

## PROTON ACCEPTOR ABILITY OF HALIDES OF THE GROUP IV A ELEMENTS\*

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Received December 30th, 1976

Proton acceptor ability of chlorine in the  $R_3MCl$  (A),  $R_2MCl_2$  (B), and  $R_3MCH_2Cl$  (C) compounds with  $R =$  alkyl, and  $M = C, Si, Ge,$  and  $Sn$  was measured by hydrogen bond IR spectra. This property is shown to be in agreement with the  $M-Cl$  bond heterogeneity in the series A and B, in corresponding organosilicon compounds is strongly influenced by back bonding.

Molecular features mainly affecting physico-chemical properties of the organic compounds of the group IVa elements<sup>1-3</sup> have long been under dispute. A molecular structure of the halides  $R_3MX$  (M is the group IVa element) appears to be mainly governed by the atom M electronegativities, the variation in the electron-donating substituents R is being expected not to have noticeable influence on the differences in physico-chemical properties of these compounds. The findings of Bellama and coworkers<sup>4</sup> that electric dipole moment of monohalogen derivatives of germane and silane follow dissimilar trend together with our preliminary results on physical properties of the  $(CH_3)_3MX$  compounds<sup>5</sup> led us to spread our earlier interest in the proton acceptor ability of halogen in organosilicon compounds<sup>6</sup> to that in organometallic halides of germanium and tin. Within framework of our study of the  $\alpha$ -carbofunctional compounds of silicon<sup>7</sup> the examination of the relative proton acceptor ability of  $(CH_3)_3MCH_2Cl$  compounds is presented as well.

### EXPERIMENTAL

Trimethylchlorogermane was prepared by protodegermylation of phenyltrimethylgermane. Dry hydrogen chloride was bubbled through the solution of phenyltrimethylgermane (20 g, 0.10 mol) in absolute di-n-butyl ether (100 ml) and the reaction course was continuously checked by GC analysis. Trimethylchlorogermane was obtained by rectification (b.p. 99–100°C, 12.5 g, 82% yield). 2,2-Dimethylpropyl chloride was prepared by the treatment of 2,2-dimethylpropan-1-ol with thionyl chloride in the presence of stoichiometric amount of pyridine in di-n-butyl ether and obtained from the distillation fraction boiling at 85°C by preparative gas chromatography.

\* Part XXIV in the series Organogermanium Compounds; Part XXIII: This Journal 41, 581 (1976).

Trimethylchlorostannane was supplied by Merck-Schuchardt, di-n-butylchlorostannane by Lachema, Brno; dimethyldichlorogermane<sup>8</sup>, trimethylchloromethylgermane<sup>8</sup>, and 2,2-dichloropropane<sup>8</sup> were prepared and characterized earlier, and trimethylchloromethylstannane was from the laboratory stock.

Proton acceptor ability,  $\Delta\nu(\text{OH})$ , was determined from the IR spectra of hydrogen bonds as reported before<sup>6</sup>.

## RESULTS AND DISCUSSION

Similarly to chlorine bonded to an organic skeleton<sup>9</sup> also chlorine bonded to the group IVa element M interacts in  $\text{CCl}_4$  solution with the acidic hydrogen of phenol and forms intermolecular hydrogen bond. Proton acceptor ability of chlorine in  $\text{R}_3\text{MCl}$ ,  $\text{R}_2\text{MCl}_2$ , and  $\text{R}_3\text{MCH}_2\text{Cl}$  compounds could thus be ascertained by this way and its relative values for aforementioned compounds with M is C, Si, Ge, and Sn are seen from Table I. Proton acceptor ability of chlorine in the  $\text{R}_3\text{MCl}$  compounds is always somewhat higher when compared to that of corresponding  $\text{R}_2\text{MCl}_2$  compound, what might be expected due to the mutual polar effect of chlorine atoms in the latter compounds. Increasing ability of chlorine to interact with positively charged hydrogen of phenol when going from silicon *via* carbon and germanium to tin does not correspond either to the electronegativities of the M elements<sup>10</sup>, or to the  $\text{R}_3\text{M}$  group electronegativities<sup>11</sup>. The very characteristic<sup>12</sup> M—H stretching vibration in the  $\text{X}_3\text{M—H}$  compounds was shown<sup>13</sup> to be sensitive measure of the electronic effect of the  $\text{X}_3\text{M}$ -groups and it would be therefore reasonable to find out whether relative proton acceptor ability of chlorine in  $\text{R}_3\text{MCl}$  compounds is in harmony with polar effect of the  $\text{R}_3\text{M}$ -group appraised from the force constant of the

TABLE I

Relative Proton Acceptor Ability,  $\Delta\nu^a$  in  $\text{cm}^{-1}$ , of the  $(\text{CH}_3)_3\text{MCl}$ ,  $(\text{CH}_3)_2\text{MCl}_2$ , and  $(\text{CH}_3)_3\text{.CH}_2\text{Cl}$  Compounds

Compound	M			
	C	Si	Ge	Sn
$(\text{CH}_3)_3\text{MCl}$	74	52 <sup>b</sup>	90	113
$(\text{CH}_3)_2\text{MCl}_2$	30	26 <sup>b,c</sup>	32	62 <sup>d</sup>
$(\text{CH}_3)_3\text{MCH}_2\text{Cl}$	63 <sup>e</sup>	62 <sup>b</sup>	64	67

<sup>a</sup>  $\Delta\nu$  denotes the difference between  $\nu(\text{OH})_{\text{free}}$  and  $\nu(\text{OH}\dots\text{Cl})$  for the solution of 0.02M phenol and about 1M proton acceptor  $(\text{CH}_3)_3\text{MCl}$ ,  $(\text{CH}_3)_2\text{MCl}_2$ , or  $(\text{CH}_3)_3\text{MCH}_2\text{Cl}$  in  $\text{CCl}_4$ . Experimental error was  $\pm 3 \text{ cm}^{-1}$ ; <sup>b</sup> Ref.<sup>6</sup>; <sup>c</sup> Shoulder; <sup>d</sup>  $(n\text{-C}_4\text{H}_9)_2\text{SnCl}_2$ ; <sup>e</sup> The value has to be taken with reservation because of an impurity in this compound.

M—H bond of aforementioned  $X_3MH$  hydrides. As it turns out from the Fig. 1, the plot of  $\Delta\nu(\text{OH})$  versus Taft polar constant of  $R_3M$  group  $\sigma_{R_3M}^*$  (ref.<sup>13</sup>) is linear for  $R_3M\text{Cl}$  compounds except for silylchloride. The stretching M—H frequency in  $(\text{CH}_3)_3MH$  compounds is linearly raised following the order of the decreasing electronegativity difference between the M and H elements<sup>14</sup>. No satisfactory linear relationship however holds for coupling constants between directly bonded protons and  $^{13}\text{C}$  nucleus and the group electronegativities covering the  $R_3M$  groups with the first, second, third, and the fourth row's central atom in  $R_3MX$  ( $X = \text{halogen}$ ) compounds in common, but only separate linear relationships within individual rows could be obtained<sup>15</sup>.

If we assume only very slight difference both in electronegativities of the Si, Ge, and Sn atoms<sup>10,16</sup>, and that in Taft polar constants for  $R_3M$  ( $M = \text{Si, Ge, Sn}$ ) groups<sup>13</sup>, we may suppose the M—X bond character to be mainly responsible for the observed trend of proton acceptor ability of  $R_3M\text{Cl}$  compounds (and  $R_2M\text{Cl}_2$  compounds as well). The decrease in covalent bond strength of M—Cl bonds with an increasing atomic number of atom M was claimed by Drago<sup>16</sup>, and from our data an additional support to this statement can be gained. The increase of the proton acceptor ability of chlorine in the  $R_3M\text{Cl}$  (and also  $R_2MX_2$ ) compounds following the order C, Ge, Sn is thus compatible with the increase of the heterogeneity of the M—Cl bond, the phenomenon having been discussed earlier<sup>16</sup>. The low  $\Delta\nu(\text{OH})$  values for  $(\text{CH}_3)_3\text{SiCl}$  and  $(\text{CH}_3)_2\text{SiCl}_2$  compounds are caused by back bonding<sup>1,17</sup>, the situation observed<sup>18,19</sup> also for oxygen containing  $R_3MOR'$  compounds ( $R'$  is alkyl). As to the  $R_3M\text{CH}_2\text{Cl}$  compounds, their relative proton acceptor ability is comparable, and the differences are within experimental error. Any conclusion concerning the relative role of the  $\alpha$ -effect<sup>20,21</sup> in these compounds is thus precluded.

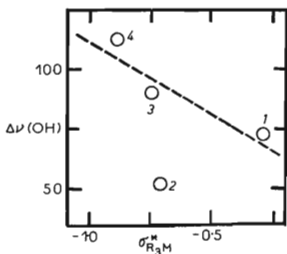


FIG. 1

Plot of  $\Delta\nu(\text{OH})$  of Phenol Due to Its Interaction with Chlorine of the  $R_3M\text{Cl}$  Compounds versus Taft Polar Constant of  $R_3M$  Group

The points 1—4 refer to  $M = \text{C, Si, Ge, Sn}$  respectively.

## REFERENCES

1. Bažant V., Chvalovský V., Rathouský J.: *Organosilicon Compounds*. Publication of the Institute of Chemical Process Fundamentals, Czech. Acad. Sci., Prague 1973.
2. Glockling F.: *The Chemistry of Germanium*. Acad. Press, London 1969.
3. Ebsworth E. A. V. in the book: *Organometallic Compounds of the Group IV Elements*, (A. G. MacDiarmid, Ed). Vol. 1. M. Dekker, New York 1968.
4. Bellama J. M., Wandiga S. O., Maryott A. A.: *Inorg. Nucl. Chem. Lett.* 7, 71 (1971).
5. Pola J., Chvalovský V.: This Journal, in press.
6. Jakoubková M., Papoušková Z., Chvalovský V.: This Journal 41, 2701 (1976).
7. Chvalovský V.: Plenary Lecture at the III. International Symposium on Organosilicon Chemistry, Madison, USA 1972.
8. Chvalovský V., Svoboda P., Cadenas J., Vaisarová V., Papoušková Z., Jakoubková M.: This Journal, in press.
9. Schleyer P. R., West R.: *J. Amer. Chem. Soc.* 81, 3164 (1959).
10. Huggins M. L.: *J. Amer. Chem. Soc.* 75, 4123 (1953).
11. Huheey J. E.: *J. Phys. Chem.* 69, 3284 (1965).
12. Kovalev I. F.: *Dokl. Akad. Nauk SSSR* 134, 559 (1960).
13. Egorov Yu. P., Morozov V. P., Kovalenko N. F.: *Ukr. Khim. Zh.* 31, 123 (1965).
14. Mathis R., Satge J., Mathis F.: *Spectrochim. Acta* 18, 1463 (1962).
15. Wels R. R.: *Progr. Phys. Chem.* 6, 111 (1968).
16. Drago R. S.: *J. Inorg. Nucl. Chem.* 15, 237 (1960).
17. Pitt C. G.: *J. Organometal. Chem.* 61, 49 (1973).
18. Ulbricht K., Jakoubková M., Chvalovský V.: This Journal 33, 1693 (1968).
19. Marchand A., Mendelsohn J., Lebedeff M., Valade J.: *J. Organometal. Chem.* 17, 379 (1969).
20. Voronkov M. G., Feshin V. P., Mironov V. F., Mikhailants S. A., Gar T. K.: *Zh. Obshch. Khim.* 41, 2211 (1971).
21. Voronkov M. G., Feshin V. P., Romanenko L. S., Pola J., Chvalovský V.: This Journal 41, 2718 (1976).

Translated by the author (J. P.).