# Charge control in the formation of complexes of phenol with unsaturated compounds containing organometallic substituents from group IV

## 6. The effect of intermolecular interactions on the resonance effects in acetylene derivatives

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The resonance donor effect of the σ,π conjugation of $R_3M$ and $R_3MCH_2$ (M = Si, Ge, Sn; R is an alklyl group) substituents with the triple bond in compounds $R_3MC{\equiv}CX$ and $R_3MCH_2C{\equiv}CX$ (X = H, R) changes on passing from isolated molecules to their H-complexes. A partial $\delta^+$ charge on the triple bond enhances σ,π conjugation; a partial $\delta^-$ charge on the triple bond has practically no effect on the resonance properties of $R_3M$ substituents, whereas the σ,π conjugation of $R_3MCH_2$ substituents diminishes owing to the effect of negative direct resonance interaction. The effect of σ,π conjugation on the effective negative charges of the carbon atoms in the —C≡C— fragments was estimated quantitatively.

**Key words:** silylacetylenes, germylacetylenes, stannylacetylenes, σ,π conjugation, negative direct resonance interaction, H-complexes, effective charge.

It is known[1,2] that, in $R_3MX$ type organic compounds of group IV elements M (M = Si, Ge, Sn, Pb; R is an allyl radical, X is a group containing an atom with lone electron pairs in the α position to M or an α,β-unsaturated hydrocarbon radical), intramolecular resonance interactions are complicated in nature. According to the additivity scheme for considering intramolecular interactions[2] widespread in organometallic chemistry, the total resonance acceptor effect of $R_3M$ with respect to X includes acceptor and donor components. According to the current concept,[2] the resonance acceptor effect of $R_3M$ (abbreviated as d,n conjugation or d,π conjugation) is due to the joint effect of unoccupied nd orbitals of M and antibonding σ* orbitals of M—C bonds; this effect is enhanced as M changes in the series Sn < Ge < Si and as the effective charge on M increases. The resonance donor effect of $R_3M$ with respect to X is σ,n- or σ,π-type hyperconjugation. When the X fragment in $R_3MX$ has an atom with lone electron pairs at the α position to M, σ,n conjugation occurs due to mixing of the σ orbitals of the M—C bond with the π and π* orbitals of X.[2]

The fact that the extent of σ,π conjugation depends on the charge on the π system is essential. This dependence has been studied in more detail for the benzene derivatives $R_3MC_6H_5$ (see Refs. 2—4). In particular, the values of the $\sigma_p$ and $\sigma^+_p$ constants are characteristic, since they reflect the total electronic effect, inductive and resonance of the $R_3M$ substituents when a small effective positive charge occurs on the aromatic ring owing to direct polar conjugation, and when a large positive charge close to unity occurs on the ring, respectively.[5] Based on the values of $\sigma_p$ and $\sigma^+_p$, for some substituents, such as $Me_3Ge$ (−0.10 and −0.21, respectively) and $Me_3Sn$ (−0.12 and −0.34), the electron-donating properties increase, for others, such as $Cl_3Si$ (+0.56 and +0.16) and $Cl_3Sn$ (+0.95 and +0.41), the electron-accepting properties sharply decrease, and for a third group of substituents, *e.g.*, $Br_3Si$ (+0.57 and −0.11) and $Ph_2BrGe$ (+0.35 and −0.05), the donor-acceptor properties are reversed.[3] This is caused by enhancement of the σ,π conjugation effect as the positive charge on the benzene ring increases.

The spectroscopy of molecular complexes is a widespread method for studying intramolecular interactions in organic and organometallic compounds.[6] One of the ways it is used is to determine of the σ constants of the $R_3M$ substituents.[6,7] When a molecular complex of the $R_3MX\cdots A$ type (A is the acceptor molecule) involving the π system of X is formed, a partial positive charge must be induced on the latter owing to the charge transfer from $R_3MX$ to A. The magnitude of this charge must affect the extent of the σ,π conjugation between $R_3M$ and X and, consequently, the value of the σ

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constants of $R_3M$ substituents, which are determined from spectroscopic data for complexes of the $R_3MX\cdot\cdot\cdot A$ type. Hence, depending on the characteristics of A and, consequently, on the type of complex and the charge on the $\pi$ system of X, it is conceivable that a set of $\sigma$ values for the $R_3M$ substituents can exist starting from $\sigma_p$ (when the positive charge on X is insignificant) to $\sigma^+_p$ (when the charge on X is close to +1). Hence, two interrelated problems arise. The first one is the problem of determining some "true" values of $\sigma^+_p$ constants, which would characterize such substituents, when, on the one hand, they are involved in a molecular complex, but, on the other hand, the partial positive charge on the $\pi$ system of X is virtually absent. The second is the problem of establishing the relationships between the above-mentioned "true" values of $\sigma_p$ and the constants $\sigma_p^0$ characterizing the total electronic effect of $R_3M$ substituents, when the $R_3MX$ molecules are involved in molecular complexes, and no direct polar conjugation occurs.

The aim of this work is to study these problems using acetylene derivatives as examples. It is known,[8] that in acetylene derivatives the transfer of electron density from the electron-donating organic substituents to the $\pi$ system *via* the resonance mechanism is somewhat greater than in the corresponding benzene derivatives. A significantly sharper enhancement occurs for the organometallic substituents $R_3M$, the $\sigma_p$ constants of which are significantly more negative in the series $R_3MC{\equiv}CH$ than in the series $R_3MC_6H_5$.[5,7] For studying the dependence of $\sigma_p$ on the charge on the triple bond, we compared the IR spectra of two types of H-complexes. In the complexes of the first type, $R_3MC{\equiv}CH\cdot\cdot\cdot B$ (B is tetrahydrofuran (THF) or N,N-dimethylformamide (DMF)), the acetylene derivatives are electron acceptors, and in the complexes of the second type $R_3MC{\equiv}CH\cdot\cdot\cdot HOPh$ and $R_3MC{\equiv}CR\cdot\cdot\cdot HOPh$, the acetylene derivatives are electron donors.

## Experimental

The compounds under study were synthesized according to the procedures described previously in Refs. 9 and 10. Freshly distilled THF, DMF, and $CCl_4$ were used throughout. The IR spectra of the respective H-complexes were recorded with a UR-20 spectrophotometer in the range 3000—3500 $cm^{-1}$.

The H-complexes of THF were studied in the 0.1—0.5 *M* range of concentrations using pure THF or a mixture of THF with $CCl_4$. The frequency shift of the $\nu({\equiv}C{-}H)$ stretching vibration due to the formation of the H-complex $\Delta\nu(CH\cdot\cdot\cdot THF) = \nu(CH, CCl_4) - \nu(CH, THF)$ is the difference of the frequencies $\nu({\equiv}C{-}H)$ in the $CCl_4$ medium and in the THF medium.

The conditions for studying H-complexes with DMF: solute concentration 0.3—0.5 *M*, concentration of DMF 2—3 *M*, in $CCl_4$. The frequency shift $\Delta\nu(CH\cdot\cdot\cdot DMF) = \nu(CH, CCl_4) - \nu(CH, DMF)$ is the difference of the frequencies $\nu({\equiv}C{-}H)$ in the $CCl_4$ medium and in the mixture of DMF with $CCl_4$.

The values of $\nu(CH, CCl_4)$ were measured in $CCl_4$ at the solute concentrations 0.02—0.05 *M*.

In the medium of THF and in the mixture of DMF with $CCl_4$, along with the frequencies of H-complexes, $\nu(CH, THF)$ and $\nu(CH, DMF)$, the absorption bands $\nu^M({\equiv}C{-}H)$ were observed, which correspond to the studied compounds $R_3MC{\equiv}CH$ not coordinated with B. The difference between the $\nu(CH, CCl_4)$ and $\nu^M({\equiv}C{-}H)$ frequencies is smaller than the standard deviation $S_Y$ in the correlation equations (9)—(12).

The values of $\sigma_p$, $\sigma_I$, and $\sigma_R$ for organic substituents and for organometallic substituents were taken from the known procedure[11] and from previously published works,[5,7,13] respectively.

## Results and Discussion

Table 1 presents the values $\Delta\nu(CH\cdot\cdot\cdot THF)$ and $\Delta\nu(CH\cdot\cdot\cdot DMF)$ in the IR spectra of H-complexes of acetylene derivatives with organic and organometallic substituents. Consideration of organic derivatives was of interest. For H-complexes

$$AH + B{-}X_i \rightleftharpoons AH\cdot\cdot\cdot B{-}X_i \qquad (1)$$

with the same AH acceptor (*e.g.*, phenol) and varying substituents $X_i$ attached to the donor center B, the following linear relationships are valid:

$$\Delta\nu(AH) = a\cdot\Delta H_{H\dots B} + b \qquad (2)$$

$$\Delta\nu(AH) = c\cdot\Delta G_{H\dots B} + d \qquad (3)$$

$$\Delta\nu(AH) = k\cdot\sigma_p(X_i) + l \qquad (4)$$

$$\Delta\nu(AH) = m\cdot\sigma_I(X_i) + n\cdot\sigma_R(X_i) + p, \qquad (5)$$

which connect the parameter $\Delta\nu(AH)$ with the variation of the enthalpy $\Delta H_{H\dots B}$ and Gibbs energy $\Delta G_{H\dots B}$ on complexing, as well as with Hammett's $\sigma_p$ constants, and the inductive $\sigma_I$ and resonance $\sigma_R$ constants of substituents $X_i$ (*cf.* Refs. 14—17). The numerical values of coefficients *a, b, c, d, k, l, m, n,* and *p* depend on the types of AH and the donor center B. The comprehensive analysis of Eqs. (4) and (5) indicated[15—17] that even when donor centers B are structurally similar (*e.g.*, a benzene ring, double or triple bond), specific values of *k, l, m, n,* and *p* are peculiar to each B. Thus, for the H-complexes of phenol with acetylene derivatives,[7,15] general relationships (4) and (5) become

$$\Delta\nu(OH) = -167\Sigma\sigma_p + 71 \qquad (6)$$
$$S_a = 8;\ S_b = 2;\ S_y = 5;\ r = 0.986;\ n = 12;$$

$$\Delta\nu(OH) = -168\Sigma\sigma_I + 148\Sigma\sigma_R + 76 \qquad (7)$$
$$S_a = 8;\ S_b = 17;\ S_c = 4;\ S_y = 5;\ r = 0.990;\ n = 12.$$

**Table 1.** The values of $\Delta\nu$ in the IR spectra of H-complexes involving $RC{\equiv}CH$ and $R_3MC{\equiv}CH$

| Compound | R or $R_3M$ | $\Delta\nu(CH\cdots THF)/cm^{-1}$ | $\Delta\nu(CH\cdots DMF)/cm^{-1}$ |
|---|---|---|---|
| **1** | *i*-Pr | — | 66* |
| **2** | Bu | — | 64* |
| **3** | *i*-Bu | 56 | 64 |
| **4** | *t*-Bu | 58 | 67, 65* |
| **5** | $C_5H_{11}$ | — | 61* |
| **6** | $PhCH_2$ | 62 | — |
| **7** | PhO | — | 75* |
| **8** | $C_6F_5CH_2$ | 71 | 81 |
| **9** | Ph | 73 | 80, 79* |
| **10** | $MeOCH_2$ | 67 | 80 |
| **11** | EtS | 67 | 77 |
| **12** | $MeOCOCH_2$ | — | 79* |
| **13** | $ClCH_2$ | 78 | 86, 78* |
| **14** | $BrCH_2$ | 77 | 84, 82* |
| **15** | EtOCO | — | 100* |
| **16** | $C_6F_5$ | 100 | 107 |
| **17** | $Me_3Si$ | 66 | 71 |
| **18** | $Et_3Si$ | 63 | 70, 64* |
| **19** | $Me_2(HC{\equiv}C)Si$ | 73 | 80 |
| **20** | $Me_2(ClCH_2)Si$ | 72 | 80 |
| **21** | $Me_3Ge$ | 61 | 67, 63* |
| **22** | $Me_3Sn$ | 56 | 69 |
| **23** | $Et_3Sn$ | 54 | 66, 59* |
| **24** | $Pr_3Sn$ | 54 | — |
| **25** | $Bu_3Sn$ | 50 | 64 |
| **26** | $(t\text{-}Bu)_3Sn$ | 54 | 63 |
| **27** | $Me(t\text{-}Bu)_2Sn$ | 59 | 65 |
| **28** | $Me_2(t\text{-}Bu)Sn$ | 54 | 64 |
| **29** | $(HC{\equiv}C)_3Sn$ | 78 | — |
| **30** | $Me(HC{\equiv}C)_2Sn$ | 74 | — |
| **31** | $Me_2(HC{\equiv}C)Sn$ | 66 | — |
| **32** | $Me_3SiCH_2$ | 58 | 68 |
| **33** | $Me_3GeCH_2$ | 59 | 68 |
| **34** | $(t\text{-}Bu)_3SnCH_2$ | 55 | 68 |

* According to the data from Ref. 13.

H-Complexes with different substituents $X_i$ in the acceptor molecule, $X_i$—AH,

$$X_i\text{—AH} + B \rightleftharpoons X_i\text{—AH}\cdots B \qquad (8)$$

have been less studied. The H-complexes considered in this work are of this type. Based on some examples presented previously,[14,18–20] one has good reason to suggest that Eqs. (2)—(5) are universally valid not only for type (1) H-complexes, but also for type (8) H-complexes.

Processing by the least-squares method indicated that, for the acetylenes with organic substituents (compounds **1**—**16**), the following linear relationships hold true at the confidence level of 95 %:

$$\Delta\nu(CH\cdots THF) = 81\sigma_p + 70 \qquad (9)$$
$$S_a = 9;\ S_b = 1;\ S_y = 4;\ r = 0.949;\ n = 10;$$

$$\Delta\nu(CH\cdots THF) = 73\sigma_I + 100\sigma_R + 72 \qquad (10)$$
$$S_a = 13;\ S_b = 22;\ S_c = 3;\ S_y = 4;\ r = 0.941;\ n = 10;$$

$$\Delta\nu(CH\cdots DMF) = 79\sigma_p + 77 \qquad (11)$$
$$S_a = 6;\ S_b = 1;\ S_y = 4;\ r = 0.966;\ n = 15;$$

$$\Delta\nu(CH\cdots DMF) = 79\sigma_I + 79\sigma_R + 77 \qquad (12)$$
$$S_a = 7;\ S_b = 10;\ S_c = 1;\ S_y = 4;\ r = 0.960;\ n = 15.$$

Relationships (9)—(12) are generally invalid for the H-complexes of compounds **17**—**34** containing organometallic substituents $R_3M$. This fact is manifested on the plots of $\Delta\nu$ *vs.* $\sigma_p$ by the deflection of the points corresponding to these compounds from the linear curves (9) and (11) (Fig. 1, curve (9)) toward lower $\sigma_p$ values. If one assumes the values of $\sigma_p$ and, consequently, $\sigma_R$ to be inadequate, then, using relationships (9)—(12), one

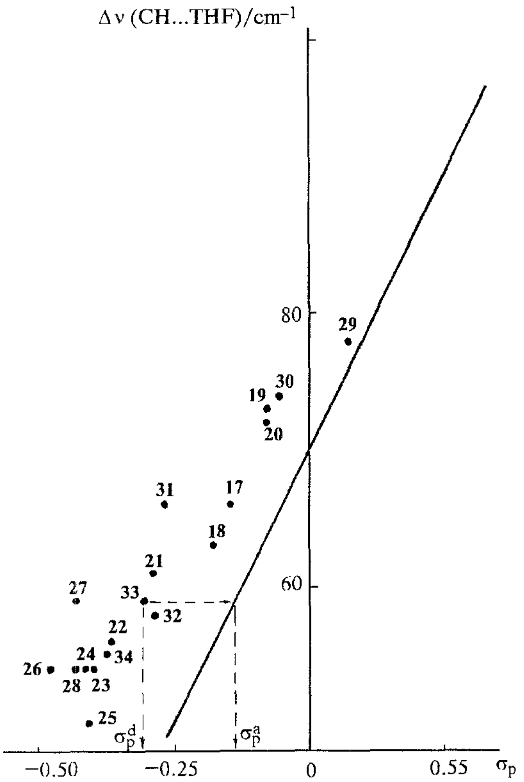


**Fig. 1.** Deviations of points (compounds **17—34**) from the straight line (9) connecting the values Δν(CH···THF) and $\sigma_p$ in compounds **3**, **4**, **6**, **8—11**, **13**, **14**, and **16**. The point numbering is the same as that in Tables 1 and 2.

can find new values of s based on the data on Δν. Let us denote these constants by $\sigma_p^a$ and $\sigma_R^a$. The superscript "a" signifies that the constants $\sigma_p^a$ and $\sigma_R^a$ of the substituents $R_3M$ can be used in the case when the compounds $R_3MC{\equiv}CH$ are acceptors of H-complexes, *i.e.*, when the latter correspond to type (8). For complexes corresponding to type (1), with organometallic acetylenes as donors, we designate the constants of $R_3M$ by $\sigma_p^d$ and $\sigma_R^d$.

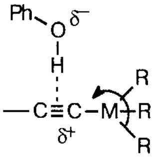
Analyzing the values of σ (Table 2), we concluded that the $\sigma_p^a$ constants are greater than the $\sigma_p^d$ constants. Hence, all of the differences $\sigma_p^a - \sigma_p^d$ (which are numerically equal to the differences $\Delta(\sigma_R) = \sigma_p^a - \sigma_R^d$) are positive. This unambiguously indicates that, during the formation of H-complexes by acetylene derivatives, the resonance effects of the substituents $R_3M$ in the $R_3M{-}C{\equiv}C$ fragments are not unchanged and, moreover, vary quite regularly. The resonance donor properties of $R_3M$ (with respect to the triple bond) are stronger in the processes of type (1) complexes than in those of type (8) due to the fact[21] that electrostatic interactions between the donor and acceptor centers of the H-complex predominate during the formation of the hydrogen bond; on the other hand, the transfer of charge from the donor molecule (B) to the acceptor molecule (AH) always occurs. This results in a partial positive charge $\delta^+$ on B and a partial negative charge $\delta^-$ on AH. The different charge signs on B and AH result in a significant difference in the conjugation of the $R_3M$-type substituents with donor and acceptor centers of H-complexes.

**Table 2.** The values of σ constants for organometallic substituents $R_3M$ in $R_3M{-}C{\equiv}CH$ and the values of $\Delta(\Delta q_\pi)$

| Compound | $R_3M$ | $\sigma_I$ | $\sigma_p^d$ | $\sigma_p^a$ | $\sigma_R^d$ | $\sigma_R^a$ | $\sigma_R^0$ | $\Delta(\sigma_R) = \sigma_R^a - \sigma_R^d$ | $\Delta(\Delta q_\pi) \cdot 10^{-3}$/au |
|---|---|---|---|---|---|---|---|---|---|
| **17** | $Me_3Si$ | −0.15 | −0.15 | −0.05 | 0.00 | 0.10 | 0.07 | 0.10 | 18 |
| **18** | $Et_3Si$ | −0.18 | −0.18 | −0.08 | 0.00 | 0.10 | 0.08 | 0.10 | 18 |
| **19** | $Me_2(HC{\equiv}C)Si$ | — | −0.08 | 0.04 | — | — | — | 0.12 | 21 |
| **20** | $Me_2(ClCH_2)Si$ | — | −0.08 | 0.03 | — | — | — | 0.11 | 20 |
| **21** | $Me_3Ge$ | −0.11 | −0.29 | −0.10 | −0.18 | 0.01 | 0.02 | 0.19 | 34 |
| **22** | $Me_3Sn$ | −0.13 | −0.37 | −0.12 | −0.24 | 0.01 | 0.01 | 0.25 | 44 |
| **23** | $Et_3Sn$ | −0.15 | −0.40 | −0.15 | −0.25 | 0.00 | 0.03 | 0.25 | 44 |
| **24** | $Pr_3Sn$ | −0.17 | −0.42 | −0.18 | −0.25 | −0.01 | — | 0.24 | 43 |
| **25** | $Bu_3Sn$ | −0.16 | −0.41 | −0.18 | −0.25 | −0.02 | — | 0.23 | 41 |
| **26** | $(t\text{-}Bu)_3Sn$ | −0.20 | −0.48 | −0.17 | −0.28 | 0.03 | 0.00 | 0.31 | 55 |
| **27** | $Me(t\text{-}Bu)_2Sn$ | −0.17 | −0.43 | −0.13 | −0.26 | 0.04 | 0.00 | 0.30 | 53 |
| **28** | $Me_2(t\text{-}Bu)Sn$ | −0.15 | −0.43 | −0.16 | −0.28 | 0.01 | 0.01 | 0.27 | 48 |
| **29** | $(HC{\equiv}C)_3Sn$ | — | 0.07 | 0.09 | — | — | — | ~0 | ~0 |
| **30** | $Me(HC{\equiv}C)_2Sn$ | — | −0.06 | 0.04 | — | — | — | 0.10 | 18 |
| **31** | $Me_2(HC{\equiv}C)Sn$ | — | −0.27 | −0.04 | — | — | — | 0.23 | 41 |
| **32** | $Me_3SiCH_2$ | −0.05 | −0.29 | −0.11 | −0.24 | −0.06 | −0.21 | 0.18 | 32 |
| **33** | $Me_3GeCH_2$ | −0.04 | −0.31 | −0.11 | −0.27 | −0.07 | −0.22 | 0.20 | 36 |
| **34** | $(t\text{-}Bu)_3SnCH_2$ | −0.05 | −0.38 | −0.12 | −0.33 | −0.07 | −0.25 | 0.26 | 46 |

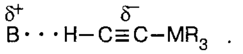
*Note.* The values of $\sigma_I$, $\sigma_p^d$, $\sigma_R^d$, and $\sigma_R^0$ were taken from works published previously.[5,7] Some values of $\sigma_p$ were calculated from the IR spectra of the H-complexes of acetylene derivatives with phenol using the well-known method.[7] It was assumed that $\sigma_p = \sigma_I + \sigma_R$. The values of $\sigma_p^a$ calculated in this work with Eqs. (9) and (11) are close to each other; hence, the average values are given in the Table.

Thus, in the H-complexes of acetylenes (donors) with phenol (acceptor) corresponding to type (1),



the occurrence of a partial positive charge on the multiple bond enforces the σ,π conjugation of the $R_3M$ substituents with the π system. This effect is manifested by substantial negative values of $\sigma_p{}^d$ and $\sigma_R{}^d$ for the majority of $R_3M$.

The opposite process occurs in the H-complexes of acetylenes (as acceptors) with THF or DMF (B, donors)



$$\overset{\delta+}{B}\cdots H{-}\overset{\delta-}{C}{\equiv}C{-}MR_3\ .$$

In this case, the occurrence of a partial negative charge on the multiple bond should not significantly affect the σ,π conjugation of the $R_3M$ substituents with the π system. Indeed, σ,π conjugation, as a typically strong resonance effect of the +M type, is invariant to a negative charge on the reaction center[5,11] (with the exception of $CH_2MR_3$ substituents, whose specific properties when σ,π conjugation occurs, will be discussed below.) The data available from the literature[2,3,5,6] on the second component of the total resonance effect of $R_3M$ with respect to a triple bond — the effect of d,π conjugation — indicates a significant dependence of this effect on the charge on M, while small variations in the charge on the π system during the formation of H-complexes apparently affect d,π conjugation only insignificantly. From Table 2, it is evident that the $\sigma_R{}^a$ values virtually coincide with $\sigma_R{}^0$, which characterize the total resonance effect of the $R_3M$ substituents with the triple bond in isolated molecules (*i.e.*, those not involved in H-complexes). The case of $R_3MCH_2$ substituents, for which the $\sigma_R{}^a$ and $\sigma_R{}^0$ values differ noticeably, will be discussed below.

The enhancement of the σ,π conjugation of the $R_3M$ and $R_3MCH_2$ substituents with the π system when it acquires a positive charge, can be estimated by the difference $\Delta(\sigma_R) = \sigma_R{}^a - \sigma_R{}^d$, and can also be expressed just in the form of the π charge transferred from the substituents to the triple bond during this enhancement. (As has been discussed in detail previously,[2] this transfer of the π charge takes place *via* the mechanism of hyperconjugation, which is the conjugation of the σ(M—C) orbitals with the π- and π* orbitals of the triple bond.) The idea is based on the predominance of electrostatic interactions during the formation of H-complexes, and, consequently, on charge control over the reaction of phenol with acetylene derivatives.[15]

From relationship (7) it follows that, for the formation of complexes of acetylenes with phenol, the resonance contribution $\Delta\nu_R$ to $\Delta\nu$ is equal to

$$\Delta\nu_R = -148\sigma_R + \text{const} \tag{13}$$

within a constant characterizing the resonance component of the constant term of the relationship (7). For an argument equal to $\sigma_R{}^a$ and $\sigma_R{}^d$, Eq. (13) is transformed to

$$\Delta\nu_R{}^a = -148\sigma_R{}^a + \text{const} \tag{14}$$

and

$$\Delta\nu_R{}^d = -148\sigma_R{}^d + \text{const.} \tag{15}$$

At the same time for all of the monosubstituted acetylenes XC≡CH, the relationship is also valid[15]

$$\Delta\nu_R = -0.83\Delta q_\pi + \text{const}', \tag{16}$$

where $\Delta q_\pi$ is the variation of the effective charge on the carbon atoms of the triple bond caused by the conjugation between X and the π system. For the cases concerned, relationship (16) becomes

$$\Delta\nu_R{}^a = -0.83\Delta q_\pi{}^a + \text{const}', \tag{17}$$

and

$$\Delta\nu_R{}^d = -0.83\Delta q_\pi{}^d + \text{const}'. \tag{18}$$

Subtracting Eq. (15) from (14) and Eq. (18) from (17) and equating the left-hand sides of the differences, one obtains

$$\Delta(\Delta q_\pi) = 148(\sigma_R{}^a - \sigma_R{}^d)/0.83, \tag{19}$$

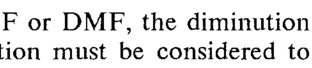
where $\Delta(\Delta q_\pi) = \Delta q_\pi{}^a - \Delta q_\pi{}^d$.

Hence, Eq. (19) makes it possible to characterize the enhancement of the σ,π conjugation of the $R_3M$ and $R_3MCH_2$ substituents with the triple bond quantitatively by the increase in the π-electron transfer from these substituents to the π system, *i.e.*, by the increase in the negative effective charge $\Delta(\Delta q_\pi)$ on the carbon atoms of the C≡C fragments (see Table 2, the last column on the left).

Let us compare the values $\Delta(\Delta q_\pi)$ with the values $\Delta q_\pi$ for the resonance interactions of the organic substituents R with the triple bond in RC≡CH.[8] The $\Delta(\Delta q_\pi)$ variation range is ~$55 \cdot 10^{-3}$ au (see Table 2), whereas[8] the π-electron exchange between the substituents and the triple bond for the moderate resonance donors $CH_2{=}CH$, $CH_3$, and F is 10, 12, and $62 \cdot 10^{-3}$ au, respectively, and varies in the range ~$(20\text{—}60) \cdot 10^{-3}$ au for typical resonance acceptors CN, COH, $COCH_3$, and $NO_2$. Hence, the increase in the σ,π conjugation of the $R_3M$ and $R_3MCH_2$ substituents with the triple bond due to the formation of H-complexes with phenol is comparable with the variation of the effective charge on the carbon atoms of the —C≡C— fragment that occurs during resonance interactions in isolated acetylene molecules containing organic substituents.

For compounds of the type $R_3MC{\equiv}CH$, the values $\Delta(\sigma_R)$ and $\Delta(\Delta q_\pi)$ depend on the nature of M and R. These values increase regularly on passing from $Alk_3SiC{\equiv}CH$ (compounds **17, 18**) to $Me_3GeC{\equiv}CH$ (compound **21**) and further to $Alk_3SnC{\equiv}CH$ (compounds **22—28**). An increase in the atomic number of M in $Alk_3MC{\equiv}CH$ is accompanied, on the one hand, by a decrease in d,π conjugation and an increase in σ,π conjugation,[22] *i.e.*, a decrease in the resonance acceptor properties (an increase in donor properties) of $Alk_3M$ with respect to the triple bond, and, consequently, a decrease in $\sigma_R{}^0$ and $\sigma_R{}^a$. On the other hand, the larger the atomic number of M in $Alk_3MC{\equiv}CH$, the larger the increase in the effect of σ,π conjugation due to the appearance of a partial charge $\delta^+$ in the formation of the H-complex with phenol along with the effect of σ,π conjugation in isolated molecules. Hence, the differences $\Delta(\sigma_R) = \sigma_R{}^a - \sigma_R{}^d$ and $\Delta(\Delta q_\pi)$ increase when M in $Alk_3MC{\equiv}CH$ varies in the series Si < Ge < Sn. The derivatives $Me_{3-n}(HC{\equiv}C)_nSnC{\equiv}CH$ (compounds **29—31**) have some peculiarities: for $n = 3$, $\Delta(\sigma_R)$ and $\Delta(\Delta q_\pi)$ are nearly zero; for $n = 1$, these quantities have the values typical for $Alk_3SnC{\equiv}CH$; and for $n = 2$, they have intermediate values. Hence, it follows that a necessary condition for both the existence of σ,π conjugation in isolated molecules and its enhancement when molecular complexes are formed is the occurrence of at least one alkyl group bonded to the M atom. Moreover, according to the literature data,[2,5] an $H_3M$ group can also participate in the σ,π conjugation with the triple bond.

For the propargyl derivatives $Alk_3MCH_2C{\equiv}CH$ (compounds **32—34**) the magnitudes of $\Delta(\sigma_R)$ and $\Delta(\Delta q_\pi)$ increase with the atomic number of M. Hence, the effect of σ,π conjugation and its enhancement when a partial charge $\delta^+$ occurs on the multiple bond increase as M changes in the series Si < Ge < Sn. However, while in the compounds $R_3MC{\equiv}CH$ the constants $\sigma_R{}^0$ and $\sigma_R{}^a$ are nearly the same, in the propargyl series they differ significantly. According to the values of the constants $\sigma_R{}^0$ ($-0.21$ to $-0.25$) and $\sigma_R{}^a$ ($-0.06$ to $-0.07$), the effect of σ,π conjugation in propargyl derivatives $Alk_3MCH_2C{\equiv}CH$ decreases on going from isolated molecules to molecules forming H-complexes with THF and DMF. When these H-complexes are formed, a partial negative charge $\delta^-$ appears on the multiple bond. Hence, in the system



$$\overset{\delta^+}{B}\cdots H-C\equiv\overset{\delta^-}{C}-CH_2-MAlk_3,$$

where B = THF or DMF, the diminution of the effect of σ,π conjugation must be considered to be a consequence of some kind of negative direct resonance interaction, in which the increase in the electron density on the C≡C bond due to the formation of the H-complex with B results in a decrease in the acceptor ability of the π orbitals with respect to the σ(M—C) orbitals of substituents $CH_2MAlk_3$. As was shown previously for *para*-disubstituted benzenes[23] and disubstituted acetylenes,[24] negative direct resonance interaction occurs when a molecule contains two substituents that are typical resonance donors. In the case considered, one of these substituents is the $CH_2MR_3$ group, for which no d,π conjugation occurs. Hence, in contrast to the $MR_3$ substituents, the $CH_2MR_3$ groups possess strong resonance donor properties in isolated molecules (a large negative value of $\sigma_R{}^0$ in contrast to small positive values $\sigma_R{}^0$ for $MR_3$). Molecules B act as the second substituent inducing the $\delta^-$ charge on the triple bond when the H-complex is formed. The negative direct resonance interaction results in only a partial realization of the potentially high resonance donor properties of the $CH_2MR_3$ group.

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