes or ketones and methylenedioxy-type biradicals. Methylenedioxy biradical ($\cdot OCH_2O\cdot$) is known as an intermediate formed in the course of unimolecular reaction of the Criegee intermediate which is produced in ozone-olefin reactions.[7–9]

Observation of CH_2CO, CH_3OH, and CH_3COOCH_3 in this study may be explained by the contribution of this mechanism. However, the C–O bond cleavage cannot be the main reaction path since the fact that the sum of the yields of CO, CO_2, and HCOOH is much higher than that of HCHO in the photolysis of EO cannot be explained by this mechanism.

Another candidate for the reaction path is the reaction 2c followed by unimolecular decompositions. Such intramolecular hydrogen abstraction has been supposed to be the main route of the pyrolysis of ozonides both in the liquid phase[10] and in the gas phase.[4] Intramolecular hydrogen abstraction in alkoxyl radicals has also been noted by Carter and co-workers.[11]

If such intramolecular hydrogen abstraction occurs to give $HCOOCH_2OH$ as an intermediate in the photolysis of EO, the overall excess energy for the reaction 2c at the wavelength of 310 nm amounts to 166 kcal mol^{-1} as shown in Fig. 2. Therefore, following types of radical-forming unimolecular decomposition rather than the aldehyde-acid pair forming reaction would predominate in the gas-phase.

$$HCOOCH_2OH \rightarrow HOCH_2O + HCO \rightarrow HCOOH$$
$$+ H + H\dot{C}O(H + CO) \qquad (3a)$$
$$\rightarrow H_2COH + HCOO \rightarrow HCHO + CO_2 + 2H \qquad (3b)$$

High yield of HCOOH, CO, and CO_2 as well as HCHO can be accounted for by this mechanism. Observation of CH_3COOH in the photolysis of PO, BO, and IO would also be explained by this mechanism.

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