Another system in which persistent luminescence has been observed is F_2 + NO, where light, presumably from FNO,[11] peaks at $[NO]_0 = 2[F_2]_0$. As previously mentioned, sharply peaked downstream emission has also been observed in the F + H_2[3] and F + CH_3OH[4] reactions. These systems are all more complicated than O_3 + NO, containing possibilities of series and parallel reactions. Their detailed analysis has not yet been completed.

Experimental Section

Chemiluminescence from the NO + O_3 reaction was studied in a 2-in. diameter Teflon-coated Pyrex flow tube at 25 °C and 4.3 Torr with luminescence observed ca. 70 cm downstream of the mixing zone by a cooled R406 photomultiplier. The flow velocity was 25 cm/s. A steady flow of ozone was obtained in O_2 diluent by directing the output from a Wellsbach Model T406 ozonizer directly into the flow tube. At full voltage the ozonizer produces ca. 2% ozone, at which concentration the titration is too sharply peaked to give a meaningful comparison with theory. However, when the voltage of the ozonizer is reduced to 60–75 V, it produces ca. 0.25–1.25% O_3 (as measured by the end point of the titration) and gives the titration curves shown in Figure 2. Nitric oxide (Linde) was taken directly from a lecture bottle. Its flow was adjusted by means of a Granville-Phillips metal seal series 203 variable leak. The flow from the ozonizer was measured by a Brooks mercury piston flowmeter and that of NO by directing the flow into an evacuated calibrated volume and measuring the rate of pressure increase in the volume. System pressure was measured with a 0–100 Torr MKS Baratron gauge. Flows were permitted to stabilize for several hours before taking measurements.

Acknowledgment. The author thanks Dr. A. Fontijn for several helpful conversations dealing with this work. Support of this work by the Air Force Office of Scientific Research is gratefully acknowledged.

Supplementary Material Available: Table of rates as a function of $\mathcal{J}$ and s (5 pages). Ordering information is given on any current masthead page.

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Conformational Analysis. 12. 2-Chloropropenoyl Chloride. An Electron-Diffraction Investigation of the Molecular Structure, Conformational Composition, Anti–Syn Energy and Entropy Differences, and Potential Hindering Internal Rotation

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Abstract: The molecular structure of 2-chloropropenoyl chloride ($CH_2{=}CCl{-}C{=}OCl$) has been investigated at three temperatures by gas-phase electron diffraction. Two conformers were identified, a more stable anti form and a less stable planar (or near planar) syn form. The mole fractions of the anti form with uncertainties estimated at 2σ were found to be 0.775 (98) at 303 K, 0.704 (71) at 377 K, and 0.660 (75) at 475 K and correspond to $\Delta E° = E_s° - E_a° = 3.8(\sigma{=}2.2)$ kJ·mol^{-1} and $\Delta S_s° = S_s° - S_a° = 2.7(\sigma{=}5.6)$ J·mol^{-1}·K^{-1}. The energy difference and the root-mean-square torsional amplitudes for the two conformers were used to calculate a torsional potential of the form $2V = \sum V_i(1 - \cos i\phi)$ through three terms. The results are $V_1 = 2.1(\sigma{=}1.3)$, $V_2 = 7.5(\sigma{=}1.2)$, and $V_3 = 1.7(\sigma{=}0.3)$, all in kJ·mol^{-1}. No temperature dependence of the distances and angles was found. The following values, with estimated 2σ uncertainties, of the principal bond distances (r_g) and bond angles ($\angle_\alpha$) are for a "best model" comprising averages of the results from the three temperatures. (The atom numbering corresponds to the arrangement $C_1{=}C_2{-}C_3$; except for $\angle C_2{-}C_3{-}Cl$ and the torsion angles, the parameter values for the anti and syn forms were assumed equal.) $r(C_3{=}O) = 1.189$ (2) Å, $r(C{=}C) = 1.342$ (3) Å, $r(C{-}C) = 1.496$ (3) Å, $\langle r(C{-}Cl)\rangle = 1.753$ (2) Å, $\Delta r(C{-}C) = r(C_3{-}Cl) - r(C_2{-}Cl) = 0.041$ (6) Å, $r(C_3{-}Cl) = 1.774$ (4) Å, $r(C_2{-}Cl) = 1.733$ (4) Å, $\angle C{-}C{=}O = 125.5$ (6)°, $\angle C{=}C{-}C = 122.0$ (6)°, $\angle C_3{-}C_2{-}Cl = 118.3$ (4)°, $\langle \angle C_2{-}C_3{-}Cl\rangle = 113.4$ (3)°, $\Delta\angle C_2{-}C_3{-}Cl = \angle C_2{-}C_3{-}Cl(\text{syn}) - \angle C_2{-}C_3{-}Cl(\text{anti}) = 3.0°$ (assumed). The conformations of the molecule are discussed in relation to those of similar molecules.

Substitution of the aldehyde proton in conjugated aldehydes with a halogen atom has been shown to affect strongly the relative energies of the rotational conformers. In gaseous propenal[1] ($CH_2{=}CH{-}CH{=}O$) the form with the double bonds anti to each other predominates, and the energy difference $\Delta E_{s-a}° = E_s° - E_a°$ was measured to be 7.11 ± 0.17 kJ·mol^{-1}. For gaseous propenoyl chloride[2] and propenoyl fluoride[3] ($CH_2{=}CH{-}CX{=}O$) substantially greater proportions of the syn conformer are present, with $\Delta E_{s-a}° = 1.0 \pm 1.7$ kJ·mol^{-1} and 0.42 ± 0.08 kJ·mol^{-1}, respectively. For fumaraldehyde[4] ($O{=}CH{-}CH{=}CH{-}C{=}O$) only the anti–anti conformer was observed, but in fumaryl chloride[5] ($O{=}CCl{-}CH{=}CH{-}CCl{=}O$) three different conformers (anti–anti, anti–syn, and syn–syn) with about equal energies were identified.

Our investigations of conjugated systems are intended to provide the structural data that will permit a better understanding of the conformational behavior of such systems. 2-Chloropropenoyl chloride (Figure 1; hereafter CPC) is an especially interesting case because of its structural similarity to 2,3-dichloro-1,3-butadiene,[6] oxalyl chloride,[7] and propenoyl chloride,[2] which have different conformational properties: although the more stable form is the anti form in each case, the second form in 2,3-dichloro-1,3-butadiene and oxalyl chloride is gauche (respectively about 15% and 60% at high temperatures), but in propenoyl chloride it is planar or near planar syn. We had expected the conformers of CPC to

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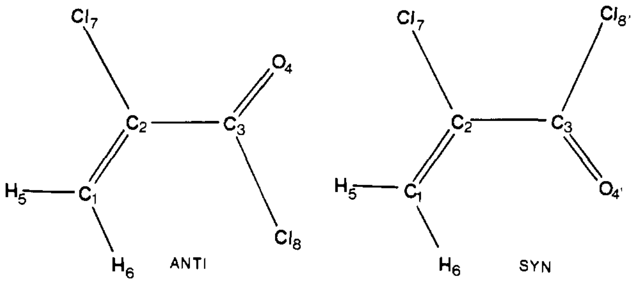

Figure 1. Diagrams of conformers of 2-chloropropenoyl chloride with atom numbering.

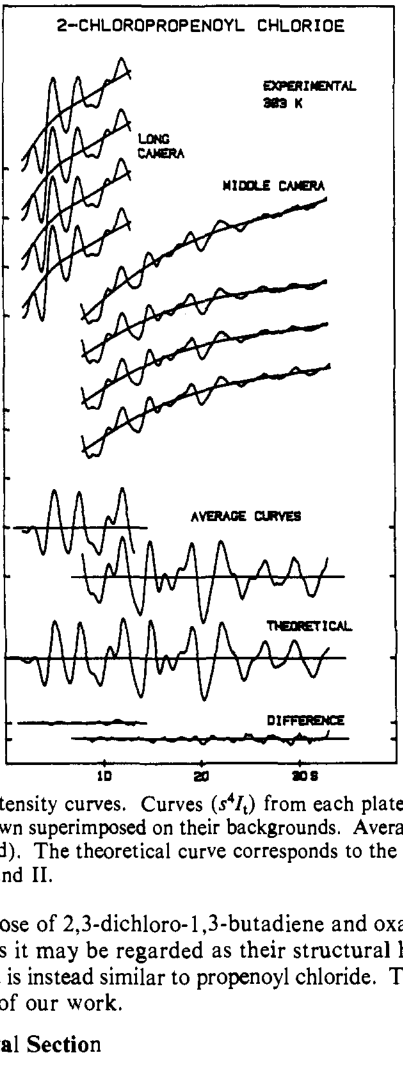

Figure 2. Intensity curves. Curves (s^4I_t) from each plate magnified 7 times are shown superimposed on their backgrounds. Average curves are $s(s^4I_t$ − backd). The theoretical curve corresponds to the 303 K model of Tables I and II.

resemble those of 2,3-dichloro-1,3-butadiene and oxalyl chloride inasmuch as it may be regarded as their structural hybrid. Remarkably, it is instead similar to propenoyl chloride. The following is a report of our work.

Experimental Section

The sample of CPC (>98% by GC) obtained from Willow Brook Chemical Co. was used without further purification.

Diffraction photographs were made in the Oregon State apparatus at nozzle-tip temperatures of 303, 377, and 475 K. Experimental conditions were as follows: sector shape, r^3; plates, 8 × 10 in Kodak projector slide, medium contrast; ambient apparatus pressure during exposure, (0.5–2.0) × 10^{-5} Torr; exposure times, 1.25–4.0 min; beam currents, 0.38–0.60 μA; nominal nozzle-to-plate distances, 75 cm (long camera) and 30 cm (middle camera); nominal electron wavelengths, 0.058 Å; wavelength standard, CO_2 with r_a(C=O) = 1.1646 Å and r_a(O···O) = 2.3244 Å. Three plates from each of the two camera distances were selected for analysis at each of the three temperatures. The procedures for obtaining the leveled total scattered intensity distribution ($s^4I_t(s)$) and the molecular intensity ($sI_m(s)$) have been described.[8,9] The ranges of data were $2.00 \leq s/\text{Å}^{-1} \leq 13.00$ and $8.00 \leq s/\text{Å}^{-1} \leq 33.00$. The data interval was $\Delta s = 0.25$ Å^{-1}. Figure 2 shows curves of the total scattered intensities and the final backgrounds for the experiment at 303 K. Corresponding figures for the other temperatures as well as all the intensity and background data are available as supplementary material (see the paragraph at the end of the paper).

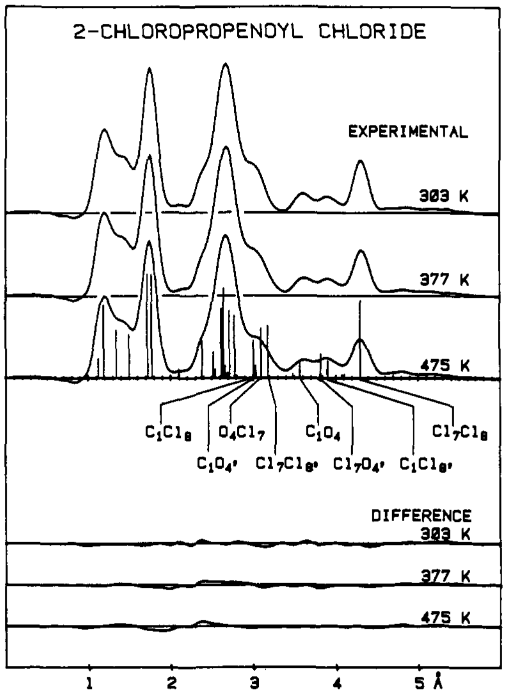

Figure 3. Radial distribution curves. The vertical lines indicate interatomic distances; their lengths are proportional to the weight of the terms. Only the important conformationally dependent distances are labeled; the rest can be identified using Table II. Difference curves are experimental minus theoretical.

The radial distribution curves (Figure 3) were calculated in the usual way by Fourier transformation of functions $I'_m(s) = Z_CZ_{Cl}A_C^{-1}A_{Cl}^{-1}sI_m(s)\exp(-Bs^2)$ with $B = 0.0020$ Å^2. Amplitudes ($F_i = s^2A_i$) and phases for all calculations were obtained from tables.[10]

Structure Analysis

The presence of more than one conformer in the gaseous sample is seen in the temperature dependence of certain torsion-sensitive peaks in the radial distribution curve. Those at 4.3 and 3.6 Å decrease as the temperature is increased, whereas those at 3.2 and 3.9 Å increase. The former may be assigned to the Cl···Cl and Cl_7···O_4 distances in the anti form of CPC and the latter in good part to these distances in a nearly planar syn form. Preliminary theoretical radial distribution curves were consistent with this interpretation.

In most of our analyses of systems similar to CPC it has been satisfactory to assume that the structures of the two conformers differed only in the value of the torsion angle about the conjugated bond. That was not the case, however, in propenoyl chloride[2] for which significantly better fits were obtained with a model that incorporated differences in the values of the C–Cl distances and the C–C–Cl angle in the two forms. The differences were attributed to steric interaction that could, in CPC, affect the parameter values of both chlorine atoms. Such a model for CPC would doubtless have unrefinable geometrical parameters, however. The parameter set below, which allowed sufficient flexibility to obtain excellent fits to our data, is the result of tests and other considerations based on experience. It includes the assumptions that neither the distances C_2–Cl_7 and C_3–Cl_8 nor the angle C_3–C_2–Cl_7 changed in the two conformers but allows for a difference in the values of C_2–C_3–Cl_8. The set is r(C–H), r(C=O), r(C=C), r(C–C), $\langle r(\text{C–Cl})\rangle = 0.5[r(\text{C}_3\text{–Cl}) + r(\text{C}_2\text{–Cl})]$, $\Delta r(\text{C–Cl}) = r(\text{C}_3\text{–Cl}) - r(\text{C}_2\text{–Cl})$, ∠C=C–C, $\angle\text{C}_3\text{–C}_2\text{–Cl}$, $\langle\angle\text{C}_2\text{–C}_3\text{–Cl}\rangle = 0.5[\angle\text{C}_2\text{–C}_3\text{–Cl(syn)} + \angle\text{C}_2\text{–C}_3\text{–Cl(anti)}]$, $\Delta\angle\text{C}_2\text{–C}_3\text{–Cl} = \angle\text{C}_2\text{–C}_3\text{–Cl(syn)} - \angle\text{C}_2\text{–C}_3\text{–Cl(anti)}$, ∠C–C=O, ∠C=C–H. Depending upon type of model, to be described later, other parameters were needed: ϕ(S), the torsion angle of the syn form; σ(A) and σ(S), the root-mean-square amplitudes of torsional vibration of the two forms; V_0(S) and α_0(S), parameters that describe a double-minimum torsional potential for the syn form.

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Table I. Values of Parameters Used To Define the Structure of 2-Chloropropenoyl Chloride[a]

	303 K		377 K		475 K		"best" values[b]	
	2S[c]	2M[d]	2S[c]	2M[d]	2S[c]	2M[d]	2S[c]	2M[d]
r(C–H)	[1.115]	[1.115]	[1.115]	[1.115]	[1.115]	[1.115]	[1.115]	[1.115]
r(C=O)	1.186 (4)	1.183 (4)	1.190 (3)	1.189 (3)	1.189 (3)	1.189 (2)	1.189 (2)	1.188 (2)
r(C=C)	1.339 (7)	1.331 (7)	1.344 (5)	1.341 (5)	1.342 (6)	1.340 (6)	1.342 (3)	1.339 (3)
r(C–C)	1.496 (8)	1.490 (8)	1.496 (5)	1.493 (6)	1.497 (6)	1.497 (7)	1.496 (3)	1.494 (4)
$\langle r(\text{C–Cl})\rangle^e$	1.753 (3)	1.750 (3)	1.752 (2)	1.752 (2)	1.754 (2)	1.754 (2)	1.753 (2)	1.752 (2)
$\Delta r(\text{C–Cl})^e$	0.037 (13)	0.040 (12)	0.047 (8)	0.048 (8)	0.028 (13)	0.036 (11)	0.041 (6)	0.043 (6)
∠C–C=C	123.1 (11)	124.6 (11)	122.4 (9)	124.4 (10)	121.5 (6)	124.7 (11)	122.0 (6)	124.6 (6)
∠C–C–H	119.6 (92)	119.2 (83)	122.3 (68)	120.6 (69)	119.7 (65)	116.4 (58)	120.7 (42)	118.4 (39)
$\angle C_3–C_2–Cl$	117.7 (8)	117.7 (14)	117.9 (8)	118.1 (9)	118.5 (4)	118.4 (9)	118.3 (4)	118.2 (6)
$\langle\angle C_2–C_3–Cl\rangle^e$	113.3 (7)	112.7 (12)	113.8 (6)	113.0 (7)	113.2 (5)	112.6 (7)	113.4 (3)	112.8 (5)
$\Delta\angle C_2–C_3–Cl^e$	[3.0]	[3.0]	[3.0]	[3.0]	[3.0]	[3.0]	[3.0]	[3.0]
∠C–C=O	125.3 (13)	125.3 (12)	125.3 (9)	125.7 (10)	125.9 (9)	125.3 (10)	125.5 (6)	125.4 (6)
$\sigma_A{}^e$	17.6 (4)	13.5 (48)	19.6 (34)	14.4 (39)	21.3 (45)	10.4 (40)		
$\sigma_S{}^e$	36.5 (226)		37.7 (128)		39.7 (124)			
$V_o{}^e$		[4.0]		[4.0]		[4.0]		
$\phi_o{}^e$		146.3 (101)		145.1 (87)		145.9 (115)		
% anti	77.5 (98)	79.8 (87)	70.4 (71)	73.0 (60)	66.0 (75)	67.7 (55)		
R^f	0.094	0.090	0.069	0.071	0.071	0.071		

[a] Distances (r_g) in angstroms, angles in degrees. Values in parentheses are estimated 2σ, those in brackets are assumed. [b] Weighted average of results from three temperatures. [c] Results for a "double-σ" torsional model, see text. [d] Results for a model with a double minima in the torsional potential function for the syn conformer, see text. [e] See test for definitions. [f] $R = [\sum w_i\Delta_i/\sum w_i(s_iI_i(\text{obsd}))^2]^{1/2}$, where $\Delta_i = s_iI_i(\text{obsd}) - s_iI_i(\text{calcd})$.

The structure refinements were carried out by least-squares[11] adjustment of a theoretical intensity curve to the two average experimental curves for each temperature with use of a unit weight matrix. Conversion of the structurally consistent set of r_α distances to r_g and r_a for use in the scattered intensity formula was done in a way similar to that described for propenoyl chloride.[2] No vibrational frequencies have been reported for CPC. We used the force field developed for propenoyl chloride,[2] modified for the additional chlorine substitution. Tables of symmetry coordinates and force constant values are available in the supplementary material. Anharmonicity constants κ were included for the bonds only, with values ($\times 10^6$) 11.71, 0.92, 1.28, 2.02, and 2.54 Å^3 for C–H, C=O, C=C, C–C, and C–Cl, respectively, estimated from the diatomic approximation.[12,13] Preliminary work revealed that the quality of fit was insensitive to reasonable variation in the C–H distance and in the angle difference $\Delta\angle C_2–C_3–Cl$. These were assigned reasonable values, the latter similar to that found in propenoyl chloride. The preliminary work also helped us decide the makeup of groups of amplitudes amenable to refinement.

Following these determinations, refinements were carried out for several models that represented the torsional aspects of the structural problem in different ways. In the simplest of these no special cognizance was taken of a possible large-amplitude torsional motion; i.e., the parameters σ were ignored. Refinement of this torsionally stiff model led to near-planar conformations for both forms (ϕ_A = 10–15°, ϕ_s = 155–165°). This is a typical result for planar molecules undergoing large-amplitude torsional motion. In a "double-σ" (or 2S) model this motion was simulated as described earlier,[2] by five pseudoconformers for each of the two forms which were assumed to have planar equilibrium conformations. The pseudoconformers were given weights determined by a Gaussian torsional potential; the refinable parameters descriptive of the torsion were σ(A) and σ(S). In a third model (2M) the assumption of planarity for the syn form was replaced by introduction of a double-minimum potential specified by a barrier height V_0 and an angle position $\alpha_0 = 180 - \phi_0$ for one of the minima with respect to the planar syn angle: $V(\alpha) = V_0(1 + (\alpha/\alpha_0)^4 - 2(\alpha/\alpha_0)^2)$. Refinements of the torsionally rigid model and the 2S model went smoothly to convergence. For the 2M model high correlation prohibited simultaneous adjustment of the parameters V_0 and α_0. We tested models with V_0 set at several values in the range $0 \leq V_0/\text{kJ·mol}^{-1} \leq 12.0$ and found fits that were significantly poorer only at the upper end. The quality of fit obtained for each of the three models, judged from both the R factors and the appearance of the radial distribution curves, was about equally good.

Results

Refinements of the three models gave similar values for the bond lengths, bond angles, and the conformational composition of the system at each temperature. However, because the representation of torsional effects differs in the three models, a direct comparison of torsional parameter values, particularly for the syn form, has little significance. A firm conclusion may nevertheless be had from the collection of results related to the torsional problem: all of these are consistent with large-amplitude librational motion in both the anti form and a planar or nearly planar syn form of the molecule. In view of this conclusion the torsionally rigid model is unrealistic and will not be further discussed. Table I contains results for the two dynamic models 2S and 2M, the latter with an arbitrary choice of V_0. Other choices of V_0 in the range cited above led to similar parameter values. Inasmuch as there is no experimental basis for selection of best model type, we have elected to present the distances and amplitudes calculated from the 2S (planar anti, planar syn) model. These are given in Table II; values for the corresponding parameters in the 2M model are similar. Table III is the correlation matrix for the parameters of Table I measured at 303 K.

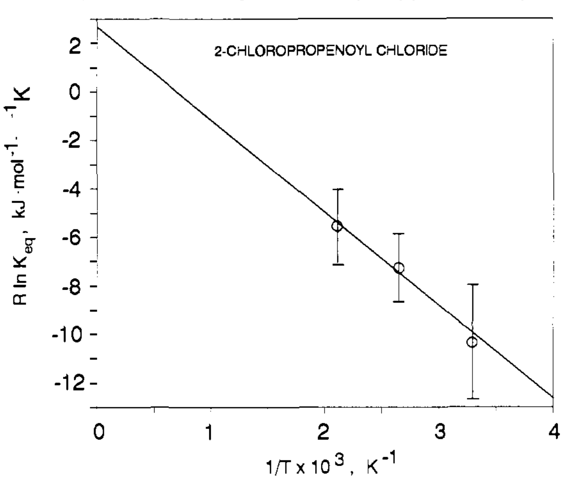

Figure 4. van't Hoff plot of conformational composition data. $K_{eq} = N_S/N_A$. Half-lengths of the bars are estimated standard deviations. Least-squares straight line.

Although anharmonicity of vibration in principle should lead to systematic change in parameter values with temperature changes, these are expected to be insignificant for bond lengths and bond angles. From Tables I and II it can be seen that, of the refined parameters, only the conformational composition and the root-mean-square torsonal amplitudes show systematic variation with temperature. "Best" values for the other parameters may therefore be calculated as weighted averages; these values are included in Table I.

Discussion

The geometrical parameter values for CPC and some related molecules are listed in Table IV. Similar values are generally

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Table II. Selected Distances (r_g) and Amplitudes (l) for 2-Chloropropenoyl Chloride from Model 2S[a,b]

	303 K		377 K		475 K	
	r	l^c	r	l^c	r	l^c
C-H	[1.115]	0.077	[1.115]	0.077	[1.115]	0.077
C=O	1.186 (4)	0.033	1.190 (3)	0.032	1.189 (3)	0.036
C=C	1.339 (7)	0.038 }(7)	1.344 (5)	0.036 }(5)	1.342 (6)	0.041 }(5)
C-C	1.496 (8)	0.043	1.496 (5)	0.043	1.497 (6)	0.048
C_2-Cl	1.734 (7)	0.050	1.730 (4)	0.052	1.740 (7)	0.054
C_3-Cl	1.771 (7)	0.050	1.777 (4)	0.052	1.768 (7)	0.055
$C_2{\cdot}H_5$	2.115 (94)	0.104	2.147 (67)	0.105	2.138 (80)	0.069
$C_2{\cdot}O_4$	2.381 (11)	0.062	2.388 (9)	0.065	2.393 (9	0.069
$C_1{\cdot}C_3$	2.489 (19)	0.067	2.485 (14)	0.069	2.473 (14)	0.074
$C_1{\cdot}Cl_7$	2.654 (12)	0.062 }(11)	2.660 (7)	0.061 }(8)	2.670 (9)	0.055 (8)
$C_3{\cdot}C_7$	2.763 (15)	0.065	2.763 (13)	0.064	2.781 (9)	0.060
			Anti Form			
$O_4{\cdot}Cl_8$	2.615 (18)	0.063 }(11)	2.611 (9)	0.056 }(8)	2.605 (10)	0.058 }(8)
$C_2{\cdot}Cl_8$	2.711 (13)	0.064	2.721 (11)	0.059	2.704 (13)	0.055
$Cl_7{\cdot\cdot}Cl_8$	4.339 (9)	0.064 (9)	4.346 (7)	0.067 (8)	4.344 (9)	0.079 (11)
$C_1{\cdot\cdot}Cl_8$	2.928 (37)	0.104 }(26)	2.931 (34)	0.109 }(25)	2.891 (26)	0.090 }(18)
$C_4{\cdot\cdot}Cl_7$	3.030 (31)	0.113	3.040 (32)	0.120	3.068 (19)	0.102
$C_1{\cdot\cdot}O_4$	3.575 (15)	0.063 (21)	3.579 (11)	0.069 (19)	3.571 (12)	0.074 (24)
			Syn Form			
$O_4{\cdot}Cl_8$	2.579 (20)	0.059 }(11)	2.575 (10)	0.056 }(8)	2.569 (11)	0.052 }(9)
$C_2{\cdot}Cl_8$	2.756 (13)	0.062	2.769 (11)	0.062	2.752 (13)	0.059
$Cl_7{\cdot\cdot}Cl_8$	3.044 (17)	0.128 (27)	3.065 (12)	0.138 (21)	3.066 (13)	0.125 (20)
$C_1{\cdot\cdot}Cl_8$	4.028 (12)	0.066 }(7)	4.038 (10)	0.070 }(6)	4.015 (11)	0.080 }(7)
$O_4{\cdots}Cl_7$	3.890 (10)	0.060	3.893 (10)	0.063	3.911 (7)	0.073
$C_1{\cdot\cdot}O_4$	2.904 (22)	0.108	2.901 (16)	0.108	2.890 (15)	0.119

[a] In angstroms. [b] Quantities in parentheses are estimated 2σ, those in brackets are assumed. [c] Quantities in braces were refined as a group. All the C·Cl and O·Cl amplitudes were refined as one group. Amplitudes without attached uncertainties were calculated from the force field and were not refined.

Table III. Correlation Matrix (×100) for Parameters of 2-Chloropropenoyl Chloride at 303 K

	σ_{LS}[a]	r_1	r_2	r_3	r_4	$\angle_5$	$\angle_6$	$\angle_7$	$\angle_8$	$\angle_9$	σ_{10}	σ_{11}	r_{12}	l_{13}	l_{14}	l_{15}	l_{16}	l_{17}	% anti
1. r(C=O)	0.0013	100	55	39	−22	21	−27	10	1	−41	21	2	0	−4	37	−18	−10	−2	−16
2. r(C=C)	0.0024		100	62	−22	11	−43	26	−25	−45	25	5	−3	32	42	−21	−25	−1	−23
3. r(C-C)	0.0027			100	−24	17	−45	7	−31	−51	27	6	8	26	44	−25	−21	−1	−26
4. ⟨r(C-Cl)⟩	0.0007				100	23	14	−20	−6	12	6	1	−2	8	4	−4	13	−1	4
5. ∠C-C=C	0.39					100	−9	−73	24	−49	−11	−27	−1	9	55	6	69	3	2
6. ∠C=C-H	3.24						100	−13	4	65	−26	4	−7	−22	−54	26	21	1	34
7. ∠C_3-C_2-Cl	0.29							100	−33	4	38	30	10	1	−14	−25	−74	−3	−14
8. ⟨∠C_2-C_3-Cl⟩	0.24								100	−26	28	−24	5	−12	−7	0	36	7	29
9. ∠C-C=O	0.46									100	−48	4	−10	−20	−72	41	−3	3	33
10. σ_A	1.55										100	4	13	10	23	−57	−32	0	−5
11. σ_S	7.55											100	7	2	−10	−37	−56	−7	−57
12. Δr(C-Cl)	0.0046												100	−14	39	−9	−7	1	−22
13. l(C=O)	0.0022													100	19	−6	−8	2	−12
14. l(O·Cl)	0.0036														100	−20	17	1	−28
15. l(Cl···Cl)	0.0030															100	42	14	57
16. l(C···Cl)	0.0088																100	6	47
17. l(C···O)	0.0073																	100	20
18. % anti	0.035																		100

[a] Standard deviations from least-squares refinements. Distances (r) and vibrational amplitudes (l) in angstroms, angles (∠) in degrees.

Table IV. Parameter Values for 2-Chloropropenoyl Chloride and Related Molecules[a]

	2-chloropropenoyl chloride	propenoyl chloride	fumaryl chloride	oxalyl chloride	2,3-dichloro-1,3-butadiene
r(C=O)	1.188 (2)	1.192 (2)	1.911 (2)	1.181 (2)	
r(C=C)	1.341 (3)	1.339 (2)	1.334 (5)		1.337 (2)
r(C-C)	1.495 (3)	1.484 (2)	1.488 (3)	1.528 (3)	1.472 (4)
r(C_3-Cl)	1.773 (3)	1.788 (2)	1.783 (2)	1.745 (2)	
r(C_2-Cl)	1.731 (3)				1.745 (2)
∠C-C=O	125.5 (6)	125.2 (2)	125.5 (4)	124.3 (2)	
∠C-C=C	122.0 (6)	123.4 (4)	125.2 (6)		126.1 (2)
∠C_2-C_3-Cl	113.4 (3)	114.1 (3)	114.6 (3)	111.8 (2)	
∠C_3-C_2-Cl	118.3 (4)				115.2 (3)
ref	this work	2	5	7	6

[a] Distances (r_a) in angstroms, angles in degrees. Parenthesized values are estimated 2σ. For all molecules the results are weighted averages of values from experiments at three or more different temperatures.

associated with the same molecular skeleton, as for example those for corresponding bonds and bond angles in CPC and propenoyl chloride, which have the backbone C=C—C=O. Fumaryl chloride has the backbone O=C—C=C—C=O, and the bonds and bond angles associated with the propenoyl moiety in this molecule are similar to those in the propenoyl compounds. The C=C—C angle in fumaryl chloride, however, is larger than in the propenoyl compounds; its value, similar to that in 2,3-di-

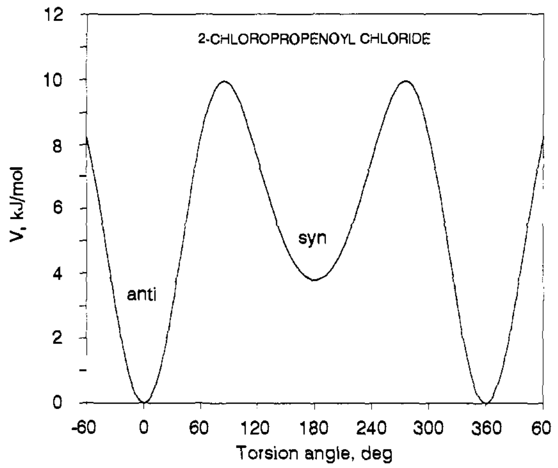

Figure 5. Potential for torsion around the conjugated single bond.

chloro-1,3-butadiene, appears to reflect the C_4 rather than the C_3O moiety. In view of these considerations, it is not surprising that the bond distances in oxalyl chloride with its O=C—C=O backbone are rather different from those in the other molecules.

In general, the bond length within the backbones of the molecules cited are in accord with conventional views about the relative importance of conjugation in the different backbone chains. This is most clearly seen in the value of the conjugated C–C single bond in CPC. Regarded as a "hybrid" of the weakly conjugated oxalyl chloride and the strongly conjugated 2,3-dichloro-1,3-butadiene, CPC is expected and found to have a C–C distance intermediate between its isoelectronic "parents". The same comparison, however, fails to predict correctly the planar or near planar conformation of CPC from the distinctly gauche forms of both parents. We suggest that the different syn conformations of these molecules are the result of different degrees of conformational stabilization (C=C—C=C > C=C—C=O > O=C—C=O) opposed by differing steric effects. The syn form of 2,3-dichloro-1,3-butadiene is nonplanar despite the strong conjugation because of even stronger repulsion between methylene hydrogens which that form would place in very close proximity. A coplanar syn form of oxalyl chloride would experience weaker van der Waals repulsion than would the butadiene, but the weak O=C—C=O conjugation is insufficient to overcome it. The coplanar or nearly coplanar syn form for CPC has about the same level of steric repulsion between opposite ends of the molecule as oxalyl chloride, but in this case the conjugation effect dominates.

The observed temperature dependence of the sample composition affords estimates of the energy and entropy differences between the two conformers. Figure 4 is a plot of the data in the form $R \ln K_{eq} = -\Delta E°/T + \Delta S°$, where $k_{eq} = N_s/N_a$, $\Delta E° = E_s° - E_a°$, and $\Delta S° = S_s° - S_a°$. The results are $\Delta E = 3.8(\sigma{=}2.2)$ kJ·mol^{-1} and $\Delta S° = 2.7(\sigma{=}5.6)$ J·mol^{-1}·K^{-1}. These values are somewhat higher than the values found for propenoyl chloride[2] ($\Delta E° = 1.0(\sigma{=}0.8)$ kJ·mol^{-1}, $\Delta S° = -0.6(\sigma{=}2.1)$ J·mol^{-1}·K^{-1}). The values observed for $\Delta E°$ in oxalyl chloride[7] (5.8(σ=1.5) kJ·mol^{-1}) and in 2,3-dichloro-1,3-butadiene[6] (9.2(σ=2.3) kJ·mol^{-1}) are both larger than the value determined for CPC.

With adoption of the 2S model it is possible to calculate a crude potential function of the form $2V = \sum V_i(1 - \cos i\phi)$ for internal rotation in CPC. The method has been described.[2,7] The results in kJ/mol are $V_1 = 2.1(\sigma{=}1.3)$, $V_2 = 8.0(\sigma{=}0.5)$, and $V_3 = 1.7(\sigma{=}0.3)$; the function is plotted in Figure 5. It is also possible to estimate the torsional frequencies for the anti and syn forms. The estimate is based on the rough approximation that torsional motions are harmonic in the angle displacements; from the three temperatures the average values are $k_A = RT/\sigma_A{}^2 = 0.045$ (11) aJ·rad^{-2} and $k_s = 0.012$ (5) aJ·rad^{-2}. The torsional wave numbers are $\omega_A = 44$ (6) cm^{-1} and $\omega_s = 23$ (5) cm^{-1}. No measurements of the vibrations are on record for comparison.

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Supplementary Material Available: Tables of total intensities, final backgrounds, average molecular intensities, symmetry coordinates, force constants, and figures equivalent to Figure 2 for 377 and 475 K (42 pages). Ordering information is given on any current masthead page.

Conformational Analysis. 13. 2-Fluoroethanol. An Investigation of the Molecular Structure and Conformational Composition at 20, 156, and 240 °C. Estimate of the Anti–Gauche Energy Difference

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Abstract: The gas-phase molecular structure and anti–gauche conformational composition of 2-fluoroethanol have been investigated at 20, 156, and 240 °C with use of electron-diffraction data, augmented by rotational constants and dipole moment data from microwave spectroscopy. Because of the combined influence of the gauche effect and the internal O–H···F hydrogen bond, both of which stabilize the gauche conformer, the amounts of the anti form at the two lower temperatures were too small to detect. At the highest temperature the mole fraction of the anti form was measured to be 0.098 ($2\sigma = 0.067$). Values of some of the important distances (r_g) and angles ($\angle_\alpha$) with uncertainties estimated at the 95% confidence level are C–O = 1.432 (16) Å, C–C = 1.518 (6) Å, C–F = 1.398 (24) Å, ⟨C–H,O–H⟩ = (4C–H + O–H)/5 = 1.091 (18) Å, Δ(C–H,O–H) = C–H–O–H = 0.137 (36) Å, ∠CCO = 112.3 (14)°, ∠CCF = 108.5 (8)°, ∠COH = 105.8° (assumed), ∠HCH = 111.7 (50)°, ∠OCCF = 64.0 (8)°, ∠CCOH = −54.6 (78)°. A crude estimate of the conformational energy difference is $\Delta E = E_a° - E_g°$ = 2.7 (+1.8 − 1.5) kcal/mol. It was not possible to obtain a reliable measure of the energy of the internal hydrogen bond.

Some years ago a gas-phase electron-diffraction investigation of 2-fluoroethanol[1] (Figure 1; hereafter FE) was reported from this laboratory as one of the earliest in a series of studies of internal hydrogen bonding in disubstituted ethanes. The gauche form was