an explanation for the different behavior of carbon and silicon.

The difference between carbon and silicon is due to the increase in atomic size (from C to Si) having an effect on bond formation and, in particular, on favoring a greater number of bonds formed. For example, increasing the size of the central atom increases the separation between it and the donor atoms and implies diminished repulsion between the effective nuclear charges of their atomic cores. An increase in the coordination number in the cluster of atoms is then favored both by the diminished repulsion between cores and by the consequential reduction in localization (the mutual repulsion) of valence electrons within the larger cluster.[30]

Conclusions

We have gone some way to answering the four equations posed in the introduction. In brief the answers are the following:

(i) Nucleophilic addition to silicon is the major pathway in silane and methylsilanes. The formation of a *stable* five-coordinate intermediate in such an exothermic reaction depends both upon possible decomposition modes of the intermediate, and upon its ability to dissipate (some of) its excess energy of formation.

(ii) Theoretical calculations predict that H^- and MeO^- should react with silane without energy barriers to form $[H_4SiNu^-]$. In contrast, the hydrogens of methylsilanes should initially trap a basic nucleophile (e.g., HO^-, MeO^-) and there is then a small energy barrier (20 to 35 kJ mol^{-1}) to be overcome before the five-coordinate adduct is formed. The predicted H-bonded intermediates are not detected in ICR experiments.

(iii) The energy barriers described in ii (above) do not affect the rates of the reactions which (within experimental and computational error) are equal to the collision rates.

(iv) Theoretical calculations show that silicon can (in theory) form stable five-coordinate adducts even with the bulkiest of donor atoms. This contrasts with carbon, which is unable to form five-coordinate adducts even with the smallest donor atoms. This difference is unlikely to result solely from steric factors.

Experimental Section

ICR spectra were measured with a Dynaspec ICR 9 spectrometer. Spectra can either be obtained in the 0–5 eV range (primary negative ions formed by dissociative thermal electron capture) or in the range 40–80 eV (primary negative ions formed by dissociative secondary electron capture). The latter range gives the better sensitivity, hence spectra were obtained at a nominal 70 eV. Other reaction conditions are the following: $\omega_c/2\pi$ = 153.7 kHz; RONO pressure 5×10^{-6} torr; pressure of silyl compound 1×10^{-5} torr. In the case of $[RO^- \cdot\cdot HOR]$ experiments, HCO_2R was also added at a partial pressure of 5×10^{-6} torr. The ion current was in the 10^{-10} A range, emission current 0.2 μA, and ion transit time 1×10^{-3} s.

Alkyl nitrites were prepared on the day of the ICR experiment by a standard method.[31] Silane was prepared from tetrachlorosilane by reaction of lithium aluminum hydride,[32] and trifluoromethylsilane was prepared by a standard method.[33]

Acknowledgment. We are grateful to Charles H. DePuy for the rate data presented in Table II. This project was wholly supported from a grant from the Australian Research Grants Scheme. We thank the University of Adelaide Computing Centre for facilities.

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[30] As an illustration, the most stable crystalline forms of the native group 4A elements display the following coordination numbers (bonds to nearest neighbors): C 3, Si 4, Ge 4, Sn 6, and Pb 12. This is an example of an increase in coordination number down a group in the Periodic Table, yet it cannot be attributed to increasing atomic size since the relative sizes of any atom to its neighbors is constant (and equal) in any one of these elemental structures. It must be inferred that the capacity of larger atoms to achieve higher coordination number is related to the characteristics of the longer bonds formed. For an example of a model that relates coordination number to variations of repulsions between atomic cores, see: Allison, G. B.; Sheldon, J. C. *Inorg. Chem.* **1967**, *6*, 1493.

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Cyclopropylidenemethanone: A Quasi-Symmetrical Molecule

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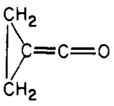
Abstract: The structure of cyclopropylidenemethanone has been investigated via microwave spectroscopy. Analysis of the spectra of the ground and nine excited vibrational states has revealed the form of two bending potentials involving motion of the methanone group relative to the cyclopropylidene ring. The vibration perpendicular to the plane containing the ring carbon atoms has a double-minimum potential with the ground state lying just 2 cm^{-1} below the 29 cm^{-1} high central barrier. Analysis of this motion using the rigid bender method shows that the two potential minima lie 17.5° away from the ring plane. The proximity of the ground state to the top of the barrier leads to the designation of the molecule as *quasi-symmetric*, being close to C_{2v}, despite its less symmetric C_s equilibrium structure. The vibration in the plane of the ring has a near harmonic potential, with a fundamental of 154 cm^{-1}. Analysis of the Stark effect indicates a dipole moment of 2.60 (1) D.

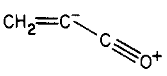
Cyclopropylidenemethanone (**1**) would be expected to have a symmetrical C_{2v} structure, with all heavy atoms in a plane were it not for the fact that the closely related molecule propadienone (**2**) has recently been shown to be kinked, the heavy atoms being in a zigzag arrangement in the methylene plane.[1,2] The question therefore arises as to whether **1** will exhibit an analogous structural abnormality. The cyclopropane ring has long been regarded as electronically similar to a double bond.[3,4] The electronic pe-



1

$CH_2{=}C{=}C{=}O$

2



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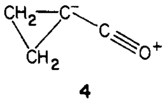

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Table I. Spectroscopic Constants of Cyclopropylidenemethanone

ν_{21}	ν_{15}	A, MHz	B, MHz	C, MHz	inertia defect amu Å^2	D_j, kHz	D_{jk}, kHz	dipole moment, D
0	0	21 164 (4)	3113.282 (3)	2825.006 (3)	−7.314 (4)	0.624 (32)	51.59 (9)	2.60 (1)
0	1	20 844 (4)	3137.466 (3)	2851.651 (4)	−8.101 (5)	0.528 (37)	−13.08 (12)	2.54 (1)
0	2	20 588 (2)	3142.686 (3)	2857.795 (2)	−8.516 (3)	0.276 (25)	24.32 (7)	2.54 (1)
0	3	20 268 (12)	3157.934 (22)	2875.504 (19)	−9.217 (17)	0.804 (140)	25.17 (98)	2.50 (1)
0	4	19 903 (2)	3170.197 (2)	2888.477 (2)	−9.844 (2)	0.452 (17)	23.32 (68)	2.50 (1)
1	0	21 832 (19)	3125.324 (21)	2830.803 (24)	−6.325 (22)	0.599 (190)	51.93 (116)	2.60 (1)
1	1	21 171 (6)	3149.877 (4)	2857.632 (4)	−7.463 (7)	0.590 (48)	−19.08 (16)	2.55 (1)
1	2	20 874 (2)	3155.088 (2)	2864.324 (3)	−7.951 (2)	0.305 (22)	21.27 (7)	2.56 (1)
2	0	23 137 (4)	3135.875 (10)	2837.916 (6)	−4.922 (4)	2.635 (67)	−79.99 (41)	
2	1	21 607 (10)	3162.243 (8)	2863.657 (7)	−6.726 (11)	0.749 (85)	−26.03 (27)	2.55 (1)

culiarity responsible for the kinking of propadienone is most simply thought of in terms of the contributions of a polar resonance structure **3**[1,2,5] so that, analogously, we are raising the question of whether **4** makes a noticeable contribution to the electronic structure of cyclopropylidenemethanone.

A more thorough theoretical investigation by means of ab initio molecular orbital calculations[6] predicted a very low frequency vibration, perpendicular to the heavy-atom plane, but left open the question of the existence of a small barrier to inversion.

We report here an investigation of cyclopropylidenemethanone by microwave spectroscopy, with particular reference to the question of planarity of the heavy-atom arrangement.

Experimental Section

Preparation of 2,2-Dimethyl-1,3-dioxan-4,6-dione-5-spirocyclopropane. Condensation of cyclopropane-1,1-dicarboxylic acid[7] with acetone in the presence of acetic anhydride and a catalytic amount of sulfuric acid[8] gave 2,2-dimethyl-1,3-dioxan-4,6-dione-5-spirocyclopropane (**5**) mp 64 °C[9] (EtOH/pentane).

Mass spectrum, *m/z* 155 (M − 15, 15%), 113 (40%), 68 (70%), 43 (100%), 40 (82%); ^{1}H NMR spectrum ($CDCl_3$) δ 1.82 (s, 3 H), 1.97 (s, 2 H).

Cyclopropylidenemethanone[10] was generated by flash vacuum pyrolysis of **5** at temperatures around 530 °C, the precursor being held at room temperature and the inlet pressure at the spectrometer cell being maintained at 0.5–1 Pa.

The microwave spectrometer was a standard 6.525-kHz Stark modulated instrument having a 3-m-long G-band cell with the sample inlet tube from the pyrolysis oven at one end and a liquid-nitrogen trap at the other, backed by a small diffusion pump and 60 L min^{-1} mechanical pump. The microwave sources were either a Monash-built microprocessor-controlled backward-wave-oscillator synthesizer or a suitable OKI klystron phase locked to the BWO synthesizer. The synthesizer was referenced to the laboratory frequency standard (Sulzer 2.5C), which is regularly calibrated against the national frequency standard. Lines were usually repetitively scanned, the spectral data being accumulated and reduced with a Sperry-Univac V75 computer system.

Center frequencies of spectral lines were determined by a least-squares fitting of a Lorentzian curve to an appropriate section of the spectrometer's digitized and averaged output. The location of center frequencies was typically reproducible to about 10 kHz. We believe that systematic errors associated with line frequencies are less than 5 kHz. Overall uncertainties for line frequencies were estimated as one-tenth of the line width (fwhm) which was generally between 80 and 180 kHz.

The electric field calibration for the Stark-effect measurements was based on measurements on OCS for which the electric dipole moment was taken to be 0.715 21 D.[11]

Results

The microwave spectrum of the pyrolysis products consisted of the rich spectrum of acetone and some additional lines that could be recognized as an ^aR branch of an asymmetric rotor with rotational constants close to those derived from the geometry of cyclopropylidenemethanone predicted by ab initio MO calculations.[6] Ultimately all lines not identifiable as acetone lines (about 250 in all) were assigned to **1**. No additional lines indicative of other species have been found. Many vibrational satellite lines (all in due course assignable to **1**) were apparent in the spectrum, indicating the presence of at least one low-frequency vibration in the molecule.

By comparison with the intensity of OCS lines at similar pressure, it appears that the mole fraction of **1** in the pyrolysate is approximately 10%. This rather low value is due to the presence of acetone and CO_2 generated in the pyrolysis reaction and presumably in part to the thermal decomposition of **1** within the pyrolysis oven.

A total of 10 separate series of spectra, attributable to 10 different vibrational states of **1**, were assigned by least-squares fitting the frequencies to a rotational Hamiltonian that included terms up to the fourth power of the angular momentum:

$$H = \tfrac{1}{2}(B + C)\tilde{J}^2 + [A - \tfrac{1}{2}(B + C)]\tilde{J}_a^{\,2} + \tfrac{1}{4}(B - C)(\tilde{J}_+^{\,2} + \tilde{J}_-^{\,2}) - D_J\tilde{J}^4 - D_{JK}\tilde{J}^2\tilde{J}_a^{\,2}$$

The inclusion of higher order terms did not improve the fit. The assigned lines were low-J ^aR-branch lines (J = 1–7). The search for ^aQ-branch lines was unsuccessful, which was not surprising because of their predicted low intensity and the spectral congestion from acetone lines.

Table I lists derived spectral parameters for the 10 spectra. Their vibrational assignments are indicated, and we now outline the method by which this was achieved.

Assignment of Vibrational States. On the basis of the MO calculations[6] we expected to observe vibrational satellites attributable to two low-frequency vibrational modes, ν_{15} out of plane (b_1 in C_{2v}) and ν_{21} in-plane (b_2). The substantial number of satellites observed indicated a relatively small energy separation between vibrational states. Attempts to obtain a vibrational assignment from observed relative intensities between the different vibrational states proved inconclusive. It was, however, possible to exploit the alternating relative intensities associated with odd and even values of K_{-1} within each rotational spectrum, due to the 10:6 proton spin weighting, to determine the parity of each otherwise unidentified vibrational state. Ultimately, this information aided in the assignment of vibrational quantum numbers.

Further help in identifying the satellites came from model calculations which indicated that an in-plane bend of the CO group relative to the ring would lead to an increase in A and in $B - C$ while for out-of-plane bending A decreases and $B - C$ shows little change. However, something more was required to achieve unambiguous vibrational labeling of each of the vibrational satellites.

From our experience of the related molecule propadienone, we anticipated that the out-of-plane bend of **1** would be far from harmonic and, very likely, correspond to a double-minimum potential function. The variation of a rotational constant, R, with vibrational quantum number, v, is expected to show a simple trend for members of the same satellite series:

$$R_v = R_e + \alpha_R\langle Q^2\rangle_v + \beta_R\langle Q^4\rangle_v + \ldots$$

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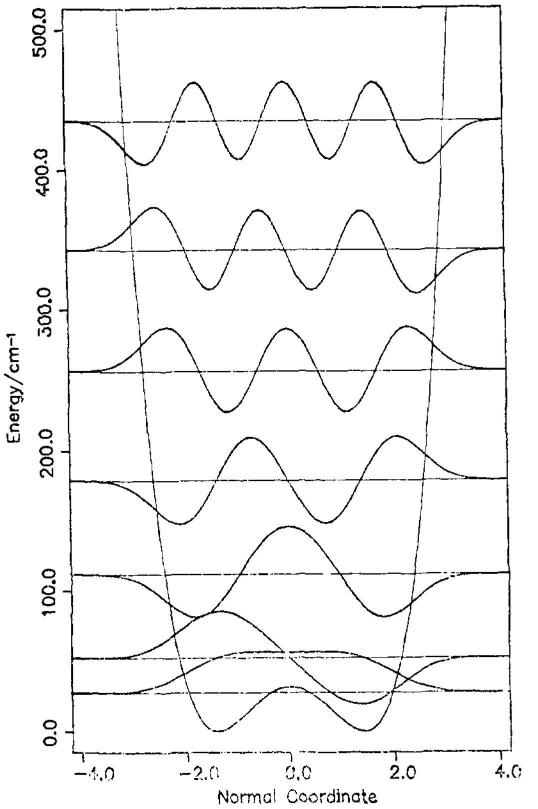

Figure 1. ν_{15} bending potential, energy levels, and wave functions of **1**. The potential energy is given by the formula $V = 7.893(Q^4 - 4.0Q^2)$ cm^{-1}. The potential minima at $Q = \pm1.42$ correspond to 17.5°.

where Q is the normal coordinate for the vibration.

By analysis of the trends of B_v and C_v (numbering the satellite series arbitrarily l..., m..., n... we inspected the ratio $(B_m - B_n)/(C_m - C_n)$ which will be virtually constant for a given vibrational sequence but different for different sequences, the value of the quotient being, very nearly, α_B/α_C) sufficient satellites were assigned to enable us to fit a simple double-minimum potential function for the out-of-plane bending mode ν_{15} and assign several other vibrational satellites. It ultimately has proved possible to apply the rigid bender analysis[12] to the motion and to obtain a corresponding effective potential function that has a central maximum 29 cm^{-1} above the minima which fall at 17.5° in the bending angle (Figure 1). Details of this work are reported elsewhere.[13]

The remaining satellite series were assigned to vibrational states that involved at least one quantum of the higher frequency ν_{21} in-plane bend, specifically $v_{21} = 1$ with $v_{15} = 0, 1, 2$ and $v_{21} = 2$, $v_{15} = 0, 1$. Variations in B and C with the different vibrational quantum numbers implied that the in-plane vibration is almost harmonic and intensity measurements indicated a frequency of the order of 200 cm^{-1}.

A more precise determination of ν_{21} became possible when we noticed a Coriolis interaction between the ($v_{15} = 3$, $v_{21} = 0$) and ($v_{15} = 0$, $v_{21} = 1$) vibrational states. The analysis of this interaction[13] indicated that these levels are separated by 6.7 cm^{-1} implying that the in-plane bending frequency ν_{21} is 154 cm^{-1}. Figure 2 summarises the lowest in-plane and out-of-plane vibrational energy levels.

Dipole Moment. Stark-effect measurements were made on the 4_{13}–3_{12} transition in nine of the ten vibrational states studied. This yielded a value for μ_a of 2.60 ± 0.01 D for the ground state. Details are given in Table I.

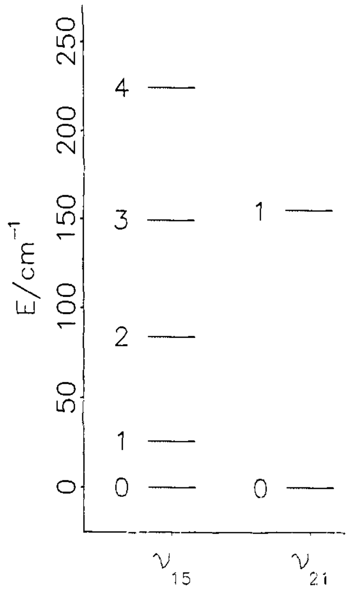

Figure 2. Lowest ν_{15} and ν_{21} energy levels, showing the near degeneracy between the $3\nu_{15}$ state and the $1\nu_{21}$ state which give rise to a Coriolis interaction.

Discussion

The inertial defect of −7.314 amu Å^2 for the ground state is consistent with four hydrogen atoms approximately 0.96 Å away from the heavy atom plane and is similar to the value of −6.694 amu Å^2 reported for cyclopropanone.[14]

The dipole moment of **1** is suprisingly high when compared with propadienone (2.30 D).[1] The interpretation of the alternating values of the dipole moments of the cumulenones up to butatrienone in terms of resonance structures has been presented before (ref 2, especially Figure 8, p 300). On this basis we might have expected the dipole moment of **1** to lie between the values for ketene (1.42 D)[15] and propadienone because the resonance structure for **1** that is the counterpart of $H_2C^+C{\equiv}CO^-$ involves a "no-bond" structure for the three-membered ring. However, it would be optimistic to hope for such a precise accounting for dipole moment trends by means of simple resonance theory.

The potential function for the out-of-plane motion for cyclopropylidenemethanone shows that this molecule is to be classified in that small group of molecules having ambiguous symmetry. It oscillates about a C_{2v} conformation that has a planar arrangement of heavy atoms, but in the ground state the vibrational wave function has virtually constant magnitude over a substantial range of the vibrational coordinate (Figure 1). Since the ground state lies just below the top of the barrier (2 cm^{-1}), it should possibly be classed as kinked and having C_s symmetry. However, it is reminiscent of molecules such as fulminic acid (HCNO)[16] and carbon suboxide (C_3O_2)[17] which have a small effective barrier to linearity rising to the vicinity of the zero-point vibrational level. The term quasi-linear has been applied to molecules like these two and so we propose that cyclopropylidenemethanone be termed *quasi-symmetric*.

From the point of view of the classical structural theory of carbon compounds one confidently expects **1** to be a symmetrical (C_{2v}) molecule with all heavy atoms in a plane, but it has now been shown that this is not correct. For propadienone there is a similar breakdown of classical structural theory so that one must be warned that structural anomalies may be associated with cumulated double bonds. It would be interesting to find out whether

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this anomaly occurs in other related systems such as butatriene or butatrienone, and we hope to report further on this in the future.

The failure of structural theory for this class of compound also extends to calculations by the method of molecular mechanics[18] and to ab initio molecular orbital calculations at the SCF level,[2] but at least in the case of propadienenone, and probably more generally, molecular orbital calculations including electron correlation[5] are consistent with the observed quasi-symmetry.

Acknowledgment. This work was supported by funding from the Australian Research Grants Scheme.

Registry No. 1, 59078-44-3.

Supplementary Material Available: A listing of frequencies and uncertainties for all measured transitions used in this work (3 pages). Ordering information is given on any current masthead page.

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The Chemistry of First-Row Transition-Metal Ions with Primary Amines in the Gas Phase: Correlations of Reactivity with Electronic Structure

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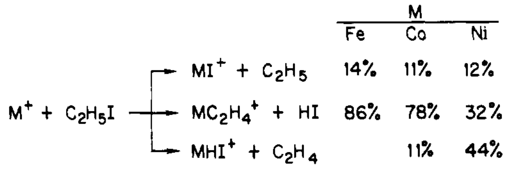
Abstract: In the past several years, an extensive body of literature has appeared in the area of gas-phase organometallic ion/molecule reactions. Most of the observed reactions can be explained by assuming that the first step of the interaction is a metal ion insertion into a bond of the organic molecule. Presented here are reactions of first-row transition-metal ions with a primary amine. They parallel the literature in that, for other types of organic molecules as well, Fe$^+$ typically inserts into many types of bonds, Ni$^+$ is very selective in this regard, Co$^+$ is intermediate between Fe$^+$ and Ni$^+$, and Mn$^+$ is frequently unreactive. An explanation of the reactivity trends of the first-row transition-metal ions is suggested, based on a consideration of the thermodynamics of the metal insertion process. The explanation uses the concept of promotion energy, the energy required to achieve a metal ion configuration conducive to the formation of two σ-bonds. Available data on excited states of these metal ions leads to an ordering in terms of these promotion energies, which appear to correlate with reactivity in terms of ability to insert into various bonds in organic molecules.

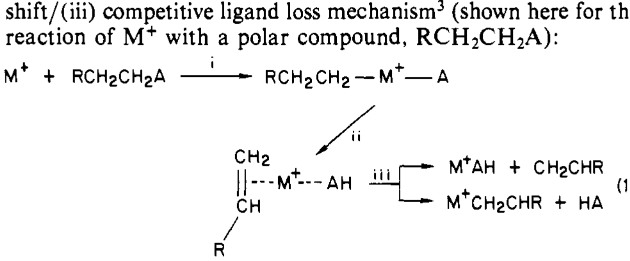
In the past several years a substantial amount of work has been published concerning the gas-phase chemistry of transition-metal ions with organic molecules.[1]

In 1979, Allison and Ridge[2] reported the bimolecular ion/molecule chemistry of Fe$^+$, Co$^+$, and Ni$^+$ with alkyl halides and alcohols. With the polar compounds studied, these three metal ions exhibited essentially the same chemistry, e.g.



	M: Fe	Co	Ni
MI$^+$ + C$_2$H$_5$	14%	11%	12%
MC$_2$H$_4$$^+$ + HI	86%	78%	32%
MHI$^+$ + C$_2$H$_4$		11%	44%

While the product distributions varied, all three ions reacted by a common mechanism involving a (i) metal insertion/(ii) β-H atom shift/(iii) competitive ligand loss mechanism[3] (shown here for the reaction of M$^+$ with a polar compound, RCH$_2$CH$_2$A):



(1)

All three transition-metal ions appeared to insert into C–I, C–Cl, and C–OH bonds.[2] In subsequent years, studies of other transition-metal ions with polar compounds such as alkyl halides appeared, with similar results. Also, subsequent papers showed that the metal insertion/β-H shift mechanism was a common one. For example, Co$^+$ also reacts with thiols,[4] alkanes,[5] alkenes,[6] nitroalkanes,[7] ketones,[4] acids,[4] and amines[8] via this general mechanism, involving metal insertion into a variety of polar and nonpolar bonds.

One type of organic molecule for which the most extensive studies have been reported with the most metal ions is alkanes. From such data, differences in the reactivity of first-row transition-metal ions became more apparent. It has been pointed out that, with alkanes, Fe$^+$ is "indescriminate" in inserting into C–H and C–C bonds, Ni$^+$ is more selective, Co$^+$ is intermediate in reactivity between these two, while Mn$^+$ and Cr$^+$ are unreactive.[9]

[†] The Dow Chemical Co.

[*] Address correspondence to this author at the Michigan State University.

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