of the solution (containing 0.3 mg. of the complex) was injected into the flash vaporizer chamber. One minute after the sample was injected, carbon tetrachloride appeared in the trap. Most of the carbon tetrachloride was eluted in the first 6 min., but small amounts appeared as late as 25 min. after sample injection. At this point the chromium complex began to be eluted. It was eluted rapidly at first and then much more slowly. Tailing was very extensive, and very small quantities of the complex were still being eluted several hours later. After 20 hr. the column was dismantled and examined to see if any of the complex remained adsorbed or had decomposed. Only 60 to 70% of the complex could be accounted for in the eluted fractions. Attempts to extract the chromium complex from the quartz with chloroform and ethanol were unsuccessful. However, destructive oxidation with potassium permanganate in sulfuric and nitric acids and subsequent treatment with sodium azide, ammonium hydroxide, and freshly prepared diphenylcarbazide showed a positive test for chromium.[7]

An early fraction of the eluate, collected over the period from 25 to 35 min. after injection, was dissolved in carbon tetrachloride and checked for optical activity. The observed rotation was $+0.043 \pm 0.008°$ at the sodium D line at 25°. The concentration of the complex was determined spectrophotometrically at 359 mμ, and the apparent specific rotation was calculated to be $+260°$. It is concluded that at least a partial resolution was accomplished.

The experiment was repeated several times under somewhat different conditions. Observed rotations ranged from $+0.034 \pm 0.003°$ to $+0.051 \pm 0.006°$ and apparent specific rotations varied between $+80$ and $+190°$.

**Acknowledgment.**—The authors wish to thank Dr. B. W. Ponder for his helpful suggestions.

[7] F. D. Snell and C. T. Snell, "Colorimetric Methods of Analysis," Vol. II, D. Van Nostrand Co., Inc., New York, N. Y., 1959, p. 214.

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## Infrared Spectral Evidence for Dative π-Bonding in Ethynylsilanes

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Many observations of the physical and chemical properties of aryl silicon compounds indicate that dative π-bonding can take place from the filled aromatic π-orbitals into the vacant 3d orbitals of silicon.[1] The direction of additions to vinylsilanes provides indirect evidence which suggests that similar π-bonding may take place involving olefinic π-electrons.[2] In $R_3Si$ compounds, it is probable that a degenerate pair of orbitals $(d_\pi)$ is available on silicon for dative π-bonding.[3] Such back-bonding might be especially favorable in ethynylsilanes, for in these compounds two equivalent dative π-bonds might be formed involving both of the acetylenic π-orbitals.

Accordingly, a study was undertaken of some of the vibrational frequencies of ethynylsilanes, and of the properties of these compounds as proton acceptors and proton donors in hydrogen bonding.[4] The C≡C and C–H stretching frequencies of the ethynylsilanes suggest substantial dative π-bonding in these compounds. This interpretation is substantiated by the hydrogen bonding results, which show that ethynylsilanes are better proton donors and poorer proton acceptors than 1-alkynes. Ethynyltrimethylstannane was studied for comparative purposes, but the results do not provide definite indication of dative π-bonding in this compound.

### Experimental

**Spectra.**—Infrared frequencies were measured with a Perkin-Elmer Model 112 spectrophotometer using a lithium fluoride prism. Acetylenes were studied as approximately 0.06 *M* solutions in reagent grade carbon tetrachloride. For the studies of acetylene basicity, phenol was present at 0.02 *M*, and the acetylene at 1 *M;* the path length was 3 mm. In the studies of hydrogen bonding acidity, the acetylenes were present at 0.6 *M* and the concentration of N,N-dimethylacetamide was 2 *M;* the path length was 1 mm. Frequency shifts were determined from logarithmic plots of the per cent transmission spectra as described previously.[4a]

**Materials.**—Methods used for the purification of phenol, N,N-dimethylacetamide, and the various acetylenes have been reported previously.[4a] Commercial acetylene gas was purified by passing through a cold trap at −80° and then through towers containing either concentrated sulfuric acid or alumina. 3,3-Dimethyl-1-butyne was prepared by the method of Cleveland and Murray[5] and was shown to be pure by gas chromatography. Bistrimethylsilylacetylene was prepared according to the method of Frisch and Young.[6] Boiling points and refractive indices of both of these acetylenes agreed with those reported in the literature.

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[1] C. Eaborn, "Organosilicon Compounds," Butterworths, London, 1960. pp. 97–103.

[2] L. H. Sommer, D. L. Bailey, G. M. Goldberg, C. E. Buck, T. S. Bye, F. J. Evans, and F. C. Whitmore, *J. Am. Chem. Soc.*, **76**, 1613 (1954); E. Larsson, *Chalmers Tek. Hogskol. Handl.*, **25**, 115 (1951).

[3] R. West, K. J. Lake, and L. S. Whatley, *J. Am. Chem. Soc.*, **83**, 761 (1961).

[4] (a) R. West and C. S. Kraihanzel, *ibid.*, **83**, 765 (1961); (b) J. C. D. Brand, C. Eglinton, and J. F. Morman, *J. Chem. Soc.*, 2526 (1960).

[5] F. E. Cleveland and M. J. Murray, *J. Chem. Phys.*, **11**, 450 (1943).

[6] K. C. Frisch and R. B. Young, *J. Am. Chem. Soc.*, **74**, 4853 (1952).

**Ethynyltrimethylsilane.**—Ethynylsodium was prepared from sodium (4.6 g., 0.20 g.-atom) and acetylene in hot xylene according to the method of Rutledge.[7] To the cool ethynylsodium slurry was added 35 ml. of freshly distilled N,N-dimethylformamide after which a solution of 20 g. (0.18 mole) of freshly distilled trimethylchlorosilane in 25 ml. of xylene was added over 2.5 hr. The reaction was slightly exothermic and was cooled to room temperature. After standing overnight the mixture was heated and material boiling to 125° collected.

The distillate was fractionated. The fraction boiling at 52–53° was shaken briefly with ice water, dried very briefly over phosphorus pentoxide, and refractionated to give 3.9 g. (22%) of pure (by gas chromatography) ethynyltrimethylsilane, b.p. 52°, $d_4^{24}$ 0.707, $n^{25}$D 1.3870. The properties agree with those recently reported by Büchert and Zeil.[8]

**Ethynyltriphenylsilane.**—Ethynylsodium was prepared from sodium (4.6 g., 0.20 g.-atom) and acetylene in liquid ammonia, after which the ammonia was allowed to evaporate. Dry tetrahydrofuran (200 ml.) was added and the mixture was refluxed to ensure the absence of ammonia. Triphenylchlorosilane (52.2 g., 0.18 mole) in 300 ml. of dry tetrahydrofuran was added over 1 hr. The mixture was stirred for 18 hr. at room temperature and then was poured onto 800 g. of ice. The resulting white solid was filtered and extracted repeatedly with ether (5 × 40 ml.) and then with heptane until no more product was present in the washings, as shown by the absence of the acetylenic CH band at 3293 cm.$^{-1}$. The organic solutions were dried with magnesium sulfate and then the solvent was removed under vacuum to give 13 g. of a crude mixture of oil and white solid. This mixture was fractionally distilled to give 8.6 g. of ethynyltriphenylsilane, b.p. 192–195° (2 mm.). This product was dissolved in heptane and passed through a silica column. The residue of the eluate was distilled to give 6.75 g. (13%) of analytically pure triphenylsilylacetylene, b.p. 191° (1.9 mm.), as a clear colorless oil. This supercooled liquid crystallized when scratched to give a white solid, m.p. 45–46°. Gilman and Aoki recently have reported an alternate preparation of triphenylsilylacetylene, but apparently they did not obtain this compound in the solid state.[9]

*Anal.* Calcd. for $C_{20}H_{16}Si$: C, 84.95; H, 5.67. Found: C, 84.78; H, 5.83.

**Ethynyltrimethylstannane.**—This previously unreported compound can be prepared by the method given above for ethynyltrimethylsilane, but separation from the solvents and N,N-dimethylformamide is difficult. The following procedure was satisfactory. Ethynylsodium was prepared from 2.3 g. (0.1 g.-atom) of sodium and excess acetylene in liquid ammonia. The ammonia was replaced with 100 ml. of dry ether. Trimethyltin chloride (20 g., 0.1 mole) in 20 ml. of ether was added under nitrogen in 0.5 hr. and the mixture was stirred for 1 hr. at room temperature. The supernatant liquid was separated and the ether was removed under vacuum. The residue was rapidly distilled to give 4.28 g. of colorless liquid, b.p. 86–92°, whose infrared spectrum contained the characteristic bands of a terminal acetylene. The infrared spectrum of a fractionally distilled sample (b.p. 92–95°) was unchanged from that of the crude material. The purity of the sample probably was between 90 and 95%, sufficient for infrared spectral studies. The compound undergoes instantaneous hydrolysis in contact with moist air.

*Anal.* Calcd. for $C_5H_{10}Sn$: C, 31.8; H, 5.34. Found: C, 32.7; H, 6.01.

**Force-Field Calculations.**—The equations of motion for a linear four-atom system (E—C≡C—H) were solved, using a simple valence force field and neglecting the perpendicular vibrations, all of which belong to a different symmetry species.[10] The C≡C and C–H force constants were taken to be 15.7 and 5.9 × $10^5$ dynes/cm., respectively, as in haloacetylenes[11] and simple alkynes.[12] Force constants for bonds from silicon and tin to digonal carbon are unknown. The approximate values $K(\text{Si—C}\equiv) = 3.8$ and $K(\text{Sn—C}\equiv) = 2.9 \times 10^5$ dynes/cm. were used in the calculations.[13] The mass of E was taken as the mass of the metal (or carbon) atom alone. Secondary mass effects seem to be negligible, since approximately the same frequencies are observed for ethynyltrimethylsilane and ethynyltriphenylsilane, and for *t*-butylacetylene and the 1-alkynes. In view of the approximate nature of the method, calculated frequencies are expected to have only relative meaning. However, the frequencies for $\nu_{C\equiv C}$ and $\nu_{C\equiv H}$ calculated for E = carbon, 2155 and 3325 cm.$^{-1}$, agree quite well with the observed frequencies for 1-alkynes.

## Discussion

The infrared absorption frequencies of the acetylenic C–H and C≡C stretching bands in substituted 1-alkynes are remarkably constant. So long as the atom attached directly to the triple bond is a carbon atom $\nu_{C-H}$ and $\nu_{C\equiv C}$ occur very near to 3315 and 2120 cm.$^{-1}$, respectively.[4,17] However, in acetylenes of type $R_3E—C\equiv C—H$, where E is a heteroatom, marked changes in these group frequencies may be produced. In the silicon- and tin-substituted compounds, $\nu_{C\equiv C}$ is decreased by about 100 cm.$^{-1}$ from that in

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(7) T. F. Rutledge, *J. Org. Chem.*, **22**, 649 (1957); **24**, 840 (1959).

(8) H. Büchert and W. Zeil, *Z. physik. Chem.* (Frankfurt), **29**, 317 (1961).

(9) H. Gilman and D. Aoki, *Chem. Ind.* (London), 1619 (1961).

(10) C. S. Kraihanzel, Thesis, University of Wisconsin, 1961.

(11) G. R. Hunt and M. K. Wilson, *J. Chem. Phys.*, **34**, 1301 (1961).

(12) B. L. Crawford and S. H. Brinkley, *ibid.*, **9**, 69 (1941); B. L. Crawford, *ibid.*, **8**, 526 (1940).

(13) These values were obtained by correcting Si–C and Sn–C simple valence force constants for bonds to tetrahedral carbon. $K$(Si–C) was taken as 3.31 × $10^5$ dynes/cm.[14] No simple valence force constant for Sn–C has been calculated, but the value is estimated as 2.5 × $10^5$ dynes/cm. for a more complete treatment.[15] The ratio of C–C force constants $K_{C(\text{tetrahedral}) - C(\text{diagonal})}/K_{C(\text{tetrahedral}) - C(\text{tetrahedral})}$ is about 1.15,[16] so $K(\text{Si—C}\equiv)$ and $K(\text{Sn—C}\equiv)$ were obtained by multiplying $K$(Si–C) and $K$(Sn–C) by this factor. The predicted frequency lowering is changed only slightly by other reasonable estimates of metal–carbon force constants.

(14) S. Silver, *J. Chem. Phys.*, **8**, 919 (1940).

(15) H. Siebert, *Z. anorg. allgem. Chem.*, **268**, 177 (1952).

(16) G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Company, Inc., Princeton, New Jersey, 1945, p. 338.

(17) R. A. Nyquist and W. J. Potts, *Spectrochim. Acta*, **16**, 419 (1960).

1-alkynes, and corresponding but smaller decreases are observed for $\nu_{C-H}$ (Table I).[18,19]

TABLE I

INFRARED FREQUENCIES AND HYDROGEN BONDING FREQUENCY SHIFTS FOR ACETYLENES, IN CM.$^{-1}$

| Compound | $\nu_{CH}$ | $\nu_{CC}$ | Ref. | $\Delta\nu_{OH}$[b] phenol | $\Delta\nu_{C-H}$[c] DMA |
|---|---|---|---|---|---|
| $RCH_2C{\equiv}CH$ | 3314 | 2119 | 4 | 90 | 72–74 |
| $(CH_3)_3CC{\equiv}CH$ | 3312 | 2105, 2135 | *a* | 95 | 74 |
| $(CH_3)_3SiC{\equiv}CH$ | 3293 | 2035 | *a* | 86 | 82 |
| $(C_6H_5)_3SiC{\equiv}CH$ | 3293 | 2037 | *a* | *d* | 93 |
| $(CH_3)_3SnC{\equiv}CH$ | 3286 | 2010 | *a* | *d* | 66 |
| $RCH_2C{\equiv}CCH_2R$ | ... | 2260, 2190 | *e* | 138 | ... |
| $(CH_3)_3SiC{\equiv}CSi(CH_3)_3$ | ... | 2107 | 8 | 126 | ... |

[a] This investigation. [b] Frequency shift of O–H band of phenol upon hydrogen bond formation to acetylene. [c] Frequency shift of C–H band of acetylene upon hydrogen bond formation to N,N-dimethylacetamide. [d] Frequency shift not determinable. [e] L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1958, p. 58.

The frequency shifts alone cannot be used to deduce information about the bonding, because the mass of E and the force constant of the E–C bond in these compounds will influence the C≡C and C–H frequencies even in the absence of any electronic effects.[20] To estimate the effect of mass and force constant differences on the C≡C and C–H frequencies in acetylenes of type $R_3E—C{\equiv}C—H$, a simple force field calculation was carried out for the four-atom system, $E—C{\equiv}C—H$, as described in the Experimental section. From this calculation a frequency shift of about −45 cm.$^{-1}$ in $\nu_{C\equiv C}$ upon replacement of carbon by silicon is predicted. The observed shift is −83 cm.$^{-1}$. Thus about half of the frequency shift is attributable to mass and simple force constant effects resulting from the replacement of C by Si. The remainder probably can be attributed to electronic effects, *i.e.*, weaking of the C≡C force constant by electron withdrawal due to dative $\pi$-bonding from carbon to silicon. The Si–C force constant also should be increased above the predicted value by such $\pi$-bonding.

For the tin compound the predicted and observed C≡C frequency shifts from 1-alkynes are −70 and −109 cm.$^{-1}$. The difference again may reflect dative $\pi$-bonding from carbon to the metal. However, the evidence is less convincing, partly because the predicted shift for tin is necessarily more approximate.[13]

Practically no change in the C–H stretching absorption frequency is predicted from changes in the mass of E and in the E–C force constant. A small decrease in $\nu_{C-H}$ is observed upon substitution of silicon or tin for carbon, perhaps reflecting C–H bond weakening in these compounds compared to alkylacetylenes. However, the C–H and C≡C modes in acetylenes are known to interact strongly, and the small changes in $\nu_{C-H}$ also might result from this interaction.

**Hydrogen Bonding Studies.**—Silicon is inductively electron-releasing toward carbon, and so in the absence of dative $\pi$-bonding silyl acetylenes would be expected to be more basic and less acidic then comparable carbon compounds. However, data in Table I show that observed effects are just the opposite. For instance, when mixed with phenol ethynyltrimethylsilane gives a smaller O–H frequency shift than does *t*-butylacetylene, indicating lower $\pi$-electron availability in the silicon than in the carbon compound. Similarly, bis-(trimethylsilyl)-acetylene appears to have abnormally low basicity toward phenol. Also, ethynyltrimethylsilane gives a larger C–H shift upon hydrogen bonding to dimethylacetamide than does its carbon analog, indicating that the silicon compound is the better proton donor. The frequency shift for ethynyltriphenylsilane with dimethylacetamide is even larger. The pronounced acidic behavior of ethynyltriphenylsilane in proton exchange has been demonstrated recently.[21] These effects all imply that dative $\pi$-bonding takes place from the acetylenic group to silicon, in agreement with the above deductions from the infrared frequencies.

The basicity of the tin compound could not be measured because it was rapidly cleaved by phenol. However, it appears to be only a weak proton donor, and it seems likely that in this compound the effect of any dative $\pi$-bonding on the acidity is outweighed by the inductive electron-releasing effect.

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(18) Similar changes in frequency are observed for ethynyl groups bonded to oxygen or sulfur,[10] or halogens.[11]

(19) The complete infrared spectrum of ethynyltrimethylsilane has been published recently by Büchert and Zeil[8]; our frequencies agree well with those reported.

(20) The monohaloacetylenes provide a case in point; there are substantial differences in $\nu_{C\equiv C}$ among these molecules, but Hunt and Wilson's[11] normal coördinate treatment indicates that the frequency shifts are due entirely to differences in the mass of the halogen and in the halogen–carbon force constants.

(21) R. E. Dessy, Y. Okuzumi, and A. Chen, *J. Am. Chem. Soc.* **84**, 2899 (1962).