Molecular structure and conformation of propionyl chloride as determined by gas-phase electron diffraction

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MOLECULAR STRUCTURE AND CONFORMATION OF PROPIONYL CHLORIDE AS DETERMINED BY GAS-PHASE ELECTRON DIFFRACTION

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ABSTRACT

The molecular structure of propionyl chloride, CH_3CH_2—COCl, has been investigated by gas-phase electron diffraction at nozzle temperatures of 293, 367 and 488 K. Rotational constants from microwave spectroscopy were also included in the analysis. The molecules exist as a mixture of two conformers with the methyl group and the chlorine atom *anti* (torsion angle $\angle\phi = 0°$) or *gauche* ($\angle\phi = 120°$) to each other and with the *anti* form the more stable. The composition (mole fraction) of the vapor with uncertainties estimated at 2σ was found to be 0.77(0.10), 0.65(0.13) and 0.53(0.11) at 293, 367 and 488 K, respectively. These values correspond to an energy difference $\Delta E = E_g - E_a = 6$ ($\sigma = 2$) kJ mol^{-1} and an entropy difference $\Delta S = 7$ ($\sigma = 6$) J mol^{-1} K^{-1}. The results at 488 K for the distance (r_a) and angle ($\angle_\alpha$) parameters, with estimated uncertainties of 2σ, are: $r(C—H) = 1.123(11)$ Å, $r(C=O) = 1.181(5)$ Å, $r(C—C=) = 1.522(13)$ Å, $r(C—C—) = 1.526(15)$ Å, $r(C—Cl) = 1.800(6)$ Å, $\angle C—C=O = 127.1(6)°$, $\angle C—C—Cl = 112.0(3)°$, $\angle C—C—C = 112.3(8)°$, $\angle\phi$ (*gauche*) $= 120.0(7.7)°$. A normal coordinate calculation was made by developing a valence force field. Using 29 force constants, the 24 vibrational frequencies were calculated with an average deviation from experimental values of 5 cm^{-1}.

INTRODUCTION

We have recently investigated by electron diffraction a series of molecules with general formula CH_2X—COY (X = Y = Cl [1], X = Y = Br [2], X = Br, Y = Cl [2], X = Cl, Y = H [3]) and for all observed mixtures of two conformers with different X—C—C—Y torsion angles. In the haloacetyl halides [1, 2] (X, Y = halogen) a low-energy form with X and Y *anti* to each other was found, while in chloroacetaldehyde [3] X and Y (Cl and H) were almost *syn* in the most stable conformer. We were also interested in investigating molecules with X or Y being a CH_3-group. A methyl group and a chlorine atom have almost the same van der Waals radius, but quite different electronegativity, and it would be of interest to see the conformational effect of the different substituents. In this paper we present our results (Fig. 1) for propionyl chloride (X = CH_3, Y = Cl), later we hope to present results for chloroacetone (X = Cl, Y = CH_3).

Microwave spectroscopy investigations [4, 5] of propionyl chloride have shown that the most stable form of this molecule has CH_3 and Cl *anti*
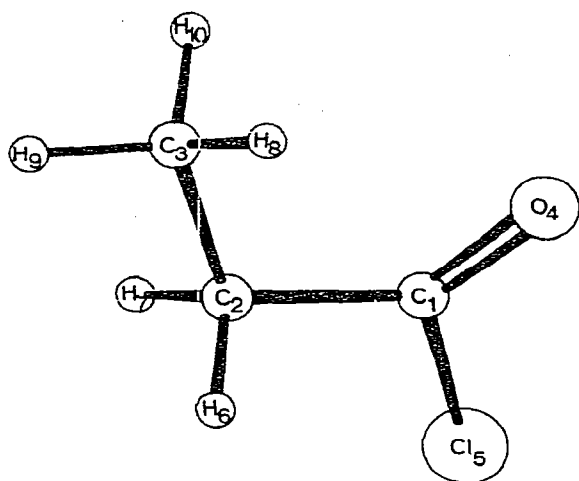
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Fig. 1. Propionyl chloride. Diagram of the *anti* conformer with atomic numbering.

(C—C—C—Cl torsion angle $\angle\phi = 0°$), but these investigations could not detect any second conformer. However, a vibrational spectroscopy investigation [6] observed a second conformer present both in liquid and gas phase, but could not determine accurately the torsion angle of this second form. Electron diffraction should be able to determine the conformational equilibrium in propionyl chloride and also determine bond distances, bond angles and torsion angles as well as some vibrational amplitudes. To improve the accuracy of the investigation, the observed rotational constants [4, 5] were included as experimental data in our analysis. Two conformers were observed, and in order to determine energy and entropy differences between these conformers, the electron diffraction experiment was repeated at three different temperatures.

EXPERIMENTAL AND DATA REDUCTION

A commercial sample of propionyl chloride was obtained from Aldrich Chem. Co. (>97%) and was used without further purification. Electron diffraction photographs were recorded at 293, 367 and 488 K with a Balzers Eldigraph KDG-2 [7, 8] using a rotating sector with angular opening proportional to r^3 and Kodak Electron Image plates at nominal nozzle-to-plate distances of 50 and 25 cm. The electron wavelength was determined by voltage measurements, calibrated against gaseous benzene [9]. The experimental conditions are summarized in a supplementary publication [10]. Reduction of the data was done in the usual way [11, 12], and a calculated background [13] was subtracted from the data for each plate to yield the experimental molecular intensity distribution in the form $sI_m(s)$. The averages of the molecular intensities are shown in Fig. 2, the data for the
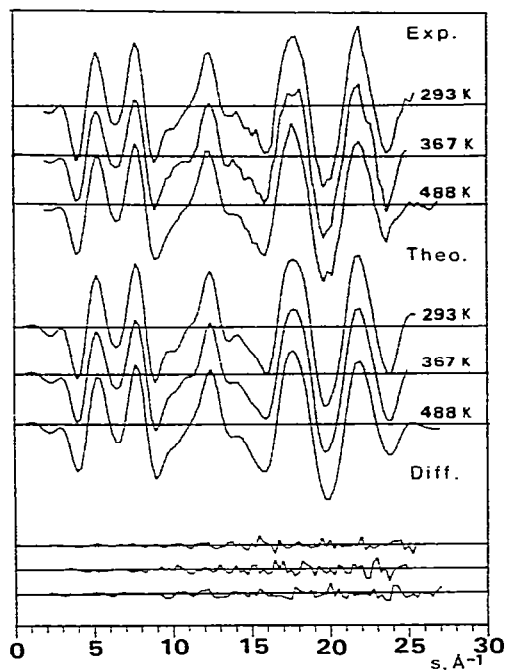
Fig. 2. Propionyl chloride. Intensity curves in the form $sI_m(s)$. Experimental curves are composites of all plates and all camera distances. Theoretical curves were calculated using parameter values shown in Tables 3 and 4. All curves are on the same scale. $\Delta s = 0.25$ Å^{-1}.

total intensities and the backgrounds are available as a supplementary publication [10]. Electron scattering amplitudes and phase shifts were calculated by the use of Hartree—Fock potentials for C, O and Cl [14], while molecular bonded potentials were used for H [15].

FORCE FIELD CALCULATION

Calculation of vibrational quantities were made with a valence force field. The initial valence force constants were transferred from 1-butene [16] and acetyl chloride. The latter force field was developed to be consistent with the one for 1-butene. Thus, for acetyl chloride, a 19 parameter force field reproduced the 15 observed frequencies [17] to an average deviation of 3 cm^{-1}.

From the initial force field for propionyl chloride, an improved fit to the observed *anti* frequencies [6] was obtained by a least squares refinement, giving an average deviation of 5 cm^{-1}. For the *gauche* conformer almost all the initial force constants obtained from 1-butene and acetyl chloride were used unchanged.

The force field for propionyl chloride is given in Table 1, and in Table 2 are listed observed and calculated frequencies along with the potential energy distribution. These force constants were then used to calculate root-

TABLE 1

Valence force field for anti/gauche conformers of propionyl chloride

Type	Coordinate(s) involved	Value[a]	Type	Coordinate(s) involved	Value[a]
Stretch	$O=C$	11.05	*Out of plane*	$=C-Cl$	0.41
	C_1-C_2	4.97			
	C_2-C_3	4.29	*Stretch/stretch*	$C-H/C-H$ (CH_2)	0.06
	$C-Cl$	2.62		$C-H/C-H$ (CH_3)	0.08
	$C-H$ (CH_2)	4.64		$C_1-C_2/C-Cl$	0.78/0.70
	$C-H$ (CH_3)	4.84			
			Stretch/bend	$C-C/C-C-C$	0.22
Bend	$O=C-C$	0.76/0.87		$C-Cl/O=C-Cl$	0.53/0.61
	$O=C-Cl$	1.26/0.92		$C-Cl/C-C-Cl$	0.50
	$C-C-Cl$	1.20/0.95		$C-C/C-C-H$ (CH_2)	0.22
	$C-C-C$	0.83		$C-C/C-C-H$ (CH_3)	0.32
	$C-C-H$ (CH_2)	0.69			
	$C-C-H$ (CH_3)	0.64	*Bend/bend*	$C-C-H/C-C-H$	−0.02/−0.0
	$H-C-H$ (CH_2)	0.53		(CH_2, $C-C$ common)	
	$H-C-H$ (CH_3)	0.54		$C-C-H/C-C-H$	−0.01
				(CH_3, $C-C$ common)	
Torsion	C_1-C_2	0.06		$C-C-H/C-C-H$	0.05
	C_2-C_3	0.07		(CH_2, $C-H$ common)	
				$C-C-H/C-C-H$	0.11
				(trans, $C-C$ common)	

[a]Units for force constants are mdyn A^{-1} for stretching and mdyn A rad^{-2} for bending, out-of-plane and torsion, with corresponding units for interaction constants.

mean-square amplitudes of vibration (l), perpendicular amplitudes (K) and centrifugal distortion constants (δr).

STRUCTURE ANALYSIS

Radial distribution (RD) curves, Fig. 3, were calculated in the normal manner from the intensity curves shown in Fig. 2. The origin of the various peaks in the RD-curves are indicated on the figure. Approximate values for the geometrical parameters were obtained from the experimental RD-curves and from structures reported for related molecules [1, 18]. The temperature dependence of the area under the peak at 4.1 A in the experimental RD-curves clearly showed the presence of more than one conformer. This peak represents the longest carbon—chlorine distance in the *anti* form and the amount of *anti* is seen to decrease with increasing temperature. Calculation of theoretical RD-curves for various combinations of conformers (*anti*, *gauche* and *syn*), Fig. 4, revealed that the conformational mixture consisted of *anti* (C—C—C—Cl torsion angle $\angle\phi = 0°$) and *gauche* ($\angle\phi = 120°$), with about equal amounts of the two forms present at the highest temperature (488 K).

TABLE 2

Propionyl chloride. Observed [6] and calculated frequencies in cm^{-1} and potential energy distribution in %

Anti			Approximate description	Gauche	
Obs.[a]	Calc.	P.E.D.[b]		Obs.[a]	Calc.
a' 2981	2992	C$_3$—H(100)	asym.str. CH$_3$		2992
2959	2949	C$_3$—H(96)	sym.str. CH$_3$		2949
2897	2907	C$_2$—H(98)	sym.str. CH$_2$		2906
1805	1805	O=C(79)	str. O=C	1833	1797
1472	1462	H—C$_3$—H(84)	asym.def. CH$_3$		1457
1424	1425	H—C$_2$—H(75)	def. CH$_2$	1400	1433
1385	1392	C—C$_2$—H(41)C—C$_3$—H(29) H—C$_3$—H(28)	sym.def. CH$_3$		1385
1339	1345	C—C$_2$—H(41)C—C$_3$—H(29) H—C$_3$—H(26)	wag CH$_2$		1334
1084	1082	C$_2$—C$_3$(28)C$_1$—C$_2$(26)	str. C—C	1127	1121
1016	1021	C—C$_3$—H(52)	rock CH$_3$		1030
926	922	C$_2$—C$_3$(40)C—C$_3$—H(25)	str. C—C	908	913
689	699	C—Cl(29)O=C—C(22)	bend O=C—C	576	596
441	445	C—Cl(50)O=C—Cl(22)	str. C—Cl		433
359	356	C—C—Cl(30)	bend C—C—Cl	383	377
229	229	C—C—C(48)C—C—Cl(25)	bend C—C—C	257	229
a" 2999	2999	C$_3$—H(100)	asym.str. CH$_3$		2992
2936	2929	C$_2$—H(100)	asym.str. CH$_3$		2930
1456	1457	H—C$_3$—H(91)	asym.str. CH$_2$		1460
1261	1264	C—C$_2$—H(86)	twist CH$_2$		1229
1088	1075	C—C$_2$—H(46)C—C$_3$—H(41)	rock CH$_3$	1073	1051
790	792	C—C$_2$—H(54)C—C$_3$—H(45)	rock CH$_2$	804	792
505	509	w(=C—Cl)(87)	wag =CCl	576	577
196	197	t(C$_2$—C$_3$)(94)	tors. C$_2$—C$_3$		187
71	74	t(C$_1$—C$_2$)(94)	tors. C$_1$—C$_2$		77

[a] Observed frequencies from gas phase. [b] w and t denotes out-of-plane wag and torsion, respectively. Only contributions larger than 20% are included.

Least squares refinements [19] of the structure were made at each temperature by simultaneously fitting a single theoretical intensity curve to the two average experimental curves and the three calculated rotational constants to the experimental ones. Because of the effect of vibrational averaging, the r_a distances used to calculate theoretical intensity curves are inappropriate for rotational constants. We therefore defined our models in terms of the geometrically consistent $r_\alpha^0 = r_z$ set of distances which were used to calculate rotational constants B_Z related to the observed B_0 by

$$B_Z = B_0 + 1/2 \ \Sigma \alpha_s^{harm}$$

The r_a distances for the temperature of interest (T) were generated from the r_α^0 set of the model according to [20]
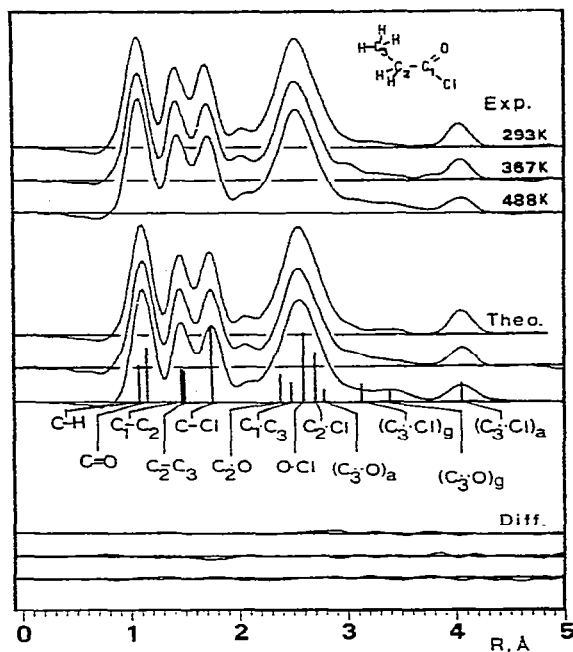
Fig. 3. Propionyl chloride. Radial distribution curves calculated from the intensity curves of Fig. 2 after multiplication by $Z_C Z_{Cl}/(f'_C f'_{Cl})$ and with an artificial damping constant $B = 0.002$ A². Unobserved experimental intensity data from the region $0 < s < 1.75$ were taken from theoretical curves. The vertical lines indicate the important distances in the final model; lengths of the lines are proportional to the weights of the distances. All curves are on the same scale.

$$r_a^T = r_\alpha^0 + (3/2)a_3[(l^2)^T - (l^2)^0] + \delta r^T + K^0 - (l^2)^T/r_\alpha^0$$

The Morse function anharmonicity constants a_3 were given the diatomic molecule value [21] for bonds and otherwise assumed to be zero. Values for l, δr and K as well as α^{harm}, were calculated from the above mentioned force field.

In the least squares refinements the two conformers were assumed to have the same geometry except for the C—C—C—Cl torsion angle. For the *anti* conformer a dynamic model was used where the *anti* conformer was represented by five distinct forms with different torsion angles, each weighted according to a gaussian potential function. The r.m.s. amplitude for the torsional vibration (τ) was calculated from the observed frequency for the torsion, and the weights for the five pseudo-conformers were then calculated from τ [12]. Only an average value was determined for the C—H bonds, and the two different C—C bonds were refined as an average value and a split. Among the vibrational amplitudes for the interatomic distances, only the value for the C—Cl bond was refined, while the others were kept constant at the values calculated from the valence force field shown in Table 1. The
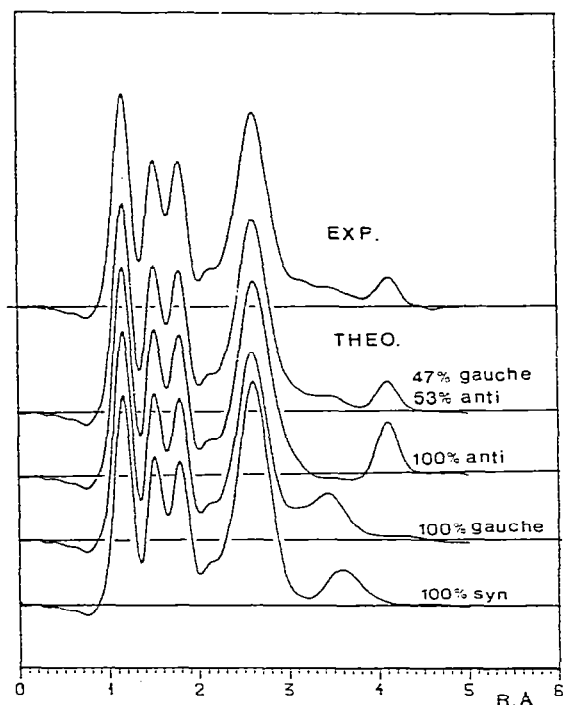
Fig. 4. Propionyl chloride. Theoretical radial distribution curves for different conformers or mixture of conformers compared with the experimental curve for the 488 K data. All curves are on the same scale.

results of the final least squares refinements are listed in Tables 3 and 4. The theoretical intensity and RD-curves calculated from these results together with experimental and difference curves are shown in Figs. 2 and 3. Table 5 gives the correlation matrix for the high temperature experiments, the other two correlation matrices are similar.

DISCUSSION

Molecular structure

As can be seen from Table 3, the results obtained for propionyl chloride at the three different temperatures are consistent; all geometrical parameters are nearly constant. In Table 6 some of the important geometrical parameters in molecules with the general formula CH_2X—COY are shown. In all of these molecules the central carbon—carbon bond distances are almost the same. The length of the carbonyl bond seems to depend somewhat on the substituent Y, with a shorter carbonyl bond when Y = halogen than when Y = H. This has also been observed in other molecules [18]. $r(C=O)$ and $\angle C$—$C=O$ show a correlation with a larger angle when the bond distance is short.

TABLE 3

Final structural[a, b] results for propionyl chloride at different temperatures

Parameter	293 K		367 K		488 K	
	$r_a/\angle_\alpha$	l	$r_a/\angle_\alpha$	l	$r_a/\angle_\alpha$	l
C—H	1.107(11)	[0.079]	1.103(14)	[0.079]	1.123(11)	[0.079]
C=O	1.187(5)	[0.038]	1.191(7)	[0.038]	1.181(5)	[0.039]
(C—C)[c]	1.524(5)		1.521(7)		1.524(5)	
Δ(C—C)[d]	—0.002(30)		0.010(37)		0.004(26)	
C—Cl	1.795(5)	0.049(6)	1.798(7)	0.057(9)	1.800(6)	0.061(5)
∠C—C=O	127.0(7)		126.8(9)		127.1(6)	
∠C—C—Cl	112.1(4)		112.9(5)		112.0(3)	
∠C—C—C	112.7(7)		112.7(1.1)		112.3(8)	
∠C—C—H₆	102.0(4.1)		112.5(5.4)		104.7(3.7)	
∠H₇—C—H₆	105.3(9.8)		105.4(10.4)		[105.0]	
∠C—C—H₈	109.6(2.3)		104.2(3.4)		109.4(2.7)	
∠φ₁[e]	117.5(11.4)		128.4(14.4)		120.0(7.7)	
∠φ₂[f]	18.0(23.7)		36.2(28.9)		4.4(44.0)	
τ[g]	[9.6]		[10.7]		[12.4]	
% anti	76.5(9.8)		65.2(13.1)		52.9(10.8)	
R_L[h]	0.063		0.086		0.061	
R_S[h]	0.081		0.117		0.089	

[a] Distances (r_a) and root-mean-square amplitudes (l) in Ångströms, angles in degrees.
[b] Parenthesized uncertainties are 2σ and include estimates of systematic error and correlation. Quantities in square brackets were not refined.
[c] (C—C) = $0.5(r(C_1—C_2) + r(C_2—C_3))$.
[d] Δ(C—C) = $r(C_2—C_3) — r(C_1—C_2)$.
[e] ∠φ₁ is the *gauche* CCCCl torsion angle relative to 0° for the *anti* form.
[f] ∠φ₂ is the CCCH₉ torsion angle relative to 0° when $C_3—H_9$ is *anti* to $C_1—C_2$.
[g] τ is the r.m.s. amplitude for the $C_1—C_2$ torsional oscillation in the *anti* form, calculated from the observed frequency.
[h] R_L and R_S are the agreement factor for the long camera and short camera curves, respectively. $R = |\Sigma w_i \Delta_i^2/(w_i I_i(\text{obs.}))^2|^{1/2}$ where $\Delta_i = I_i(\text{obs.}) — I_i(\text{calc.})$.

The structures of chloroacetyl chloride (X = Cl, Y = Cl) and propionyl chloride (X = CH₃, Y = Cl) are very similar. Both bond distances, bond angles and the torsional angles of the two conformers are almost the same in the two molecules. The large difference in electronegativity between CH₃ and Cl therefore seems to have only a small effect on these parameters.

The electron diffraction and microwave data are entirely consistent. In the final combined analysis, the three observed rotational constants agreed with the calculated values to within less than 1.5 MHz for all experiments, and even an analysis based solely on the electron diffraction data yielded results consistent with those presented in Tables 3 and 4.

Energy and entropy differences of the conformers

The measured variation of sample composition with temperature makes it possible to determine energy and entropy differences between the *gauche* and *anti* conformers by use of the formula

TABLE 4

Dependent distances and r.m.s. amplitudes of vibration for propionyl chloride[a]

Distances	293 K		367 K		488 K	
	r_a	l[b]	r_a	l[b]	r_a	l[b]
C_1-C_2	1.525(16)	0.049	1.516(18)	0.049	1.522(13)	0.051
C_2-C_3	1.523(16)	0.051	1.526(21)	0.052	1.526(15)	0.054
$C_2 \cdot H_8$	2.161(29)	0.109	2.090(42)	0.110	2.173(32)	0.113
$C_1 \cdot H_6$	2.057(50)	0.108	2.183(67)	0.109	2.102(47)	0.111
$C_3 \cdot H_6$	2.242(43)	0.110	2.118(88)	0.111	2.233(37)	0.114
$C_1 \cdot C_3$	2.535(10)	0.075	2.529(16)	0.079	2.528(13)	0.087
$C_2 \cdot O_4$	2.428(9)	0.060	2.422(10)	0.062	2.422(8)	0.067
$C_2 \cdot Cl_5$	2.755(11)	0.066	2.762(13)	0.070	2.753(10)	0.078
$O_4 \cdot Cl_5$	2.608(8)	0.060	2.606(9)	0.063	2.606(7)	0.069
$C_1 \cdots H_8$	2.927(205)	0.185	2.917(266)	0.197	2.806(362)	0.217
$C_1 \cdots H_9$	3.460(38)	0.107	3.377(66)	0.109	3.486(26)	0.113
$C_1 \cdots H_{10}$	2.647(155)	0.185	2.497(161)	0.197	2.734(351)	0.217
$H_8 \cdot H_9$	1.818(40)	0.127	1.863(48)	0.127	1.847(47)	0.128
$C_3 \cdots O_4$ (A)	2.857(14)	0.112	2.847(22)	0.123	2.845(17)	0.139
$C_3 \cdots Cl_5$	4.138(10)	0.072	4.145(12)	0.078	4.136(10)	0.086
$O_4 \cdots H_6$	3.049(40)	0.117	3.146(38)	0.119	3.084(26)	0.123
$Cl_5 \cdots H_6$	2.774(62)	0.137	2.993(114)	0.141	2.824(73)	0.150
$O_4 \cdots H_8$	3.058(221)	0.261	3.109(281)	0.285	2.847(616)	0.321
$Cl_5 \cdots H_8$	4.538(87)	0.162	4.502(120)	0.172	4.466(149)	0.187
$O_4 \cdots H_9$	3.909(59)	0.129	3.840(100)	0.137	3.942(32)	0.149
$Cl_5 \cdots H_9$	4.892(32)	0.122	4.812(51)	0.126	4.915(27)	0.133
$O_4 \cdots H_{10}$	2.580(272)	0.261	2.395(290)	0.285	2.724(599)	0.321
$Cl_5 \cdots H_{10}$	4.366(66)	0.162	4.241(67)	0.172	4.421(148)	0.187
$C_3 \cdots O_4$ (G)	3.467(44)	0.116	3.525(50)	0.127	3.470(30)	0.143
$C_3 \cdots Cl_5$	3.207(84)	0.193	3.101(103)	0.214	3.166(59)	0.246
$O_4 \cdots H_6$	2.472(76)	0.132	2.649(104)	0.138	2.518(66)	0.148
$Cl_5 \cdots H_6$	3.643(24)	0.189	3.731(25)	0.202	3.680(24)	0.224
$O_4 \cdots H_7$	3.008(58)	0.138	3.103(62)	0.141	3.038(45)	0.149
$Cl_5 \cdots H_7$	2.863(141)	0.104	3.081(113)	0.106	2.924(89)	0.111
$O_4 \cdots H_8$	3.571(171)	0.191	3.653(180)	0.204	3.474(205)	0.226
$Cl_5 \cdots H_8$	3.830(194)	0.291	3.729(316)	0.319	3.602(431)	0.361
$Cl_5 \cdots H_9$	4.422(36)	0.137	4.402(37)	0.145	4.410(77)	0.158
$Cl_5 \cdots H_{10}$	4.045(175)	0.197	3.877(198)	0.215	4.140(211)	0.243
$O_4 \cdots H_{10}$	3.671(139)	0.235	3.577(177)	0.255	3.799(295)	0.285
$Cl_5 \cdots H_{10}$	2.646(220)	0.321	2.372(210)	0.354	2.642(348)	0.403

[a] Distances (r_a) and root-mean-square amplitudes (l) are in Ångströms. Parenthesized uncertainties are 2σ and include estimates of systematic error and correlation. [b] For the torsion-sensitive distances in the *anti* form where a dynamic model was used, vibrational amplitudes were calculated without contribution from the C—C torsion.

$$K = N_g/N_a = 2e^{\Delta S/R}e^{-\Delta E/RT}$$

where N_g and N_a are the fractions of *gauche* and *anti* molecules and the factor 2 is the statistical weights of the two forms. Assuming ΔS and ΔE to be temperature independent in the actual temperature-interval, they can be

TABLE 5

Correlation matrix ($\times$ 100) for propionyl chloride at 488 K

	σ_{LS}^a	r_1	r_2	r_3	Δr	r_4	L_1	L_2	L_3	L_4	L_5	L_6	L_7	l_1	α
C—H	0.0026	100	—52	8	4	—8	—10	0	8	—18	—11	—3	—5	—19	8
C=O	0.0010		100	—2	19	10	12	31	—17	20	—7	6	4	20	—5
$\langle$C—C$\rangle$	0.0009			100	22	2	3	—14	—34	—2	—22	3	4	—26	—1
Δ(C—C)	0.0065				100	41	70	—7	10	37	—39	—18	—2	—8	32
C—Cl	0.0011					100	56	—20	—44	32	—6	—4	—4	3	4
$\angle$CCO	0.21						100	—54	—23	16	25	—21	—19	—2	37
$\angle$CCCl	0.11							100	36	31	—74	9	20	8	—16
$\angle$CCC	0.27								100	—40	—40	—12	15	—8	5
$\angle$CCH$_3$	2.16									100	—28	1	—2	18	7
$\angle$CCH$_8$	0.90										100	—3	—22	12	5
$\angle\phi_1{}^b$	2.56											100	—14	—2	—9
$\angle\phi_2{}^c$	14.68												100	7	—55
l(C—Cl)	0.0012													100	—8
%anti	0.036														100

[a] Standard deviations from least squares. Distances and amplitudes are in Ångstroms, angles in degrees.
[b] $\angle\phi_1$ is the CCCCl torsional angle for the *gauche* conformer.
[c] $\angle\phi_2$ is the HCCC torsional angle.

TABLE 6

Comparison of parameter values for some CH_2X-COY molecules

	CH_3-COH X = H, Y = H	CH_3-COCl X = H, Y = Cl	$CH_2Cl-COH$ X = Cl, Y = H	$CH_2Cl-COCl$ X = Cl, Y = Cl	CH_3CH_2-COCl X = CH$_3$, Y = Cl	$CH_2Br-COBr$ X = Br, Y = Br	$CH_2Br-COCl$ X = Br, Y = Cl
$r(C-C)$	1.515(4)	1.506(3)	1.521(5)	1.519(8)	1.522(13)	1.513(20)	1.519(18)
$r(C-X)$	1.107(6)	1.105(5)	1.782(4)	1.782(27)	1.526(15)	1.915(20)	1.935(12)
$r(C-Y)$	1.128(4)	1.798(2)	1.103(12)	1.775(25)	1.800(6)	1.987(20)	1.789(11)
$r(C=O)$	1.210(4)	1.187(4)	1.206(3)	1.180(4)	1.181(5)	1.175(13)	1.188(9)
$\angle C-C=O$	124.1(3)	127.2(5)	123.3(6)	126.5(12)	127.1(6)	129.4(17)	127.6(13)
$\angle C-C-Y$	115.3(3)	111.6(6)	112.4(38)	111.2(13)	112.0(3)	110.7(15)	111.3(11)
$\angle C-C-X$	109.0(9)	—	110.4(3)	112.5(19)	112.3(8)	111.7(18)	111.0(15)
$\angle \phi_1$ [a]	0	0	162	0	0	0	0
$\angle \phi_2$ [b]	—	—	0	121.5(65)	120.0(77)	105.0	110.0
Method	ED, MW	ED, MW	ED	ED	ED, MW	ED	ED
Dist. type	r_g	r_g	r_a	r_a	r_a	r_a	r_a
Ref.	18	18	3	1	This work	2	2

[a] $\angle \phi_1$ is the XCCY torsional angle for the low-energy conformer. $\angle \phi_1$ is 0° when C–X and C–Y are *anti* to each other. [b] $\angle \phi_2$ is the XCCY torsional angle for the high-energy conformer in those molecules where more than one form has been observed.
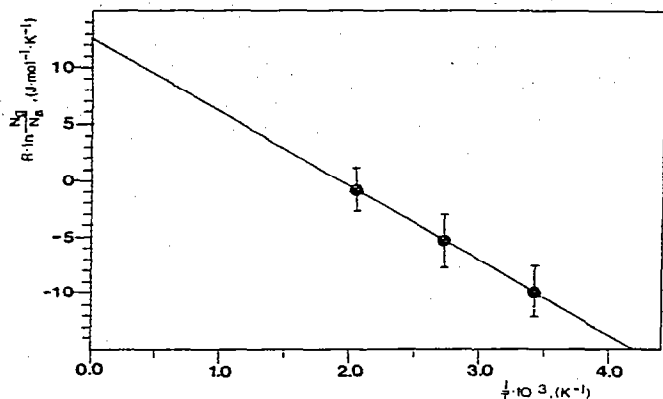
Fig. 5. Propionyl chloride. Van't Hoff plot of composition data. The half-lengths of the vertical bars indicate 1σ. Least-squares straight line.

determined from a straight line fitted to the $(R \ln K, 1/T)$ points (Fig. 5). The best-fit (least squares) line leads to the following values with estimated standard deviations $\Delta E = E_g - E_a = 6 \pm 2$ kJ mol^{-1} and ΔS (excluded the contribution from the fact that there are two enantiomeric *gauche* forms) $= 7 \pm 6$ J mol^{-1} K^{-1}. The value for ΔE is considerably higher than the value reported from the spectroscopic study [6] (3.5 kJ mol^{-1}). However, no uncertainty was reported in that work and that makes it difficult to judge how different the two values really are. For chloroacetyl chloride the values were determined to be: $\Delta E = 5 \pm 2$ kJ mol^{-1} and $\Delta S = 3 \pm 4$ J mol^{-1} K^{-1}. The change in ΔE as a result of substituting one of the chlorine atoms in chloro-acetyl chloride with a CH_3—group is therefore small, if any at all. The large uncertainties in ΔS prevent meaningful comparisons here.

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