80 mV more negative and the wave height is about one-half of that of the CpC wave.

At 0° in pH 4.5 McIlvaine buffer, CpU shows one ill-defined wave close to background discharge; I and $E_{1/2}$ are similar to those of CpC wave I (Table I).

(2) **Cyclic Voltammetry.** At scan rates below 1 V/sec, CpG and CpU produce a faint inflection near background discharge. At higher scan rates, the peak for CpU becomes visible; its E_p becomes more negative and the $i_p/ACv^{1/2}$ ratio increases rapidly with increasing v (Figures 3 and 9; Table IV).

(3) **Ac Polarography.** At 25°, CpU and CpG have the same general total ac pattern as CpC, showing the depression from background centered around −0.6 V but only rounded peak I at about −1.2 V (Table V; Figure 8).

CpU does not show distorted current oscillations below pH 8; CpG exhibits such oscillations at all pH's in addition to the pitlike formations.

The height of peak I above background for both compounds increases with increasing pH to pH 5 and then decreases. For CpG, the base current is depressed below that of the background at potentials more negative than peak I.

CpG shifts the background discharge to more positive potential. The magnitude of the shift is about 150 mV at pH 2 and, as with CpC, is proportional to pH up to pH 5 and then decreases to vanish at pH 8. CpU shifts background discharge by a relatively small but variable magnitude of 10 to 40 mV, which is apparently pH independent. At pH 4.0, the magnitude of the positive background shift for the dinucleoside phosphates increases in the order CpU < CpC < CpG.

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Conformational Analysis. I. Molecular Structure, Composition, Trans–Gauche Energy and Entropy Differences, and Potential Hindering Internal Rotation of Gaseous Oxalyl Chloride as Determined by Electron Diffraction

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Abstract: Electron-diffraction patterns obtained from gaseous oxalyl chloride at 0, 80, and 190° reveal it to consist of a mixture of trans and gauche conformers instead of the generally supposed trans and cis. The greater stability of the trans and gauche forms relative to the cis may be understood in terms of the "bent" single-bond pair concept of the carbon–oxygen double bond. Assuming that the geometries of the two conformers differ only in the torsion angle about the C–C bond, some of the more important parameter values at 0° with estimated errors of 2σ are $r_{C=O} = 1.182$ Å (0.002), $r_{C-C} = 1.534$ Å (0.005), $r_{C-Cl} = 1.744$ Å (0.002), $\angle$CCO = 124.2° (0.3), $\angle$CCCl = 111.7° (0.2), ϕ (the gauche torsion angle relative to 0° for the trans form) = 125.0° (5.8), $l_{C=O} = 0.0380$ Å (0.0025), $l_{C-C} = 0.0482$ Å (0.0026), $l_{C-Cl} = 0.0532$ Å (0.0026), and δ (the rms torsion amplitude for the trans conformer) = 22.1° (3.3). The mole fractions of the trans conformer at 0, 80, and 190° were found to be 0.676 (0.084), 0.513 (0.100), and 0.424 (0.102), respectively, from which the energy difference ($\Delta E° = E°_g - E°_t$) was calculated to be 1.38 ($\sigma = 0.35$) kcal/mol and the entropy difference ($\Delta S° = S°_g - S°_t$) to be 2.3 ($\sigma = 1.0$) cal mol^{-1} deg^{-1}. For an assumed hindering potential of the form $2V = V_1(1 - \cos\phi) + V_2(1 - \cos 2\phi) + V_3(1 - \cos 3\phi)$, a value with estimated standard deviation of 13.2 ± 4.2 kcal/mol was obtained for $V^* = V_1 + 4V_2 + 9V_3$. This together with two other conditions on the V_i's imposed by the experimental results gave $V_1 = 1.01 \pm 0.22$, $V_2 = 0.85 \pm 0.19$, and $V_3 = 0.98 \pm 0.43$, all in kcal/mol. The barrier separating the trans from the gauche conformer is 2.00 ± 0.42 and that separating the two gauche forms is 0.61 ± 0.44 kcal/mol.

During the past 2 decades oxalyl chloride has been the subject of a number of experimental and interpretive spectroscopic studies involving infrared work on the gas,[1-5] liquid or solution,[1-3,5] and solid;[5,6] Raman on the liquid[1-5] and solid;[5] and ultraviolet on the gas,[7-10] liquid,[7] and solid.[11] An important concern in most of this work was the composition of the material, *i.e.*, the possible existence of more than one rotational conformer. The solid phase appears to consist only of the expected coplanar s-trans form (symmetry D_{2h}), and although some of the results for the gas and liquid phases have been interpreted[2,4] as consistent with the presence of just this form, the weight of the evidence seems to favor as well the presence in these phases of a second conformer generally agreed to be the coplanar s-cis rotamer (symmetry C_{2v}). The composition of liquid oxalyl chloride at room temperature was estimated[5] to be 15–20% cis with the trans form the more stable by 2.2–2.8 kcal/mol.[1,5] No evidence for a cis form was found in an X-ray diffraction investigation of the crystal[12] nor in

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(1) B. D. Saksena and R. E. Kagarise, *J. Chem. Phys.*, **19**, 987 (1951).

(2) J. S. Ziomek, A. G. Meister, F. F. Cleveland, and C. E. Decker, *ibid.*, **21**, 90 (1953).

(3) B. D. Saksena, R. E. Kagarise, and D. H. Rank, *ibid.*, **21**, 1613 (1953).

(4) J. L. Hencher and G. W. King, *J. Mol. Spectrosc.*, **16**, 158 (1965).

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(7) B. D. Saksena and R. E. Kagarise, *ibid.*, **19**, 999 (1951).

(8) J. W. Sidman, *J. Amer. Chem. Soc.*, **78**, 1527 (1956).

(9) B. D. Saksena and G. S. Jauhri, *J. Chem. Phys.*, **36**, 2233 (1962).

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(11) H. Shimada, R. Shimada, and Y. Kanda, *Spectrochim. Acta, Part A*, **23**, 2821 (1967).

(12) P. Groth and O. Hassel, *Acta Chem. Scand.*, **16**, 2311 (1962).

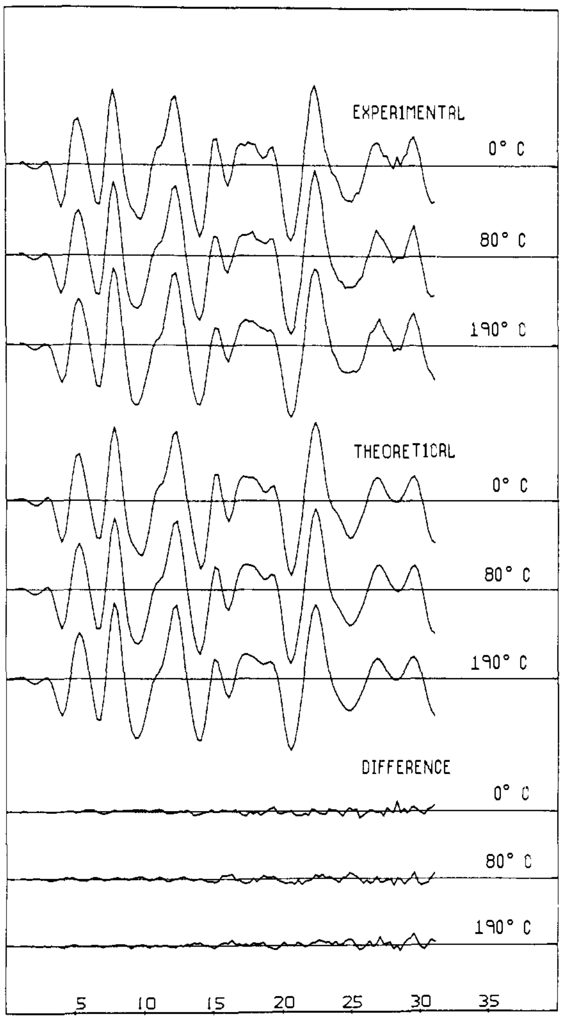

Figure 1. Intensity curves for oxalyl chloride. The experimental curves are composites of data from the long and intermediate nozzle-to-plate distance experiments. The theoretical curves were calculated from the parameter values of Table I.

an electron-diffraction investigation of the gas;[13] however, the molecule did not appear to be strictly coplanar in the crystal, and in the gas-phase work it was necessary to assume a large amplitude of torsional vibration in order to obtain a satisfactory fit to the observed intensity distribution.

Several years ago an electron-diffraction investigation of oxalyl chloride was undertaken in this laboratory[14] as a part of a program of study of conjugated systems. Experiments were carried out at nozzle temperatures of about −15 and 135°. Although the work was not completed, it was clear that the two sets of data differed by more than could be accounted for by only a trans species of molecule present at each temperature. Recently we have again become interested in the oxalyl chloride problem, stimulated in part by the somewhat controversial spectroscopic picture, by our broader interest in conjugated systems, and by the hope of obtaining accurate values for the energy and entropy differences of the two suspected conformers. The latter objective requires experiments at a minimum of three temperatures if statistical error estimates are desired. It seemed best that the conditions of these experiments be otherwise as similar as possible, and accordingly we decided to ignore the old data and to begin anew.

Experimental Section

Materials. Oxalyl chloride (98%) from the Aldrich Chemical Co. was used without further purification. Before each experiment, however, the bulb containing the sample was pumped for several minutes.

Apparatus and Procedure. Diffraction photographs were made in the Oregon State apparatus at nozzle-tip temperatures of 0, 80, and 190° under the following conditions: plates, 8 × 10 in. Kodak lantern slide (medium); sector, angular opening proportional to r^3; beam currents, 0.4–0.5 μA; exposure times, 0.5–3.0 min; ambient apparatus pressure during exposure, 0.4–0.8 $\times 10^{-5}$ Torr; electron wavelength, 0.05702–0.05707 Å as determined by calibration against diffraction patterns from gaseous CO_2 (r_a(C–O) = 1.1646 Å and r_a(O···O) = 2.3244 Å);[15] nozzle-to-plate distances, 74.982 and 29.984 cm. For each temperature three plates from the long and four from the intermediate distance were selected for analysis which was carried out in the way described previously.[16] Data from each temperature covered the approximate ranges $1.00 \leqslant s \leqslant 13.00$ (long distance) and $7.00 \leqslant s \leqslant 32.00$ (intermediate distance) in intervals $\Delta s = 0.25$ ($s = 4\pi\lambda^{-1}\sin\theta$; 2θ is the scattering angle). Smooth, hand-drawn backgrounds were subtracted from plots of the reduced data to yield intensity curves sI_m in a form corresponding to the formula[17]

$$sI_m(s) = k\sum_{i\neq j} n_{ij}A_iA_jr_{ij}^{-1}V_{ij}\cos|\eta_i - \eta_j|\sin r_{ij}s \qquad (1)$$

The 21 sets of data (seven at each temperature) comprising these curves were used in the eventual structure refinement.[18]

Trial Structures

Deductions of the trial structures for the three temperatures were based upon radial distribution curves calculated according to

$$D(r) = \frac{2}{\pi}\Delta s\sum_{s_{min}}^{s_{max}} I_m'(s)\exp(-Bs^2)\sin rs \qquad (2)$$

The $I_m'(s)$ were composites of the data at a given temperature obtained by summing the several sets from each camera distance, scaling the resulting pair of sum sets by comparison of values in the region of overlap ($7.00 \leqslant s \leqslant 13.00$), averaging the overlapping data, and multiplying the result by $Z_{Cl}Z_OA_{Cl}^{-1}A_O^{-1}$. Data for the unobserved region $0 \leqslant s \leqslant 1.00$ were at first omitted, and in later calculations taken from models close to the final one. The convergence coefficient B was given the value 0.0020 in all cases. The composite curves, on the same scale and before multiplication with the factor $Z_{Cl}Z_OA_{Cl}^{-1}A_O^{-1}$, are shown in

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(13) K. Hjortaas, *Acta Chem. Scand.*, **21**, 1379 (1967).

(14) B. Haas and K. Hedberg, unpublished work.

(15) See V. Plato, W. Hartford, and K. Hedberg, *J. Chem. Phys.*, **53**, 3488 (1970), for sources of these values.

(16) G. Gundersen and K. Hedberg, *ibid.*, **51**, 2500 (1969).

(17) The n's are numbers of symmetrically equivalent interatomic distances of magnitude r, the V's are vibration factors, the A's are electron scattering amplitutes multiplied by s^2, and the η's are the phases of scattered waves. The electron scattering amplitudes were obtained from Schafer, Yates and Bonham's tables [L. Schafer, A. C. Yates, and R. A. Bonham, *J. Chem. Phys.*, **55**, 3055 (1971)] as follows. Tabulated values ($\Delta s = 1$) for accelerating potentials of 40 and 70 kV were linearly interpolated to yield values corresponding to the 44 kV used in our experiments. After multiplication by s^2 the results were smoothed, interpolated by fitting a cubic equation to four points to yield values at $s = 0.25$, and again smoothed. The phases were obtained by interpolating tabulated values at 10, 40, 70, and 100 kV with the aid of a cubic equation to yield values at 44 kV followed by an additional interpolation as described for the amplitudes.

(18) These data will appear immediately following this article in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JACS-73-1003. Remit check or money order for $4.00 for photocopy or $2.00 for microfiche.

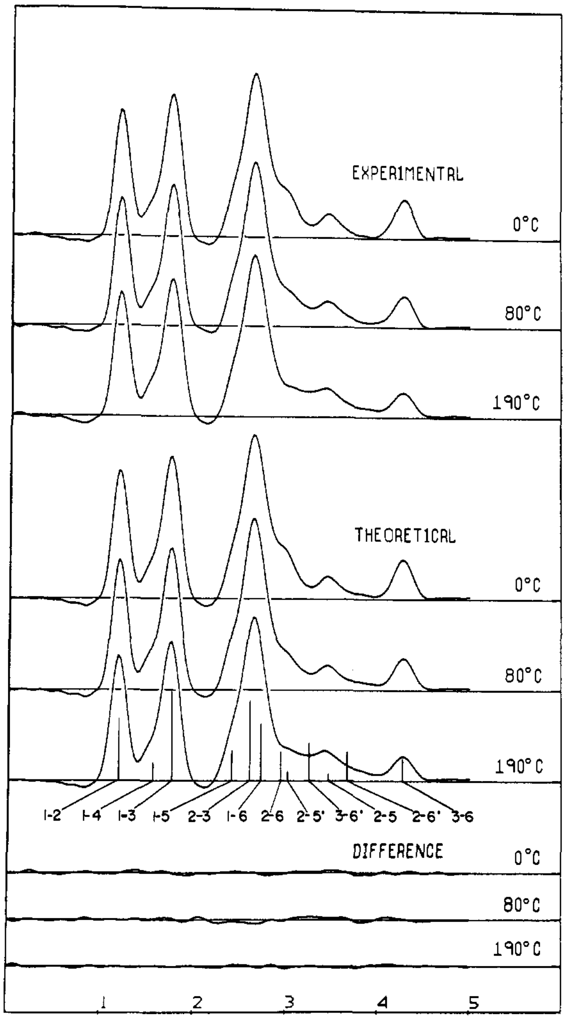

Figure 2. Radial distribution curves for oxalyl chloride. The curves were calculated from the intensity curves of Figure 1 with $B = 0.0020$. Unobserved experimental intensity data for the region $0 \leq s \leq 1.00$ were taken from the theoretical curves. The vertical lines indicate the interatomic distances of the final models; the lengths of the lines are proportional to the weights of the distances.

Figure 1 and the radial distribution curves, also on the same scale, are shown in Figure 2.

The radial distribution curves are very similar throughout the range $r < 2.8$ Å (where the nontorsion-sensitive distances appear) and quite different for $r > 2.8$ Å. Assignments of interatomic distances to the peaks for $r < 2.8$ Å are obvious in most respects; these are indicated by the vertical bars shown in Figure 2. A theoretical radial distribution curve calculated for the trans form of the molecule based on these distance values is in very poor agreement with the experimental curves for $r > 2.8$ Å (compare curves A and D, Figure 3). One notes particularly the well-resolved peak at 4.2 Å, which corresponds to the Cl···Cl distance in the trans molecule; its area is much smaller at each of the experimental temperatures than in curve D. We conclude that gaseous oxalyl chloride must contain a second conformer in substantial proportion at each of our experimental temperatures. Our data do not support the conclusion from the earlier electron-diffraction work[13] that the molecule is coplanar trans with large amplitude of torsional oscillation.

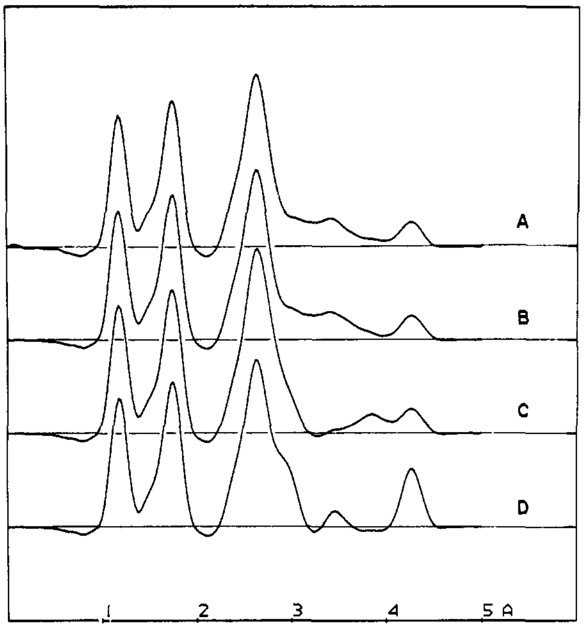

Figure 3. Comparison of radial distribution curves: (A) experimental at 190°; (B) theoretical for 42.4% trans, 57.6% gauche; (C) theoretical for 45.0% trans, 55.0% cis; (D) theoretical for pure trans.

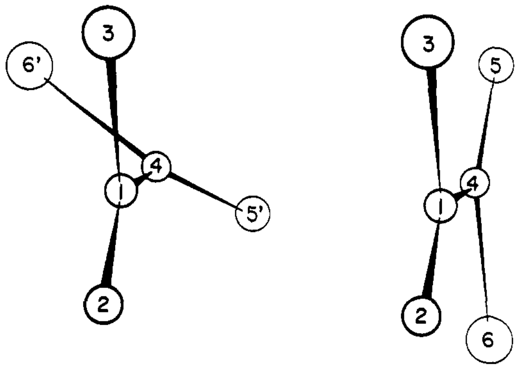

Figure 4. Diagrams of the gauche and trans forms of oxalyl chloride with atom numbering.

The outcome of our effort to identify the second conformer was mildly surprising. Assuming that the structures of this conformer and the trans differ from each other only in the torsion angle[19] (∠OCCl, OCCl), it was impossible to fit the radial distribution curves well over the distance range $r > 2.8$ Å with any mixture of cis and trans conformers. This may be seen in the appearance of curve C, Figure 3, compared with curves A and D. Curve C, which represents a mixture containing approximately equal amounts of cis and trans conformers, has a trans Cl···Cl peak at 4.2 Å in good agreement with the observed peak, but is in poor agreement with the observed curve over the range $2.8 < r < 4.0$ Å. Because neither the cis nor trans conformers have distances in the region of 3.2 Å (compare curves C and D) where distances are required experimentally, and because only the trans form can account for the 4.2 Å peak, it may be concluded that the cis conformer cannot be present in significant amounts. A gauche form (Figure 4) with

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(19) The assumption, although not true in an exact sense, is surely plausible because the nontorsion-sensitive distances can be fit very precisely with parameter values reasonable for a single conformer.

Table I. Final Structural Results[a,b] for Oxalyl Chloride at Different Temperatures

	0°		80°		190°	
Parameter[c]	r	l[d]	r	l[d]	r	l[d]
C=O	1.182 (0.002)	0.0380 (0.0025)	1.181 (0.002)	0.0350 (0.0027)	1.180 (0.002)	0.0422 (0.0027)
C—C	1.534 (0.005)	0.0482 (0.0026)	1.524 (0.005)	0.0479 (0.0026)	1.526 (0.005)	0.0506 (0.0028)
C—Cl	1.744 (0.002)	0.0532	1.745 (0.002)	0.0529	1.745 (0.002)	0.0556
$C_1\ldots O_5$	2.405 (0.005)	0.0606 (0.0040)	2.398 (0.005)	0.0583 (0.0040)	2.397 (0.006)	0.0662 (0.0046)
$C_1\ldots Cl_6$	2.716 (0.005)	0.0656	2.710 (0.006)	0.0633	2.713 (0.006)	0.0712
$O_2\ldots Cl_3$	2.598 (0.004)	0.0606	2.595 (0.004)	0.0583	2.596 (0.004)	0.0662
$O_2\ldots Cl_6$	2.955 (0.006)	0.0961 (0.0105)	2.933 (0.006)	0.1175 (0.0182)	2.945 (0.007)	0.1283 (0.0231)
$O_2\ldots O_5$	3.445 (0.006)	0.0585 (0.0142)	3.449 (0.006)	0.0506 (0.0181)	3.438 (0.007)	0.0665 (0.0289)
$Cl_3\ldots Cl_6$	4.254 (0.007)	0.0716 (0.0096)	4.272 (0.007)	0.0764 (0.0131)	4.260 (0.008)	0.0811 (0.0189)
$O_2\ldots Cl_6'$	3.672 (0.035)	0.2508 (0.0756)	3.686 (0.053)	0.3108 (0.0818)	3.646 (0.030)	0.2878 (0.0816)
$O_2\ldots O_5'$	3.001 (0.028)	0.1808	2.982 (0.039)	0.2408	3.006 (0.024)	0.2178
$Cl_3\ldots Cl_6'$	3.197 (0.070)	0.1808	3.158 (0.102)	0.2408	3.239 (0.057)	0.2178
∠CCO	124.2 (0.3)		124.4 (0.3)		124.2 (0.3)	
∠CCCl	111.7 (0.2)		111.8 (0.3)		111.9 (0.3)	
ϕ[e]	125.0 (5.8)		128.1 (9.0)		121.5 (4.6)	
δ[f]	22.1 (3.3)		16.2 (5.0)		20.5 (6.1)	
% trans	67.6 (8.4)		51.3 (10.0)		42.4 (10.2)	
R[g]	0.103		0.129		0.116	

[a] Distances (r) and root-mean-square amplitudes (l) in ångströms; angles in degrees. [b] Parenthesized values are 2σ and include estimates of systematic error. [c] Unprimed items refer either to nontorsion-sensitive distances or to torsion-sensitive distances in the trans conformer. Primed items refer to torsion-sensitive distances in the gauche conformer. [d] Bracketed quantities were refined, with constant differences, as a group. [e] Average torsion angle in gauche form relative to 0° for the trans conformation. [f] Root-mean-square amplitude of torsional motion in the trans conformer. [g] $R = [\Sigma w_i\Delta_i^2/(\Sigma w_i I_i^2(\text{obsd}))]^{1/2}$, where $\Delta_i = I_i(\text{obsd}) - I_i(\text{calcd})$.

torsion angle equal to about 120° (relative to 0° for the trans) does have distances in the 3.2 Å region, however, and preliminary calculations quickly showed that mixtures of gauche and trans forms could account for the observed distance spectrum. Comparison of curve B, Figure 3, with curve A illustrates this point.

Structure Refinements

Refinements of the structures were carried out by the method of least squares based on intensity curves[20] in the form of eq 1, adjusting a single theoretical curve to the seven sets of data simultaneously. A unit weight matrix was used and the harmonic vibration approximation $V_{ij} = \exp[-\langle l_{ij}^2\rangle s^2/2]$ was assumed. The gaseous mixtures were assumed to consist of only gauche and trans conformers having the same structures except for torsion angle.[19] Thus, in addition to a composition parameter there were six geometrical parameters, conveniently chosen to be $r_{C=O}$, r_{C-C}, r_{C-Cl}, ∠CCO, ∠CCCl, and ϕ_g (the torsion angle of the gauche form). In early refinements a seventh geometrical parameter, ϕ_t, was included to test the possibility of noncoplanarity for the trans conformer; it was discarded in favor of a torsional amplitude parameter (δ) which was felt to be more appropriate. The amplitude parameters were taken to be (the atom numbering is shown in Figure 4) $l_{C=O}$, $l_{C-Cl} = l_{C-C} + \Delta$, $l_{15} = l_{23} = l_{16} + \Delta'$, l_{25}, l_{26}, l_{36}, and $l_{36}' = l_{25}' = l_{26}' + \Delta''$, and δ, the root-mean-square amplitude of the torsional oscillation of the coplanar form. The Δ's were assumed constants. The parameter δ was not handled in the same way as the l's because, even though the torsional vibration might be regarded as harmonic, the distance distribution for a given atomic pair arising from torsional motion in the trans conformer is not symmetrically disposed with respect to the equilibrium distance. In order to approximate the correct distance distribution, the values of all torsion-sensitive distances for the trans conformer were calculated at values of ϕ, the torsion angle, corresponding to $\phi = 0, \pm0.25\delta, \pm0.50\delta, \cdots \pm2.00\delta$.[21] These were weighted according to the (Gaussian) angle-distribution function and the set of terms normalized. Thus, a given torsion-sensitive distance in the trans conformer was represented by a total of nine distance terms, each of which was assumed to be affected by molecular frame vibrations described by a single l value.[22] It seemed unnecessary to describe the assumed harmonic torsional motion in the gauche conformer in the same way because the distance distribution arising from this motion is more nearly symmetric about the equilibrium distance.

Final Results and Discussion

Molecular Structure. The final structural results are summarized in Table I; the theoretical intensity and radical distribution curves corresponding to these models of the mixtures are shown in Figures 1 and 2 together with difference curves. The error estimates in Table I, which include estimates of contributions from systematic error and correlation among the observations, were calculated as described previously.[23] As expected, the values for most of the distances and angles show little or no variation with temperature, while the amplitude values on the whole tend to increase with increasing temperature. We regard the consistency of the values of individual distances and angles as good; except for $r_{O_2\ldots Cl_6}$ the differences with temperature are encompassed by the sums of the associated errors. Accordingly, each of the three sets of results in Table I (aside from the composition) may be taken as a fair statement of the structure of

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(20) K. Hedberg and M. Iwasaki, *Acta Crystallogr.*, 17, 529 (1964).

(21) The angle distribution is given by $\exp[-(\Delta\phi)^2/(2\langle\delta^2\rangle)]$. The distances of a given type corresponding to the two values $\pm\Delta\phi$ are identical, of course.

(22) It seemed unnecessary to give the different distance terms different l values because the torsional amplitude was found to be small.

(23) M. M. Gilbert, G. Gundersen, and K. Hedberg, *J. Chem. Phys.*, 56, 1692 (1972). The error in δ was obtained from $2\sigma_\delta = 2\sqrt{2}\sigma_{LS}$ where σ_{LS} was taken from the least-squares refinement.

both forms of oxalyl chloride. The correlation matrix from the refinement of the 0° data is given in Table II; the other correlation matrices are similar. To the extent that the assumption of essentially identical structures (exclusive of torsion angle) for the gauche and trans conformers plays a role, all geometrical and amplitude parameter values in Table I are weighted averages for the two forms. However, there is no evidence that the structures of the two forms are significantly different.

Energy and Entropy Differences of the Conformers. The measured variation of sample composition with temperature allows one to determine the energy and entropy differences between the trans and gauche conformers by use of the formula

$$\frac{N_g}{N_t} = 2e^{\Delta S^\circ/R}e^{-\Delta E^\circ/RT} \tag{3}$$

where N_g and N_t are the fractions of gauche and trans molecules and the factor 2 is the ratio of the statistical weights of the gauche to the trans forms. The results (Figure 5) are $\Delta E^\circ = E^\circ_g - E^\circ_t = 1.38$ ($\sigma = 0.35$) kcal/mol and $\Delta S^\circ = S^\circ_g - S^\circ_t = 2.3$ ($\sigma = 1.0$) cal mol^{-1} deg^{-1}. Our value for ΔE° is lower than the values obtained from spectroscopic measurements (2.2 ± 0.2 kcal/mol;[5] 2.8 kcal/mol[1]), but we attach no special significance to the difference because the spectroscopic measurements were made on the liquid phase. Our value for ΔS° is slightly lower than the 3 cal mol^{-1} deg^{-1} calculated[5] from all fundamental frequencies except the torsional based on an assumed cis–trans interconversion, but it falls well within the range 2–4 cal mol^{-1} that seems to have been observed for similar conformational equilibria.[5]

Conformation and Bonding. The existence of a gauche conformer, instead of the generally accepted cis, in equilibrium with the trans form presents a very interesting bonding problem. In the simple, conventional view, both the trans and cis forms should be stabilized by conjugation and destabilized by repulsions between eclipsed atoms; to the extent that these repulsions are greater in one form, the other will predominate. However, this picture of the bonding does not easily account for the absence of the cis and the presence of substantial amounts of a gauche conformer with a torsion angle about 120° from that of the trans.

An appealingly simple explanation of the trans–gauche composition of oxalyl chloride may be had by viewing the bonding in terms of contributions from structures involving the concepts of, first, π-system conjugation and second, double bonds formed from a pair of "bent" single bonds.[24] The π-system conjugation may be regarded as stabilizing the trans and cis conformers relative to noncoplanar forms and the bent-bond structures as stabilizing the trans and gauche conformers, which are seen to have staggered bond configurations, relative to the eclipsed-bond cis and skew (60°) forms. If it is imagined that the conformations reflect balances between conjugation stabilization (E_C), repulsions between peripheral atoms ($E_A = E_A(\mathrm{Cl}\cdots\mathrm{Cl}) + E_A(\mathrm{O}\cdots\mathrm{O})$; $E_A' = 2E_A(\mathrm{O}\cdots\mathrm{Cl})$), and peripheral-bond electron-pair repulsions (E_B); one may assign respectively to the trans, cis, gauche, and skew forms the relative energies $E_A' - E_C$, $E_A - E_C + E_B$, 0, and E_B. From the dominance of the trans, the presence of the gauche, and the absence of the cis and skew forms, one may write that E_B, $E_B + E_A - E_C \gg 0 > E_A' - E_C$. It may be concluded that $E_B \gg 0$, $E_C > E_A'$, and $E_B \gg E_C - E_A$.

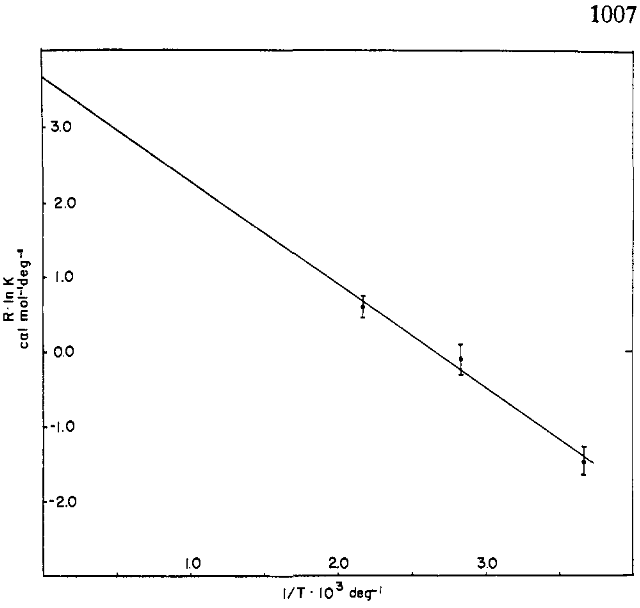
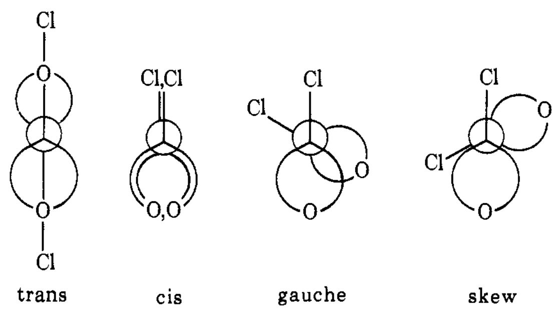


Figure 5. Arrhenius plot of mixture-composition data ($K = N_g/N_t$). The half-lengths of the vertical bars indicate 1σ. Least-squares straight line.



The bent-bond concept provides a plausible explanation for the structures of other similar conjugated molecules as well. For example, glyoxal[25] and butadiene[26] appear to exist nearly entirely in the trans conformation at room temperature, suggesting the atom repulsions are weak relative to conjugation stabilization. On the other hand, hexafluorobutadiene[27] and hexachlorobutadiene[28] as well as certain other halogen-stubstituted butadienes exist mostly if not entirely in the gauche conformation; in these cases the interatom repulsions are presumably much greater than in, say, oxalyl chloride because of the additional interactions between central and terminal halogen atoms.

Table III contains the values of the geometrical parameters of several related compounds. It is clear that conjugation has relatively little effect on the carbon–oxygen bond length, for this bond is about equally long in glyoxal (or oxalic acid) and acrolein, molecules

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(24) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, pp 136–142.

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Table II. Correlation Matrix for Parameters of Oxalyl Chloride at 0°[a]

	r_{C-C}	$r_{C=O}$	r_{C-Cl}	∠CCO	∠CCCl	δ	ϕ	l_{C-C}
σ[b]	0.0015	0.0005	0.0005	0.093	0.082	1.16	2.05	0.0006
	1.000	−0.003	−0.145	−0.345	−0.109	0.248	−0.193	−0.273
		1.000	−0.075	−0.128	0.324	0.113	−0.094	0.072
			1.000	0.286	−0.048	0.156	−0.100	0.143
				1.000	−0.639	−0.535	0.024	−0.071
					1.000	0.399	−0.057	0.243
						1.000	−0.338	0.049
							1.000	0.070
								1.000

[a] Distances (r) and root-mean-square amplitudes (l) in ångströms; angles in degrees. [b] Standard deviations from least-squares.

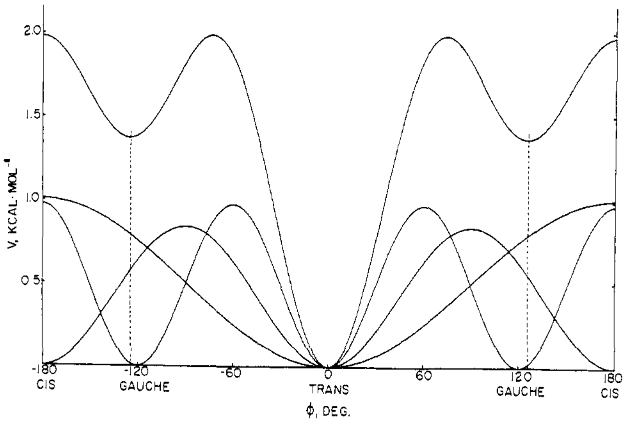

Figure 6. Form of hindering potential. The dashed lines indicate the measured gauche torsion angle.

in which conjugation is expected to be involved to different extents. Moreover in oxalyl chloride, which contains a substantial amount of gauche conformer and in which, therefore, conjugation may be assumed to play a substantially smaller role, this bond is only 0.02 Å shorter than in the other molecules. The carbon–carbon bond lengths (with the possible exception of that for oxalic acid which seems somewhat long) are generally in accord with these ideas, they diminish as conjugation increases.

The agreement (Table III) between the geometries of oxalyl chloride deduced from the previous[13] and current studies is quite satisfactory in view of the previous study's assumption of a pure trans conformation for the molecule.

Rotational Barrier. For molecules such as oxalyl chloride the potential hindering internal rotation may be written in the form

$$2V(\phi) = V_1(1 - \cos\phi) + V_2(1 - \cos 2\phi) + V_3(1 - \cos 3\phi) + \ldots \quad (4)$$

where higher terms in the series are assumed to be negligible. A power series expansion in which terms larger than ϕ^2 are ignored leads to the harmonic approximation formula[29]

$$V(\phi) = {}^1\!/_4 V^*\phi^2 \quad (5)$$

where $V^* = V_1 + 4V_2 + 9V_3$. The information about rotational barriers so far as electron diffraction is concerned is contained in the distance distributions which reflect the torsional motions. After taking account of the effect of frame vibrations, these distributions are determined by the known relationship between distances and torsion angle and the probability distribution of angle

$$p'(\phi) = Q^{-1}\exp\{-V(\phi)/RT\} \quad (6)$$

which in the harmonic approximation of angle displacements (eq 5) becomes

$$p'(\phi) = Q^{-1}\exp\{-V^*\phi^2/4RT\} \quad (7)$$

The agreement between the experimental radial distribution curves and the theoretical ones (which are based upon assumed harmonic torsion-angle displacements) suggests that eq 8 may be applied with confidence to our results. Because $p'(\phi)$ is Gaussian, the values of δ allow calculation of V^* according to

$$V^*/4RT = 1/2\delta^2 \quad (8)$$

The results are 7.4, 17.8, and 14.5 kcal/mol at 0, 80, and 190°, respectively. Since V^* should be temperature independent, we take the average 13.2 ± 4.2 kcal/mol, as the best overall value for oxalyl chloride. It is pleasing that it is in good agreement with the 11.1 kcal/mol estimated from spectroscopic measurements,[5] and that it is comfortably smaller than the value estimated[29] (also from spectroscopic measurements) for butadiene where the conjugated single bond has more double-bond character.

In order to evaluate the barrier separating the trans and gauche forms of oxalyl chloride it is necessary to evaluate the individual components of V^*. It is possible to identify three conditions from the electron diffraction results which allow this to be done. They are the measurements of V^*, the condition of a potential minimum at the measured gauche angle, and the measurement of ΔE which is equal to $V(\phi)$ at the gauche angle. These conditions may be respectively formulated as

$$V_1 + 4V_2 + 9V_3 = 13.2 \text{ kcal/mol} \quad (9)$$

$$V_1 - 2.42V_2 + 0.95V_3 = 0 \quad (10)$$

$$0.787V_1 + 0.671V_2 + 0.017V_3 = 1.38 \text{ kcal/mol} \quad (11)$$

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(29) W. G. Fateley, R. K. Harris, F. A. Miller, and R. E. Witkowski, *Spectrochim. Acta*, 21, 231 (1965).

$l_{C=O}$	l_{15}	l_{36}	l_{25}	l_{26}	l_{36}	% trans
0.0007	0.0011	0.0033	0.0050	0.0035	0.0266	0.0296
−0.080	−0.291	−0.128	0.001	−0.334	−0.107	0.018
0.053	−0.054	−0.032	−0.016	−0.123	−0.042	0.008
0.101	0.067	−0.040	0.019	−0.067	−0.033	0.044
−0.131	−0.008	0.275	0.085	0.468	0.133	0.062
0.173	−0.269	−0.182	0.036	−0.301	−0.042	−0.024
0.086	0.035	−0.333	−0.030	−0.419	−0.246	0.251
0.060	0.135	−0.216	−0.026	0.106	0.650	−0.544
0.535	0.162	0.025	−0.038	−0.055	−0.017	−0.044
1.000	0.190	−0.002	−0.063	−0.119	−0.030	−0.064
	1.000	−0.069	−0.183	0.004	−0.012	−0.133
		1.000	0.103	0.467	−0.408	0.562
			1.000	0.173	0.181	0.145
				1.000	0.040	0.399
					1.000	−0.689
						1.000

Table III. Some Geometrical Parameter Values for Oxalyl Chloride and Related Molecules[a]

Parameter	Oxalyl chloride[b]	Oxalyl chloride[c]	Glyoxal[d]	Oxalic acid[e]	Acrolein[f]
r_{C-C}	1.528 ± 0.005	1.534 ± 0.003	1.525 ± 0.003	1.548 ± 0.004	1.481 ± 0.004
$r_{C=O}$	1.181 ± 0.002	1.189 ± 0.002	1.207 ± 0.007	1.208 ± 0.003	1.209 ± 0.002
r_{C-Cl}	1.745 ± 0.002	1.749 ± 0.003			
∠CCO	124.2 ± 0.3	124.1 ± 0.5	121.2 ± 0.2	123.1 ± 0.9	124.7 ± 0.7
∠CCCl	111.8 ± 0.2	112.4 ± 0.5			

[a] Distances in ångströms, angles in degrees. [b] This investigation. [c] Reference 13. [d] Reference 25. [e] Z. Nahlovsky, B. Nahlovsky, and T. G. Strand, *Acta Chem. Scand.*, **24**, 2617 (1970). [f] M. Traetteberg, *ibid.*, **24**, 373 (1970).

which yield the values with standard deviations V_1 = 1.01 ± 0.22, V_2 = 0.85 ± 0.19, and V_3 = 0.98 ± 0.43, all in kcal/mol. Figure 6 shows the form of the potential and its components. The barrier separating the trans from the gauche conformer is calculated to be 2.00 ± 0.42 kcal/mol and that separating gauche from gauche, 0.61 ± 0.44 kcal/mol.

Torsional Frequencies. Insofar as the quadratic approximation of the potential (eq 5) is valid, it is possible to calculate the torsional frequency for the trans conformer from the usual formula $\nu = (2\pi)^{-1}(k/\mu_I)^{1/2}$ where k is equal to $V^*/2$ and μ_I is the reduced moment of inertia. The result is 55 cm^{-1}, in perfect agreement with the observed value assigned to this mode.[5] The analogous calculation for the torsional frequency of the gauche conformer, which has not been observed, is perhaps less valid since the potential well is much shallower. However, it is interesting that the value predicted in the quadratic approximation from $k = (d^2V/d\phi^2)_{\phi=125}$ is about 30 cm^{-1}, in a range apparently experimentally inaccessible to the spectroscopic workers.

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