Infrared Spectra and Kinetics of Decomposition of Primary Ozonides in the Liquid Phase at Low Temperatures

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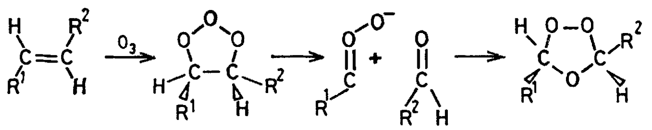
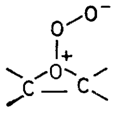
A low-temperature i.r. cell has been developed for *in situ* studies of the intermediates of the ozonolysis of alkenes in the liquid phase at temperatures down to −178 °C. The i.r. spectra of 1,2,3-trioxolans (primary ozonides) formed from the following alkenes have been observed: hex-1-ene, *cis*-di-isopropylethylene, *trans*-diethylethylene, *trans*-di-isopropylethylene, and *trans*-di-t-butylethylene. All have characteristic bands in three spectral regions, 690, 970, and 1 100 cm^{-1} and at higher temperatures decompose with the formation of 1,2,4-trioxolans (final ozonide) and peroxy-compounds. The decay of the i.r. bands at 690 cm^{-1} has been used to study the kinetics of the decomposition of the primary ozonides over a range of temperatures. The reactions are first order and have the following *A* and *E* factors: *trans*-diethylethylene, $10^{5.3}$ s^{-1}, 29 ± 6 kJ mol^{-1}; *trans*-di-isopropylethylene, $10^{8.4}$ s^{-1}, 40 ± 3 kJ mol^{-1}; *trans*-di-t-butylethylene, 10^{11} s^{-1}, 60 ± 13 kJ mol^{-1}. The activation energies for the decomposition of the primary ozonides from *cis*-di-isopropylethylene and hex-1-ene are estimated to be lower than 14 kJ mol^{-1}. The observed parameters and the effects of substitution indicate incipient π-bonding and charge separation in the C–O bonds of the transition state and also considerable orientation of solvent molecules.

RECENTLY, there has been a resurgence of interest in the mechanism and application of the ozonolysis of alkenes.[1-3] There has been much controversy between two mechanisms which have been proposed for these unusual reactions where the strong C=C bond is broken and the 1,2,4-trioxolans rather than the expected 1,2,3-trioxolans are produced. Both the Murray aldehyde interchange mechanism [4] and the Bauld–Bailey modification [5] of the original Criegee mechanism [6] attempt to explain the unexpected finding that the *cis* : *trans* ratios of the 1,2,4-trioxolans depend on the geometry of the parent alkene. However, recent results,[7,8] including those of Murray,[9] indicate that there is little experimental evidence for, or a need to involve, the aldehyde interchange mechanism. Therefore the modified Criegee mechanism is used as the basis for discussing the results of the present studies. The reaction is assumed to proceed in three stages: (*a*) a 1,3 dipolar cycloaddition to give an unstable 1,2,3-trioxolan,[10] also called the primary ozonide (I) (there is some evidence that this step may be preceded by the formation of a charge transfer or π-complex [11,12]); (*b*) the decomposition of the primary ozonide (I) to *syn*- and *anti*-zwitterions (II) and carbonyl fragments; and (*c*) the recombination of the zwitterion and carbonyl moieties in the reverse sense to form the 1,2,4-trioxolan also called the final or stable ozonide (III), *syn*- and *anti*-zwitterions forming predominantly the *cis*- and *trans*-final ozonide, respectively. The three reactions fall into the $[_{\pi}4_s + _{\pi}2_s]$ classification and are symmetry allowed.[13] The influence of the parent alkene geometry arises because of the preferential formation of the *syn*-zwitterions from the *cis*-alkene and the preferential formation of the *cis*-final ozonide from the recombination of the *syn*-zwitterions, and *vice versa* for *anti*-zwitterions and the *trans*-alkene.

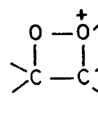


(I) (II) *anti* or *syn* (III) *cis* and *trans*

The structure of the primary ozonide (I) is still not established unequivocally but all the experimental evidence is consistent with a 1,2,3-trioxolan geometry although three-membered ring structures such as the peroxy-epoxide (IV) cannot be excluded.[14] The primary ozonide from *trans*-di-t-butylethylene is a crystalline solid at −78 °C which on reduction gives a racemic diol indicating an intact alkene C–C bond in the primary ozonide.[15-17] Similar diols are obtained from other *trans*-alkene primary ozonides [4,18] but as yet *cis*-alkene primary ozonides have proved too unstable for such direct chemical evidence of their structures to be obtained, although n.m.r. studies at −130 °C by Greenwood and Durham [19] indicate their occurrence and structural similarity to the *trans*-primary ozonides. The n.m.r. spectra of the *trans*-primary ozonides have only a single proton resonance from the methine group, showing that they are equivalent [17,18] and that the Staudinger molozonide (V) can be discounted. Hull *et al.*[20] have condensed ozone and alkenes onto caesium bromide windows at −175 °C and have observed i.r. absorption bands in the solid phase which they assign to primary ozonides. The i.r. spectra of solutions of alkenes in carbon disulphide ozonised *in situ* are in substantial agreement with those observed in solid matrices.[21] In both cases characteristic bands, which decay irreversibly during a warming–cooling cycle, are found in three regions, 690, 970, and 1 100 cm^{-1}. These are assigned to O–O–O and C–O dominant modes in a 1,2,3-trioxolan structure but in the absence of isotopic substitution



(IV)



(V)

experiments these assignments are speculative even if reasonable.

Rouse[22] using CNDO/2 methods and Hiberty[23] using SCF-MO have concluded that the 1,2,3-trioxolan is the most stable structure and the former author has shown that the most stable conformer is the O–O half chair with several other conformers lying within 5 kJ mol^{-1}.

Although it is known qualitatively that the stability of the primary ozonides is highly dependent on the structure of parent alkene, the *trans*-alkene ozonides being much more stable than the *cis* or terminal alkene ozonides, there is almost no quantitative kinetic data on their decomposition. The most careful kinetic study is that of Greenwood and Durham[24] who used n.m.r. to follow the decomposition of the primary ozonide from *trans*-diethylethylene in CCl_2F_2. Unfortunately the first-order rate constant of the decomposition was determined only at -100 and -103 °C so that the activation energy of 33 kJ mol^{-1} is subject to considerable uncertainty. These authors found marked differences in rate constants and product distribution in CCl_2F_2 and perdeuteriodimethyl ether as solvents. Razumovskii and Berezova[25] determined the rate of decomposition of the primary ozonide from hex-1-ene by the rather indirect method of 'quenching' the reaction by adding ethanol to the ozonised solution in diethyl ether at selected times and determining the drop in yield of the final ozonide. An A factor of 10^9 s^{-1} and an activation energy of 29 kJ mol^{-1} are reported.

There have been two recent theoretical attempts to estimate the activation energy for the decomposition of ethylene primary ozonide. Hiberty[23] has used SCF-MO methods to show that the '*O*-envelope' conformation of 1,2,3-trioxolans is the most stable form of the ethylene primary ozonide, and that it cleaves to the zwitterion and formaldehyde with an activation energy of 71 or 46 kJ mol^{-1} depending on whether configuration interaction is taken into account. Similarly Leroy and Sana calculate an activation energy in the range 5—22 kJ mol^{-1} for the same reaction.[26]

There is a clear deficiency of reliable kinetic information on this important second step in the ozonolysis of alkenes and a need to obtain the Arrhenius parameters for this reaction so that the effects of substitution and stereochemistry can be understood and predicted. We describe the development and use of a low-temperature i.r. cell to produce and observe the i.r. spectra of a wide range of primary ozonides in carbon disulphide and liquid ethane. The decay of the i.r. spectra of several primary ozonides has been used to determine their rate of decomposition over a range of temperatures so as to obtain the Arrhenius parameters for a series of substituted ozonides.

EXPERIMENTAL

Materials.—Alkenes and aldehydes were obtained from commercial sources and were >99.7% pure in all cases by g.l.c. Spectroscopic carbon disulphide and Research grade ethane contained no detectable impurities. Carbon disulphide solutions were freshly prepared immediately before each ozonolysis and the last traces of oxygenated compounds and acid impurities were removed by passing the solutions through activated alumina and Amberlyst A21 ion exchange resin.

Ozone was made by passing pure dry oxygen through a glow discharge sustained in a concentric double-walled soda-glass vessel by application of 12 kV.[27] The residual oxygen was removed from the 4 vol % ozone stream by preferentially adsorbing the ozone onto 60—80 silica gel cooled to -78 °C in a U tube with taps at both ends.[28] The ozone is adsorbed as a bright blue band which slowly extends through the silica gel bed. After saturation (*ca.* 2×10^{-3} moles of ozone) the ozone was desorbed from the silica gel by warming and swept by a nitrogen stream into a 50 cm^3 evacuated bulb. This nitrogen–ozone mixture was then used for the *in situ* ozonolysis of the alkene solutions in the infrared cell as described below.

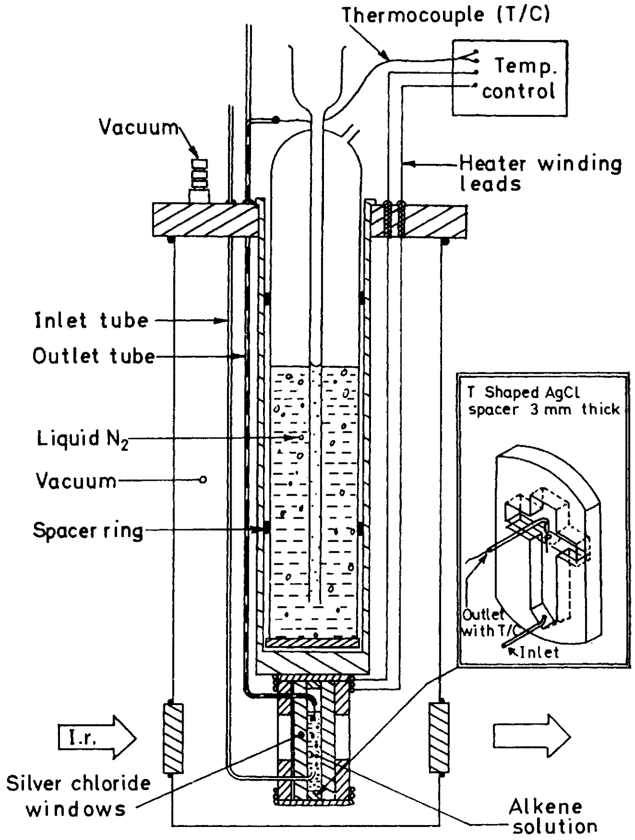


FIGURE 1 Modified Beckman VLT2 cell: ●, vacuum seal

Low-temperature I.r. Cell for in situ *Ozonolysis.*—Because of their instability the primary ozonides have to be prepared and studied in the spectrometer cell itself. No commercial i.r. cell is available which allows a gas to be reacted with a liquid at low temperatures while spectra are simultaneously and subsequently recorded. A Beckman VLT2 low temperature unit has been modified considerably to allow this to be done. (The unit as purchased only allows liquid samples to be introduced at room temperature and their i.r. spectra recorded at low temperatures.) Figure 1 is a schematic drawing of the modified cell. The most important modifications are as follows.

(*a*) Gas entry and exit was *via* stainless steel tubes brazed to the two filling ports of the VLT2 cell. Lengths of nylon tubing were attached to tubes and were fed out of the vacuum chamber through neoprene septa sealed into the top plate. The outlet tube was wider (1.5 mm) than the inlet tube (0.6 mm) so that a thermocouple could be inserted into the solution contained in the cell.

(*b*) The i.r. cell itself was made by interposing between two silver chloride window plates a third silver chloride plate with its central region cut out to form a crucifix shape as shown in the inset of Figure 1. The resulting cell with a long path length of 3.5 mm is needed to prevent the bubbles of gas from lifting the solution out of the cell but this length requires careful selection of solvents and the use of dilute alkene solutions (*ca.* 0.04M). The initial problems of liquid foaming and lifting which occurred even with this ' wide ' cell were eventually solved by using the crucifix cross section shown; the film-bubble expands suddenly on reaching the shoulder and collapses back into the liquid. The cell was gas-sealed by coating the contacting silver chloride windows with silver nitrate solution and judiciously tightening the cell compression bolts and cycling the cell temperature between −78 and 60 °C between tightenings. A good gas-tight seal was judged to have been made when a good vacuum could be maintained in the outer jacket and when solutions in the cell were retained for several hours.

(*c*) The measurement of the temperature of the solution itself is crucial since we found that temperature differences and lags of up to 10 °C could exist between the block temperature (given by a thermocouple embedded in a blind hole in the block) and the solution temperature. Such errors at low temperatures can make the determination of Arrhenius parameters virtually useless. A Comark 1619 AB chromel–alumel couple, protected with a thin nylon sleeve was, with difficulty, introduced into the cell through the outlet tube and the temperature calibrated by determining the m.p.s or b.p.s of reference liquids in the cell.

Procedure.—Carbon disulphide solutions. When the cell had been cooled to a selected temperature the carbon disulphide solution of the alkene was sucked carefully into the cell through the nylon inlet tube, the liquid flow being controlled by a needle valve in the pumped exit line. After the i.r. spectra of the alkene solution had been recorded the nylon inlet tube was transferred to the bulb containing the ozone–nitrogen mixture and the needle valve adjusted so that about two bubbles (*ca.* 1 mm diameter) per second were sucked through the alkene solution. Spectra could be recorded during ozonolysis and also at any desired temperature after ozonolysis using the Beckman TEM-IC variable temperature control unit. The ability to warm and then recool the samples before recording their spectra is an invaluable aid for assigning i.r. bands to unstable intermediates which, unlike those of stable products, diminish or disappear during these warming–recooling cycles.

Liquid ethane solutions. Ethane was used as solvent below −107 °C but in this case the alkene solution was prepared in the cell itself. A small quantity of alkene was introduced into the cell (enough to give a 0.04M solution) at room temperature, and the cell then cooled to −175 °C while being purged with a stream of helium. At −175 °C ethane gas was substituted for the helium and the cell was filled with liquid ethane, the alkene dissolving in the ethane as shown by the appearance of the alkene i.r. bands. Control of temperature and concentration is more difficult with liquid ethane but it, like carbon disulphide, is a very convenient solvent for our studies since it is transparent below 770 cm^{-1} and has very little absorption in the 1 000—1 200 cm^{-1} region.

Spectra were recorded with a Perkin-Elmer 137 prism spectrometer. The narrowing of lines at low temperature was so marked that it was not possible to use a room temperature Vernier variable path length cell containing the alkene solution for reference beam compensation and the reference beam intensity had to be reduced with a comb attenuator.

RESULTS

I.r. Spectra.—The spectral changes accompanying the ozonolysis of *trans*-di-t-butylethylene in CS_2 are shown in Figure 2, for illustration. The alkene bands diminish on ozonolysis and new bands appear. The new bands, which are asterisked, themselves disappear on warming the solution to −50 °C and recooling to −78 °C and are replaced by those of stable products such as the final ozonides and peroxides. We thus assign such temperature-sensitive

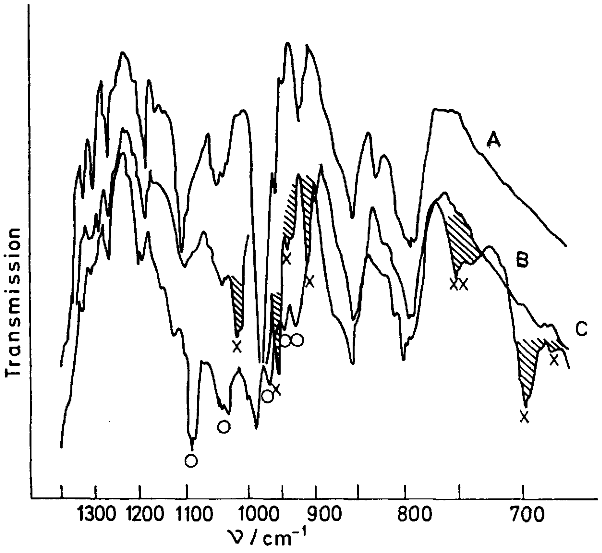


FIGURE 2 Ozonolysis of *trans*-DIPE in CS_2 at −105 °C: A, before ozonolysis; B, after ozonolysis; C, after warming cycle. ×, Primary ozonide; ○, stable ozonolysis product

TABLE 1

Absorption bands of primary ozonides

Alkene	Solvent	*t*/°C	Band position/cm^{-1}
Hex-1-ene	C_2H_6	−175 ± 1	692, 725, 740, 975, 1 001, 1 230, 1 275
cis-Di-isopropylethylene	C_2H_6	−177 ± 1	689, 726, 735, 970, 980, 1 020, 1 030, 1 070
trans-Diethylethylene	CS_2	−105 ± 1	695, 878, 939, 954, 1 010
trans-Di-isopropylethylene	CS_2	−105 ± 1	673, 692, 735, 750, 905, 925—930, 949, 954, 985, 1 010
trans-Di-t-butylethylene	CS_2	−105 ± 1	699, 745, 755, 784, 802, 892, 915, 935, 962, 995
Results from ref. 30			
Propene			680, 715, 825, 910, 971, 1 110, 1 210
trans-But-2-ene			690, 705, 900, 1 110, 1 185
cis-But-2-ene			710, 890, 1 019, 1 050, 1 110, 1 180

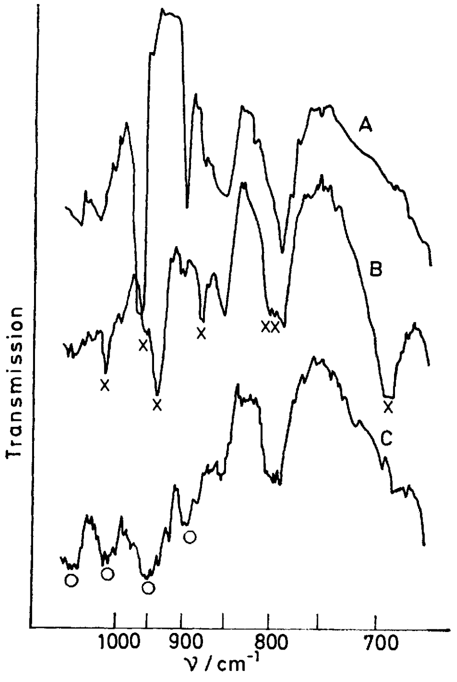


FIGURE 3 Ozonolysis of *trans*-diethylethylene in CS_2 at −109 °C: A, before ozonolysis; B, after ozonolysis; C, after warming cycle. ×, Primary ozonide; ○, stable ozonolysis product

bands to the primary ozonides. They are consistent with a five-membered 1,2,3-trioxolan structure. The primary ozonide bands from other alkenes in carbon disulphide at −78 °C and liquid ethane at −175 °C are similarly assigned and are shown and listed in Figures 3—6 and in Table 1.

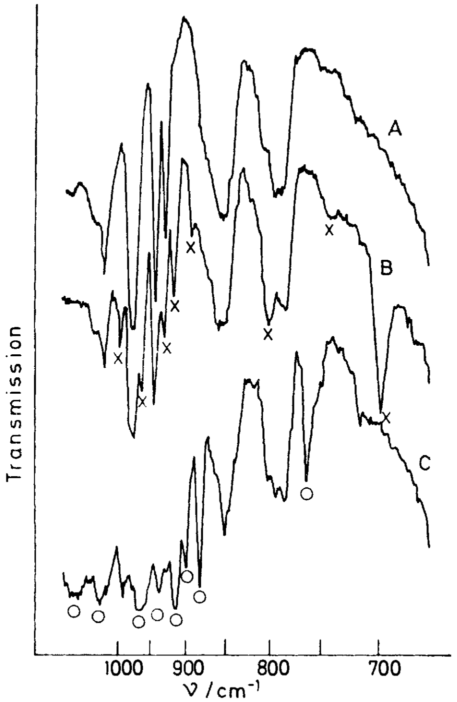


FIGURE 4 Ozonolysis of *trans*-di-t-butylethylene in CS_2 at −105 °C: A, before ozonolysis; B, after ozonolysis; C, after warming cycle. ×, Primary ozonide; ○, stable ozonolysis product

Although direct comparison is not possible since different alkenes were used, our spectra are in general agreement with those observed by Hull *et al.*[20] in the solid state, with the exception that we do not observe bands at 1 010 and 1 226 cm^{-1}. Such bands appear on standing or slight warming and we attribute them to the final ozonide and believe they are also best attributed to final ozonides in the case of the solid-state spectra. At low enough temperatures the primary ozonide bands persist for several hours but all eventually decay to be replaced by those of the final ozonide.[20,29] In addition to the final ozonide bands there is a growth of a broad absorption envelope between 1 100 and 800 cm^{-1} which is probably due to cyclic peroxides and oligomers formed by zwitterion–zwitterion association reactions. The size of this envelope varies with the primary ozonide, being greatest for *trans*-diethylethylene and least for *trans*-di-t-butylethylene.

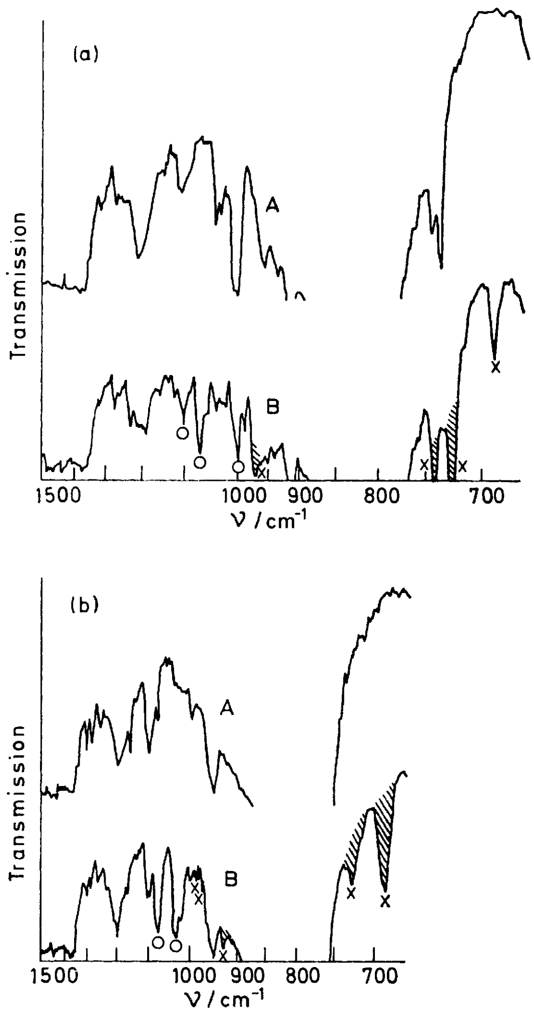


FIGURE 5 (a) Ozonolysis of hex-1-ene in liquid ethane at −176 °C: (b) ozonolysis of *cis*-DIPE in liquid ethane at −177 °C: A, before ozonolysis; B, after ozonolysis. ×, Primary ozonide; ○, stable ozonolysis product

Kinetics of the Decomposition of Primary Ozonides.—Having established the occurrence of a number of persistent primary ozonides during ozonolysis and obtained their i.r. spectra we have used the rate of decay of their spectral

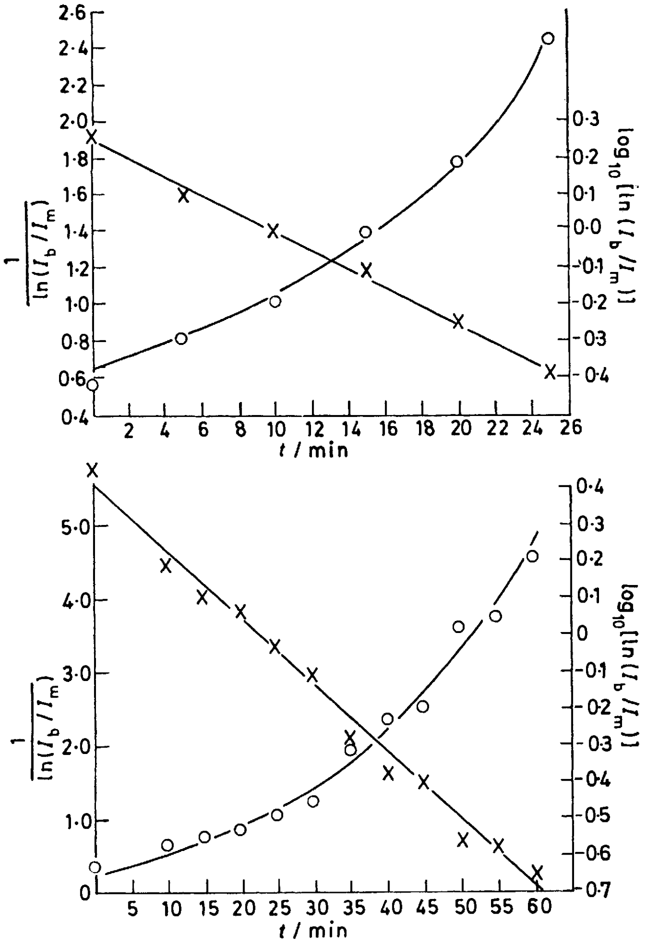


FIGURE 6 Comparison of first- and second-order treatments of data on the decomposition of two primary ozonides: (a) *trans*-DIPE at −82.1 ± 0.3 °C; (b) *trans*-di-t-butylethylene at −59 °C

bands to determine their rates of decomposition over a range of temperatures. The bands centred at *ca.* 690 $\mathrm{cm^{-1}}$ were selected because they are characteristic of primary ozonides,[20,22] strong, and free of interference from reactants and products. The applicability of Beer's Law is shown by the correspondence between the amount of ozone introduced into the alkene solutions and the optical density (O.D.) given by $\log_{10} I_m/I_b$ where I_m is the transmittance of the primary ozone band and I_b that of the solvent at the ozonide band position (estimated from the transmittance on each side of the band).

If the decomposition of the primary ozonide follows a first-order rate law then equation (1) applies, and if a second-order rate law, equation (2) where $\mathrm{O.D.}_0$ and $\mathrm{O.D.}_t$ are the initial optical density and that at time t, k_1 and k_2

$$\log \mathrm{O.D.}_0 - \log \mathrm{O.D.}_t = -2.303k_1t \qquad (1)$$

$$\mathrm{O.D.}_0^{-1} - \mathrm{O.D.}_t^{-1} = k_2t/\varepsilon l \qquad (2)$$

are the first- and second-order rate constants, ε the extinction coefficient, and l the path length. Good first-order plots were obtained over two half-lives as illustrated in Figure 6 for the case of *trans*-di-isopropylethylene and *trans*-di-t-butylethylene. The second-order plots of optical density of the same data show decided curvature (Figure 6). Hull *et al.* have employed similar procedures in using i.r. spectral bands to study the gas-phase decomposition of the final ozonides of selected alkenes.[30]

Rate Parameters of the Primary Ozonides of trans-*Alkenes.*—Accurate rate constants over a range of temperatures have been obtained for the ozonides of the three *trans*-alkenes in which the CH_2 groups adjacent to the double bond are progressively substituted by methyl groups.

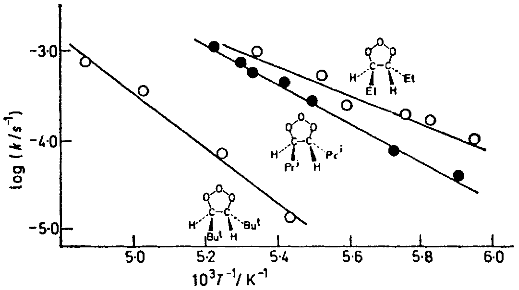


FIGURE 7 Arrhenius plots for ozonide decomposition

Table 2 lists the first-order rate constants and the Arrhenius parameters obtained from the good ln k_1 *versus* T^{-1} plots of these values (Figure 7). It is worth noting that if the cell block temperature rather than the actual solution temperature is used the Arrhenius parameters are considerably lower, for example, values of 22 kJ $\mathrm{mol^{-1}}$ and $2.3 \times 10^2\ \mathrm{s^{-1}}$ are obtained for the primary ozonide of *trans*-di-isopropylethylene.

Rate of Decomposition of cis-*Di-isopropylethylene* (*DIPE*) *Primary Ozonide.*—At −105 °C only the i.r. bands of the final ozonide of *cis*-DIPE are seen indicating that the primary ozonide, if formed, is converted into the final ozonide in <1 min, *i.e.* the rate constant for its decomposition is $>10^{-2}\ \mathrm{s^{-1}}$. In liquid ethane at −178 °C new bands at 689, 728, 970, 980, 1 020, and 1 022 $\mathrm{cm^{-1}}$ are observed indicating the presence of a primary ozonide. The decay of these bands at −178 °C is too slow to allow us

TABLE 2

Rate constants and Arrhenius parameters for the decomposition of primary ozonides

Parent alkene	Solvent	T/K	$\log_{10}k$/ $\mathrm{s^{-1}}$	$\log_{10}A$/ $\mathrm{s^{-1}}$	E/kJ $\mathrm{mol^{-1}}$
trans-Diethylethylene	CS_2	173.5	−3.80	5.3 ± 1.3	29 ± 6
	CCl_2F_2	173	−3.27	6.7	33 *
trans-Di-isopropylethylene	CS_2	174	−4.22	8.4 ± 1.5	40 ± 5
trans-Di-t-butylethylene	CS_2	190.5	−5.00	11.0 ± 2	60 ± 7
cis-Di-isopropylethylene	Ethane	95	<-5	~3	<20
	CS_2	168	>-2		
Hex-1-ene	Ethane	95	<-5	~3	<20
	CS_2	168	>-2		

* Results from F. L. Greenwood and L. J. Durham, *J. Org. Chem.*, 1969, **34**, 3363.

to measure the rate constant with any accuracy but we estimate that $k < 10^{-5}$ s^{-1}. These two limits indicate that the activation energy is *ca.* 14 kJ mol^{-1} but that the A factor is very low indeed, 10^2—10^3 s^{-1}.

*Decomposition of the Hex-*1*-ene Primary Ozonide.*—The behaviour of hex-1-ene is very similar to that of the *cis*-DIPE in that only at −175 °C were bands obtained which could be assigned to the primary ozonide. The decay of the primary ozonide was again too slow at −175 °C to allow us to measure the rate constant with any accuracy. We estimate similar A and E values to those estimated for the *cis*-di-isopropylethylene primary ozonide.

DISCUSSION

I.r. Spectra of Pre-zwitterion Intermediates

Primary Ozonides.—In two previous publications [12,21] we reported the detection of pre-zwitterion intermediates by i.r. spectroscopy of ozonized alkene solutions at very low temperatures. The internal alkene, *trans*-di-isopropylethylene-formed pre-zwitterion intermediates with a half-life of *ca.* 30 min at −78 °C,[12] whilst for the terminal alkene 2,4,4-trimethylpent-1-ene similar intermediates could only be observed in liquid ethane solutions below −165 °C.[21] In both cases the intermediates were assumed to be the cyclic 1,2,3-trioxolan. In the latter case, however, at the lowest temperatures (*ca.* −182 °C), short-lived absorptions and a red colour, both of which disappeared on warming to −165 °C to give tioxolan, were attributed to a loose π-complex preceding the formation of the trioxolan. The present study confirms and extends the general pattern of observations made earlier and Table 1 lists the i.r. absorption bands which have been observed for a series of additional terminal and internal alkenes and attributed to pre-zwitterion intermediates.

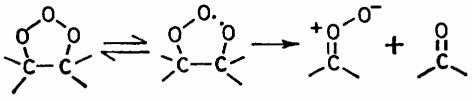
For the terminal alkene hex-1-ene and the *cis*-di-isopropylethylene (DIPE) the pre-zwitterion intermediates are again observed only in liquid ethane solution (at −175 °C) whilst for the internal alkenes, *trans*-diethylethylene and di-t-butylethylene, the intermediates can be observed at *ca.* −105 °C. In general, bands between 650 and 900 cm^{-1} are solely attributable to pre-zwitterion intermediates which disappear unequivocably on warming to form the familiar stable ozonides. The unstable intermediates also have bands between 900 and 1 100 cm^{-1}, which on warming show a general shift to higher absorbance energies giving a broad fairly poorly resolved band typical of stable ozonides and other stable ozonolysis products. This is particularly well observed in Figure 4. The normal vibrational modes for a five-membered ring are complex (see for example the analysis by Kühne and Günthard [29] of the spectra of stable ozonides), and we can only comment qualitatively that the bands observed for the pre-zwitterion intermediates below 900 cm^{-1} are best attributed to motions in a cyclic tioxolan structure where the O–O vibration predominates whilst the higher frequency bands at 900—1 100 cm^{-1} are due in part to modes where the C–O motion predominates in the ring vibrations. We have previously [12,21] compared the location of these bands to those found for cyclic ethers and cyclic peroxides. The spectra of the trioxolan prepared from 2,5-dimethylhex-3-ene and $^{18}O_3$ provide support for the band assignments.[31] Bands originally found near 950 cm^{-1} are shifted *ca.* 10 cm^{-1} by substitution of the heavier isotope. The use of a simple model of a C–O mode involving only one oxygen leads to a prediction of a downshift of *ca.* 20 cm^{-1}. Bands near 700 cm^{-1} are downshifted by at least 50 cm^{-1} which is consistent with the predominant motion being associated with at least two oxygen atoms.

Occasionally weak bands are observed above 1 200 cm^{-1} which invariably increase in intensity on warming. These bands might well be attributable to skeletal modes of the primary ozonide but we consider they are best attributed to small concentrations of stable product formed, for example, in the cell entry tube which is at higher temperatures.

π-Complexes.—In only one of the experiments reported here was an observation made which might be attributed to a loose π-complex between ozone and an alkene. When hex-1-ene was ozonized at liquid ethane temperatures and then warmed slightly a sharp band at *ca.* 980 cm^{-1} diminished disproportionately to other product bands. This is in part similar to the observation previously reported,[21] where a band at 978 cm^{-1} was assigned to the ν_3 band of ozone in a π-complex with 2,4,4-trimethylpent-1-ene. In the current work, however, we did not have sufficient transmission at *ca.* 660 cm^{-1} to detect a weaker band that might be attributed to the ν_2 ozone band in a similar complex. Likewise we could not say with certainty that there was a distinct colour change on warming. The evidence for a π-complex for hex-1-ene is therefore less strong than for the 2,4,4-trimethylpent-1-ene but probably serves to emphasise that we need an alternative approach, *e.g.* u.v. spectroscopy, to affirm the formation of an aliphatic type π-complex.

Mechanism and Kinetics of 1,2,3*-Trioxolan Decomposition*

The Concerted Cleavage and Two-stage Biradical Mechanism.—It is difficult to distinguish between the concerted 1,3 cyclo-reversion reaction already discussed and the possible two-stage route involving biradical intermediates if the first cleavage is reversible and the second cleavage rate determining.[32,33] As O'Neal and Blumstein [33] have noted it is difficult to explain many of the products and observations of gas-phase ozonolysis without involving the participation of biradical intermediates (VI) which, in addition to the formation of zwitterions, undergo intramolecular hydrogen transfer reactions to both the oxy and peroxy positions with the subsequent production of dicarbonyl and keto-hydro-



(VI)

peroxide products. The absence of such products in liquid-phase ozonolysis suggests either that the concerted mechanism is dominant or that there is a marked solvent effect which disfavours the intramolecular transfer reactions. Flizsar [34] has argued that the direction of cleavage in unsymmetric ozonides can only be explained by a concerted cleavage but also only if the initial weakening is at the C–C bond and not at the O–O bond. Our results are discussed in terms of the concerted mechanism but we cannot exclude a biradical mechanism in which the second stage is rate determining.

The detailed model suggested by Lattimer *et al.*[13] is used as a basis for discussion of the present results. The trioxolan is a mixture of several conformers of very similar energies with the carbon half-chair and the carbon oxygen half-chair being slightly favoured by *ca.* 6 kJ mol⁻¹.[23] The cyclo-reversion reaction occurs through a transition state having an oxygen envelope conformation, the direction of motion of oxygen away from or toward the R group determining whether an *anti*- or *syn*-zwitterion is formed. The important interactions are the *gauche–trans*-interaction between the R groups and ring bonds, across-ring interactions, and those between the substituents on adjacent carbon atoms.[13]

Enthalpy changes. The heat of formation of the zwitterion fragment needs to be known for the enthalpy change ΔH for the concerted cleavage reaction to be calculated. Two extreme thermochemical values can be estimated for the simplest zwitterion $\overset{+}{C}H_2O\overset{-}{O}$.

1. No π-bonding in the zwitterion (*i.e.* the C–H bond strength in the methylperoxyl radical is similar to that in methanol).

$$D(\mathrm{H-CH_2OO^{\cdot}}) \simeq D(\mathrm{H-CH_2OH}) \simeq 394\ \mathrm{kJ\ mol^{-1}} \quad (3)$$

$$\therefore\ \Delta H^{\circ}_{f}(\mathrm{^{\cdot}CH_2OO^{\cdot}}) \simeq H_f(\mathrm{CH_3OO^{\cdot}}) + D(\mathrm{H-CH_2OO^{\cdot}}) - H_f(\mathrm{H^{\cdot}}) \simeq 204\ \mathrm{kJ\ mol^{-1}} \quad (4)$$

2. Appreciable π-bonding in the zwitterion (*i.e.* $\mathrm{CH_2{=}\overset{+}{O}{-}\overset{-}{O}}$ or $\mathrm{CH_2{=}O{\rightarrow}O}$, the C–H bond strength is similar to that in the methoxyl radical).

$$D(\mathrm{H-CH_2OO^{\cdot}}) \simeq D(\mathrm{H-CH_2O}) \simeq 88\ \mathrm{kJ\ mol^{-1}} \quad (5)$$

$$\Delta H_f^{\circ}(\mathrm{^{\cdot}CH_2OO^{\cdot}}) \simeq -102\ \mathrm{kJ\ mol^{-1}} \quad (6)$$

Wadt and Goddard [2] have estimated $\Delta H_f(\mathrm{^{\cdot}CH_2OO^{\cdot}})$ to be 119 and 140 kJ mol⁻¹ using GVB and CI methods respectively while Hiberty [23] obtained 101 kJ mol⁻¹ by using SCF-MO theory. These indicate some degree of π-bonding in the zwitterion. Using an estimated value of 29 kJ mol⁻¹ for ΔH_f° of the primary ozonide by group additivity methods [32] the following values are calculated for the enthalpy of decomposition of the primary ozonide of ethylene to the zwitterion and formaldehyde in the gas phase (Table 3).

Kinetic Parameters for the Decomposition of 1,2,3-*Trioxolans.—Activation energies.* The value of 29 ± 6 kJ mol⁻¹ for the decomposition of the *trans*-diethyloxolan in CS_2 is in good agreement with that of 33 kJ mol⁻¹ obtained by Greenwood and Durham in CF_2Cl_2.[24] Because of the narrower range of temperature used in the n.m.r. studies (3 °C) a better comparison is that between the rate constant of 1.6×10^{-4} s⁻¹ at −99.5 °C determined here and the value of 5.4×10^{-4} found by n.m.r. The three-fold difference could be within the overlapping experimental errors of both methods but a solvent effect may well be involved and was indeed reported by Greenwood and Durham.

We have found a marked solvent effect for the *trans*-di-isopropylethylene ozonide in that its half-life in pentane at −78 °C is about five times longer than in carbon disulphide.[12,35] The Arrhenius parameters obtained by Razumovskii and Berezova [25] for the hex-1-ene would result in a half-life of seconds so that the fact that we did not observe this ozonide is not unexpected, but here also solvent effects may be important.

TABLE 3

Method	CI	GVB	SCF	No π-bonding	Full π-bonding
ΔH/kJ mol⁻¹	54	33	15	118	−189

TABLE 4

Group	k_1 at −82 °C/s⁻¹	σ_R
Et	12.6×10^{-4}	−0.094
Pr^i	9.6×10^{-4}	−0.086
Bu^t	0.1×10^{-4}	−0.078

All the activation energies lie well below the enthalpy change of +118 kJ mol⁻¹ calculated assuming no π-bonding in the zwitterion. Hiberty's [24] estimate of 46 kJ mol⁻¹ for the decomposition of the ethylene trioxolan lies quite close to the range of values reported here but this may be fortuitous since it is an estimate for the gas-phase reaction. The value of 5 kJ mol⁻¹ calculated by Leroy and Sana appears to be too low. In order to explain the experimental activation energies it is clearly necessary to involve some degree of π-bonding in the zwitterion and also in the transition state, both at the carbon centre about to become the zwitterion and at that about to become the aldehyde. Such incipient π-bonding will result in charge development and as discussed below this has important consequences for the magnitude of the enthalpies and entropies of activation for the decomposition.

Effects of substituents. As shown in Table 2 there are very substantial changes in activation energy as the CH_2 groups β to the trioxolan ring are progressively substituted. Using the oxygen envelope conformation for the transition state,[13] these effects can be discussed in terms of three factors.

(*a*) Incipient π-bonding in the transition state. The extent of π-bonding and charge separation will depend on the R groups. The order of stabilisation of the charge on the carbon atoms in the trioxolan ring will be $CH_3CH_2 > (CH_3)_2CH > (CH_3)_3C$ viewed either in terms of hyperconjugation or electron release to achieve maximum electroneutrality.[34] The reduced stabilisation as the series is ascended results in an increase in activation energy as found experimentally. Although there is no linear Hammett relationship between rate constants and hyperconjugation σ_R values there is a clear trend of decreasing rate constants and increasing activation energy with increasing σ_R (Table 4). Fliszar *et al.*[34] have found similar group effects on the relative rates of cleavage of unsymmetric trioxolans, in that the preferential formation of the zwitterions is in the same descending order as that found here.

(*b*) Solvent effects. These could be important because of the charge separation in the transition state. Indeed there are marked effects of solvents on ozonolysis [24] and the whole pattern of products can be changed by using different solvents and complexing agents.[36,37] Even though CS_2 has no dipole moment its high polarisability (n_D 1.629 5) may assist charge development. Polarisation of the solvent by the transition state will lower the activation energy and the degree of polarisation will increase with increase in charge development. As already discussed, π-bonding and charge development decrease with increase in methyl substitution and hence an increase in activation energy is expected, *i.e.* the solvent further discriminates between the effects of substitution on the energy of activation. Another effect of methyl substitution could be that increasing bulk hinders solvent access and hence reduces stabilisation of the transition state.

(*c*) *gauche* Interactions between substituents and ring bonds.[13] As the trioxolan passes through the oxygen envelope conformation of the transition state there is an increasing *gauche* interaction between the *trans*-R groups and the ring O–O bonds. The bulkier the alkyl group the larger will be such repulsive interactions and hence the larger will be the activation energies for decomposition.

It is difficult to estimate the relative magnitude of these three factors but there is a clear need for further studies of solvent effects on the kinetics of decomposition of trioxolans.

Entropy of activation. The *A* factors are all well below the value of 10^{13} s^{-1} usually associated with ring opening reactions [38] but we believe that they are not experimental artefacts. The entropy losses listed in Table 2 indicate an increased rigidity in the transition state and its associated solvent molecules. Story *et al.*[39] have also found anomalously low *A* factors, as low as $10^{4.1}$, for the decomposition of hydrotrioxides in polar solvents and ascribe these to solvent orientation effects. The *A* factors for the decomposition of disubstituted 1,2,3-trioxolans (final ozonides) in the gas phase are also very low, *e.g.* for the isobutyl ozonide $A = 10^9$ s^{-1}.[30] The *A* factors observed in this study, and the very large change of 10^5 produced by methyl substitution, are again explicable in terms of solvent and incipient π-bonding effects.

(*a*) Incipient π-bonding. The larger the degree of C=O character in the transition state, the more rigid will be the transition state, the stiffening of the C–O bonds and attendant rocking and bending modes tending to compensate for the weakening of the O–O and C–C bonds which are about to break. Hyperconjugation in the transition state will tend to restrict rotation about the α-C–C bond and to stiffen the rocking modes. In addition the low frequency ring puckering mode of the cyclic five-membered ring,[22] as illustrated by the calculated small energy difference between the trioxolan conformers, could be lost in forming the exaggerated oxygen envelope configuration of the transition state. We estimate a maximum entropy loss of 30 J mol^{-1} K^{-1} from these factors compounded in the following way: stiffening of C–O vibrations *ca.* 4 J mol^{-1} K^{-1}; loss of rocking modes *ca.* 14 J mol^{-1} K^{-1}; loss of ring-puckering modes *ca.* 8 J mol^{-1} K^{-1}; and loss of C–C rotations *ca.* 8 J mol^{-1} K^{-1}. Thus the stiffening of the transition state alone cannot account for the entropy losses of 88 and 147 J mol^{-1} K^{-1} found experimentally for the case of the diethyl- and di-isopropyltrioxolans but would account for those in the di-t-butyl derivative.

(*b*) Solvent orientation. The remaining entropy loss may arise because the charge separation in the transition state leads to a greater orientation of the solvent molecules. The higher the charge development (*i.e.* the lower the degree of substitution of the methylene α to the C=C bond) the greater the orientation and hence the greater the entropy loss in forming the transition state and its accompanying sheath of solvent molecules. In this context it is worth noting that Wadt and Goddard [2] have calculated a high dipole moment of 3.03 D for the CH_2OO zwitterion, indicating that the transition state could be highly polar.

A rough estimate of this effect can be obtained from the entropy of fusion of carbon disulphide, 27.2 J mol^{-1} K^{-1}. If the carbon disulphide molecules orientated by the charges in the transition state are regarded as being ' frozen ' we can use this value to determine the number of CS_2 molecules frozen, $n_s^‡$ in the transition state. If the total entropy losses shown in Table 2 arise in this way the number of molecules involved are 5.5, 3, and 1.5 with increasing substitution. If there is a contribution of 24 J mol^{-1} K^{-1} from a stiffening of the transition state then the numbers become 4, 2, and 0. These estimates do not appear unreasonable especially since it is known that the solvent can have such marked effects on the ozonolysis reaction.

The instability of the cis-*di-isopropylethylene and hex*-1-*ene primary ozonides.* In contradiction of the theoretical predictions of Rouse [22] the ozonide of *cis*-DIPE does have an energy minimum of sufficient depth (*ca.* 14 kJ mol^{-1} s^{-1}) so that it does exist, albeit at very low temperatures, *ca.* −175 °C. Its finite life time under these conditions may also arise because of a low *A* factor for its decomposition although this has not been measured in this work. The instability of the *cis*-isomer is a natural consequence of the large repulsive interactions between two *gauche*-isopropyl groups on adjacent carbon atoms in the trioxolan. Since such interactions could easily exceed 20 kJ mol^{-1} [32] the activation energy of

40 kJ mol^{-1} found for the *trans*-isomer could readily be reduced to below 20 kJ mol^{-1} for the *cis*-isomer.

The low stability of the 1,2,3-trioxolan from hex-1-ene is perhaps a little surprising but is likely to result from the greater degree of π-bonding at the carbon centre about to become formaldehyde and from a reduction in *gauche*-interactions, since only one alkyl group is present.

We have shown that most alkenes will probably form primary ozonides at low enough temperatures and in suitable solvents. The very marked effects of substitution on both the enthalpy and entropy of activation of the decomposition of the primary ozonides provide important information on incipient π-bonding and charge separation in the transition state for these reactions. The range of alkenes needs to be extended and accurate rate parameters determined at low temperatures for the less stable trioxolans. The use of other techniques such as n.m.r. in addition to i.r. is currently being undertaken as are our studies of the reactions in different solvents, so as to examine further the very large effects of solvent on both the entropy and energy of activation indicated by the present work.

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