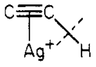
sp carbon), a positive correlation is seen in four cases. Figure 2 shows a linear relationship between change in IR stretching frequency and both k_1 and rate/[complex]. There is no linear relationship between change in proton NMR chemical shift and both k_1 and rate/[complex] (Figure 3). However, as k_1 and rate/[complex] increase, there is an increase (nonlinear) in change in chemical shift. The nonlinearity is caused by the diyne, 1,5-hexadiyne. Monoynes exhibit a nearly linear dependence.

The dependence of deuterium exchange upon change in terminal sp C–H stretching frequency caused by π coordination implies that initial π coordination can dispose the resulting complex to C–H bond activation. Chrisment and Delpuech have found that acidity of noncoordinated terminal alkynes correlates well with ≡CH stretching vibration changes.[34] In our case, cause of the linear relationship may be as simple as electron withdrawal by the π-coordinated electronegative silver ion weakening the C–H bond and raising the ground-state energy of the reactant complex. At the other extreme is direct interaction between silver ion and the terminal C–H bond. Formation of a nonlinear 2-electron, 3-center bond between silver ion and terminal C–H bond (**3**) would remove electron density from the C–H bond and weaken it. The formation of nonlinear 2-electron, 3-center bonds has been observed in the ground state by neutron diffraction analysis[35] and supported by solution studies.[36] Consistent with our observation of alkyne C–H bond activation, the 3-center interaction in cyclohexenylmanganese tricarbonyl renders the bridging hydrogen acidic, thereby permitting deprotonation and electrophilic substitution.[37]



3

The increasing downfield chemical shift upon silver ion π coordination that correlated with increasing k_1 and rate/[complex] can be explained by the same principles as for the IR changes. π coordination of silver ion could deshield the terminal proton by inductive electron withdrawal and thereby activate the terminal C–H bond. A 2-electron, 3-center interaction with silver ion would deform the C≡C—H bond angle to <180°; the resulting anisotropic effect would deshield the terminal proton. Greater deshielding due to greater strength of 2-electron, 3-center interaction would be reflected in more facile terminal C–H bond activation.

Acknowledgment. We thank Central Michigan University, the Research Corp., and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work.

Registry No. RC≡CH·AgOTf (R = 1-hexyne), 74910-01-3; RC≡CH·AgOTf (R = 3-methyl-1-pentyne), 74915-00-7; RC≡CH·AgOTf (R = 3,3-dimethyl-1-butyne), 74915-01-8; RC≡CH·AgOTf (R = 1,5-hexadiyne), 83573-31-3; Ag^{1+}, 14701-21-4; 1-hexyne, 693-02-7; 3-methyl-1-pentyne, 922-59-8; 3,3-dimethyl-1-butyne, 917-92-0; 1,5-hexadiyne, 628-16-0; 1-hexyne-*1*-d_1, 7299-48-1; 3-methyl-1-pentyne-*1*-d_1, 83573-30-2; 3,3-dimethyl-1-butyne-*1*-d_1, 6833-44-9; deuterium, 7782-39-0; silver triflate, 2923-28-6.

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Why Life Exists[†]

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The chemical inertness of tetracoordinated carbon, on which life depends, is commonly attributed to the fact that carbon has no d AOs, or empty or doubly occupied AOs, in its valence shell. Silicon is much more reactive than carbon because it can use 3d AOs to form additional bonds. The same argument is used to explain the inability of the second period elements to form hypervalent compounds. This interpretation is now shown to be probably incorrect. The special features of second period elements are probably due solely to the smaller size of their atoms.

Life is made possible by the stability of carbon compounds of very varied types, even when they are thermodynamically unstable, as a result of the slowness of reactions involving them, and this in turn is due primarily to the unreactivity of quadrivalent carbon. This inertness is commonly attributed to the fact that carbon has only four AOs in its valence shell so it can form at most four electron-pair bonds. Quadrivalent carbon can therefore form a bond to some other atom or group only if one of the preexisting bonds is broken, either before or in concert with formation of the new bond. The energy required to weaken or break the preexisting bond represents a barrier to the reaction in question, even if the net effect is exothermic. While the other typical group 4 elements resemble carbon in being quadrivalent, their valence shells include d AOs as well as s and p AOs. Consequently they can form electron-pair bonds to more than four other atoms, so they can react by direct addition, to form pentacoordinated adducts, without the need to break preexisting bonds. The consequent lack of an activation barrier naturally makes such reactions much faster than in the case of carbon. For example, whereas carbon tetrachloride reacts only very slowly with cold water, silicon tetrachloride

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[†] Dedicated to Rowland Pettit, a founding member of our research group.

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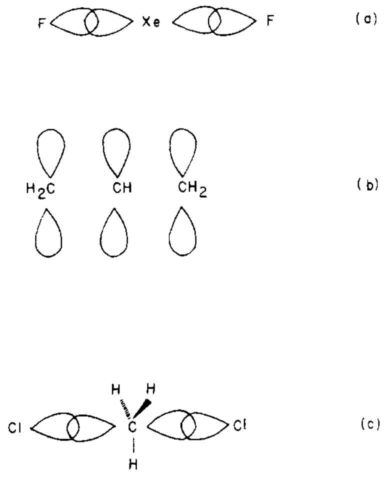


Figure 1. Orbitals in (a) xenon difluoride, (b) allyl anion, and (c) the transition state for a S_N2 reaction.

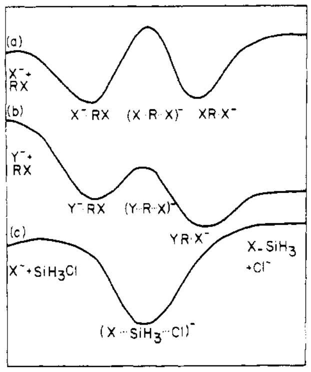


Figure 2. Minimum energy reaction paths for (a) a degenerate S_N2 reaction, (b) an exothermic S_N2 reaction, and (c) addition of X^- to CH_3SiCl.

reacts violently. Furthermore, the barriers to reaction on carbon can be controlled by varying the strengths of the bonds broken during them. For example, addition to unsaturated carbon takes place more easily than substitution on saturated carbon because addition involves breaking a π bond and π bonds are in general weaker than σ bonds. Carbon compounds therefore not only are relatively inert, even when they are thermodynamically unstable, but also can be made to react in a controlled manner. These are the features that make life, as we know it, possible.

The existence of life undoubtedly depends on the reluctance of carbon to expand its coordination shell and a similar reluctance undoubtedly accounts for the analogous differences in behavior between the second period elements and elements from the later periods, in particular the inability of the former to form hypervalent compounds in which they exert valencies greater than the group norm, of phosphorus pentafluoride or sulfur hexafluoride. The attribution of this difference to the lack of d AOs in the valence shells of the second period elements is not, however, well founded. Our purpose here is to show that the differences between the second and later periods can in fact be explained convincingly in another way.

In 1951 Hach and Rundle[1] suggested the possibility of three atoms being linked together by a three-center four-electron bond by using a p AO of one atom to bind two others, and in 1963 Rundle[2] pointed out that the bonding in the xenon fluorides (which had just been discovered) was probably of this type. Thus in xenon difluoride (**1**), as Figure 1a shows, a p AO of xenon can interact with AOs of two fluorine atoms to form a three AO system entirely analogous to the three AO π system (Figure 1b) in allyl anion **2**. In both cases exactly four electrons have to be accommodated, and can be accommodated, in the resulting three-center MOs, since one of them is bonding and another nonbonding. In the allyl anion, to a first approximation, the average π-electron densities on the terminal and central carbon atoms are 1.5 and 1, respectively, the formal negative charge being half on one terminal atom and half on the other. Since the distribution of the delocalized π electrons in **1** should be similar and since the xenon p AO is initially full, the three-center FXeF bond will involve loss of one electron from xenon to the fluorine atoms. Since the ionization energy of xenon is large and since those of the other inert gases increase in the order Xe < Kr < Ar < Ne < He, this interpretation explains nicely why xenon forms covalent compounds only with very electronegative elements, why krypton combines only with fluorine, and why no compounds of argon, neon, or helium are known. In recent years similar three-center four-electron bonds have been proposed for a wide variety of other inorganic compounds, and it now seems to be generally accepted[3] that bonding of this kind can lead to the formation of stable products.

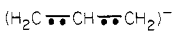
The transition state for an S_N2 reaction on carbon, for example that between chloride ion and methyl chloride

$$\mathrm{Cl^- + R{-}Cl \rightarrow \underset{\textbf{3}}{[Cl\cdots R\cdots Cl]^-} \rightarrow Cl{-}R + Cl^-} \qquad (1)$$

has a similar structure, the entering and leaving groups and carbon being held together by a three-center four-electron bond (Figure 1c). Furthermore, no problems arise here from electron transfer between atoms of different electronegativity because the formal negative charge remains on the chlorine atoms, the carbon atom remaining neutral. The relationship between the reactants (e.g., $CH_3Cl + Cl^-$) and the corresponding adduct (e.g., **3**) is moreover the same as that between orthogonal allyl anion **4**, where there are only two-center bonds, and allyl anion **2** itself, where there is a three-center π bond. Since there is no doubt that **2** is much lower in energy than **4**, **3** should likewise be much lower in energy than (**3** + Cl^-). Yet there seems no doubt[4] that the intermediate (e.g., **3**) in an S_N2 reaction is a transition state, not a stable intermediate, i.e., a saddlepoint on the potential surface and not a minimum. The high energy of this species is indeed responsible for the activation barrier that makes compounds of tetracoordinated carbon so unreactive. Thus we have turned around the traditional problem of explaining why tetracoordinated compounds of silicon are more reactive than those of carbon into explaining why the former are unexpectedly unreactive.

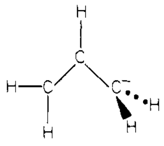
XeF_2

1



$(H_2C \cdots CH \cdots CH_2)^-$

2



4

Detailed MNDO calculations[5] for a wide range of S_N2 reactions have confirmed the conclusion, from experiment[4] and ab initio studies[6] of a few simple examples, that the

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[1] Hach, R. J.; Rundle, R. E. *J. Am. Chem. Soc.* **1951**, *73*, 4325.

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Table I. Energies and Lengths of Forming/Breaking Bonds in Relevant Species in S_N2 Reactions of Methyl Halides

reactants		heats of formation, kcal/mol				bond lengths,[a] Å	
Y^-	RX	$(Y^- + RX)$	$(Y^- RX)$[b]	$(Y\cdots R\cdots X)^-$	$(YR X^-)$	CX	CY
F^-	CH_3F	−78.7	−83.9	−38.9	−83.9	1.64 (1.35)	
Cl^-	CH_3Cl	−77	−83.6	−75.0	−83.6	2.14 (1.80)	
Br^-	CH_3Br	−48	−53.9	−45.9	−53.9	2.21 (1.88)	
CN^-	CH_3F	−6.4	−10.6	29.2	−5.1	1.75 (1.35)	1.66 (1.45)
H^-	CH_3F	12.2	4.8	11.6	−29.5	1.67 (1.35)	1.27 (1.10)
F^-	CH_3Br	−28.1	−35.6	−29.1	−103.3	2.05 (1.88)	2.16 (1.35)
Cl^-	CH_3Br	−65.2	−70.8	−60.4	−69.4	2.22 (1.88)	2.13 (1.80)
CH_3O^-	CH_3Br	−50.7	−55.9	−39.2	−91.4	2.12 (1.88)	2.00 (1.40)

[a] First value, bond length of the transition state; value in parentheses bond length of reactant (RX) or product (RY).
[b] Initial charge-dipole adduct.

Table II. Energies and Lengths of Forming/Breaking Bonds in Relevant Species in S_N2 Reactions of Silicon Halides

reactants		heats of formation, kcal/mol		bond length of transitn state,[a] Å	
Y^-	R_3SiX	$Y^- + R_3SiX$	$(Y\cdots SiR_3\cdots X)^-$	SiX[a]	SiY
H^-	H_3SiH	84.4	24.7	1.52 (1.43)	1.52
F^-	H_3SiF	−103.7	−176.2	1.75 (1.65)	1.75
Cl^-	H_3SiCl	−90.0	−130.3	2.26 (2.11)	2.26
Br^-	H_3SiBr	−49.9	−87.7	2.37 (2.22)	2.37
Cl^-	Cl_3SiCl	−182.3	−272.7	2.21 (2.09)	2.21
Cl^-	CH_3SiH_2Cl	−117.4	−152.5	2.28 (2.12)	2.28
Cl^-	$(CH_3)_3SiCl$	−168.7	−191.7	2.34 (2.14)	2.34
Me_2N^-	H_3SiCl	−24.6	−88.8	2.34 (2.11)	1.87
MeO^-	H_3SiOCH_3	−105.6	−146.4	1.84 (1.72)	1.84
MeO^-	H_3SiCl	−75.8	−142.7	2.34 (2.11)	1.80

[a] Bond length in R_3CX in parentheses.

potential surface for a degenerate S_N2 reaction of an anion X^- with RX

$$X^- + R\text{-}X \rightarrow X\text{-}R + X^- \qquad (2)$$

has the form indicated in Figure 2a. RX and X^- first combine to form a charge-dipole complex which rearranges via a symmetrical transition state (cf. **3**) to a mirror-image complex that can then dissociate. In exothermic S_N2 reactions, the calculated potential surfaces have the same general form but are skewed (Figure 2b). Here there is no barrier to the reaction at low pressures in the gas phase but a barrier remains in solution.

Table I shows the heats of formation calculated by MNDO for the reactants and transition states for several reactions of this kind, together with the lengths of the forming/breaking bonds in the transition state and of the bond to the leaving group in the reactant. The calculations were carried out by using the standard MNDO procedure[7] and parameters,[7-9] the geometries of the various species being found by minimizing their energies with respect to all geometrical variables by the gradient procedure included in our standard[10] MNDO computer program. The stationary points were characterized by the McIver–Komornicki procedure,[11] i.e., calculating and diagonalizing the Hessian (force constant) matrix. Calculations for the reactions studied previously[5] gave results agreeing with the earlier ones.

If the traditional explanation of the reactivity of silicon is correct, the potential surface for the S_N2 reaction of a silyl derivative should have the same form as that of its methyl analogue, if contributions by 3d AOs are not taken into account. To check this, we carried out analogous MNDO calculations for the reactions of halosilanes **5** with various anions by using published[12] parameters for silicon. These of course refer to the current version of MNDO where d AOs are not taken into account.

$$\underset{\textbf{5}}{R_3SiX} \qquad \underset{\textbf{6}}{(X\cdots SiR_3\cdots X)^-}$$

The results obtained in this way were quite different from those for the reactions of the corresponding halomethanes. In each case the anion combined exothermically and without activation with the halosilane to form a symmetrical adduct (**6**). There is of course no question of 3d AOs being involved in **6** since d AOs are not included in the current version of MNDO. Table II shows the heats of formation calculated for the reactants and adducts for the reactions of various nucleophiles with various halosilanes together with the lengths of the relevant bonds to silicon.

This conclusion is not at all surprising, given that other hypervalent compounds of the main group elements of groups 4B, 5B, 6B, and 7B can be interpreted very satisfactorily in similar terms.[3] For example, the difference in length and strength between the axial and equatorial PF bonds in PF_5 can be easily understood if the two axial fluorine atoms are in fact linked to phosphorus by a single three-center four-electron bond. The conclusion that d AOs play only a minor role in such cases is also very reasonable. Since the energies of the relevant (*n*d) AOs of such atoms are much greater than those of the other (*n*s, *n*p) valence shell AOs and since the nd AOs are empty, interactions between the latter and the orbitals used in bonding would be expected to be small. The only cases where participation by d AOs would be expected to be

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(10) Available from the Quantum Chemistry Program Exchange (QCPE).

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(12) Dewar, M. J. S.; Rzepa, H. S.; Mckee, M. L. *J. Am. Chem. Soc.* **1978**, *100*, 3607.

important are those involving atoms whose relevant d AOs have a principal quantum number *less* than that of the valence shell s and p AOs and where the d shell is partly empty or only just filled. This condition is met only by the transition metals, and there d AOs undoubtedly play a major role in bonding.

Why then does carbon differ from the other group 4 elements in forming unreactive quadrivalent species? In particular, why are the three-center four-electron bonds in transition states for nucleophilic substitution on carbon so weak? For that matter, in the same vein, why do nitrogen and oxygen fail to form hypervalent compounds? The ionization potentials of the lone-pair electrons in amines and ethers are far less than that of xenon, which reacts easily with fluorine. Why then do amines and ethers not react likewise with fluorine to form compounds of the type R_3NF_2 or R_2OF_2?

There can be only one reason for this, i.e., the smaller size of the second period elements. In **3**, the ClCH bond angles are 90°. Because carbon is so small, this brings the chlorine and hydrogen atoms too close together for comfort. The resulting steric repulsions destabilize **3**. Since the steric requirements of lone pairs are considerable, steric repulsions could also destabilize hypervalent compounds of nitrogen or oxygen. In this way one can explain the peculiarities of the second period elements without having to invoke participation by d AOs in the case of the later periods.

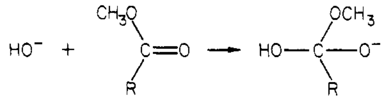
This conclusion is strongly supported by the bond lengths listed in the tables.

In the substitutions on silicon, the bond on the "leaving group" X in the intermediate is only 6–7% longer than it is in the reactant. This would be expected, because the bond energy of the three-center bond in a compound of this type should not be much less than that of the analogous two-center bond.[12] Indeed, the calculated heats of reaction for formation of these intermediates are large (Table II). Similar arguments apply to the analogous three-center bonds in hypervalent compounds of the third period elements, where the lengths of the corresponding bonds are also only a little greater than those of the corresponding two-center ones.

In the transition states for the degenerate S_N2 reactions of halide ions with methyl halides, however, the carbon–halogen bond is longer by ca. 25% than in the reactant. This difference cannot be attributed to absence of d AOs on carbon because the calculations for the chlorosilanes were carried out without inclusion of d AOs. Since there is no other reason why the three-center bonds should be any weaker for carbon than silicon, the only possible explanation seems to lie in increased steric repulsions due to the smaller size of the carbon atom.

It is interesting to note that many years ago Evans[13] suggested that steric repulsions might be the major controlling factor in S_N2 reactions of alkyl compounds. This view was, however, immediately challenged by Ingold et al.,[14] and their interpretation prevailed. It now appears that steric effects in such reactions are even more important than Evans thought.

The problem in the second period is that there simply is not enough room to pack additional groups round the central atom, in the geometry required for the formation of one or more linear three-center four electron bonds. This problem does not arise if the coordination number of the central atom is reduced. Consider for example nucleophilic attack on carbonyl, as in hydrolysis of an ester.



(3)

Here the adduct contains tetrahedral tetracoordinated carbon, which of course is its normal state. Repulsions between the anion and substrate no longer impede addition because the groups attached to carbon bend away from the anion as it approaches. MNDO calculations indicate that these reactions, if exothermic, do indeed take place without activation, like the additions of anions to **5** (Figure 2c). The heats of reaction are of course less than in the case of **5** because the addition involves breaking of a bond to carbon, albeit a π bond. Our discussion therefore accounts for the special features of carbon chemistry on which life depends.

Acknowledgment. This work was supported by the Air Force Office of Scientific Research (Grant No. AFOSR 79-0008) and the Robert A. Welch Foundation (Grant No. F-126). The calculations were carried out by using a Digital VAX 11-780 computer purchased with grants from the National Science Foundation and The University of Texas at Austin.

Registry No. Carbon, 7440-44-0.

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