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Internal Rotation in Some Oxalyl Halides. A Theoretical Investigation

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Abstract: Ab initio molecular orbital theory is used to study internal rotation in oxalyl fluoride, oxalyl chlorofluoride, and oxalyl chloride. The theoretical results indicate the presence of both trans and cis conformations for oxalyl fluoride and oxalyl chlorofluoride with the trans conformation being somewhat more stable than the cis. Oxalyl chloride on the other hand is predicted to have trans and gauche conformations with no stable cis conformation and with the trans conformation being the more stable. These results are compared with those derived from spectroscopic studies. An examination of the factors determining the shape of the energy curves is given.

Extensive use has been made of molecular orbital theory in recent years to study the change in the energy of molecules with internal rotation about single bonds.[1-3] Pople and his co-workers[4] have investigated the internal rotation about the carbon-carbon bond in glyoxal (CHO-CHO) and have predicted the existence of both a trans and a cis conformation with the former being more stable by 6.1 kcal/mol, in close agreement with another theoretical study of Pincelli, Cadioli, and David[5] who obtained a separation of 6.4 kcal/mol for the two conformations, and it is to be compared with an experimental value of 3.2 kcal/mol.[6] However, except for a somewhat limited theoretical treatment of oxalyl chlorofluoride using the CNDO/2 method by Pople and Segal,[7] no theoretical calculations have been published on the halogen derivatives of glyoxal and in particular on oxalyl chloride, oxalyl chlorofluoride, and oxalyl fluoride.

Experimental investigations of internal rotation in the oxalyl halides have been the subject of a large number of publications by many workers with significantly different interpretations of the data occurring, resulting in considerable controversy. Most of the publications have dealt with oxalyl chloride, beginning with the observation of its Raman spectrum in the liquid state by Kohlrausch and Wittek.[8] These authors made no assignments for the observed spectrum. Ziomek et al.[9] first reported the infrared spectrum of the liquid state and though no assignments were made they concluded from the fact that only two coincidences were observed between infrared and Raman frequencies that only the trans isomer was present. Saksena and Kagarise[10] obtained an infrared and Raman spectrum of the liquid and an infrared spectrum of the vapor and studied the intensity variation of the observed bands. Their conclusion was that more than one conformation was present in both liquid and vapor states and that the conformations were the trans and cis forms with the trans being more stable by 2.8 kcal/mol. There then followed a set of three more publications by Ziomek et al.,[11] by Saksena et al.,[12] and by Kagarise[13] attempting to support their respective interpretations. An x-ray analysis of solid oxalyl chloride was published by Groth and Hassel[14] indicating the presence of only a trans conformation. Hencher and King[15] analyzed the infrared and Raman spectrum of the liquid and vapor and concluded that only the trans conformation existed and Balfour and King[16] interpreted the uv spectrum in terms of only the trans conformation. Hjoortas[17] published a short note on the electron diffraction spectrum, whose analysis indicated only the presence of a trans conformation in the vapor phase. Fleury et al.[18-20] published a series of papers which concluded that oxalyl chloride exists as a cis-trans mixture with an energy difference of around 2 kcal/mol, the trans conformation being the more stable. Durig and Hannum[21] studied the infrared spectrum of the solid, liquid, and gas and the Raman spectrum of the solid and liquid and concluded that only the trans conformation was present in the solid while both cis and trans were present in the liquid and gas with the trans conformation being more stable by 2.2 kcal/mol. From the torsional vibration at 55 cm^{-1} they obtain a value of V^* ($= V_1 + 4V_2 + 9V_3$) equal to 11.1 kcal/mol. Finally Hagen and Hedberg[22] analyzed the electron diffraction data for the gaseous oxalyl chloride and concluded that there were two conformations but that these were the trans and the gauche with the trans being more stable by 1.38 kcal/mol and the barrier to rotation being 2.00 kcal/mol. In summary the experimental data, particularly the more recent work, supports the existence of two conformers but there is still uncertainty as to whether the less stable conformer is the cis or the gauche.

The experimental data on oxalyl fluoride have also been subject to different interpretations though there have been fewer papers published on this molecule. The infrared spectrum

Table I. Optimized Geometries and Total Energies for the Trans Conformations of the Oxalyl Halides Using the 4-31G Extended Basis Set

	$(COF)_2$	COFCOCl	$(COCl)_2$
C-Cl, Å		1.745	1.745
C=O, Å	1.181	1.181	1.181
C-F, Å	1.338	1.338	
C-C, Å	1.500	1.510	1.520
∠OCCl, deg		123	123
∠CCCl, deg		113.7	113.2
∠OCF, deg	122.8	125.4	
∠CCF, deg	111.8	111.8	
$E(0)$, hartrees	−423.725 35	−783.386 84	−1143.051 05

of the liquid and vapor and the Raman spectrum of the liquid were first reported by Hencher and King[23] who concluded that only the trans conformation existed. Balfour and King[24] analyzed the uv spectrum of oxalyl fluoride on the assumption that only the trans structure was present. Durig et al.[25] investigated the infrared spectrum of the solid and vapor and the Raman spectrum of the solid and liquid and concluded that only the trans conformation existed in the solid state but that both trans and cis conformations were present in the liquid and gaseous states with a value for V^* of 12.4 kcal/mol for internal rotation from the trans to the higher energy cis form. Goubeau and Adelhelm[26] also concluded from a study of the infrared and Raman spectrum in various states that there was both a trans and a cis conformation present in the liquid and gaseous states with the trans form being the more stable.

Hencher and King[23] and Goubeau and Adelhelm[26] concluded from an investigation of the infrared and Raman spectrum of oxalyl chlorofluoride in various states that only the trans conformation exists. The uv spectrum of oxalyl chlorofluoride was interpreted by Balfour and King[24] on the basis of only a trans conformation existing.

The purpose of this study is to carry out accurate molecular orbital calculations on the energies of these three oxalyl halides as a function of the dihedral angle to determine whether there is more than one energy minima, which dihedral angles these minima correspond to, and the barriers to internal rotation between different conformations if more than one appears to be present.

Method and Results

All calculations were carried out using the GAUSSIAN 70 ab initio molecular orbital program developed by Hehre et al.[27] using one or other of the Gaussian basis sets, STO-3G, STO-4G, and 4-31G. The bond lengths and angles for oxalyl chloride were based on those obtained by Hagen and Hedberg[22] optimized to give minimum energy in the trans conformation using the 4-31G extended Gaussian basis set. The initial geometries for the oxalyl chlorofluoride and the oxalyl fluoride were based on the optimized set of bond lengths and angles obtained for oxalyl chloride and on values given for formyl fluoride (HCFO).[28] These were then optimized in the trans configuration using the 4-31G extended Gaussian basis set. The geometries used for all three molecules along with the total energies, in hartrees, of the trans conformations are given in Table I. The trans conformation is taken to be the unrotated conformation in all cases, i.e., the dihedral angle ϕ equals 0° for the trans conformation and equals 180° for the cis conformation. Table II gives the relative energies

$$\Delta E(\phi) = E(\phi) - E(0)$$

for a variety of conformations.

All three oxalyl halides were investigated using the STO-4G Gaussian basis set and oxalyl fluoride was also studied over the complete range of dihedral angles using the 4-31G extended Gaussian basis set. When the 4-31G extended Gaussian basis set was applied to oxalyl chloride convergence was obtained for the trans and the 60° conformations but conformations with a larger dihedral angle failed to converge. With oxalyl chlorofluoride convergence was obtained only with the trans conformation. Various attempts involving geometry modification, i.e., treating the molecules as nonrigid rotors, variation of the scaling parameter in the initial Extended Hückel calculation, and variation of the scaling parameters for the 3sp Gaussian functions of chlorine, were made without achieving convergence. Alternative molecular orbital configurations were also utilized without success.

Table II. Relative Energies $\Delta E(\phi)$ (kcal/mol) for Oxalyl Halide Conformations

Molecule	$\Delta E(0)$	$\Delta E(60)$	$\Delta E(90)$	$\Delta E(120)$	$\Delta E(180)$
$(COF)_2$					
(a) 4-31G	0	3.99	5.23	3.74	0.54
(b) STO-4G	0^a	2.34	3.06	2.34	0.13
COFCOCl					
STO-4G	0^a	2.61	3.20	2.22	0.28
$(COCl)_2$					
STO-4G	0^a	2.75	3.32	2.80	4.90

[a] $E(0)$ for $(COF)_2$ using STO-4G basis set is −421.510 88 hartrees. $E(0)$ for COFCOCl using STO-4G basis set is −779.927 99 hartrees. $E(0)$ for $(COCl)_2$ using STO-4G basis set is −1138.345 52 hartrees.

Table III. Properties Associated with Internal Rotation in the Oxalyl Halides

Molecule	Basis set	Barriers to internal rotation, kcal/mol	Energy diff of conformations, kcal/mol	% of less stable conformation at 298 K
$(COF)_2$	4-31G	5.23	0.54	29
	STO-4G	3.06	0.13	45
COFCOCl	STO-4G	3.20	0.28	38
$(COCl)_2$	STO-4G	3.32	2.80	2

Discussion

As mentioned earlier the geometry optimization calculations were carried out for the trans conformation of the oxalyl halides and the energy changes, as a function of dihedral angle, were determined assuming the molecules to be rigid rotors; i.e., the only geometry change made was in the dihedral angle. Initial geometry optimization calculations, dealing particularly with the C-C bond and using the STO-3G basis set, were found to lead to C-C bond lengths much longer than would be expected (e.g., 1.577 Å for oxalyl fluoride as compared to 1.500 Å using the 4-31G basis set). This is in agreement with the results obtained by previous workers.[2,3]

The results obtained for oxalyl fluoride agree qualitatively with those obtained by Durig et al.[25] and Goubeau and Adelhelm[26] who proposed the existence of both a trans and a cis conformation in the gaseous state and indicated the trans conformation was the more stable. The value of V^* of 24.7 kcal/mol obtained using the results for V_1, V_2, and V_3 given in Table IV and discussed later is approximately twice that determined experimentally by Durig et al.[25] (12.4 kcal/mol). The barriers to internal rotation, energy differences of the conformations and the percentage of the cis conformation present at room temperature (298 K) are given in Table III. The results for oxalyl chlorofluoride are supportive of the ex-

Table IV. Potential Constants (kcal/mol) for Internal Rotation

Molecule	V_1	V_2	V_3
$(COF)_2$[a]	0.08	4.90	0.29
COFCOCl	−0.18	3.14	0.30
$(COCl)_2$	2.86	0.87	2.04

[a] 4-31G basis set.

perimental data of Hencher and King[23] and Goubeau and Adelhelm[26] in so far as they conclude that the trans conformation is the more stable. However, they do indicate a significant presence of the cis conformation though somewhat less than for the oxalyl fluoride. The results do suggest that further experimental work is required, particularly with a view to determining the presence of the cis conformation and an evaluation of the barrier to internal rotation. Again the barrier to internal rotation and other relevant data for oxalyl chlorofluoride are summarized in Table III.

The calculations on oxalyl chloride are the most interesting, particularly in terms of their comparison with the large number of experimental results and the varying conclusions associated with them. The calculations would appear to support the conclusions of Hagen and Hedberg[22] that the stable conformations are a trans and gauche form with the former being the more stable. The theoretical data suggest a somewhat less stable gauche form than do the experimental results though this might be modified if a more sophisticated basis set calculation could be performed. Also the theoretical barrier to internal rotation is somewhat higher than is the experimental one. It should be noted of course that there are two gauche conformations. The small percentage of the gauche conformation (2%) makes comprehensible the conclusions of many of the workers that only a trans conformation was present. It is of interest that the energy difference for the trans and gauche conformations (2.80 kcal/mol) is close to the energy difference determined by Durig and Hannum[21] for the trans-cis mixture (2.2 kcal/mol). By extrapolation from the results on oxalyl fluoride, use of a more sophisticated basis set would tend to increase the barrier to rotation and the energy difference of the conformations further decreasing the percentage of the gauche conformation.

Internal rotation in the oxalyl halides is adequately described by the truncated Fourier expansion $2V(\phi) = V_1(1 - \cos\phi) + V_2(1 - \cos 2\phi) + V_3(1 - \cos 3\phi)$ where ϕ is the dihedral angle and V_1, V_2, and V_3 are respectively the onefold, twofold, and threefold barriers. The values for these barriers in the three oxalyl halides are given in Table IV. The dominant term in both oxalyl fluoride and oxalyl chlorofluoride is obviously the V_2 term leading to minima in both the trans and cis conformations. The barrier to internal rotation can then be reasonably attributed to loss of stabilization due to conjugation in going from a planar to a nonplanar configuration. The V_1 term in both molecules is very small indicating little or no change in the degree of steric interaction in the two conformations. The V_2 term, though small, seems to be the major factor influencing the slightly lower stability of the cis relative to the trans conformation and is attributable to nonbonding n–n, n–π, or π–π interactions.

The situation in oxalyl chloride is quite different with the V_2 term now playing a much smaller part. All three terms contribute to the stability of the trans conformation but both the V_1 and V_3 terms are strongly destabilizing for the cis conformation indicating much greater steric effects due to Cl–Cl nuclear repulsion and larger nonbonded interactions. The V_3 term is the one which leads to the minimum in the gauche configuration and also contributes significantly to the barrier between the trans and gauche conformations.

Our inability to achieve convergence for oxalyl chloride and oxalyl chlorofluoride at dihedral angles significantly different from 0° (trans) using the 4-31G basis set was disturbing. Attempts to overcome this problem by assuming nonrigidity in the molecular framework on internal rotation were not successful. Calculations were carried out using a wide range of C–C bond lengths and OCCl angles without achieving convergence. Variation of the initial extended Hückel guess and of the scaling parameters for the linear combinations of Gaussians also failed to result in convergence. Modification of the molecular orbital configuration was also unsuccessful. The problem may be the result of the limited basis sets available to us and could probably be eliminated by using a more sophisticated basis set. It should perhaps be noted that we have experienced similar nonconvergence problems with a number of other molecules some containing only "first" row elements.

The valence molecular orbitals of the oxalyl halides are important in determining the structure and properties of the oxalyl halides and of particular importance in determining the lowest energy electronic transitions is the ordering of these orbitals. The only experimental evidence available is from the analysis of the ultraviolet spectrum of these molecules by

Table V. Oxalyl Halide Orbital Energies in Hartrees[a]

	Trans						Cis/gauche					
Molecule	4-31G			STO-4G			4-31G			STO-4G		
$(COF)_2$	−0.5335	$10a_g$	n_a	−0.3803	$10a_g$	n_a	−0.5422	$10a_1$	n_a	−0.3810	$10a_1$	n_a
	−0.5799	$2b_g$	π_b	−0.4330	$2b_g$	π_b	−0.5766	$2a_2$	π_a	−0.4325	$2a_2$	π_a
	−0.6099	$9b_u$	n_b	−0.4637	$2a_u$	π_a	−0.5884	$9b_2$	n_b	−0.4616	$9b_2$	n_b
	−0.6163	$2a_u$	π_a	−0.4681	$9b_u$	n_b	−0.6205	$2b_1$	π_b	−0.4650	$2b_1$	π_b
	−0.6673	$9a_g$	n_a	−0.4985	$9a_g$	n_a	−0.6868	$9a_1$	n_a	−0.5067	$9a_1$	n_a
COFCOCl	−0.4928	$23a'$	n	−0.3835	$23a'$	n				−0.3821	$23a'$	n
	−0.5014	$4a''$	π	−0.4192	$4a''$	π				−0.4194	$4a''$	π
	−0.5133	$22a'$	n	−0.4297	$22a'$	n				−0.4280	$22a'$	n
	−0.5836	$3a''$	π	−0.4567	$3a''$	π				−0.4592	$3a''$	π
	−0.5878	$21a'$	n	−0.4753	$21a'$	n				−0.4847	$21a'$	n
$(COCl)_2$	−0.4708	$13a_g$	n_a	−0.3890	$13a_g$	n_a				−0.3825	16a	
	−0.4944	$12a_g$	n_a	−0.4291	$3b_g$	π_b				−0.4265	15a	
	−0.4946	$3b_g$	π_b	−0.4293	$3a_u$	π_a				−0.4314	15b	
	−0.5021	$3a_u$	π_a	−0.4328	$12a_g$	n_a				−0.4361	14b	
	−0.5184	$12b_u$	n_b	−0.4472	$12b_u$	n_b				−0.4475	14a	

[a] Highest occupied ground state molecular orbitals.

Balfour and King[16,24] which indicate that the lowest lying electronic transitions are $\pi^* \leftarrow n$. Until recently the ordering of the valence molecular orbitals in the related molecules glyoxal[29] and biacetyl[30] suggested an ordering of n_a, n_b, π_b, π_a in order of increasing ionization potential (here a and b subscripts denote C_2 rotational symmetry). However, a recent ab initio calculation on glyoxal by Dykstra and Schaefer[31] indicates an ordering n, π, n, π in both the trans and cis conformations. Table V shows the energies of the five highest occupied orbitals in the three oxalyl halides in the cis and trans conformations for oxalyl fluoride and oxalyl chlorofluoride and in the gauche and trans conformations for oxalyl chloride. The results for oxalyl fluoride are based on use of the 4-31G basis set and the STO-4G basis set while those for oxalyl chlorofluoride and oxalyl chloride show the data for both the STO-4G and 4-31G basis sets in the trans conformation but only for the STO-4G basis set in the other conformation. It is clear that in all three molecules studied, and with both basis sets, the highest occupied orbital in the conformations listed is a nonbonding orbital. As a result the lowest energy electronic transitions would be expected to arise from this orbital as is found experimentally. In oxalyl fluoride the results obtained for both the trans and cis conformations using the 4-31G basis set agree with those found for glyoxal,[31] i.e., n, π, n, π from highest occupied down with a reversal in the π_a and π_b orbitals in going from the trans to the cis conformation. The results obtained for oxalyl fluoride using the STO-4G basis set in the trans conformation indicate a different ordering, n_a, π_b, π_a, n_b. However, it should be noted that the π_a and n_b orbitals are almost degenerate in this calculation. The oxalyl chlorofluoride data give the ordering n, π, n, π in all instances. The results obtained for oxalyl chloride using the minimum basis set indicate an ordering in the trans conformation of n_a, π_b, π_a, n_a with the latter three orbitals all having very similar energies while the 4-31G basis set indicates a relative destabilization of one of the n orbitals relative to the two π orbitals resulting in a n_a, n_a, π_b, π_a ordering similar to that suggested by Turner[29] for glyoxal and Sidman and McClure[30] for biacetyl. Again however it should be noted that the latter three orbitals are nearly degenerate. These results indicate the importance of the basis set in determining the order of the valence molecular orbitals. They also indicate however the possibility of low energy electronic transitions arising from π molecular orbitals. It should perhaps be emphasized that the results obtained here are not quantitively rigorous since we are using a limited basis set and the energy differences between different conformers are of the order of only a few kilocalories per mole. The results obtained here cannot be considered in isolation from experimental data but hopefully do suggest possible fruitful areas to investigate both experimentally and, using more sophisticated basis sets, theoretically.

The computations were carried out using an IBM 370/158 computer. Typical computations were of the order of 15 min for the STO-4G basis set calculations and 90 min for the 4-31G basis set calculations.

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