Atmospheric Degradation of Glycidaldehyde: Photolysis and Reaction with OH Radicals

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Epoxide aldehydes have recently been detected among the oxidation products of aromatic hydrocarbons. Many epoxides are toxic and very little is known about their atmospheric fate. The products and kinetics of the atmospheric oxidation, OH radical reaction, and photolysis of glycidaldehyde have been investigated in a large volume reactor at 298 K using in situ long-path FT-IR spectroscopy for the analysis. A rate coefficient of \( k = (1.69 \pm 0.04) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) has been determined for the reaction of glycidaldehyde with the OH radical using the relative kinetic technique. The UV absorption spectrum of glycidaldehyde was measured in the range 220–380 nm from which upper limits of its photolysis frequencies in the troposphere have been deduced, e.g., \( \lambda \sim 1.0 \times 10^{-4} \text{ s}^{-1} \) (for July 1, noon, and 50° N). The OH radical initiated photooxidation of glycidaldehyde yields CO, CO\(_2\), formic acid, formic acid anhydride, formaldehyde, and hydroperoxymethyl formate as major products. A reaction mechanism is postulated to account for the product formation.

Introduction

Glycidaldehyde is the simplest epoxide aldehyde and has been classified as an animal carcinogen substance based on long-term in vitro animal carcinogenicity studies and inhalation studies in humans (1). Recently glycidaldehyde along with other epoxides has been identified by means of GC–MS as products in the OH radical initiated degradation of benzene and toluene (2). Although the yields were not determined and may not be particularly high, their importance in atmospheric chemistry arises principally from their high toxicity. The atmospheric chemistry of epoxides has received very little attention and to our knowledge nothing is presently known about the atmospheric fate of glycidaldehyde.

In this study glycidaldehyde has been synthesized and the kinetics and products of its OH radical initiated degradation under atmospheric conditions investigated. The UV spectrum of glycidaldehyde has also been recorded in an attempt to access the relative importance of its loss via reaction with OH radicals compared to photolysis.

Experimental Section

Synthesis of Glycidaldehyde. Glycidaldehyde was prepared on the basis of a method described in the literature (3) through aqueous oxidation of acrolein by H\(_2\)O\(_2\) under strictly controlled pH conditions (8.0–8.5) at a temperature between 25 and 30 °C.

\[
\text{H}_2\text{C}={\text{C}}_{\text{C}}=\text{H} + \text{H}_2\text{O}_2 \quad \text{pH 8.0–8.5} \\
\text{H}_2\text{C}={\text{C}}_{\text{C}}=\text{H} + \text{H}_2\text{O}
\]

The method has been simplified on two points. First, the reaction mixture was lyophilized overnight to reduce the amount of water instead of using a circulating evaporator. Second, the product was extracted in dichloromethane, and the organic phase was distilled under reduced pressure. This variation replaced the extraction with warm cyclohexanone and the time-consuming rectification on an Oldershaw column. The NMR and infrared spectra showed that the product was essentially pure. A GC–MS determination of the purity was unsuccessful. The density of glycidaldehyde has been determined and may not be particularly high, their importance in atmospheric chemistry arises principally from their high toxicity. The atmospheric chemistry of epoxides has received very little attention and to our knowledge nothing is presently known about the atmospheric fate of glycidaldehyde.

\[
\text{OH} + \text{glycidaldehyde} \rightarrow \text{products} \\
\text{OH} + \text{ethene} \rightarrow \text{products}
\]

The initial concentrations of glycidaldehyde and ethene were in the range \((3–6) \times 10^{-3} \text{ molecules cm}^{-3}\) and the photolysis of \(~10^{14} \text{ molecules cm}^{-3}\) of H\(_2\)O\(_2\) with the UV lamps was employed as the OH radical source:

\[
\text{H}_2\text{O}_2 + \text{hv} (\lambda = 254 \text{ nm}) \rightarrow 2\text{OH}
\]

Mixtures of glycidaldehyde/ethene/H\(_2\)O\(_2\)/air were photolyzed for approximately 30 min, and the degradation of the compounds was monitored in situ using FTIR spectrometry with a resolution of 1 cm\(^{-1}\). Experiments were carried out to test for possible contributions to the measured glycidaldehyde decay rate under the experimental conditions employed through wall loss and photolysis, such losses for ethene are known to be negligible. The wall loss of glycidaldehyde was very low \((<10^{-5} \text{ s}^{-1})\). In the tests for contributions due to photolysis a large excess of propene was added to a mixture of glycidaldehyde and air the purpose of which was to scavenge any OH radicals which might be produced in the reactor, e.g. from reactions of impurities at the reactor wall, and thus ensure that the measured decay was actually due to photolysis. The levels...
of "rogue" OH radical production were found to be very low and no difference was found between experiments performed with and without addition of propene. Tests showed, however, the photolysis of glycidaldehyde to be nonnegligible and consequently this loss process had to be taken into account in the kinetic analysis. The following equation has been used to evaluate the kinetic data:

\[
\ln \left( \frac{[\text{glycidaldehyde}]}{[\text{glycidaldehyde}]_0} \right) - k_p t = k_1 \ln \left( \frac{[\text{ethene}]}{[\text{ethene}]_0} \right) - k_2 \ln \left( \frac{[\text{ethene}]}{[\text{ethene}]_0} \right)
\]

where \([\text{glycidaldehyde}]_0\) and \([\text{ethene}]_0\) represent the concentrations of glycidaldehyde and ethene at the initial time \(t_0\); \([\text{glycidaldehyde}]\) and \([\text{ethene}]\) represent the concentrations of glycidaldehyde and ethene at the reaction time \(t\); \(k_1\) and \(k_2\) are the rate coefficients for the reactions of OH with glycidaldehyde and ethene, respectively. \(k_p\) is the photolysis frequency of glycidaldehyde and also includes a small contribution due to wall loss. Plots of \(\ln (\frac{[\text{glycidaldehyde}]}{[\text{glycidaldehyde}]_0}) - k_p t\) against \(\ln (\frac{[\text{ethene}]}{[\text{ethene}]_0})\) resulted in straight lines with a slope of \(\frac{k_1}{k_2}\) and zero intercept.

The spectra for the product analyses were recorded under conditions similar to those given above but without the inclusion of ethene in the reactant mixture.

**UV Absorption Spectrum.** The UV absorption spectrum of glycidaldehyde was measured in a 480-L volume reactor equipped with multiple reflection mirror optics for simultaneous in situ measurement in the UV and IR. The UV spectrometer consists of a modified 22-cm monochromator (SPEX) and a diode array detector (EG & G PAR 1412). A spectral resolution of 0.6 nm was achieved with a grating of 1200 lines/mm covering a spectral range of 70 nm on the diode array detector. The UV and IR light sources were a deuterium lamp and a globar, respectively. The optical pathlengths in the UV and IR were preadjusted to 39.1 and 51.6 m, respectively. The wavelength scale was calibrated using atomic emission lines from a low-pressure mercury lamp.

The infrared absorption–concentration behavior of glycidaldehyde was calibrated in the reactor by means of precise vapor pressure measurements using a Baratron pressure gauge and the absorption peak at 842.5 cm\(^{-1}\). After gaseous glycidaldehyde had been added, the reactor was filled with \(N_2\) to 1000 mbar, and the absorbance of the peak at 842.5 cm\(^{-1}\) was measured. The infrared spectra were recorded with a Nicolet 520 FT-IR spectrometer using a resolution of 1 cm\(^{-1}\). A plot of absorbance against concentration (molecules per cubic centimeter) resulted in straight line in
According to Lambert–Beer’s law, \(\ln(I/I_0) = -cl\). A value of the absorption coefficient \((842.5 \text{ cm}^{-1})\) \((2.45 \pm 0.12) \times 10^{-4} \text{ ppm}^{-1} \text{ m}^{-1}, \text{ base e}\) was obtained.

Calibrated UV spectra of glycidaldehyde were obtained by simultaneously measuring the UV and IR spectra of the compound in the chamber at a total pressure of 1000 mbar with a spectral resolution of 0.6 nm. The concentration of glycidaldehyde was determined from the corresponding IR absorption and the cross sections of glycidaldehyde were subsequently obtained from a regression of optical depth against concentration.

Results and Discussion

**OH Kinetic Studies.** Figure 1 shows a plot of the kinetic data evaluated according to eq I using data from four experiments. Reasonable linearity is observed. Combined photolysis and wall losses contributed \(\pm 3\%\) to the decay of glycidaldehyde under the conditions employed. Using a value of \(k_2 = 8.52 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\) for the reference hydrocarbon results in a rate coefficient of \(k_1 = (1.69 \pm 0.04) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\) for the reaction of OH radicals with glycidaldehyde. The error is the 2\(\sigma\) standard deviation of the linear regression fit and only reflects the precision of the measurements. This work is the first determination of a rate coefficient for the reaction of OH with glycidaldehyde.

Taking, e.g. a global mean value of \((9.7 \pm 0.6) \times 10^5 \text{ cm}^{-3}\) for the OH radical concentration \((6, 7)\) would imply a global atmospheric lifetime \(\tau\) of \(~17\) h for glycidaldehyde through reaction with OH radicals.

In common with other unsaturated epoxides, the reaction of OH radicals with glycidaldehyde is expected to proceed via a H atom abstraction \((8, 9)\). Glycidaldehyde has 4 H atoms from which H atom abstraction by OH radicals can occur, one attached to the aldehyde group and the other three situated on the epoxide ring. The rate coefficients for the reactions of OH with ethene oxide, formaldehyde, acetaldehyde, and propional are \(1.13 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\), \(0.94 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\), \(1.58 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\), and \(1.96 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\), respectively. Comparing these rate coefficients, the rate coefficient for H atom abstraction from the epoxide ring is approximately 100 times smaller than H atom abstraction from an aldehyde.

### TABLE 2. Product Yields of the OH Initiated Oxidation of Glycidaldehyde at 298 ± 2 K in 1000 mbar of Synthetic Air in the Absence of NOx as Function of Time

<table>
<thead>
<tr>
<th>reaction time (min)</th>
<th>yield, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>FAN HCOOH HCHO CO(_2) CO HPMF ketene</td>
</tr>
<tr>
<td>3.12</td>
<td>43 ± 6 23 ± 3 22 ± 4 20 11 ± 2 6 1</td>
</tr>
<tr>
<td>10.9</td>
<td>29 ± 4 39 ± 3 15 ± 2 46 45 ± 4 7 1</td>
</tr>
<tr>
<td>20.35</td>
<td>55 ± 3 11 ± 2 56 68 ± 4 4 &lt; 1</td>
</tr>
<tr>
<td>33.20</td>
<td>6 ± 3 3 9 ± 2 69 86 ± 9 3 &lt; 1</td>
</tr>
</tbody>
</table>

*Yields of CO\(_2\) are subject to a high degree of uncertainty due to fluctuations in the background levels in the gas used to purge the external optical in the experimental setup.*

**FIGURE 3.** Gas-phase infrared absorption spectrum of glycidaldehyde in 1000 mbar of synthetic air at 298 ± 2 K.

**FIGURE 4.** The upper trace shows a residual product spectrum obtained from a glycidaldehyde/H\(_2\)O\(_2\)/air mixture after ~5 min of irradiation with 32 UV lamps and subtraction of absorptions from glycidaldehyde, H\(_2\)O, and water. The middle trace shows an infrared spectrum of formic acid anhydride, H(O)COC(O)H, in air and the lower trace an infrared spectrum of hydroperoxymethyl formate, HOOCH\(_2\)OC(O)H, in air.

**FIGURE 5.** Concentration-time profiles of the products observed in the reaction of OH radicals with glycidaldehyde at 298 ± 2 K in 1000 mbar of synthetic air.
group. The measured rate coefficient for the reaction of OH with glycidaldehyde of $k = (1.69 \pm 0.04) \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ lies between those measured for acetaldehyde and propanal which strongly supports that the reaction proceeds predominantly via H atom abstraction from the aldehyde group.

**UV Absorption Cross Section and Photolysis Frequency.**

The UV absorption spectrum was recorded in 4 sections: 215–280, 260–325, 310–375, and 355–420 nm. At the present experimental sensitivity, absorptions from glycidaldehyde above 350 nm were below the detection level. The various portions of the spectrum have been merged using a procedure which compensates for any differences, for example in concentration, in the regions of overlap. Below 250 nm and particularly below 230 nm the spectrum was noisy due to a combination of low lamp intensity and low sensitivity of the diode array. Therefore the result plotted in Figure 2 shows only the region 230–375 nm. Values of the UV absorption cross section have been calculated according to Lambert–Beer’s law, eq III:

$$\ln \frac{I}{I_0} = \varepsilon c l$$

In Figure 2, two absorption maxima are discernible. The strongest absorption with a maximum about 300 nm is very similar in form to the absorption features observed for simple aldehydes (12) and also for unsaturated carbonyl compounds, e.g., methacrolein or methyl vinyl ketone (9). The maximum is close to those reported for the simple carboxyls such as formaldehyde, acetaldehyde, and acetone. A weaker absorption which peaks at 230 nm is thought to be from the epoxide ring.

From the absorption data an upper limit of the photolysis frequency, $J$, for glycidaldehyde in the troposphere can be estimated by using the following:

$$J(s^{-1}) = \sum_{\lambda=250nm}^{\lambda=420nm} \sigma(\lambda)\phi(\lambda)J(\lambda)$$

where $\sigma(\lambda)$ is absorption cross section of glycidaldehyde averaged over a wavelength interval $\lambda_i$ centered at $\lambda$ (base e, in cm$^2$ molecule$^{-1}$); $\phi(\lambda)$ is the primary quantum yield for the loss of glycidaldehyde averaged over the wavelength interval $\lambda_i$ centered at $\lambda$; $J(\lambda)$ represents actinic flux (in photons cm$^{-2}$ s$^{-1}$) summed over the wavelength interval $\lambda_i$ centered at $\lambda_i$, at a solar zenith angle $\theta$ for July 1, noon at a latitude of 50° N (13). Table 1 summarizes the data of this calculation. Assuming a primary quantum yield $\phi(\lambda) = 1$ gives an upper limit of $J \leq 0.96 \times 10^{-4}$ s$^{-1}$ for the photolysis frequency of glycidaldehyde in the troposphere under the given conditions (July 1, noon and 50° N). A similar calculation for 40° N results in a value of $J \leq 1.03 \times 10^{-4}$ s$^{-1}$.

For comparison the importance of photolysis of glycidaldehyde in the atmosphere has been assessed by another procedure. The photolysis frequency of glycidaldehyde has been determined in 1000 mbar of synthetic air in the 1080-L reactor by monitoring the concentration decrease of glycidaldehyde on irradiation with 32 fluorescent lamps as described in the Experimental Section. The evaluation of the recorded spectra resulted in a first-order decay and a photolytic rate constant of $1.9 \times 10^{-5}$ s$^{-1}$. To adjust the measured NO$_2$ photolysis rate constant measured in the reactor to atmosphere conditions eq V was used:

$$J(\text{atmosphere}) = \frac{k_{\text{NO}_2(\text{atmosphere})}}{k_{\text{NO}_2(\text{reactor})}} \frac{1}{k_{\text{NO}_2(\text{reactor})}}$$

where $k_{\text{NO}_2}$ is the photolysis rate constant for NO$_2$ in the atmosphere at noon and in the reactor as indicated and $J$ represents the photolysis frequency for glycidaldehyde in the atmosphere at noon and in the reactor as indicated. Using a value of $k_{\text{NO}_2(\text{reactor})} = 2.7 \times 10^{-3}$ s$^{-1}$ determined under the experimental conditions in this laboratory and a literature value of $k_{\text{NO}_2(\text{atmosphere})} = (8.5 \pm 0.5) \times 10^{-3}$ s$^{-1}$ (14) results in an approximative value of $6.0 \times 10^{-4}$ s$^{-1}$ for the photolysis frequency of glycidaldehyde at July 1, noon and 40° N. The ratio of the values of $J$ determined from the comparison with NO$_2$ photolysis rates and the UV absorption spectrum of $\sim 0.58$ suggests that the photolysis quantum efficiency is probably only of the order of 60%.

These first estimations of the photolysis frequency suggest that photolysis will probably be somewhat more important than removal with OH radicals.

**Product Studies.** Figure 3 shows the gas-phase infrared spectrum of glycidaldehyde in the range of 4000 to 800 cm$^{-1}$. In the liquid-phase spectrum of glycidaldehyde reported in the literature (3) an absorption at $5.75 \mu$ ($1739$ cm$^{-1}$) has been assigned to a carbonyl absorption and bands at $8.15 \mu$ ($1227$ cm$^{-1}$) and $11.76 \mu$ ($850$ cm$^{-1}$) to epoxide vibrations. In the gas-phase spectrum shown in Figure 3 the corresponding carbonyl band is centered at $1754$ cm$^{-1}$ and the epoxide absorption bands are located at $1162$ and $835$ cm$^{-1}$.

Figure 4, upper trace, shows the residual product spectrum which is obtained after $\approx 5$ min irradiation of a glycidaldehyde/H$_2$O$_2$/air mixture with $32$ UV lamps and subtraction of absorptions due to glycidaldehyde, H$_2$O$_2$, and water. The middle and lower traces show the infrared spectra of formic acid anhydride (HOCOCO(OH), hereafter abbreviated to FAN) and hydroperoxymethyl formate (HOOCOOC(OH), hereafter abbreviated to HPMF), respectively. An inspection of Figure 4, upper trace, shows the products consist of carbon.
monoxide, carbon dioxide, formic acid, formaldehyde, FAN, and HPMF. Careful inspection of the residual spectrum after subtraction of carbon monoxide showed the formation of ketene in low yields.

The product formation yields and estimated errors (where appropriate) are tabulated in Table 2 for selected reaction times. The quoted errors are estimated total errors and include uncertainties for the subtraction procedure and the calibration spectra. Under the conditions of this work the error was of the order of 15% for middle concentrations and usually somewhat higher for low concentrations. Normally in studies of this type it is a common practice to plot the yields of the products versus the consumption of the reactant to obtain information on the overall mass balance. However, such an analysis in this particular case is of very limited use because of the instability of the major primary product and uncertainties in the yields of the ensuing products as outlined below.

The absolute yield of CO₂ is subjected to a high degree of uncertainty due to fluctuations in its concentration in the air used to purge the external optics in the experimental setup. The CO₂ concentration values given in Table 2 and shown in Figure 5 are only intended to indicate the concentration trend. Figure 5 shows the concentration–time profiles for all the positively identified products in the reaction of OH with glycidaldehyde during the entire observation period. Error bars have been omitted in Figure 5 to preserve clarity. From Figure 5 and Table 2 it is evident that FAN is the major product at short reaction times and that it undergoes further oxidation as the reaction progresses producing CO, CO₂, and HCOOH.

Due to the slowness of the glycidaldehyde photolysis rate under the present experimental conditions the photolysis products could not be unambiguously determined. However, the photolysis products are anticipated to be identical to those produced in the OH-initiated oxidation since the major pathway is expected to be loss of the aldehyde functional group, –CHO, which is equivalent to the OH radical reaction pathway as discussed below.

**Mechanism of the Reaction of OH Radicals with Glycidaldehyde.** On the basis of the kinetic and product information given above a reaction mechanism for the OH
aldehyde group, radical mainly reacts via H atom abstraction from the aldehyde group, –CHO, to give a carbonyl radical (I) which combines with an oxygen molecule to yield a peroxy radical (II). Under the NOx-free conditions of the present study the peroxy radical undergoes self-reaction or cross reactions with other peroxy radicals to form the corresponding oxy radical, in this case an oxiranyl carboxy radical (III). Reaction of the peroxy radical (II) with HO2 to form an instable peroxy acid is also a further possibility.

The oxiranyl carboxy radical (III) is expected to lose carbon dioxide and form an oxiranyl radical (IV). Niki et al. (15) have investigated the Cl-initiated reaction of ethene oxide in O2/N2 diluent systems in which the initial step is also formation of an oxiranyl radical. With the exception of chlorine-containing compounds the products observed by Niki et al. are very similar to the products observed in this study. As in the work of Niki et al. the major fate of the oxiranyl radical (IV) is addition of O2 to form a peroxy radical (V) followed by further self-reactions or cross reactions to form an oxiranoxy radical (VI). Carbon—carbon bond fission of the oxiranyl radical (IV) can lead to the formation of ketene as indicated in Figure 6; however, this appears to be only a minor pathway.

The further reactions of the oxiranyl radical (VI), as outlined in Figure 7, determine the final product distribution. Two important intermediate products observed in the system, FAN and HPMF, are formed from the alkyl-type radical, CH2OC(OH), which results from C—C bond scission of the oxiranoxy radical (VI). The CH2OC(OH) radical adds O2 to form a peroxy radical, OOC(O)CH2OC(OH), for which there are three possible reaction routes: (i) reaction with HO2 to form hydroperoxymethyl formate (HPMF), (ii) self-reaction or possibly cross reaction to form formic acid anhydride (FAN) and hydroxymethyl formate, and (iii) self-reaction or cross reaction to form an oxy radical, OCH2OC(O)H. Further reactions of the oxy radical will yield FAN, HCHO, and CO2 as indicated in Figure 7.

The oxiranoxy radical (VI) may also undergo C—O scission and form glyoxal as the main product. However, this is obviously not an important pathway since under the experimental conditions in this work glyoxal was always below the detection limit.

Neither FAN nor HPMF is thermally stable. In the gas phase, HPMF is known to decompose to FAN and water (16), and FAN further decomposes to formic acid and carbon monoxide (17). Examination of Figure 5 and Table 2 shows a clear increase in the concentrations of formic acid and CO as the concentration of FAN decreases. Experiments in this laboratory on samples of pure synthesized FAN (17) have shown that its decay can be qualitatively described by:

\[ \text{HC(O)OC(O)H} \rightarrow \text{HCOOH} + \text{CO} \]

however, the stoichiometry of HCOOH and CO to another as well as to the decay of FAN is not given. The missing products as well as the magnitude of the observed decay are in line with a mainly heterogeneous decomposition of FAN at the reactor surface.

Niki et al. (15) assigned the absorption bands in their study of Cl-initiated reaction of ethylene oxide to hydroxymethyl formate, CH2(OH)OC(O)H, based on a comparison with a spectrum obtained from an ozone-ethene system. This identification has recently been shown to be incorrect and that the absorptions are actually due to hydroperoxymethyl formate (HPMF) (16–19). Thamm et al. (16) have synthesized HPMF by the ozonolysis of ethyl vinyl ether in solution and characterized it by NMR and mass spectrometry. The recorded IR spectrum of the pure compound in the gas phase has confirmed that the intermediate observed in the gas-phase ozonolysis of ethene is HPMF and not hydroxymethyl formate as previously thought. It is interesting to note that although the ozonolysis studies (16–19) have shown that FAN and HPMF are two important products of the gas-phase ozonolysis of ethene they are formed via a completely different mechanisms to the OH-initiated oxidation of glycidaldehyde, i.e., from reactions of the stabilized Criegee biradical, CH2O2.

In Figure 7 the formation of hydroxymethyl formate, CH2(OH)OC(O)H, has been proposed as one of the possible products of the self-reaction of the peroxy radicals, OOC(O)CH2OC(O)H. Figure 8 shows the residual product spectrum of the glycidaldehyde/H2O2/air system after ~15 min of irradiation with 32 UV lamps and subtraction of all the identified product spectra including HPMF. The residual
The spectrum still shows absorption bands which are very similar to those of HPMF. The main difference lies in the region of the OH stretching mode. The insert in Figure 8 displays this region. Two relatively strong absorption bands at 3320 and 3583 cm\(^{-1}\) are tentatively attributed to the cis and trans isomers of hydroxymethyl formate, i.e.:

\[ \text{cis-Form} \quad \text{trans-Form} \]

The lower frequency at 3320 cm\(^{-1}\) is attributed to the cis isomer whose O–H bonding is weakened by the intramolecular hydrogen bond, whereas the O–H vibration in the trans form is expected to behave normally.

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**Literature Cited**


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