Low-Temperature Infrared Studies of Simple Alkene–Ozone Reactions

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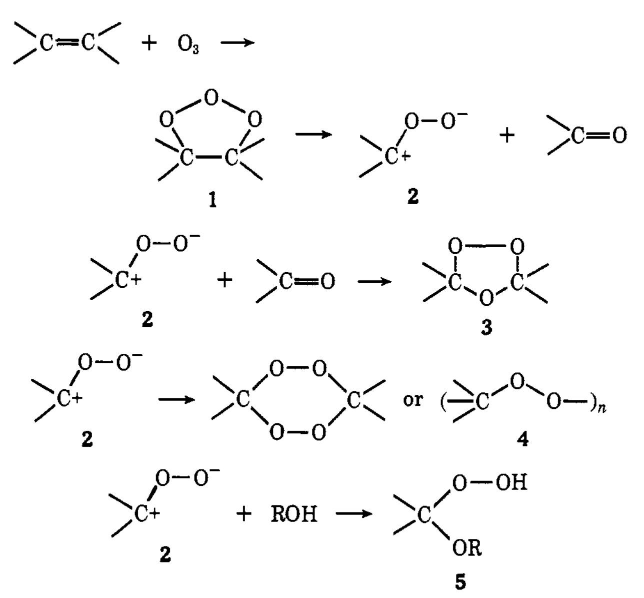
Abstract: The reactions of O_3 with C_2H_4, C_3H_6, i-C_4H_8, *cis*- and *trans*-2-C_4H_8, c-C_5H_8, c-C_6H_{10}, trimethylethylene, tetramethylethylene, and toluene have been studied in the condensed phase in the temperature range of −175 to −80° by infrared spectroscopy. At −175°, two species are formed, tentatively identified as a π complex and a primary ozonide (presumably the 1,2,3-trioxolane). The only exceptions were with C_2H_4, which did not produce the π complex, and with toluene, which did not produce the ozonide. On warming the π complex appears to revert to reactants, but the primary ozonide decomposes to products stable at room temperature. These include the secondary ozonides, ketones, aldehydes, acids, and polymeric material. The results are discussed in terms of both the Criegee and Story mechanisms. However, our finding of a single primary ozonide must temper the considerable speculation as to the number of intermediate species involved in the ozonation of olefins.

The mechanistic sequence by which ozone reacts with olefins has been the subject of a great deal of investigation over a long period of time.[1] The mechanism proposed by Criegee and Werner[2] (Scheme I) has received substantial experimental support.[3–19]

Scheme I



The quantitative trapping of the intermediate zwitterion **2** in alcohol solvents[3,4] to give the alkoxy hydroperoxides **5**, the incorporation of ^{18}O from labeled aldehydes into the ether oxygen of the product secondary ozonides **3**,[8,9] and the observation of mixed (or cross) ozonides from the ozonolysis of unsymmetrical olefins[12,13] all clearly delineate the reactivity and presence of the zwitterion **2**.

The primary ozonides **1** are highly unstable and the demonstration of their existence required that the reaction be carried out at low temperatures. Criegee and Schröder[14] obtained a crystalline material upon ozonolysis of *trans*-di-*tert*-butylethylene at −78° in pentane which upon warming to −60° gave, with explosive decomposition, the normal room-temperature ozonolysis products. The primary ozonide **1** has also been observed by Greenwood and Durham in the nmr for a series of cis and trans olefins.[15–18] They find, in general, that the primary ozonides from trans olefins are stable to about −100°, and Bailey and coworkers[19] have confirmed the symmetrical nature of the primary ozonide of *trans*-di-*tert*-butylethylene by nmr. The corresponding primary ozonide from cis olefins appears to be much less stable and Durham and Greenwood[16] report them to be unstable above −130°. The structure of the primary ozonide from the cis olefins seems less certain but by analogy with the trans olefins it is proposed as **1**.

The sequence observed by Greenwood and by Bailey and their collaborators then corresponds to initial formation of primary ozonide which upon decomposing goes to aldehyde, secondary ozonide, and oligomer (produced by reactions of the zwitterion with one or more zwitterions).[15–21]

The Criegee mechanism predicts that the secondary ozonides **3** would not retain any stereospecificity of the primary ozonides **1** and furthermore the ether oxygen in

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

(2) R. Criegee and G. Werner, *Justus Liebigs Ann. Chem.*, **546**, 9 (1949).

(3) R. Criegee, *ibid.*, **564**, 9 (1953).

(4) R. Criegee, *Rec. Chem. Progr.*, 18, 111 (1957).

(5) S. Fliszár and J. Renard, *Can. J. Chem.*, **45**, 533 (1967).

(6) S. Fliszár, D. Gravel, and E. Cavalieri, *ibid.*, **44**, 1013 (1966).

(7) J. Renard and S. Fliszár, *ibid.*, 47, 3533 (1969).

(8) S. Fliszár and J. Carles, *J. Amer. Chem. Soc.*, **91**, 2637 (1969).

(9) S. Fliszár, J. Carles, and J. Renard, *ibid.*, **90**, 1364 (1968).

(10) J. Castonguay, M. Bertrand, J. Carles, S. Fliszár, and Y. Rousseau, *Can. J. Chem.*, **47**, 919 (1969).

(11) G. Klutsch, J. Grignon, J. Renard, and S. Fliszár, *ibid.*, **48**, 1598 (1970).

(12) N. L. Bauld, J. A. Thompson, C. E. Hudson, and P. S. Bailey, *J. Amer. Chem. Soc.*, **90**, 1822 (1968).

(13) S. Fliszár and J. Carles, *Can. J. Chem.*, **47**, 3921 (1969).

(14) R. Criegee and G. Schröder, *Chem. Ber.*, **93**, 689 (1960).

(15) F. L. Greenwood, *J. Org. Chem.*, **30**, 3108 (1965).

(16) L. J. Durham and F. L. Greenwood, *Chem. Commun.*, 24 (1968).

(17) L. J. Durham and F. L. Greenwood, *J. Org. Chem.*, **33**, 1629 (1968).

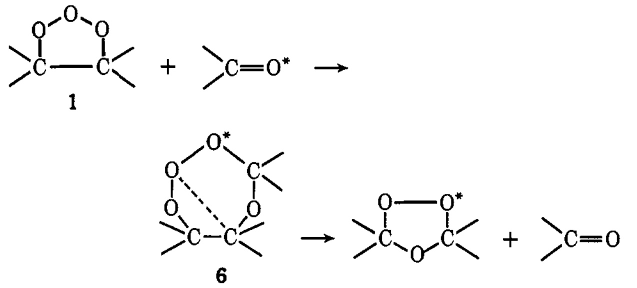
(18) F. L. Greenwood and L. J. Durham, *ibid.*, **34**, 3363 (1969).

(19) P. S. Bailey, J. A. Thompson, and B. A. Shoulders, *J. Amer. Chem. Soc.*, **88**, 4098 (1966).

(20) S. Fliszár, D. Gravel, and E. Cavalieri, *Can. J. Chem.*, **44**, 67 (1966).

(21) S. Fliszár and J. B. Chylinska, *ibid.*, **46**, 783 (1968).

Scheme II



3 would come exclusively from the carbonyl fragment. Story and his coworkers found that in some cases part of the stereospecificity was retained,[22] and they proposed an additional scheme in which the carbonyl compound reacted with the primary ozonide.[23] The carbonyl O is designated with an asterisk and should appear in the peroxide position. Subsequent labeling experiments[24,25] with ^{18}O showed that this could occur. However, Fliszár and his coworkers[13,26] have argued that both of the above observations could still be consistent with the Criegee mechanism, and Scheme II has not been established beyond question.

Because the nmr method is limited to temperatures greater than about −130° and is limited by solubilities of the various substrates and freezing points of the various useful solvents, it was decided to see if some other method could not be devised for following the ozone–olefin reactions at even lower temperatures. The following is a description of such a method and the results obtained.

Experimental Section

Apparatus. All work was done using a Perkin-Elmer Model 225 grating infrared spectrometer over the wavelength range 4000–250 cm^{-1}. The low-temperature cell was of standard design;[27] the external and internal windows were CsBr. The external CsBr windows were sealed to the cell body with Apiezon Q and the seal around the Cu–constantan thermocouple was Apiezon W. The copper window frame assembly was attached to the Cu-glass seal area with a soft solder. Dow Corning silicone grease was used as the seal lubricant for the large rotatable joint. None of the construction materials appeared to be affected by the presence of the small amounts of O_3 used in this study.

The temperature of the sample window was measured with a copper–constantan thermocouple which was attached to the lower end of the window frame. The junction potentials were determined by a direct reading potentiometer (Honeywell Model 2732). The temperature readings were calibrated by observing directly on the window the melting point of ethylene (mp −169.5°) from which it was found that the potentiometer readings needed essentially no correction in the region.[28]

Chemicals. The ozone was produced as needed in a static electric discharge (Tesla coil) through O_2 and collected at −196°. Pumping with an oil diffusion pump removed substantially all the excess oxygen.

The ethylene was Matheson research grade, and the propene, isobutylene, and *cis*- and *trans*-2-butene were all Matheson C.P. grade. The trimethylethylene was obtained from Eastman Organic Chemicals, the tetramethylethylene from Peninsular ChemResearch, Inc., and the cyclopentene, cyclohexene, and toluene from Matheson Coleman and Bell. Each was distilled into an evacuated 1000-ml storage bulb and used without further purification.

Procedure. The following is the general procedure employed for all the olefins except ethylene and propylene. The cell was cleaned and then evacuated overnight with an oil diffusion pump. Then the internal window was cooled to −185° using liquid N_2 as coolant in the cold finger and the olefin (0.05–0.25 mmol obtained by multiple expansion) was condensed all at once on the window and a spectrum then taken. A 10-cm CsBr compensation cell was used in the reference beam. In control experiments, where the olefin was warmed and cooled to effect annealing, the only changes in the spectra observed were some sharpening of peaks and small variations in relative intensities; no new peaks appeared.

The ozone (prepared as described, 0.1–0.2 mmol) was then admitted to the cell at −185° in the same manner as the olefin. The ozone was observed to condense (blue color) on the copper parts of the cold finger, but no change was observed in the olefin. After all the ozone had been admitted, the cell was then pumped with the diffusion pump for about 10 min while maintaining the temperature at −185°. The cell was then removed from the vacuum line and another spectrum taken. In general no change was observed in the olefin spectrum. Presumably the ozone condensed on the copper parts of the cold finger because they were slightly colder than the window,[29] and the high volatility of ozone allowed it to move to the coldest point on the cold finger. There was no appreciable warming of the window in the ir beam as long as there was liquid N_2 in the cold finger.

The cell was warmed and reaction was initiated by pouring out the liquid N_2. Most warmings were done with the cell removed from the ir beam, except where noted. The copper parts of the cold finger warmed most rapidly and the ozone distilled from the copper to the cold CsBr window. This began to occur at −175° and the blue ozone color could be seen on the window at this temperature. The time it took to warm to −170 to −175° was about 5 min. At this point liquid N_2 was added to quench the reaction and the cell cooled again to −185°. The ozone could be seen to distill off the cold window back onto the copper parts of the cold finger. A spectrum was then taken at −185°. Further warming was effected in the same manner; *i.e.*, the liquid N_2 was poured out of the cold finger and the cell allowed to warm to the desired temperature, at which point the liquid N_2 was again introduced into the cold finger and the window cooled back to −185° and a spectrum taken. In this way spectra over a sequence of temperatures −175, −160, −150, −130, −110, −90, and −80° could be obtained. It was necessary to cool the cell to −185° before taking spectra to ensure that the infrared beam did not further warm the sample.

Certain observations are relevant. The ozone was generally all reacted by −150°. In experiments where unreacted ozone was removed by pumping on the cell while warming it to −160° (after having allowed some reaction to take place by performing a warm-cool cycle to −160°), the results were identical with those obtained when the ozone was not removed. At times when unreacted ozone was still present it always recondensed on the copper part of the cold finger on recooling. In addition, the more volatile olefins, those with four or fewer carbon atoms, all distilled to the copper portion of the cold finger by about −130° leaving behind only the reaction products. Except as will be noted in the Results section, none of the reaction products were sufficiently volatile to distill off the window when liquid N_2 was readded to the cold finger after each warming cycle. Upon removing the liquid N_2, the window took about 15 min to reach −150° and about 30 min to reach −110°.

After the last warming cycle and spectrum (generally ∼−90°) the cell was connected to the vacuum again and was allowed to warm to room temperature while the volatiles were collected in a liquid N_2 trap. The cell was then recooled to −185° and a spectrum taken of the remaining nonvolatile polymer. The material in the trap was transferred to a 10-cm CsI gas cell and its spectrum taken for product analysis purposes. The material in the 10-cm CsI cell was then recondensed onto the low-temperature cell window

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[22] R. W. Murray, R. D. Youssefyeh, and P. R. Story, *J. Amer. Chem. Soc.*, 88, 3143 (1966).

[23] P. R. Story, R. W. Murray, and R. D. Youssefyeh, *ibid.*, 88 3144 (1966).

[24] C. E. Bishop and P. R. Story, *ibid.*, 90, 1905 (1968).

[25] P. R. Story, C. E. Bishop, J. R. Burgess, R. W. Murray, and R. D. Youssefyeh, *ibid.*, **90**, 1907 (1968).

[26] S. Fliszár and J. Renard, *Can. J. Chem.*, 48, 3002 (1970).

[27] A modified version of the cell described by E. L. Wagner and D. F. Hornig, *J. Chem. Phys.*, **18**, 296 (1950), allowing direct sample introduction onto the cold window through a 4-mm bore stopcock was used. The apparatus is described completely by P. Miller, Jr., M.S. Thesis, The Pennsylvania State University, 1962, p 9.

[28] T. A. Ford, P. F. Sato, and M. Falk, *Spectrochim. Acta, Part A*, **25**, 1650 (1969).

[29] Wagner and Hornig[27] quote a temperature differential of about 5° for a similar apparatus.

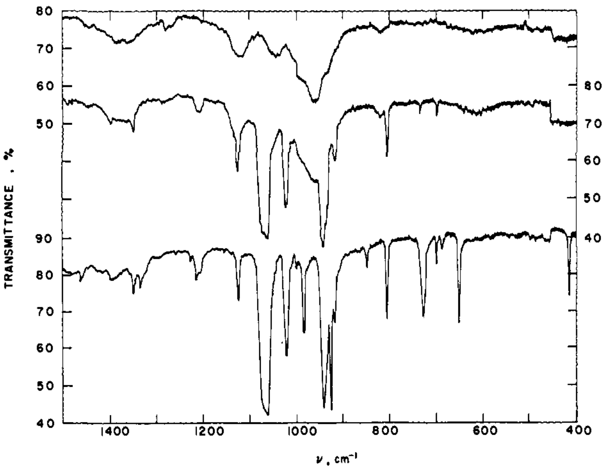

Figure 1. Infrared spectra from the ethylene–O_3 reaction. The lowest spectrum is that initially formed and was taken after the reaction mixture had been warmed to −100° and recooled to −185°. The uppermost spectrum is of the polymeric product and was taken after the cell was warmed to room temperature, evacuated, and recooled to −185°. The middle spectrum is of the final products and was taken after the gaseous products were first removed at room temperature and then returned to the cell and recooled to −185°.

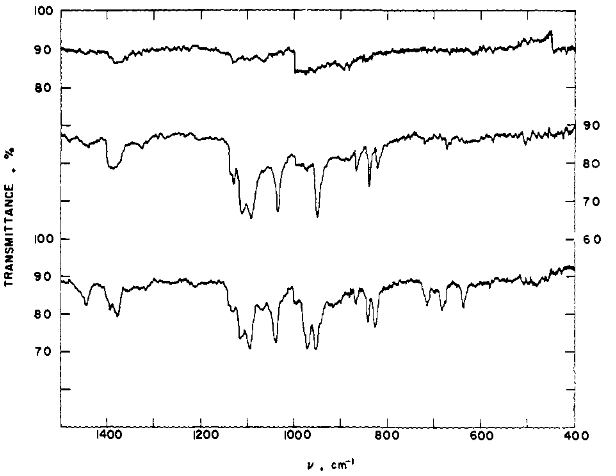

Figure 2. Infrared spectra from the propylene–O_3 reaction. The lowest spectrum is that initially formed and was taken after the reaction mixture had been warmed to −130° and recooled to −185°. The middle spectrum is of the final products and was taken after the reaction mixture had been warmed to −100° and recooled to −185°. The uppermost spectrum is of the polymeric product and was taken after the cell was warmed to room temperature and evacuated.

at −185° and the spectrum taken. Sometimes this condensed sample was annealed by warming and cooling as described above and further spectra were taken.

In the cases of ethylene and propylene a slightly different procedure was necessary because of their high volatility. Both the ozone and the olefins (ethylene and propylene) have appreciable vapor pressures at −170 to −175° and, when the experiments were carried out as described above, reaction did not take place on the window, but instead occurred in the gas phase. The products condensed on the cold finger but essentially none condensed on the window.

The modified procedure was to add the ozone first to the window cooled to ∼−200°. The low temperature was achieved by pumping on the liquid N_2 coolant in the cold finger thereby cooling the liquid N_2 below its normal boiling point. Solid N_2 crystals were observed in the coolant. It was found that when the ozone was admitted to the window cooled to −200° it remained on the window (as observed by the blue color) for a sufficiently long time to allow the ethylene or propylene to be condensed on top of it and thereby obtain reaction products on the window. The above described warming–cooling cycles were then performed. It should be noted that when this inverse addition technique was used with a less volatile olefin (tetramethylethylene), the results were in accord with those obtained when the addition was performed in the standard manner.

The products stable at room temperature were identified from known spectra. Except for the secondary ozonides, most have been listed by Pierson, *et al.*[30] The infrared spectra obtained of ethylene, propylene, and isobutylene secondary ozonides are virtually identical with those reported by Garvin and Schubert.[31] Genuine samples of the secondary ozonides from *cis*- and *trans*-2-butene were obtained by the ozonolysis of *cis*- and *trans*-2-butene at −78° in Freon 11 solution. The resulting ozonides had virtually identical infrared spectra. Actually two secondary ozonides, cis and trans, should be present,[12,13] but the differences in composition are sufficiently subtle so that by ir the product ozonides may be treated as if they were identical. That is, ir spectral analysis is not the method of choice for determining subtle compositional differences of the secondary ozonide products.

Caution. In the course of the above work no serious or destructive explosions occurred but the potential was always there. Certain notes of caution are in order.

(1) Whenever ozone and olefin manage to get in the gas phase at the same time an explosion will result. This is especially to be noted for ethylene and propylene. Also, if the cold finger is warmed too quickly so the ozone does not condense on the window first before going into the gas phase (this occurs when the window temperature rises to about −160°), then the olefin may vaporize as the temperature rises and an explosive situation is obtained. As mentioned, when the quantities of materials indicated were used, no serious or destructive explosions occurred. Keeping the amounts of ozone small is never a bad policy.

(2) All products obtained should be treated as potentially explosive. Certainly the initial primary ozonides are explosive; in particular, the primary ozonide from cyclopentene does in fact decompose explosively. By keeping the quantities small no problems however were encountered.

(3) In addition, ozone itself is an explosive poisonous gas and should be treated as such.

Results

When O_3 is condensed on an olefin at about −170°, reaction occurs which produces a primary ozonide and/or a π complex. With warming the π complex appears to revert to reactants, but the primary ozonide decomposes to products stable at room temperature. These include secondary ozonides, ketones, aldehydes, acids, and polymeric material. The reaction was studied with nine olefins and toluene and the reactions were monitored by infrared absorption. The spectra obtained at various points in the reaction sequence are shown in Figures 1–10. The following is a description by temperature region of the experimental results.

−175 to −150°. The reactions were initiated by warming to −175 to −170° and observing the ozone distil onto the window. The samples often became cloudy at this point. The spectra showed marked changes, that is, new peaks with simultaneous decrease of the olefin peaks. Continued warming to −160° generally gave maximum amount of product. Further warming did not result in significantly increased peak intensities. Except for two bands, the increasing peaks maintained a constant relative intensity ratio. In Table I are listed the prominent bands for each of the initial low-temperature products.

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[30] R. A. Pierson, A. N. Fletcher, and E. St. Clair Gantz, *Anal. Chem.*, **28**, 1218 (1956).

[31] D. Garvin and C. Schubert, *J. Phys. Chem.*, **60**, 807 (1956).

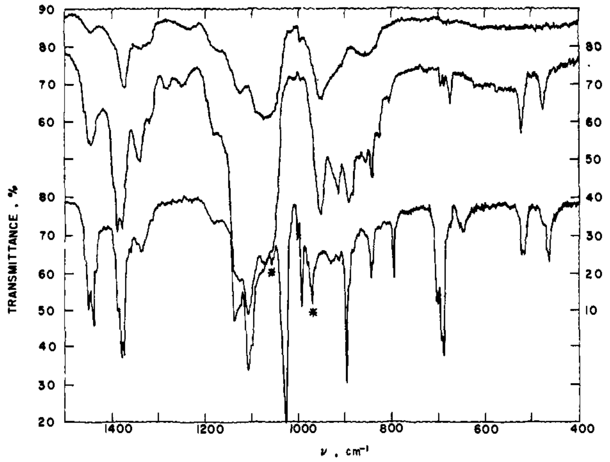

Figure 3. Infrared spectra from the *trans*-2-butene-O_3 reaction. The lowest spectrum is that initially formed and was taken after the reaction mixture had been warmed to −150° and recooled to −185°. Unreacted olefin bands are marked with an asterisk. The middle spectrum is of the final products and was taken after the reaction mixture was warmed to −90° and then recooled to −185°. The uppermost spectrum is of the polymeric product and was taken after the cell was warmed to room temperature, evacuated, and recooled to −185°.

Table I. Low-Temperature Product Ir Bands (cm^{-1}) for the Initial Ozone–Olefin Reaction Products

	Low-temperature product band assignments[a]					
	C–O		O–O–O			Other prominent
Substrate	ν_a	ν_s	ν_a	ν_s	ν_δ	ir bands
O_3 (gas)[b]			1042	1103	701	2111
Toluene[c]			1026	1082	705	2090
	1125	1214	927	983	687	730, 650
	1110	1210	825	971 or 910	680	715, 635
	1110	1185	900	995	690	1383, 1378, 1028, 705
	1110	1180	890	1019	710	1050, 450
	1155	1226	790	980 or 950	698	670
	1168	1200	883	948	670	1370, 1037, 730, 708
	1148	1197	852	953	682	1370, 721
	1114	1216	936	1011	680	800, 425
	1143	1186	850	950	680	1030, 965

[a] Assuming the product is the 1,2,3-trioxolane. [b] From ref 33. [c] Spectrum of toluene–O_3 complex.

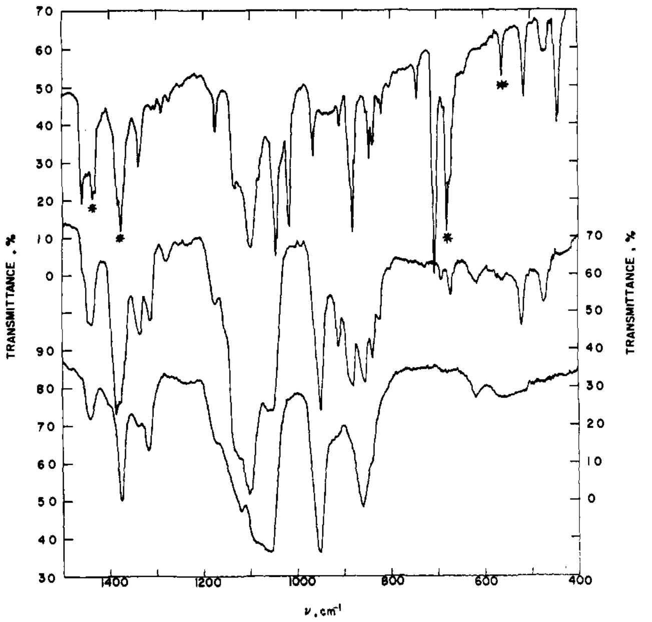

Figure 4. Infrared spectra from the *cis*-2-butene-O_3 reaction. The uppermost spectrum is that initially formed and was taken after the reaction mixture had been warmed to −130° and recooled to −185°. Unreacted olefin bands are marked with an asterisk. The middle spectrum is of the final products and was taken after the gaseous products were first removed at room temperature and then returned to the cell and recooled to −185°. The lowest spectrum is of the polymeric product and was taken after the cell was warmed to room temperature and evacuated.

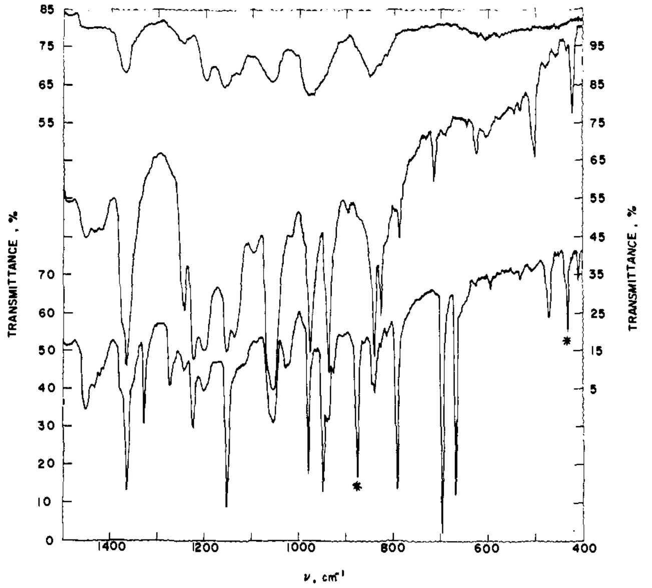

Figure 5. Infrared spectra from the isobutene-O_3 reaction. The lowest spectrum is that initially formed and was taken after the reaction mixture had been warmed to −130° and recooled to −185°. Unreacted olefin bands are marked with an asterisk. The middle spectrum is of the final products and was taken after the reaction mixture had been warmed to −100° and then recooled to −185°. The uppermost spectrum is of the polymeric product and was taken after the cell was warmed to room temperature, evacuated, and recooled to −185°.

Everyone of the nine olefins yields a product which shows strong bands in the 650–730- and 950–1050-cm^{-1} regions. We associate these bands with the primary ozonides. In Table I are listed the tentative band assignments based on a cyclic five-membered 1,2,3-trioxolane structure. The assignments are of course speculative since no isotope substitution work has been done, and the molecules are complex. Where there is no rational basis upon which to make a choice the other possible bands are listed. The C–O stretching frequencies were assigned in the general region 1150–1060 cm^{-1} after Bellamy[32] with the antisymmetric stretch the more intense. The trioxy group was assigned in analogy to ozone both by relative intensity and approximate band position. That is, the antisymmetric O–O–O stretch was considered the most intense band and the symmetric stretch and the O–O–O bending vibration considered to be about equally intense. The

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[32] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Wiley, New York, N. Y., 1958, p 115.

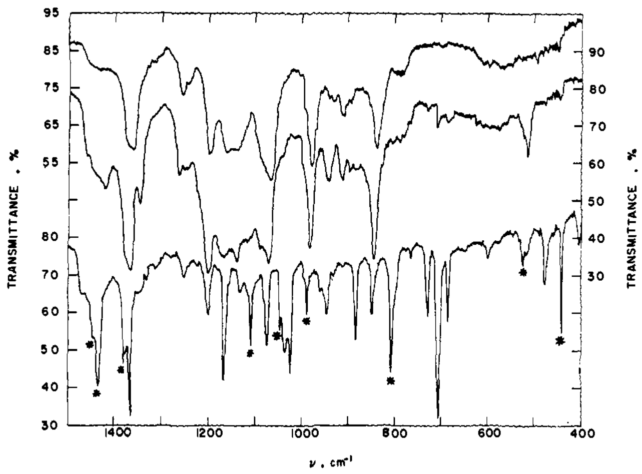


Figure 6. Infrared spectra from the trimethylethylene-O_3 reaction. The lowest spectrum is that initially formed (plus olefin) and was taken after the reaction mixture had been warmed to −130° and recooled to −185°. The unreacted olefin bands are marked with an asterisk. The middle spectrum is of the final products and was taken after the reaction mixture had been warmed to −100° and then recooled to −185°. The uppermost spectrum is of the polymeric product and was taken after the cell was warmed to room temperature, evacuated, and recooled to −185°.

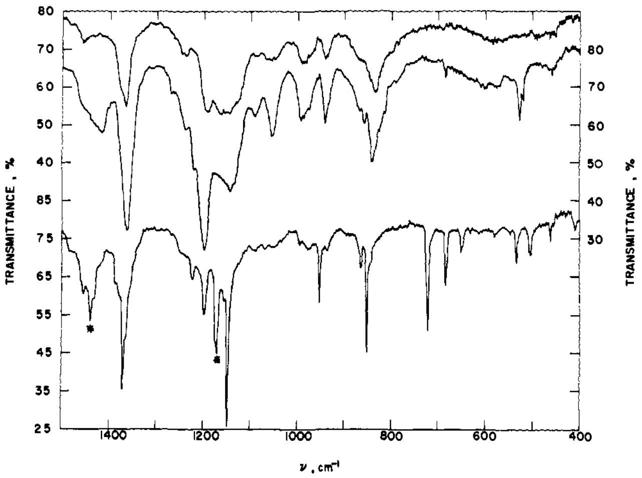


Figure 7. Infrared spectra from the tetramethylethylene-O_3 reaction. The lowest spectrum is that initially formed (plus olefin) and was taken after the reaction mixture had been warmed to −90° and recooled to −185°. The unreacted olefins bands are marked with an asterisk. The middle spectrum is of the final products and was taken after the reaction mixture was warmed to −75° and then recooled to −185° The uppermost spectrum is of the polymeric product and was taken after the cell was warmed to room temperature and evacuated.

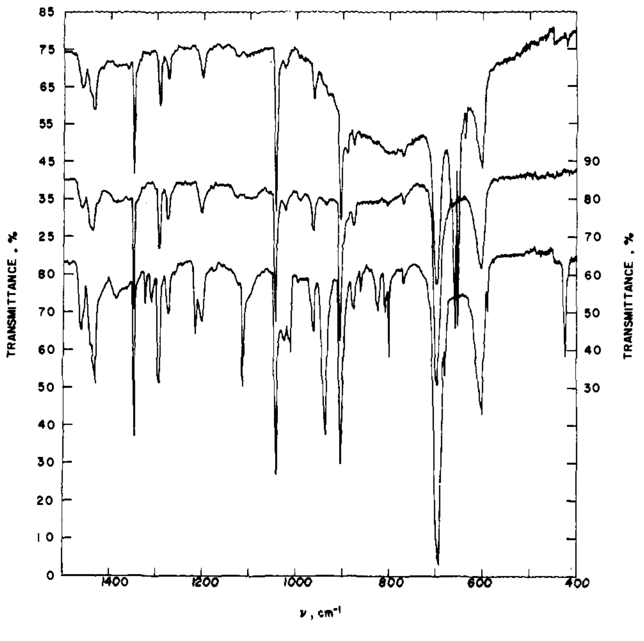


Figure 8. Infrared spectra from the cyclopentene-O_3 reaction. The lowest spectrum is that initially formed (plus olefin) and was taken after the reaction mixture had been warmed to −140° and recooled to −185°. The middle spectrum corresponds to that of the olefin and was taken after the cell was warmed to −120° and recooled to −185°. The uppermost spectrum is of the final products (H_2O, CO_2) plus unreacted olefin and was taken after the gaseous products were first removed at room temperature and then returned to the cell and recooled to −185°.

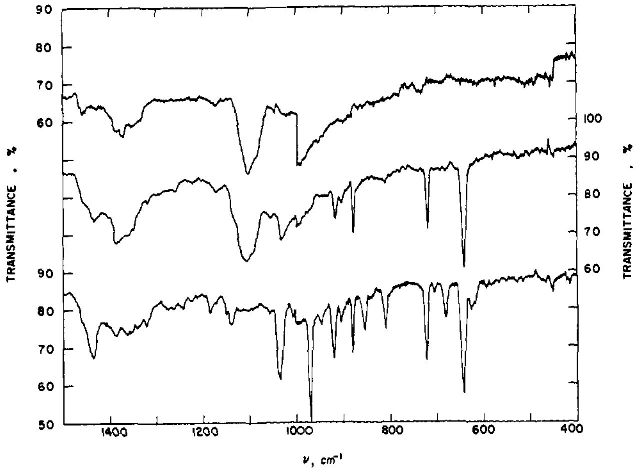


Figure 9. Infrared spectra from the cyclohexene-O_3 reaction. The lowest spectrum is that initially formed (plus olefin) and was taken after the reaction mixture had been warmed to −165° and recooled to −185°. The band at 1030 cm^{-1} decreases in intensity on successive warmings but the other bands do not. The middle spectrum corresponds to that of the olefin and polymer and was taken after the cell was warmed to −130° and recooled to −185°. The uppermost spectrum is of the polymeric product and was taken after the cell was warmed to room temperature, evacuated, and recooled to −185°.

assignments are reasonable enough to enable the assertion that the five-membered trioxolane structure is consistent with the spectra observed.

The two bands which do not belong to the primary ozonides are a strong one at about 1030 cm^{-1} and a weak one at about 2100 cm^{-1}. These bands increase to a maximum intensity at about −160° and disappear in the −155 to −140° region without producing additional primary ozonide. The gas-phase spectrum of ozone has bands at 1042 and 2110 cm^{-1},[33] so these appear to correspond to ozone bands. Ozone also shows a series of bands at 2100, 1000, and 700 cm^{-1} when trapped in an argon matrix at 4 °K.[34]

In the reaction of toluene and ozone it can be seen that the 1026- and 2090-cm^{-1} bands are accompanied by a 705-cm^{-1} band and these are the only prominent

(33) D. J. McCaa and J. H. Shaw, *J. Mol. Spectrosc.*, **25**, 374 (1968).

(34) J. Schwager and A. Arkell, *J. Amer. Chem. Soc.*, **89**, 6006 (1967).

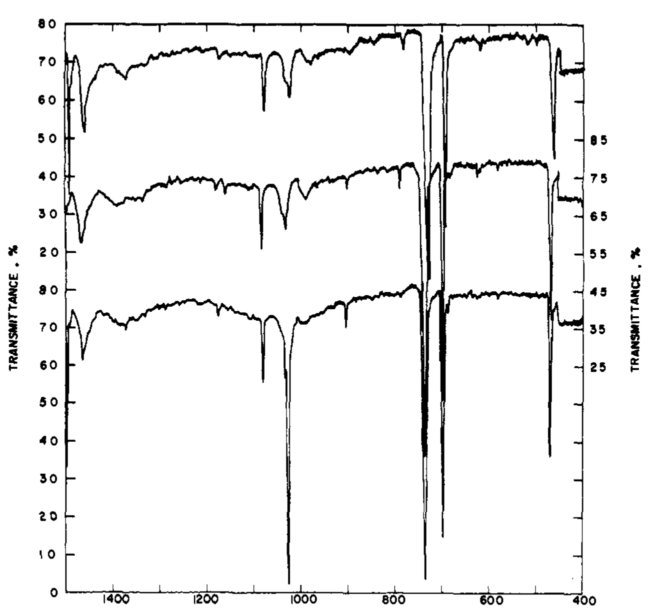


Figure 10. Infrared spectra from the toluene-O_3 reaction. The uppermost spectrum is of pure toluene and was taken at −185°. The lowest spectrum was taken after the cell was warmed to −170° and recooled to −185°. A new sharp band at 1024 cm^{-1} is readily apparent. This band disappears on further warming to −150° and recooling to −185° as shown in the middle spectrum.

new bands. The appearance of these bands is accompanied by the appearance on the window of a canary yellow color. The ultraviolet spectrum displays a band with a maximum at 3850 Å which is due neither to toluene nor ozone. The yellow color, the uv band, and the ir bands all disappear on warming above −150° giving back the spectrum of pure toluene, and the ozone can be recovered. (The cell is recooled to −185° before the spectrum is taken, but the ozone freezes in the cold finger and not on the cell window.) The reaction is reversible since again warming the sample to −170° gives back the yellow color, uv spectrum, and the abovementioned ir bands.

In a run using *n*-butane as the substrate, the warming sequence to −150° resulted in no changes of the spectra other than those attributable to annealing; *i.e.*, there were no new bands in the ozone region or elsewhere. The only compound that did not display this 1030-cm^{-1} band variation was ethylene, although the band in tetramethylethylene was weak and therefore somewhat ambiguous.

−150 to −130°. With two exceptions the compounds formed in the temperature region <−150° retained their spectral identity in this temperature region, neither increasing nor decreasing in intensity. The olefins with four or less carbon atoms generally distilled off the windows in this region.

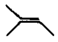
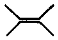
The two exceptions were cyclopentene and cyclohexene. The initial products from these two compounds both decomposed to yield other materials in this temperature region. The cyclopentene initial product decomposed explosively, with a distinct clicking sound and on one occasion with a flash of light. The spectrum after decomposition at −130° displayed nothing but peaks attributable to unreacted cyclopentene. Further warming had no effect on the spectrum. The products obtained on warming the cell to room temperature and collecting the materials in the liquid N_2 trap indicated the presence of H_2O, CO_2, and acetylene as well as some noncondensable gas.

Cyclohexene was less violent but nontheless decomposed in the −150 to −130° range. Its spectrum after decomposition displayed ketonic absorption at 1710 cm^{-1} and broad bands in the 1100–900-cm^{-1} range which did not change on further warming. The volatile products on collection showed the presence of H_2O and CO_2 as well as a small amount of material that could have been secondary ozonide (band at 1080 cm^{-1}). The major product, however, was a nonvolatile polymer that remained on the CsBr window despite pumping at room temperature with a diffusion pump.

−130 to −100°. In this temperature region the initial products from propylene, *cis*-2-butene, isobutene, and trimethylethylene decompose in a quiet, seemingly nonexplosive manner. The decompositions were almost always accompanied by some crystallinity change; *i.e.*, they could be seen to occur by a change in the opacity of the film. For isobutylene the spectrum was scanned in the region 1000–600 cm^{-1} several times while the temperature was allowed to rise (*i.e.*, no liquid N_2 in the cold finger). No spectral changes, besides slight band broadening, were observed until the decomposition point was reached, at which point the changes in the spectrum was very sudden, occurring in a 5° temperature range over a period of about 2–3 min. The product spectrum then remained virtually unchanged on further warming.

The product spectra obtained from the decomposition of the primary ozonides of propylene, *cis*-2-butene, and trimethylethylene also remained unchanged upon further warming. The product spectra, incidently, could be reproduced by returning the collected products from the gas phase at room temperature to the cooled window at −185°. In Table II are listed the decomposition temperatures for the initial ozone reaction products as well as the products of this decomposition.

Table II. Primary Ozonide Decomposition Temperatures and Products

Olefin	Dec temp, °C	Products Major	 Minor
	−100 to −80	Sec[a] ozonide	H_2CO, HCOOH
	−130 to −100	Sec ozonide	Polymer, H_2CO
	−100 to −90	Sec ozonide	Polymer, CH_3CHO, CH_3COOH
	−130 to −100	Sec ozonide, polymer	CH_3CHO, CH_3COOH
	−115 to −110	Sec ozonide, ketonic products (HCOOH, H_2CO, $(CH_3)_2CO$)	Polymer
	−130 to −100	$(CH_3)_2CO$	CH_3CHO, polymer, sec ozonide[b]
	−90 to −75	$(CH_3)_2CO$	Polymer, dimer
	−150 to −130	H_2O, CO_2, C_2H_2, non-cond gas	
	−150 to −130	Ketonic polymer	CO_2, H_2O, sec ozonide (?)

[a] Sec = secondary. [b] Probably 2-butene ozonide. Also no CH_3COOH observed.

The products include the secondary ozonide, polymer, and aldehydes, ketones, and acids. For propylene, isobutene, and trimethylethylene, the parent secondary ozonide and two cross ozonides could have been formed, in principle, from either Scheme I or II. Such cross ozonides have been observed in reactions of more complex olefins at higher temperatures (> −78°).[13,26,35] Actually only one cross ozonide would be expected for isobutene and trimethylethylene, since the ketone fragments do not readily re-form oxonides.[1] The ozonide produced from the trimethylethylene may have been the 2-butene ozonide. However in the case of propylene, which could form two cross ozonides, only the propylene secondary ozonide was produced. To check this striking result we reacted propylene with O_3 at −78° in Freon 114. Only the parent secondary ozonide, but neither of the cross ozonides, was produced.

−100 to −80°. The initial products produced from the reaction of ozone with ethylene, *trans*-2-butene, and tetramethylethylene all decomposed in this region, again seemingly without violence.

As with isobutene, the spectrum of the *trans*-2-butene initial product was scanned in the 1000–600-cm^{-1} region during warming. It also displayed no spectral changes, other than a slight band broadening, until its decomposition temperature, which was the same as the decomposition temperature determined during an ordinary warming experiment.

Again the product spectra obtained after decomposition of the three olefins were unaffected by further warming and could be reproduced by recondensing the room temperature products on the cooled cell window.

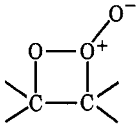
The products, listed in Table II, were secondary ozonide, polymer, aldehydes, ketones, and acids. With tetramethylethylene, no secondary ozonide was produced, in keeping with the supposition that ketones will not produce secondary ozonides by either Scheme I or II. We also did not find either the alcoholic dimers of the zwitterion **2** or the 3-propanediol reported by Story and Burgess[36] for the tetramethylene–O_3 reaction, possibly because of their low yield (~10%).[36] (They first reported these as hydroperoxides, but later suggested alcohols.) Our conditions were considerably different from theirs, and we could have easily overlooked minor amounts of this product.

In a uv experiment, using *trans*-2-butene as the substrate, the O_3 band at 2600 Å was observed, and its intensity appeared to decrease monotonically over the temperature range −170 to −90°. This is to be contrasted with the behavior of the 1030- and 2100-cm^{-1} bands in the ir which disappeared sharply at −140°. No other bands were observed in the uv.

Discussion

Primary Ozonide. The Criegee mechanism as shown in Scheme I implies the existence of a discrete unstable intermediate which is depicted as a 1,2,3-trioxolane structure **1** and is the precursor of another highly reactive intermediate, the zwitterion **2**, that has never been seen spectroscopically but whose reactions are well characterized.

The additional hypothesis proposed by Story and coworkers is depicted by Scheme II and involves a seven-membered ring intermediate **6**. More recently Story and coworkers[37,38] have found that a large excess of C_2H_5CHO and higher aldehydes can react with the primary ozonide to completely suppress secondary ozonide formation. Since in their mechanism, Scheme II, low concentrations of the same aldehydes react with the primary ozonide to produce secondary ozonide, they require two primary ozonides, one of which must be a precursor to the other, and not in equilibrium with it. A large excess of the aldehyde would remove the precursor and thus inhibit secondary ozonide production, whereas otherwise the secondary primary ozonide would be produced and further react with the aldehyde to yield secondary ozonide by Scheme II. They thus proposed the Staudinger molozonide **7**[39] as the precursor primary ozonide. Either primary ozonide could also produce secondary ozonide by the Criegee mechanism, Scheme I.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Our results clearly indicate two molecular species, unstable at room temperature but stable at −170°. One of these is probably a π complex (see next section), and the other a primary ozonide. When warmed the π complex appears to decompose back to starting materials and not to the primary ozonide. In addition, the similarity observed in the spectrum of the complex when compared to reactants indicates no great change in molecular geometry. Therefore the complex is unlikely to be the second intermediate required by the Story mechanism. The other species, the primary ozonide, is converted, over a very narrow temperature range, to the ordinarily observed high-temperature ozonolysis products.

Each of the primary ozonides had a strong band around 1000 and 700 cm^{-1}. The latter absorption provides an identifying band since none of the secondary ozonides, polymers, or ketonic–acidic products have a strong band here. The only interfering absorption is the out-of-plane bending of some of the olefinic starting materials, which can readily be distinguished by their presence in the spectra of the starting material. The similarity of the positions of the ir absorptions of all these primary products would indicate that they all possess the same basic structural unit, whether **1** or **7** it would be difficult to state. The decomposition temperatures for the *cis*- and *trans*-2-butene primary products (−130 to −100, −100 to −90°, respectively) correspond very well with those observed by Durham and Greenwood[17] (−130, −100 to −90°). The smaller alkenes gave some secondary ozonide and decomposition products even on the first warming to −175° and it seems likely that the excess energy of reaction is less easily dissipated for the smaller molecules, and the primary product decomposes to some extent. A similar phenomenon has been observed in the nmr studies.[17]

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[35] S. Fliszár and M. Granger, *J. Amer. Chem. Soc.*, **91**, 3330 (1969).

[36] P. R. Story and J. R. Burgess, *ibid.*, **89**, 5726 (1967).

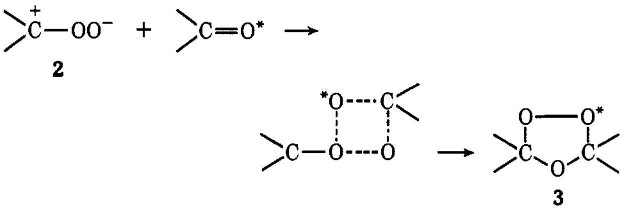
[37] P. R. Story, J. A. Alford, J. R. Burgess, and W. C. Ray, *ibid.*, **93**, 3042 (1971).

[38] P. R. Story, J. A. Alford, J. R. Burgess, and W. C. Ray, *ibid.*, **93**, 3044 (1971).

[39] H. Staudinger, *Chem. Ber.*, **58**, 1088 (1925).

Thus it is likely that the primary ozonide observed by us is the same as that seen by Durham and Greenwood, namely the symmetrical 1,2,3-trioxolane **1**. This does not rule out the Story mechanism, but it does limit it. For one thing the role of the primary ozonides **1** and **7** would be reversed since **1** must now be the precursor to **7**. The latter would be produced as the former decomposed and would be so reactive that no evidence of it would be seen by infrared analysis. A further difficulty with the Story mechanism is that it does not explain either the solvent or concentration effect on the degree of retained stereospecificity, as observed by Fliszár and Carles.[13]

The Story mechanism was proposed to account for retention of stereospecificity and the fact that ^{18}O in an aldehyde can be incorporated into the peroxy bond of the secondary ozonide **3**. Both facts appear to conflict with the Criegee mechanism, Scheme I. Recently, however, Fliszár and coworkers[13,26,35] have argued that both apparent inconsistencies can in fact be reconciled with the Criegee mechanism. The retention of stereospecificity would be the result from two forms of the zwitterion, the syn and anti forms, as suggested by Criegee.[40] The equilibrium between these two species would be influenced by both the nature and concentration of the olefin. The incorporation of ^{18}O into the peroxy bridge of the secondary olefin could occur *via* exchange in the intermediate. We wish to point out



that this scheme could only account for 50% ^{18}O in the peroxy bridge unless the first of the above reactions was reversible, so that isotope exchange would occur. As far as we know there is no evidence for or against isotope exchange, Story, *et al.*,[25] reported 68% labeling in the peroxy bridge in the *trans*-diisopropylethylene ozonation, which would require isotope exchange for the Fliszár scheme to hold. However, a recalculation by Carles and Fliszár[41] gave 43%, so isotope exchange is not necessary.

The products of the primary ozonide decompositions are what one would expect, except that no secondary cross ozonides are produced. The simple unhindered olefins give mostly secondary ozonides and small amounts of polymer and ketonic–acidic material. As the structures get more complex (trimethylethylene and tetramethylethylene) the products become increasingly polymeric and ketonic–acidic. The only unusual cases are cyclopentene and cyclohexene primary ozonides. They are the most unstable of all the primary ozonides (decompose at −150 to −130°) and give fragmentation products (CO_2, C_2H_2, H_2O). With either structure for the primary ozonide, the increased restraints imposed by the bicyclic structure on the primary ozonides of cyclopentene and cyclohexene would greatly reduce their stability.[42] In the fragmentation of such primary ozonides the ordinary partition of the excess energy between rotational–vibrational and translational modes is here inhibitied by the cyclic nature of the substrates to a purely rotational–vibrational energy distribution. Subsequent fragmentation of these vibrationally hot molecules is therefore not unexpected. In ozonolysis studies in solution at −78°, unsubstituted five-membered rings give poor yields of secondary ozonide and cyclohexene gives mostly polymeric material,[19] which is in accord with the above.

The failure to detect cross ozonides is surprising. One possibility is that the Criegee mechanism applies exclusively and the resulting fragments are trapped in a cage and recombine. However in this case no oligomers of the zwitterion should have been produced, and we discard this explanation. The other possibility is that for these small olefins, cleavage of the primary ozonides occur to produce one set of fragments predominantly. These fragments then either recombine *via* Scheme I, or the aldehyde fragment attacks a neighboring primary ozonide *via* Scheme II, insertion being predominantly to produce only one set of products.

π **Complex.** The toluene reaction with ozone in the region −175 to −150° produces no ozonide but does give a reversible reaction. The product does not appear to be too structurally different from the starting materials since the ir of neither toluene nor ozone changes greatly. However, the fact that there is an interaction is confirmed by the uv band with peak absorption at 3850 Å. The correspondence between the disappearance of the 3850-Å band in the uv and the disappearance of the 2090-, 1026-, and 705-cm^{-1} bands in the ir tends to confirm that they are due to the same species. Most likely this is a charge-transfer complex.

The 2100- and 1030-cm^{-1} bands in the ir that appear and disappear over the temperature range −175 to −150° for the simple olefins, however, admit to several possible explanations: (1) condensed O_3; (2) dissolved or trapped O_3; (3) complex formation (π or σ); (4) some entirely different species (product or otherwise).

The first possibility can be ruled out by the experiment with *n*-butane as substrate in which no O_3 could be condensed and retained on the window. The fourth explanation would seem to be ruled out by the similarity between the band positions of gaseous ozone and those observed here. The possibility of O_3 dissolving during reaction and becoming trapped in the solid matrix cannot be completely ruled out. The experimental difficulties are great, and the simultaneous occurrence of product-forming reaction complicates the spectral analysis. In addition, the utilization of surface sites for reaction makes it difficult to demonstrate that a complex can be re-formed with further addition of ozone once reaction has taken place.

Nevertheless the evidence favors the formation of a complex. The ir bands at 2100 and 1030 cm^{-1} probably reflect this complex formation in the olefins, for they disappear at the same temperature as those in the toluene-O_3 complex. In the *trans*-2-butene experi-

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[40] R. Criegee, "Peroxide Reaction Mechanisms," Interscience, New York, N. Y., 1962, p 29.

[41] J. Carles and S. Fliszár, *Can. J. Chem.*, 47, 1113 (1969).

[42] P. D. Bartlett and P. Gunther, *J. Amer. Chem. Soc.*, 88, 3288 (1966).

ments the O_3 uv band disappeared gradually as the temperature was raised, whereas the ir bands disappeared quickly over a small temperature range. Furthermore, if the ratio of the ir and uv extinction coefficients for O_3 are the same in the vapor phase and when condensed at $-185°$, then the 2100- and 1030-cm^{-1} bands were too intense by a factor of 10 to be condensed O_3.

If the above species is a complex it could be either a π or σ complex. The possibility of such complexes has been suggested by several workers.[1,38,43,44] Evidence for a π complex from 1-mesityl-1-phenylethylene and other mesityl compounds has been given very recently by Bailey, *et al.*[43]

The considerable speculation as to the number of species involved in the transformation of olefin to high-temperature products by reaction with ozone[1,37,38] must be tempered by the existence of a single primary ozonide at temperatures above $-175°$. The implications suggest that any new species to be invoked must either be transitory on the way to products from the primary ozonide (such as the zwitterion **2** or the Staudinger molozonide **7**) or be transitory on the way to primary ozonide at $-175°$ (such as a π complex).

Conclusion

The reaction of ozone with simple olefins and the subsequent product transformations can be followed in the ir in the temperature range -175 to $-80°$. The results indicate the possibility of a π complex and the formation of one primary ozonide characterized by strong bands around 1000 and 700 cm^{-1}. The primary ozonide decomposes to yield the normal ozonolysis products observed at higher temperatures.

Acknowledgment. This work was supported by the Environmental Protection Agency through the Office of Air Programs under Grants No. AP 00018 and AP 01044, for which we are grateful.

(43) P. S. Bailey, J. W. Ward, and R. E. Hornish, *J. Amer. Chem. Soc*,, **93**, 3552 (1971).

(44) D. G. Williamson and R. J. Cvetanović, *ibid*., 90, 4248 (1968).

Photolysis of Sulfur Dioxide in the Presence of Foreign Gases. II. Thiophene

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Abstract: The SO_2 photosensitized decomposition of thiophene vapor was studied at 25 ± 3° with irradiation from a mercury arc (effective λ = 3130, 3022, and 2967 Å). Two types of products were formed. Type I products are those produced in the direct photolysis of thiophene, *i.e.*, C_2H_2, CH_2CCH_2, CH_3CCH, CS_2, CH_2CHCCH, and polymer. Type II products are H_2 (the major product), CH_2CO, and SCO. Traces of C_2H_4 and C_3H_6 were also found. Experiments with NO, which quenches the triplet states of SO_2, and with N_2, which quenches the emitting singlet state of SO_2, as well as experiments in which the triplet emitting state ${}^3SO_2$ was directly produced by radiation >3600 Å established that ${}^3SO_2$ was not the sensitizing state, that type I products came from sensitization of $SO_2{}^*$ and $SO_2{}^{**}$ (the nonemitting singlet and triplet states of SO_2, respectively), and that type II products came mainly, if not entirely, from sensitization by ${}^1SO_2$ (the emitting singlet state) and $SO_2{}^*$. A simplified mechanism is presented which adequately explains the results, and a number of rate constant ratios are obtained.

The interest in the mechanism of the reactions between electronically excited SO_2 and different added gases has increased in the last years mainly because of the general concern about the nature of the chemical processes taking place in SO_2 polluted atmospheres. Since the ozone present in the atmosphere absorbs the radiation lying in the 2000–3000 Å region, the wavelengths of interest are those larger than 2900 Å which correspond to energies lower than 99 kcal/mol. Thus, under atmospheric conditions, the high OS–O bond dissociation energy (132 kcal/mol at 298°K) precludes its direct photodecomposition. Hence, the reactions of atmospheric importance are those of electronically excited SO_2, principally when excited into the first singlet band, centered at 2900 Å.

The mechanism for the primary photophysical processes in SO_2 when excited into this band is

$$SO_2 + h\nu \longrightarrow {}^1SO_2 \tag{I_a}$$

$${}^1SO_2 + SO_2 \longrightarrow 2SO_2 \tag{1a}$$

$$\longrightarrow {}^3SO_2 + SO_2 \tag{1b}$$

$${}^1SO_2 \longrightarrow SO_2 + h\nu_f \tag{2a}$$

$$\longrightarrow SO_2 \tag{2b}$$

$$\longrightarrow {}^3SO_2 \tag{2c}$$

$${}^3SO_2 \longrightarrow SO_2 + h\nu_p \tag{3a}$$

$$\longrightarrow SO_2 \tag{3b}$$

$${}^3SO_2 + SO_2 \longrightarrow 2SO_2 \tag{4a}$$

$$\longrightarrow SO_3 + SO \tag{4b}$$