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Conformational Analysis. 8. Propenoyl Chloride. An Electron-Diffraction Investigation of the Molecular Structure, Composition, Syn–Anti Energy and Entropy Differences, and Potential Hindering Internal Rotation

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Abstract: The molecular structure of propenoyl chloride (acrylyl chloride) has been investigated by gas-phase electron diffraction at 20, 102, 207, and 370 °C. Two distinct conformers were identified, a more stable planar anti form and a less stable planar (or near planar) syn form. The structures of the two forms differ slightly in the length of the C–Cl bond and in the size of the C–C–Cl bond angle, but the data are otherwise consistent with insignificant differences in the values of the remaining parameters. There is no discernable temperature dependence of the structural parameters, and the composition changes only slightly. The average bond lengths (r_a) and bond angles ($\angle_\alpha$) from the four temperatures are $r(\mathrm{C{-}H}) = 1.100\ (6)$ Å, $r(\mathrm{C{=}O}) = 1.192\ (2)$ Å, $r(\mathrm{C{=}C}) = 1.339\ (2)$ Å, $r(\mathrm{C{-}C}) = 1.484\ (4)$ Å, $r(\mathrm{C{-}Cl_A}) = 1.804\ (3)$ Å, $r(\mathrm{C{-}Cl_S}) = 1.772\ (4)$ Å, $\angle\mathrm{C{=}C{-}H} = 121.5\ (18)°$, $\angle\mathrm{C{-}C{=}O} = 125.2\ (2)°$, $\angle\mathrm{C{=}C{-}C} = 123.4\ (7)°$, $\angle\mathrm{C{-}C{-}Cl_A} = 116.3\ (8)°$, $\angle\mathrm{C{-}C{-}Cl_S} = 111.8\ (15)°$; the parenthesized quantities are estimated 2σ. The mole fractions of the anti form were found to be 0.605 (66), 0.630 (61), 0.567 (73), and 0.556 (93) at 20, 102, 207, and 370 °C and correspond to $\Delta E° = E_S° - E_A° = 0.25$ ($\sigma = 0.18$) kcal·mol^{-1} and $S_S° - S_A° = \Delta S° = -0.15$ ($\sigma = 0.5$) cal·mol^{-1}·K^{-1}. The energy difference together with the force constants of the torsional modes of the two conformers were used to calculate a torsional potential of the form $V(\phi) = {}^1/_2\sum V_i\,(1 - \cos i\phi)$ through three terms. The results are $V_1 = 0.064$, $V_2 = 3.4$, $V_3 = 0.16$, all in kcal·mol with uncertainties of about 0.2 kcal·mol. The structure is discussed.

A series of investigations[1-6] in this laboratory has been concerned with the gas-phase structures of simple conjugated molecules in which torsion about a central single bond may yield mixtures of conformers. In those cases where more than one conformer has been detected (oxalyl chloride,[2] oxalyl bromide,[3] and formaldazine[5]), the lower energy form has the expected anti arrangement of the double bonds and the higher energy form a gauche conformation with torsion angles differing by 115–135° from the anti. By measuring the temperature dependence of the composition of these compounds, estimates of the energy and entropy differences of the conformers have been obtained.

In contrast to the oxalyl halides where substantial amounts of the higher energy conformers are found at room temperature, both 1,3-butadiene and glyoxal are found almost entirely as the planar anti form. For example, although the Raman spectrum[7] of 1,3-butadiene and the microwave spectrum[8] of glyoxal lead to the conclusion that syn forms are also present, the electron-diffraction data[9,10] (even at elevated temperatures in the case of butadiene[9b]) have been successfully interpreted assuming their absence. It is thus not surprising that propenal (acrolein), a formal hybrid of 1,3-butadiene and glyoxal, exhibits similar conformational behavior: electron diffraction[9a,10] and microwave spectroscopy[11] show the molecules in the gas to be predominantly anti, and an interpretation of the vibrational spectra[12] points to the higher energy form as planar syn.

The differing conformational properties of the oxalyl halides and propenal led us to be interested in the conformational properties of one of their formal hybrids, propenoyl chloride (acrylyl chloride, Figure 1). One expects, and IR and Raman measurements[13-16] reveal it to be so, that this substance will have a greater proportion of a higher energy conformer than does propenal at the same temperature. This circumstance affords opportunity for positive identification of the form of the second conformer (this form has generally been described as s-cis (syn) by analogy with propenoyl fluoride[17]) and for determination of the energy and entropy differences of the species. There has been some structural work on gaseous propenoyl chloride: an early electron-diffraction study[18] by the visual method showed the low-energy form to be the expected planar anti and a microwave investigation[19] that yielded four independent rotational constants for this form and proved it to be planar. The parameter values from the diffraction work are, of course, imprecise by modern standards, and those from the microwave study are necessarily incomplete.

Experimental Section

The sample of propenoyl chloride (>98%) was obtained from the Aldrich Chemical Co. and further purified by fractional distillation through a 40-cm column packed with glass helices. A middle fraction was selected for the experiments.

Diffraction photographs were made in the Oregon State apparatus at nozzle-tip temperatures of 293, 375, 480, and 643 K. Experimental conditions were as follows: sector shape, r^3; plates, 8 × 10 and 5 × 7 in Kodak projector slide, medium contrast; ambient apparatus pressure during exposure, 5.0×10^{-6}–2.0×10^{-5} torr; exposure times, 0.5–8 min; beam currents, 0.40–0.68 μA; nozzle-to-plate distances, 74.461–74.962 cm ("long camera"), 29.988–30.103 cm ("middle camera"), and 12.045–12.125 cm ("short camera"); electron wavelengths,

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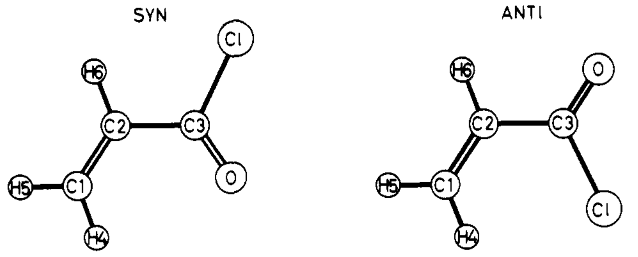

Figure 1. Diagrams of conformers of propenoyl chloride.

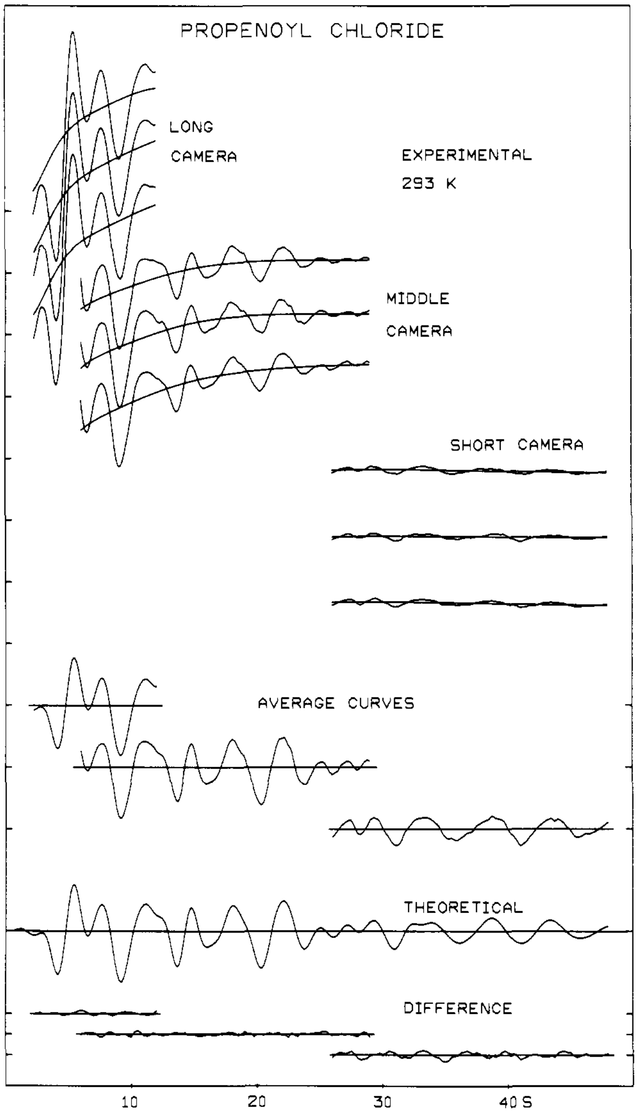

Figure 2. Intensity curves for 293 K. Experimental: s^4I_T magnified fivefold to show better the undulations, shown superimposed on their backgrounds. Average: sI_m for each camera distance. Theoretical: sI_m for the model of Tables I and II. Difference: average of the experimental minus the theoretical.

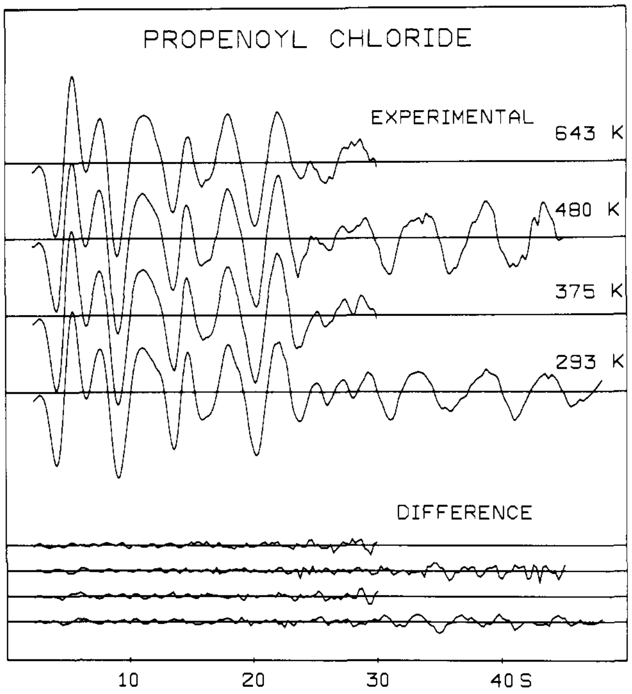

Figure 3. Intensity curves for four temperatures. Experimental: sI_m composites of average curves from each camera distance ($sI_m = s(s^4I_T$ – background)). Difference: experimental minus theoretical.

0.05746–0.05843 Å; wavelength standard, CO_2 with r_a(C═O) = 1.1646 Å and r_a(O··O) = 2.3244 Å. For analysis of the structure at 293 K we selected three plates from each of the three camera distances, at 375 and 643 K three plates each from the long and middle distances, and at 480 K three plates from the long, three from the middle, and four from the short. The procedures for obtaining the leveled total scattered intensity distribution ($s^4I_t(s)$) and the molecular intensity ($sI_m(s)$) have been described.[20,21] The ranges of the data (s in Å^{-1}) were $2.25 < s < 12.00$ from the long camera, $6.00 < s < 29.00$ (293 K) and $7.00 < s < 30.00$ (375, 480, 643 K) from the middle camera, and $26.00 < s < 48.00$ (293 K) and $25.00 < s < 45.00$ (480 K) from the short camera. The data interval was $\Delta s = 0.25$. Figure 2 shows curves of the total scattered intensities and the final backgrounds for the experiment at 293 K. Corresponding figures for the other temperatures as well as all the intensity and background data are available as supplementary material.

Radial distribution curves ($rD(r)$) were calculated in the usual way by the fourier transformation of functions $I'_m(s) = sI_m(s)Z_CZ_{Cl}A_C^{-1}A_{Cl}^{-1}\exp(-Bs^2)$ with $B = 0.0009$ Å^2 for the 293 and 480 K curves and $B = 0.0025$ Å^2 for the 375 and 643 K curves. Amplitudes and phases for all calculations were obtained[20] from tables.[22] The experimental $rD(r)$ curves are seen in Figure 4 and the intensity composites from which they were calculated in Figure 3.

Structure Analysis

Assignment of the torsion-insensitive peaks of the radial distribution curves was straightforward, following which the evidence for the expected two conformers could be sorted out. The peak at 3.95 Å is due mainly to the vicinal (torsion-sensitive) C··Cl distance in a syn form with a torsion angle rather larger than the 110–135° found in the oxalyl halides and formaldazine, and the peak at 3.55 Å is due the vicinal C··O distance in the planar anti form of the molecule. That the syn form is the higher energy one can be seen in the slight increase in area of the syn peak accompanied by a slight decrease in the area of the anti as the temperature is increased. The relative areas of the two peaks indicate that roughly half of the molecules have the anti conformation.

Our initial attempts to refine the structure(s) were based on the assumption that the geometries of the two forms differed only in the torsion angle. The agreement obtained with this model was not wholly satisfactory: the region $20 < s < 30$ Å^{-1} of the intensity curves was not well reproduced and the vibrational amplitude for the C–Cl bond was unreasonably large. Accordingly, the model was modified to incorporate structural differences other than torsion angle between the two forms. The parameters chosen were r(C—H), r(C═O), r(C═C), r(C—C), $\langle r(\text{C—Cl})\rangle = |r(\text{C—Cl}_A) + r(\text{C—Cl}_S)|/2$, $\Delta r(\text{C—Cl}) = r(\text{C—Cl}_A) - r(\text{C—Cl}_S)$, ∠(C═

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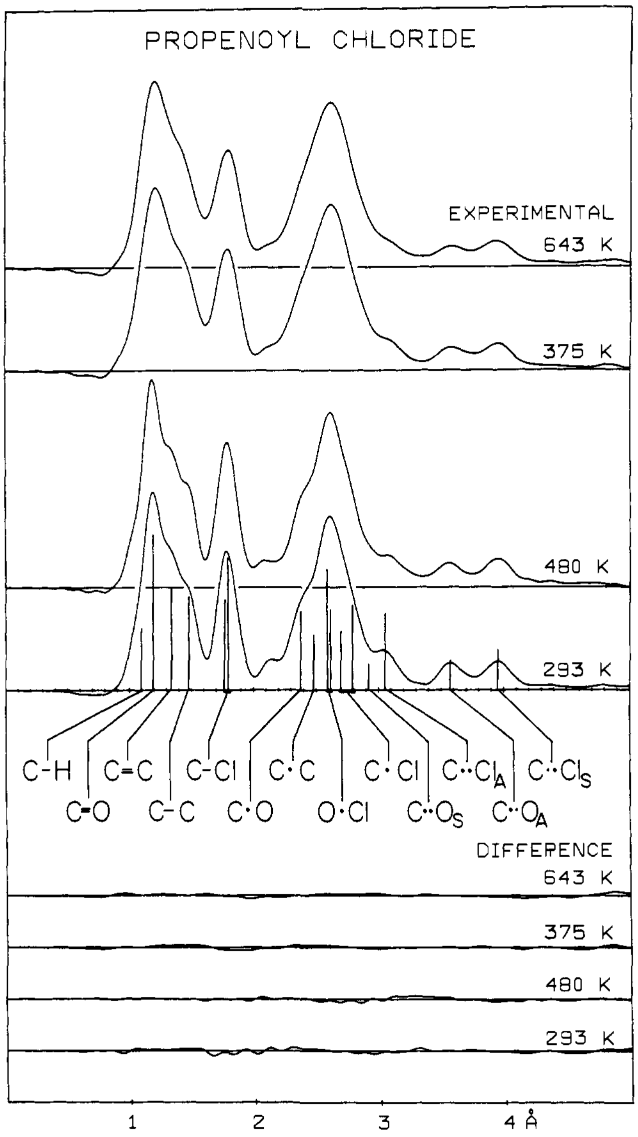

Figure 4. Radial distribution curves for four temperatures. The vertical lines indicate the interatomic distances; their lengths are proportional to the weights of the terms. Difference curves are experimental minus theoretical.

C—H), ∠(C—C=O), ∠(C—C=C), ⟨∠(C—C—Cl)⟩ = |∠(C—C—Cl$_A$) + ∠(C—C—Cl$_S$)|/2, Δ∠(C—C—Cl) = ∠(C—C—Cl$_A$) - ∠(C—C—Cl$_S$), ∠ϕ_S (the syn torsion angle), and σ_A and σ_S (the two root mean square amplitudes of torsional vibration). The rotational constants[19] for the anti form provide a valuable constraint on the refinements. The three constants for the species $C_3H_3O^{35}Cl$ were incorporated as observations after conversion of the B_0 values to B_Z according to $B_Z = B_0 + {}^1/_2\sum_s \alpha_s^{\text{har}}$ (A_Z = 5545.62 MHz, B_Z = 3817.91 MHz, C_Z = 2261.29 MHz; $B_Z I_Z$ = 505379 MHz·u·Å^2).

The $r_Z = r_\alpha^0$ distances compatible with the B_Z's must be converted to r_a for use in the diffraction equations. The necessary correction[23] as well as the α^{har} (above) were calculated from quadratic force fields for each conformer obtained by symmetrizing sets of value for bond stretches, angle bends, out-of-plane bends, and torsions taken from similar molecules and adjusting the symmetry constants to fit the observed[13-16] fundamental frequencies with good accuracy. Since our only interest in the force field lay in the α's, the r_α^0 to r_a corrections, and the amplitudes of vibration calculable from it, and since these are normally not very sensitive to small changes in force constant values, we made no attempt to investigate the force field further. Tables of the symmetry coordinates, force constant values, and calculated and observed frequencies are available in the supplementary material.

Table I. Values of Parameters Used to Define the Structure of Propenoyl Chloride[a]

parameter	293 K	375 K	480 K	643 K
r(C—H)	1.096 (10)	1.097 (11)	1.093 (10)	1.137 (17)
r(C=O)	1.193 (2)	1.196 (3)	1.191 (2)	1.191 (3)
r(C=C)	1.338 (4)	1.341 (5)	1.338 (3)	1.346 (8)
r(C—C)	1.483 (4)	1.485 (5)	1.484 (5)	1.484 (6)
⟨r(C—Cl)⟩[b]	1.784 (3)	1.788 (4)	1.787 (3)	1.792 (3)
Δr(C—Cl)[b]	0.029 (13)	0.021 (14)	0.044 (13)	0.032 (13)
∠C=C—H	123.9 (36)	124.6 (40)	119.1 (29)	119.9 (41)
∠C=C—C	123.4 (6)	123.0 (8)	123.8 (6)	123.1 (11)
∠C—C=O	124.8 (4)	125.2 (5)	125.2 (4)	125.9 (5)
⟨∠C—C—Cl⟩[b]	114.1 (5)	113.6 (10)	114.0 (4)	113.6 (6)
Δ(∠C—C—Cl)[b]	4.7 (10)	5.7 (21)	3.7 (7)	4.9 (13)
σ_A[c]	15.3	17.3	19.6	22.7
σ_S[c]	18.7	21.3	24.0	27.7
% anti	60.5 (66)	63.0 (61)	56.7 (73)	55.6 (93)
R[d]	0.096	0.068	0.091	0.074

[a] Distances (r_a) in angstroms, angles ($\angle_\alpha$) in degrees. [b] See text for definitions. [c] Root mean square torsional amplitudes calculated from torsional frequencies. [d] $R = [\sum w_i \Delta_i^2 / \sum w_i (s_i I_i(\text{obsd}))^2]^{1/2}$ where $\Delta_i = s_i I_i(\text{obsd}) - s_i I_i(\text{calcd})$.

The structure refinements were done by least-squares[24] adjustment of a theoretical intensity curve simultaneously to the average curves from each camera distance and to the three B_Z rotational constants. A unit weight matrix was used for the diffraction data, and the rotational constants were weighted several times more heavily than each intensity measurement. Anharmonicity constants κ were included for the bonds only, with values (×10^6) 11.71, 0.92, 1.28, and 2.02 Å^{-3} for C—H, C=O, C=C, and C—C, respectively, estimated from the diatomic approximation.[25] The very large number of structural and vibrational parameters required for complete specification of the system was reduced to a managable level by setting most of the nonbond amplitudes involving a hydrogen atom at the calculated values and by refining others as groups in the usual way.

Refinement Results. A structural question of great interest is the matter of the equilibrium value for the torsion angle in the syn form of the molecule. We investigated this question carefully in terms of two different types of models each consisting of two conformers. In the first and simplest of these no special cognizance was taken of possible large-amplitude torsional motion; i.e., the parameters σ_A and σ_S were ignored, the effects of torsional motion thereby being absorbed in the vibrational amplitudes of the torsion-sensitive distances. Refinement of this torsionally stiff model led to a value for the syn torsion angle corresponding to near planarity (ϕ_S = 158°). Since this is the result expected for a planar molecule undergoing large-amplitude torsional motion, our second model was designed to represent such motion in both of the conformers. As before,[2] this was done by positioning five torsional pseudoconformers for each form of the molecule at angles $\Delta\phi = \phi - \phi_0$, where $\phi_{0,A} = 0°$ and $\phi_{0,S} = 180°$, equal to 0, $\sigma/2$, σ, $3\sigma/2$, and 2σ with weights proportional to $\exp|-(\Delta\phi)^2/2\sigma^2|$. The quantities σ are thus the root mean square amplitudes of the torsional motion for the two conformers. The agreement obtained with this "double-σ" model was about the same as that gotten with the torsionally stiff model. Since the values σ_A and σ_S that resulted[26] were, taking into account their rather large uncertainties, consistent with prediction on the basis of the observed frequencies, we adopted the calculated values for the final refinements. The agreement obtained with this model was insignificantly different from that obtained with the stiff model and from the model incorporating σ_A and σ_S as adjustable parameters. The final results

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(26) The values of σ_A and σ_S obtained at 20, 102, and 207 °C were 9 ± 5° and 33 ± 7°; 10 ± 10° and 27 ± 9°; and 17 ± 6° and 26 ± 7°. The values at 370 °C had such large uncertainties as to be meaningless.

Table II. Selected Distances (r), Amplitudes (l), and Vibration-Rotation Corrections (Δr) in Propenoyl Chloride[a,b]

	293 K			375 K			480 K			643 K		
atom pair	r_a	l	$\Delta r \times 10^3$	r_a	l	$\Delta r \times 10^3$	r_a	l	$\Delta r \times 10^3$	r_a	l	$\Delta r \times 10^3$
C−H	1.096 (10)	0.077	22	1.097 (11)	0.077	17	1.093 (10)	0.077	16	1.137 (17)	0.077	17
C=O	1.193 (2)	0.048 (3)	2	1.196 (3)	0.041	3	1.191 (2)	0.040 (2)	3	1.191 (3)	0.048	3
C=C	1.338 (4)	0.047 (3)	5	1.341 (5)	0.046 (4)	5	1.338 (3)	0.042 (3)	6	1.346 (8)	0.053 (6)	5
C−C	1.483 (4)	0.053 (4)	2	1.485 (5)	0.052	2	1.484 (4)	0.048 (3)	3	1.484 (6)	0.062	4
$C_2{\cdot}H_4$	2.145 (33)	0.104	17	2.160 (37)	0.106	18	2.098 (29)	0.108	18	2.140 (37)	0.112	7
$C_1{\cdot}H_6$	2.143 (33)	0.099	15	2.157 (37)	0.100	15	2.095 (29)	0.101	15	2.147 (37)	0.104	14
$C_3{\cdot}H_6$	2.149 (48)	0.101	9	2.151 (54)	0.102	9	2.201 (37)	0.104	10	2.236 (61)	0.108	12
$C_1{\cdot}C_3$	2.480 (6)	0.068} (7)	1	2.479 (7)	0.071} (7)	1	2.484 (8)	0.069} (7)	2	2.484 (10)	0.077} (9)	3
$C_2{\cdot}O$	2.374 (5)	0.063}	2	2.382 (7)	0.065}	2	2.375 (5)	0.062}	2	2.383 (7)	0.068}	2
						Anti Form[c]						
C−Cl	1.799 (6)	0.065 (4)	1	1.799 (6)	0.063 (4)	2	1.810 (6)	0.060 (4)	3	1.808 (7)	0.069 (6)	4
O·Cl	2.592 (8)	0.069} (4)	1	2.586 (9)	0.066} (8)	1	2.599 (7)	0.071} (5)	1	2.585 (8)	0.077} (7)	1
$C_2{\cdot}Cl$	2.794 (7)	0.067}	1	2.796 (8)	0.064}	1	2.793 (8)	0.068}	1	2.793 (11)	0.074}	2
$C_1{\cdot}Cl$	3.065 (7)	0.097 (14)	0	3.051 (8)	0.125 (22)	−2	3.054 (7)	0.125 (3)	−1	3.044 (10)	0.150 (33)	−2
$C_1{\cdot}O$	3.572 (7)	0.074 (14)	0	3.577 (7)	0.097 (20)	0	3.573 (7)	0.081 (18)	1	3.581 (9)	0.087 (23)	1
						Syn Form[c]						
C−Cl	1.770 (9)	0.065 (4)	1	1.778 (10)	0.063 (4)	2	1.767 (7)	0.060 (4)	3	1.776 (8)	0.069 (6)	4
O·Cl	2.623 (16)	0.069} (5)	1	2.638 (23)	0.066} (8)	1	2.605 (10)	0.071} (5)	1	2.619 (18)	0.077} (7)	1
$C_2{\cdot}Cl$	2.696 (12)	0.067}	1	2.691 (17)	0.064}	1	2.699 (12)	0.068}	2	2.693 (19)	0.074}	2
$C_1{\cdot}O$	2.898 (12)	0.105	0	2.902 (14)	0.116	0	2.908 (13)	0.128	0	2.913 (18)	0.147	−1
$C_1{\cdot}Cl$	3.980 (11)	0.074 (17)	1	3.978 (13)	0.066	1	3.982 (11)	0.074	2	3.985 (15)	0.086 (25)	3

[a] Values in angstroms. Parenthesized quantities are estimated 2σ, those in curly brackets were refined as a group, those without attached uncertainties were calculated from the force field and were not refined. [b] $\Delta r = r_a - r_\alpha{}^\circ$. [c] Amplitudes for C−Cl anti and syn and for O·Cl and $C_2{\cdot}Cl$ anti and syn refined as groups.

Table III. Correlation Matrix (×100) for Parameters of Propenoyl Chloride

	$\sigma_{LS} \times 100$[a]	r_1	r_2	r_3	r_4	$\langle r_5\rangle$	Δr_6	$\angle_7$	$\angle_8$	$\angle_9$	$\langle\angle_{10}\rangle$	$\Delta\angle_{11}$	%	l_{13}	l_{14}	l_{15}	l_{16}	l_{17}	l_{18}	l_{19}	l_{20}	l_{21}
1. r(C—H)	0.34	100	18	24	6	−4	−4	−30	<1	19	−11	−4	4	20	−14	−24	−19	−17	−17	1	−7	−9
2. r(C=O)	0.07		100	47	5	−13	−10	−11	−29	−9	8	12	14	18	−29	−10	10	14	−5	<1	5	−8
3. r(C=C)	0.12			100	46	−14	−18	−19	−51	−21	−8	28	20	48	−6	−30	22	2	−2	−1	10	−10
4. r(C—C)	0.12				100	−13	−26	−7	−41	−26	−23	29	23	24	21	−6	30	4	−11	<1	12	−10
5. ⟨r(C—Cl)⟩	0.12					100	−52	53	−6	68	−5	15	52	−12	2	<1	15	7	−54	−4	−7	29
6. Δr(C—Cl)	0.46						100	−71	−9	−28	54	−62	−5	−5	−1	4	−52	7	68	−35	−16	1
7. ∠C=C—H	127							100	11	35	−30	51	25	−13	3	11	41	3	−57	23	12	18
8. ∠C=C—C	21								100	15	−30	−16	18	−27	−2	10	−12	−33	1	37	<1	15
9. ∠C—C—O	15									100	−18	2	−50	−19	−6	−1	−9	3	46	8	−14	23
10. ⟨∠C—C—Cl⟩	17										100	−62	−56	−1	−7	3	−27	11	24	−54	−24	33
11. Δ(∠C—C—Cl)	35											100	41	12	4	−4	43	7	−31	37	28	−20
12. % anti	2.3												100	15	2	14	14	−6	−6	43	30	−54
13. l(C=O)	0.06													100	15	−11	27	5	9	−1	8	−5
14. l(C=C)	0.08														100	32	5	5	7	−2	2	<1
15. l(C—C)	0.10															100	1	2	2	<1	1	5
16. l(C—Cl)	0.10																100	13	−14	19	19	2
17. $l(C_1{\cdot}C_3)$	0.22																	100	25	−18	<1	5
18. l(O·Cl)	0.17																		100	−19	−1	−14
19. $l(C_1{\cdot}Cl)_a$	0.47																			100	14	−23
20. $l(C_1{\cdot}O)$	0.48																				100	−12
21. $l(C_1{\cdot}Cl)_s$	0.59																					100

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

Table IV. Parameter Values for Propenoyl Chloride and Related Molecules[a]

	propenoyl chloride				
	U	KHC[b]	this work[c]	butadiene[d]	oxalyl chloride
r(C=O)	1.20 (2)	[1.192 (20)]	1.192 (2)		1.182 (2)
r(C=C)	1.36 (2)	[1.345 (10)]	1.339 (2)	1.345 (2)	
r(C—C)	1.44 (3)	1.476 (10)	1.484 (4)	1.465 (3)	1.534 (5)
$r(C—Cl_A)$	1.74 (2)	1.816 (20)	1.804 (3)		1.744 (2)
$r(C—Cl_S)$			1.772 (4)		
∠C—C=O	125.0 (20)	[127.2 (30)]	125.2 (2)		124.2 (3)
$\angle C—C—X_A$	110.0 (30)	116.3 (10)	116.3 (8)		111.7 (2)
$\angle C—C—X_S$			111.8 (15)		
∠C—C=C	120.0 (30)	122.6 (15)	123.4	123.3 (3)	
ref	18	19		10	2

[a] Distances in angstroms, angles in degrees. Parenthesized uncertainties may have different meanings in the different investigations. [b] Quantities in square brackets were assumed. [c] Weighted average of values from four temperatures. [d] r_g-type distances have been converted to r_a.

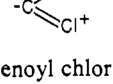
are given in Tables I and II. Table III is the correlation matrix from the 20 °C experiment. Figures 3 and 4 show curves for the several experiments.

Discussion

Apart from the effect of temperature on the isomeric composition and on the torsional amplitudes of the conformers of propenoyl chloride, one does not expect to see regular changes in the values of the geometrical parameters obtained from our experiments at different temperatures. Tables I and II reveal no obvious trends. The "best" values for the distances and angles may be estimated by forming a weighted average in the usual way. The results are given in Table IV. These are seen to be in very good agreement with the results from the earlier studies. The agreement with the microwave work, especially, is striking in view of the many structural assumptions required to complete the microwave analysis.

Although the values of geometrical parameters other than the torsion angle are surely different for the conformers of simple systems, we have heretofore always found the differences small enough to be ignored. It is surprising, therefore, that it was found necessary to take account of differences in the C–Cl bond lengths and the C–C–Cl bond angles in the two forms of propenoyl chloride in order to obtain the expected quality of fit between experimental and theoretical intensities. The difference between the bond lengths is small and the values themselves unremarkable, but the average angle difference of 4.5° is striking. Since the average C–C–Cl angle in the syn compound is very similar to those in oxalyl chloride[1] (111.7 (2)°) and acetyl chloride[27] (111.6 (6)°), the angle in the anti form must be viewed as unusual. It seems likely that the increased size of this angle in the anti form is a consequence of repulsive interaction between the atoms Cl and H(4). As measured, the average over the four temperatures of the Cl··H(4) distance in the anti form is very near the average of the Cl··H(6) distance in the syn (2.60 Å vs. 2.64 Å), both well below the van der Waals distance of about 3.0 Å. If the anti form were to have the same C–Cl bond length and C–C–Cl bond angle as the syn, the Cl··H(4) distance would drop to about 2.45 Å and the energy of repulsion would increase by about 40%.

As seen from Table IV, the conjugated single bond in butadiene is almost 0.07 Å shorter than that in oxalyl chloride. Propenoyl chloride, a formal hybrid of these molecules, is expected, and found, to have a conjugated single bond length between those of its parents. Since the relative lengths of these bonds presumably reflect the relative amounts of electron delocalization, one expects to find accompanying effects in the other parts of the conjugated system. Thus, the C=C bond in propenoyl chloride is slightly shorter than in butadiene and the C=O bond is slightly longer than in oxalyl chloride. It is also noteworthy that the C–Cl bond is substantially longer in propenoyl chloride than in oxalyl chloride: contributions from doubly bonded structures of the sort



tend to be reduced in propenoyl chloride by the effective conjugation stabilization between the C=O and C=C groups.

Perhaps the most interesting question about the propenoyl chloride system concerns the torsion angle of the syn form. As mentioned earlier, our results are consistent with a torsionally stiff, near-planar (ϕ_S = 158°) syn form or with a planar form undergoing large-amplitude torsional motion. The former is quite unlikely, but a similar model with a low barrier at the planar syn position is not. Because such a potential would lead to a distribution of molecules along the torsional coordinate approximately the same as that given by the one with a minimum at the planar syn position, our experiment cannot distinguish between the two possibilities. Since the two forms in propenoyl fluoride are known to be planar syn and planar anti,[17] it seems probable that this is also the case for the chloride. The issue may ultimately be settled by further analysis of the microwave spectrum[19] in which lines attributed to a syn form have been identified but not assigned.

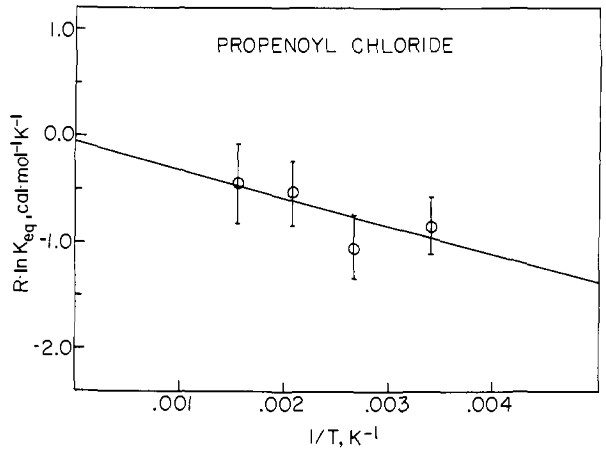


Figure 5. van't Hoff plot of isomeric composition data. $K_{eq} = N_S/N_A$. Half-lengths of the bars are estimated standard deviations. Least-squares straight line.

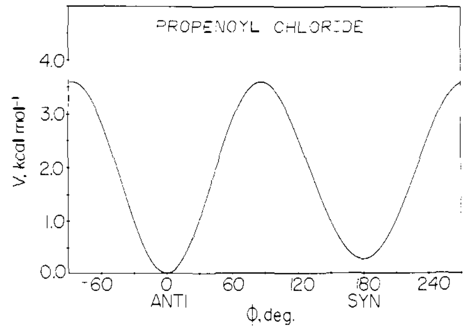


Figure 6. Potential for torsion around the conjugated single bond.

Our measurements of the temperature dependence of the sample composition afford estimates of the energy and entropy differences of the two conformers. Figure 5 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 $\Delta E°$ = 0.25 (σ = 0.18) kcal·mol^{-1} and $\Delta S°$ = -0.15 (σ = 0.5) cal·mol^{-1}·K^{-1}. The energy difference has been estimated from the temperature dependence of infrared intensities to be about 0.6[13] and 0.25 kcal·mol[14] and from an analysis of the torsional transitions[15] to be about 0.6 kcal·mol. Taking into account the rather large uncertainties in some of these measurements, the agreement is quite satisfactory.

The torsional potential for propenoyl chloride, assumed to have the form $V(\phi) = {}^1/_2\sum V_i\,(1 - \cos i\phi)$, may be determined through three terms from the electron-diffraction measurements of the torsional amplitudes and the energy difference of the two conformers in a way similar to that discribed previously.[2] However, the average torsional wavenumbers corresponding to these amplitudes,[26] $\omega_A = 162 \pm 60$ cm^{-1} and $\omega_S = 62 \pm 25$ cm^{-1}, corresponding to values for k_A and k_S rather different from these in our force field which fit the observed[14,15] wavenumbers of ω_A = 106 cm^{-1} and ω_S = 80 cm^{-1}. With use of the force-field k's and the electron-diffraction measurement of $\Delta E°$, we obtain from $k_\phi = \partial^2 V(\phi)/\partial\phi^2$ evaluated at ϕ = 0° and 180° the equations

$$k_A = 8.205\ \text{kcal·mol}^{-1} = V_1/2 + 2V_2 + 9V_3/2$$

$$k_S = 5.470\ \text{kcal·mol}^{-1} = -V_1/2 + 2V_2 - 9V_3/2$$

$$\Delta E° = 0.25\ (36)\ \text{kcal·mol}^{-1} = V_1 + V_3$$

The results are $V_1 = -0.064$, $V_2 = 3.4$, and $V_3 = 0.16$ with uncertainties (based on the uncertainty for $\Delta E°$) of about 0.2 kcal·mol. A plot of the potential is shown as Figure 6. Values for four coefficients of the series have also been obtained from analysis of the torsional transitions;[15] they are $V_1 = 0.27$, $V_2 =$

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[27] Tsuchiya, S.; Kimura, M. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 736.

4.9, V_3 = 0.38, and V_4 = −0.35 kcal/mol.

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Supplementary Material Available: Tables of total intensities, final backgrounds, average molecular intensities, symmetry coordinates, force constants and wave numbers, and figures equivalent to Figure 2 for 375, 480, and 643 K (44 pages). Ordering information is given on any current masthead page.

Multitechnique Depth Profiling of Small Molecules in Polymeric Matrices

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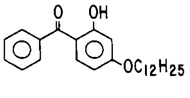
Abstract: A multitechnique approach has been used to determine the depth profile of a small molecule in a polymeric matrix as a function of heating. The molecule, 2-hydroxy-4-(dodecyloxy)benzophenone, was solubilized in a polyalkylmethacrylate/2-butoxyethanol carrier and applied as a thin film (0.2 μm thick) to the surface of a bisphenol A polycarbonate sheet. Upon heating, the partition of this molecule between the polymethacrylate and the polycarbonate was determined by transmission ultraviolet absorption spectroscopy after selective chemical etching. Infrared attenuated total reflectance sampling showed the disappearance of the substituted benzophenone from a surface layer ca. 0.3–0.4 μm thick. Demonstrated for the first time, the deuterium depth profile obtained by secondary ion mass spectrometry using a deuterated analogue clearly shows the diffusion of this molecule into the polycarbonate interior to a depth of ca. 3 μm. Direct transmission infrared analyses of serially cut microtome slices confirm these observations.

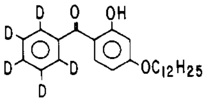
The characterization of a polymer's interfacial region and the study of the chemistry that occurs there are topics of considerable scientific interest and practical importance. For instance, small molecules are added to polymeric matrices to aid processing, prevent photodegradation, reduce flammability, or otherwise enhance the material's overall performance.[1] In a number of cases, the location of such an additive is crucial. As an example, the photodegradation of bisphenol A polycarbonate (PC) is clearly a surface phenomenon[2] in which any stabilizer added to protect the polymer from light-induced chemistry must be concentrated over or in the PC interfacial region. There are few analytical methods that have been routinely used to map the positions of small molecules in either man-made or biosynthetic polymers such that the resulting molecular distributions might be correlated with the polymer's chemical and physical properties.

We wish to describe a multitechnique approach to determine the in-depth distribution of a topically applied small molecule as a function of subsequent heating. The molecule, 2-hydroxy-4-(dodecyloxy)benzophenone (DOBP),[3] a typical UV stabilizer, is initially contained in a thin polyalkylmethacrylate (PAMA) film on the surface of a PC sheet.

DOBP-d_5 has three spectroscopically useful labels: a UV chromophore with $\epsilon > 10^4$ M^{-1} cm^{-1}, an infrared absorbing carbonyl functionality, and deuterium. As analyzed by their respective methodologies, ultraviolet spectroscopy (UV), Fourier transform infrared spectroscopy (FT-IR), and secondary ion mass spectrometry (SIMS), each of these labels is free of interference from other components of the experimental system. This report correlates the results of these several different techniques which seek an answer to a common question: What is the depth distribution of DOBP? While the example given is quite specific, we feel that in principle the approach is applicable to a wide range of polymeric systems.



DOBP



DOBP-d_5

Table I. Selective Chemical Etching: Partition of DOBP as a Function of Heating Time (130 °C)

heating time, min, 130 °C	% DOBP[a]		
	volatilized[b]	in PAMA[c]	in PC[d]
0	0	100	0
2.5	<1	23	76
5	0	17	83
10	11	13	76
15	0	17	83
20	<1	16	83
30	19	10	71
45	8	13	79
60	16	10	74
120	24	7	69
180	33	0	67

[a] All absorbances were measured at 292 nm. The initial DOBP absorbance before heating and etching was 0.75. The precision is ±10% of the given value. [b] % DOBP volatilized = ((initial absorbance − absorbance before etching)/initial absorbance)100. [c] % DOBP in PAMA = ((absorbance before etching − absorbance after etching)/initial absorbance)100. [d] % DOBP in PC = (absorbance after etching/initial absorbance)100.

Results and Discussion

A. Selective Chemical Etching—UV Analysis. A solution of 2.5 wt % DOBP, 2.0 wt % PAMA, and 95.5 wt % 2-butoxyethanol was flow coated onto a 10-mil PC film and allowed to air-dry for 30 min at room temperature. The differential UV absorption

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(1) (a) Hawkins, W. L. "Polymer Stabilization"; Wiley-Interscience: New York, 1972. (b) Ranby, B.; Rabek, J. F. "Photodegradation, Photooxidation and Photostabilization of Polymers"; Wiley-Interscience: New York, 1975.

(2) (a) Factor, A.; Chu, M. L. *Polym. Degradation Stab.* **1980**, *2*, 203. (b) Clark, D. T.; Munro, H. S. *Ibid.* **1982**, *4*, 441. (c) Clark, D. T.; Munro, H. S. *Ibid.* **1983**, *5*, 227.

(3) DOBP is a registered trademark of Eastman Chemical Company.

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