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Low-Temperature Infrared Studies of Some Chloroethylene–Ozone Reactions

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Abstract: The reactions of ozone with the haloethylenes C_2Cl_4, CH_2CCl_2, *cis*- and *trans*-CHClCHCl, and CH_2CHCl have been examined by low temperature infrared spectroscopy. An unstable primary ozonide was detected only from vinyl chloride. It did not rearrange into a secondary ozonide but decomposed instead into HCOOH, HCl, CO_2, polymer, and presumably CO and O_2. Two isomeric forms of the primary ozonide were present. Other solid chloroethylenes gave unstable π complexes, characterized by a weak infrared band at 1030 cm^{-1}, which reverted to the reactants or produced other products upon warming. The present results support a non-Criegee mechanism as a dominant path of ozonolyses of chloroethylenes except in the case of vinyl chloride, where both the ozonide and nonozonide reaction paths are nvolved.

An earlier report[1] from this laboratory described how a low temperature infrared spectroscopic technique can be used to gain mechanistic information on reactions of ozone with simple olefins. In particular, when these reactions were carried out at temperatures near the boiling point of liquid nitrogen, many gave two unstable primary products. One product was identified as a π complex on the basis of its decomposition back to the reactants upon warming and since its O_3-group frequencies and the temperature dependence of such bands were similar to those observed with the yellow-colored O_3-toluene π complex. The second product was a primary ozonide (1,2,3-trioxolane) which on warming isomerized into the better known and more stable secondary ozonide (1,2,4-trioxolane) or decomposed into acids, carbonyl products, and polymers.

In the present investigation the above spectroscopic method was used to examine the reactions of ozone with C_2Cl_4, CH_2CCl_2, *cis*- and *trans*-CHClCHCl, and CH_2CHCl. Studies of the gas phase ozonolysis of C_2Cl_4,[2] CH_2CCl_2,[3] and CHClCHCl[4] have already been reported from our laboratory and a preliminary note on the CH_2CHCl reaction[5] has appeared. Also, Williamson and Cvetanović[6] have reported the ozonolyses of chloroethylenes in CCl_4 solutions.

Experimental Section

The liquid chloroethylenes C_2Cl_4 (J. T. Baker Co.), CH_2CCl_2 (Fisher Scientific Co.), and CHClCHCl (Aldrich Chemical Co.) were degassed several times and distilled in a vacuum line into storage vessels. The stated purity of each isomeric CHClCHCl was better than 98% and was satisfactory for our infrared studies. The infrared spectra of C_2Cl_4 and CH_2CCl_2 also showed no impurity absorption bands under our experimental conditions. Matheson Co. was the source of CH_2CHCl which was distilled in the vacuum line at reduced temperatures and pressures to give a sample with no apparent impurities. Pressures of the haloethylenes were measured with an oil manometer containing Kel-F No. 3 oil (3M Co.). A Tesla coil discharge of purified oxygen gas cooled to liquid nitrogen temperature gave ozone for each experiment. Excess oxygen in an ozone sample was removed by pumping on the mixture at liquid nitrogen temperature with a glass single-stage oil diffusion pump.

Our Pyrex glass low temperature infrared cells were similar to that used previously.[1] A copper–constantan thermocouple attached to the window holder frame permitted estimation of the sample window temperatures. Generally, the olefin in excess was condensed on the low temperature window first, and then ozone was added to the cell. Under normal experimental conditions, ozone did not condense on the window but accumulated instead on the copper section of the cold finger which was in direct contact with the liquid nitrogen. When the liquid nitrogen refrigerant was removed, however, the ozone distilled over to the low temperature window and imparted a blue color to it. Recooling of the cell, however, caused the ozone to distill back to the colder copper sections of the cell. In addition to the initial spectrum taken before the first warming of the sample, spectra were recorded repeatedly after warming to various temperatures and recooling each time to liquid nitrogen temperature. The infrared spectra were taken on Perkin-Elmer Model 225 and 521 grating spectrophotometers.

Results

C_2Cl_4. When solid C_2Cl_4 at liquid nitrogen temperature was exposed to ozone, a new infrared band which was weak but sharp appeared at 1030 cm^{-1}. On warming the solid this band grew weaker until it disappeared at temperatures near −130 °C. By appropriately controlling the temperature of the sample window the 1030-cm^{-1} band could be made to appear or disappear reversibly. Other absorption bands in the spectrum remained unchanged during this warming process. No evidence of an ozonolysis reaction was observed on further warming of the solid to about −80 °C where the sample started to sublime off the low temperature window. Neither was an ozonide observed from the liquid phase reaction of C_2Cl_4 with ozone. The products in this case were similar to those observed from the gas phase reaction[2] and consisted mostly of CCl_2O and CCl_3CClO with a smaller amount of $\overline{CCl_2CCl_2O}$. Traces of HCOOH and an explosive solid residue were also detected.

CH_2CCl_2. As in the tetrachloro compound, the 1030-cm^{-1} band was the only new feature in the initial spectrum of solid CH_2CCl_2 after it was exposed to ozone at liquid nitrogen temperature. This new band grew weaker on warming and was no longer observable at temperatures near the melting point

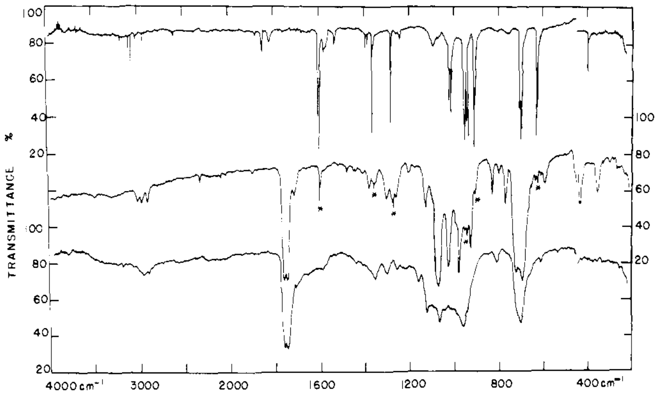

Figure 1. Infrared spectra of vinyl chloride and its ozonolysis products at liquid nitrogen temperature. Upper curve, initial vinyl chloride; middle curve, products after reaction at −170 °C, asterisks identify original olefin bands; lower curve, after warming to 0 °C and redepositing of evolved gaseous products.

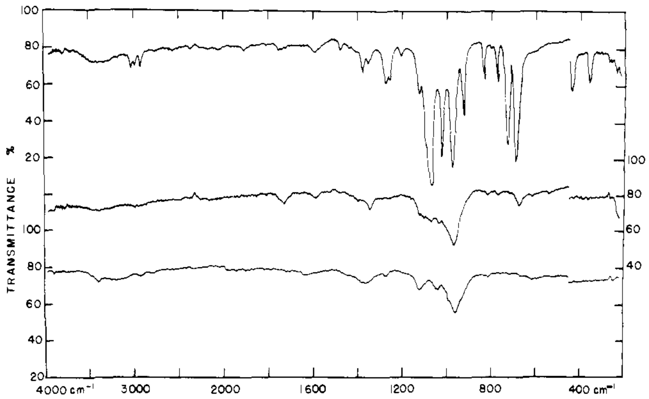

Figure 2. Infrared spectra of ozonolysis products of vinyl chloride and ethylene at liquid nitrogen temperature. Upper curve, vinyl chloride ozonide; middle curve, polymer from the decomposition of vinyl chloride ozonide; lower curve, polymer from the decomposition of ethylene ozonide.

of the sample. Again as in the C_2Cl_4 case the appearance or disappearance of the 1030-cm^{-1} band was reversible. No ozonolysis reaction of CH_2CCl_2 was evident until the sample liquefied near −120 °C. When a liquefied sample which had been warmed to approximately −90 °C was recooled to liquid nitrogen temperature, its spectrum now showed absorption bands due to phosgene and the acid chloride ClH_2CClO, both of which had been observed in the gas phase reaction.[3] However, no bands attributable to ozonides were present. Most prominent in the spectrum of the solid reaction mixture were broad bands at 1800 and at 720 cm^{-1} due respectively to CCl_2O and to ClH_2CClO. The gas phase spectrum of the reaction mixture showed in addition that HCOOH was present.

CHClCHCl. The 1030-cm^{-1} band observed with the previous two chloroethylenes was not present in the initial spectrum of *cis*- or *trans*-CHClCHCl at liquid nitrogen temperature after the ozone was introduced into the low temperature cell. This band appeared only when the sample was warmed to about −150 °C. However, concomitantly a doublet band at 1760 cm^{-1} and a broad band near 715 cm^{-1} both due to formyl chloride[7] appeared during the warming of the sample to this temperature. Further warming to near −120 °C caused the HCClO bands to become more intense but the 1030-cm^{-1} band disappeared. Finally, above −120 °C the HCClO bands themselves started to disappear from the spectrum of the sample. Within our experimental uncertainties, identical results were obtained from the cis and the trans isomers, and the spectra showed no evidence that the olefin had isomerized during the appearance or disappearance of the 1030-cm^{-1} band and the bands due to HCClO. Again, no ozonides were detected either from the solid phase or the liquid phase reaction. The vapor phase spectra of the products of these condensed phase reactions generally showed small amounts of HCOOH, CCl_2O, and HCl, the latter being one of the decomposition products of HCClO. Explosive polymeric liquid residues were also formed in the liquid phase ozonolysis reaction. On ignition this clear residue turned into a white, nonvolatile solid.

CH_2CHCl. Since the 1030-cm^{-1} region of the spectrum of solid vinyl chloride was obscured by one of its fundamental bands, it was not possible to detect in this system the presence or absence of the weak 1030-cm^{-1} peak when the solid olefin at liquid nitrogen temperature was exposed to ozone. Furthermore, on warming the sample to about −170 °C after ozone introduction, new intense absorption bands due to the products of the ozonolysis reaction appeared in this and other regions of the spectrum. These new bands continued to grow while those of the parent olefin became weaker as the sample was warmed repeatedly to near this temperature until finally the ozone was consumed. These changes are illustrated by the middle spectrum in Figure 1. Here, approximately 0.13 mmol of vinyl chloride whose solid spectrum is shown by the upper curve in the figure was reacted with 0.18 mmol of ozone by warming to near −170 °C five times and recooling after each warming. The absorption bands of the residual CH_2CHCl in this colorless reaction mixture are identified by asterisks in the middle spectrm of this figure.

Formyl chloride is one of the products of the ozonolysis of vinyl chloride solid, and its absorption bands in the middle spectrum of Figure 1 consist of the intense doublet at 1760 cm^{-1}, a weak peak at 1303 cm^{-1}, a broad band of moderate intensity at 715 cm^{-1} which is overlapped by a pair of intense product peaks at 729 and 692 cm^{-1}, and a weak overlapped band near 450 cm^{-1} (point of grating change in the spectrum). These peak frequencies and relative band intensities are similar to those in the gas phase spectrum of HCClO.[7] Neither HCClO nor other ozonolysis products displaying the middle spectrum of Figure 1 changed on further warming of the sample to about −150 °C but above this temperature vinyl chloride itself started to sublime off the window. Also, at about −120 °C the absorption bands of HCClO began to decay indicating sublimation of this species from the low temperature window. The remaining bands in the spectrum showed no further changes until the sample was warmed to near −70 °C. Above this temperature prominent peaks in the spectrum started to decay and finally near −40 °C the spectrum no longer resembled the initial scan. This irreversible change is illustrated by the lower spectrum in Figure 1. In this case, the reaction products which gave the middle spectrum were removed from the low temperature cell by warming to 0 °C while pumping. The recovered sample was then redeposited on the low temperature window and subjected to an annealing by warming to −130 °C. Under these conditions HCClO did not decompose completely and its characteristic infrared bands are still visible at 1760 and 715 cm^{-1}. However, comparison of the middle and lower spectra of Figure 1 shows that the other ozonolysis products have undergone extensive decompositions.

The infrared spectrum of the products of vinyl chloride ozonolysis from which formyl chloride had been removed by fractional sublimation is illustrated by the upper spectrum of Figure 2. In this case 0.12 mmol of vinyl chloride was reacted with 0.10 mmol of ozone at about −160 °C and the excess olefin and the product HCClO were sublimed off the window at −90 °C. When this sample was decomposed by warming to

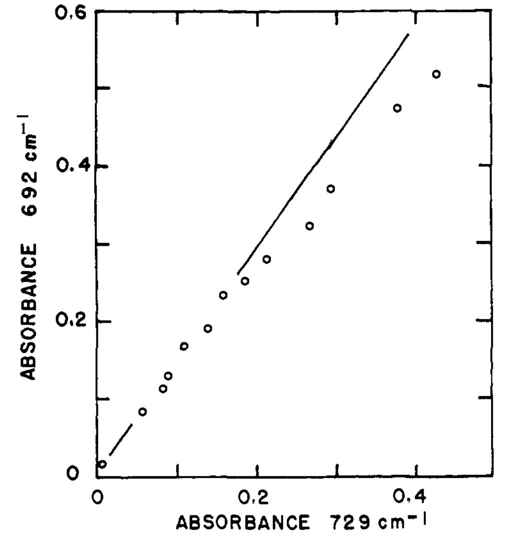

Figure 3. Intensity correlation of the 692- and 729-cm^{-1} bands of isomeric vinyl chloride ozonides.

Table I. Infrared Spectrum of Vinyl Chloride Primary Ozonide, Liquid Nitrogen Temperature

Frequency, cm^{-1} [a]	Assignment
3020 w	CH stretch
2990 w	CH stretch
2913 w	CH stretch
1480* vw	CH_2 deformation
1406 vw	CH_2 deformation (isomer)
1378 m	CH rock
1351 m	CH wag
1279* m	CH_2 wag
1259 m	CH_2 wag (isomer)
1200 vw	CH_2 rock
1129 m	CC stretch
1069* vs	Ring stretch
1026 vs	Ring stretch (isomer)
977* vs	Ring stretch
928 vs	Ring stretch (isomer)
832* m	Ring bend
776 m	Ring bend (isomer)
729* vs	CCl stretch
692 vs	CCl stretch (isomer)
436* m	Ring bend
360 m	Ring bend (isomer)
260 vw	CCl wag

[a] Bands identified by asterisks are assigned to the less stable ozonide.

about −40 °C, its spectrum changed to that shown by the middle curve of Figure 2. Here, the peaks at 1730 and 670 cm^{-1} are due to formic acid while the broad absorptions around 1000 cm^{-1} arise from a white, polymeric material which pumped off slowly at room temperature. During the decomposition process such as the one illustrated by the top two spectra in Figure 2, the products HCOOH, CO_2, HCl, and some gas not condensable at liquid nitrogen temperature were obtained. However, only HCOOH could be detected from the decomposition of the polymeric material whose quantity was usually small.

From the increase in the relative intensities of the absorption bands in the upper spectrum of Figure 2 during the initial reaction of vinyl chloride with ozone near −170 °C, it was evident that these bands belonged to a primary ozonolysis product which formed independently along with another primary product HCClO. Furthermore, since its spectrum resembled that of the primary ozonide (1,2,3-trioxolane) of ethylene,[1,5] it was reasonable to assign the present initial product to the primary ozonide of vinyl chloride. However, closer examinations of its spectra and their peak frequencies, which are summarized in Table I, revealed that actually two different primary ozonides having similar molecular structures were produced in the ozonolysis of vinyl chloride. These ozonides presumably are isomers and they give rise to pairs of infrared bands in 400, 700, 800, 1000, and 1270 cm^{-1} regions. Although the rapid reaction rate did not permit the observation of differences in the growth of these ozonides, their decay rates were measurable and showed some distinctions. For example, the variations in relative intensities of the 700-cm^{-1} pair, which are assigned to the C–Cl stretch modes, are illustrated in Figure 3. The nonlinear variation shown here as well as in Figure 4 for the weaker and more difficult to follow 800-cm^{-1} pair may be contrasted with the approximate linear dependence of the relative intensities of the 832- and 729-cm^{-1} bands (Figure 5). These correlations suggest that the 832- and

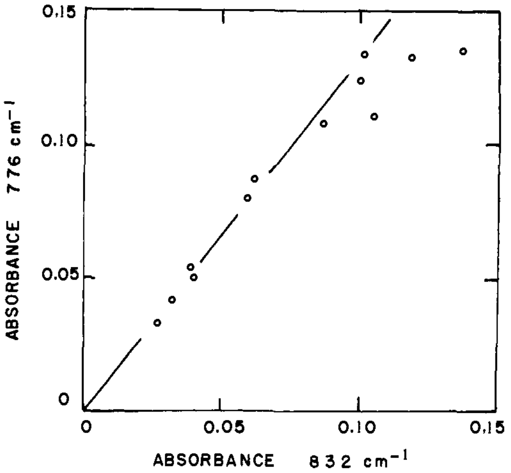

Figure 4. Intensity correlation of the 776- and 832-cm^{-1} bands of isomeric vinyl chloride ozonides.

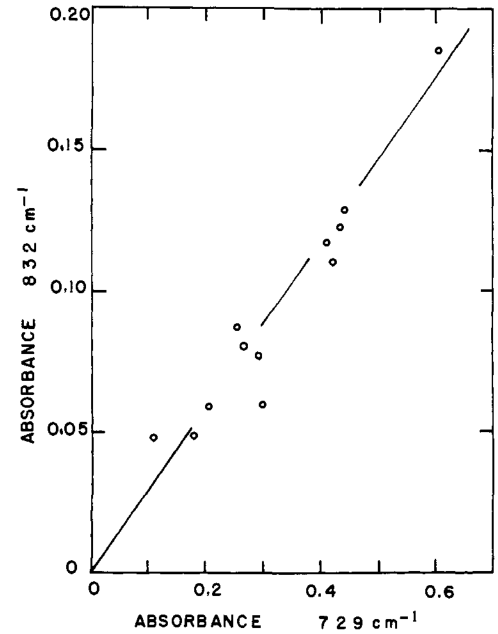

Figure 5. Intensity correlation of the 729- and 832-cm^{-1} bands of a vinyl chloride ozonide.

729-cm^{-1} bands belong to the same species while the 776- and 692-cm^{-1} bands are due to the second isomer. Overlapping of bands made relative intensity measurements in the 1000-cm^{-1} region difficult, but here too the 1069- and 977-cm^{-1} bands appeared to decay faster than did the 1026- and 928-cm^{-1} pair. The faster decaying bands which are associated with the less stable isomer of the vinyl chloride primary ozonides are identified by asterisks in Table I. Other band assignments presented in this table are based on those of ethylene ozonides[5] and of vinyl chloride.[8]

Discussion

The absence of ozonides and the detection of π complexes during the initial stages of the low-temperature ozonolysis reactions of C_2Cl_4, CH_2CCl_2, and CHClCHCl are consistent with the previous interpretations of the corresponding gas phase reactions of these chloroethylenes.[5] As in the hydrocarbon olefins[1] the weak π complexes of these chloroethylenes are formed reversibly and are characterized by essentially an unchanged olefin vibrational spectrum and by a single new infrared band at 1030 cm^{-1} which is only 12 cm^{-1} below the frequency of the antisymmetric stretch fundamental[9] of gaseous ozone.

Although the possibility of the 1030-cm^{-1} band arising from O_3 trapped in the matrix during the exothermic ozonolysis reaction could not be ruled out completely in the earlier study of the hydrocarbon olefins, the present results, particularly those from the C_2Cl_4 matrix which is inert and has a much higher melting point, indicate the unlikelihood of this band being due to dissolved O_3 contrary to the suggestion of Alcock and Mile.[10] The latter investigators observed a red-colored material during the ozonolysis of 2,4,4-trimethylpentene-1 in liquid ethane at -18 °C which they suggested was the π complex with infrared bands at 978 and 669 cm^{-1}. Their interpretation, however, is in conflict with an earlier observation[1] that the ozonolysis of none of the nine monoolefins produced such red materials and that the primary ozonides have characteristic infrared bands in the reported regions.

The presence of the 1030-cm^{-1} band in the initial low temperature spectra of C_2Cl_4 and CH_2CCl_2 after introduction of room temperature gaseous ozone and the absence in CHClCHCl indicate that the reaction activation energy for the formation of the complex is greater for CHClCHCl than for those of CH_2CCl_2 and C_2Cl_4. These π complexes once formed evidently serve as necessary intermediates in a non-Criegee reaction path in view of gas phase kinetic arguments proposed earlier.[5]

The 1030-cm^{-1} region was obscured by the vinyl chloride infrared bands but formyl chloride and two different vinyl chloride primary ozonides were observed as independent primary products. The two vinyl chloride primary ozonides (Table I) are assigned to 1,2,3-trioxolane in which the chlorine atom occupies an axial or an equatorial position as expected on the basis of the primary ozonide conformation, for example as proposed by Lattimer, Kuczkowski, and Gillies.[11] Generally in monohalocycloalkanes, the equatorial CCl stretch is reported to be at a higher frequency than the axial CCl band frequency.[12] If this observation is applicable to the present heterocyclic ozonides, then the less stable isomer whose bands are identified by asterisks in Table I is the vinyl chloride primary ozonide having an equatorial chlorine atom. Unfortunately, neither this ozonide nor its isomer rearranged into the expected secondary ozonides, so comparison of the interpretation with the recent observation of Lattimer, Mazur, and Kuczkowski[13] is not possible. The latter authors showed by microwave spectroscopy that the fluorine atom in vinyl fluoride secondary ozonide occurs predominantly in the axial position.

The decay products of vinyl chloride primary ozonides must be H_2COO and HCClO since no H_2CO was observed. However, the occasional presence of small amounts of CO_2 among the decomposition products suggests that H_2CO and HCClOO may be formed part of the time. The latter formyl chloride zwitterion or diradical may rearrange into chloroformic acid which is known to decompose very rapidly into CO_2 and HCl.[14] Also, under acidic condition (HCl) small amounts of H_2CO may polymerize and become easily hidden in the background spectrum of our samples. Since CO_2 was not observed all the time and its quantity appeared to be variable, experimental conditions such as dielectric effects may determine the extent to which the species HClOO or H_2COO is formed. Formyl chloride also was not detected during the decomposition of the primary ozonide due partly to the strong formic acid carbonyl band obscuring the spectrum, but this compound is known to decompose rapidly by a heterogeneous process to give HCl and CO.[4] Positive identification of HCl was made in this study and most of the noncondensable gas evolved during the decomposition is believed to be CO. The source of the major product HCOOH must be H_2COO and its polymer which are also formed in the ethylene case.[1] In fact an infrared spectrum of the latter polymer shown by the bottom spectrum in Figure 2 is very similar to that of the polymer (middle spectrum in this figure) obtained from the decomposition of vinyl chloride primary ozonide.

Since Gozzo and Camaggi[15] had reported earlier that low temperature liquid phase ozonolysis of C_2F_4 gave its secondary ozonide, we attempted to examine this system also. However, the vapor pressure of C_2F_4 at liquid nitrogen temperature was too high and led to only vapor phase reaction giving the expected O_2 and CF_2O as products. Ozonolysis was attempted in CCl_4 solutions at reduced temperatures, but here too we observed from the infrared spectra only CF_2O and another minor product, presumably $\overline{CF_2CF_2O}$, with sharp Q branches at 1255, 1028, 908, and 895 cm^{-1}. These products have also been reported by Gozzo and Camaggi. Finally, in addition to the vinyl fluoride secondary ozonide reported by Lattimer, Mazur, and Kuczkowski,[13] a secondary ozonide from *cis*- and *trans*-CHFCHF has been observed by Gillies.[16] In all of these systems, since complex products were obtained, both the π-complex mechanism and the Criegee path may be involved as is evidently the case in the present vinyl chloride system. A similar situation may exist in the ozonolysis of 1,2-dichloro olefin since Griesbaum and Hofmann[17] have reported recently the detection of small amounts of secondary ozonide from the liquid phase ozonolysis of *trans*-2,3-dichlorobutene, the latter yield depending rather strongly on the solvent used.

Acknowledgment. We thank Professor R. L. Kuczkowski for providing us with preprints of ozonolysis studies conducted in his laboratory. This work was supported by Grant 800874 from the Environmental Protection Agency and by the Center for Air Environment Studies for which we are grateful.

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Vinylic Radicals Are Intermediates in the Oxidation of Vinylic Lithium Reagents to Lithium Enolates by Dioxygen, But Not by Lithium *tert*-Butyl Peroxide[1]

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Abstract: (*E*)- and (*Z*)-1-lithio-1-propene (**1**) and (*E*)- and (*Z*)-1-lithio-1-phenyl-1-butene (**2**) react with dioxygen at −78 °C and yield the corresponding lithium enolates with partial loss of stereochemistry around the double bond. Reactions of **1** and **2** with lithium *tert*-butyl peroxide yield enolates with retention of configuration. These stereochemical observations implicate free vinylic radicals in reactions of vinylic lithium reagents with dioxygen, and exclude them in reactions with lithium *tert*-butyl peroxide.

Transformation of an organolithium or -magnesium reagent to the corresponding alcoholate by reaction with dioxygen ordinarily occurs in two distinct steps:[3]

$$\mathrm{RM} + \mathrm{O_2} \rightarrow \mathrm{ROOM} \qquad (1)$$

$$\mathrm{ROOM} + \mathrm{RM} \rightarrow 2\mathrm{ROM} \qquad (2)$$

Formation of an intermediate organic peroxide by reaction between the organometallic reagent and dioxygen has been proposed to require initial single-electron transfer to dioxygen;[4] this electron transfer may or may not generate a free radical, R·, depending on the solvation or extent of aggregation of the organometallic species.[5] The mechanism(s) of conversion of organic peroxides to alcoholates has not been carefully examined, but a related reaction—that of di-*tert*-butyl peroxide with ethyllithium, yielding, inter alia, lithium *tert*-butoxide and ethyl *tert*-butyl ether—has free alkyl and alkoxyl radical intermediates.[6]

Here we describe stereochemical evidence that indicates that vinylic radicals are intermediates in the oxidation of vinylic lithium reagents to lithium enolates by dioxygen, but not by lithium *tert*-butyl peroxide. *E* and *Z* diastereomers of appropriately substituted vinylic lithium reagents, and of the derived lithium enolates, can be prepared with high stereoselectivity and proved to be stereochemically stable under the conditions required for these oxidations. Vinylic radicals undergo rapid *Z*-*E* isomerization ($k_i = 10^8$–$10^{10}\ \mathrm{s^{-1}}$ for vinyl radical itself).[7-9] Thus, if free vinylic radicals are intermediates in oxidation of diastereomerically pure *Z* or *E* vinylic lithium reagents, the product lithium enolates will be formed as a mixture of diastereomers.[10] Conversely, if the products of reaction are generated with retention (or inversion) of stereochemistry, vinylic radicals are not intermediates.

These studies contribute to the body of mechanistic information which will eventually rationalize the nucleophilic and electron-transfer pathways followed in reactions of organometallic compounds. They also provide a new method for the stereoselective generation of enolates, and may have applications in synthesis.[11]

Results

(*E*)- and (*Z*)-1-lithiopropene ((*E*)- and (*Z*)-**1**) were prepared by reaction of lithium metal with (*E*)-1-chloropropene and (*Z*)-1-bromopropene, respectively, in diethyl ether solution.[10,12] (*Z*)-1-Lithio-1-phenyl-1-butene ((*Z*)-**2**) was obtained by a lithium-halogen exchange reaction between *n*-butyllithium and (*E*)-1-bromo-1-phenyl-1-butene in hexane solution at 22 °C or THF solution at −78 °C,[13] and (*E*)-1-lithio-1-phenyl-1-butene ((*E*)-**2**) by reaction of *n*-butyllithium with (*Z*)-1-bromo-1-phenyl-1-butene in THF solution at −78 °C.[13] The diastereomers of **1** and **2** are configurationally stable at the temperatures used for the oxidation studies (−78 °C).[10,12,13] The lithium enolates **3** and **4**, generated by oxidation of the lithium reagents **1** and **2**, can be assayed for diastereomeric composition by acylation with acetic anhydride, and analysis by GLC of the resulting enol acetates **5** and **6**. The yields and isomeric composition of the enolate anions formed by oxidations of these reagents were determined by quenching the reaction mixtures with excess acetic anhydride, and analyzing the resulting enol acetates by GLC (Scheme I). Before the compositions of these mixtures of enol acetates could be used as the basis for conclusions concerning the stereochemistry of conversion of vinylic lithium reagents to lithium enolates, however, it was necessary to establish that (a) conversion of lithium enolate to enol acetate proceeded in high yield without isomerization, (b) the lithium enolates were stereochemically stable under the oxidative conditions used to generate them from the vinylic lithium reagents, and (c) neither diastereomer of the pairs of enolates was destroyed oxidatively at a much faster rate than the other.

Authentic lithium enolates were prepared by treating enol acetates with an excess of methyllithium. If stereochemically pure (>99%) (*Z*)- or (*E*)-**5** or -**6** was converted to lithium enolate by this procedure, and then quenched with acetic anhydride, the original enol acetate was obtained in >90% yield, with no detectable loss of stereochemistry. The yields and stereochemistry of the enol acetates obtained by acylation with acetic anhydride thus accurately reflect the composition of the lithium enolates from which they were derived.