Thus, the *number* of H_2O molecules in the clathrate structure would not be expected to be equal to the number of minima; i.e., we would not expect to find only *eight* molecules of water surrounding CH_4 as a consequence of the existence of *eight* shallow minima.

In CH_3OH, the interaction between its OH group and H_2O is the dominant feature in the attractive region of the isoenergy map (see Figures 5 and 6). The figures show two regions of pronounced minima, one corresponding to a standard hydrogen bond between an H_2O molecule and the methanol OH group, and the other in the direction of the lone pairs of the oxygen atom. The two minima persist out of the plane, as shown in Figure 6. On this basis, we might expect that the OH of CH_3OH will take the place of an OH of H_2O when CH_3OH is in solution. Since the OH of CH_3OH assumes a different orientation for each conformation (for example, S, P, E), the $H_2O\cdots H_2O$ network is expected to be different for each conformation. These differences might alter the relative stabilities for the S, P, and E conformations.[22] However, it might be difficult for a Monte Carlo simulation to settle this small energetic detail (the barrier is only about 1 kcal/mol) with present-day water–water potentials for studies of solutions. The strength of the interaction between the OH group of methanol and H_2O is larger enough to perturb the water molecules in the CH_3 region of methanol (see Figures 5 and 6). On this basis, water molecules solvating the CH_3 group of CH_3OH might resemble the solvation of CH_4 around the methyl group but not around the hydroxyl group. However, the isoenergy contour maps alone are *not sufficient* to allow a more precise prediction of the organization of H_2O molecules about the methyl group of methanol in aqueous solution.

These $CH_4\cdots H_2O$ and $CH_3\cdots H_2O$ potentials have been used, together with an $H_2O\cdots H_2O$ potential,[11] in Monte Carlo studies of the hydration of methane and methanol; for details, see ref 7 and 8.

A number of points on the water–methanol potential surface have been computed with a larger basis set, (11s, 7p, 1d) for C and O atoms and (6s, 1p) for H atoms; as above, the CP and the dispersion corrections were added.[34] As expected these data confirm the potential reported in Table II; the largest difference is a decreased attraction for the first minimum (the one shown in the upper half of Figures 5 and 6) which now becomes as deep as the second minimum (the one shown in the lower half of Figures 5 and 6).

Acknowledgment. This work was supported in part by research grants from the National Science Foundation (PCM79-20279) and from the National Institute of General Medical Sciences of the Institutes of Health, U.S. Public Health Service (GM-14312).

Registry No. Water, 7732-18-5; methane, 74-82-8; methanol, 67-56-1.

Supplementary Material Available: Tables IV–VII giving the geometries for the $CH_4\cdots H_2O$ and CH_3—$OH\cdots H_2O$ systems and the corresponding interaction energies (SCF, SCF + CP, and SCP + CP + E_{disp}) (30 pages). Ordering information is given on any current masthead page.

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Microwave Spectrum, Dipole Moment, and Substitution Structure of Peroxyformic Acid

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Contribution from the Laboratory for Physical Chemistry, Swiss Federal Institute of Technology, CH-8092 Zurich, Switzerland. *Received July 29, 1982*

Abstract: The microwave spectra of peroxyformic acid (HCOOOH) and seven isotopic species have been investigated from 12 to 40 GHz. Rotational constants and all quartic centrifugal distortion constants have been adjusted from measured transition frequencies for the parent species. Measurements of the Stark splittings of three transitions have yielded the components of the permanent electric dipole moment $\mu_a = 0.922$ (1) D, $\mu_b = 1.050$ (2) D, and $\mu_{total} = 1.398$ (2) D. From the inertia defect and the absence of any μ_c dipole component, we concluded the molecule to be planar. A complete substitution structure resulted from the analysis of all singly and one doubly substituted isotopic species. The stable conformation is characterized by an intramolecular hydrogen bond. No other conformer with an estimated energy difference of less than 700 cm^{-1} could be found. Ab initio SCF calculations with full geometry optimization were performed in a search of possible conformers. Three stable conformers were found which all feature a planar structure and which are higher in energy by 700 to 5000 cm^{-1} than the conformer measured.

1. Introduction

The structures and conformations of peroxy acids have been inferred in the past mostly from theoretical calculations. The microwave spectrum is known only for peroxyacetic acid.[1] From the microwave spectroscopic data of the parent species and the CH_3COOOD species, it was concluded that the peroxy acid moiety is planar, featuring an intramolecular hydrogen-bonded conformation. Infrared spectra have been recorded previously for peroxyformic acid[2,3] and partially assigned. The vibrational spectrum provided the first evidence of an intramolecular hydrogen bond. The interpretation of the vibrational spectrum was consistent with a planar structure.[4]

The first attempt to elucidate the conformation of peroxy acids was based on dipole moment considerations from measurements of the dielectric constant in solution.[5] A conformation with a dihedral angle of 72° for the peroxy group was suggested.

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Over the last 10 years many semiempirical and ab initio self-consistent field (SCF) calculations were performed.[6–15] In the earlier calculations different planar conformations of the peroxy acid moiety were found to have the lowest energy. The latest ab initio calculation with an extended basis[15] confirmed earlier results that the cis planar form with an intramolecular hydrogen bond is the most stable conformation. The best ab initio calculations are now consistent with the observed conformation of peroxyacetic acid.

In this paper we report the measurement of the microwave spectrum of peroxyformic acid in the frequency range from 12 to 40 GHz. Rotational transitions up to $J = 50$ have been assigned for the parent species in the vibrational ground state. Rotational constants and centrifugal distortion constants have been adjusted to the measured transition frequencies. The electric dipole components have been determined from the Stark splittings of three suitably chosen transitions. A complete substitution structure was deduced from the analysis of the microwave spectra of all singly substituted isotopic species. No evidence of other conformers was obtained in the microwave spectrum.

In order to derive reliable estimates for the energy differences of the less stable conformers, ab initio SCF calculations with a 4-21G basis set augmented by p and d functions were carried out with full geometry optimization. Four different conformers were located through internal rotations around the C–O and O–O bonds. The structure of the most stable conformer compares well with the substitution structure.

2. Experimental Details

2.1 Chemicals. The reaction of formic acid with hydrogen peroxide (concentration >95%)

$$HCOOH + H_2O_2 = HCOOOH + H_2O$$

rapidly leads to an equilibrium.[16] Sulfuric acid or metaboric acid added to the reaction mixture absorbs the water and shifts the equilibrium in favor of peroxyformic acid.[17] These compounds act simultaneously as catalysts.

Because of the explosive risks[18] of peroxyformic acid, only portions of 3 mmol were prepared at a time by mixing 150 mg of HBO_2 (prepared from H_3BO_3 by heating at 80–90 °C in vacuo) or 150 μL of H_2SO_4 (91%) with 75 μL of H_2O_2 (concentrated to >95% by distilling water off at 45 °C and 15 torr from commercial 30% solutions of H_2O_2[19]) at 0 °C. Pure HCOOH (115 μL) was then added dropwise to the reaction mixture. The mixture was allowed to warm and stand at room temperature for 1 h. Subsequently it was cooled to 77 K with liquid nitrogen and evacuated. Upon warming to room temperature the mixture was allowed to expand into a 5-L Pyrex bulb, reaching finally a pressure of 8–10 torr. The gaseous mixture was used for the microwave measurements without further purification. It contained mainly peroxyformic acid with traces of formic acid, hydrogen peroxide, and water. It could be stored in the glass bulb for up to 1 week without much decomposition. All synthetic work was done behind safety shields.

Deuterated, ^{13}C, and ^{18}O species of peroxyformic acid were prepared from appropriately substituted formic acid or hydrogen peroxide. Details of the synthesis of all isotopic species will be given elsewhere.[20]

2.2. Microwave Measurements. The microwave spectra were recorded with conventional Stark-modulated spectrometers with 30-kHz square-wave modulation and phase-sensitive detection. Phase-stabilized backward wave oscillators served as radiation sources over the 12–40-GHz range. A 4-m long aluminum X-band absorption cell of our own design[21] was used for all measurements and was kept at room temperature (22 ± 2 °C). Since the peroxyformic acid sample decomposed rapidly in the absorption cell, the cell was equipped with a flow system. For the broad band surveys a pressure of 40 mtorr was selected. The pressure was reduced to 10–20 mtorr for accurate frequency measurements of absorption lines. The center frequencies were averaged from sweeps in both directions. The output of the spectrometer was digitized and stored in a PDP-8/E computer. A parabola was fitted to the central part of the absorption line and its maximum was determined. The frequency measurements should be accurate to within 20 kHz in this way.

3. Assignments and Results

3.1. Parent Molecule. Rotational transitions of peroxyformic acid were predicted from rotational constants based on the ab initio optimized geometry given by Petrongolo[9] for the hydrogen-bonded conformer. A broad band scan over the 18–40-GHz range revealed a number of transitions for which the Stark components were clearly resolved. Three Q-branch transitions were readily assigned. $A - C$ and $\kappa = (2B - A - C)/(A - C)$ were determined from plots of the transition frequencies vs. κ in the usual manner. Assigning an R-branch transition allowed the determination of all three rotational constants A, B, and C. Further transitions could then easily be assigned and checked by their Stark pattern. In a stepwise manner the range of the J values was increased. Finally over 40 transitions including μ_a- and μ_b-type R- and Q-branch transitions up to $J = 50$ were assigned for the vibrational ground state of peroxyformic acid between 12 and 40 GHz. Further checks on the correctness of the assignments came from microwave–microwave double resonance measurements.[22] A list with all accurately measured transition frequencies is available as supplementary material.

The measured transition frequencies were subjected to an iterative least-squares fit of the three rotational constants and the five quartic centrifugal distortion constants in Watson's asymmetric reduction for a prolate I^r basis.[23] Since less transitions have been assigned for the isotopic species, the fit was restricted without a loss in accuracy to a well-balanced set of 28 μ_a- and μ_b-type R- and Q-branch transitions with $J \leq 17$. This set was similar for all isotopic species in order to avoid any systematic influence from the fitting procedure. The results of the adjusted parameters with their standard deviations are given in Table I. Differences between measured and calculated transition frequencies from these constants reach at most 22 kHz with a mean residual error of 11 kHz for all transitions with $J \leq 17$. The mean residual error is smaller than the estimated accuracy of the frequency measurements. At higher J values the errors increase systematically owing possibly to higher order centrifugal distortion effects.

For the low J μ_a-type transitions three different satellites from vibrationally excited states were observed. They belong to the two lowest out-of-plane and the lowest in-plane vibrational modes with frequencies below 500 cm^{-1}. It was found that the μ_b-type rotational transitions of the excited out-of-plane modes showed considerable deviations from the rigid rotor predictions. No detailed analyses of the satellite spectra have yet been performed.

The broad scan was surveyed carefully in order to detect other transitions of possible conformers of peroxyformic acid. Essentially no stronger transition within a few percent of the strongest observed remained unassigned either to peroxyformic acid and its satellites or to impurities like formic acid and hydrogen peroxide. Therefore, we can set a lower limit of 700 cm^{-1} (2 kcal/mol) to the energy difference of other conformers.

3.2. Isotopic Species. The microwave spectra of all singly substituted isotopic species of peroxyformic acid were recorded

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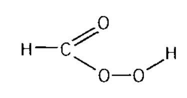
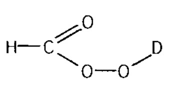
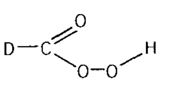
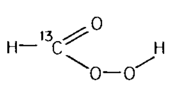
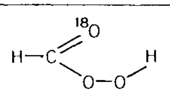
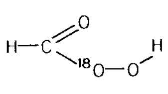
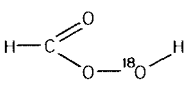
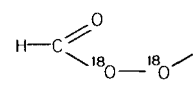
Table I. Rotational Constants (MHz), Centrifugal Distortion Constants (kHz), and Moments of Inertia (u Å^2)[a] of Isotopic Species of Peroxyformic Acid[b]

								
A	20251.568 (3)	19203.045 (4)	18686.739 (3)	20049.981 (2)	19778.600 (3)	19489.021 (8)	19830.311 (7)	19027.801 (7)
B	7624.382 (1)	7595.532 (1)	7443.049 (1)	7561.8883 (8)	7278.364 (1)	7548.988 (3)	7266.697 (3)	7212.332 (2)
C	5534.063 (1)	5438.586 (1)	5318.507 (1)	5486.0578 (7)	5315.7569 (9)	5436.370 (2)	5313.265 (2)	5225.258 (2)
Δ_J	6.98 (2)	7.09 (3)	6.21 (2)	6.80 (1)	6.45 (2)	6.65 (5)	6.53 (3)	6.33 (4)
Δ_{JK}	−21.4 (1)	−19.5 (2)	−17.7 (1)	−21.1 (1)	−20.1 (1)	−19.4 (3)	−20.9 (3)	−18.7 (3)
Δ_K	67.6 (1)	54.4 (2)	50.0 (1)	66.0 (1)	64.09 (7)	63.5 (4)	66.1 (2)	62.3 (3)
δ_J	2.277 (6)	2.33 (1)	2.047 (7)	2.224 (5)	2.072 (7)	2.20 (2)	2.08 (2)	2.05 (2)
δ_K	10.5 (1)	10.4 (2)	9.2 (1)	10.2 (1)	10.1 (2)	9.8 (4)	10.0 (4)	9.5 (4)
I_a	24.955057 (4)	26.317651 (5)	27.044796 (4)	25.205961 (2)	25.551811 (4)	25.931474 (9)	25.485180 (8)	26.560034 (8)
I_b	66.28459 (1)	66.53635 (1)	67.89946 (1)	66.832387 (8)	69.43580 (1)	66.94659 (3)	69.54728 (3)	70.07151 (2)
I_c	91.32152 (2)	92.92471 (1)	95.02272 (1)	92.12062 (1)	95.071889 (9)	92.96259 (4)	95.11647 (4)	96.71848 (4)
Δ°	0.08187	0.07070	0.07847	0.08227	0.08427	0.08452	0.08401	0.08696
σ^c	11	18	15	10	13	31	28	26

[a] Conversion factor of 505379.05 MHz u Å^2. [b] Numbers in parentheses represent one standard deviation. [c] Mean residual error of a measured transition frequency (kHz).

Table II. Measured Stark Splitting Coefficients (Hz V^{-2} cm^2) and Permanent Electric Dipole Moment (D) of Peroxyformic Acid[a]

		$\Delta\nu/E^2$	
transition	M	obsd	calcd
3(1,2)-3(0,3)	±1	1.17 (1)	1.18
	±2	3.65 (1)	3.65
	±3	7.79 (1)	7.78
2(1,2)-1(1,1)	0	1.00 (1)	1.01
	±1	28.1 (2)	27.7
3(1,2)-3(2,1)	±1	10.5 (1)	10.7
	±2	24.07 (6)	24.04
	±3	46.2 (1)	46.1
μ_a	0.922 (1)	μ_c	0[b]
μ_b	1.050 (2)	μ_{total}	1.398 (2)

[a] Numbers in parentheses represent one standard deviation.
[b] Assumed; see text.

over the same frequency range from 12 to 40 GHz as for the parent molecule. The ^{18}O:^{16}O isotope mixing ratio of 1:1 used for the preparation of the peroxy-substituted species allowed not only the observation of the two singly but also of the doubly substituted species $HCO^{18}O^{18}OH$. Assignments of the spectra of isotopic species were readily made along the same lines as for the parent molecule. Transitions with $J > 25$ have not been assigned since they do not improve the accuracy of the rotational constants significantly. All accurately measured frequencies of rotational transitions for all isotopic species are collected in a table available as supplementary material. Rotational constants and centrifugal distortion constants were adjusted in separate least-squares fits for each isotopic species from a common set of transitions. They are listed also in Table I.

4. Permanent Electric Dipole Moment

The electric dipole moment of peroxyformic acid was determined from the measurements of the splittings for a total of eight Stark components of three different rotational transitions. Only those components were included which exhibited a purely quadratic Stark effect within experimental accuracy. The electric field in the Stark cell was calibrated with OCS assuming a dipole moment of $\mu = 0.715210$ D.[24] The measured Stark slopes and their standard deviations are listed in Table II. Theoretical splitting coefficients were calculated from second-order perturbation sums. The squares of the components of the electric dipole moment in the principal axes system were determined in a weighted least-squares fit with the help of these coefficients. The small negative value obtained first for μ_c was well within the error limits. It was neglected in the final fit in accordance with the finding of a planar structure from the inertia defect. The final results are shown in Table II.

5. Substitution Structure

The rotational constants in Table I are converted to moments of inertia for all isotopic species. The moments of inertia and the inertia defects are included in Table I. Small positive values for the inertia defects $\Delta = I_c - I_a - I_b$ were found between 0.071 and 0.087 u Å for all isotopic species. This is conclusive evidence for the molecule being perfectly planar.

The substitution coordinates of all nuclei in peroxyformic acid were calculated in the principal axes system of the parent molecule. The method of Kraitchman[25] for planar molecules was applied which considers only I_b and I_c. The same calculation was repeated with the general three-dimensional equations for the substitution coordinates. The results of the latter calculation are numerically equal with values obtained from the formulas of Rudolph[26] for planar molecules, if the c coordinates are disregarded. The bond

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Table III. Substitution Structure of Peroxyformic Acid[a]

bond lengths and angles	Kraitchman[b]	Kraitchman[c]	least squares[d]	ab initio[e]	formic acid[27]	hydrogen peroxide[28]
$d(C-H_1)$	1.095	1.094	1.090 (2)	1.078	1.097	
$d(C-O_1)$	1.202	1.203	1.208 (3)	1.195	1.202	
$d(C-O_2)$	1.336	1.337	1.332 (2)	1.352	1.343	
$d(O_2-O_3)$	1.445	1.445	1.445 (2)	1.439		1.475
$d(O_3-H_2)$	1.015	1.017	1.014	0.995	0.972	0.950
$d(H_2-O_1)$	1.861	1.855	1.857 (3)	1.885		
$\angle(H_1CO_1)$	127.0	127.0	126.6 (2)	126.9	124.1	
$\angle(H_1CO_2)$	108.3	108.3	109.0	109.7	111.0	
$\angle(O_1CO_2)$	124.7	124.7	124.4 (2)	123.4	124.9	
$\angle(CO_2O_3)$	110.5	110.5	110.7 (1)	110.7		
$\angle(O_2O_3H_2)$	99.2	98.9	98.9	101.0		94.8
$\angle(O_3H_2O_1)$	122.5	122.8	122.7	120.8		
$\angle(H_2O_1C)$	83.1	83.1	83.0 (1)	84.1		

[a] Bond lengths in Å, angles in deg. [b] Equations with I_b and I_c for planar molecules used. [c] General three-dimensional equations with I_a, I_b, and I_c used. [d] Numbers in parentheses represent one standard deviation. [e] Optimization stopped if bond lengths were within 0.002 Å and angles within 0.2°. For details see text.

Table IV. Fully Optimized Structural Parameters[a] for Different Conformations of Peroxyformic Acid and Their SCF Energies (au) and Electric Dipole Moments (D) from ab Initio Calculations

bond lengths angles	conformer I		conformer II		conformer III		conformer IV
	4-21G	4-21G*	4-21G	4-21G*	4-21G	4-21G*	4-21G
$d(C-O_1)$	1.202	1.195	1.189	1.182	1.190	1.184	1.189
$d(C-H_1)$	1.074	1.078	1.078	1.082	1.075	1.081	1.082
$d(C-O_2)$	1.364	1.352	1.376	1.361	1.385	1.362	1.377
$d(O_2-O_3)$	1.476	1.439	1.472	1.439	1.474	1.454	1.471
$d(O_3-H_2)$	0.981	0.955	0.970	0.946	0.969	0.940	0.975
$\angle(O_1CO_2)$	123.0	123.4	126.4	127.1	120.8	122.1	121.3
$\angle(O_1CH)$	127.4	126.9	127.3	126.7	127.3	126.7	125.2
$\angle(CO_2O_3)$	111.5	110.7	110.6	110.2	107.1	104.7	116.3
$\angle(O_2O_3H_2)$	102.1	101.0	98.0	97.2	98.6	98.8	105.8
E_T(SCF)	−262.87225	−262.94117	−262.87222	−262.93450	−262.87190	−262.93800	−262.84984
ΔE_T(SCF)[b]	0.00	0.00	0.02	4.20	0.22	2.00	14.06
μ		1.57		3.11		3.37	

[a] Bond lengths in Å, angles in deg. [b] Energy differences in kcal/mol.

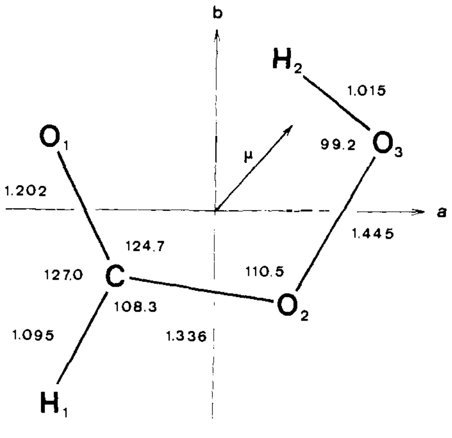

Figure 1. Peroxyformic acid: atomic numbering scheme, dipole moment, and substitution structure (bond lengths in Å, bond angles in deg).

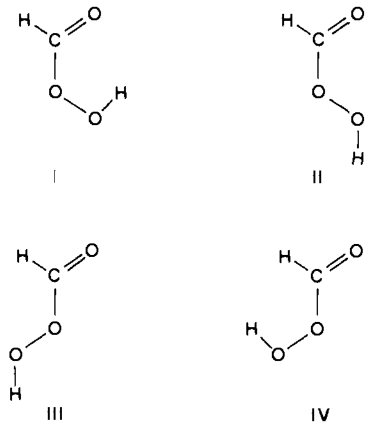

Figure 2. Four planar conformers of peroxyformic acid considered in the SCF ab initio calculations.

lengths and bond angles were determined from both sets of substitution coordinates. They are shown in Table III. Errors from the propagated standard deviations of the moments of inertia are smaller than the least significant digit of the results given.

Bond lengths and bond angles were also determined in a least-squares fit of the differences of the moments of inertia upon isotopic substitution.[29] The doubly substituted species could be included in this fit. The results are included in Table III. They nearly coincide with the values from the substitution structure. The errors in parentheses reflect the systematic contributions from the normal vibrations to the moments of inertia.

Peroxyformic acid represents a favorable case for the structure determination with the microwave method. No nucleus is near a principal axis, and an accurate structure is obtained. Systematic errors are larger than the inaccuracies of the experimental data. The result for the substitution structure is shown in Figure 1.

6. Ab Initio SCF Calculations

A complete geometry optimization with respect to 13 internal coordinates has been carried out for peroxyformic acid. The TEXAS program with the ab initio SCF gradient method was used.[30]

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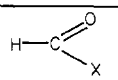
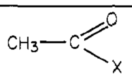
Table V. Comparison of Permanent Electric Dipole Moments (D) between Formyl and Acetyl Derivatives[35]

X	 $HC(=O)X$	 $CH_3C(=O)X$
H	2.339 (13)	2.69
OH	1.415 (10)	1.70 (2)
OOH	1.398 (2)	2.384 (5)
OCH_3	1.77 (3)	1.7
F	2.02 (2)	2.96 (3)
NH_2	3.71 (3)	3.7

Split-valence 3-21G[31] and 4-21G[32] basis sets were chosen for the first calculations. Finally the 4-21G* basis set was employed which includes a set of d functions on carbon and oxygen with exponents of 0.75 and 0.80, respectively, and p functions on hydrogen with exponents of 1.2. The optimizations were stopped when the changes in all structural parameters were less than 0.002 Å and 0.2° for the bond lengths and bond angles, respectively.

Four planar conformers shown in Figure 2 were considered in the calculations. In conformer I the hydrogen of the peroxy group forms an intramolecular hydrogen bond with the carbonyl oxygen. The other conformers were obtained from conformer I by 180° rotations about the O–O and C–O bonds. No further conformers could be located when both angles for these internal rotations were simultaneously varied in steps of 30°.

The optimized geometrical parameters and the SCF energies of these four conformers from calculations with the 4-21G and 4-21G* basis sets are summarized in Table IV. The calculated SCF energies for the 4-21G basis set clearly indicate that conformer IV is about 14 kcal/mol less stable than the other three conformers which have nearly the same SCF energies. On the other hand, the results of the 4-21G* basis set which includes polarization functions show that conformer I is more stable than conformers II and III by 4.2 and 2.0 kcal/mol, respectively. Comparing the optimized geometrical parameters from both basis sets it is noted that the bond lengths of O_2-O_3 and O_3-H_2 are about 0.03 Å shorter for the 4-21G* basis set. The bond angles and other parameters are not seriously affected by the inclusion of the polarization functions.

The permanent electric dipole moments were calculated for conformers I–III which might be observed in the microwave spectrum. The results are included in Table IV. The values for the conformers II and III are twice as large as that for conformer I. These data might stimulate further searches for the unknown conformers.

7. Discussion

The conformation of peroxycarboxylic acids has been subject to a long dispute. Giguere[2] and Brooks[4] interpreted the vibrational spectrum of peroxyformic and peroxyacetic acid on the basis of the planar cis conformation I (see Figure 2) of the peroxycarboxylic acid moiety. It was found that this form is stabilized by an intramolecular hydrogen bond. However, Swern et al.[5] proposed a nonplanar conformation with a dihedral angle of 72° for the peroxy group. They used a bond moment model for the calculation of the electric dipole moment of the molecule. The calculated value was forced to coincide by a rotation of the hydroxyl group around the peroxy bond with experimental dipole moments which were determined from dielectric constants of higher members of peroxycarboxylic acids in solution.

The conformation of peroxyacetic acid was shown to be in the planar cis form, analogous to conformer I of peroxyformic acid. This result was obtained from the analysis of the rotational spectra of the parent and the OD species.[1] Although this fact was demonstrated unambiguously in 1976, some recent papers on the theoretical calculations did not take notice of the experimental data. Peroxyacetic acid is not a favorable molecule for a complete structural analysis by the microwave method. The rotational spectrum is complicated by the internal rotation of the methyl group with a low barrier. Furthermore, three nuclei are located near a principal axis which would lead to considerable errors in the substitution structure.

Various quantum chemical calculations were reported[6–15] which tried to make a decision between the different conformations proposed. The results depended on the degree of sophistication of the calculations and no consistency was obtained. Even the planar trans conformer II was suggested as the most stable conformer.[14]

The substitution structure of peroxyformic acid is compared with the structures of hydrogen peroxide and formic acid in Table III. The bond lengths C—H_1 and C=O_1 are almost equal between peroxyformic and formic acid. The three bond angles around the carbon are equally similar for the two molecules. The bond length C–O_2 is definitely shorter in peroxyformic acid than in formic acid. The bond length O_2–O_3 is much shorter and the bond length O_3–H_2 longer in peroxyformic acid than those found in hydrogen peroxide. These trends might be rationalized in view of the intramolecular hydrogen bond in peroxyformic acid which pulls some electron density away from the O_3–H_2 bond. Similarly the bond angle $O_2O_3H_2$ opens upon formation of the hydrogen bond in peroxyformic acid with respect to the analogous angle in hydrogen peroxide.

Previous experiences with ab initio calculations of energy differences between conformers[33,34] showed that the results very critically depend on the choice of the basis set. Even qualitatively wrong results are likely to be obtained for minimal basis sets. Furthermore, it is known that p and d functions are essential for an adequate description of hydrogen bonding. The results of our calculations with the 4-21G* basis set are qualitatively consistent with those of Bock et al.[15] However, the small energy differences between conformer I and conformers II and III of 4.2 and 2.0 kcal/mol, respectively, are more than twice as large in our calculations than the values of 1.50 and 0.94 kcal/mol of Bock et al.[15] The larger differences agree better with the microwave results where a careful search did not reveal any other conformer with an energy difference of less than 2 kcal/mol. The results of Bock et al.[15] suggest that conformer III should be present in equilibrium at room temperature with a fraction of 20%. This conformer would not have escaped our attention. It is believed that our calculation describes the intramolecular hydrogen bond especially more accurately. This supposition is further supported by the good agreement of the calculated structural parameters with those of the substitution structure.

The calculated electric dipole moment of 1.57 D agrees well with the experimental value of 1.398 D. The dipole moment of peroxyformic acid is considerably smaller than that of peroxyacetic acid, 2.384 D,[1] which compares well with the dipole moments of the higher homologues of 2.3 to 2.4 D from dielectric constant measurements.[5] The other conformers have substantially larger dipole moments than the most stable conformer. This fact is of help in further attempts to detect other conformers in the microwave spectrum. A comparison of the electric dipole moments of formyl and acetyl derivatives is shown in Table V. It is noticed that a difference of nearly 1 D is found for the OOH and F substituents. For all other substituents much smaller differences are observed.

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ETHZ granted free computer time.

Registry No. HBO_2, 13460-50-9; H_2O_2, 7722-84-1; HCOOH, 64-18-6; HC(O)OOH, 107-32-4; HC(O)OOD, 84057-56-7; DC(O)OOH, 84057-57-8; $H^{13}C(O)OOH$, 84057-58-9; $HC(^{18}O)OOH$, 84057-59-0; $HC(O)O^{18}OH$, 84082-02-0; $HC(O)^{18}OOH$, 84057-60-3; $HC(O)^{18}O^{18}OH$, 84057-61-4.

Supplementary Material Available: Listings of measured rotational transition frequencies of HCOOOH, HCOOOD, DCOOOH, $H^{13}COOOH$, $HC^{18}OOOH$, $HCO^{18}OOH$, $HCOO^{18}OH$, and $HCO^{18}O^{18}OH$ in the vibrational ground state (Table VI) (3 pages). Ordering information is given on any current masthead page.

Small-Molecule Chemisorption on $NiSi_2$: Implications for Heterogeneous Catalysis

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Abstract: The chemisorption of O_2, CO, CO_2, H_2, N_2, and CH_3OH on the clean (111) surface of nickel disilicide ($NiSi_2$) was studied under ultrahigh vacuum conditions. Samples were characterized by high-resolution electron energy loss spectroscopy (EELS), low-energy electron diffraction (LEED), and Auger electron spectroscopy (AES) with experiments carried out between 170 and 300 K. The vibrational spectra clearly indicate that O_2, CO, and CO_2 dissociate on $NiSi_2(111)$ at 170 K. Adsorbed CH_3OH yielded only a methoxide species, even at 300 K. We found no evidence for either molecular H_2 or molecular N_2 adsorption, although atomic hydrogen is strongly bound to the silicide surface. The implications of these unusual findings with respect to both heterogeneous catalysis by supported metal particles and strong metal-support interactions (SMSI) are discussed.

It is generally accepted that of the factors which most significantly influence the performance of a catalyst (as measured by parameters such as activity and selectivity), many are "local" in origin.[1] These can be structural—steps, kinks, and other surface defects[2]—or perturbations in site geometries and local band structure due to alloying and/or compound formation.[3] The catalytic consequences of the latter processes can be both dramatic and technologically important. It is largely for this reason that there continues to be considerable interest in the characteristics of metals in unusual chemical and structural environments. While single-crystal metal and alloy surfaces have been well studied,[2,3] little attention has been given to the corresponding surfaces of intermetallic compounds. This omission is significant in that both the nature of the chemistry exhibited by these materials and their structure can be unique. For example, in recent studies on the activity of nickel-silicon intermetallic compounds as catalysts for CO hydrogenation, unusual chemisorption behavior was observed.[4,5] It was found that these materials have chemisorption properties similar to those of supported metal catalysts which are believed to be influenced by strong metal-support interactions (SMSI).[6] The origin of the SMSI effect, an abnormally low activity for both CO and H_2 chemisorption, is unknown at present. It has been postulated by Tauster[6] and others[7] that SMSI, induced by the high-temperature reduction of supported metal salts, *may* be the result of intermetallic compound formation. Thus, data on the chemistry of well-characterized intermetallic compound surfaces would address several important issues in catalysis by transition metals.

In this paper we describe a detailed study of the chemisorption properties of a well-ordered, single-crystal (111) surface of nickel disilicide ($NiSi_2$). This material is easily prepared[8] and is characterized by an unusual structure in which coordinately unsaturated nickel surface atoms are bonded *only* to silicon nearest neighbors. The chemisorption properties of nickel in this material, with respect to small adsorbate molecules (H_2, O_2, N_2, CO, CO_2, CH_3OH) incapable of bridging between Ni atoms, is found to be dramatically different from that of bulk metal. The implications of these findings with respect to heterogeneous catalysis by supported metal particles is discussed.

Experimental Section

$NiSi_2$ samples were grown epitaxially on highly polished and etched Si(111) single crystal wafers. In a typical preparation, nickel was electron beam evaporated onto the substrate at a pressure of the order of 10^{-7} torr to a film thickness of 1200 Å. Vacuum-annealing ($\lesssim 10^{-7}$ torr) at 573 K for 30 min produced a polycrystalline Ni_2Si film, while further annealing at 1073 K resulted in the growth of an epitaxial disilicide.[9] Previous studies have shown that comparable procedures produce well-ordered, stoichiometric surfaces.[9]

Our analysis is based primarily on data obtained by high-resolution electron energy loss spectroscopy (EELS).[10,11] In this technique a collimated beam of monoenergetic electrons (1-10 eV incident energy, 5-10 meV, or 40-80 cm^{-1} full width at half-maximum) is scattered from a crystal surface and the energy distribution of the specularly reflected beam recorded. The incident electrons excite surface vibrational modes (surface phonons, adsorbate and adsorbate-substrate vibrations) and therefore lose energy corresponding to the frequency of the vibration involved. Both theory and experiment have shown this inelastic scattering process to occur by a long-range electron-dipole interaction.[11] Due to the nature of this interaction and to the high dielectric constant of the substrate, the incident electrons will couple only to vibrations which are perpendicular to the sample surface. This orientational selection rule greatly simplifies the interpretation of the observed spectra.

All experiments were carried out in an ultrahigh vacuum chamber (diffusion and titanium-sublimation pumped) with a base pressure near 1×10^{-11} torr. The system was equipped for Auger electron spectroscopy (AES), low-energy electron diffraction (LEED), ion sputtering, as well as for high-resolution electron energy loss spectroscopy. The design of the high-resolution EELS spectrometer is similar to that described by

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