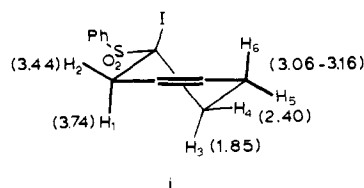


Ogata and Aoki<sup>14</sup> have previously observed the formation of acetoxy-, vicinal diacetoxy-, and iodoacetoxyalkanes upon oxidation of iodoalkanes with peroxyacetic acid in acetic acid. These results are consistent with the solvolysis or elimination of an intermediate iodoso compound followed by further reaction of any olefin formed with peracid or acyl hypiodite. Under these conditions primary iodides gave acetoxy compounds, whereas alcohols were isolated in the present work. More recently, Beeley and Sutherland have proposed an elimination of hypiodous acid to account for olefin formation during the Baeyer-Villiger oxidation of an iodonorbornane.<sup>15</sup>

**Acknowledgment.** We thank the Dow Chemical Co., the National Science Foundation, and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

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- (12) Complete oxidative or base elimination of the 1:1 mixture of diastereomers **7** produced **8a** and **8b** in a 48:52 ( $52 \pm 5\%$   $d_1$ ,  $m$ -CPBA in  $\text{CH}_2\text{Cl}_2$ ) or 47:53 ( $53 \pm 3\%$   $d_1$ , EtOK in EtOH) ratio.
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Hans J. Reich,<sup>16\*</sup> Steven L. Peake

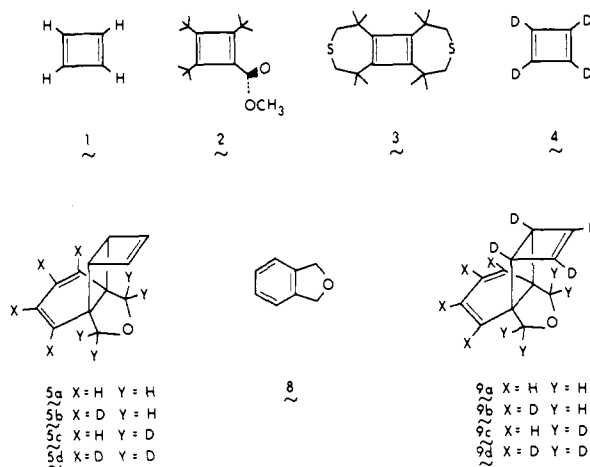
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Received March 31, 1978

## Cyclobutadiene Is Not Square

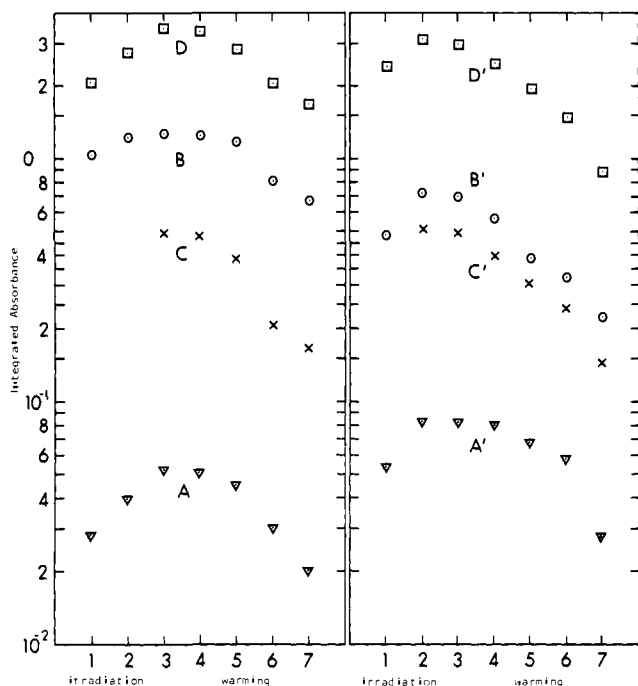
Sir:

The most crucial current issue of cyclobutadiene chemistry concerns the ground-state geometry of the parent compound **1**.<sup>1</sup> The full characterization of simple crystalline derivatives



(**2** and **3**), in which the electronic state of the system is only slightly perturbed, has led to the unambiguous demonstrations (a) that the ground states of **2**<sup>2</sup> and **3**<sup>3</sup> are singlet and (b) that their cyclobutadiene rings are not square, but rectangular. These results contrast to those for **1**. While repeated failures to observe ESR signals (ascribable to a triplet state) strongly indicate a singlet ground state for **1**,<sup>2a</sup> an IR spectral analysis has concluded that **1** detained in an argon matrix possesses a square geometry.<sup>4</sup> However, this conclusion is, in essence, based on the assignment of an absorption at  $1240\text{ cm}^{-1}$  to a C—C stretching vibration.<sup>5</sup> Although some theoretical treatments have proposed a square triplet (ST) (excited) state<sup>4a,6</sup> or an "effectively" square singlet (SS) ground state<sup>7</sup> for the matrix-isolated species, more recent calculations conclude that the ST lies above the SS in the energy surface of the system and a rectangular singlet (RS) represents the ground state of **1**.<sup>8,9</sup> Earlier we emphasized the necessity of further IR studies on both **1** and its perdeuterio derivative **4**.<sup>1a,5a</sup> The spectral evidence presented herein now disproves the previous conclusion that the ring is square and is only consistent with a geometry less symmetrical than  $D_{4h}$ , very likely rectangular, for **1**.

Of the known photoprecursors (**5a**,<sup>10</sup> **6**,<sup>1b,5b</sup> and **7**<sup>4</sup>) of **1**, irradiation (medium-pressure mercury lamp, Vycor filter) of **5a** in an argon matrix (7K, guest-host ratio 1:100-500) proceeds most efficiently to provide the highest concentration of **1**, but the concurrent generation of phthalan **8** masks several regions of the infrared spectrum. However, deuterium incorporation in **5a** as indicated in **5b-d** shifts the IR absorptions of **8**, and use of all these precursors has permitted the careful inspection of the vibrational modes of **1** in the entire region from  $4000$  to  $400\text{ cm}^{-1}$ . Thus IR spectra of the photolysates of **5a** and **5d** recorded with a Nicolet 7199 FT-IR interferometer (resolution  $0.5\text{ cm}^{-1}$ , 100-500 scans averaged) clearly showed that, in addition to the two reported bands at  $1240$  and  $572\text{ cm}^{-1}$ , there were observed, for the first time, two weak absorptions at  $1523$  and  $723\text{ cm}^{-1}$  (below  $1700\text{ cm}^{-1}$ ), which had escaped previous detection. The appearance of these bands from other precursors **6** and **7** was subsequently confirmed. The deuterio series including **9a-d**, **10**, and **11** behaved correspondingly to the protio series, exhibiting, after irradiation, absorptions which increased in intensity upon irradiation of all of the precursors (**5a,d**, **6**, **7**, and **9a,b**, **10**, and **11**) employed and decreased upon warming to  $35\text{ K}$ .<sup>11</sup> Figures 1-3 show the



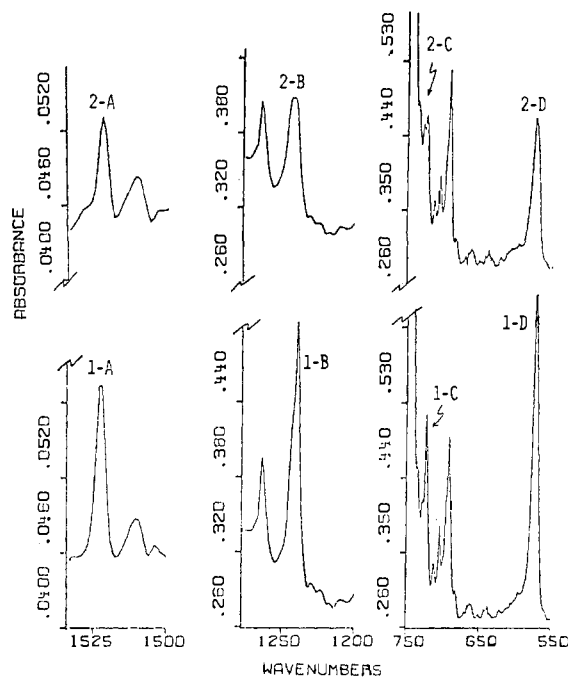
**Figure 1.** Relative intensities of bands A-D and A'-D' (see Table I) during irradiation and warming. For **1** (photoprecursor **5a**): 1, irradiation for 30 min; 2, 75 min; 3, 120 min; 4, warming at 28 K for 60 min; 5, at 33 K for 60 min; 6, at 35 K for 60 min; 7, at 35 K for 90 min. For **4** (photoprecursor **9b**): 1, irradiation for 90 min; 2, 270 min; 3, warming at 25 K for 60 min; 4, at 34 K for 60 min; 5, at 35 K for 60 min; 6, at 35 K for 90 min; 7, at 35 K for 120 min. Integrated absorbance is expressed in logarithmic scale.

**Table I.** IR Absorptions of **1** and **4**

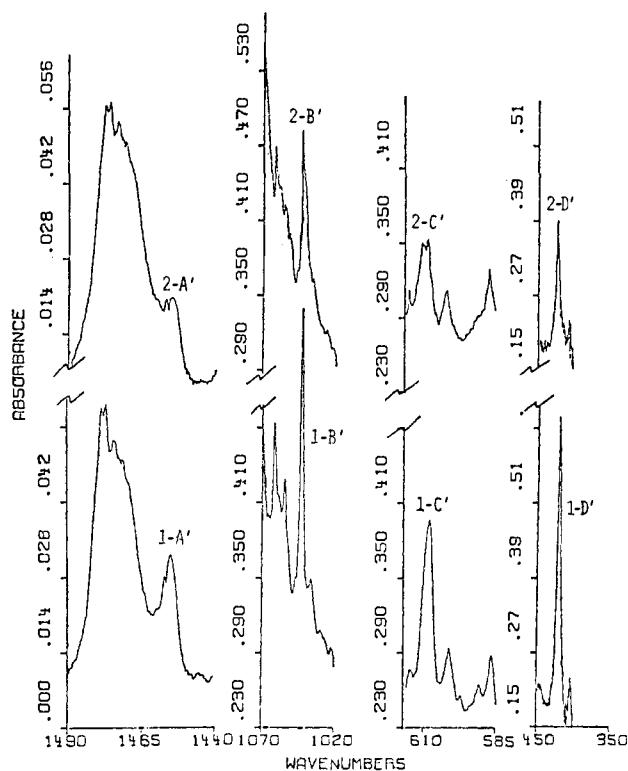
precursor	band	wavenumber, $\text{cm}^{-1}$	rel intensity <sup>a</sup>
<b>C<sub>4</sub>H<sub>4</sub> (1)</b>			
<b>5a,d</b>	A	1523	1.4
	B	1240	41.1
	C	723	12.4
	D	572	100.0
<b>6</b>	A	1527-1528, 1530	2.2
	B	1242, 1245	38.9
	C	718, 721	9.0
	D	576, 591	100.0
<b>7</b>	A	1529, 1531	1.4
	B	1241, 1244	35.0
	C	719, 721	6.8
	D	574, 576	100.0
<b>C<sub>4</sub>D<sub>4</sub> (4)</b>			
<b>9a,b</b>	A'	1456	2.9
	B'	1043	21.0
	C'	609 <sup>b</sup>	16.2
	D'	421	100.0
<b>10</b>	A'	1460, 1464	3.6
	B'	1044, 1046	20.3
	C'	608, 609	27.8
	D'	425, 432	100.0
<b>11</b>	A'	1450, 1455	2.5
	B'	1044, 1047	21.8
	C'	608, 609	20.4
	D'	423, 426	100.0

<sup>a</sup> Relative integrated absorbances of the bands averaged over several runs.

relative intensities of the absorptions during these processes. It is noted that each absorption of the photoproducts derived from precursors **6** and **7**, and **10** and **11**, which generate CO<sub>2</sub> upon photolysis, appears as a doublet (see Table I), possibly



**Figure 2.** Photographs of selected regions of original unsmoothed IR spectra of **1** generated from **5a**: 1-A-1-D, after irradiation of **5a** at 7 K for 120 min; 2-A-2-D, after warming the photolysate at 35 K for 60 min.



**Figure 3.** Photographs of selected regions of original unsmoothed IR spectra of **4** generated from **9b**: 1-A'-1-D', after irradiation of **9b** at 7 K for 270 min; 2-A'-2-D', after warming the photolysate at 35 K for 120 min.

owing to the weak interaction of CO<sub>2</sub> located in the vicinity of **1** in the matrix.<sup>5,12</sup>

The three facts, (a) that all the bands consistently appear from several different precursors, (b) all of them split when CO<sub>2</sub>-generating precursors are used, and (c) the relative intensities are maintained constant at any stage of the photochemical and thermal processes, constitute convincing evidence that the absorptions listed in Table I are indeed attributable to vibrations of **1** or **4**. If these criteria for the assignment of

the bands to **1** or **4** stand the test of time, it immediately follows that the appearance of four absorptions below  $1700\text{ cm}^{-1}$  excludes the possibility of the square ring since group theory predicts for this geometry (point group  $D_{4h}$ ) only three IR-active vibrations in addition to the C—H stretching vibration which appears at  $\sim 3000\text{ cm}^{-1}$ . The band at  $1523\text{ cm}^{-1}$  which shifts to  $1456\text{ cm}^{-1}$  upon deuteration is undoubtedly due to the C=C stretching vibration and corroborates this conclusion.

The spectra presented are consistent with a rectangular geometry for **1** and **4**, point group  $D_{2h}$ . The application of the product rule<sup>13</sup> to the present data leads to the following symmetry assignment of vibrations A–D and A'–D' (see Table I): the pairs of vibrations B and C and B' and C' have  $B_{2u}$  symmetry<sup>14</sup> (product rule ratio: theoretical 1.927, observed 1.918 where the C—H and C—D stretching frequencies are assumed to have the harmonic ratio 1.363); D and D' are the sole  $B_{3u}$  out-of-plane hydrogen and deuterium vibrations (product rule ratio: theoretical 1.363, observed 1.357); and finally the C=C stretching vibrations (A and A') and unobserved vibrations (vide infra) that correspond primarily to H–C–C and D–C–C bending motions have  $B_{1u}$  symmetry. The isotope shifts indicate that B ( $1240\text{ cm}^{-1}$ ) is due largely to H–C–C in-plane bending motion and clearly not primarily to the C—C stretching motion which contributes mainly to C ( $723\text{ cm}^{-1}$ ). In **4** the vibrations B' and C' ( $1043$  and  $609\text{ cm}^{-1}$ ) are both heavy mixtures of these two motions.<sup>15,16</sup> Thus the conclusion derived from the earlier IR analysis completely loses its ground.<sup>17</sup> It is already noted that one  $B_{1u}$  vibration has not been identified. Although the presence of some very weak absorptions at  $\sim 1000\text{ cm}^{-1}$  in the case of **1** and at  $\sim 750\text{ cm}^{-1}$  in **4** is indicated in the spectra, we judge that their intensities are too small to be confirmed with the present sophistication of instrumentation.

Obviously, the number of observed bands enables one to exclude the geometries of symmetry higher than that allowed by group theory, but does not necessarily define the exact symmetry of the molecule. The present study, at minimum, provides the answer to the recent controversial cyclobutadiene problem and the chemistry of this system has now become mutually consistent. The evidence, both theoretical and experimental, points to the conclusion that the cyclobutadiene ring in the ground state is not square but very likely rectangular.<sup>18,19</sup>

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- Following *J. Chem. Phys.*, **23**, 1997 (1955), the *x* axis is perpendicular to the ring, and the *z* axis cuts the C=C bonds.
- The geometry suggested earlier<sup>2a</sup> and a set of reasonable force constants reproduced the observed frequencies well through a GF normal coordinate calculation.<sup>13</sup>  $C_4H_4$ :  $B_{1u}$ , 1540, 974 (not observed);  $B_{2u}$ , 1223, 740;  $B_{3u}$ , 574.  $C_4D_4$ :  $B_{1u}$ , 1455, 713 (not observed);  $B_{2u}$ , 1054, 604;  $B_{3u}$ , 422. Assignments are as reported in the text. Internal coordinates: 4 C—H, 2 C=C, 2 C—C, 4 H—C—C, 4 H—C=C, 4 out-of-plane H—C—C<sub>2</sub>. Geometry assumed:  $r_{C-C} = 1.37\text{ \AA}$ ,  $r_{C=C} = 1.51\text{ \AA}$ ,  $r_{C-H} = 1.08\text{ \AA}$ , H—C—C angle =  $135^\circ$ . Force constants: C—H, 4.85; C=C, 7.425; C—C, 2.55 (all mdyn  $\text{\AA}^{-1}$ ); H—C—C and H—C=C, 0.367 mdyn  $\text{\AA}$ ; out-of-plane H—C—C<sub>2</sub>, 0.2105 mdyn  $\text{\AA}$  (all interaction force constants 0.0).
- The isotope shifts are definitely inconsistent with the assignment of B ( $1240\text{ cm}^{-1}$ ) primarily to C—C stretching vibration.
- This  $1241\text{ cm}^{-1}$  band shifts to  $1237\text{ cm}^{-1}$  in the spectrum of  $^{13}C_3H_4$ ,<sup>5c</sup> but this result alone contributes very little to the assignment.
- All the deuterated photoprecursors were at minimum 98% rich in deuterium content and full experimental details of the syntheses of these compounds and the matrix work are available on request. (F.A.S.-B., Ph.D. Thesis, University of Alberta.)
- The authors thank Drs. K. Sakan, R. L. Sobczak, and S. Ohta for their preparations of deuterated precursors, Mr. A. Clement for his technical assistance, Professor G. L. Closs for valuable suggestions, and the National Research Council of Canada for financial support.
- Inquiries may be addressed to S.M. at either the University of Alberta or the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Mass. 02139.

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## Isomerism and Charge Distribution in Mixed-Metal Polyoxoanion Clusters: Oxygen-17 Nuclear Magnetic Resonance Structure Determinations of *cis*- $V_2W_4O_{19}^{4-}$ and *cis*- $HV_2W_4O_{19}^{3-}$

Sir:

Mixed-metal polyoxoanion clusters have recently attracted attention as reversible oxidants in the homogeneous catalytic oxidation of olefinic and aromatic hydrocarbons.<sup>1–3</sup> Characterization of structure and charge distribution clearly provides a first step toward understanding the reactivity of these species. Although x-ray crystallographic studies have characterized the overall metal–oxygen frameworks in several mixed-metal polyanions,<sup>4–6</sup> in no case have the relative positions of the different metal atoms within the framework been determined. Infrared,<sup>7</sup>  $^{51}V$  NMR,<sup>8–10</sup>  $^{31}P$  NMR,<sup>9–11</sup> and  $^{17}O$  NMR<sup>6,12,13</sup> studies have likewise failed to unambiguously establish metal atom configurations for specific mixed-metal isomers. We report here an  $^{17}O$  NMR study of  $V_2W_4O_{19}^{4-}$  which establishes a *cis* relationship between vanadium atoms in its octahedral metal array, and demonstrates that negative charge on the surface of the cluster is concentrated on the unique oxygen atom bonded to both vanadiums.

X-ray crystallography has provided a structural model for  $V_2W_4O_{19}^{4-}$  in  $\alpha$ -( $CN_3H_6$ )<sub>4</sub> $V_2W_4O_{19}$  consistent with the *cis* or *trans* structures shown in Figure 1a and 1b, or a mixture of the two.<sup>4</sup> Assuming that the pertinent resonances may be observed, sufficiently resolved, and assigned,  $^{17}O$  NMR spectroscopy should allow assignment of a *cis* or *trans* structure on the basis of one or more of the following structural features: (1) only the *cis* structure possesses an  $OV_2$  oxygen, i.e., an oxygen bonded to two vanadiums, (2) all  $OW$  oxygens bonded to a single tungsten are symmetry equivalent in the *trans* structure as are the  $OW_2$  oxygens bonded to two tungstens, whereas the *cis* structure contains two nonequivalent types of