Microwave Spectrum and Structure of Ethylene Ozonide: Effects of Large Axes Rotations in Structure Calculations

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Rotational spectra for 14 isotopic species of ethylene ozonide have now been assigned. The consistency of the Kraitchman substitution structure was checked by calculating the O_p–O_p bond distance six ways; the values ranged from 1.458 to 1.502 Å. This variation was attributed to an amplification of residual vibrational effects by large axes rotations upon isotopic substitution. Estimates of errors produced from this effect were made and a procedure was developed for choosing r_s parameters in which the effect is minimized. This gave the following ring parameters: $d(CO_e) = 1.416$ Å, $d(CO_p) = 1.412$ Å, $d(OO) = 1.461$ Å, $<CO_eC = 104.8°$, $<O_eCO_p = 105.5°$, $<CO_pO_p = 99.3°$.

INTRODUCTION

Although organic ozonides are well-known products of the ozonolysis of alkenes, there have been few investigations of their structural parameters. Previous studies include investigations by electron diffraction of ethylene ozonide (*1, 2*); analyses of microwave spectra for ethylene (*3*), propylene, and *trans*-2-butene ozonides (*4*); and an X-ray diffraction study of 3-carbomethoxy-5-anisyl-1,2,4-trioxacyclopentane (*5*). The prior spectroscopic report established that ethylene ozonide has the O–O half-chair conformation (C_2 symmetry). Structural parameters (r_0) were derived from rotational constants of seven isotopic species. These included the normal isotopic species, the singly substituted ^{13}C species, and two D_1 and three D_2 species. In subsequent studies dealing with the mechanism of ozonolysis (*6, 7*), the rotational constants of the singly substituted oxygen-18 species were reported but structural parameters were not derived. Besides these isotopic species, there have been additional studies of five other isotopically enriched species in our laboratory including the doubly and triply enriched oxygen-18 species, the 1,1-D_2 species, and the D_4 species. Improved data were also obtained for the three D_2 species reported previously (*3*).

This large number of isotopic data allowed a recalculation of the r_0 structure and the determination of the complete r_s structure. An empirical evaluation of the Kraitchman procedure was made by calculating the O_p–O_p bond distance six different ways. This gave an unexpectedly large variance in that r_s parameter. However, good agreement could be obtained by correcting the r_s coordinates for the effect of large rotations of the principal axes upon isotopic substitution. From this analysis a procedure was identified for estimating the best r_s structure. These more reliable parameters (as well as the

Table 1.　Ground State Transition Frequencies (MHz)

$\nu_{obs} - \nu_{calc}$ in parenthesis.

Transition	$HD_aCOOCHD_eO$ (cis)	$HD_eCOOCHD_eO$ (trans)	$HD_aCOOCHD_aO$ (trans)	D_2COOCH_2O	D_2COOCD_2O
$1_{11}-2_{02}$	20120.07(0.01)	19775.70(0.05)	20450.44(-0.01)	20097.32(-0.08)	18571.38(0.02)
$1_{11}-2_{20}$	33407.60(0.02)	33616.79(0.01)	33249.17(0.01)	33426.39(-0.03)	31185.86(0.02)
$1_{10}-2_{21}$	28255.46(0.00)	28512.94(-0.02)	27997.50(-0.04)	28361.86(0.06)	27187.98(-0.01)
$1_{01}-2_{12}$	20992.77(0.10)	20865.26(0.02)	21102.06(0.08)	21043.05(-0.09)	20051.61(0.06)
$2_{12}-3_{03}$	29213.17(-0.02)	28804.67(-0.05)	29589.91(0.06)	29233.74(-0.03)	27474.42(0.05)
$2_{11}-3_{22}$	36936.04(-0.06)	37033.66(0.01)	---	37053.62(-0.04)	35429.61(-0.04)
$2_{02}-3_{13}$	---	29009.10(0.02)	29674.21(0.05)	29396.27(0.01)	27860.05(0.04)
$2_{21}-3_{12}$	34087.16(-0.01)	33445.49(-0.01)	34723.71(0.00)	33954.46(0.06)	30478.62(-0.02)
$3_{13}-4_{04}$	---	---	38453.65(-0.09)	---	35871.45(-0.07)
$3_{03}-4_{14}$	---	---	38460.84(-0.01)	38013.05(0.09)	35940.81(-0.02)

recalculated r_0 values) have some significant differences from the values previously reported (*3*).

EXPERIMENTAL DETAILS

Samples. Ethylene ozonide was made by the reaction of ethylene with ozone at low temperature in a solvent such as methyl chloride or CF_2Cl_2. The procedure was discussed previously (*3, 7*). Enriched reactants were employed to obtain the new isotopic

Table 2.　Ground State Transition Frequencies (MHz)

$\nu_{obs} - \nu_{calc}$ in parenthesis.

Transition	$H_2CO^{18}OCH_2^{18}O$	$H_2C^{18}O^{18}OCH_2O$	$H_2C^{18}O^{18}OCH_2^{18}O$
$1_{01}-2_{02}$	21083.22(0.05)	20975.53(0.01)	20601.08(0.09)
$1_{10}-2_{11}$	27132.15(0.04)	27765.08(-0.01)	26590.43(0.04)
$1_{10}-2_{21}$	28445.77(-0.02)	----	----
$1_{11}-2_{20}$	34494.74(0.01)	----	----
$1_{11}-2_{12}$	---	20943.95(0.03)	20248.53(0.07)
$2_{21}-3_{22}$	35864.24(-0.04)	----	----
$2_{12}-3_{13}$	29613.70(0.02)	29726.46(0.10)	28960.09(-0.06)
$2_{02}-3_{03}$	29652.31(-0.01)	29726.46(-0.12)	----
$2_{21}-3_{12}$	35658.41(-0.01)	----	----
$2_{21}-3_{22}$	----	----	35129.08(-0.05)
$2_{11}-3_{12}$	----	----	36122.40(-0.02)

Table 3. Ground State Rotational Constants (MHz) and Moments of Inertia ($u\text{Å}^2$).

Species[a]	A	B	C	I_a	I_b	I_c
$H_2\overline{COOCH_2O}$	8243.84(4)[b]	8093.80(4)	4584.74(2)	61.3035[c]	62.4399	110.2300
$H_2^{13}\overline{COOCH_2O}$	8233.28(4)	7928.25(4)	4530.18(2)	61.3821	63.7437	111.5576
$HD_e\overline{COOCH_2O}$	8203.59(2)	7576.80(1)	4418.74(1)	61.6043	66.7005	114.3711
$HD_a\overline{COOCH_2O}$	8050.30(4)	7668.24(2)	4500.84(2)	62.7773	65.9051	112.2848
cis $HD\overline{COOCHDO}$	7971.71(2)	7225.89(2)	4340.32(2)	63.3962	69.9396	116.4375
trans $HD_e\overline{COOCHD_eO}$	8084.21(1)	7175.83(1)	4260.35(1)	62.5140	70.4275	118.6231
trans $HD_a\overline{COOCHD_aO}$	7861.33(3)	7287.46(1)	4413.55(1)	64.2863	69.3487	114.5056
$D_2\overline{COOCH_2O}$	8005.35(3)	7205.29(3)	4345.87(1)	63.1298	70.1396	116.2888
$D_2\overline{COOCD_2O}$	7689.05(2)	6534.36(2)	4120.83(1)	65.7267	77.3413	122.6394
$H_2\overline{COOCH_2{}^{18}O}$	8094.14(16)	7877.01(3)	4469.11(2)	62.4373	64.1584	113.0820
$H_2C^{18}\overline{OOCH_2O}$	8143.49(2)	7831.46(2)	4480.96(1)	62.0589	64.5315	112.7830
$H_2C^{18}\overline{OOCH_2{}^{18}O}$	8026.57(2)	7588.67(2)	4366.09(1)	62.9629	66.5961	115.7502
$H_2C^{18}O^{18}\overline{OCH_2O}$	7825.73(16)	7793.92(8)	4383.33(5)	64.5788	64.8423	115.2947
$H_2C^{18}O^{18}\overline{OCH_2{}^{18}O}$	7825.94(9)	7440.34(5)	4269.37(3)	64.5770	67.9238	118.3725

[a] The constants for the first four species and the two single substituted ^{18}O species are taken from References 3 and 7.

[b] The uncertainty is twice the standard deviation obtained from the frequency fit.

[c] $B \cdot I = 505\ 376\ u\text{Å}^2$.

species reported here. The doubly and triply enriched ^{18}O species were obtained using O_3 prepared from ^{18}O-labeled O_2 gas (54% ^{18}O) (7). The

$$\overline{HDCOOCHDO} \quad \text{and} \quad \overline{D_2COOCD_2O}$$
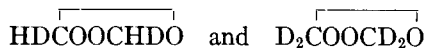
species were synthesized starting with DHCCHD (98% D, *cis–trans* mixture) and D_2CCD_2 (98%), respectively. The

$$\overline{D_2COOCH_2O}$$
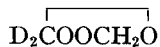
species was obtained using the ozonide product from the ozonolysis of the ethylene mixed with 99% deuterated formaldehyde (7).

Spectrometer. A conventional 80 kHz Stark spectrometer cooled with dry ice was employed (8). All transitions reported here were obtained using klystrons. Frequencies are accurate to ±0.1 MHz. The ^{13}C assignment (3) was rechecked by recorder tracing using locked klystrons but this produced no significant differences from the previous report.

Assignment. The analysis employed standard techniques and computations. The transitions observed for the additional isotopic species are listed in Tables 1 and 2.[1] The assignments were confirmed by Stark splittings, expected intensities, the frequency fit, and the expected position of transitions predicted from the structure. Rotational

[1] In the tables and the text, H_e and H_a indicate the equatorial and axial hydrogen atoms. They correlate with H_A and H_B, respectively, in Ref. (3). Also, O_e and O_p represent the ether and peroxide oxygen atoms.

Table 4. Atom Coordinates (Å) Calculated by Different Methods.

		r_0 14 Isotopes	r_s Single subst.	r_s Double subst.	r_s Preferred[a]
O_e	b	1.2097	1.2076		1.2076
O_p	+a	0.6741	0.6792	0.6740	0.6740
	-b	0.9232	0.9176	0.9214	0.9214
	+c	0.2827	0.2816	0.2816	0.2816
C	+a	1.1129	1.1091		1.1091
	b	0.3448	0.3312		0.3443
	+c	0.1695	0.1687		0.1687
H_{ax}	+a	1.3871	1.3863	1.3859	1.3859
	b	0.3018	0.2934	0.2986	0.2986
	+c	1.3396	1.2301	1.2297	1.2297
H_{eq}	+a	1.9343	1.9331	1.9334	1.9334
	b	0.6441	0.6439	0.6420	0.6420
	±c	0.4794	0.4791	0.4806	0.4806

[a] Hydrogen and peroxy coordinates calculated from double substitution species. Ether oxygen b and carbon a and c from single substitution. Carbon b from first moment equation.

constants were obtained by least-squares fitting of the observed transitions. The rotational constants and moments of inertia are listed in Table 3. As noted previously (3), the spectrum is characteristic of a species with a high barrier to pseudorotation. The only unusual aspect of the spectral assignment was the occurrence of large rotations in the principal axes upon isotopic substitution at the oxygen positions. While the normal isotopic species obeyed b dipole selection rules, the three ^{18}O enriched species that also have a C_2 axis followed a dipole selection rules. For the

$$\overline{CH_2{}^{18}OOCH_2O} \quad \text{and} \quad \overline{CH_2{}^{18}OOCH_2{}^{18}O}$$
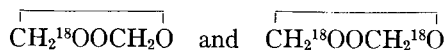
species, the angle between the new b inertial axis and the C_2 symmetry axis (b axis) in the normal isotopic species was 41° and 68°, respectively, and both a and b dipole transitions had appreciable intensities. These unusually large rotations occurred because the normal isotopic species is a near-oblate symmetric top. This makes the orientation of the principal axes very sensitive to mass changes at certain positions.

RESULTS

Table 4 lists the r_0 coordinates of the atoms obtained by fitting the moments of inertia of the 14 isotopic species (9) and the Kraitchman r_s coordinates obtained by single substitution at each position (10). Table 5 lists the ring structural parameters derived from these coordinates and also the original r_0 structure obtained from fitting the moments of only 7 isotopic species (3). It is observed that the bond parameters vary over about 0.02 Å, a range considered not unusual. Ordinarily the substitution structure would be the preferred data set, provided there are no significant problems arising in the analysis from small coordinates or some other vibrational effect (11). Costain has shown for a number of simple molecules that vibrational effects cancel significantly by this procedure (12). He obtained parameters close to equilibrium values and found high consistency when parameters were derived from different isotopic species.

Table 5. Ring Structural Parameters Calculated by Different Methods

	r_o Orig paper 7 Species	r_o All 14 Species	r_s Single Subst.	r_s Preferred
$C-O_e$	1.436Å	1.420Å	1.424Å	1.416Å
$C-O_p$	1.395	1.416	1.395	1.412
O_p-O_p	1.470	1.462	1.471	1.461
$\sphericalangle CO_eC$	102.8°	104.9°	104.0°	104.8°
$\sphericalangle O_eCO_p$	106.2	105.3	105.8	105.5
$\sphericalangle CO_pO_p$	99.2	99.3	99.3	99.3

Because of the large number of isotopic data on ethylene ozonide, the consistency of structural data obtained from different isotopic species could be examined to test the reliability of the Kraitchman calculations. Table 6 lists the O_p-O_p distance when it is calculated six different ways using alternative sets of isotopic species. The values for calculations I–IV were obtained from Kraitchman's equations for single substitution (13). Calculation V and VI were obtained using the Kraitchman formulas applicable for symmetrical double substitution in a molecule with C_2 symmetry (cf. Appendix). It is obvious that difficulties exist with these calculations; the O_p-O_p distance varies over 0.05 Å, at least one order of magnitude larger than expected by this procedure!

The source of these large deviations is related to the large rotations of the principal axes that occur upon changing the mass of an oxygen atom (vide supra). These large rotations in effect amplify the small vibrational contributions that do not cancel in the substitution procedure. To identify this effect we were aided by previous discussion on error analysis in Kraitchman structures (13–17). In particular, the last reference has reported similar effects in furan, a planar near-oblate top.

Table 6. Peroxide Bond Distance Calculated by Kraitchman's Equations for Different Isotopic Species.

	Parent $O_eO_pO_p$	Subst. $O_eO_pO_p$	Distance O_p-O_p
I	16 16 16	16 16 18	1.471Å
II	18 16 16	18 16 18	1.455
III	18 18 18	18 16 18	1.464
IV	16 18 18	16 16 18	1.502
V	16 16 16	16 18 18	1.461
VI	18 18 18	18 16 16	1.461

The following equation can be used to estimate the error in a_s, the coordinate obtained from the single-substitution equations. Similar equations can be obtained for b_s and c_s after cyclic permutation of a, b, and c.

$$|a_s{}^*| - |a_s| = |2a_s\mu|^{-1}\left\{\left[1 + \frac{P_{bb}{}' - P_{bb}}{P_{bb} - P_{aa}}\right]\left[1 + \frac{P_{cc}{}' - P_{cc}}{P_{cc} - P_{aa}}\right]\delta a\right.$$

$$+ (P_{aa}{}' - P_{aa})\left[1 + \frac{P_{cc}{}' - P_{cc}}{P_{cc} - P_{aa}}\right]\left(\frac{\delta b}{P_{bb} - P_{aa}}\right)$$

$$\left. + (P_{aa}{}' - P_{aa})\left[1 + \frac{P_{bb}{}' - P_{bb}}{P_{bb} - P_{aa}}\right]\left(\frac{\delta c}{P_{cc} - P_{aa}}\right)\right\}. \quad (1)$$

In this equation $a_s{}^*$ is the corrected substitution coordinate, and P_{aa} and $P_{aa}{}'$ represent the ground-state planar second moments of the parent and substituted species, respectively. The reduced mass $\mu = M(M' - M)/M'$, where M and M' are the molecular weights of the two species. δa, δb, and δc, represent the error estimates in $P_{aa}{}' - P_{aa}$, $P_{bb}{}' - P_{bb}$, and $P_{cc}{}' - P_{cc}$ that arise from vibrational effects that do not entirely cancel. An empirical definition of δa, δb, and δc would rely on the operational definition of the r_s coordinate and the criterion that a "good" r_s parameter is isotopically invariant (16).[2]

Two possible theoretical interpretations of δa, δb, δc come to mind. In one case they could be equated to the differences in the vibration–rotation interaction constants (15) [or pseudoinertial defects (13)] upon isotopic substitution. Application of Eq. (1) would then result in estimates of equilibrium coordinates. The equation might also be used to estimate the average structure. Kuchitsu et al. (14) have shown that Kraitchman's equations employing ground-state moments can be used for this purpose provided that shrinkage effects are properly taken into account. These are the small differences in the average bond distances due to vibrational anharmonicity when a heavier atom is incorporated into a molecule (11, 14). In this application of Eq. (1), δa, etc., would be a correction to the differences in ground-state moments arising from this shrinkage effect. (They should also contain the differences in the harmonic part of the vibration–rotation constants, although this is believed to be small.)

For molecular systems that are fairly asymmetric, the contribution from δa, etc., may not lead to large inconsistencies between isotopic species. The δ's are expected to be small, (about $|0.005|$ uÅ^2 or less), and the terms in the denominators of Eq. (1), $P_{bb} - P_{aa}$ and $P_{cc} - P_{aa}$, reduce their effect. However, for a near-oblate top such as ethylene ozonide, where $P_{bb} - P_{aa}$ ranges from -0.26 to -3.3 uÅ^2, the effect of the δ's can be amplified. To illustrate this, it is convenient to write Eq. (1) as

$$|a_s{}^*| - |a_s| = K_1^a\delta a + K_2^a\delta b + K_3^a\delta c. \quad (2)$$

The factors K_i^a depend only on the experimental moments of inertia, masses, and the substitution coordinate. Their values are listed in Table 7 for the peroxy atom coordinates in four isotopic species of ethylene ozonide along with a_s, $a_s{}^*$, etc. The corrections

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[2] Although this variance is small in several cases (12), it has been shown recently that the r_s structure is not necessarily isotopically invariant (15).

Table 7. The r_s and Estimated r_s^* Peroxide Oxygen Coordinates and Bond Distance (Å) for Different Isotopic Species

	$O_e\ O_p\ O_p$	$O_e\ O_p\ O_p$	$O_e\ O_p\ O_p$	$O_e\ O_p\ O_p$
Parent [a]	16 16 16	18 16 16	18 18 18	16 18 18
Substituted	16 16 18	18 16 18	18 16 18	16 16 18
a_s	0.6792	0.9549	0.9044	0.8575
b_s	0.9175	0.6705	0.6799	0.7002
c_s	0.2816	0.2821	0.2718	0.2715
$|a_s^*|-|a_s|$ [b]	-0.0027	-0.0010	0.0028	0.0180
$|b_s^*|-|b_s|$	0.0055	0.0058	0.0005	-0.0179
$|c_s^*|-|c_s|$	-0.0019	-0.0019	-0.0017	-0.0017
r_s:$d(O_p O_p)$	1.471	1.455	1.464	1.502
r_s^*:$d(O_p O_p)$	1.464	1.464	1.464	1.467
$K_1{}^a$, $K_2{}^a$, $K_3{}^a$	0.09,-0.32 -0.01	0.10,-0.18 0.00	-0.19,-0.05 0.00	-1.42,-0.08 0.00
$K_1{}^b$, $K_2{}^b$, $K_3{}^b$	0.38,-0.01 0.08	0.44,0.00 0.04	-0.12,0.00 0.08	-0.07,0.00 1.56
$K_1{}^c$, $K_2{}^c$, $K_3{}^c$	0.48,0.00 0.00	0.48,0.00 0.00	-0.42,0.00 0.00	-0.42,0.00 0.00
$I_{bb}-I_{aa}$ [c]	1.1364	1.7211	3.3468	0.2636

[a] C_2 axis in parent species along $\underline{b}$ axis for 16, 16, 16 species and along $\underline{a}$ axis for the others. [b] Estimated using equation 2, the values of K_i^x listed in this table and the values of δx discussed in text. [c] In uÅ^2 for parent species.

$|a_s^*|-|a_s|$, etc., were estimated with assumed values of $\delta a = \delta b = 0.006$ uÅ^2 and $\delta c = -0.002$ uÅ^2 for a ^{16}O to ^{18}O isotopic substitution and values with opposite signs for the reverse mass change.

It is seen that the assumed set of δ's produces satisfactory agreement among the four O_p–O_p distances (r_s^*). The values assumed for the δ's are not very precise. They were first chosen by inspection, noting that they were roughly twice the changes observed in the planar second moments when the ether oxygen on the symmetry axis is substituted (cf. Table 8). Another set can be obtained by solution of four simultaneous equations,

Table 8. Planar Second Moments (uÅ^2) for Isotopic Substitution on Symmetry Axis

$O_e\ O_p\ O_p$	P_{aa}	P_{bb}	P_{cc}
16 16 16 [a]	55.6832	54.5468	6.7567
18 16 16	57.4016	55.6805	6.7568
16 18 18	57.7791	57.5156	7.0632
18 18 18	60.8596	57.5129	7.0642

[a] C_2 axis along $\underline{b}$ inertial axis for this species and along $\underline{a}$ axis for the other three.

Table 9.   Preferred r_s Structural Parameters for
Ethylene Ozonide.

Bond Lengths (Å)[a]		Bond Angles deg.		Dihedral Angles deg.	
CH_{eq}	1.091	COC	104.8	$C_1O_eC_2O_p$	-16.25
CH_{ax}	1.097	COO	99.3	$C_1O_pO_pC_2$	-49.48
CO_e	1.416	OCO	105.5°	$O_eCO_pO_p$	40.78
CO_p	1.412	HCH	113.3°	$C_1O_eC_2H_{eq}$	-131.32
OO	1.461	O_eCH_{eq}	110.8°	$C_1O_eC_2H_{ax}$	102.75
		O_eCH_{ax}	109.8°		
		O_pCH_{eq}	106.7°		
		O_pCH_{ax}	110.4°		

[a] Uncertainties based on experimental error is $\pm$ 0.002Å in
bond lengths and $\pm$ 0.5° for angles. Dihedral angles are
defined in Ref. 3.

again assuming the same δ's for each isotopic species. This gave values of $r_s{}^* = 1.462$ Å, $\delta a = 0.0065$, $\delta b = 0.006$, $\delta c = -0.005$ uÅ².

Considering the magnitudes of the δ's and the good agreement for $d(O_p\text{-}O_p)$ that they produce, the major difficulty in using Kraitchman's equations appears to have been identified, i.e., amplification of vibrational effects due to large axes rotations. It is not clear, however, whether this empirical procedure has given a bond distance closer to the equilibrium or the average value.

This error analysis was also made for the calculations of the ether oxygen, carbon, and hydrogen single-substitution coordinates in order to determine the effect of axes rotations on their values. This indicated that the error in the oxygen b, the carbon a, and hydrogen a and c were between 0.001 and 0.004 Å. The carbon c coordinate was overestimated as much as 0.006 Å, while the carbon and hydrogen b coordinates were underestimated between 0.009 and 0.017 Å. These estimates were made using the same values for the δ's employed in the peroxy oxygen calculations except for the estimates of the ether oxygen where values one-half as large were employed (cf. Table 8).

To minimize these vibrational effects and to obtain the most reliable r_s structures with the fewest assumptions, the following choice for r_s coordinates was made. The ether oxygen b coordinate was taken from the single-substitution calculation. The coordinates for O_p, H_e, and H_a were obtained using Kraitchman's equations for symmetrical disubstitution. It is shown in the Appendix that the error in their b coordinates is reduced to a level typical of a good substitution calculation because the symmetry axis is preserved in those species. While the error analysis is not as definitive for the a and c coordinates by this procedure, it appears that they also should be quite reliable. The good agreement for the two calculations of $d(O_pO_p)$ using double-substitution data supports this (cf. Table 6). The carbon a and c coordinates were calculated using the single-substitution data and the b coordinate was obtained from the first moment equation. The carbon b

coordinate increased by about 0.013 Å using this procedure consistent with the previous estimate that it was underestimated by 0.016 Å using the single-substitution equations. These coordinates and the derived structural parameters are listed in Tables 4, 5, and 9 as r_s preferred. A standard estimate of propagation of errors based on experimental uncertainties alone indicates that these parameters are reliable to ±0.002 Å and ±0.5°. An estimate of model errors based on the residual vibrational effects in the r_s structure was made and indicates that those errors are the order of 0.002–0.004 Å for bond lengths and a few tenths of a degree for angles. These estimates were made using Eq. (1) or (6) and plausible estimates for δa, δb, and δc to give the equilibrium structure. Hence, an estimate of the total error would indicate that the parameters in Table 9 are within 0.006 Å (bond lengths) and 0.70° (bond angles) of the equilibrium values.

DISCUSSION

Structure. The structural parameters obtained here have two noteworthy differences from the earlier report (3). First, the large difference of 0.04 Å between the CO_e and CO_p bond distances was not confirmed in this new analysis; both bond distances are now well within the range 1.41–1.44 Å usually observed for C–O single bonds. It appears that $d(CO_e) > d(CO_p)$, but the difference is not unambiguously established; it seems unlikely to be greater than about 0.01 Å. A difference in the same direction was also indicated in propylene ozonide (4), although the estimated uncertainties are large: $d(CO_e) = 1.423 \pm 0.020$, $d(O_p-CHCH_3) = 1.399 \pm 0.019$, and $d(O_p-CH_2) = 1.411 \pm 0.005$ Å. A small difference in the observed direction might be reconciled with the greater electronegativity of the O–O linkage.

A second result is a shortening of the O_p-O_p distance by about 0.01 Å. Since 1.47–1.48 Å is the typical value for a peroxy linkage, the value in ethylene ozonide (1.461 Å $= r_s$) may at first appear slightly low. In addition, it is the only ring parameter that falls markedly outside the error estimates reported in the ED study. That study obtained $r_g = 1.487$ (−0.006, +0.004). However, this discrepancy is not disturbing. Some (perhaps most) of the difference probably arises because r_s and r_g are defined differently. Also, the discussion of uncertainties in determining r_g indicates that the reported standard deviations could be too small (2).

Hydrogen peroxide and propylene ozonide are the only other peroxy compounds, excluding

$$F_2O_2 \quad \text{and} \quad \overline{HBOBHOO},$$

for which spectroscopic data are available for comparison. In propylene ozonide the O–O distance was estimated to be 1.471 ± 0.013 Å (4). The available spectroscopic data for H_2O_2 have been evaluated recently and shown to be consistent with $r_e = 1.452 \pm 0.004$ Å and $r_0 = 1.464 \pm 0.003$ Å (18). These values are shorter than previous estimates, although a neutron diffraction study obtained 1.453 ± 0.007 Å (19). The literature regarding other O–O distances obtained largely by X-ray diffraction has recently been summarized (20). Values between 1.44 and 1.48 Å are commonly found and most studies report error estimates of about 0.01–0.04 Å. In summary, the O–O distance for ethylene ozonide appears within the range of values reported for similar systems.

Structure determination. The large deviation in the peroxy bond distances using Kraitchman's equations points out the care that must be exercised in estimating even large coordinates for a near-symmetric top. For ethylene ozonide, sizable discrepancies were observed even when $I_b - I_a$ was 1.74 uÅ^2. Equation (1) can compensate adequately for this effect if $I_b - I_a$ is not too small and if reasonable estimates can be made for the δ's. The surplus of data on ethylene ozonide made it easier to obtain plausible estimates for these quantities. Application of this equation may be more ambiguous in other systems where fewer isotopic data are available and a more arbitrary choice must be made for the δ's. Some guidelines for estimating their values based on theoretical models or empirical data would obviously prove valuable. Several analyses have already provided some such insights (*11, 13–16, 21*).

Finally, it is interesting to note the two r_0 structures in Table 5 obtained by fitting the structural parameters in a least-squares sense to either 7 or all 14 isotopic species. The first calculation is close to the single-substitution r_s structure, while the latter calculation is close to the preferred r_s structure. Similar observations that the r_0 structures are sensitive to the choice of isotopic species and also can be close to a good r_s calculation have recently been made (*9*).

<center>APPENDIX</center>

Kraitchman Equations for Double-Substituted Molecules With C_2 Symmetry

Chutjian (*22*) has extended Kraitchman's equations for isotopic substitution of single atoms to multiple isotopic substitution of symmetrically equivalent atoms. From his general formulas, the equations for double substitution in a molecule with C_2 symmetry can be derived.

$$z_s = [(\Delta I_x + \Delta I_y - \Delta I_z)/2\mu_2]^{\frac{1}{2}}, \tag{3}$$

$$y_s = [(I_z'I_y' - RS - R\Delta I_z)/2\Delta m(I_y - I_x)]^{\frac{1}{2}}, \tag{4}$$

$$x_s = [(I_x'I_y' - RS - S\Delta I_z)/2\Delta m(I_x - I_y)]^{\frac{1}{2}}. \tag{5}$$

The primed and unprimed I's and ΔI's have the usual meaning; z is the symmetry axis; Δm is the atomic mass difference between the parent atom and the substituted atom; $\mu_2 = 2M\Delta m/(M + 2\Delta M)$; $R = I_x + \mu_2 z_s^2$ and $S = I_y + \mu_2 z_s^2$.

Vibration effects should be minimized in calculating the z coordinate because no rotation terms enter into Eq. (3). Defining, δx as the error in $I_z' - I_x$, etc., the following expression can be derived.

$$|z_s^*| - |z_s| = (\delta x + \delta y - \delta z)/4\mu_2 z_s. \tag{6}$$

For ethylene ozonide, $|z_s^*| - |z_s|$ is expected to be no greater than ±0.002 Å. The oxygen z_s coordinate for the last two calculations in Table 6 are 0.9214 and 0.9058 Å, in reasonable agreement with the estimates for z_s^* in Table 7 using single-substitution data. The values obtained for the hydrogen coordinates listed in Table 4, however, do not correlate as readily with estimates of z_s^* using single-substitution data unless values for δb are assumed in Eq. (1) that have different signs for the two species and are 50 to 75% smaller than the values used in the peroxy oxygen estimates.

Error estimates for the x and y coordinates result in more complicated expressions. Inspection of Eqs. (4) and (5) indicates that estimates of x_s and y_s are aided by the large denominators and, consequently, vibrational effects should be minimized. Some support for this is obtained by noting that the r_s values for the oxygen atoms in calculations V and VI (Table 6) are 0.6740, 0.2815 and 0.6781, 0.2718. These are in good agreement with the r_s* values in Table 7. For the hydrogen atoms, the r_s* values using Eq. (1) suggest small deviations for the single-substitution calculations; the double-substitution r_s values in Table 4 are also close to these estimates. It therefore appears that the double-substitution equations are also the preferred method for calculating the x_s and y_s coordinates for ethylene ozonide.[3]

Pierce's Equations.

There are enough isotopic data to apply the Pierce double-substitution method (*23*) to locate the peroxy oxygen atom. The procedure can be formulated where the differences between the $^{16}O_p{}^{16}O_p{}^{16}O_e$, $^{18}O_p{}^{16}O_p{}^{16}O_e$ species and the $^{16}O_p{}^{16}O_p{}^{18}O_e$, $^{18}O_p{}^{16}O_p{}^{18}O_e$ species are taken. However, for this isotopic combination, only the coordinate along the symmetry axis can be calculated. Since the change in mass in the two coordinate systems is on the symmetry axis, the other two coordinates should not alter for a rigid rotor.

When this coordinate was calculated using the Pierce procedure, a value of 0.9263 Å was obtained. This value, while close to the double-substitution value of 0.9214 Å, is sufficiently different to require some examination. Ordinarily, vibrational contributions are expected to cancel even better than in the usual Kraitchman analysis. Upon inspecting Pierce's equations, it became apparent that the difficulty arose because the symmetry axis switches from the b axis in the normal species to the a axis in the $^{18}O_e$ $^{16}O_p$ $^{16}O_p$ species. Consequently the large axis rotation terms did not effectively cancel. An error analysis indicated that because of this the Pierce procedure would overestimate the b coordinate by 0.002–0.003 Å. This brings the coordinate into better agreement with the double-substitution result.

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[3] It was pointed out to us by Dr. L. Nygaard that Eqs. (3)–(5) can be more simply expressed as $\mu_z z_s{}^2 = \Delta P_z$; $2\Delta m x_s{}^2 = \Delta P_x[1 + \Delta P_y/(P_y - P_z)]$ and $2\Delta m y_s{}^2 = \Delta P_y[1 + \Delta P_x/(P_x - P_y)]$. With these expressions, it is clearer that vibrational effects will be minimized when calculating x_s and y_s for ethylene ozonide.

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