Table X. Typical FT NMR Acquisition Parameters

parameter	^{1}H	^{13}C{^{1}H}	^{31}P{^{1}H}
total scans	32	240	32
sweep width, Hz	3000	13 000	10 000
Fourier no.	16K	16K	8K
cycle time, s	3.0	1.5	1.5
pulse width, μs	2	9	9

Experimental Section

The variable-temperature 101.2-MHz ^{31}P{^{1}H} and 62.9-MHz ^{13}C{^{1}H} pulsed FT NMR spectra were recorded on a Bruker WM250 NMR system at the University of Vermont using a custom-built cold nitrogen gas delivery system, modified superconducting magnet cavity, and Bruker BVT-1000 temperature control unit. Temperature measurement is accurate to ±3 K for ^{1}H spectra and ±4 K for ^{13}C{^{1}H} and ^{31}P{^{1}H} spectra. Due to the error in temperature measurement, we do not report $\Delta H^\ddagger$ and $\Delta S^\ddagger$ values. The variable-temperature 270-MHz ^{1}H FT NMR spectra were recorded on a Bruker HX270 NMR system at the NSF Regional Instrumentation Center, Yale University. All spectra were obtained by using quadrature-phase detection. Typical acquisition parameters are listed in Table X. All NMR samples were sealed after a minimum of three freeze–pump–thaw cycles using a vacuum below 0.1 torr.

Certain phosphines were synthesized by using literature procedures. Others were purchased. All reactions were performed under nitrogen and manipulated inside nitrogen-flushed glovebags. All solvents used in synthesis and workup were either thoroughly degassed or distilled under nitrogen. Diethyl ether and tetrahydrofuran were freshly distilled from sodium and benzophenone ketal.

Di-*tert*-butylphosphine (**1**),[32] di-*tert*-butylmethylphosphine (**2**),[33] di-*tert*-butylethylphosphine (**3**),[34] di-*tert*-butylbenzylphosphine (**4**),[35] and di-*tert*-butylisopropylphosphine (**5**)[34] are all known compounds and were synthesized by literature procedures: NMR data, see text.

Tri-*tert*-butylphosphine (**6**) and di-*tert*-butylphenylphosphine (**7**) were purchased from Strem Chemicals Co. and used without further purification: NMR data, see text.

Supplementary Material Available: Figures 1, 2, 5, 6, 9–16, 19, 24, and 26 of NMR spectra (**1–6**) and Tables IS, IIS, IIIS, IVS, VS, and VIS of bond angles and bond lengths (**1–7**) (40 pages). Ordering information is given on any current masthead page.

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Structure and Conformations of 4-Chloro-1-butanol: Electron-Diffraction Evidence for Internal Hydrogen Bonding

Otto Bastiansen, Liv Fernholt, Kenneth Hedberg,* and Ragnhild Seip

Contribution from the Department of Chemistry, University of Oslo, P.B. 1033, Blindern 0315, Oslo 3, Norway. Received July 15, 1985

Abstract: Internal hydrogen bonding is generally believed to occur in the free molecules of substances that have suitable, properly oriented, donor and acceptor groups, as in 2-chloro- or 2-fluoroethanol. However, such bonding is difficult to establish by purely structural means because the orientation of the skeletal atoms is also influenced by a "gauche effect" when the donator and acceptor groups are separated by only one skeletal torsion angle. Accordingly, we have investigated the structure of 4-chloro-1-butanol, a molecule in which any gauche effect should be minimal, for evidence of internal hydrogen bonding. If rotation about each C–C bond is assumed to generate three potential energy minima, this molecule has 14 conformers that are characterized by different distances between the heavy atoms, only one of which has the Cl and O atoms within hydrogen-bonding distance. Since it is not possible to determine the composition of such a complicated mixture of conformers by electron diffraction, calculations from molecular mechanics were used to predict a composition *exclusive of any assumed contribution to the energy from hydrogen bonding*. Refinement of models in which the mole fraction of the hydrogen-bonded conformer was allowed to adjust led to large increases over that predicted from molecular mechanics. We take these results as strong evidence for the existence of internal hydrogen bonding. Values for the structural parameters and conformational composition are presented.

The problem of internal hydrogen bond formation is an intriguing one. Evidence for the existence of such bonds is found in the structures of many molecules in which internal rotation plays a role, such as glycol and glycerol,[1] and in the 2-haloethanols, molecules of particular interest in connection with the work to be described here. In the cases of 2-chloro-[1-4] and 2-bromoethanol,[2,5] for example, the lower energy of the gauche ($\phi \simeq 55°$) forms relative to the anti ($\phi \simeq 180°$) stands in contrast to the relative energies of these forms in the corresponding 1,2-dihaloethanes[5-8] in which the anti form is the lower energy one and has been attributed to the stabilizing effect of O–H···X bond formation. This satisfying picture is clouded by the results for 2-fluoroethanol[9,10] and 1,2-difluoroethane:[6,11,12] the more stable form for the former is of course gauche; the latter, however, is not the

expected anti but is also gauche.

The stability of the gauche forms of such 1,2-disubstituted compounds with electronegative substituents has been accounted

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*On sabbatical leave. Permanent address: Department of Chemistry, Oregon State University, Corvallis, Oregon 97331.

Table I. Steric Energies[a] of Conformers of 4-Chloro-1-butanol

| conformer | | MM2[b] | | model A[c] | model B[c] | model D[c] |
no.	symbol[d]	E_s	%[e]	E_s	E_s^f	E_s^f
1	AAA	10.406	15.1	15.51 (−377)	19.12 (−544)	11.76
2	G⁻AA	11.782	17.9	14.18 (−209)	13.89 (+795, −167)	13.14
3	AAG⁻	11.970	16.7	12.55 (+272, −126)	11.67 (+167, −105)	13.26
4	G⁻AG⁺	12.611	13.1	11.84 (+272, −126)	11.63 (+230, −209)	13.97
5	G⁻AG⁻	13.276	10.3	14.31 (−251)	16.23 (−377)	14.64
6	AG⁻A	14.259	7.0	15.06 (+544, −167)	17.28 (−293)	15.56
7	G⁻G⁻A	15.368	4.6		13.60 (+502, −167)	16.82
8	AG⁻G⁻	15.619	4.2			17.07
9	G⁻G⁺A	15.736	4.0			
10	G⁻G⁻G⁻	15.778	3.9	12.93 (+502, −167)	15.56 (−355)	17.15
11	G⁻G⁺G⁺	18.129	1.6	11.34 (+126, −84)	11.05 (+84, −63)	9.83 (+33, −29)
12	AG⁻G⁺	19.359	1.0			
13	G⁻G⁻G⁺	21.418	0.5			
14	G⁻G⁺G⁻	23.058	0.3			

[a] In kJ/mol. [b] From molecular mechanics. [c] From least-squares refinements. [d] See text. [e] Composition calculated from Boltzmann formula. [f] Estimated 3σ uncertainties in parentheses.

for in terms of a "gauche effect",[13] which may also be expected to operate strongly in the case of 1,2-difluoroethane, and to some extent in the case of 1,2-dichloroethane. Although the hydroxyl group is known[2,9] to be oriented toward rather than away from the halogen atoms in the 2-haloethanols, the question remains as to how important hydrogen bonding is for the determination of conformational stability, or indeed whether hydrogen "bonds" actually exist in these compounds.[2]

It seems likely that at least some understanding of the role of internal hydrogen bonding in the halogen-substituted alcohols could be gained from investigations of the conformational composition of longer chain compounds in which the gauche effect is expected to be negligible. If rotation about the O–C bond is disregarded, the molecule 3-chloropropanol has five distinct conformers (two enantiomorphic pairs and an extended form) arising from the anti and (two) gauche forms generated by rotations about the C–C bonds, each assumed to give rise to three potential minima. The dominant conformer is a gauche–gauche form that places the C–O and C–Cl bonds on opposite sides of the $C_1C_2C_3$ plane.[14] This result supports the notion of a negligible gauche effect, but none of the conformers has a structure favorable for hydrogen bond formation. On the other hand, the molecule 4-chloro-1-butanol (hereafter CB) has 14 distinct conformers of which only one (an enantiomorphic pair) is favorable for O–H···Cl bonding. Without a gauche effect, evidence for the formation of a hydrogen bond in the molecule would be the existence of this form in amounts greater than expected. Accordingly, we decided to investigate the CB system by electron diffraction from the gas. No previous diffraction work on the molecule is known to us, but a study of a similar system, 4-penten-1-ol, has recently been completed.[15]

Experimental Section

The sample of 4-chloro-1butanol (Fluka) was purified in our laboratory by Else Kloster-Jensen, to whom we are very grateful.

The diffraction patterns were made in the Balzers Eldigraph KDG-2[16,17] with use of an r^3 sector and a nominal electron wavelength of 0.059 Å calibrated against benzene. In order to avoid decomposition of the compound, the temperature was kept as low as possible by using a doughnut-shaped nozzle.[18] Six plates were made at a nominal nozzle-to-plate distance of 500 mm and five at 250 mm; the nozzle temperature was about 42 °C. The experimental data were treated in the usual way.[19]

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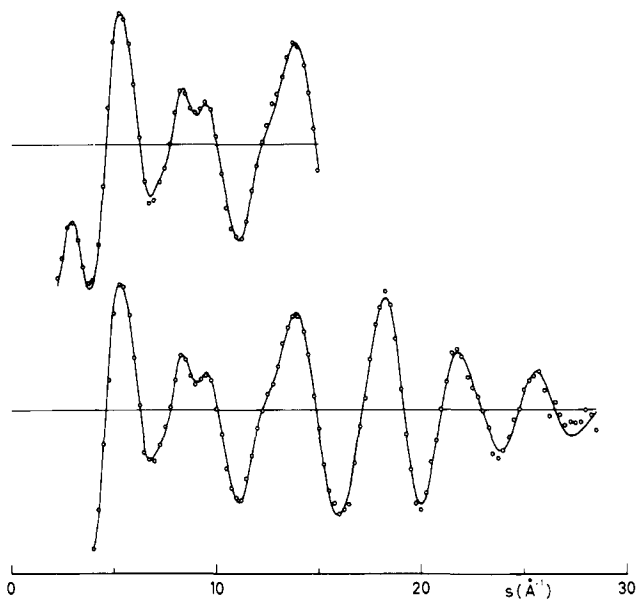(19) Andersen, B.; Seip, H. M.; Strand, T. G.; Stølevik, R. *Acta Chem. Scand.* **1969**, *23*, 3224.

Figure 1. Intensity curves. The experimental values are indicated by the circles; the solid line is the curve for model B.

The complex scattering factors were calculated[20] by using Hartree–Fock potentials[21] for Cl, O, and C and a molecular bonded potential for H.[22] The molecular intensities were modified by multiplication with the factor $s/f_{Cl}f_C$. The average modified molecular intensities ranged from $s = 2.25$ to 15.00 Å⁻¹ (long camera distance) with data points at the interval $s = 0.125$ Å⁻¹ and from $s = 4.00$ to 28.50 Å⁻¹ (shorter distance) with $s = 0.25$ Å⁻¹. The intensity curves are shown in Figure 1 and the corresponding radial distribution curve in Figure 2.

Structure Analysis

The conformations of CB of importance to the electron-diffraction analysis include the many combinations of rotations, both positive and negative, about the three C–C bonds; rotations about the C–O bond affect only vicinal nonbond distances to H_5 (Figure 2) that cannot be reliably measured. If one assumes the rotational potential for each C–C bond to have three minima corresponding to two gauche and an anti conformation of the adjacent bonds to heavy atoms, there are 27 different possible conformers of which 13 occur as enantiomorphic pairs. Thus, including the single extended form with C_s symmetry there are 14 conformations to be considered. Symbols for these are given in Table I where the letters from left to right refer to rotations about the bonds C_1–C_2, C_2–C_3, and C_3–C_4, respectively. The symbol G⁺G⁻A, for example,

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Table II. Parameter Values Obtained from Molecular Mechanics[a]

parameter	conformer no.[b]								
	1	2	3	4	5	6	7	10	11
$r(C-O)$	1.410	1.409	1.410	1.410	1.409	1.410	1.409	1.409	1.409
$r(C_1-C_2)$	1.533	1.534	1.534	1.534	1.534	1.533	1.534	1.534	1.534
$r(C_2-C_3)$	1.537	1.534	1.538	1.538	1.538	1.538	1.539	1.539	1.539
$r(C_3-C_4)$	1.534	1.534	1.535	1.535	1.535	1.534	1.534	1.535	1.535
$r(C-Cl)$	1.787	1.787	1.787	1.787	1.787	1.788	1.788	1.786	1.787
$r(O-H)$	0.943	0.942	0.943	0.942	0.942	0.943	0.942	0.942	0.942
$r(C-H)$[c]	1.116	1.116	1.115	1.115	1.115	1.115	1.115	1.115	1.115
$\angle COH$	108.7	108.8	108.8	108.7	108.8	108.8	108.9	108.7	108.9
$\angle CCO$	108.7	109.1	108.8	109.2	109.2	108.6	109.2	109.3	109.8
$\angle C_1C_2C_3$	111.7	112.5	111.6	112.4	112.4	113.3	114.4	114.6	114.6
$\angle C_2C_3C_4$	111.3	111.3	113.5	113.5	113.5	113.0	113.1	115.5	116.1
$\angle CCCl$	111.2	111.3	112.4	112.4	112.5	111.2	111.3	112.4	112.5
$\angle HCH$[c]	108.6	108.4	108.2	108.1	108.0	108.4	108.0	107.3	107.4
$\angle CCCO$	179.9	62.9	179.9	63.1	62.0	175.9	56.4	55.7	72.8
$\angle CCCC$	180.0	179.2	−177.0	−178.0	175.7	65.7	62.9	58.6	−65.6
$\angle CCCCl$	180.0	−179.9	−67.3	−67.2	66.7	176.8	176.1	62.2	−63.2
$\angle CCOH$	180.0	−179.3	178.9	179.8	178.8	−178.7	178.4	177.7	176.9

[a] Distances (r) in Ångstroms; angles in degrees. [b] See Table I and text. [c] Average values.


```
              H41  H31  H21  H11
               |    |    |    |
        Cl — C4 — C3 — C2 — C1 — O — H5
               |    |    |    |
              H42  H32  H22  H12
```
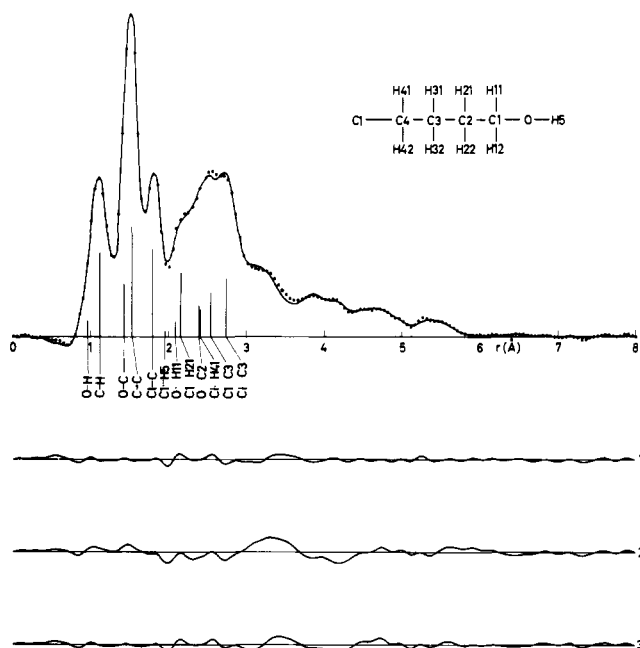
Figure 2. Radial distribution curve. The experimental curve is indicated by dots superimposed on the theoretical curve for model B drawn with a solid line. The differences between experiment and the theoretical curves for models B, C, and D are denoted by 1, 2, and 3, respectively. The vertical lines locate the principle interatomic distances not subject to torsion.

designates a 60° counterclockwise rotation of the O–C₁ bond from the position eclipsing C₂–C₃, a 60° clockwise rotation of the C₁–C₂ bond from that eclipsing C₃–C₄, and a 180° rotation of the C₂–C₃ bond from that eclipsing C₄–Cl.

The analysis began with the reasonable assumption that corresponding bond distances and bond angles in the conformers, as well as the vibrational amplitudes for bond and geminal distances, do not differ significantly. With these assumptions the structural parameters that define a model of 4-chloro-1-butanol are the bond lengths $r(C-C)$, $r(C-O)$, $r(C-Cl)$, and $r(C-H)$; the bond angles $\angle CCC$, $\angle CCO$, $\angle CCCl$, and $\angle HCH$; the torsion angles around the three C–C bonds; and, in the case of a mixture, the mole fractions of the conformers. In order to ascertain how well each conformer alone could be made to fit the data, a number of test refinements were first carried out in which the more important bond distances, bond angles, and amplitudes were refined. An important result of this preliminary work was the discovery that, although no conformer gave a satisfactory fit to the experimental torsion-sensitive distance distribution seen in the radial distribution curves, some conformers were distinctly better than others. Included in
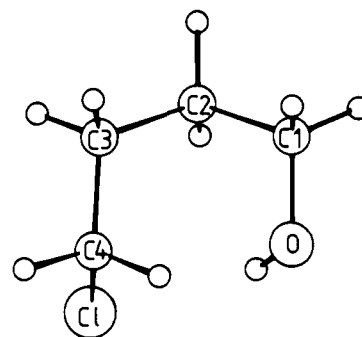
Figure 3. Model of the conformer with possible hydrogen bonding $(G^-G^+G^+)$.

this better group was $G^-G^+G^+$ (Figure 3), the only form that afforded reasonable opportunity for O–H⋯Cl bonding. As expected, combinations of these better fitting conformers also gave better than average fits to experiment.

There was, of course, no way in which a model of the system containing arbitrary mole ratios of the 14 conformers could be refined to provide a result for the system composition because the nonlinear least-squares method used for fitting electron-diffraction data requires an initial model suitably close to the final one. It seemed likely that such a model could be found by the methods of molecular mechanics. We used the program MM2[23] to calculate both the structures and the steric energies of the 14 conformers *exclusive of contributions from possible O–H⋯Cl hydrogen bonds* and then calculated the corresponding mole ratios based on assumption of a Boltzmann distribution. The energies and mole ratios for the fully relaxed structures are given in the third column of Table I. The calculated structures for most conformers reckoned to be present in amounts greater than 1% are given in Table II.

The main refinements of the structure were designed to determine the extent to which O–H⋯Cl hydrogen bonding is important in CB. This problem amounted to a determination of the mole ratios of the conformers: an excess of $G^-G^+G^+$ over the amount calculated with assumption of no hydrogen bonding would constitute evidence for the presence of such bonding. The problem itself was, of course, completely intractable without simplifications that reduced drastically the enormous (in principle) number of independent geometrical and vibrational parameters. With respect to the structural parameters, most of the simplifications were based on the results of the molecular mechanics calculations. One was the assumption that conformers calculated to be present in amounts less than about 5% could be ignored (except for $G^-G^+G^+$, of course, and for $G^-G^-G^-$ for reasons explained below) without

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Table III. Calculated Amplitudes[a] for Important Conformers of 4-Chloro-1-butanol

distance type[b]	conformer no.								
	1	2	3	4	5	6	7	10	11
bonds									
C–O	0.0468	0.0468	0.0468	0.00468	0.0468	0.0468	0.0468	0.0468	0.0468
⟨C–C⟩[c]	0.0493	0.0493	0.0493	0.0494	0.0494	0.0494	0.0494	0.0494	0.0494
C–Cl	0.0491	0.0491	0.0491	0.0491	0.0491	0.0491	0.0491	0.0491	0.0491
O–H	0.0692	0.0692	0.0692	0.0692	0.0692	0.0692	0.0692	0.0692	0.0692
⟨C–H⟩[d]	0.0782	0.0782	0.0782	0.0782	0.0782	0.0782	0.0782	0.0782	0.0782
geminal									
C·O[e]	0.0772	0.0772	0.0771	0.0772	0.0772	0.0772	0.0772	0.0772	0.0770
⟨C·C⟩[e]	0.0790	0.0790	0.0788	0.0787	0.0787	0.0786	0.0785	0.0781	0.0779
C·Cl	0.0808	0.0808	0.0805	0.0805	0.0805	0.0808	0.0808	0.0805	0.0805
O·H	0.118	0.118	0.118	0.0118	0.118	0.118	0.118	0.118	0.118
⟨C·H_c⟩[f]	0.119	0.119	0.119	0.119	0.119	0.119	0.119	0.119	0.119
C·H_0	0.105	0.105	0.105	0.105	0.105	0.105	0.105	0.105	0.105
Cl·H	0.124	0.124	0.123	0.124	0.124	0.124	0.124	0.124	0.124
H·H[c]	0.183	0.184	0.185	0.186	0.186	0.184	0.186	0.189	0.190
torsion sensitive[g]									
C··O	0.0796	0.153	0.0796	0.153	0.153	0.0799	0.151	0.151	0.149
C··C	0.0811	0.0812	0.0812	0.0812	0.0814	0.155	0.154	0.152	0.151
C··Cl	0.0807	0.0807	0.166	0.166	0.166	0.0810	0.0811	0.165	0.164
C···O	0.103	0.153	0.102	0.158	0.151	0.150	0.267	0.270	0.240
C···Cl	0.108	0.108	0.168	0.169	0.168	0.155	0.153	0.289	0.276
O····Cl	0.101	0.214	0.227	0.157	0.263	0.142	0.297	0.322	0.415

[a] In Ångstroms. [b] Number of dots indicates number of bond angles separating the atoms. [c] Average. Largest difference between values for same conformer was 0.0001 Å. [d] Largest difference in values was smaller than 0.0001 Å. [e] Largest difference in values was 0.0006 Å. [f] Largest difference in values was 0.003 Å. [g] Amplitudes for torsion-sensitive distances between a heavy atom and hydrogen have been omitted. Their values fell in the range 0.10–0.36 Å.

Table IV. Refinement Results for 4-Chloro-1-butanol[a]

Parameter Values Common to All Models[b]

bonds			geminal distances			bond angles	
	r_a/Å	l/Å		r_a/Å	l/Å		∠/deg
C–O	[1.430]	0.051 (4)	C·O	2.389 (15)	0.076 ⎫	CCO	107.7 (7)
C–C	1.526 (2)	0.053	C·C	2.537 (8)	0.077 ⎬ (10)	CCC	112.4 (7)
C–Cl	1.796 (4)	0.061 (4)	C·Cl	2.743 (13)	0.079 ⎭	CCCl	111.1 (6)
C–H	1.108 (4)	0.074 (5)	O·H	2.088 (13)	0.110 ⎫ (9)		
			C·H	2.157 (12)	0.111 ⎭		

Percentage Composition[c]

conformer[d]	model A		model B		model C	model D
	obsd	calcd[e]	obsd	calcd[e]	calcd[e]	obsd
1	2.5 (75)	17.6	0.6 (74)	16.7	16.0	9.6
2	8.3 (88)	20.9	8.8 (84)	19.8	19.0	11.3
3	15.5 (100)	19.5	20.8 (100)	18.5	17.6	10.7
4	20.4 (131)	15.3	21.0 (124)	14.4	13.8	8.4
5	8.2 (113)	12.0	3.7 (118)	11.5	10.9	6.6 (50)[f]
6	6.0 (52)	8.2	1.7 (62)	7.8	7.4	4.8
7	[0.0]		10.1 (86)	5.1	4.9	3.0
8	[0.0]		[0.0]		4.5	2.9
10	13.7 (118)	4.5	4.8 (120)	4.4	4.2	2.4
11[g]	25.4 (82)	2.0	28.5 (78)	1.9	1.7	40.3 (50)
R[h]	0.084		0.083		0.145	0.100

[a] Quantities in square brackets were assumed; those in curly brackets were refined in groups. [b] Uncertainties are estimated 3σ. [c] Uncertainties are 2σ. [d] See Table I for identification of conformers. [e] From molecular mechanics. See text. [f] Uncertainty for group as a whole. [g] Hydrogen-bonded conformer. [h] $R = \sum W\Delta_s^2 / \sum W(I_s^{obsd})^2$ where $\Delta = I^{obsd} - I^{calcd}$.

significant effect on the results of the refinements. Other assumptions were equality of the lengths of all bonds of the same type (C–C or C–H, etc.) irrespective of conformation, equal values for all bond angles defined by bonds between the same types of atoms (CCC, CCCl, etc.), and methylene group geometry characterized by the plane of the CH_2 group as bisector of the opposite R_1CR_2 angle. (The extent to which these assumptions are justified may be seen by comparing the parameter values of Table II. We regard the assumptions as excellent.) The torsion angles for each conformer were assigned the values calculated for them, and the COH and HCH bond angles and the O–H distance were each given an approximate average value suggested by the calculations. As a consequence of these assumptions the structure and composition of CB are specified by values for seven geometrical parameters and the mole fractions of the numbers of con-

formers (minus one) to be considered. The geometrical parameters were chosen to be the bond lengths r(C–O), r(C–C), r(C–Cl), and r(C–H) and the bond angles ∠CCO, ∠CCC, and ∠CCCl. Most of the large number of vibrational amplitude parameters arising from the several hundred interatomic distances in the CB system were obviously nonrefinable. In order to elicit reasonable values for these amplitudes, we carried out normal coordinate calculations[24] for each conformer of interest. The simple force field for the calculations comprised internal force constants (stretches, bends, and torsions) with values taken from similar molecules. The amplitude values for the more important distances obtained from the calculations are given in Table III. The

(24) Hedberg, L. Abstracts, 7th Austin Symposium on Gas Phase Molecular Structure, Austin, Texas, 1978, 49.

Table V. Correlation Matrix (×100) for Models A and B[a]

		σ_{LS}^b (×100)	r_1	r_2	r_3	$\angle 4$	$\angle 5$	$\angle 6$	l_7	l_8	l_9	l_{10}	l_{11}	X_{12}	X_{13}	X_{14}	X_{15}	X_{16}	X_{17}	X_{18}	X_{19}
1.	r(C–C)	0.0762	100	39	15	–15	–23	–27	–16	–8	22	–6	18	0	2	0	–4	–3	2	11	0
2.	r(C–Cl)	0.136		100	14	–36	–27	–49	21	–3	14	7	–33	1	–4	–7	–9	–5	5	17	0
3.	r(C–H)	0.178			100	10	13	–3	–22	0	–1	–6	–3	0	2	1	1	0	–1	1	0
4.	$\angle$CCO	24.1	A			100	36	45	–12	–5	–5	–7	30	–2	9	13	12	4	–10	–18	0
5.	$\angle$CCC	22.4					100	34	–10	7	–11	–47	33	–4	22	20	15	2	–13	–9	0
6.	$\angle$CCCl	18.0						100	2	1	0	11	26	–4	21	17	14	7	–13	10	0
7.	l(C–O)	0.138							100	15	32	4	–23	1	–4	–2	–7	0	0	19	0
8.	l(C–Cl)	0.139								100	13	1	24	1	–2	–1	–1	3	0	2	0
9.	l(C–H)	0.152									100	0	–17	0	0	0	–4	–1	0	13	0
10.	l(C·O)	0.430								σ_{LS}^b	100	14	0	–4	–5	–4	0	3	12	0
11.	l(O·H)	1.08								(×100)		100	–1	6	6	8	6	–6	–8	0
12.	$X(1)^c$	3.76								3.7			100	–77	0	–86	–11	60	1	0
13.	$X(3)$	5.02								5.0			–80	100	–4	74	1	–61	6	0
14.	$X(6)$	2.62								3.1			13	–32	100	–24	–50	25	–1	0
15.	$X(2)$	4.40								4.1			–85	67	–21	100	36	–78	–1	0
16.	$X(5)$	5.66	B							5.9			–1	–14	–13	34	100	–60	16	0
17.	$X(4)$	6.53								6.2			57	–51	16	–77	–58	100	–15	0
18.	$X(11)$	4.11								3.9			–5	17	–23	0	0	–11	100	0
19.	$X(10)$									6.0			17	–34	38	–13	–13	7	–77	100

[a] Model A: upper triangular array; model B: lower triangular array. [b] Standard deviations for least squares. Distance (r) and amplitudes (l) in ångstroms, angles ($\angle$) in degrees; X's are mole fractions. [c] Numbers in parentheses designate conformer. See Table I.

amplitudes for all torsion-sensitive distances except H···H (terms for individual H···H interactions are of negligible weight) were assigned their calculated values. Certain other amplitudes were grouped together as single parameters with differences held at those determined by the calculated values; the set of these amplitude parameters is evident from Table IV.

Refinements of the CB system were carried out by least-squares adjustment of intensity curves with use of procedures previously described.[19] Shrinkage corrections were regarded as negligible compared to other assumptions and ignored. Early tests showed that the parameter r(C–O) was highly correlated with certain amplitudes, and we elected not to attempt its refinement. Several model systems consisting of seven or more conformers were investigated. In one of the first of these, six of the conformers calculated from molecular mechanics to be the most abundant, together with a seventh, G⁻G⁻G⁻ (No. 10), that the preliminary testing had shown to provide one of the best fits of any single species, and an eighth, the possibly hydrogen-bonded one G⁻G⁺G⁺ (No. 11), were included at starting concentrations taken from the calculations but scaled proportionately upward to total 100%. The results of this refinement are in given Table IV as model A. In a succeeding refinement the number of conformers was increased to 10 by inclusion of G⁻G⁻A (No. 7) and AG⁻G⁻ (No. 8), but the amount of No. 8 obtained a negative value. When the refinement was repeated with the amount of No. 8 set to zero and the structural and amplitude parameters held at the values found for model A, the results tabulated as model B were obtained. Model C represents a system with the mole fractions of the 10 most abundant conformers held at the values from the MM2 calculations and model D a system of the same 10 conformers in which the mole fraction of the hydrogen-bonded species was allowed to adjust against that of the rest of the group with relative mole fractions taken from MM2.

The values of the agreement factor R (Table IV) indicate clearly that models A and B provide the best fits to the diffraction data and model C the worst; the quality of the fits is seen graphically in the difference curves of Figure 2. Figure 4 shows the locations of the torsion-sensitive distances in each of the conformers of model B. Correlation matrices for the parameters of models A and B are presented in Table V.

Discussion

The most interesting feature of our results is the strong evidence they hold for the existence of internal O–H···Cl hydrogen bonding: models A, B, and D in Table IV all provide a much better fit than does model C in which the mole fraction of the hydrogen-bonded conformer was held at the value calculated assuming no O–H···Cl interaction. Further, when allowed to vary as in models A, B, and D in Table IV, the mole fraction of the hydrogen-bonded
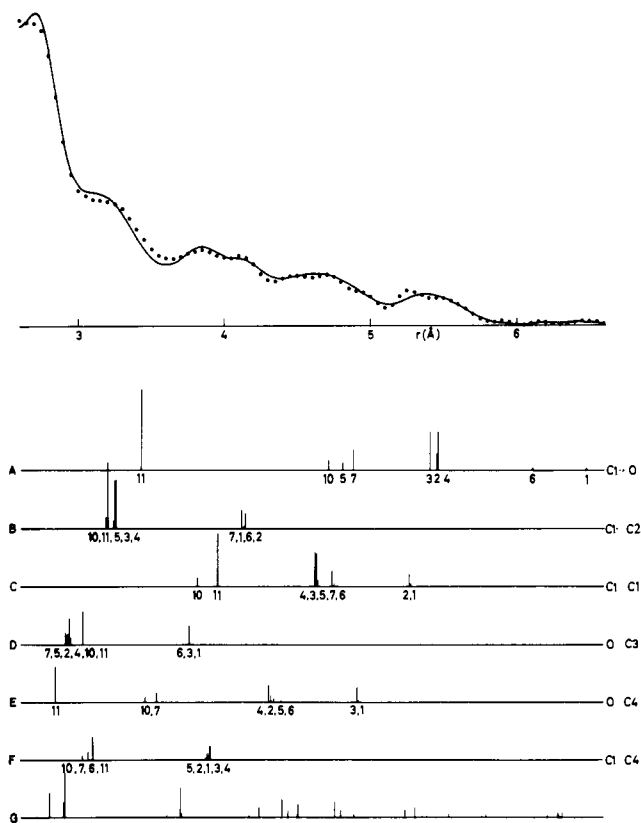

Figure 4. Distribution of torsion-sensitive distances for model B. The curves are the outer portion of the radial distance distribution (Figure 2). The vertical lines denote the most important distances for each of the conformers of model B. The terms are labeled at the right-hand side of the figure. The line labeled G shows the distribution of Cl···H distances in all conformers of model B.

conformer (No. 11) is observed to be very much larger than that calculated with the assumption of no hydrogen bond energy. Since the uncertainties associated with the amounts of this conformer leave little doubt that the difference is significant, the case for internal hydrogen bonding rests first and foremost on the reliability of the steric energy calculations from molecular mechanics. Judged from experience, there is no reason to distrust the calculations for a straightforward system such as CB. So far as the present work is concerned, we note that the calculated composition is in quite good agreement with experiment, apart from the amounts of conformers 1 and 2 that have been depleted (models

A and B) in favor of 11. As model D shows, however, maintenance of the relative amounts, calculated from MM2, of all possible conformers except No. 11 leads to only slightly poorer overall agreement than when the amounts of the conformers are allowed to refine freely. A more direct comparison of the experimental and theoretical results is obtained by transformation of the experimental compositions into steric energies. Since the experimental compositions provide only relative energies, it was necessary to scale them. This was done by use of the formula $E_s(\text{ED}) - E_s(\text{MM2}) = RT \ln [X(\text{ED})/X(\text{MM2})]$, where the X's are mole fractions. The results, given in Table I, are in very good agreement with those from the MM2 calculations; only the values for conformer AAA differ by more than the experimental uncertainty. All in all, we find no evidence in our experimental results that the MM2 energies are unreliable for those CB conformers incapable of hydrogen bond formation.

If it is assumed that the major difference between the MM2 and the experimental composition of the CB system is due to O–H⋯Cl hydrogen bonding, the difference provides a rough estimate of the energy of the hydrogen bond. Models A, B, and D have estimated steric energies for the hydrogen-bonded conformer G⁻G⁺G⁺ that differ respectively by 6.7 ± 1.3, 7.1 ± 0.8, and 8.4 ± 0.4 kJ/mol from the MM2 result obtained with the assumption of no hydrogen bonding. Not surprisingly, these values are smaller than the energies of such bonds to atoms more electronegative than chlorine. They are also smaller than the energy difference of 10.9 (+7.9, −3.3) kJ/mol between the gauche and anti forms of 2-chloroethanol.[3]

Since our investigation of CB made use of torsion-angle values for the various conformers calculated from MM2, the O⋯Cl distance in the hydrogen-bonded conformer, as in the other conformers, was restricted to a range determined by the uncertainties in the bond lengths and bond angles. This range is centered at about 3.4 Å (Figure 4), a value not much different from the 3.17 Å O⋯Cl distance found for the gauche conformer in 2-chloroethanol. It is not known how reliable the hydrogen-bonded O⋯Cl distance is because the parameters that determine it are highly correlated with its associated amplitude of vibration. Refinements designed to test the matter gave values over the approximate range 3.1–3.9 Å.

Selectivity of Proton Abstraction from Propyne on the Ag(110) Surface

J. M. Vohs, B. A. Carney, and M. A. Barteau*

Contribution from the Center for Catalytic Science and Technology, Department of Chemical Engineering, University of Delaware, Newark, Delaware 19716. Received June 26, 1985

Abstract: Propyne reacts with oxygen atoms adsorbed on the Ag(110) surface via proton transfer to produce water. At 200 K this reaction is selective toward formation of stable surface methyl acetylides. At 300 K proton abstraction from the methyl group of propyne competes with methyl acetylide formation. Surface methyl acetylides were thermally stable to 500 K; surface propargyl species were unstable and could not be isolated before decomposing to deposit surface carbon. The activation energy difference for proton abstraction from the two ends of propyne was determined to be 3.2 kcal/mol based on results from XPS and TPD experiments. This difference is in good agreement with the calculated stabilities for methyl acetylide and propargyl anions and with the relative rates of proton abstraction in the gas phase. XPS spectra for adsorbed methyl acetylide species demonstrate greater polarization of the acetylenic π-orbitals than for adsorbed HC_2 species; these results support previous polarization models for alkyl substituent effects on gas-phase acidities.

I. Introduction

The unravelling of reaction mechanisms and the connection of surface chemistry to the physical and chemical properties of solids represent one of the great challenges in modern heterogeneous catalysis. In the absence of mechanistic information obtained by methods such as in situ spectroscopies or isotopic labeling, perhaps the most common approach to rationalization of heterogeneously catalyzed reactions is to borrow plausible mechanisms from homogeneous chemistry, both catalytic and noncatalytic. It is not surprising that these connections are most highly developed for some of the simplest reactions, e.g., proton-transfer reactions. The chemistry and product distribution of the heterogeneously catalyzed cracking of hydrocarbons, for example, appear to be well described by reactions observed in acid and superacid solutions.[1,2]

While it is tempting to apply the well-developed concepts of proton-transfer reactions in solution to the large number of hydrogen-abstraction reactions occurring on surfaces, particularly those of ionic solids, this approach may be both qualitatively and quantitatively misleading for certain reactions. For example, the relative acidities of organic acids in the gas phase are dramatically different from those in aqueous solution. It is not clear how such properties may change when these molecules are adsorbed on a solid surface, or how one can quantitatively relate the acid–base properties of a solid catalyst to those of an adsorbed indicator when the latter have been determined in solution. Likewise, although reactions such as the dehydration and dehydrogenation of alcohols are classic test reactions which have been used to characterize the acid–base properties of solid catalysts, recent studies have reported results (e.g., the production of ethylene from ethanol on basic MgO[3]) which suggest that the reaction selectivity may not be related straightforwardly to the mechanisms of acid and base catalysis usually postulated.

We have chosen the base-catalyzed isomerization of alkynes as a test reaction for the transferability of acid–base mechanisms from homogeneous media to solid surfaces. These isomerizations

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