considerable amount of diradical character and cannot be adequately described by a closed-shell restricted Hartree–Fock method. (4) The triplet state ($^3A''$) is predicted to lie about 25 kcal/mol above the ground-state singlet $^1A'$. (5) The triple-bond harmonic stretching frequency for singlet cyclopentyne is predicted to be 1828 cm^{-1}, while the analogous stretching frequency for the triplet state is 1622 cm^{-1}.

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Registry No. Cyclopentyne, 1120-58-7.

Supplementary Material Available: Cartesian coordinates of the optimized molecular structures (C_{2v} and C_s symmetries) and harmonic frequencies and normal modes (in internal valence coordinates) for the lowest singlet (at the GVB/3-21G level of theory) and triplet (at the ROHF/3-21G level of theory) electronic states of cyclopentyne (13 pages). Ordering information is given on any current masthead page.

Electron Diffraction Investigation of Pseudorotation in 1,3-Dioxolanes

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Abstract: The gas-phase structures of 1,3-dioxolane, 2-methyl-1,3-dioxolane, and 2,2-dimethyl-1,3-dioxolane have been determined by least-squares analysis of gas-phase electron-diffraction patterns. Various rigid single conformer models, conformational mixtures of envelope and twist forms of the molecules, and pseudorotational models were tested. For 1,3-dioxolane the best results were obtained by using a pseudorotational model with a twofold barrier of about 0.3 kcal/mol. For 2-methyl-1,3-dioxolane a rigid model with the methyl group in the equatorial position gave the best fit. For 2,2-dimethyl-1,3-dioxolane a pseudorotational model with a twofold barrier of 1.1 ± 0.3 kcal/mol with the twist form being the more stable conformer gave the best agreement. These results are compared with previous experimental and theoretical results.

It is quite well-established that cyclopentane does not exist as static twist or envelope forms, instead it is constantly undergoing a large amplitude pseudorotational motion with nearly no barrier. We have recently been interested in the effects of exocyclic substitution on the pseudorotational potential function of cyclopentane. We have found that monosubstituted cyclopentanes like chlorocyclopentane[1] and cyanocyclopentane[2] have a hindered pseudorotational potential function which depends strongly on the nature of the substituents and that the stable conformers are the axial and equatorial forms. However, not enough experimental data are yet available to understand and predict the effect of substituents on the potential function.

One other way to influence the pseudorotational potential of cyclopentane is to make endocyclic substitution. Five-membered rings like tetrahydrofuran and 1,3-dioxolane are good candidates for these studies in that the oxygen atoms do not increase the barrier so much that only one conformer can be observed. For example, silacyclopentane has a twofold barrier of 4 kcal/mol,[3] and only the twist form is observed in the gas phase.[4] The molecular structure of tetrahydrofuran has been reported by Geise et al.[5] and the electron diffraction data were consistent with free pseudorotation. Other spectroscopic studies[6,7] have also shown this to be the case. We therefore decided to study the dioxolanes because there are available experimental and theoretical data for 1,3-dioxolane and for 2-methyl-1,3-dioxolane suggesting the presence of pseudorotational motion. The most stable form on the potential function of 1,3-dioxolane had not been resolved, and the twist, envelope, and a hybrid half-twist forms have all been proposed. We also felt that a more complete and perhaps detailed understanding of the pseudorotational motion could emerge if related dioxolanes were analyzed simultaneously by using the same procedures and programs. We have therefore chosen to study the molecular structures of 1,3-dioxolane, 2-methyl-1,3-dioxolane, and 2,2-dimethyl-1,3-dioxolane with particular attention paid to the pseudorotational motion of these compounds.

Cremer et al.[8,9] have employed ab initio molecular orbital calculations to study the effects of oxygen substituents in cyclopentane. Their findings indicated that nonadjacent oxygen substituents lowered the barrier to planarity but increased the barrier to pseudorotation while adjacent oxygen atoms raised both barriers. They found that the most stable forms in the first several members of the series were predicted to be twist instead of envelope. Cremer and Pople[8] noted that for 1,3-dioxolane the twist minimum was obtained by using 4-31G basis and that STO-3G gave the envelope form as minimum. However, the bond lengths and the methylene geometry in 1,3-dioxolane were fixed in these studies. Norskov-Lauritsen and Allinger[10] in their study on the treatment of

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(1) Hilderbrandt, R. L.; Shen, Q. *J. Phys. Chem.* **1982**, *86*, 587.

(2) Hilderbrandt, R. L.; Leavitt, H.; Shen, Q. *J. Mol. Struct.* **1984**, *116*, 38.

(3) Laane, J. *J. Chem. Phys.* **1969**, *50*, 1946.

(4) Shen, Q.; Hilderbrandt, R. L.; Mastryukov, V. S. *J. Mol. Struct.* **1979**, *54*, 121.

(5) Geise, H. J.; Adams, W. J.; Bartell, L. S. *Tetrahedron* **1969**, *25*, 3045.

(6) Engerholm, G. G.; Luntz, A. C.; Gwinn, W. D.; Harris, D. O. *J. Chem. Phys.* **1969**, *50*, 2446.

(7) Lafferty, W. J.; Robinson, D. W.; St. Louis, R. V.; Russell, J. W.; Strauss, H. L. *J. Chem. Phys.* **1965**, *42*, 2915.

(8) Cremer, D.; Pople, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 1358.

(9) Cremer, D. *Isr. J. Chem.* **1983**, *23*, 72.

(10) Norskov-Lauritsen, L.; Allinger, N. L. *J. Comp. Chem.* **1984**, *5*, 326.

0002-7863/86/1508-6888$01.50/0

the anomeric effect in molecular mechanisms calculations predicted the envelope form of 1,3-dioxolane to be 0.52 kcal/mol lower in energy than the twist form.

The pseudorotational motion of 1,3-dioxolane has been investigated by both microwave[11] and far-infrared spectroscopic methods.[12,13] Greenhouse and Strauss[12] concluded from their far-infrared study of tetrahydrofuran and 1,3-dioxolane that both compounds had barriers to pseudorotation of about 0.15 kcal/mol. Durig and Wertz[13] interpreted their near- and far-infrared data for 1,3-dioxolane in terms of free pseudorotation. Baron and Harris[11] recorded the microwave spectrum of 1,3-dioxolane in the region from 8 to 35 GHz and concluded that the barrier to pseudorotation was 135 cal/mol and that both the bend and twist forms were maxima on the potential energy surface with twist slightly higher in energy. No attempt to determine the structure by using rotational constants was made.

Durig and co-workers[14] reported an infrared and Raman spectroscopic study of 2-methyl-1,3-dioxolane and its d_4 analog. They assigned the 58-cm^{-1} band to the ring puckering mode and calculated the barrier to the pseudorotational motion to be about 1.3 kcal/mol. The potential function was not obtained. No structural information is available for 2-methyl-1,3-dioxolane and 2,2-dimethyl-1,3-dioxolane.

Experimental Section

1,3-Dioxolane (DOX), 2-methyl-1,3-dioxolane (MDOX), and 2,2-dimethyl-1,3-dioxolane (DMDOX) were obtained from Aldrich Chemical Co. and were used without further purification. Electron diffraction data were collected on Kodak Electron Image plates (4 × 5 in.) by using the North Dakota State University apparatus. All experiments were carried out at room temperature. The exposure times were in the range of 45–70 s for the long camera plates and 120–160 s for the short camera plates; and the ambient pressure was maintained at 2×10^{-5} torr. An accelerating voltage of 40 keV was used, and the plate distances were measured with a precision cathetometer. They were for DOX 253.49 nm and 99.67 mm, for MDOX, 253.49 mm and 99.67 mm, and for DMDOX 251.41 mm and 99.51 mm. Benzene plates were recorded under identical conditions as the samples for calibration. For each molecule three plates for each camera distance were selected for analysis. They were traced on the microcomputer controlled densitometer at intervals of 0.15 mm. These data were corrected for emulsion saturation, plate flatness, and sector imperfections and were interpreted to integral units of $q = [(40/\lambda)\sin(\theta/2)]$. Least-squares analysis of the interpolated intensity data were carried out by using the procedure outlined by Gundersen and Hedberg,[15] and the elastic scattering factors and phase shifts were calculated by Schafer et al.[16]

Molecular Mechanics Calculations

Allinger's MM2 molecular mechanics program[17] was used to calculate the energy of the various conformations exhibited by DOX, MDOX, and DMDOX. We have carried out calculations with and without the inclusion of the oxygen lone pairs. With the inclusion of these lone pairs MM2 predicted the envelope form of DOX to be 0.36 kcal/mol lower in energy than the twist form. For MDOX, the equatorial form was found to be 2.0 kcal/mol more stable than the axial form. The twist form converged to the equatorial form during the refinement. For DMDOX, the twist form was calculated to be only 0.15 kcal/mol lower in energy than the envelope form.

With the exclusion of the oxygen lone pairs, the results are slightly different. The twist form of DOX gave the lowest energy, and envelope was 0.59 kcal/mol higher in energy. For MDOX, the equatorial form was found to be a stable minimum. The axial form converged to the equatorial form, but the twist form converged to a form with C_4 as the apex of the envelope form of the five-membered ring. This hybrid form is 0.20 kcal/mol lower in energy than the equatorial form. The twist form of DMDOX was 0.91 kcal/mol lower in energy than the envelope. It appeared that the inclusion of the oxygen lone pairs lowered the energy of the envelope form by about 0.8 kcal/mol.

Table I. Results from MM2 Calculations[a]

confrmr, rel energy, paramrs	DOX		MDOX		DMDOX	
	twist 0.36	envelope 0.0	equatorial 0.0	axial 2.0	twist 0.0	envelope 0.15
τ(C–C)	1.527	1.536	1.536	1.534	1.526	1.534
τ(C_5–O)	1.417	1.420	1.420	1.420	1.416	1.534
τ(C_2–O)	1.426	1.420	1.421	1.421	1.429	1.423
τ(C–H)	1.118	1.118	1.118	1.118	1.118	1.117
τ(C–C_m)			1.532	1.537	1.539	1.539
CCO	102.5	104.8	104.5	105.1	102.6	105.1
∠COC	105.0	104.0	104.2	104.9	105.4	105.1
∠OCO	109.8	105.8	105.5	106.7	109.2	106.1
∠C_mCC_m					110.5	110.5
∠OCC_m			110.7	111.4	108.9	109.2
∠HCC_m			111.1	109.8		
τ5123	−13.6	−40.4	−40.9	34.3	−11.6	−35.9
τ1234	−11.8	39.5	39.5	−36.5	−13.8	35.9
τ2345	30.0	−22.5	−22.1	23.7	31.5	−21.4
τ3451	−38.9	−1.4	2.2	−3.3	−38.7	0.0
τ4512	31.4	24.7	25.6	−18.3	30.3	21.4

[a] Oxygen lone pairs are included in these calculations. Distance parameters are in units of Å, angles are in deg, and C_m is the exocyclic carbon atom. τ12341234 corresponds to the torsional angle $O_1C_2O_3C_4$; see Figure 1 for atom numbering. DOX, MDOX, and DMDOX are 1,3-dioxolane, 2-methyl-1,3-dioxolane, and 2,2-dimethyl-1,3-dioxolane, respectively. Energy is in units of kcal/mol.

Table I summarizes the results from MM2 calculations with the inclusion of the oxygen lone pairs. It appears that the C–C and C–O bonds are different in the different conformations. The C–C bonds in twist are shorter than in envelope, and the two different C–O bonds (C_5–O and C_2–O) are identical in envelope and different in twist. The C_2–O bonds are slightly longer than the C_5–O bonds in all three dioxolanes. The C–C bond of the exocyclic methyl group is slightly longer than the C–C bond in the ring. The ∠CCO ring angle is 2° larger in envrlope than in twist.

Data Analysis

There is no available force field for any one of these three molecules so we adapted the force field reported by Synder and Zerbi[18] for aliphatic ethers. This valence force field, developed from studying ten ethers, includes stretch and bend force constants, and stretch–stretch, stretch–bend, and bend–bend interactions. Unfortunately it did not include a value for the OCO bending force constant so the averaged value of the CCO and COC constants was used. This force field gave rather small l_{ij} values for the geminal nonbonded C⋯C, C⋯O, and O⋯O distances.

(A) 1,3-Dioxolane. Rigid Model. Figure 1 shows the twist form for DOX. The geometrical parameters chosen were as follows: (1) the C–C bond length; (2) an average C–O bond length; (3) an average C–H bond length; (4) the ∠CCO angle; (5) the ∠HCH angle, with no rocking of the methylene group; (6) τ, torsional angle $O_1C_5C_4O_3$, and (7) ψ, the angle between the plane $O_1C_2O_3$ and the plane formed by atoms O_3 and O_1 and midpoint of C_4–C_5 bond. The combination of parameters 6 and 7 generates the twist and envelope forms; for example, $\tau = 0.0°$ and $\psi = 30°$ gives envelope, while $\tau = 40°$ and $\psi = 0.0°$ gives twist.

Models with only the twist form and envelope form were tested, and the radial distribution curves are shown in Figure 3. The twist form alone appeared to give a better fit to the experimental data than the envelope. The discrepancies were mainly in the geminal C⋯C, C⋯O, and O⋯O nonbonded distances. This is reasonable since the five-membered ring is shaped differently in the two conformers. It suggested that a model with a mixture of twist and envelope should be tested. Unfortunately in this model, both of the parameters ψ and τ could not be refined

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(11) Baron, P. A.; Harris, D. O. *J. Mol. Spectrosc.* **1974**, *49*, 70.

(12) Greenhouse, J. A.; Strauss, H. L. *J. Chem. Phys.* **1969**, *50*, 124.

(13) Durig, J. R.; Wertz, W. *J. Chem. Phys.* **1968**, *49*, 675.

(14) Durig, J. R.; Kizer, K. L.; Karriker, J. M. *J. Raman. Spectrosc.* **1973**, *1*, 17.

(15) Gundersen, G.; Hedberg, K. W. *J. Chem. Phys.* **1969**, *51*, 2500.

(16) Schafer, L.; Yates, A C.; Bonham, R. A. *J. Chem. Phys.* **1971**, *55*, 3055.

(17) Molecular Mechanics II (QCPE 423). Profeta, Jr., S. *QCPE Bull.* **1981**, *1*, 57.

(18) Synder, R. G.; Zerbi, G. *Spectrochim. Acta* **1967**, *23A*, 391.

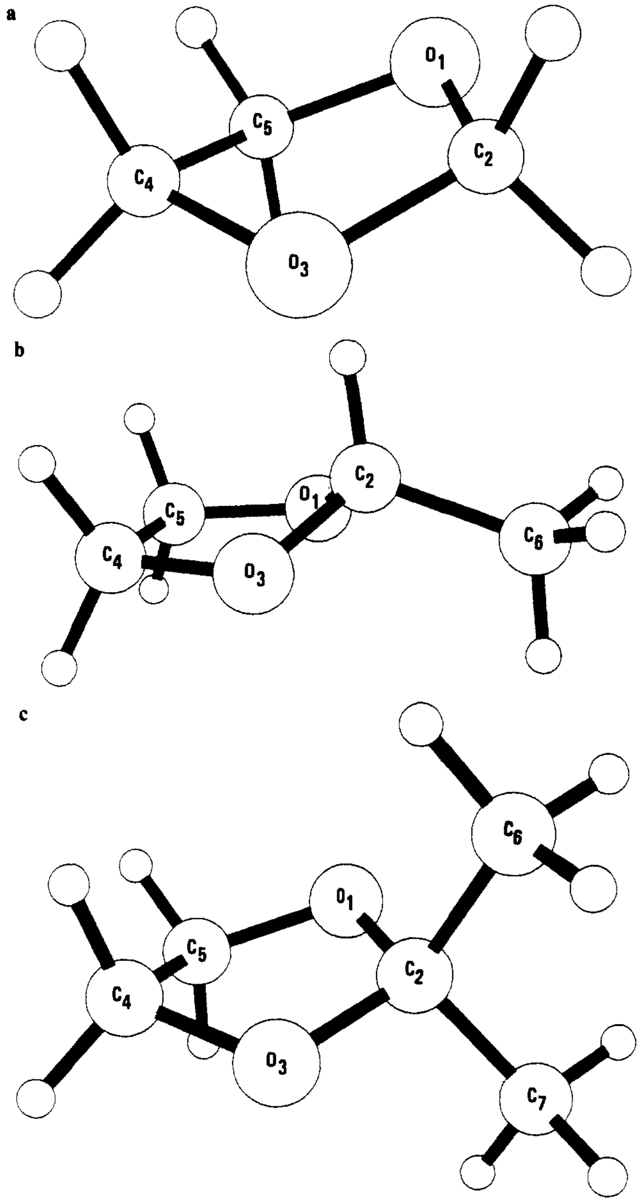

Figure 1. Atomic Numbering used in defining structural parameters for (a) 1,3-dioxolane (twist), (b) 2-methyl-1,3-dioxolane (equatorial), (c) and 2,2-dimethyl-1,3-dioxolane (twist).

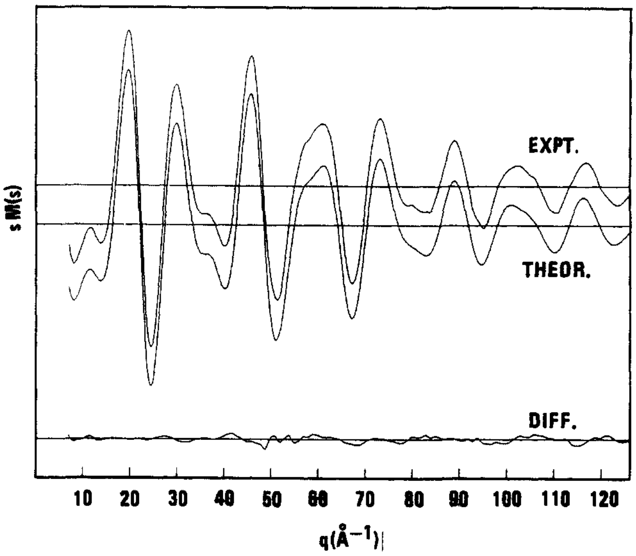

Figure 2. Levelled experimental and theoretical intensity curves for 1,3-dioxolane (dynamic model).

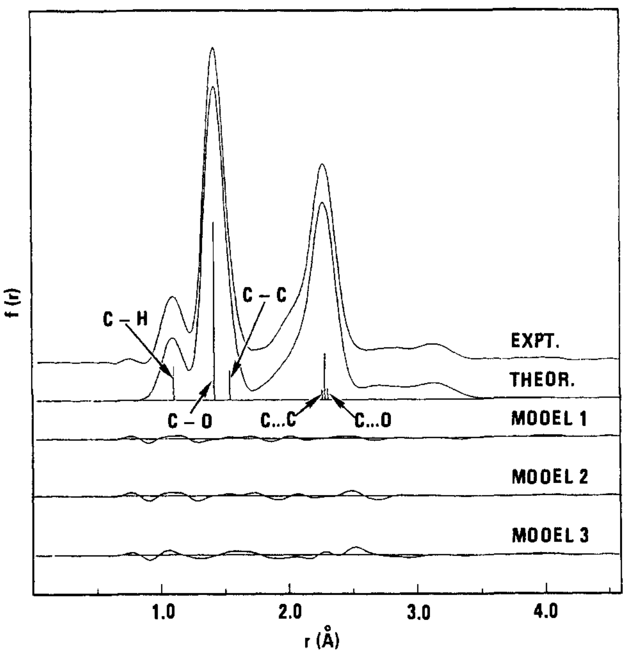

Figure 3. Radial distribution curves for 1,3-dioxolane: model 1 = dynamic model, model 2 = twist, and model 3 = envelope.

simultaneously, and the mole fraction of the conformers was strongly correlated with the values assigned to these two parameters. Test refinements showed that percent twist could vary from 85 to 65 depending on these parameters. The two-conformer model did not improve the *R* factor of the long camera distance data, in fact inclusion of envelope sometimes made the fit to the long camera data worse.

In all of our tests to this point only an averaged value of C–O was used. The ground state rotational constants available from MW[11] were incorporated into the analysis attempting to resolve these two distances. The usual B_z to B_0 vibrational corrections were not made since (a) the corrections are not obvious and trivial in a pseudorotating molecule where the rotational constants are strongly vibrational level dependent[19] and (b) we felt that the uncorrected rotational constants would suffice for preliminary tests. The ED/MW refinements showed that the twist model gave better agreement than the envelope model. The average C–O model reproduced the observed rotational constants to within 3 MHz while the model with two C–O bonds gave values within 0.2 MHz. When the C–O bonds were allowed to differ, the MW/ED refinements favored a model with the C_2–O bond shorter than C_4–O bond by 0.028 Å and a C–C bond length of 1.559 (6) Å. The results are summarized in Table II.

Pseudorotation Model. In view of the spectroscopic data which all suggested a rather small barrier to pseudorotation and the fact that the static models tested did not give satisfactory fit, we decided to test the pseudorotation model in the analysis of the electron diffraction data. A twofold potential function of the form

$$V(\phi) = \frac{V_2}{2}(1 - \cos 2\phi)$$

was used, where ϕ is the pseudorotational phase angle, and V_2 is the barrier. In order to allow for a smooth variation of the values of τ and ψ during the pseudorotational motion, the following equations were incorporated into the model

$$\tau = \tau_0 \sin \phi$$

and

$$\psi = \psi_0 \cos \phi$$

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(19) Tamagawa, K.; Hilderbrandt, R. L. *J. Phys. Chem.* **1983**, *87*, 5508.
(20) Astrup, E. E. *Acta Chem. Scand.* **1973**, *27*, 3271.
(21) Blukis, U.; Kasai, P. H.; Myers, R. J. *J. Chem. Phys.* **1963**, *38*, 2753.
(22) Almeningen, A. Kolsokes, P.; Seip, H. M.; Willadsen, T. *Acta Chem. Scand.* **1969**, *23*, 3398.
(23) Clark, A. H.; Hewitt, T. G. *J. Mol. Struct.* **1971**, *98* 33.

Table II. Least-Squares Results for 1,3-Dioxolane[a]

parameters	envelope	twist	twist ED/MW	dynamic
τ(C–H)	1.122 (8)	1.107 (7)	1.105 (6)	1.106 (6)
τ(C–C)	1.546 (9)	1.538 (9)	1.559 (6)	1.542 (6)
$\tau(C–O)_{AV}$	1.422 (2)	1.422 (2)		1.423 (1)
$\tau(C_2–O)$			1.411 (7)	
$\tau(C_5–O)$			1.439 (5)	
∠CCO	105.1 (6)	102.0 (9)	101.0 (3)	101.0 (4)
∠HCH	115.0 (fixed)	120 (7)	109.1 (23)	118 (5)
τ1543[b]	0.0	36 (7)	39.0 (10)	41.8 (31)
ψ[c]	34 (3)			34 (fixed)
V_2[d]				0.3 (fixed)
g[e]	0.31	0.35	0.38	0.39
l_{C-H}	0.074 (7)	0.065 (6)	0.067 (6)	0.065 (5)
l_{C-O}	0.053 (1)	0.049 (1)	0.049 (fixed)	0.050 (1)
$l_{C\cdots C}$	0.063 (4)	0.071 (1)	0.071 (3)	0.060 (fixed)
$l_{O\cdots H}$	0.13 (fixed)	0.13 (fixed)	0.091 (13)	0.17 (2)
R[f]	0.077	0.071	0.075	0.061

[a] Distance parameters are reported as τ_g values in Å whereas angles in deg are reported as τ_α parameters corrected for shrinkage effects. The quoted errors are three standard deviations obtained from the least-squares analysis plus an estimate of the systematic error. [b] Torsional angle defined by atoms $O_1C_5C_4O_3$. [c] ψ is the angle formed by the $O_1C_2O_3$ plane and the plane formed by atoms O_3 and O_1 and midpoint of C_4–C_5 bond. [d] Barrier of the twofold potential function in kcal/mol. [e] q is the puckering amplitude for the ring. [f] R factors are defined as $R = [(\Sigma W_i(I_{(obsd)} - I_{(calcd)}{}^2)/\Sigma W_i I^2{}_{(obsd)})]^{1/2}$.

where τ_0 is the value of the twist angle for the twist conformer, and ψ_0 is the value for the ψ angle for the envelope form. The twofold potential function has a minimum at the twist ($\phi = 90°$) and a maximum at the envelope ($\phi = 0°$) form. Nine conformations were included in the analysis as the phase angle varies from 0 to 180°. In the refinements using this model it was impossible to refine the value of V_2 simultaneously with the other parameters, and therefore refinements with the value fixed at 2, 1, 0.5, and 0.3 kcal/mol were carried out. The R factors for the long camera data for these refinements were 3.49, 3.34, 2.89, and 2.50 %, respectively. The least-squares results are summarized in Table II and the intensity and the radial distribution curves are shown in Figure 2 and 3, respectively.

(B) 2-Methyl-1,3-dioxolane. Rigid Model. The geometrical parameters chosen for this molecule are very similar to those for DOX. In addition we have assumed the exocyclic C–C bond to be of the same length as the endocyclic C–C bond so the C–C parameters represents an averaged value. One additional parameter was introduced, the $\angle OC_2C_m$ where C_m is the exocyclic methyl carbon atom. The parameter list is shown in Table III. Figure 4 shows the radial distribution curve which clearly reveals that equatorial is the major species in the gas phase at room temperature. A static equatorial form was used as a model in the analysis, and the best least-squares results are summarized in Table III.

Attempts to refine a two-conformer model were all met with very little success. A two-conformer model of equatorial/axial gave a small negative percentage (5–10%) for the axial form. A mixture of equatorial/twist gave a slight positive percentage (up to 15%) for the twist form. Neither of these two-conformer models gave an improvement in the R factor. All of our analyses showed no strong evidence for the presence of the axial conformer in the gas phase but a small amount of the twist cannot be totally ruled out. Careful inspection of the radial distribution led to the same conclusion since the $C_6\cdots C_4$ distances for the axial and twist forms are located in the 3.0- and 3.5-Å region where no error is really evident in the equatorial model. The intensity and radial distribution curves for the static axial form model are shown in Figures 4 and 5, respectively.

(C) 2,2-Dimethyl-1,3-dioxolane. Rigid Model. The geometry was defined by using averaged C–C and C–O bond lengths. The two methyl groups were placed on the C_2 atom by using the single parameter $\angle C_mC_2C_m$ (where C_m's are the methyl group carbon atoms) and the assumption that the lines bisecting the valence angles $C_mC_2C_m$ and OC_2O were colinear. The parameter list is shown in Table III.

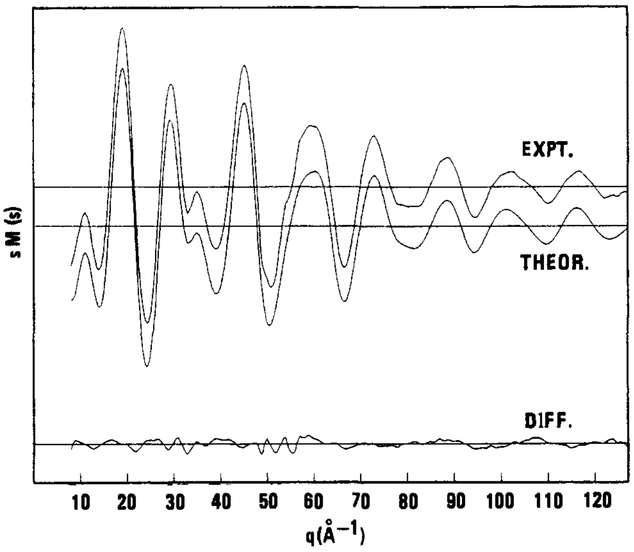

Figure 4. Levelled experimental and theoretical intensity curves for 2-methyl-1,3-dioxolane (equatorial).

Table III. Least-Squares Results for 2-Methyl-1,3-dioxolane and 2,2-Dimethyl-1,3-dioxolane[a]

	MDOX		DMDOX	
parameters	equatorial	twist	mixture (T/E)[b]	dynamic
τ(C–H)	1.102 (9)	1.106 (5)	1.107 (4)	1.108 (4)
$\tau(C–C)_{AV}$	1.522 (7)	1.525 (4)	1.525 (3)	1.526 (3)
$\tau(C–O)_{AV}$	1.422 (2)	1.428 (2)	1.427 (2)	1.428 (2)
∠CCO	105.2 (10)	104.0 (5)	102.8 (5)[c]	101.9 (3)
$\angle HC_mC$[d]		115.8 (24)	111.3 (18)	112.8 (27)
$\angle COC_m$	110.9 (10)			
$\angle C_mCC_m$		97.3 (23)	111.7 (14)	114.0 (83)
∠HCH	118 (fixed)	115 (fixed)	115 (fixed)	115 (fixed)
τ1543*e* (T)	0.0	32.2 (30)	29.6 (31)	35.4 (24)
ψ[f] (E)	32.6 (35)		33.7 (36)	38.1 (55)
%T			66 (7)	
V_2[g]				1.1 (0.3)
q[h]	0.30	0.30	0.28	0.34
l_{C-H}	0.069 (7)	0.074 (4)	0.074 (3)	0.074 (3)
l_{C-C}	0.054 (fixed)	0.054 (4)	0.054 (3)	0.057 (4)
l_{C-O}	0.049 (2)	0.053 (2)	0.053 (2)	0.054 (2)
$l_{C_6\cdots C_3}$	0.084 (2)	0.18 (3)	0.105 (28)	0.081 (3)
$l_{C\cdots C/C\cdots O}$	0.060 (10)	0.097 (10)	0.086 (9)	0.077 (4)
$l_{C\cdots H}$	0.13 (fixed)	0.11 (fixed)	0.11 (fixed)	0.13 (2)
R[i]	0.101	0.061	0.047	0.045

[a] Distance parameters are reported as τ_g values in Å whereas angles are reported in deg as τ_α parameters corrected for shrinkage effects. The quoted errors are three standard deviations obtained from the least-squares analysis plus an estimate of the systematic error. MDOX and DMDOX are 2-methyl-1,3-dioxolane and 2,2-dimethyl-1,3-dioxolane, respectively. [b] T and E are the twist and envelope conformers. [c] The value for the envelope form is 2° larger (104.8). [d] Kc_m corresponds to the exocyclic carbon atoms. [e] τ1543 defines the torsional angle $O_1C_5C_4O_3$. [f] ψ is the angle formed by the $O_1C_2O_3$ plane and the plane formed by atoms O_3 and O_1 and midpoint of C_4–C_5 bond. [g] Barrier of the twofold potential function in kcal/mol. [h] q is the puckering amplitude for the ring. [i] R factors are defined as

$$R = [(\Sigma W_i(I_{(obsd)} - I_{(calcd)})^2)/\Sigma W_i I^2_{(obsd)}]^{1/2}$$

With the presence of two exocyclic methyl groups on the C_2 atom there are only two likely conformers for DMDOX: twist and envelope. Static models of pure twist and pure envelope were both tested, and the refinements clearly showed a perference for the twist conformer. This model gave a very small value for the valence angle $\angle C_mCC_m$. A two conformer model (twist/envelope) was introduced with the assumption that all the geometrical parameters of the two forms are identical except for the values of ψ, τ, and ∠CCO where the value for envelope was assumed to be 2° larger than the value for twist. It is interesting to note that a much better fit was obtained when this difference was introduced

Table IV. Comparison of Geometrical Parameters between 1,3-Dioxolane and Related Molecules[a]

parameter	dimethoxymethane	dimethyl ether	tetrahydrofuran	1,2,4-trioxacyclopentane	1,3,5-trioxane	DOX
rC–O	1.382 (4) 1.438 (4)	1.410 (3)	1.428 (2)	1.415 (3)	1.411 (2)	1.423 (1)
∠OCO	114.3 (7)			105.3 (8)	111.0 (7)	108.7 (24)
∠COC	114.6 (5)	111.7		105.9 (11)	109.2 (10)	105.8 (24)
method	ED	MW	ED	ED	ED	ED
ref	20	21	5	22	23	this work

[a] Distances in Å and angles in deg. MW = microwave and ED = electron diffraction studies.

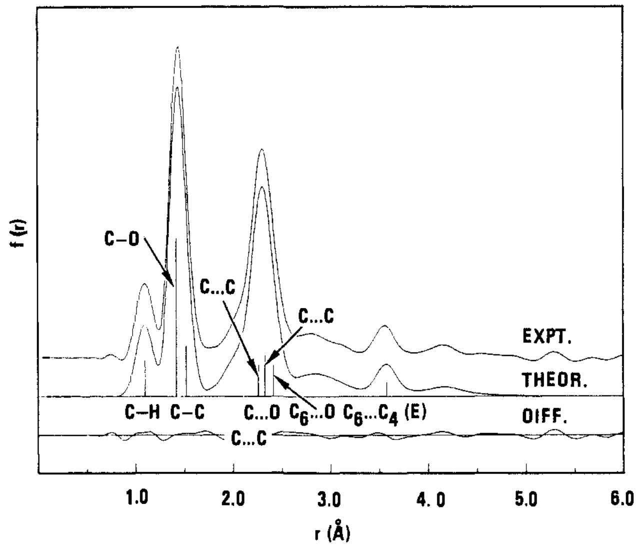

Figure 5. Radical distribution curves for 2-methyl-1,3-dioxolane (equatorial).

into the two-conformer model. In these refinements the values for both ψ and τ were refined, and twist was found to be twice as abundant as envelope. Table III shows the final least-squares results for the two conformer model.

Pseudorotation Model. A twofold potential function of the type used in analyzing DOX was adopted for DMDOX. A total of nine conformers were included in the analysis as the phase angle ϕ varies from 0 to 180°. Both τ_0 and ψ_0 were refined along with V_2, and the results are shown in Table III. A value of 1.1 ± 0.3 kcal/mol was obtained for V_2. The intensity and radial distribution curves for this model are shown in Figures 6 and 7, respectively. The final least-squares results are summarized in Table III.

Discussion

Molecular Structure. Electron diffraction in the present study is not capable of resolving all of the different C–O and C–C distances. Perhaps, with the proper vibrational corrections to the rotational constants a combined ED/MW analysis could resolve the C–O distances in DOX. The situations in MDOX and DMDOX are even more complex in that the exocyclic methyl group introduces an extra C–C bond, and there is no MW data available for either one. Microwave data would be of great value in the analysis of MDOX which, we believe, has a higher pseudorotational barrier and thus proper B_z to B_3 corrections could be made. Nevertheless, the average bond lengths obtained in this study should be reliable. The average C–C bond lengths in MDOX and DMDOX are identical; however, they are shorter than the C–C bond in DOX. The C–C bond length in DOX is not well-determined, and the error limit is rather large. The average C–O bond lengths are essentially identical in all three molecules. The differences in the ∠CCO angles are due to the geometrical difference of the ring for the twist and envelope forms. The puckering amplitudes decrease from DOX > MDOX = DMDOX. Table IV compares some of the major geometrical parameter values obtained for the dioxolanes and related ethers.

Conformation. Both far-infrared[12-13] and microwave[11] spectroscopic studies found a very small barrier to pseudorotation for DOX, and our electron diffraction data are consistent with this interpretation. We can further infer from our data that the stable conformer is very likely twist. This result agrees with Cremer's theoretical calculations[8,9] but is in disagreement with the results of MM2 calculations and the microwave spectroscopic[11] results. We believe the MM2 force field, with the inclusion of the oxygen lone pairs, may have over-estimated the stability of the envelope form by about 0.8 kcal/mol. This is consistent both in DOX and DMDOX. In DMDOX, ED found the twist to be 1.1 kcal/mol lower in energy, and MM2 gave a value of 0.18 kcal/mol. In

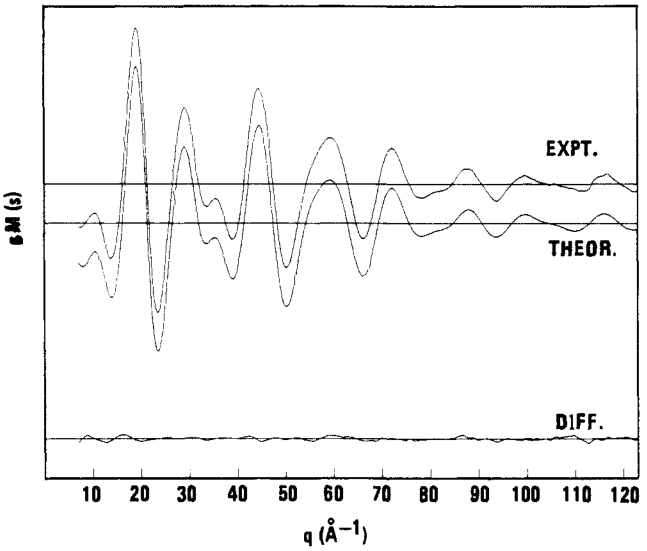

Figure 6. Levelled experimental and theoretical intensity curves for 2,2-dimethyl-1,3-dioxolane (dynamic model).

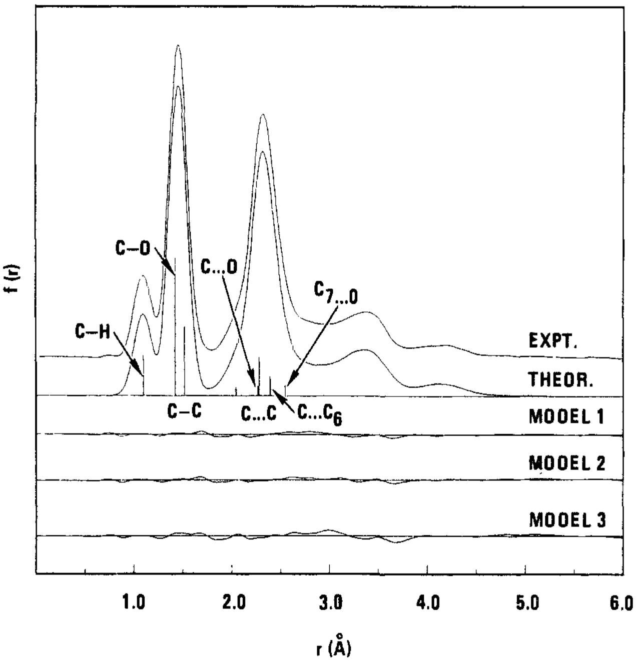

Figure 7. Radial distribution curves for 2,2-dimethyl-1,3-dioxolane: model 1 = dynamic model, model 2 = twist + envelope, and model 3 = twist.

MDOX where twist does not play a role, MM2 predicts a difference of 2.0 kcal/mol between equatorial and axial which is consistent with the ED result where only equatorial was observed.

For MDOX equatorial is the only conformation found in substantial quantity. MM2 calculations seem to suggest twist is neither a minimum nor a maximum on the pseudorotational trajectory. Equatorial is definitely the lowest energy form in agreement with the experiment. We believe that due to the repulsive forces of the methyl group, axial might very well be a maximum on the potential surface. Thus the pseudorotation of MDOX is governed by a onefold function with high barrier at axial and minimum at equatorial. For DMDOX a dynamic model with a twofold potential function fit the ED data very admirably, and the barrier was found to be 1.1 ± 0.3 kcal/mol.

It is very likely that the barrier in DOX is less than 1.1 kcal/mol (the barrier obtained for DMDOX) because with the absence of the two bulky methyl groups the pseudorotation in DOX should be less hindered. In summary, this study suggests that DOX has a very low barrier to pseudorotation with twist as the minimum; MDOX can be described by using a onefold potential with equatorial as the minimum, and DMDOX has a twofold barrier of 1.1 kcal/mol with twist as the minimum energy conformer.

At the conclusion of this research we became aware of the fact that Professor Kenneth Hedberg, Department of Chemistry, Oregon State University, had also recently completed a gas phase electron diffraction study of DOX. We have compared our results with those of Professor Hedberg, and we find no significant differences in any of the reported structural parameters.

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Registry No. DOX, 646-06-0; MDOX, 497-26-7; DMDOX, 2916-31-6.

Supplementary Material Available: Tables of correlation matrixes and intensity data (12 pages). Ordering information is available on any current masthead page.

Oscillations and Bistability in the Cu(II)-Catalyzed Reaction between H_2O_2 and KSCN

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Abstract: The reaction between H_2O_2 and KSCN catalyzed by $CuSO_4$ exhibits three different types of bistability as a function of flow rate in a continuous flow stirred tank reactor at 25 °C. Two steady states and one oscillatory state are involved. The system is one of the few examples in which oscillations can appear in batch configuration as well. The color, the potential of a Pt electrode, and the rate of oxygen gas evolution oscillate for a wide range of reagent concentrations. The chemistry which accounts for the observed behavior is discussed briefly.

The rapidly growing interest in and number of examples of oscillatory and related phenomena suggest that chemical oscillations and multistability are a frequent rather than an exceptional form of behavior in far-from-equilibrium systems. It is still a problem to find the proper conditions under which these phenomena can occur. Mathematical models are capable of predicting these behaviors from solutions to the appropriate differential equations, although wide gaps still exist between the models and the real chemical systems. A few authors claim that an oscillatory chemical reaction can be constructed by design. It is perhaps fairer to say that until now only some general requirements have been established (e.g., far-from-equilibrium conditons, feedback, nonlinear kinetics, etc.) which may result in oscillations under certain combinations of the constraints. A semiempirical approach of constructing oscillatory chemical systems was successfully applied in recent years, and the technique coupled with a little luck, and fantasy has led to the discovery of dozens of new oscillators.[1] In spite of the large number of examples, only a few are based on really different chemistry, whereas the majority represent variations with more or less essential modifications of the so-called "minimal" versions. An effort to classify the known liquid-phase chemical oscillators was made in a recently published monograph[2] in which three basic groups were distinguished: the classes of iodate, bromate, and chlorite oscillators.

Some very recent results have shown that species other than oxyhalogens can also give rise to oscillations, bistability, and excitability in solution. Examples are the oxidation of benzaldehyde by oxygen in glacial acetic acid with $CoBr_2$ catalyst,[3] the oxidation of methylene blue by oxygen in strongly alkaline medium in the presence of sulfite and sulfide,[4] and the oxidation of sulfide ion with hydrogen peroxide in nearly neutral solution.[5] In the H_2O_2–S^{2-} reaction, among other periodic responses, pH oscillations of some 3–4 units were observed.

The new oscillatory reaction reported in this paper may represent a member of a fundamentally new group. It has an initial composition of KSCN–H_2O_2–$CuSO_4$–NaOH; it shows several types of bistability; it oscillates in color, in potential of a Pt electrode and in the rate of gas evolution; but it gives no pH oscillations. For the oscillation, the pH must be above 9 and the periodicity appears in both batch and flow configurations.

Experimental Section

Materials. Stock solutions of KSCN and NaOH were prepared using analytical grade chemicals dissolved in distilled water previously passed through an ion-exchange column filled with oxycellulose to remove any trace metal impurities. After this treatment of the water, atomic absorption spectrophotometry indicated no measurable amount of metal ion contamination. The concentrations of KSCN and NaOH were checked by the Volhard and acid–base titration methods, respectively. The H_2O_2 solutions were always freshly made by dilution of commercially available Fisher Certified ACS 30% or Reanal 30% product, and kept in poly-

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(1) Epstein, I. R.; Kustin, K.; De Kepper, P.; Orbán, M. *Sci. Am.* **1983**, *248*, (3), 112–123.

(2) Epstein, I. R.; Orbán, M. *Oscillations and Traveling Waves in Chemical Systems*; Field, R. J., Burger, M., Eds.; Wiley: New York, 1984; Chapter 8, pp 257–286.

(3) Jensen, J. H. *J. Am. Soc.* **1983**, *105*, 2639–2641.

(4) Burger, M.; Field, R. J. *Nature (London)* **1984**, *307*, 720–721.

(5) Orbán, M.; Epstein, I. R. *J. Am. Chem. Soc.* **1985**, *107*, 2302–2305.

0002-7863/86/1508-6893$01.50/0