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# Conformational Analysis. 21. The Torsional Problem in Oxalyl Chloride. An ab Initio and Electron-Diffraction Investigation of the Structures of the Conformers and Their Energy and Entropy Differences

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The structure and conformational properties of oxalyl chloride, which experiences internal rotation about the C–C bond, have been reinvestigated by electron diffraction from the gas at 0, 80, and 190 °C and by extensive ab initio calculations. Complete structure optimizations at a very high level (MP2/TZ2P, 166 basis functions) revealed, in addition to the anti form at  $\angle\text{ClCCCl} = 180^\circ$ , a second stable form (gauche) with  $\angle\text{ClCCCl} = 89.8^\circ$  characterized by a very shallow minimum in the energy; earlier theoretical results for oxalyl chloride had been inconsistent with the existence of a second form known from experiment to be present. The electron diffraction analysis was based on dynamic models that comprised a set of pseudoconformers spaced at regular intervals around the torsional coordinate  $\phi = \angle\text{ClCCCl}$  and Boltzmann weighted according to a three-term torsional potential  $V(\phi) = \frac{1}{2}\sum_i V_i[1 - \cos i(180 - \phi)]$ . For the more elaborate model results from the ab initio calculations were incorporated in the form of distance and angle differences among the pseudoconformers; in a second, simpler model these differences were omitted so that the structures of the pseudoconformers differed only in their torsion angles. A theoretical force field for the anti form was also evaluated ab initio, scaled to fit the observed wavenumbers, and used in each model to calculate the usual corrections for vibrational averaging. The results for the analysis of the 0 °C data for the more elaborate (preferred) model are as follows ( $r_g/\text{\AA}$ ;  $\angle_o/\text{deg}$  with  $2\sigma$  uncertainty estimates):  $r(\text{C}=\text{O}) = 1.184(2)$ ,  $r(\text{C}-\text{C}) = 1.548(8)$ ,  $r(\text{C}-\text{Cl}) = 1.749(3)$ ,  $\angle\text{CCO} = 123.8(4)$ ,  $\angle\text{CCCl} = 111.8(3)$ , and  $\angle\text{ClCCCl}_{\text{gauche}} = 76(18)$  where  $0^\circ$  corresponds to cis; results at the other temperatures are similar. Values of the potential constants, which should be temperature independent, are found in the ranges (kcal/mol)  $1.45 \leq V_1 \leq 1.99$ ,  $-0.40 \leq V_2 \leq 0.03$ , and  $0.43 \leq V_3 \leq 1.05$ ; the average values are  $V_1 = 1.59(83)$ ,  $V_2 = -0.11(38)$ , and  $V_3 = 0.74(39)$ . The estimated mole fractions of the anti form at 0, 80, and 190 °C are 0.67, 0.62, and 0.43, from which the internal energy difference  $\Delta U^\circ = U_g^\circ - U_a^\circ$  is calculated to be  $0.75(50)$  kcal mol<sup>-1</sup> and the entropy difference  $\Delta S^\circ = S_g^\circ + R \ln 2 - S_a^\circ$  to be  $1.31(148)$  cal mol<sup>-1</sup> K<sup>-1</sup>. The simpler model gives similar results.

## Introduction

Investigations of the molecular structure of oxalyl chloride are many in number and span a period of over 40 years. Interest in the molecule centers on the ease with which internal rotation can occur around the conjugated carbon–carbon single bond, thereby affording the possibility for generation of more than one conformer as suggested by Figure 1. By 1970 it had become clear from spectroscopic and X-ray work that the molecule assumed an anti conformation (symmetry  $C_{2h}$ ) in the crystal, but in fluid phases certain differences in the spectra indicated the presence of an additional conformer.<sup>1</sup> This conformer was widely thought to be a planar syn form (symmetry  $C_{2v}$ ), but in 1973 it was shown by our electron-diffraction study of the gas<sup>2</sup> to be gauche with a torsion angle  $\text{ClCCCl}$  of about  $65^\circ$  (anti =  $180^\circ$ ) and to be less stable than the anti by about 1.4 kcal/mol. These conclusions were verified by a subsequent unpublished study<sup>3</sup> of the molecule based on a more elaborate model, one in which the conformational distribution was assumed to be determined by a torsional potential of the form  $2V(\phi) = \sum_i V_i[1 - \cos i(180 - \phi)]$  with  $i = 1, 2$ , and 3. Among the refined parameters were the constants

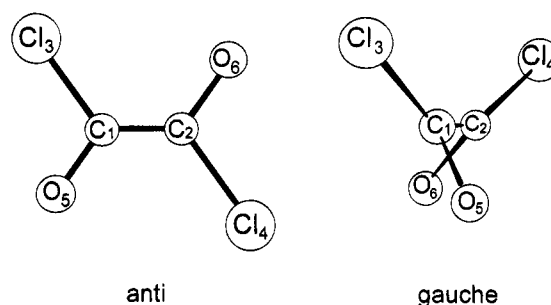


Figure 1. Model of conformers of oxalyl chloride.

$V_i$ . In addition to the potential minimum for the anti at  $\phi = \angle\text{ClCCCl} = 180^\circ$ , a second minimum was found at  $\phi$  equal to about  $86^\circ$ .

From the experimental side there has thus seemed to be no doubt about the existence of a second conformer in gaseous oxalyl chloride or about its identity as gauche. Recently, however, an extensive ab initio investigation<sup>4</sup> of the molecule opened the question anew. This work comprised a detailed investigation of the basis set dependence of the torsional potential. Structure optimizations were carried out at the HF level with bases ranging from 3-21G\* to TZ2P over the range  $0^\circ \leq \angle\text{ClCCCl} \leq 180^\circ$ . A number of single-point MP2/HF calculations were also done, as well as one series of optimiza-

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tions at the MP2/DZP level. Surprisingly, only the compact HF/3-21G\* and the HF/DZ((P)) (polarization functions only on the chlorine atom) resulted in stable second conformers: from the former a planar syn form and from the latter a gauche form with a torsion angle of about  $60^\circ$  from planar syn. Nearly all the results, however, showed at least a dip in the potential in the approximate range  $70^\circ \leq \angle \text{ClCCCl} \leq 110^\circ$  that suggests some kind of stabilizing force for a gauche type of conformer. Since the theoretical torsional potentials, at least those from the higher level calculations, tend to have values less than about  $1.0 \text{ kcal mol}^{-1}$  in this region, these results also suggest that the (anti) molecule undergoes large-amplitude torsional motion.

The contrasting pictures provided by the experimental results (two stable conformers) and the theoretical ones just cited (only one stable conformer) has led us to reexamine the electron diffraction aspect of the work. The point of interest is whether the limitations of the models used for our previous experimental work could have led to the wrong conclusion about the conformational composition. The first of these models was built on the assumption that two conformers were present, and the structures of these conformers differed only in the torsion angles.<sup>2</sup> It was recognized that the latter part of this assumption could not be wholly correct, but any reasonable deviations from it seemed quite unlikely to affect conclusions about the identity of the conformers and their energy difference. Nevertheless, to the extent that the theoretical potentials might have merit, the two-conformer model could not by its nature represent a fair test of them because the parameters of this model would necessarily have accommodated themselves to give the best possible fit to the data. The second (cosine potential) model<sup>3</sup> provided a better test, both because the assumed presence of two conformers was dropped and because estimates of the effects of vibrational averaging ("shrinkage") were included. However, it also contained an assumption that could be viewed as weakening the experimental case for the existence of two stable conformers in that no allowance had been made for the changes in the bond lengths and bond angles indicated by the ab initio results to be a consequence of torsion angle change. We emphasize that other features of both models made them quite sophisticated ones for the time, and both gave excellent fits to the data from experiments at three temperatures.

In view of the widespread use of ab initio calculations for structure prediction, it seemed worthwhile to test against our diffraction data a model incorporating additional assumptions drawn from the theoretical data. This model would be based on the three-term cosine potential described above, but the pseudoconformers would include the changes in the parameters obtained by comparison of ab initio optimized structures at various fixed values of the torsion angle  $\text{ClCCCl}$ . Details of this model and the results obtained from it are the subjects of this paper.

## Experimental Section

The diffraction photographs were those on which the original study was based;<sup>2</sup> the experimental conditions are described there. The data were obtained by retracing<sup>3</sup> the plates used in the published work.<sup>2</sup> (The principal reason for the retracing was a desire to make use of improved photometric equipment.) Instead of the hand-drawn backgrounds from the earlier work, computer-generated ones were removed and the data processed by our usual methods.<sup>5</sup> The electron-scattering amplitudes were taken from tables.<sup>6</sup> In addition to the data from the three original sample temperatures (0, 80, and  $190^\circ\text{C}$ ), additional data were obtained at still higher temperatures, 405 and  $525^\circ\text{C}$ .<sup>3</sup> The new high-temperature data were intended to improve the

reliability of the conformational energy measurements, but unfortunately extensive sample decomposition occurred at both higher temperatures and the data were found unsuitable for inclusion in the new study.<sup>3b</sup>

## Design of the Model

Any model of a system of molecules responsible for an electron-diffraction pattern necessarily is built on certain assumptions that may carry important consequences for some of the parameter measurements. For molecules such as oxalyl chloride wherein the main matter of interest is the torsional potential function, it has been our practice to represent this potential by a series of the type  $2V(\phi) = \sum_i V_i [1 - \cos i(180 - \phi)]$ , with  $i = 1, 2$ , and  $3$ , and to represent the system by a set of pseudoconformers chosen at suitable intervals of  $\phi$  each weighted by a Boltzmann factor determined by the potential.<sup>7</sup> The problem to be faced in the design of the more elaborate model was the selection of appropriate additional assumptions concerning the structures and vibrational properties of the pseudoconformers. We decided to construct a model (henceforth model A) invoking certain results of ab initio calculations for the former and the results of such calculations coupled with normal coordinate analyses for the latter. It was done as follows. A set of pseudoconformers was defined at suitable intervals of the torsion angle  $\angle \text{ClCCCl}$ , and the structures were optimized with use of the programs GAUSSIAN 90<sup>8</sup> and SPARTAN<sup>9</sup> as described in the following section. The normal frequencies and Cartesian force constants were then calculated for the optimized anti form. These were converted to symmetrized internal force constants and scaled to fit the observed wavenumbers<sup>10</sup> with a new version of the program ASYM20.<sup>11</sup> Using the set of force constants derived for the anti form and omitting the very low-frequency torsional mode, the root-mean-square amplitudes, perpendicular amplitude corrections, and centrifugal distortions were calculated with ASYM20 for the molecular frames of each pseudoconformer.<sup>12</sup> (Details and interpretations of these results will be presented in a future article.) The structure of each pseudoconformer was defined in terms of the parameters of the anti conformer ( $\phi = 180^\circ$ ), to which were added the differences between parameter values for the form in question and the anti form obtained from comparison of the optimized ab initio structures. The vibration properties of each pseudoconformer were defined in a similar fashion: each distance was assigned an amplitude determined by the difference between its calculated value and that calculated for the anti form.

As a result of this procedure, the structures and vibrational amplitudes of the entire system were defined in terms of these properties for the anti conformer. The parameters to be fitted for this model A of the oxalyl chloride system were chosen as the distances  $r(\text{C}=\text{O})$ ,  $r(\text{C}-\text{C})$ ,  $r(\text{C}-\text{Cl})$ ; the angles  $\angle(\text{C}-\text{C}=\text{O})$  and  $\angle(\text{C}-\text{C}-\text{Cl})$ ; several groups of vibrational amplitudes; and the potential constant  $V_1$ ,  $V_2$ , and  $V_3$  in the three-term potential function. Thirteen pseudoconformers spaced at  $15^\circ$  intervals over the range  $0^\circ \leq \phi \leq 180^\circ$  were included. The structures were defined in  $r_\alpha$  space wherein distances are free from the effects of harmonic vibration ("shrinkage"), and the usual corrections to  $r_a$  and  $r_g$  were applied.<sup>13</sup>

In the introductory paragraphs we have referred to our unpublished reanalysis of the oxalyl chloride data. The model for this work will henceforth be designated B. Model B differs from A principally in that the bond distances and bond angles of the pseudoconformers were assumed to be unaffected by torsion. Minor differences in the way the frame amplitudes for the pseudoconformers were estimated and assigned also exist.

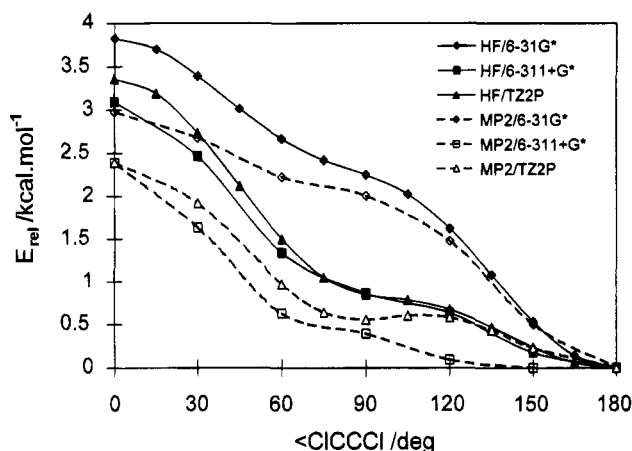


Figure 2. Energy dependence of optimized structures on torsion angle for several basis sets.

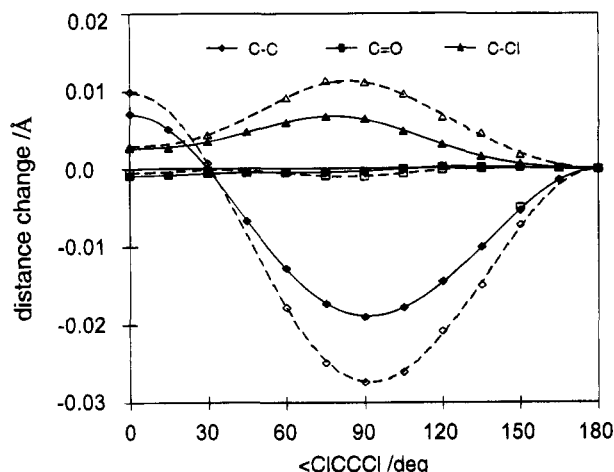


Figure 3. Theoretical variation of bond length with torsion angle from HF/6-31G\* basis (solid lines) and MP2/6-31G\* (dotted lines).

### Quantum Mechanical Calculations

To help us decide which particular set of structural parameter differences to use for setting up the several pseudoconformers of model A, geometry optimizations at several levels of ab initio theory were carried out for selected pseudoconformers. Some based on smaller basis sets were repeats of those carried out before;<sup>4</sup> for logistical reasons the earlier results were not readily accessible. The current calculations included complete structure optimizations over the range  $0^\circ \leq \phi \leq 180^\circ$  at several levels: HF/6-31G\* and HF/TZ2P<sup>4</sup> at  $15^\circ$  intervals and MP2/6-31G\*, HF/6-311+G\*, MP2/6-311+G\*, and MP2/TZ2P at  $30^\circ$  intervals except for a couple of extra points for the last. With addition of the HF and MP2 sets of calculations using the standard 6-31G\* and 6-311+G\* bases, and the MP2/TZ2P set, our results constitute a significant extension of the earlier theoretical work<sup>4</sup> on this molecule. A second reason for these calculations was a desire to verify the important conclusion from the earlier work that there is no theoretical basis for the existence of a stable second conformer. The MP2 optimizations with the large bases were carried out for this purpose. To our surprise, however, the complete optimizations at the MP2/TZ2P level revealed a very shallow minimum in the region of  $\phi = 90^\circ$ —the only theoretical suggestion of a possible stable gauche conformer we found. Energy curves from several levels of theory are shown in Figure 2, and Figures 3 and 4 show the predicted variation of structural parameters with torsion angle for two of these. Equilibrium parameter values from the calculations at several levels are given in Table 1.

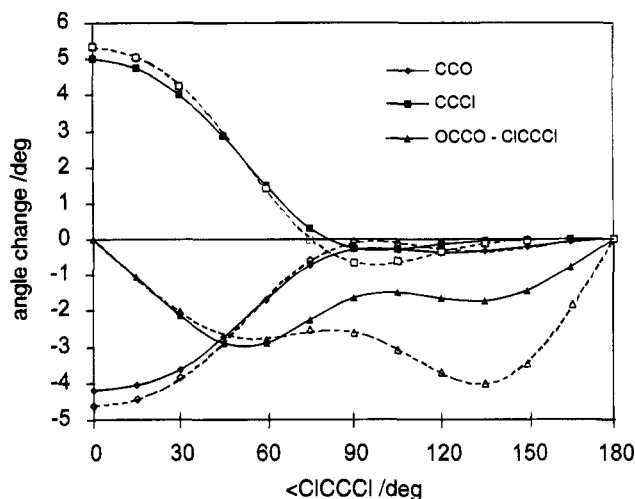


Figure 4. Theoretical variation of bond angle with torsion angle from HF/6-31G\* basis (solid lines) and MP2/6-31G\* (dotted lines).

### Refinement Conditions and Results

The 13 pseudoconformers comprising the model described above generate a total of 117 interatomic distances which, given the assumed conformational changes, are specified by only five geometrical parameters. Because these changes were found to be similar for all basis sets, we elected to use the results of the relatively inexpensive HF/6-31G\* optimizations in our model with an eye toward future work on more complicated systems. The nine vibrational amplitudes associated with the distances characterizing each pseudoconformer are linked throughout the set of pseudoconformers by the differences calculated as described above—again, those derived from force fields based on the ab initio results. Refinements of the five geometrical parameters, nine amplitude parameters, and three potential constants defining both models A and B were carried out in the usual way by fitting of the corresponding theoretical intensity curves simultaneously to the two average experimental curves for each temperature.<sup>14</sup> The process converged smoothly in every case.

Results are summarized in Tables 2 and 3. Values for the bond lengths, bond angles, and torsion-insensitive distances in Table 2 are averages over all pseudoconformers, each Boltzman weighted according to the torsional potential; values of the torsion-sensitive distances are for the  $180^\circ$  pseudoconformer. All experimental amplitude values (Table 3) are similarly weighted average "frame" amplitudes—amplitudes from which the effect of torsion is not included. The calculated amplitudes are for the  $180^\circ$  pseudoconformer. The correlation matrix for the parameters of the preferred model (A) for the  $0^\circ$  experiment is found in Table 4; the correlation matrices for both models at the other temperatures are similar. Intensity and radial distribution curves for the preferred model are shown in Figures 5 and 6.

### Discussion

As mentioned above, the earlier theoretical study of the torsional dependence of the energy of oxalyl chloride identified only one stable conformer (the planar anti form) even at very high levels of theory. It was therefore unexpected that extension of one series of these calculations to the MP2/TZ2P level from the MP2/TZ2P/HF/TZ2P would predict a second stable conformer—a gauche (or skew) one with a C1CCCC1 torsion angle equal to  $89.8^\circ$ . To the extent that higher levels of theory should be more reliable, this result is pleasing because it removes, at least qualitatively, the former inconsistency between theory and

TABLE 1: Results of Optimizations of Oxalyl Chloride from Different Levels of *ab Initio* Theory<sup>a</sup>

	$r_e(\text{C}=\text{C})$	$r_e(\text{C}-\text{C})$	$r_e(\text{C}-\text{Cl})$	$\angle_e(\text{CCO})$	$\angle_e(\text{CCCl})$	$E$ , hartrees
HF/6-31G*	1.165	1.545	1.736	123.2	113.3	-1144.403 225 2
MP2/6-31G*	1.202	1.547	1.744	123.9	112.1	-1145.308 991 4
HF/6-311+G*	1.158	1.549	1.734	123.5	113.2	-1144.518 190 3
MP2/6-311+G*	1.193	1.554	1.743	124.0	112.2	-1145.631 403 5
HF/TZ2P	1.156	1.547	1.744	123.8	112.8	-1145.541 942 5
MP2/TZ2P	1.188	1.549	1.761	124.6	111.4	-1145.736 725 8
MP2/TZ2P(gau) <sup>b</sup>	1.187	1.522	1.773	124.5	110.7	-1145.735 840 0

<sup>a</sup> Distances in angstroms and angles in degrees. Unless indicated, all results are for the anti form. <sup>b</sup> Gauche angle is equal to 89.78°.

TABLE 2: Distances, Bond Angles, Composition, and Rotational Potential Constants for Models of Oxalyl Chloride<sup>a,b</sup>

parameter	0 °C				80 °C				190 °C			
	model A		model B		model A		model B		model A		model B	
	$r_a, \angle_a$	$r_g$	$r_a$	$r_a, \angle_a$	$r_a, \angle_a$	$r_g$	$r_a$	$r_a, \angle_a$	$r_a, \angle_a$	$r_g$	$r_a$	$r_a, \angle_a$
$r(\text{C}=\text{O})$	1.180(2)	1.184	1.183	1.180(2)	1.179(2)	1.183	1.182	1.179(2)	1.181(2)	1.184	1.183	1.181(2)
$r(\text{C}-\text{C})$	1.545(8)	1.548	1.545	1.544(8)	1.532(10)	1.535	1.533	1.531(10)	1.545(12)	1.548	1.545	1.544(11)
$r(\text{C}-\text{Cl})$	1.747(3)	1.749	1.748	1.747(2)	1.745(3)	1.748	1.747	1.745(3)	1.748(3)	1.751	1.749	1.748(3)
$r(\text{C}_1\text{O}_6)$	2.413(7)	2.415	2.413	2.413(7)	2.399(9)	2.402	2.400	2.399(9)	2.408(10)	2.410	2.408	2.409(10)
$r(\text{O}_5\text{Cl}_3)$	2.604(4)	2.605	2.604	2.602(4)	2.598(6)	2.600	2.599	2.599(6)	2.605(5)	2.607	2.605	2.605(6)
$r(\text{C}_1\text{Cl}_4)$	2.724(7)	2.727	2.725	2.722(6)	2.716(10)	2.718	2.717	2.713(10)	2.733(15)	2.735	2.732	2.730(12)
$r(\text{O}_6\text{Cl}_3)$	2.927(6)	2.929	2.926	2.921(6)	2.917(12)	2.918	2.913	2.907(12)	2.929(14)	2.931	2.926	2.920(12)
$r(\text{O}_5\text{O}_6)$	3.480(8)	3.481	3.480	3.472(8)	3.470(11)	3.471	3.470	3.456(10)	3.480(11)	3.481	3.480	3.465(11)
$r(\text{Cl}_3\text{Cl}_4)$	4.306(9)	4.308	4.307	4.307(8)	4.294(15)	4.295	4.294	4.297(13)	4.309(18)	4.311	4.309	4.316(13)
$\angle(\text{CCO})$	123.8(4)			124.1(3)	124.0(6)			124.1(5)	123.7(6)			123.7(5)
$\angle(\text{CCCl})$	111.8(3)			111.7(3)	111.8(6)			111.7(5)	111.9(6)			111.9(5)
$V_1$	1.99(102)			1.48(66)	1.45(84)			1.13(64)	1.49(70)			1.57(66)
$V_2$	-0.40(71)			-0.10(50)	0.02(72)			0.11(62)	0.03(67)			-0.11(63)
$V_3$	0.81(26)			0.75(32)	1.05(50)			1.12(58)	0.43(37)			0.19(42)
$X(\text{anti})^c$	0.67			0.65	0.62			0.59	0.43			
$R^d$	0.068			0.067	0.098			0.096	0.091			0.090

<sup>a</sup> Distances in angstroms, angles in degrees, and potential constants in kcal mol<sup>-1</sup>. Uncertainties in parentheses are estimated 2σ for distances and angles and 1σ for potential constants; uncertainties for  $r_g$  and  $r_a$  are similar to those for  $r_a$ . <sup>b</sup> For model values for all distances and angles except  $r(\text{O}_6\text{Cl}_3)$ ,  $r(\text{O}_5\text{O}_6)$ , and  $r(\text{Cl}_3\text{Cl}_4)$  are averages from Boltzmann weighting of pseudoconformer distribution. <sup>c</sup> Estimated mole fraction.

<sup>d</sup> Quality-of-fit factor  $R = [\sum w_i \Delta_i^2 / \sum w_i (s_i I_i(\text{obsd}))^2]^{1/2}$  where  $\Delta_i = s_i I_i(\text{obsd}) - s_i I_i(\text{calcd})$ .

TABLE 3: Root-Mean-Square Amplitudes of Vibration for Model A of Oxalyl Chloride<sup>a</sup>

	0 °C			80 °C			190 °C		
	model A	model B	calcd <sup>b</sup>	model A	model B	calcd <sup>b</sup>	model A	model B	calcd <sup>b</sup>
$l(\text{C}=\text{O})^c$	0.034(4)	0.034(3)	0.037	0.033(4)	0.033(4)	0.037	0.036(3)	0.036(3)	0.038
$l(\text{C}-\text{C})^c$	0.061(9)	0.062(9)	0.054	0.057(13)	0.056(12)	0.055	0.063(12)	0.063(11)	0.058
$l(\text{C}-\text{Cl})^c$	0.048(3)	0.049(3)	0.052	0.049(4)	0.049(4)	0.055	0.054(4)	0.055(4)	0.058
$l(\text{C}_1\text{O}_6)^c$	0.063(8)	0.063(6)	0.059	0.061(8)	0.060(8)	0.062	0.065(8)	0.066(8)	0.066
$l(\text{O}_5\text{Cl}_3)^c$	0.056(5)	0.056(5)	0.056	0.060(7)	0.060(8)	0.059	0.061(7)	0.062(6)	0.064
$l(\text{C}_1\text{Cl}_4)^c$	0.065(8)	0.064(7)	0.066	0.072(12)	0.072(15)	0.071	0.078(14)	0.081(13)	0.078
$l(\text{O}_6\text{Cl}_3)^c$	0.082(13)	0.080(13)	0.093	0.124(22)	0.125(41)	0.103	0.112(40)	0.122(51)	0.115
$l(\text{O}_5\text{O}_6)^c$	0.068(21)	0.068(10)	0.057	0.065(29)	0.065(29)	0.060	0.077(43)	0.078(43)	0.064
$l(\text{Cl}_3\text{Cl}_4)^c$	0.067(10)	0.064(10)	0.066	0.079(14)	0.079(19)	0.073	0.088(25)	0.081(25)	0.051

<sup>a</sup> In angstroms. Quantities in parentheses are estimated 2σ uncertainties. <sup>b</sup> From scaled quantum mechanical symmetrized force field. See text.

<sup>c</sup> Experimental values for models A and B are Boltzmann-weighted averages over all pseudoconformers.

the results of both spectroscopic and electron diffraction experiments. However, as Figure 2 shows, the quantitative aspects of the torsional potential yielded by even this level of theory do not inspire much confidence: the curve for the MP2/TZ2P calculation is very flat over a substantial range of torsion angle in the region of the gauche form, and the predicted gauche-anti barrier is extremely small—about 0.03 kcal/mol. All in all, it must be concluded that the theoretical evidence for the existence of a stable second conformer in gaseous oxalyl chloride is weak at best.

Curves of the torsional potential  $V(\phi)$  from experiment are plotted in Figure 7 as a function of  $\phi = \angle \text{ClCCl}$  together with the  $E(\phi)$  values from the MP2/TZ2P calculations. In principle, the  $V(\phi)$  curves should be temperature independent and thus be similar. There are clearly substantial differences, but given the difficulty of evaluating the individual  $V_i$  from the diffraction data, the agreement among them seems satisfactory. At a suitable level of theory the  $E(\phi)$ , also temperature

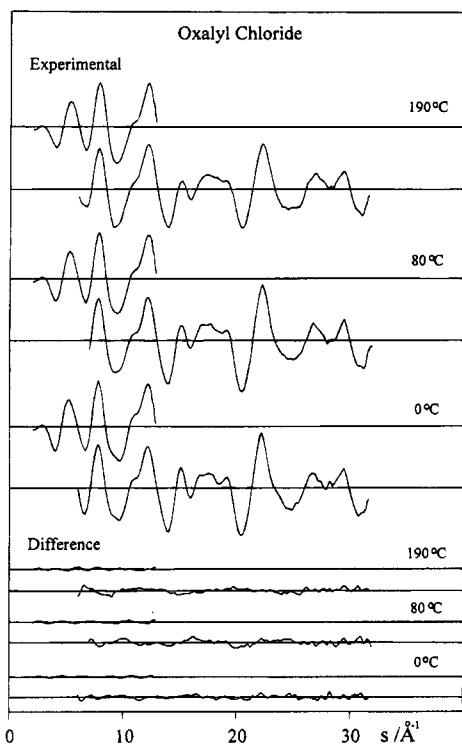
independent, should be comparable to the correct  $V(\phi)$ . The average  $V(\phi)$  and the  $E(\phi)$  curves are indeed similar as is seen by their shapes and by comparison of the potential constants for the former and those representing a fit to the latter ( $V_1/\text{kcal mol}^{-1} = 1.59$  and 1.88,  $V_2 = -0.11$  and  $-0.64$ , and  $V_3 = 0.74$  and 0.56 respectively for  $V(\phi)$  and  $E(\phi)$ ). They also agree quantitatively on the syn-anti energy differences, but their predictions of the gauche-anti energy difference and the equilibrium gauche torsion angle differ by about 0.5 kcal mol<sup>-1</sup> and about 12°. Taking into account the uncertainties in  $E(\phi)$  revealed by our extensive set of *ab initio* optimizations, and on the experimental side the uncertainties inherent in our model assumptions which carry over into  $V(\phi)$ , we feel this agreement is very satisfactory.

The geometrical parameter values and the amplitudes from this work are in excellent agreement with our early published ones with the possible exception of the C-C bond, which was found to be slightly smaller in the early work ( $r_a = 1.534(5)$ ,

**TABLE 4: Correlation Matrix ( $\times 100$ ) for Model A for Experiment at 0 °C**

	$\sigma_{LS}^a$	$r_1$	$r_2$	$r_3$	$\angle_1$	$\angle_2$	$V_1$	$V_2$	$V_3$	$l_1$	$l_2$	$l_3$	$l_4$	$l_5$	$l_6$	$l_7$	$l_8$	$l_9$
$r(C=O)$	0.051	100	-1	-11	-8	22	-3	2	-5	-5	-12	-4	7	-2	4	-9	<1	-3
$r(C-C)$	0.280		100	-4	-41	-20	12	-18	-4	-9	4	-35	30	-21	16	-46	-5	-31
$r(C-Cl)$	0.062			100	30	-17	2	4	-8	8	40	-7	13	-3	4	6	4	6
$\angle(C-C=O)$	14.0				100	-64	-50	51	-6	-7	15	-3	-32	-19	-43	31	-9	23
$\angle(C-C-Cl)$	11.3					100	43	-43	15	16	-10	28	-3	8	10	-13	13	-7
$V_1$	50.7						100	-95	63	-7	-2	-9	24	22	41	19	30	6
$V_2$	35.7							100	-74	6	2	10	-25	-24	-44	-3	-25	8
$V_3$	13.3								100	-12	-1	-8	2	6	14	23	26	13
$l(C=O)$	0.087									100	12	44	-3	18	11	-7	2	3
$l(C-C)$	0.315										100	-14	<1	-13	-7	-3	2	<1
$l(C-Cl)$	0.080											100	-16	20	4	4	4	10
$l(C_1 \cdots O_6)$	0.215												100	31	41	-13	-2	-13
$l(O_5 \cdots Cl_3)$	0.149													100	79	7	2	-7
$l(C_1 \cdots Cl_4)$	0.263														100	-4	7	-17
$l(Cl_3 \cdots O_6)$	0.430															100	16	2
$l(O_5 \cdots O_6)$	0.724																100	4
$l(Cl_3 \cdots Cl_4)$	0.336																	100

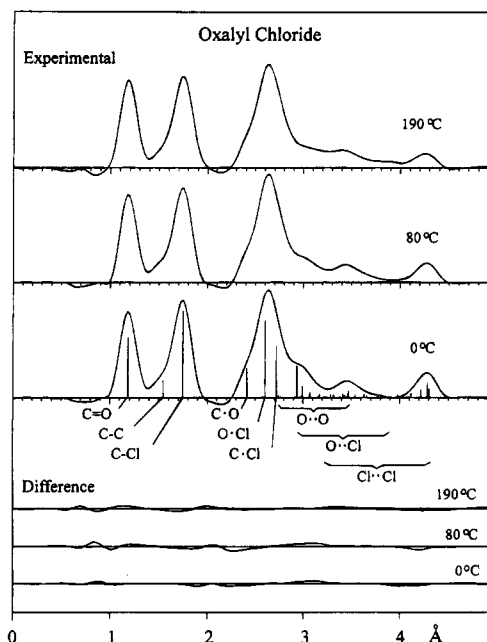
<sup>a</sup> Standard deviations ( $\times 100$ ) from least-squares refinements. Distances ( $r$ ) and amplitudes ( $l$ ) are in angstroms, and angles ( $\angle$ ) are in degrees.



**Figure 5.** Averaged experimental intensity ( $sI_m(s)$ ) curves. The shorter (longer) curves are from the longer (shorter) camera distances. The difference curves are experimental minus theoretical.

1.524(5), and 1.526(5) Å at 0, 80, and 190 °C). This agreement is especially satisfying, for it implies that results obtained from the simpler models so often used in the past in similar conformational problems can still be accepted with confidence. According to the theoretical results summarized in Figures 3 and 4, one should expect some small changes in the average values of some of the parameters as the temperature of the mixture is increased and the relative amount of the gauche form increases correspondingly. The largest change is expected in the length of the C–C bond, which should become smaller. There is a small decrease in the experimental value of this parameter for both models as the temperature increases from 0° to 80°, but the trend is not observed in the next step.

The matters of greatest experimental interest for oxalyl chloride are the equilibria between conformers and the associated thermodynamic quantities. The equilibria are somewhat complicated to evaluate from the dynamic model, but a rough approximation may be gotten from analyzing the torsional



**Figure 6.** Radial distribution curves. The bars marking the distances are proportional to the weights of the terms. The symbols separated by two dots designate torsion-sensitive distances. The convergence factor  $B$  was equal to 0.0025 Å<sup>-2</sup>. Difference curves are experimental minus theoretical.

distribution in terms of a pair of Gaussians, the areas of which are identified with the amounts of the conformers. The analysis was done as follows. The torsional potential defined by the three refined values of the  $V_i$  for a given temperature was first calculated over the range 0–180° at 15° intervals. A Gaussian representing the anti form located at  $\phi = \angle ClCCl = 180^\circ$  was defined by a height and a width parameter, and a second Gaussian for the gauche form was defined by similar parameters plus a position parameter  $\phi_{0,g}$ . The sum of these Gaussians was then least-squares-fitted to the distribution determined by the refined  $V_i$  by adjustment of the five parameters. The relative areas of the Gaussians (that for the gauche doubled to take account of the degeneracy of this form) were taken to represent the relative amounts of the components. For model A the mole fractions of the anti form at 0, 80, and 190 °C are 0.67, 0.62, and 0.43. For model B it was not possible to obtain a value from the highest temperature data; the values at 0 and 80 °C are 0.65 and 0.59. A van't Hoff plot of these data for model A (Figure 8) yields the results  $\Delta U^\circ = U_g^\circ - U_a^\circ = 1.13(18)$  kcal

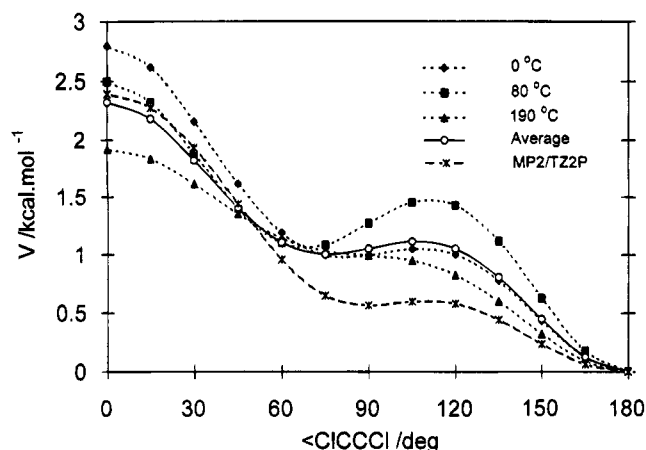


Figure 7. Torsional potential curves for oxalyl chloride.

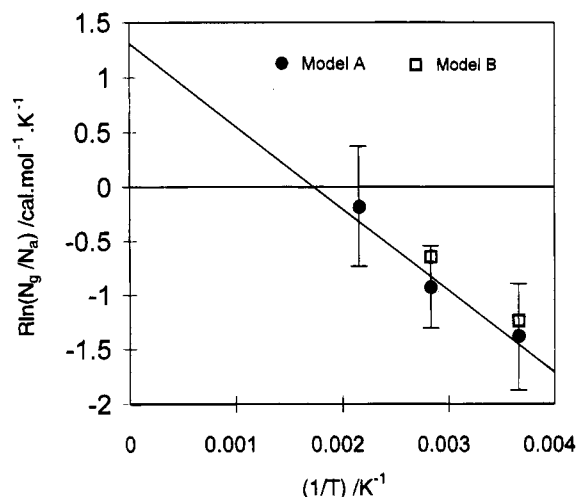


Figure 8. Van't Hoff plot of the anti-gauche equilibrium constants.

$\text{mol}^{-1}$  and  $\Delta S^\circ = S_g^\circ - S_a^\circ = 2.63(56) \text{ cal mol}^{-1} \text{ K}^{-1}$  ( $2\sigma$  uncertainties) for the equilibrium  $N_A \rightleftharpoons N_G$ . A similar plot for model B was not possible because the procedure was unsuccessful for the highest temperature data. However, the two points for the lowest temperatures of this model are seen to be consistent with those for model A. As with the structural parameters, it is gratifying that the thermodynamic results determined many years ago from the much simpler two-conformer, nondynamic model of oxalyl chloride ( $\Delta E^\circ =$

$0.75(50) \text{ kcal mol}^{-1}$  and  $\Delta S^\circ = 1.31(148) \text{ cal mol}^{-1} \text{ K}^{-1}$  are in excellent agreement with those from model A.

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**Supplementary Material Available:** Tables of the average intensity curves for experiments at 0, 80, and 190 °C (3 pages). Ordering information is given on any current masthead page.

## References and Notes

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- (12) Evaluation of these differences was made simple by fitting a function to the parameter changes obtained from the ab initio calculations. The value for any parameter of a pseudoconformer defined by any torsion angle was thus obtained by adding the calculated difference to the corresponding parameter value for the anti form.
- (13)  $r_g(T) = r_a(T) + \delta r(T) + K(T)$ ,  $r_a(T) = r_g(T) - l(T)^2/r$ .  $K$ ,  $\delta r$ , and  $\rho^2$  are respectively a perpendicular amplitude correction, centrifugal distortion, and mean-square vibrational amplitude;  $r_g$  is the thermal average distance, and  $r_a$  is the distance consistent with the electron-scattering theory.
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