Proton Exchange of Neopentyl Alcohol in Acetic Acid

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The rate of proton exchange between neopentyl alcohol and acetic acid has been measured in glacial acetic acid at 25°. This rate is found to be first order in alcohol, with a first-order rate constant, k_{HOAc}, of $(6.7 \pm 0.3) \times 10^5$ sec.$^{-1}$. Addition of cyanoacetic or trichloroacetic acid (RCO_2H) to the solution increases the rate according to the equation rate/$[ROH] = k_{HOAc}\chi_{HOAc} + k_{RCO_2H} \times \chi_{RCO_2H}$, where χ is the mole fraction. Values of k_{RCO_2H} for cyanoacetic and trichloroacetic acid are $(8.8 \pm 0.3) \times 10^6$ and $(2.5 \pm 1.0) \times 10^8$ sec.$^{-1}$, respectively. A Brønsted plot of log k vs. pK_A (measured in water) for the three acids is nicely linear with a slope of 0.55 ± 0.05. On the basis of these data and others from the literature, the mechanism of proton transfer between an alcohol and a carboxylic acid is discussed.

Proton exchange between carboxylic acids and alcohols or water[1-4] is of interest because of the possibility that this reaction might proceed through an intimate ion-pair intermediate. In previous studies,[1-4] the carboxylic acid is the *solute*, and the reaction of interest is first order in the carboxylic acid. When the solvent is methanol, the reaction proceeds by way of a cyclic transition state that involves one molecule of acid and two of methanol.[3] Moreover, for a series of substituted benzoic acids the pseudo-first-order rate constant increases with the acid dissociation constant, K_A, of the carboxylic acid according to a Brønsted relationship with a slope of 0.53.[1] This slope does not differentiate between either of the reaction mechanisms considered previously. If the reaction were to proceed through an intimate ion-pair intermediate, a slope close to one would be expected, whereas a slope close to zero would be expected for a concerted proton transfer.[1]

In this paper we report a study in which a carboxylic acid (glacial acetic acid) is the solvent and an alcohol (neopentyl alcohol) is the solute. Rates of proton exchange were measured by the nuclear magnetic resonance (n.m.r.) technique. Neopentyl alcohol was employed instead of methanol to avoid possible complications resulting from esterification.[5] With this system, the proton exchange is first order in alcohol; that is, the reaction now involves one molecule of alcohol instead of two. (Recall that reaction of RCO_2H with methanol as the solvent involves two molecules of methanol.[3]) The number of acetic acid molecules participating in the reaction could not be determined since the n.m.r. of the COOH protons is a singlet.

Addition of cyanoacetic acid or trichloroacetic acid to the acetic acid solution increases the rate of proton exchange. The additional reaction is first order in alcohol and first order in the added carboxylic acid. The over-all rates, R, were represented by the rate law

$$\frac{R}{[ROH]} = k_{HOAc}\chi_{HOAc} + k_{RCO_2H}\chi_{RCO_2H} \qquad (1)$$

where χ is the mole fraction. Values of the rate constants at 25° are as follows: $k_{HOAc} = (6.7 \pm 0.3) \times 10^5$ sec.$^{-1}$, $k_{CNCH_2CO_2H} = (8.8 \pm 0.3) \times 10^6$ sec.$^{-1}$, and $k_{Cl_3CCO_2H} = (2.5 \pm 1.0) \times 10^8$ sec.$^{-1}$. For these three acids, a Brønsted plot of log k obtained in this work vs. pK_A (measured in water) is nicely linear with a slope of 0.55 ± 0.05. This slope is indistinguishable from that obtained previously[1] for substituted benzoic acids in methanol. In addition, the first-order rate constants in methanol are of the same order of magnitude as those now observed in acetic acid.

As with the previous work in methanol,[1] it is difficult to suggest a simple reaction mechanism that can give an adequate explanation of all the data. However, it is clear that the value of the Brønsted slope, near 0.5, is not confined to one specific solvent. Indeed, because of the large difference in solvent and dielectric properties between methanol and acetic acid, one is tempted to conclude that this peculiar Brønsted slope is quite independent of the solvent.

Experimental

Materials. Neopentyl alcohol (Aldrich Chemical Co., White Label) was fractionated through an efficient spinning-band column. The middle fraction was then redistilled through a small all-glass apparatus to remove any metallic impurities that might have been introduced rom the gold-plated steel spinning band. The middle fraction obtained in this distillation had m.p. 56–57.5° (sealed tube) and was used in the kinetic experiments.

Cyanoacetic acid (Eastman Organic Chemicals, White Label) was recrystallized twice from 40:60 benzene–acetone and dried *in vacuo* over silica gel, as recommended by Feates and Ives,[6] m.p. 70–71°.

Trichloracetic acid was purified according to Grunwald and Price.[7]

Glacial acetic acid (C.P. reagent) was analyzed for water by Karl Fischer titration.[8] Acetic anhydride was added (slightly more than was necessary to react with the water), and the mixture was refluxed over chromium trioxide and distilled.[9] The middle fraction used in the rate measurements was dry to Karl Fischer reagent and contained 0.047 M acetic anhydride, as determined by Kilpi's method.[10]

Formamide (Eastman Organic Chemicals, White Label) was purified by freezing and partial thawing.

(1) E. Grunwald and S. Meiboom, *J. Am. Chem. Soc.*, **85**, 2047 (1963).
(2) Z. Luz and S. Meiboom, *ibid.*, **85**, 3923 (1963).
(3) E. Grunwald, C. F. Jumper, and S. Meiboom, *ibid.*, **85**, 522 (1963).
(4) H. Feldbauer and A. Weller, *Z. physik. Chem.* (Frankfurt), **33**, 263 (1962).
(5) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 357.

(6) F. S. Feates and D. J. G. Ives, *J. Chem. Soc.*, 2798 (1956).
(7) E. Grunwald and E. Price, *J. Am. Chem. Soc.*, **86**, 4517 (1964).
(8) A. H. Fainberg and S. Winstein, *ibid.*, **78**, 2776 (1956).
(9) E. Grunwald and E. Price, *ibid.*, **86**, 2965 (1964).
(10) S. Kilpi, *Suomen Kemistilehti*, **13B**, 19 (1940).

The remaining solid was allowed to melt and used in the n.m.r. experiments.

Rate Measurements. Rates of proton exchange were measured by the n.m.r. method.[11] For the solutions studied, the COOH and OH proton resonances of the acid and alcohol are collapsed to a single resonance line because the proton exchange is relatively fast. Spin-echo measurements of the transverse (T_2') and longitudinal (T_1) relaxation times for this line were made using a Varian D-P 60 spectrometer modified by Meiboom.[12] Alexander's[13] method was employed to avoid interference beats due to the CH_3 protons of acetic acid. For all the experiments, the COOH–OH proton system was in the region of exchange narrowing and eq. 2 was employed.[11] In this equation, T_2' is the experimental

$$\Delta = \frac{1}{T_2'} - \frac{1}{T_2} = p(1 - p)\delta^2\tau \qquad (2)$$

value which includes exchange broadening, T_2 is the hypothetical value without exchange, p is the fraction of OH protons in the COOH–OH proton system, δ is the chemical shift between the OH and COOH proton resonance lines, and τ is the relaxation time due to exchange. The relation between τ and R, the rate of proton exchange per liter per second, is given by eq. 3; the

$$\frac{1}{\tau} = \frac{R([OH] + [COOH])}{[OH][COOH]} \qquad (3)$$

brackets indicate molar concentrations. T_2 was estimated from the experimental value of T_1 using eq. 4. In this equation, the additive term is the average differ-

$$\frac{1}{T_2} = \frac{1}{T_1} + 0.042 \qquad (4)$$

ence between $1/T_2'$ and $1/T_1$ found for the COOH protons in acetic acid solutions for which exchange broadening is negligible.[14] Values of T_2' and T_1 for mixtures of acetic acid with cyanoacetic acid or trichloroacetic acid agreed well with eq. 4.

Because the rate of exchange between COOH and OH could not be reduced sufficiently to resolve the two lines, the chemical shift, δ, could not be measured directly. Instead, two indirect methods were employed. The first method is based on the development given in eq. 6 to 8 of ref. 3. In this method, neopentyl alcohol was added to acetic acid. The shift of the OH–COOH resonance relative to the CH_3 resonance of acetic acid was linear in p with a slope of $\delta + i$. δ is the desired chemical shift and i is the medium effect of neopentyl alcohol on the CH_3 vs. COOH chemical shift. To evaluate i, this medium effect is assumed to be the same as the medium effect of neopentyl alcohol on the HC vs. NH_2 proton chemical shift of formamide when this alcohol is dissolved in formamide. The results were $\delta + i = 440 \pm 5$ c.p.s. and $i = 0 \pm 50$ c.p.s.

The second method consists of measuring two chemical shifts: (1) between OH and $C(CH_3)_3$ protons of neopentyl alcohol in dilute solution in formamide, and

(2) between CO_2H protons of acetic acid and $C(CH_3)_3$ protons of neopentyl alcohol in dilute solution in acetic acid.[15] Assuming that changing from formamide to acetic acid has no significant effect on the former chemical shift, δ is found to be 417 ± 1 c.p.s., in good agreement with the value obtained by the first method. For the rate calculations, a weighted average value of 420 c.p.s. (2640 radians/sec.) was used.

All of the kinetic solutions were checked for evidence of esterification by measuring the line width as a function of time. The initial measurement was made about 10 min. after preparation of the solution; later measurements, made after about 1 hr., gave the same result.

A number of properties of solutions of cyanoacetic acid in acetic acid were measured in connection with the rate calculations. In the following, [$CNCH_2COOH$] denotes molar concentration: density $= 1.042 + 0.019[CNCH_2COOH]$, at about $23°$; total moles of COOH protons per liter of solution $= 17.36 - 0.103 \cdot [CNCH_2COOH]$, at about $23°$; chemical shift (in c.p.s.) of COOH vs. CH_3 protons $= -579.5 + 5.73[CNCH_2-COOH]$, at $25°$.

Results

Kinetic results are summarized in Table I. Since the values of the exchange broadening, Δ, have standard errors of ± 0.010 sec.$^{-1}$, the standard errors of $R/[ROH]$ range from 5 to 10%. Within these limits, the reaction is clearly first order in alcohol. Furthermore, the increase of k is linear in the concentration of the added cyanoacetic acid with only the point at 0.569 M cyanoacetic acid deviating by more than 10% from the average relationship.

Table I. Pseudo-First-Order Rate Constants, k, for OH–COOH Proton Exchange of Neopentyl Alcohol in Dry Acetic Acid at 25.0°

[ROH], M	[Other acid], M	Δ, sec.$^{-1}$	$10^{-5}R/$ [ROH], sec.$^{-1}$
0.184		0.102	7.2
0.218		0.131	6.6
0.379		0.227	6.5
0.321	$CNCH_2CO_2H$, 0.238	0.174	7.3
0.367	$CNCH_2CO_2H$, 0.569	0.195	7.4[a]
0.309	$CNCH_2CO_2H$, 0.955	0.112	10.9
0.347	$CNCH_2CO_2H$, 1.426	0.102	13.4
0.322	$CNCH_2CO_2H$, 1.403 and Ac_2O, 0.19	0.087	15.0
0.218	$Cl_4CCH_2CO_2H$, 0.0102	0.105	8.2

[a] Omitted from least-squares fit to eq. 1.

In water at 25.0°, the K_A values for acetic, cyanoacetic, and trichloroacetic acid are 1.76×10^{-5}, 3.37×10^{-3}, and 0.9, respectively.[16] The corresponding rate constants, based on eq. 1, are $(6.7 \pm 0.3) \times 10^5$, $(8.8 \pm 0.3) \times 10^6$, and $(2.5 \pm 1.0) \times 10^8$ sec.$^{-1}$. Figure 1 shows a Brønsted plot of these data. This plot is linear with remarkable accuracy over almost 5 pK_A units, and it is fit by eq. 5.

$$\log k = 0.55 \log K_A + 8.39 \qquad (5)$$

(11) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 222.

(12) S. Meiboom and D. Gill, *Rev. Sci. Instr.*, **29**, 688 (1958).

(13) S. Alexander, *ibid.*, **32**, 1066 (1961).

(14) For a more complete discussion, see E. Grunwald and E. Price, *J. Am. Chem. Soc.*, **86**, 2965 (1964).
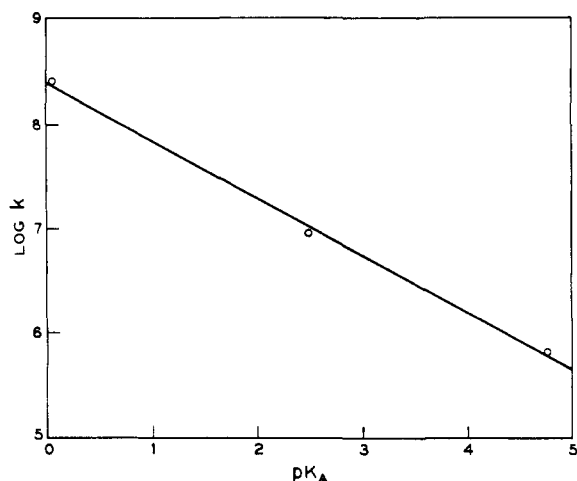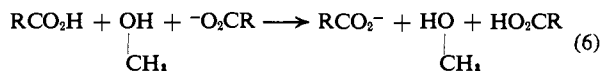
(15) Because of OH–CO_2H proton exchange, the CO_2H proton resonance is not a separate line in the presence of alcohol. However, chemical shift measurements of the CO_2H–OH average resonance vs. the $C(CH_3)_3$ resonance could be extrapolated readily to infinite dilution.

(16) (a) D. A. MacInnes and T. Shedlovsky, *J. Am. Chem. Soc.*, **54**, 1429 (1932); (b) B. Saxton and L. S. Darken, *ibid.*, **62**, 846 (1940); (c) E. Grunwald and E. Price, *ibid.*, **86**, 4517 (1964), and references cited therein.

Figure 1. Brønsted plot for proton exchange of neopentyl alcohol with a series of carboxylic acids: log k in acetic acid vs. pK_A in water (data at 25°).

Figure 2. Some plausible mechanisms for proton exchange.

Discussion

In this study, the phenomenon being observed is proton exchange between the COOH groups *in the bulk solvent* and the OH groups in the alcohol solute. This process can be represented formally as taking place in two steps: (1) exchange of acid molecules between the bulk solvent and the solvation shell of the alcohol, and (2) proton exchange between an alcohol molecule and an acid molecule in its solvation shell.

We believe that the second step in our formal scheme is rate determining for two reasons. First, step 1 is a diffusion step, and its specific rate probably should be appreciably greater than the observed value of k_{HOAc}.[17] Second, the rate of diffusion should be fairly insensitive to acid strength, whereas the observed rate is clearly dependent upon the acid strength, as indicated by the value of the Brønsted slope (eq. 5).

For the rate-determining (second) step, one can propose two different mechanisms similar to those shown in Figure 2: (1) a concerted proton transfer with rate constant $k_{1concerted}$, and (2) a two-step process involving an ion-pair intermediate. On the basis of the arguments presented earlier,[1] one would expect a Brønsted slope close to zero for the concerted process and one close to unity for the two-step process. These predictions are supported by at least some results obtained in other proton-transfer processes. For example, a Brønsted slope close to zero is observed for process 6, which is believed to be concerted.[1] Furthermore, a

$$\begin{array}{c} RCO_2H + OH + {}^-O_2CR \longrightarrow RCO_2^- + HO + HO_2CR \\ | \qquad\qquad\qquad | \\ CH_4 \qquad\qquad\qquad CH_4 \end{array} \quad (6)$$

Brønsted slope close to unity is observed for proton exchange between $NH_4^+X^-$ and acetic acid, where X is the conjugate base of a hydroxylic acid.[7] This exchange reaction appears to involve a two-step mechanism that is somewhat analogous to the two-step process described above.

The experimental Brønsted slope, 0.55, does not fit either of these descriptions. There are also other difficulties when we pursue discussion in terms of these two

(17) For example, the lifetime of an acetic acid molecule in the solvation shell of NH_3 has been estimated as $<10^{-8}$ sec.: E. Grunwald and E. Price, *J. Am. Chem. Soc.*, **86**, 2970 (1964).
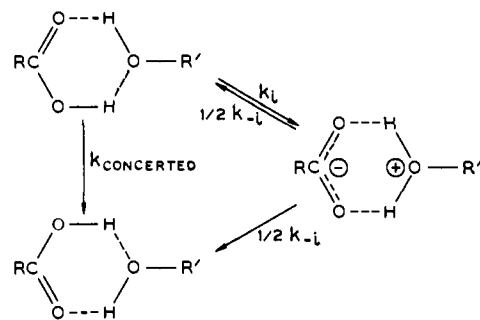
mechanisms. For an ion-pair mechanism the transition state should have considerable ionic character, and one would expect a substantial decrease in the rate constant when the dielectric constant of the solvent is decreased. Actually, the rate constant for proton exchange between acetic acid and solvent water is about 1000 times greater than that for exchange between benzoic acid and solvent methanol.[2,3] On the other hand, the latter rate constant is somewhat smaller than that for the exchange between acetic acid *solvent* and neopentyl alcohol, despite the very large decrease in dielectric constant. These inconsistent solvent effects could indicate that the reaction mechanism changes when the solvent is changed from methanol to acetic acid. That such a change is occurring is clear from the fact that the number of alcohol molecules involved in the process changes from two in methanol to one in acetic acid. However, since the Brønsted slopes for the two solvents are equal, the effect of this change on the charge distribution in the transition state probably is not a fundamental one.[18]

Additional evidence which tends to oppose a two-step mechanism such as that shown in Figure 2 is the very large value that must be inferred for the rate constant of the second step. The first, and rate-determining, step (with rate constant k_i) in this mechanism is the reaction of alcohol as a base to give a conjugate acid that is part of an ion pair in which the two OH protons of ROH_2^+ are depicted as equivalent. Reversal of this reaction (with rate constant k_{-i}) therefore can lead to proton exchange, with a probability of $^1/_2$. Hence the experimental rate constant, k_{HOAc}, is equal to $^1/_2 k_i$,[19] or $k_i = 1.34 \times 10^6$ sec.$^{-1}$.

k_{-i} is obtained from k_i according to $k_{-i} = k_i/K_i$, where K_i is the ionization constant of the alcohol in acetic acid. The order of magnitude value of K_i has been estimated as 5×10^{-8} (see Appendix). Therefore, the order of magnitude value of k_{-i} is 10^{13} sec.$^{-1}$. This value is very large.[20] It is somewhat larger, even,

(18) In deriving the Brønsted slope for methanol,[1] both rate and acid dissociation constants have been measured in methanol. On the other hand, in the present study the rate constants were obtained in acetic acid and the K_A values in water. It has been shown, however, that the relative acid strength of acetic and trichloroacetic acid is almost the same in acetic acid as in water.[7]

(19) In more general versions of this mechanism, the two protons in ROH_2^+ are nonequivalent with respect to solvation and the probability is P rather than $^1/_2$ that the cycle $ROH \rightarrow ROH_2^+ \rightarrow ROH$ will lead to proton exchange. Then $k_i = k_{HOAc}/P$. Since $P \leq 1$, k_{HOAc} is a lower bound to k_i, and k_{HOAc}/K_i is a lower bound to k_{-i}.

(20) Since the completion of our manuscript, Ryan and Futrell have reported the rate constant for a somewhat similar proton-transfer process in the *gas phase*, whose magnitude indicates that the very large value that must be inferred for k_{-i} might indeed be correct. For the reaction, $CH_3CHOH^+ + CH_3CH_2OH \rightarrow CH_3CHO + CH_3CH_2OH_2^+$, the second-order rate constant has the enormously high value of 1.9×10^{12} M^{-1} sec.$^{-1}$ in the gas phase, and reaction appears to take place at

than the frequency kT/h which, according to transition-state theory, represents translation along the reaction coordinate in the transition state. Thus, this calculation indicates that the lifetime of the ion pair that is depicted as an intermediate in the two-step mechanism would have to be comparable to that of a transition state.

In conclusion, we believe that the transition state for proton exchange between an alcohol and a carboxylic acid has considerable polar character because of the peculiar value of the Brønsted slope. Furthermore, we believe that the configuration of the reacting system that most nearly resembles an ion pair is extremely short-lived—too short-lived to respond to any of the usual kinetic methods for detecting metastable reaction intermediates.

Appendix

K_i for the neopentyl alcohol was estimated by two independent methods that agreed to better than one order of magnitude. The first method relates K_i solely to data for electrolytes in glacial acetic acid. The relation is given in eq. 7. In this equation, the K_D values

$$K_i = \frac{[ROH_2{}^+OAc^-]}{[ROH]} = K^{ROH_2{}^+ClO_4{}^-} \times$$

$$\frac{K_D{}^{ROH_2{}^+ClO_4{}^-}}{K_D{}^{ROH_2{}^+OAc^-}} \frac{K_{auto}}{K_A{}^{HClO_4}} \quad (7)$$

every collision. Since the lifetime of the collision complex is almost certainly less than 10^{-11} sec. and probably less than 10^{-12} sec., the time required for proton transfer appears to be less than 10^{-12} sec.: K. R. Ryan and J. H. Futrell, *J. Chem. Phys.*, **42**, 824 (1965).

are ion-pair dissociation constants, $K_{auto} = [AcOH_2{}^+] \times [AcO^-]$, K_A is the formal acid dissociation constant, and $K^{ROH_2{}^+ClO_4{}^-}$ is the equilibrium constant for reaction of a primary alcohol with perchloric acid (eq. 8).

$$K^{ROH_2{}^+ClO_4{}^-} = \frac{[ROH_2{}^+ClO_4{}^-]}{[ROH][HClO_4]} \quad (8)$$

Values of the latter at 25° are 4.4 for methanol and 7.4 for ethanol,[21] for an average value of 6. Since perchloric acid is a strong acid in HOAc, $K_A{}^{HClO_4} \approx K_D{}^{AcOH_2{}^+ClO_4{}^-}$, which in turn should be approximately equal to $K_D{}^{ROH_2{}^+ClO_4{}^-}$. The value of $K_D{}^{ROH_2{}^+OAc^-}$ should be at least approximately equal to K_D for other hydrogen-bonded acetate ion pairs such as pyridium acetate, for which the value is 1×10^{-6}.[22] The value for K_{auto} is 3.5×10^{-15}.[23] As a result, pK_i is estimated as 7.7.

The second method[15] involves the use of the approximate relationship

$$K_i \text{ (in HOAc)} \approx 1 \times 10^9 K_B \text{ (in H}_2\text{O)} \quad (9)$$

Reported values of K_B for primary alcohols in water[24,25] range from 10^{-15} to 10^{-17}, a plausible average being 5×10^{-17}. As a result, pK_i is estimated as 7.0.

The average estimate for pK_i, based on both methods, is 7.3.

(21) I. M. Kolthoff and S. Bruckenstein, *J. Am. Chem. Soc.*, **78**, 1 (1956).
(22) S. Bruckenstein and I. M. Kolthoff, *ibid.*, **78**, 10 (1956).
(23) S. Bruckenstein and I. M. Kolthoff, *ibid.*, **78**, 2974 (1956).
(24) For a recent review, see E. M. Arnett in "Progress in Physical Organic Chemistry," Vol. 1, S. G. Cohen, A. Streitwieser, Jr., and R. Taft, Ed., Interscience Publishers, New York, N. Y., 1963, pp. 223–403.
(25) G. D. Giles and C. F. Wells, *Nature*, **201**, 606 (1964).

Electron Spin Resonance Spectra of Some Group IV-B Substituted Biphenyl Anion Radicals. Dative π-Bonding

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The preparation of the previously unreported compounds, $4\text{-}(CH_3)_3MC_6H_4C_6H_5$ and $4,4'\text{-}(CH_3)_3MC_6H_4C_6H_4M\text{-}(CH_3)_3$ ($M = Si, Ge, Sn$), and their reduction with alkali metals and with a dropping mercury electrode are described. The uninegative radical anions thus produced give well-resolved electron magnetic resonance spectra, which are interpreted and discussed in terms of a simple molecular orbital model involving the d-orbitals of the substituent. For the carbon–silicon and carbon–germanium bonds, the calculated π-bond orders are approximately 0.18 and 0.13, respectively. The Coulomb and resonance integrals, which are consistent with the correct spin densities, suggest that silicon is more electropositive than germanium.

Introduction

The role of dative π-bonding ($d\pi$–$p\pi$ bonding) in the chemistry of the higher analogs of carbon (Si, Ge, Sn, Pb) has received a great deal of attention. Stone and Seyferth have presented a review of some physical and chemical evidence for the existence of π-bonding in silicon compounds[2]; and, on the basis of the high C–M overlap integrals (M = Si, Ge, Sn, Pb), Craig, *et al.*, concluded that π-bonding should be important in the chemistry of unsaturated derivatives of these elements.[3]

Since Stone and Seyferth's review, several papers dealing with dative π-bonding in group IV-B compounds

(2) F. G. A. Stone and D. Seyferth, *J. Inorg. Nucl. Chem.*, **1**, 112 (1955).
(3) D. P. Craig, A. Maccoll, R. S. Nyholm, L. E. Orgel, and L. E. Sutton, *J. Chem. Soc.*, 332 (1954).