TABLE IV

INFRARED SPECTRAL DATA FOR $(CH_3)_n(C_6H_5)_{3-n}MCO_2H$

| Compd | $\nu$, C=O, cm$^{-1}$ CCl$_4$ | $\nu$, C=O, cm$^{-1}$ KBr | $\nu$, MCO$_2$H, cm$^{-1}$ (CCl$_4$) | $\nu$, MCH$_3$, cm$^{-1}$ (CCl$_4$) |
|---|---|---|---|---|
| $Me_3CCO_2H$ | 1693 | 1686 | | |
| $Me_2PhCCO_2H$ | 1693 | 1670 | | |
| $MePh_2CCO_2H$ | 1696 | 1675 | | |
| $Ph_3CCO_2H$ | 1706 | 1670 | | |
| $Me_3SiCO_2H$ | 1654 | 1646 | 572 | 707, 624 |
| $Me_2PhSiCO_2H$ | 1645 | 1636 | 588 | 649, 631 sh |
| $MePh_2SiCO_2H$ | 1647 | 1636 | 593 | 661 |
| $Ph_3SiCO_2H$ | 1654 | 1633 | 600 | |
| $Me_3GeCO_2H$ | 1648 | 1650 | 563 sh | 614, 575 |
| $Me_2PhGeCO_2H$ | 1646 | 1640 | 566 sh | 607, 584 |
| $MePh_2GeCO_2H$ | 1654 | 1647 | 570 | 595 |
| $Ph_3GeCO_2H$ | 1663 | 1642 | 575 | |

TABLE V

INFRARED SPECTRAL DATA FOR $(XC_6H_4)_3GeCO_2H$

| X | $\nu$, C=O, cm$^{-1}$ CCl$_4$ | $\nu$, C=O, cm$^{-1}$ KBr | $\nu$, MCO$_2$H, cm$^{-1}$ (CCl$_4$) |
|---|---|---|---|
| H | 1663 | 1642 | 575 |
| *p*-$CH_3$ | 1652 | 1647 | 563 |
| *m*-$CH_3$ | 1654 | 1642 | 575 |
| *p*-$CH_3O$ | 1655 | 1654 | 573 |
| *m*-$CH_3O$ | 1659 | 1645 | 580 |
| *p*-F | 1656 | 1650 | 573 |
| *m*-F | 1662 | 1650 | 580 |
| *p*-$CF_3$ | 1663 | 1661 | 572 |
| *n*-$CF_3$ | 1667[a] | | |

[a] Not isolated.

TABLE VI

PROTON MAGNETIC RESONANCE DATA FOR $(CH_3)_3MCO_2H$

| M | $\delta$, ppm[a] CH$_3$ | $\delta$, ppm[a] OH[b] | Peak area ratio |
|---|---|---|---|
| C | 1.22 | 12.53 | 1:8 |
| Si | 0.26 | 12.01 | 1:8.6 |
| Ge | 0.46 | 11.96 | 1:9.2 |

[a] Spectra determined in CCl$_4$, 22–35 w/v %, using TMS as an internal standard at 60 MHz. [b] Position slightly affected by concentration.

Both the position of the carbonyl stretching frequency and the chemical shift of the acidic proton of the acids, $Me_3MCO_2H$, in relation to their carbon analog suggest that there is little $\pi$ ($\pi \rightarrow$ d) bonding in the ground state of the acid form and the observed order is mainly the result of the inductive properties of the group IVb elements.

**Registry No.**—$Me_3SiCO_2^-$, 31593-89-2; $Me_2PhSiCO_2H$, 17878-13-6; $MePh_2SiCO_2H$, 18414-58-9; $Ph_3SiCO_2H$, 18670-88-7; $Ph_3GeCO_2H$, 22718-99-6.

**Acknowledgments.**—The authors gratefully acknowledge the financial support of the Dow Corning Corp., Midland, Mich., and a grant from the National Science Foundation for the Cary Model 14 spectrophotometer. One of us (J. E. D.) is grateful to NASA for a traineeship, 1967–1969.

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# Carboxysilanes and -germanes. III.[1,2] Ionization Constants of Triorganosilane- and Triorganogermanecarboxylic Acids in Ethanol–Water and Dimethyl Sulfoxide Media

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Ionization constants of the following carboxylic acids have been determined by a spectrophotometric method: $Me_nPh_{3-n}MCO_2H$, where M = C, Si and Ge, $n$ = 0–3, in ethanol–water media and where M = C and Ge, in dimethyl sulfoxide; $(XC_6H_4)_3GeCO_2H$, where X = H, *p*-Me, *m*-Me, *p*-OMe, *m*-OMe, *p*-F, *m*-F, and *p*-$CF_3$, in ethanol–water media and X = H, *p*-Me, *m*-Me, *p*-OMe, in dimethyl sulfoxide. The relative order of acidity, $R_3SiCO_2H \approx R_3GeCO_2H > R_3CCO_2H$, is explained in terms of $\pi$ ($\pi \rightarrow$ d) bonding between the $\pi$ orbitals of the $CO_2^-$ group and the vacant nd orbitals of the metalloid with steric hindrance to anion solvation playing a smaller role. The transmission of substituent effects through the phenyl group and germanium also are discussed.

In a previous paper,[3] we reported the ionization constants of a number of acids of the type, $R_3MCO_2H$, where R = Me and/or Ph and M = C, Si, and Ge, in ethanol–water media. Since the triorganosilanecarboxylic acids are susceptible to base-catalyzed decarbonylation,[4] a new potentiometric method was developed for the determination of the ionization constants in acidic media.[5] In all cases studied, the silane- and germanecarboxylic acids were found to be more acidic than their carbon analogs. It was suggested that the observed order of acidity is the result of stabilization of the silane- and germanecarboxylate ions relative to their carbon analog by $\pi$ ($\pi \rightarrow$ d) bonding between the $CO_2^-$ group and the metalloid which overcomes the inductive effect ($+I$) of the metalloid. Also it was suggested that $\pi$ ($\pi \rightarrow$ d) bonding becomes an important factor in anion stability since there is a full negative charge on which to operate; *i.e.*, in the anion form there is a demand for charge delocalization by $\pi$ ($\pi \rightarrow$ d) bonding.

In this study we have determined the ionization con-

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(1) For preliminary reports on this work, *cf.* O. W. Steward, J. E. Dziedzic, J. S. Johnson, and J. O. Frohliger, Abstracts, Fourth International Conference on Organometallic Chemistry, Bristol, England, July 1969, D18; O. W. Steward, J. E. Dziedzic, and J. O. Frohliger, Abstracts, 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968, INOR 118.

(2) Part II: O. W. Steward, J. E. Dziedzic, and J. S. Johnson, *J. Org. Chem.*, **36**, 3475 (1971).

(3) O. W. Steward, H. W. Irwin, R. A. Gartska, and J. O. Frohliger, *J. Chem. Soc. A*, 3119 (1968).

(4) A. G. Brook and H. Gilman, *J. Amer. Chem. Soc.*, **77**, 2322 (1955).

(5) J. O. Frohliger, R. A. Gartska, H. W. Irwin, and O. W. Steward, *Anal. Chem.*, **40**, 1408 (1968).

TABLE I

p$K_a$ VALUES OF $R_3MCO_2H$ IN 45% ETHANOL–WATER AT 25°

| Acid | Registry no. | No. of determinations | p$K_a$ Found ($\sigma$)$^a$ | p$K_a$ Lit.$^b$ ($\sigma$)$^a$ |
|---|---|---|---|---|
| $MeCO_2H$ | 64-19-7 | 11 | 5.61 (0.01) | 5.64 (0.06) |
| $Me_3CCO_2H$ | 75-98-9 | 23 | 6.41 (0.08) | |
| $Me_3SiCO_2H$ | 31593-12-1 | 48 | 6.60 (0.04) | |
| $Me_3GeCO_2H$ | 22776-20-1 | 24 | 6.20 (0.03) | |
| $Me_2PhCCO_2H$ | 826-55-1 | 11 | 6.05 (0.01) | 6.00 (0.03) |
| $Me_2PhSiCO_2H$ | 17878-13-6 | 16 | <6.06$^c$ | 5.96 (0.10) |
| $Me_2PhGeCO_2H$ | 31593-16-5 | 22 | 6.00 (0.02) | |
| $MePh_2CCO_2H$ | 5558-66-7 | 11 | 5.81 (0.01) | 5.77 (0.04) |
| $MePh_2SiCO_2H$ | 18414-58-9 | 11 | <6.0$^c$ | 5.66 (0.05) |
| $MePh_2GeCO_2H$ | 31593-18-7 | 33 | 5.69 (0.01) | |

$^a$ Standard deviation. $^b$ Reference 3. $^c$ Base-catalyzed decomposition of the acid.

TABLE II

p$K_a$ VALUES OF $R_3MCO_2H$ IN 76% ETHANOL–WATER AT 25°

| Acid | No. of determinations | p$K_a$ Found ($\sigma$)$^a$ | p$K_a$ Lit.$^b$ ($\sigma$)$^a$ |
|---|---|---|---|
| $MeCO_2H$ | 12 | 6.57 (0.02) | 6.78 (0.02) |
| $Me_3CCO_2H$ | 19 | 7.96 (0.05) | |
| $Me_3SiCO_2H$ | 24 | 7.74 (0.02) | |
| $Me_3GeCO_2H$ | 20 | 7.43 (0.03) | |
| $Me_2PhCCO_2H$ | 6 | 7.45 (0.04) | 7.45 (0.02) |
| $Me_2PhSiCO_2H$ | 12 | 7.28 (0.05) | |
| $Me_2PhGeCO_2H$ | 22 | 7.33 (0.04) | |
| $MePh_2CCO_2H$ | 12 | 7.15 (0.09) | 7.20 (0.03) |
| $MePh_2SiCO_2H$ | 10 | 7.04 (0.05) | 7.03 (0.09) |
| $MePh_2GeCO_2H$ | 35 | 7.04 (0.12) | |
| $Ph_3CCO_2H$ | 10 | 6.78 (0.02) | 6.70 (0.03) |
| $Ph_3SiCO_2H$ | 9 | 6.10 (0.10) | 6.23 (0.04) |
| $Ph_3GeCO_2H$ | 11 | 6.27 (0.03) | 6.32 (0.02) |

$^a$ Standard deviation. $^b$ Reference 3.

TABLE III

p$K_a$ VALUES OF $R_3MCO_2H$ IN DIMETHYL SULFOXIDE AT 25°

| Acid | No. of determinations | p$K_a$ ($\sigma$)$^a$ |
|---|---|---|
| $MeCO_2H$ | 10 | 11.41 (0.02)$^b$ |
| $Me_3CCO_2H$ | 13 | 12.39 (0.12) |
| $Me_3GeCO_2H$ | 18 | 11.13 (0.07) |
| $Me_2PhCCO_2H$ | 16 | 11.10 (0.05) |
| $Me_2PhGeCO_2H$ | 18 | 10.20 (0.06) |
| $MePh_2CCO_2H$ | 24 | 10.00 (0.04) |
| $MePh_2GeCO_2H$ | 12 | 9.39 (0.08) |
| $Ph_3CCO_2H$ | 21 | 9.29 (0.07) |
| $Ph_3GeCO_2H$ | 6 | 8.43 (0.06) |

$^a$ Standard deviation. $^b$ Lit. p$K_a$ = 11.4 [I. M. Kolthoff and T. B. Reddy, *Inorg. Chem.*, **1**, 189 (1962)]; p$K_a$ = 11.6 [C. D. Ritchie and R. E. Uschold, *J. Amer. Chem. Soc.*, **89**, 1721 (1967)].

stants for the complete series of acids, $Me_nPh_{3-n}MCO_2H$, where M = C, Si, and Ge and $n$ = 0–3, in ethanol–water and, where M = C and Ge, in dimethyl sulfoxide by a spectrophotometric technique.[6] This study also has been extended to a series of triarylgermanecarboxylic acids with substituent groups on the aromatic rings. These data allow us to elaborate on the importance of the role of $\pi$ ($\pi \rightarrow$ d) bonding in stabilizing the conjugate base forms of the silane- and germanecarboxylic acids.

## Experimental Section

The solvents, dimethyl sulfoxide (Fisher Certified Reagent Grade) and 95% ethanol (Commercial Solvents Corp.) were purified and the 45 and 76%[7] ethanol–water solutions were prepared as described previously.[6] The synthesis and properties of the triorganosilane- and triorganogermanecarboxylic acids used in this study are reported in previous papers in this series.[2,3] The ionization constants of the carboxylic acids were determined in 45 and 76% ethanol–water and dimethyl sulfoxide at 25 ± 0.1° by a simplified spectrophotometric procedure described elsewhere.[6] A Cary Model 14 spectrophotometer was employed for absorptivity measurements, and calculations were carried out on a Control Data G-20 computer.

## Results

The ionization constants, in terms of p$K_a$ values, of the acids, $R_3MCO_2H$, in 45 and 76% ethanol–water and dimethyl sulfoxide are given in Tables I–IV. The p$K_a$ values of the triphenyl derivatives were not determined in 45% ethanol–water because of their low solubility. In some cases, as specified in the tables, base-catalyzed decarbonylation of the acids prevented the determination of the ionization constants.

The ionization constants of the acids determined by both the potentiometric and spectrophotometric[6] methods in most all cases agree within the experimental error. The spectrophotometric method is favored because of its simplicity and its adaptability to both protic and aprotic solvent systems. One disadvantage of the spectrophotometric method is that it may not be applicable if the carboxylic acids are extremely sensitive to base-catalyzed decarbonylation in the solvent employed.

## Discussion

While ultraviolet spectral studies of triorganosilane- and triorganogermanecarboxylic acids and their conjugate base forms indicate that $\pi$ ($\pi \rightarrow$ d) bonding occurs between the metalloid and the carboxyl group, particularly in reference to the excited state, infrared and proton magnetic resonance studies suggest there is little $\pi$ ($\pi \rightarrow$ d) bonding in the ground state of the acid form.[2] A study of the ionization constants of the carboxylic acids, $R_3MCO_2H$, gives results related to the ground state and allows one to compare the relative stabilities of the acid and conjugate base forms.

Inductive, resonance, and steric effects can influence the ionization equilibrium of the carboxylic acids. These effects would be expected to exert their main influence on the equilibrium by changing the stability of the carboxylate ion where there is a full negative charge

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(6) J. O. Frohliger, J. E. Dziedzic, and O. W. Steward, *Anal. Chem.*, **42**, 1189 (1970).

(7) Throughout this paper, per cent (%) will represent percentage by weight.

TABLE IV

$pK_a$ VALUES OF $(XC_6H_4)_3GeCO_2H$ AT 25°

| X | Registry no. | No. of determinations | $pK_a$, 76% EtOH-$H_2O$ | No. of determinations | $pK_a$, DMSO |
|---|---|---|---|---|---|
| H | 22718-99-6 | 11 | 6.27 (0.03)[a] | 6 | 8.43 (0.06)[a] |
| *p*-Me | 2887-10-7 | 15 | 7.34 (0.04) | 13 | 9.59 (0.04) |
| *m*-Me | 31593-21-2 | 10 | 6.79 (0.02) | 27 | 8.93 (0.09) |
| *p*-OMe | 31593-22-3 | 23 | 7.17 (0.04) | 36 | 9.13 (0.03) |
| *m*-OMe | 31593-23-4 | 10 | 6.48 (0.01) |  | <8.3[b] |
| *p*-F | 31593-24-5 | 12 | 6.02 (0.08) |  | <8.3[b] |
| *m*-F | 31593-25-6 | 13 | 5.69 (0.01) |  |  |
| *p*-$CF_3$ | 31593-26-7 | 23 | 4.85 (0.05) |  |  |

[a] Standard deviation. [b] Base-catalyzed decomposition of the acid.

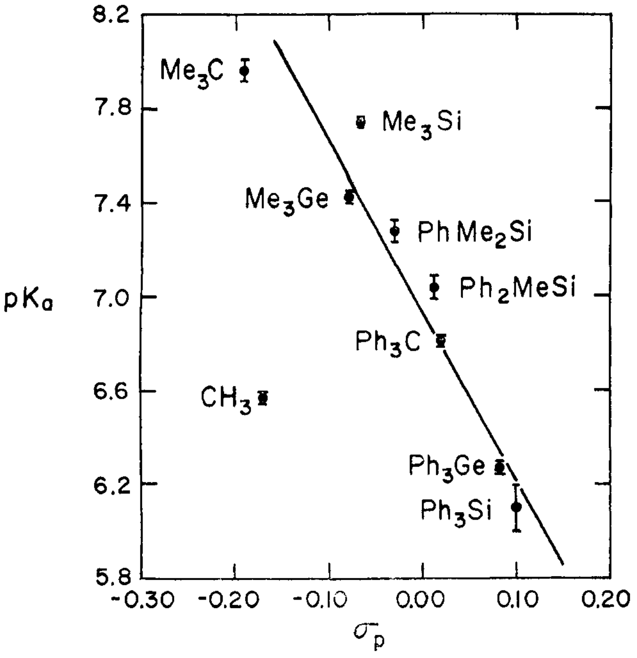

Figure 1.—Plot of the $pK_a$ of $R_3MCO_2H$, 76% ethanol-water, *vs.* the $\sigma_p$ value for the $R_3M$ group: slope, −6.70; $\bar{r}$, 0.947; $\bar{s}$, 0.20.

on which to operate.[8,9] Inductive, resonance, and steric effects will contribute to both the enthalpy and entropy of ionization since the stability of the carboxylate ion is a function of electronic and solvation effects which are not separable. In the above acids, the most important steric effect probably arises from exclusion of solvent molecules from the vicinity of the carboxylate ion.[10]

The order of acidity of the carbon, silicon, and germanium analogs of the acids, $R_3MCO_2H$, in the various solvent systems follow: 45% ethanol-water, Si ≈ Ge ⩾ C; 76% ethanol-water, Si ≈ Ge > C; dimethyl sulfoxide, Ge > C. In only one case is a reversal of the above order observed; in 45% ethanol-water, $Me_3SiCO_2H$ is a slightly weaker acid than $Me_3CCO_2H$. Also, it has been reported that $GeH_3CO_2H$ is more acidic than $CH_3CO_2H$ in aqueous solution.[11]

Based on inductive effects alone, the order of acidity of a series of the acids would be C > Si ≈ Ge.[12] From the proximity of the group IVb atoms to the carboxyl group in the acids, $R_3MCO_2H$, large differences in acidity would be expected due to the differences in the electronegativities of carbon and silicon or germanium.[13] However, the differences in the ionization constants of the carbon, silicon, and germanium acids are quite small and the relative acidity is not in accord with the inductive order.

In order to explain the observed order of acidity, the steric effect or resonance effect (−*R*) must overcome the inductive effect (+*I*) of the metalloid. Based on the covalent radii of C, Si, and Ge,[14] steric inhibition of anion solvation would lead to the following order of acidity for the acids, Ge ⩾ Si > C. $\pi$ ($\pi \rightarrow$ d) bonding between the carboxylate ion and the metalloid would lead to the following order of acidity, Si ⩾ Ge > C, and was proposed in a previous paper to explain the observed order of the series, $Ph_3MCO_2H$.[3] The following discussion of the experimental data is presented to differentiate between the two alternatives.

The relative order of the $pK_a$ values of the acids, $R_3MCO_2H$, and the substituted benzoic acids, *p*-$R_3MC_6H_4CO_2H$,[15] are similar. Linear-free-energy correlations are observed between the $\sigma_p$ values for the $R_3M$ groups and the $pK_a$ values of the acids, $R_3MCO_2H$, in 76% ethanol-water and dimethyl sulfoxide media; *cf.* Figures 1 and 2. The $\sigma_p$ values used in the correlations are the values obtained from the ionization constants and reactions of *p*-$R_3MC_6H_4CO_2H$.[16]

The above correlations indicate that the interaction between the group IVb element and the functional group in the carboxylic acids, $R_3MCO_2H$ and *p*-$R_3MC_6H_4CO_2H$, and/or the corresponding conjugate base forms are of the same type. Steric effects arising from exclusion of solvent molecules from the vicinity of the carboxylate ion must be constant or of relatively minor importance for the acids, $R_3MCO_2H$, in the light of the above correlations. Only the $\sigma_p$ values which

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[8] K. B. Wiberg, "Physical Organic Chemistry," Wiley, New York, N. Y., 1964, pp 280–288.

[9] C. D. Ritchie and R. E. Uschold, *J. Amer. Chem. Soc.*, **90**, 2821 (1968).

[10] G. S. Hammond in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, 1956, pp 426–428.

[11] P. M. Kuznesof and W. L. Jolly, *Inorg. Chem.*, **7**, 2574 (1968).

[12] R. W. Bott, C. Eaborn, and T. W. Swaddle, *J. Organometal. Chem.*, **5**, 233 (1966).

[13] E. A. V. Ebsworth in "Organometallic Compounds of the Group IV Elements," Vol. I, Part I, A. G. MacDiarmid, Ed., Marcel Dekker, New York, N. Y., 1968, pp 1–104.

[14] $r_C$ = 0.77, $r_{Si}$ = 1.15, $r_{Ge}$ = 1.21 Å: V. Schomaker and D. P. Stevenson, *J. Amer. Chem. Soc.*, **63**, 37 (1941).

[15] J. Chatt and A. A. Williams, *J. Chem. Soc.*, 4403 (1954); 688 (1956).

[16] The $\sigma_p$ values were calculated from the data of Chatt and Williams,[15] using the correlations reported by Jaffé,[17] or were taken from the work of Benkeser, *et al.*:[18] $Me_3C$, −0.19; $Me_3Si$, −0.07; $Me_3Ge$, −0.08; $Me_2PhSi$, −0.03; $MePh_2Si$, +0.01; $Ph_3C$, +0.02; $Ph_3Si$, +0.10; $Ph_3Ge$, +0.08.

[17] H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).

[18] R. A. Benkeser, C. E. DeBoer, R. E. Robinson, and D. M. Sauve, *J. Amer. Chem. Soc.*, **78**, 682 (1956); R. A. Benkeser and R. B. Gosnell, *J. Org. Chem.*, **22**, 327 (1957).

provide for a $+I$ effect and a $-R$ effect, transmitted to the point of attachment of the carboxyl group,[19] give satisfactory correlations.

Steric effects are important in determining the acidity of carboxylic acids as illustrated by the large deviation of the point for acetic acid from the regression line for the solvent 76% ethanol–water. Smaller deviations from the regression line also can be accounted for in terms of steric effects, *e.g.*, the p$K_a$ of $Me_3SiCO_2H$ is greater than $Me_3GeCO_2H$ in 76% ethanol–water. In dimethyl sulfoxide, a dipolar aprotic solvent, steric effects appear to be less important as the point for acetic acid falls much closer to the regression line.

Acid–base equilibria are very sensitive to solvation effects. The largest effect for acids of similar structure is proposed to arise from differences in anion solvation.[20] Thus, changes in p$K_a$ values on changing solvent systems should reflect steric hindrance to anion solvation due to differences in the basicity and molecular size of the solvent molecules. In Table V, the changes in the p$K_a$ values, Δp$K_a$, of the acids, $R_3MCO_2H$, on changing the solvent from 45 to 76% ethanol–water and from 76% ethanol–water to dimethyl sulfoxide are listed.

TABLE V

SOLVENT EFFECTS ON THE p$K_a$ VALUES OF $R_3MCO_2H$

| Acid | Δp$K_a$, 45% EtOH–$H_2O$ to 76% EtOH–$H_2O$ | Δp$K_a$, 76% EtOH–$H_2O$ to DMSO |
|---|---|---|
| $MeCO_2H$ | 0.96 | 4.84 |
| $Me_3CCO_2H$ | 1.55 | 4.43 |
| $Me_3SiCO_2H$ | 1.14 | |
| $Me_3GeCO_2H$ | 1.22 | 3.71 |
| $Me_2PhCCO_2H$ | 1.40 | 3.65 |
| $Me_2PhSiCO_2H$ | 1.38 | |
| $Me_2PhGeCO_2H$ | 1.33 | 2.87 |
| $MePh_2CCO_2H$ | 1.34 | 2.85 |
| $MePh_2SiCO_2H$ | 1.38 | |
| $MePh_2GeCO_2H$ | 1.35 | 2.34 |
| $Ph_3CCO_2H$ | | 2.51 |
| $Ph_3GeCO_2H$ | | 2.16 |

The changes in the ionization constants of the acids, $Me_nPh_{3-n}MCO_2H$, where $n = 1, 2$, on changing the solvent from 45 to 76% ethanol–water are relatively constant, Δp$K_a$ = 1.33–1.40, indicating that steric effects on anion solvation are about the same for these acids. Acetic acid which has quite different steric requirements for anion solvation shows a much smaller change in p$K_a$. For the acids, $Me_3MCO_2H$, which show the largest deviations from the linear-free-energy relationship, 76% ethanol–water, greater differences in the p$K_a$ values are observed indicating some differences in the steric requirements for solvation.

The change in the ionization constants of the acids, $R_3MCO_2H$, where M = C and Ge, on changing the solvent from the protic solvent, 76% ethanol–water, to the aprotic solvent, dimethyl sulfoxide, vary over a considerable range, Δp$K_a$ = 2.16–4.43. Since dimethyl sulfoxide is a better solvent than ethanol–water for large anions,[20] much smaller changes in Δp$K_a$ are observed for $Ph_3MCO_2H$. However, the differences in the Δp$K_a$ values for the carbon and germanium derivatives with the same organic groups are quite small, Δp$K_a$ (C) − Δp$K_a$ (Ge) ≈ 0.6. The smaller change in p$K_a$ for the acids, $R_3GeCO_2H$, could result from less steric hindrance to anion solvation. However, a greater demand for anion stabilization by $\pi$ ($\pi \rightarrow$ d) bonding in the solvent dimethyl sulfoxide, a poorer ionizing solvent for carboxylic acids, could account for the smaller change.

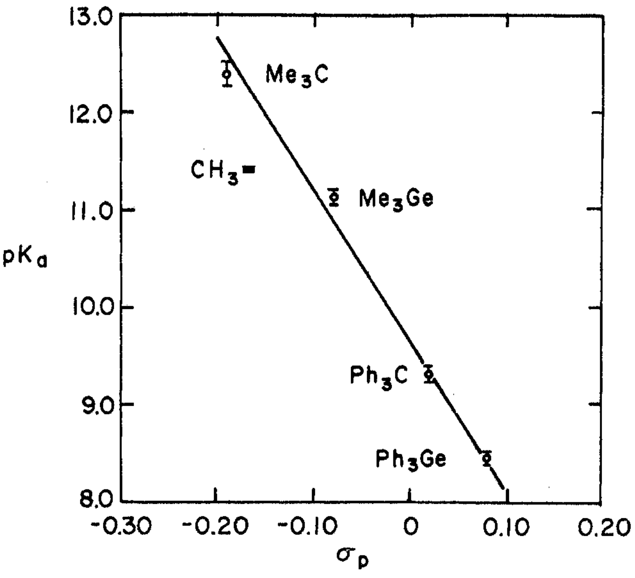

Figure 2.—Plot of the p$K_a$ of $R_3MCO_2H$, dimethyl sulfoxide, *vs.* the $\sigma_p$ value for the $R_3M$ group: slope, −15.0; $\bar{r}$, 0.993; $\bar{s}$, 0.19.

The ionization constant of $H_3GeCO_2H$ has been measured in aqueous solution.[11] This acid was found to be a stronger acid than acetic acid by 1.2 p$K_a$ units. While steric hindrance to anion solvation must be reduced considerably from the alkyl derivatives, the observed order of acidity is maintained.

From the above correlations and the overall consistency of the relative order of acidity for the acids, $R_3MCO_2H$, in the solvent systems employed, the proposal that $\pi$ ($\pi \rightarrow$ d) bonding between the metalloid and the $CO_2^-$ group overcomes the inductive influence of the metalloid seems most reasonable. The $\pi$ ($\pi \rightarrow$ d) bonding interaction is probably important only in the conjugate base forms of the acids where there is a demand for stabilization of the full negative charge.[3] Steric inhibition to anion solvation undoubtedly causes some variations in the observed order but remains fairly constant for the series studied.

Recently, Wilson, Zuckerman, *et al.*,[21] have reported the p$K_a$, Δ$H$, and Δ$S°$ values for a series of substituted benzoic acids including *m*- and *p*-$Me_3MC_6H_4CO_2H$, where M = C and Si. In this paper, they suggest that the greater acidity of the silicon derivatives can be accounted for in terms of anion–solvation effects resulting from the larger size and more strongly hydrophobic nature of the trimethylsilyl group as compared to the *tert*-butyl group and conclude that a $\pi$ ($\pi \rightarrow$ d) bonding explanation is not necessary. However, they fail to consider the effect of internal contributions, *i.e.*, inductive and $\pi$ ($\pi \rightarrow$ d) bonding effects, on anion solvation. Contributions from these effects will appear in both Δ$H$

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[19] C. Eaborn, "Organosilicon Compounds," Butterworths, London, 1960, pp 98–103.

[20] B. W. Clare, D. Cook, E. C. F. Ko, Y. C. Mac, and A. J. Parker, *J. Amer. Chem. Soc.*, **88**, 1911 (1966).

[21] J. M. Wilson, A. G. Briggs, J. E. Sawbridge, P. Tickle, and J. J. Zuckerman, *J. Chem. Soc. A*, 1024 (1970).

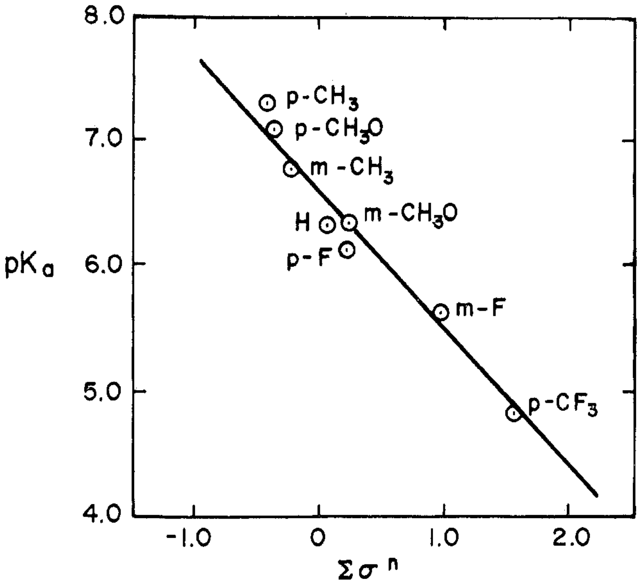

Figure 3.—Plot of the p$K_a$ of $(XC_6H_4)_3GeCO_2H$, 76% ethanol–water, *vs.* the $\sigma^n$ values for X: slope, −0.97; $r$, 0.956.

and $\Delta S°$ of ionization. While the values of $\Delta S°$ of ionization for *m*-$Me_3MC_6H_4CO_2H$, where M = C and Si, are about the same, $\Delta S°$ is higher for *p*-$Me_3SiC_6H_4CO_2H$ than *p*-$Me_3CC_6H_4CO_2H$. $\pi$ ($\pi \rightarrow$ d) bonding could account for the higher entropy of ionization of the *p*-$Me_3Si$ derivative by reducing the anion solvation requirements through anion stabilization. The higher $\Delta H$ of ionization for the *p*-$Me_3Si$ derivative, then, partially compensates for the reduced demand for solvation.

The relative hydrogen-bonding acidity of the acids, *m*- and *p*-$Me_3MC_6H_4CO_2H$, where M = C and Si, in carbon tetrachloride and pyridine media, determined by pmr, have been reported by Zuckerman and Fenton:[22] *m*- and *p*-*tert*-butyl > *m*- and *p*-trimethylsilyl. The same order of chemical shifts is observed for the acidic proton of the acids, $Me_3MCO_2H$, in carbon tetrachloride.[2] Since pmr chemical shifts for a rapidly exchanging proton indicate the average environment of the proton and little anion formation is expected in the above media, in line with the above proposal, the inductive order rather than the $\pi$ ($\pi \rightarrow$ d) bonding order is expected and observed.

**Transmission of Substituent Effects.**—The ability of various groups, Z, to transmit substituent effects to the reaction site, Y, for several series of substituted benzene derivatives, ArZY, which differ only in the nature of Z, has been determined semiquantitatively by comparing the reaction constants, $\rho$, of these derivatives with the reaction constant, $\rho^0$, for a series of derivatives, ArY. The value for the transmission of substituent effects through phenyl, Z = $-C_6H_4-$, has been reported: $\rho/\rho^0 = 0.30 \pm 0.04$.[17] More specifically, for the base-catalyzed saponification of *p*-$ArC_6H_4CO_2Et$ and $ArCO_2Et$ in 88% ethanol-water at 30°, $\rho/\rho^0 = 0.25$.

Since a linear-free-energy relationship is observed between the p$K_a$ values of the acids, $R_3MCO_2H$, and the substituent constants for the groups, $R_3M$, the value for the transmission of substituent effects through the phenyl group can be evaluated by comparing the reaction constant for this series with the reaction constant for the ionization of a series of substituted benzoic acids, $XC_6H_4CO_2H$. In 76% ethanol–water at 25°, $\rho^0/\rho = 0.26$,[23] in dimethyl sulfoxide at 25°, $\rho^0/\rho = 0.18$.[9]

The value for the transmission of substituent effects through the phenyl group calculated for the ethanol–water system shows good agreement with the literature value; however, in dimethyl sulfoxide a much lower value is obtained. The effect of solvent on transmission of inductive and resonance effects through phenyl has not been extensively investigated and the literature value is based on data for protic solvents only. Different steric effects in the series $R_3MCO_2H$ and $XC_6H_4CO_2H$ would be expected to have some influence on the $\rho$ values.

In order to compare the effectiveness of a metalloid to carbon for the transmission of inductive and resonance effects of substituent groups on the aromatic ring to the carboxyl group, the reaction constant for the ionization of a series of triarylgermanecarboxylic acids, $(XC_6H_4)_3GeCO_2H$, where X = H, *p*-Me, *m*-Me, *p*-OMe, *m*-OMe, *p*-F, *m*-F, and *p*-$CF_3$, were determined in 76% ethanol–water at 25°. The Hammett plot using $\sigma^n$ values[24] is shown in Figure 3.[25] Synthetic difficulties prevented the extention of the plot to compounds with more strongly electron-withdrawing substituent groups.[2] The reaction constant for the series, $(XC_6H_4)_3GeCO_2H$, $\rho = 0.97$, is of the same magnitude as calculated for the series, $XC_6H_4CH_2CO_2H$, in 76% ethanol–water, $\rho = 0.87$, from previously published data.[17] Thus, the effectiveness of Ge and $CH_2$ for the transmission of substituent effects to the carboxyl group are quite similar.

**Registry No.**—$Ph_3CCO_2H$, 595-91-5; ethanol, 64-17-5; water, 7732-18-5; dimethyl sulfoxide, 67-68-5.

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[22] D. E. Fenton and J. J. Zuckerman, *Inorg. Chem.*, **7**, 1323 (1968).

[23] The value for $\rho^0$ in 76 wt % ethanol–water, 1.77, was obtained by interpolation from the data of ref 17.

[24] P. R. Wells, *Chem. Rev.*, **63**, 171 (1963).

[25] A linear relationship of p$K_a$ in dimethyl sulfoxide at 25° *vs.* $\sigma^n$ values for $(XC_6H_4)_3GeCO_2H$, where X = H, *p*-Me, *m*-Me, *p*-OMe, *p*-F, also is observed: slope = −2.15, $r$ = 0.96.