the iridium *via* the phosphorus atoms outweighs the small substituent effect observed in intermolecular substitution. Hence, electron-withdrawing substituents which reduce electron density on the metal atom make it less susceptible to oxidative addition.

The observed deuteration of the cyclopentadienyl groups in the catalysts suggests that the reactive intermediate **1** can oxidatively add a metallocene C–H bond, perhaps *via* a "double decker" sandwich intermediate. This type of oxidative addition is presumably involved in the formation of niobocene and tantalocene dimers[8] with bridging cyclopentadienyl groups.

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# Acidities and Spectral Properties of α-Silyl and α-Germyl Carboxylic Acids and Their Carboxylates

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**Abstract:** The order of acidity observed for $R_3MCO_2H$ ($R = CH_3$ and/or $C_6H_5$, M = C, Si, Ge; R = H, M = C, Ge) is Si $\geq$ Ge $>$ C. We find this order is best explained in terms of the larger sizes and polarizabilities of Si and Ge relative to C which would facilitate stabilization of the negative charge in the conjugate base. CNDO/2 results on the model systems $H_3CCO_2H$, $H_3SiCO_2H$, and their anions are presented (with and without inclusion of d orbitals for Si) which predict the correct order of acidity and indicate $p\pi \rightarrow d\pi$ interaction is of little importance, contrary to previous suggestions. The importance of Si–O (1,3) $d\pi$–$p\pi$ interactions is also considered. For a consistent thermodynamic explanation the relative electron affinities of $CH_3\cdot$ and $SiH_3\cdot$ (Si $>$ C) appear to be the key factors. The electronic spectra of the title compounds indicate a symmetry ($C_{2v}$) forbidden $n \rightarrow \pi^*$ transition as the lowest energy transition. CNDO/2 predicts an allowed $\sigma \rightarrow \pi^*$ which cannot be ruled out at present as incorrect. $d\pi$–$\pi^*$ interactions (M = Si) do appear important in determining electronic properties for which there are significant excited-state contributions. Differences in CO stretching frequencies are explained qualitatively in terms of relative Si and C inductive effects. However, comparison of the ir ($\nu$(CO)) characteristics of the acids with those of the α-group-IV metal ketones and dihalocarbonyls (for which force constant and normal coordinate data are available) suggest kinetic effects (mass and geometric differences) and potential energy terms not involving the CO bond are more important than electronic effects for determining $\nu$(CO).

The ionization constants of a series of α-silyl and α-germyl carboxylic acids, $(C_6H_5)_n(CH_3)_{3-n}MCO_2H$ (M = C, Si, Ge)[1a] and $H_3GeCO_2H$,[1b] have been measured. An intriguing observation is the order of acidity found to be $R_3SiCO_2H \geq R_3GeCO_2H > R_3CCO_2H$. This is contrary to that expected on the basis of inductive effects, Si and Ge being more electropositive than C, but rather has been ascribed[1] to the (p–d)π bonding capabilities[2] of Si and Ge which should favor delocalization of negative charge and therefore stabilization of $R_3MCO_2^-$. Ramsey[3] has noted, however, that the highest filled π molecular orbital of the carboxylate group is *nodal* at the carbon atom and suggests that 1,3 (p–d)π bonding between M and oxygen in the anion may be important.

In addition to the acidity problem, the unusual electronic spectra and infrared carbonyl stretching frequencies exhibited by the α-group-IV metal carboxylic acids and carboxylates are of interest. In the few determinations of the electronic spectra of these compounds, the low-energy $n \rightarrow \pi^*$ transition is observed[1b,4] to be red shifted with respect to the analogous carbon compound. The bathochromic shift of this transition is similar to the dramatic shift observed in the spectra of α-silyl and α-germyl ketones[5-7] with respect to their carbon analogs. Recent work[5,7a] suggests that this shift is due to the strong positive inductive effect of silicon or germanium raising the energy of the nonbonding MO while considerable Si($d\pi$)–CO($\pi^*$)

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[1] (a) O. M. Steward, H. W. Irwin, R. A. Gartska, and J. O. Frohliger, *J. Chem. Soc. A*, 3119 (1968); (b) P. M. Kuznesof and W. L. Jolly, *Inorg. Chem.*, 7, 2574 (1968). The preparation and properties of the potassium salt are given but the acid itelf was never isolated.

[2] For a recent review of π bonding in group IVB, see C. J. Attridge, *Organometal. Chem. Rev., Sect. A*, 5, 323 (1970).

[3] B. G. Ramsey, "Spectroscopy in Inorganic Chemistry," Vol. II, C. N. R. Rao and J. R. Ferraro, Ed., Academic Press, New York, N. Y., 1971, p 249.

[4] (a) $(CH_3)_3GeCO_2H$ and $(CH_3)_3GeCO_2^-$: O. W. Steward and J. E. Dziedzic, *J. Organometal. Chem.*, **16**, P5 (1969); $(CH_3)_3SiCO_2H$: O. W. Steward and J. E. Dziedzic, *Int. Symp. Organometal. Chem., 4th* (1969). (b) It is appropriate also to include the ester $(CH_3)_3SiCO_2CH_3$: G. J. D. Peddle and R. W. Walsingham, *J. Amer. Chem. Soc.*, 91, 2154 (1969). (c) The $n \rightarrow \pi^*$ transition for phenyl-substituted α-silyl and α-germyl carboxylic acids is not observed due to masking by the phenyl $\pi \rightarrow \pi^*$ transition in the region 247–271 nm (ref 4a).

[5] F. Agolini, S. Klemenko, I. G. Csizmadia, and K. Yates, *Spectrochim. Acta, Part A*, 24, 169 (1968).

[6] A. G. Brook, *J. Amer. Chem. Soc.*, 79, 4373 (1957). The current interest in α-silyl and α-germyl ketones (ref 5, 7) has derived from Brook's striking observation that triphenylsilyl phenyl ketone is yellow.

[7] (a) H. Bock, H. Alt, and H. Seidl, *ibid.*, 91, 355 (1969); (b) B. G. Ramsey, "Electronic Transitions in Organometalloids," Academic Press, New York, N. Y., 1969, p 94 ff; (c) reference 3, p 238. (d) These references serve as excellent sources into the literature regarding electronic properties of organometalloids in general.

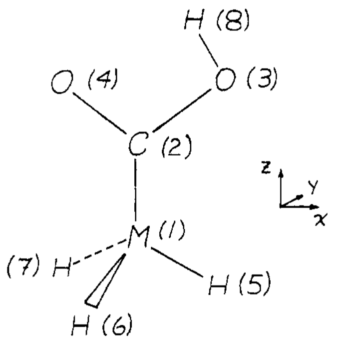

Figure 1. Orientation for $H_3MCO_2H$ and $H_3MCO_2^-$. The *y* axis is considered to be the axis of $\pi$ symmetry.

interaction in the excited state tends to lower the energy of the $\pi^*$ level. Infrared carboxyl stretching frequencies for the $\alpha$-group-IV metal carboxylic acids[4a,8,9] and their salts[1b] are abnormally shifted to lower energies with respect to their carbon analogs in a manner similar to that observed for the ketones.[10,11] The data for the ketones have been explained[12,13] in terms of the relative inductive effects of C, Si, and Ge.

In order to test Ramsey's hypothesis and to throw light on the possible electronic effects of Si and Ge on the carboxyl system, we have performed CNDO/2 molecular orbital calculations[14,15] on the two acids $H_3CCO_2H$ and $H_3SiCO_2H$ and their corresponding anions. Although $H_3SiCO_2H$ as yet has not been synthesized, we have chosen it as our model for the $\alpha$-silyl and $\alpha$-germyl carboxylic acids upon consideration of the following: (a) For the series $\alpha$-silyl and $\alpha$-germyl ketones ($RCOMR'_3$, R = $CH_3$, $C_6H_5$; R' = H, $CH_3$, $C_6H_5$; M = Si, Ge) methyl or phenyl substitution on M does not radically affect their spectroscopic properties.[5] We would expect the same to be true for $R_3MCO_2H$ and assume this is the case with regard to acidities. (b) Inclusion of three methyl or three phenyl groups would consume an excessive and, at present, unwarranted amount of computer time. For the $\alpha$-silyl compounds we have presented results which both include and exclude the silicon 3d orbitals in an effort to evaluate the importance of (p–d)$\pi$ back-bonding. This approach has been ably employed[5] in conjunction with the more approximate extended Hückel method for discussing the $\alpha$-silyl and $\alpha$-germyl ketones.

## Computational Details

Bond distances and angles[20] for $H_3CCO_2H$, $H_3SiCO_2H$, and their anions were chosen from the Chemical Society tables[21] and from Ebsworth's monograph.[22] The orientation chosen for the calculations and the atom numbering scheme are presented in Figure 1.

A revised version of Dobosh's CNINDO program from QCPE[23] was employed. This program utilizes the parameter set for the silicon atomic orbitals as presented in the paper of Santry.[24] Parameters for H, C, and O are those given in the original CNDO/2 paper.[14c]

## Results and Discussion

**Acidities.** The energy for the gas-phase reaction

$$AH \longrightarrow A^- + H^+$$

is merely the difference in energy between the anion and the acid

$$\Delta E = E_{A^-} - E_{AH}$$

since the energy of a proton is zero at infinite separation. $\Delta E$ values given in Table I gratifyingly predict the correct order of acidity.[1,25] Further, it may be seen that inclusion of d orbitals has virtually no effect on the total energy ($E_{AH}$) of $\alpha$-silyl carboxylic acid ($\sim$0.2% diminution) or its anion, and even less effect on $\Delta E$!

An explanation for the predicted acidity order is incipient upon examination of the net atomic charges given in Table I. The dramatic change in net charge of the silyl group, $\Delta q(MH_3)$ (Table I), compared to that for the methyl group upon ionization is by far the most significant feature. As the large value of $\Delta q(SiH_3)$ is obtained with or without inclusion of d orbitals further analysis of the data may be expected to reveal that d–p

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(8) H. Gilman and W. J. Trepka, *J. Org. Chem.*, **25**, 2201 (1960).

(9) J. Satge, *Ann. Chim.* (*Paris*), **6**, 519 (1961), has reported $\nu$(CO) at 1720 cm$^{-1}$ for $(C_2H_5)_3GeCO_2H$. We believe this to be too high an energy for a triorgano-$\alpha$-germyl carboxylic acid (*cf.* $\nu$(CO) at 1693 cm$^{-1}$ for $(CH_3)_3CCO_2H$, ref 4a); the compound was reported to be impure.

(10) A. G. Brook, M. A. Quigley, G. J. D. Peddle, N. V. Schwartz, and C. M. Warner, *J. Amer. Chem. Soc.*, **82**, 5102 (1960).

(11) G. J. D. Peddle, *J. Organometal. Chem.*, **5**, 486 (1966); G. J. D. Peddle, *ibid.*, **14**, 139 (1968).

(12) K. Yates and F. Agolini, *Can. J. Chem.*, **44**, 2229 (1966).

(13) R. W. Harrison and J. Trotter, *J. Chem. Soc. A*, 258 (1968).

(14) (a) J. A. Pople, D. P. Santry, and G. A. Segal, *J. Chem. Phys.*, **43**, S129 (1965); (b) J. A Pople and G. A. Segal, *ibid.*, **43**, S136 (1965); (c) *ibid.*, **44**, 3289 (1966).

(15) Our choice of the CNDO/2 method is based on the generally successful correlations of the acidities of alkanes (ref 16) and saturated alcohols (ref 16 and 17), the basicities of saturated amines (ref 16), and the reasonable qualitative correlations found between molecular orbital energies and photoelectron ionization potentials. We note the following, however. Failure of the CNDO/2 method to predict the relative acidities of cycloalkanes has been demonstrated (ref 18). This has been attributed to overemphasis of electron repulsion which would clearly be maximized in the case of anions and species with lone pairs. In our comparison of closely related species we are trusting that artifacts relating to overemphasis of electron repulsion will cancel. Also, unexpected and suspect orderings of molecular orbitals are sometimes obtained from CNDO/2 calculations and attempts at calculating molecular spectra have generally been unsuccessful without considerable reparametrizations and inclusion of configuration interaction (ref 19). Here, we wish to emphasize that correlation of spectra on the basis of one-electron transitions between CNDO/2 MO's can be qualitatively successful when combined with good intuition and available experimental data.

(16) T. P. Lewis, *Tetrahedron*, **25**, 4117 (1969).

(17) R. B. Hermann, *J. Amer. Chem. Soc.*, **92**, 5298 (1970).

(18) R. G. Jesaitis and A. Streitwieser, Jr., *Theor. Chim. Acta*, **17**, 165 (1970).

(19) H. H. Jaffe, *Accounts Chem. Res.*, **2**, 136 (1969), and references therein.

(20) Distances (Å): C–H (1.09), Si–H (1.48), C–C (1.50), SiC–(1.86), CO (1.26 in the anions, 1.24 and 1.31 for the acids), O–H (0.95). Angles: $\angle$HMH and $\angle$CMH (tetrahedral value), $\angle$MCO (118°), $\angle$OCO (124°), $\angle$COH (108°).

(21) L. E. Sutton, Ed., *Chem. Soc., Spec. Publ.*, No. 11 (1958).

(22) E. A. V. Ebsworth, "Volatile Silicon Compounds," Pergamon Press, Oxford, 1963.

(23) Quantum Chemistry Program Exchange, Department of Chemistry, University of Indiana, Bloomington, Indiana, program No. 141. This program was written originally for the IBM 360/65. We have scaled down the dimensions and organized it in overlays for an IBM 360/44 with 128K memory.

(24) D. P. Santry, *J. Amer. Chem. Soc.*, **90**, 3309 (1968): $^1/_2(I + A)_\mu = -9.0, -4.5$, and 0 eV for $\mu$ = 3s, 3p, 3d, respectively, and $(\beta^0_{Si})_{s,p} = -8.5$ eV, $(\beta^0_{Si})_d = -6$ eV.

(25) $\Delta E$ may be correlated with the free energy for the ionization reaction if it is assumed that the entropy change is zero or that the changes are equal for our comparative reactions. Although these free energies have opposite signs from those determined thermodynamically, the order of acidity calculated for these acids relative to other acids (*e.g.*, water, alcohols) is determined correctly. Presumably, reparametrization of the theory would result in free energies more consistent with thermodynamic signs without destroying the excellent agreement in relative acidities.

Table I. Energies and Net Electronic Charges for $H_3MCO_2H$ and $H_3MCO_2^-$

| | $M^a = C^0$ | $C^-$ | $Si^0$ (sp)[b] | $Si^-$ (sp)[b] | $Si^0$ (spd)[c] | $Si^-$ (spd)[c] |
|---|---|---|---|---|---|---|
| $E_{AH\text{ or }A^-}{}^d$ | −51.71 | −53.18 | −48.39 | −49.89 | −48.51 | −50.02 |
| $\Delta E^d$ | −1.47 | | −1.50 | | −1.50 | |
| $q(1)^a$ | −0.109 | −0.096 | 0.439 | 0.319 | 0.460 | 0.319 |
| $q(2)$ | 0.282 | 0.367 | 0.137 | 0.307 | 0.118 | 0.293 |
| $q(3)$ | −0.429 | $-0.582^e$ | −0.413 | $-0.537^e$ | −0.407 | $-0.517^e$ |
| $q(4)$ | −0.306 | $-0.582^e$ | −0.280 | $-0.537^e$ | −0.254 | $-0.517^e$ |
| $q(5)^e$ | 0.056 | −0.035 | −0.088 | −0.184 | −0.101 | −0.191 |
| $q(8)$ | 0.394 | | 0.381 | | 0.387 | |
| $q(MH_3)$ | 0.059 | −0.202 | 0.174 | −0.234 | 0.157 | −0.253 |
| $\Delta q(MH_3)$ | −0.261 | | −0.407 | | −0.411 | |

[a] $M^0$ refers to the acid, $M^-$ to the anion. See Figure 1 for atom numbering scheme. [b] Values using an sp basis set of atomic orbitals. [c] Values using a basis set including Si 3d orbitals. [d] Atomic units, 1 au = 27.21 eV = 627.71 kcal/mol. [e] This is an average value necessitated by the orientation chosen for the species (Figure 1).

Table II. Charge Densities and Bond Orders for $H_3MCO_2H$ and $H_3MCO_2^-$

| | π orbital ($p_y$) densities | | | | ($p_y$–$p_y$) π bond orders | | |
|---|---|---|---|---|---|---|---|
| System[a] | M(1) | C(2) | O(3) | O(4) | 1,2 | 2,3 | 2,4 |
| $C^0$ | 1.030 | 0.876 | 1.792 | 1.366 | 0.223 | 0.479 | 0.835 |
| $C^-$ | 0.935 | 0.767 | 1.626 | 1.626 | 0.211 | 0.669 | 0.669 |
| $Si^0$ (sp) | 0.877 | 0.890 | 1.790 | 1.323 | 0.179 | 0.476 | 0.853 |
| $Si^-$ (sp) | 0.787 | 0.784 | 1.605 | 1.605 | 0.174 | 0.679 | 0.679 |
| $Si^0$ (spd) | 0.780 | 0.901 | 1.784 | 1.287 | 0.185 | 0.471 | 0.848 |
| $Si^-$ (spd) | 0.702 | 0.791 | 1.585 | 1.585 | 0.183 | 0.674 | 0.674 |

| | Si d-orbital densities | | | (d–p) π bond orders | | | | |
|---|---|---|---|---|---|---|---|---|
| | *yz* | *xy* | *xz*[b] | *yz, y* | *yz, y* | *xy, y* | *xz, x*[b] | *xz, z*[b] |
| $Si^0$ (spd) | 0.050 | 0.057 | 0.051 | 1,2: 0.119 | 1,3: 0.058 | 0.039 | −0.029 | −0.087 |
| | | | | | 1,4: 0.148 | 0.030 | −0.039 | 0.073 |
| $Si^-$ (spd) | 0.051 | 0.056 | 0.053 | 1,2: 0.118 | 1,3: 0.119 | 0.060 | −0.040 | −0.099 |
| | | | | | 1,4: 0.119 | 0.009 | −0.039 | 0.098 |

[a] See footnotes *a*, *b*, and *c* in Table I. [b] It should be remembered that although these orbitals lie in the $Si–CO_2$ plane the $d_{xz}$ is π type and capable of π interaction with the $p_x$ and $p_z$ orbitals of oxygen.

($Si–CO_2$) π bonding is, at best, of secondary importance in determining the relative acidities. The inappropriateness of Si–C dative π bonding being mainly responsible for additional stabilization of $H_3SiCO_2^-$ is clearly suggested by the Si–C (d–p)π bond orders and dπ orbital electron densities set out in Table II. These quantities are calculated to be small and *the same* Si–C (d–p)π bond order, 0.118 and 0.119;[26] $Si(d_{yz})$ charge density, 0.050 and 0.051) for both acid and anion.

For assessing Ramsey's suggestion as to the importance of Si–O 1,3 (d–p)π interactions we may consider both final Si–O Hartree–Fock energy matrix elements, $F_{\mu\nu}$ (equivalent to the resonance integrals $\beta_{\mu\nu}$, in more approximate MO methods), and Si–O (d–p)π bond orders. The largest Si–O $F_{\mu\nu}$ values where d orbitals are involved are ±0.731 eV ($Si(d_{xz})$–$O(p_z)$, $H_3SiCO_2^-$); other Si–O (d–p) *F* values are of the same magnitude. Also noteworthy is the similarity in values for Si–O (p–p) and C–O (p–p) interactions (*e.g.*, 1.16 and 1.07 eV for the 1,3 ($p_z$–$p_z$) interactions in $H_3SiCO_2^-$ and $H_3CCO_2^-$, respectively). Thus, as regards the Hartree–Fock energy matrix, Si–O 1,3 (d–p) interactions are comparable to Si–O and C–O 1,3 (p–p) interactions.[27]

The Si–O 1,3 (d–p) bond orders (Table II) are small, as expected. But, a surprising result is that the 1,3 $Si(d_{yz})$–$O(p_y)$ bond order is the same as for the 1,2 $Si(d_{yz})$–$C(p_y)$ interaction in spite of the fact that corresponding overlap integrals differ by nearly a factor of 10, *e.g.*, $S(d_{yz},p_y)$: Si–C, 0.306 and Si–O, 0.044 (anion); Si–O (p–p)π bond orders are close to zero. Although the value for the Si–O (d–p)π bond order may be considered "large," it and the $F_{\mu\nu}$ values given above do not lead one to conclude that 1,3 π bonding is a major factor for anion stabilization.[28] We suggest, however, that it is a factor worthy of consideration in studies similar to this one.

Other satisfying features of the calculations are the predicted protonic nature of the hydroxyl hydrogen (Table I, $q(8)$) and the clearly hydridic character, $q(5)$, of the hydrogens bonded to silicon compared to those bonded to carbon; this is in line with currently accepted electronegativities for these atoms.[30] In addition, we note that both the silyl and the methyl hydrogens are predicted to increase their electronic charge, $q(5)$, by

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(26) (a) It is satisfying to note that the Si–C (p–p)π bond order calculated by a simple Hückel MO method using a heteroatom model (ref 26b) for the $R_3Si$ group (0.18 for $(p\text{-}(CH_3)_3SiC_6H_4)_2$) gives a value in accord with our more sophisticated treatment (see Table II). (b) M. D. Curtis and A. L. Allred, *J. Amer. Chem. Soc.*, 87, 2554 (1965).

(27) For comparison, representative values of $F_{\mu\nu}$ for M–C, 1, 2 interactions are appropriate: $H_3SiCO_2^-$, ($p_y$–$p_y$) −3.58, ($p_z$–$p_z$) 6.74, ($d_{yz}$–$p_y$) −2.26 eV; $H_3CCO_2^-$, ($p_y$–$p_y$), −5.32, ($p_z$–$p_z$), 9.88 eV.

(28) Pettit (ref 29) has given a succinct warning regarding interpretation of theoretical calculations: "In cases where dative π-bonding is thought to be present, a very small contribution from the π-bond itself to the total bond energy does not necessarily mean that it is unimportant, since its predominant feature may be the dissipation of charge from the central atom in order to create the conditions for a strong σ-bond with a shorter bond length. Under such conditions the synergic effect of a weak π-bond could be considerable." We note, however, that for our calculations essentially the same results are achieved with either an sp or spd basis set of AO's leaving our conclusions unmodified.

(29) L. D. Pettit, *Quart. Rev. Chem. Soc.*, 25, 1 (1971).

(30) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Wiley-Interscience, New York, N. Y., 1962, p 92; C. F. Shaw, III, and A. L. Allred, *Organometal. Chem. Rev., Sect. A*, 5, 95 (1970).

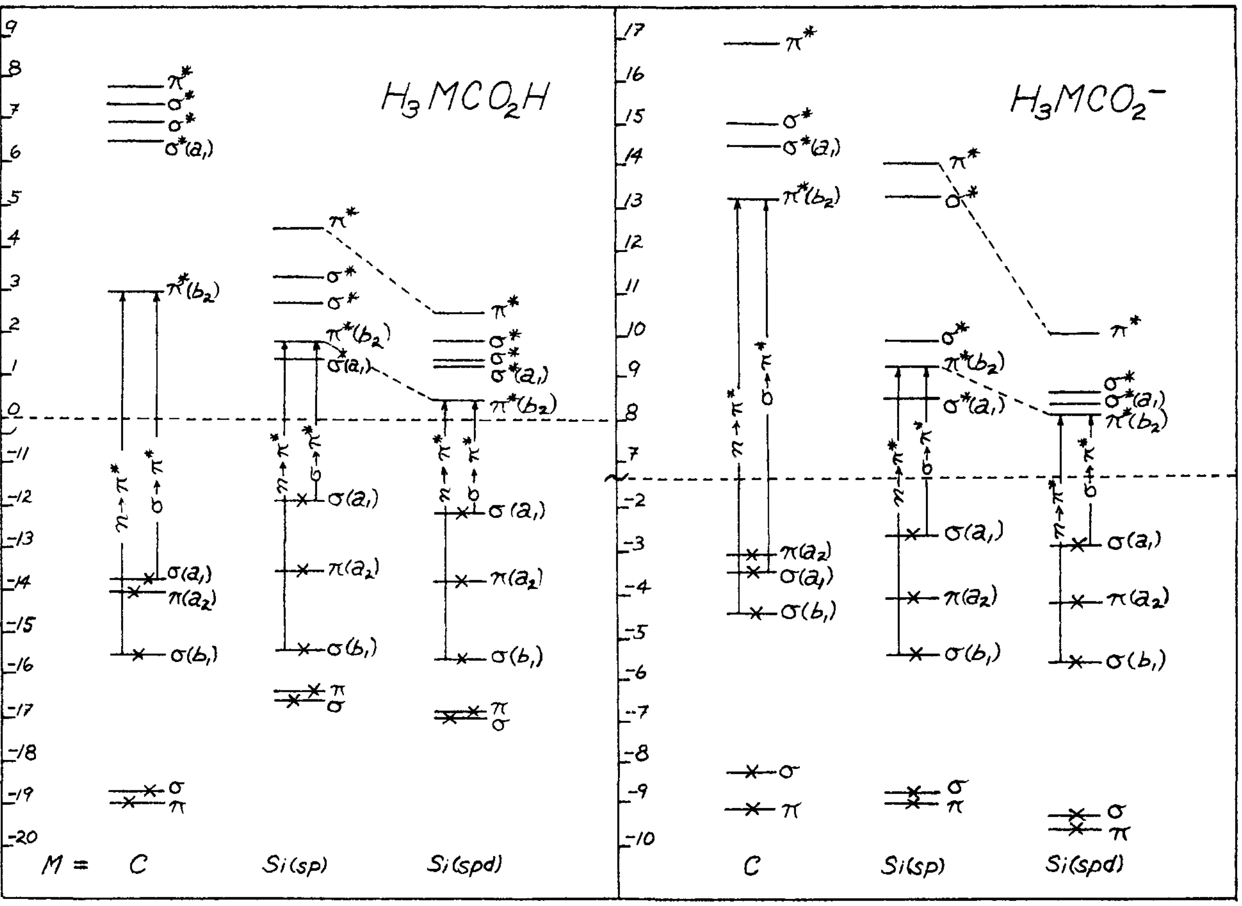

Figure 2. CNDO/2 energies of highest filled and lowest vacant MO's for acetic acid, acetate ion, α-silyl carboxylic acid, and α-silylcarboxylate ion (the latter two with sp and spd basis sets of AO's). MO's are labeled $\pi$ if their $p_y$ coefficients are nonzero; $\sigma$ if they are zero. Symmetry labels are based on $C_{2v}$ symmetry.

almost the same amount upon anion formation. Without invoking d-orbital participation, the calculations indicate that it is the large positive charge on α-silicon (+0.439) in the acid compared with that of α-carbon (−0.109) which permits the silyl group to act as the better "electron sink" upon deprotonation. (Even in the anion, silicon maintains a net *positive* charge.) Both methyl and silyl act to stabilize the anion *via* electron withdrawal.[31] Therefore, the greater accommodation and stabilization of negative charge by the silyl group (in the *gas phase*) must be attributed to the larger size of silicon and the greater diffusedness and polarizability[32] of its valence atomic orbitals (principal quantum number 3) compared with those of carbon (principal quantum number 2).

An explanation of the relative acidities of $H_3CCO_2H$ and $H_3SiCO_2H$ may also be cast in thermodynamic terms. The gas-phase ionization process can be considered as the sum of three steps:[33] (1) dissociation into two neutral radicals $H_3MCO_2\cdot$ and $H\cdot$, (2) ionization of $H\cdot$ to $H^+$, (3) anion formation, $H_3MCO_2^-$, by electron capture. For M = C or Si, if we assume the same O–H bond energy and note that the ionization potential of hydrogen is involved in both cases, then anion stabilization must depend on the relative electron affinities of $H_3CCO_2\cdot$ and $H_3SiCO_2\cdot$. Although these data are unavailable, the electron affinities of $H_3C\cdot$ (~1.08 eV)[34] and $H_3Si\cdot$ (>1.8 eV)[35] have been measured and support the view that $H_3SiCO_2^-$ should stabilize a negative charge more than $H_3CCO_2^-$.

**Electronic Spectra.** The effect of metalloid substitution on the electronic spectra of simple organic chromophores (*e.g.*, C=C, C=O, $CO_2^-$) has been extensively discussed.[7b] $CO_2H$ and $CO_2^-$ are class V chromophores[36] having a highest filled nonbonding MO and a lowest vacant $\pi^*$ MO which are predicted to suffer energy displacements (the n level to higher energy, $+I$ inductive effect; the $\pi^*$ level to lower energy, $d\pi$–$p\pi^*$ interactions) upon formation of the α-group IV metal acid or carboxylate. Assuming differences between ground-state orbital energies to be associated with electronic transitions, these displacements are expected to produce spectral red shifts for the n → $\pi^*$ transition. Also, the energy of the highest filled $\pi$ MO is expected to be affected only slightly, if at all.

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[31] There is ample evidence (experimental and theoretical) for the methyl group acting as an electron acceptor. See J. F. Sebastian, *J. Chem. Educ.*, 48, 97 (1971), and references therein; W. J. Hehre and J. A. Pople, *Tetrahedron Lett.*, 2959 (1970); and J. E. Huheey, *J. Org. Chem.*, 36, 204 (1971).

[32] W. Kauzmann, "Quantum Chemistry," Academic Press, New York, N. Y., 1957.

[33] J. I. Brauman and L. K. Blair, *J. Amer. Chem. Soc.*, **90**, 6561 (1968); A. Streitwieser, Jr., and J. H. Hammons, *Progr. Phys. Org. Chem.*, 3, 41 (1965).

[34] V. I. Vedeneyev, L. V. Gurvich, V. N. Kondrat'yev, V. A. Medvedev, and Ye. L. Frankevich, "Bond Energies, Ionization Potentials, and Electron Affinities," Edward Arnold, London, 1966.

[35] P. Potzinger and F. W. Lampe, *J. Phys. Chem.*, 73, 3912 (1969).

[36] The convenient classification of chromophores by R. West, *J. Organometal. Chem.*, 3, 314 (1965), has been logically extended: ref 3, p 202.

CNDO/2 energy level diagrams for the highest filled and lowest vacant MO's for our systems are presented in Figure 2. Taking into account that CNDO energy levels are often incorrectly ordered,[15,19] several arresting features may be noted: (1) Although intensities of observed transitions[1b,4] suggest that the lowest energy band should be forbidden ($n(b_1) \rightarrow \pi^*(b_2)$, $^1A_1 \rightarrow {}^1A_2$ ($C_{2v}$ symmetry)), the calculations predict (with or without d orbitals for silicon) an allowed $\sigma(a_1) \rightarrow \pi^*(b_2)$ transition, $^1A_1 \rightarrow {}^1B_2$, to be of lower energy (Figure 2). We note, however, that although the $\sigma(a_1) \rightarrow \pi^*(b_2)$ transition is symmetry allowed, it is polarized perpendicular to the plane of $SiCO_2$ and would therefore be weak.[37] In fact, following an approximate method for calculating intensities[37b] the intensity integral for this transition can be shown to be close to zero. Solvent effect studies which would be useful in distinguishing $n \rightarrow \pi^*$ transitions from $\pi \rightarrow \pi^*$ probably would not be of much use for distinguishing $\sigma(a_1) \rightarrow \pi^*(b_2)$ from $n(b_1) \rightarrow \pi^*(b_2)$. From the calculated similarity of the $\sigma(a_1)$ and $n(b_1)$ MO's[38] neither of which is truly "nonbonding," a hypsochromic shift would be anticipated for either type of transition upon increase of solvent polarity. Since so little data are available for the acids, it is worth noting that the lowest energy transition for the ester $(CH_3)_3SiCO_2CH_3$ is slightly blue shifted upon increasing the solvent polarity;[4b] the transition was assigned $n \rightarrow \pi^*$. (2) For $\alpha$-silyl carboxylic acid and the carboxylate another forbidden transition ($\pi(a_2) \rightarrow \sigma^*(a_1)$, $^1A_1 \rightarrow {}^1A_2$) of lower energy than the $n \rightarrow \pi^*$ is also predicted and corresponds[38] to electron transfer from the oxygens to the $MH_3$ group. (3) The lowest energy transitions are predicted to be red shifted, as observed, upon replacement of $\alpha$-silicon for $\alpha$-carbon. (4) The influence of the d orbitals of silicon on the virtual MO energies is emphasized. Only with the spd AO basis is the lowest vacant MO $\pi^*(b_2)$ hinting at a major, if not primary, role for d orbitals in determining electronic properties for which there are significant excited-state contributions.

Several low energy $\sigma \rightarrow \sigma^*$ and $n \rightarrow \sigma^*$ transitions are predicted (Figure 2) for $H_3SiCO_2H$ and $H_3SiCO_2^-$ which are not considered in the more simplified MO treatments.[36] Unfortunately, there are insufficient data to assess these CNDO results. The calculations also indicate that the low-energy transitions of $H_3SiCO_2H$ should lie at slightly higher energy than those of $H_3SiCO_2^-$. For comparison, the position of the absorption maximum for $(CH_3)_3GeCO_2H$ is 4 nm to the blue of its salt.[4a]

**Infrared Spectra.** The bathochromic shift ($\sim$50 cm$^{-1}$) of the CO stretching frequency for the $\alpha$-group-IV metal carboxylic acids with respect to their carbon analogs[4,8] suggests a considerable diminution of CO bond strength. An inductive effect argument appears to provide a qualitative explanation. The more electropositive nature of silicon relative to carbon would be expected to reduce the positive charge on the carboxyl carbon. This would weaken the $\sigma$ part of the CO bond (making it less polarized) thereby lowering $\nu$(CO). The calculated carbon (carboxyl) $\sigma$-electron densities reflect these ideas: 2.973 electrons in $H_3SiCO_2H$ (spd basis) and 2.842 electrons in $H_3CCO_2H$. Also, comparison of $q(2)$ and $q(4)$ in Table I shows that the CO double bond is considerably less polar in $H_3SiCO_2H$ than in $H_3CCO_2H$.

Further insight into this problem may be gained by considering $\nu$(CO) values for the $\alpha$-group-IV metal ketones and the dihalocarbonyls, $X_2CO$ ($X$ = F, Cl, Br). In the ketones bathochromic shifts range[10,11] from 40 to 74 cm$^{-1}$ depending on the group-IV metal and its organic substituents. Within any one series of ketones (*i.e.*, same organic moieties while varying only M), differences in $\nu$(CO) between M = Si and Ge range from only 10 to 25 cm$^{-1}$, with the silicon derivative always at lower energy. The largest reported differences between germanium and tin derivatives in any one series is 3 cm$^{-1}$. For the dihalocarbonyls, gas-phase frequency shifts of 101 and 100 cm$^{-1}$ are observed upon replacement of fluorine for chlorine and bromine, respectively.[39] As complete vibrational assignments and Urey–Bradley force constant calculations have been reported[39] for the dihalocarbonyls, one may cast these frequency shifts in molecular terms and infer how similar shifts may arise in the $\alpha$-group-IV metal ketones and carboxylic acids.

The CO stretching force constants are relatively invariant upon substitution of the heavier halogens for fluorine (12.9, 12.6, and 12.9 mdyn/Å for X = F, Cl, and Br, respectively). These values imply that the electronic contributions to the carbonyl stretching force constant are essentially identical for the dihalocarbonyls. Kinetic effects (differences in geometries and masses) and potential energy terms which depend on the carbon–halogen stretching force constants and the angular bending force constants in these molecules have been shown to account for most of the observed variations of this carbonyl group frequency.[40] A similar dependence of $\nu$(CO) on kinetic effects and the potential energy terms exclusive of the one for the CO bond should be operative in the $\alpha$-group IV metal carboxylic acids and ketones. Thus, we are warned not to expect all of the observed frequency differences to be attributable to changes in the electronic character of the CO bond. Furthermore, we note that the simple inductive argument given earlier breaks down if applied to a comparison of the $\alpha$-germyl and $\alpha$-stannyl ketones or to $Cl_2CO$ and $Br_2CO$.

The nature of the CO vibration in the ketones and the acids is currently under more quantitative investigation.[41]

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[37] (a) B. G. Ramsey, private communication. (b) H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," Wiley, New York, N. Y., 1962, p 124.

[38] The characteristics of the MO's for the six systems are qualitatively the same. As an example, we summarize for $H_3SiCO_2^-$ (spd AO basis) the nature of those MO's whose energies are given in Figure 2 beginning with the *lowest filled MO* shown: ($\pi$,$b_2$), $CO_2$–Si($d_\pi$) bonding, nodal plane between $CO_2(\pi)$ and $H_3Si$(pseudo-$\pi$,$p_\pi$) moieties; ($\sigma$,$a_2$), delocalized, large coefficients for H 1s orbitals; ($\sigma$,$b_1$), mainly O nonbonding, small contribution from C $p_x$ orbital; ($\pi$,$a_2$), localized on O's, node at C, virtually zero contribution from $SiH_3$ group; ($\sigma$,$a_1$), Si–$CO_2$ bonding, $p_z$ coefficients large, largest for O; ($\pi^*$,$b_2$), $H_3Si$(pseudo-$\pi$,$p_\pi$,$d_\pi$) coefficients large, Si–C bonding, antibonding between C and O's; ($\sigma^*$,$a_1$), main contribution from $SiH_3$ (large Si, s, $p_z$, $d_{z^2}$ coefficients); ($\sigma^*$,$b_1$), $SiH_3$ again (mainly Si($p_x$, $d_{xz}$, $d_{x^2-y^2}$) contributions); ($\pi^*$,$b_2$), Si–C($p_\pi$,$p_\pi$) antibonding but ($d_{yz}$,$p_\pi$) bonding, antibonding between C and O's.

[39] M. J. Hopper, J. W. Russell, and J. Overend, *J. Chem. Phys.*, **48**, 3765 (1968); J. Overend and J. R. Scherer, *ibid.*, 32, 1296 (1960).

[40] J. Overend and J. R. Scherer, *Spectrochim. Acta*, **16**, 773 (1960).

[41] (a) NOTE ADDED IN PROOF: At the time of submission of our manuscript we were unaware of the further studies of Steward, *et al.*, on the acidities and spectral properties of the carboxysilanes and -germanes (O. W. Steward, J. E. Dziedzic and J. S. Johnson, *J. Org. Chem.*, **36**, 3475 (1971), and O. W. Steward, J. E. Dziedzic, J. S. Johnson,

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and J. O. Frohliger, *ibid.*, **36**, 3480 (1971)). It is of particular interest to note that the lowest energy electronic transitions were all slightly red shifted upon increasing the polarity of the solvent (cyclohexane to ethanol, $\Delta\lambda_{max}$ 5–6 nm). This contrasts with the blue shift observed in a related methyl ester, $(CH_3)_3SiCO_2CH_3$ (ref 4b). (b) This work was presented at the 164th National Meeting of the American Chemical Society, New York, N. Y., 1972, Abstract INOR 133.

# Reactions between Nitrosylpentaammineruthenium(II) and Hydroxylamine or Hydrazine. Formation of (Dinitrogen oxide)pentaammineruthenium(II)

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**Abstract:** $[Ru^{II}(NH_3)_5NO]X_3 \cdot H_2O$ and hydroxylamine formed $[Ru^{II}(NH_3)_5N_2O]X_2$ (X = Cl, Br, I). The products showed a strong infrared band in the 1160-cm$^{-1}$ region ($\nu_1$ of $N_2O$) and a weak band in the 2250-cm$^{-1}$ region ($\nu_3$ of $N_2O$). The bromide salt was face-centered cubic, $a = 10.32$ Å. $[Ru^{II}(NH_3)_5NO]X_3$ and hydrazine hydrate formed, at room temperature, $[Ru^{II}(NH_3)_5N_2]X_2$ only. At $-23°$ or below a mixture of $[Ru^{II}(NH_3)_5N_2]X_2$ and $[Ru^{II}(NH_3)_5N_2O]X_2$ was obtained. The same mixture was obtained from reaction of $OH^-$ with a solution of $[Ru^{II}(NH_3)_5NO]I_3 \cdot H_2O$ and $N_2H_6I_2$ at room temperature. The properties of $[Ru^{II}(NH_3)_5N_2O]^{2+}$ are reported and mechanisms for the reactions of $[Ru^{II}(NH_3)_5NO]^{3+}$ with hydroxylamine or hydrazine suggested.

Nucleophilic attack at the nitrosyl ligand has been demonstrated for a variety of ruthenium complexes.[1-9] Particularly noteworthy are the reactions of $[Ru^{II}Cl(das)_2NO]^{2+}$ (das = *o*-phenylenebisdimethylarsine) with hydrazine, forming $[Ru^{II}ClN_3(das)_2]$,[1] and with azide ion, forming $[Ru^{II}ClN_3(das)_2]$, $N_2O$, and $N_2$.[2] A similar reaction was also found for $[Ru^{II}Cl(dipy)_2NO]^{2+}$ (dipy = 2,2′-dipyridine).[3] We have investigated reactions of nitrosylpentaammineruthenium(II), $[Ru^{II}(NH_3)_5NO]^{3+}$,[4-6] and present here the results of investigations of reactions of $[Ru^{II}(NH_3)_5NO]^{3+}$ with hydroxylamine and hydrazine which give (dinitrogen oxide)pentaammineruthenium(II), $[Ru^{II}(NH_3)_5N_2O]^{2+}$. $N_2O$ complexes of pentaammineruthenium(II) were prepared previously from $N_2O$ and $[Ru^{II}(NH_3)_5H_2O]^{2+}$.[10-12]

## Results

$[Ru^{II}(NH_3)_5NO]X_3 \cdot H_2O$ and hydroxylamine reacted rapidly, at room temperature, forming pale yellow, diamagnetic $[Ru^{II}(NH_3)_5N_2O]X_2$ (X = Cl, Br, I). Because of rapid decomposition, precipitation of the complexes as they formed was a necessity (see Experimental Section). Addition of a precipitating anion to increase yields of the more soluble salts gave products contaminated with $[Ru^{II}(NH_3)_5N_2]^{2+}$ and $[Ru^{III}(NH_3)_5OH]^{2+}$. The stability of the $N_2O$ complexes was dependent on the anion ($I^- > Br^- > Cl^-$). The iodide salt was stable for several weeks in dry air, but the chloride salt decomposed in a few days. The rate of decomposition may be an inverse function of the sample purity, since the very soluble chloride salt was difficult to obtain pure.

The complexes had properties similar to $[Ru^{II}(NH_3)_5N_2O](BF_4)_2$ prepared from $[Ru^{II}(NH_3)_5H_2O]^{2+}$ and $N_2O$.[12] The bromide and iodide salts evolved $N_2O$ on oxidation with ceric(IV) and $N_2O$, $N_2$, and $H_2O$ on dry heating. $N_2O$, 82% (±5%; mean of six determinations) of the theoretical amount, was obtained on treatment of the iodide salt with $Ce^{4+}$. Treatment of the complex prepared from $[Ru^{II}(NH_3)_5{}^{15}NO]I_3 \cdot H_2O$ and $^{14}NH_2OH$ with $Ce^{4+}$ gave $^{29}N_2O$ whose cracking pattern in the mass spectrum showed almost exclusively $^{14}NO^+$. It was concluded the product was $[Ru^{II}(NH_3)_5{}^{15}N^{14}NO]I_2$ (assuming $N_2O$ is coordinated *via* nitrogen rather than oxygen (see below)).

The infrared spectra of the complexes (Table I) showed a very strong band in the 1160-cm$^{-1}$ region ($\nu_1$ of $N_2O$) and a very weak band in the 2250-cm$^{-1}$ region ($\nu_3$ of $N_2O$), as observed for $[Ru^{II}(NH_3)_5N_2O](BF_4)_2$.[12] No bands were observed in the 700–400 cm$^{-1}$ region where metal–ammonia, metal–$N_2O$, or $\nu_2$ of $N_2O$ might be expected. The frequencies of the $N_2O$ vibrations were anion dependent, and the intensity of $\nu_3(N_2O)$ was also markedly anion dependent ($I^- >$

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