

ORBITAL HYBRIDIZATION OF HALOGEN ATOMS IN HALOGENATED HYDROCARBONS AND THE LENGTHS OF CARBON-HALOGEN BONDS

1965

SovietRxiv

View the original and related papers at <https://sovietrxiv.org/items/ru-196501.33594>

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.

Abstract

Full Text

Physical Chemistry

B. M. MIKHAILOV

ORBITAL HYBRIDIZATION OF HALOGEN ATOMS IN HALOGENATED HYDROCARBONS AND THE LENGTHS OF CARBON-HALOGEN BONDS

(Presented by Academician V. N. Kondrat'ev on 30 XI 1964)

One of the important and at the same time difficult problems of theoretical chemistry is the interpretation of the properties of carbon-halogen bonds. Despite numerous studies devoted to the nature of the C-Hal bond, its physical parameters, including interatomic distances, have not been amenable to quantitative evaluation.

In considering the problem of the chemical bond, it is now necessary to bear in mind that the most important factor determining the nature of a chemical bond is the orbital effect—the hybridization of orbitals^(1-4, 17). Orbital hybridization in carbon atoms and its influence on the properties of the carbon-carbon bond is determined in a simple way from data on the geometry of the molecule⁽¹⁷⁾. Information on the hybridization of the bonding orbitals of halogen atoms in a given molecule can be obtained from the constants of nuclear quadrupole interaction.

Until now, the use of quadrupole-interaction constants to determine the degree of hybridization of orbitals has encountered difficulties connected with the fact that they are a function both of the degree of hybridization and of the degree of ionicity of the bond, and thus in the equation

$$U_p = (1 - S)(1 - i) \quad (1)$$

there are two unknowns which must be determined from one experimental datum—the number of uncompensated p -electrons, $U_p = -eQq_{\text{mol}}/eQq_p$ ⁽⁵⁾. Therefore, in previous works various attempts were made to find relationships between the ionic character of a bond and the difference in electronegativities of the bonded atoms, so that by substituting the value of the ionic character of the bond into equation (1) the degree of hybridization of the bonding orbital of the halide could be determined^(5,6). In doing so, however, the extremely important circumstance was not taken into account that a change in the hybridization of the orbital of the halogen atom also entails a change in its electronegativity.

With the appearance of the works of Hinze, Whitehead, and Jaffé⁽⁷⁻⁹⁾, which established a dependence between these two parameters, it becomes possible to determine rather accurately the S -character of halogen orbitals and thereby to reveal its influence on the lengths of halogen-carbon bonds.

For a linear dependence⁽⁸⁾ of the electronegativity of the orbital of a chlorine atom on its S -character:

$$\chi_{\text{Cl}} = (9.38 + 9.85 S) \text{ eV}. \quad (2)$$

The ionic character of the bond⁽⁸⁾ i is determined by the expression

$$i = |n_{A_j} - 1| = |\Delta\chi/2(C_A + C_B)|, \quad (3)$$

where n_{A_j} is the number of electrons in the j -orbital of A ; $\Delta\chi$ is the difference between the electronegativities of atoms A and B ; C_A and C_B are half the difference between the ionization potentials and electron affinities for orbitals A and B , respectively; $C = \frac{1}{2}(I_v - E_v)$. The values of the ionization potentials I and affinities

to the electron E deviate comparatively little from a linear dependence on the S -character, and therefore for chlorine one may adopt:

$$I_v = (15.03 + 8.99S) \text{ eV}; \quad (4)$$

$$E_v = (3.73 + 10.72S) \text{ eV}. \quad (5)$$

From data on the molecular structure of chlorine derivatives of hydrocarbons, using the relations derived by Coulson⁽¹⁰⁾, we find the S -character of the orbitals of the carbon atoms in the bond with chlorine, and from the relation⁽⁷⁾

$$\chi_{C_j} = (5.80 + 9.15S) \text{ eV} \quad (6)$$

we determine their electronegativity. Then, from the constants of nuclear quadrupole interaction, with the aid of equations (1)–(5), we calculate the S -character of the bonding orbital of chlorine in the corresponding compound.

Table 1

Compound	U_p , kpt.	S - character of car- bon	χ_C , eV	S - character of halo- gen	χ_{Hal} , eV	i	Lit. on molec. struct.	Lit. on U_p
Cl ₂	0.99	—	—	0.01	9.48	0	(12)	(15)
CH ₃ Cl	0.682	0.211	7.73	0.20	11.35	0.150	(12)	(15)
CF ₃ Cl	0.711	0.274	8.31	0.19	11.25	0.121	(12)	(15)
CH ₂ =CHCl	0.54	0.285	8.41	0.24	11.75	0.136	(13)	(13)
C ₆ H ₅ Cl	0.663	0.298	8.53	0.24	11.75	0.132	(14)	(14)
CH≡CCl	0.726	0.500	10.38	0.24	11.75	0.054	(12)	(15)
Br ₂	0.99	—	—	0.01	8.50	0	(12)	(15)
CH ₃ Br	0.750	0.193	7.57	0.16	9.98	0.109	(12)	(15)
CF ₃ Br	0.804	0.274	8.31	0.14	9.79	0.066	(12)	(15)
CH ₃ C≡CBr	0.840	0.500	10.38	0.17	10.08	0.013	(12)	(15)
J ₂	0.940	—	—	0.06	8.55	0	(12)	(15)
CH ₃ J	0.844	0.186	7.5	0.10	8.86	0.063	(12)	(15)
C ₆ H ₅ J	0.887*	0.298	8.53	0.10	8.86	0.015	(15)	—
CH ₃ C≡CI	0.973	0.500	10.38	0.10	8.86	0.066	(12)	(15)

*Calculated value.

The calculated values of the S -character of the chlorine orbitals in methyl chloride, trifluorochloromethane, vinyl chloride, chlorobenzene, and chloroacetylene are given in Table 1. In the same way, the S -character of the orbitals of bromine and iodine atoms in bromo- and iodo-derivatives of hydrocarbons was found. To determine the degree of hybridization of the halogen orbitals in methyl bromoacetylene and iodoacetylene, in which the electronegativity of the halogen atoms is smaller than that of carbon atoms in the sp -state, equation (5) was used,

$$U_p = (1 - S)[1 + i(1 + 2C)], \quad (7)$$

where C is the shielding constant, equal to 0.13 for bromine and 0.12 for iodine⁽¹¹⁾. As is seen from the data of Table 1, the chlorine orbitals are hybridized in the bond with carbon by 19-24%, bromine by 14-17%, and iodine by 10%. Table 1 also gives the corresponding electronegativity of the bonding orbitals of the halogen atoms and the degree of ionicity of the bond i .

Information on the orbital hybridization of carbon and halogen atoms and on the degree of ionicity makes it possible to reveal the influence of these factors on the lengths of carbon-halogen bonds. For this purpose, from equation⁽¹⁷⁾

$$r_C^{\text{cov}} = (0.854 - 0.328S) \text{ \AA} \quad (8)$$

we find the covalent radius of the carbon atom in a definite state of hybridization, and from relation ⁽¹⁷⁾

$$\Delta r_C^{\text{cov}} = 0.88(n - 1) \text{ \AA} \quad (9)$$

its change as a function of the degree of ionicity of the bond. By subtracting the obtained value $r_C^{+\delta}$ (or $r_C^{-\delta}$) from the length of the carbon-halogen bond in the compound under consideration, we find the value $r_{\text{Hal}}^{-\delta}$ (or $r_{\text{Hal}}^{+\delta}$) (see Table 2). Since in chlorobenzene and chloroacetylene the S -character of the chlorine orbitals is the same (0.24), from $r_{\text{Cl}}^{-\delta}$ and i in these molecules one can find the covalent radius of chlorine at this degree of hybridization (0.921 \AA), and then, taking into account that in the chlorine molecule $S_{\text{Cl}} = 0.01$ and $r_{\text{Cl}}^{\text{cov}} = 0.994 \text{ \AA}$, obtain the dependence of the covalent radius of chlorine on the degree of hybridization

$$r_{\text{Cl}}^{\text{cov}} = (0.997 - 0.317S) \text{ \AA}. \quad (10)$$

The change in the covalent radius as a function of the degree of ionicity of the bond ($i = n - 1$) proves to be equal to

$$\Delta r_{\text{Cl}} = 1.28(n_{\text{Cl}} - 1) \text{ \AA}. \quad (11)$$

Thus, the length of the chlorine-carbon bond is

$$d(\text{C} - \text{Cl}) = r_C^{\text{cov}} + 0.88(n_C - 1) + r_{\text{Cl}}^{\text{cov}} + 1.28(n_{\text{Cl}} - 1). \quad (12)$$

Relation (12) is in good agreement with data on the molecular structure of other chlorine derivatives. With the aid of (8)–(11), the bond angles, and the constant of the nuclear quadrupole interaction, we find that the length of the C–Cl bond in CH_3Cl should be 1.779 \AA, whereas experimentally $1.781 \pm 0.005 \text{ \AA}$ was found. In CF_3Cl the calculated C–Cl bond length is 1.749 \AA, the experimental value $1.751 \pm 0.004 \text{ \AA}$. In vinyl chloride the calculated value of the C–Cl bond length is 1.736 \AA; experimental data: 1.726 \AA and 1.736 \AA (see Tables 1 and 2).

Proceeding similarly to the way this was done in the series of chlorine derivatives, we find from the data for CH_3Br , methylbromoacetylene (which differ in the hybridization of the bromine orbitals by only 1%), and Br_2 the dependence of the covalent radius of bromine on the S -character of its orbitals

$$r_{\text{Br}}^{\text{cov}} = (1.144 - 0.227S) \text{ \AA}. \quad (13)$$

The change in the radius of the bromine orbital as a function of the number of electrons localized on it is equal to:

$$\Delta r_{\text{Br}} = 1.25(n_{\text{Br}} - 1) \text{ \AA}. \quad (14)$$

Using relations (8), (9), (13), (14), the bond angles, and the constant of the nuclear quadrupole interaction with CF_3Br , one can calculate the length of the C – Br bond in this compound; it proves to be 1.901 Å, whereas experimentally 1.908 ± 0.018 Å was found (Tables 1 and 2).

From the data for CH_3J , methyliodoacetylene, and J_2 (see Table 1) we obtain the following relations for $r_{\text{J}}^{\text{cov}}$ and Δr_{J} :

$$r_{\text{J}}^{\text{cov}} = (1.348 - 0.25S) \text{ \AA}, \quad (15)$$

$$\Delta r_{\text{J}} = 1.24(n_{\text{J}} - 1) \text{ \AA}. \quad (16)$$

The calculated values of $r_{\text{C}}^{\text{cov}}$, $r_{\text{Hal}}^{\text{cov}}$, r_{C}^{δ} , r_{Hal}^{δ} , and $d(\text{C} - \text{Hal})$ are given in Table 2. Since in CH_3J and methyliodoacetylene the iodine orbitals exhibit the same degree of hybridization, it is natural to assume that it has the same character in iodobenzene as well. If, furthermore, one assumes that in iodobenzene the benzene ring is deformed in the same way as in chlorobenzene, then one can find the degree of ionicity of the C – J bond (Table 1), and from (8), (9), (15), and (16) calculate its length. It proves to be 2.085 Å, whereas experimentally 2.08 ± 0.04 Å was found (Table 2). The constant of the nuclear quadrupole interaction for $\text{C}_6\text{H}_5\text{J}^{127}$ in the gaseous state should be equal to 682.4 MHz ($u_p = 0.887$) (Table 1).

As is evident from the foregoing, the length of the carbon-halogen bond is a function of the orbital hybridization of the atoms forming it. The degree of hybridization determines the sizes of the covalent radii of the atoms, the electronegativity of the orbitals, and, thereby, the degree of ionicity of the bond*. Partial double-bond character due to the unshared electron pair of the halides is not observed. If the halides exhibited a mesomeric effect (p, π -conjugation), then the relations establishing the dependence of $r_{\text{Hal}}^{\text{cov}}$ on the S -character of the orbital and the dependence of Δr_{Hal} on i would not be valid for the halogen derivatives of both saturated and aromatic and acetylene series.

Table 2

Compound	r_C^{cov}	r_C^δ	$r_{\text{Hal}}^{\text{cov}}$	r_{Hal}^δ	$d(C - \text{Hal}), \text{calculated}$	$d(C - \text{Hal}), \text{found}$
CH ₃ Cl	0.785	0.652	0.934	1.127	1.779	1.781 ± 0.005
CF ₃ Cl	0.764	0.657	0.937	1.092	1.749	1.751 ± 0.004
CH ₂ =CHCl	0.761	0.641	0.921	1.095	1.736	1.726
CH ₂ =CHCl	0.761	0.641	0.921	1.095	1.736	1.736 ⁽¹⁶⁾
C ₆ H ₅ Cl	0.756	0.640	0.921	1.090	1.730	1.730
CH≡CCl	0.690	0.642	0.921	0.990	1.632	1.632 ± 0.061
CH ₃ Br	0.791	0.695	1.108	1.244	1.939	1.939
CF ₃ Br	0.764	0.706	1.112	1.195	1.901	1.908 ± 0.018
CH ₃ C≡CBr	0.690	0.701	1.108	1.092	1.793	1.793 ± 0.005
CH ₃ J	0.793	0.738	1.323	1.401	2.139	2.139
C ₆ H ₅ J	0.756	0.743	1.323	1.342	2.085	2.08 ± 0.04
CH ₃ C≡CJ	0.690	0.749	1.323	1.241	1.990	1.990

Mesomeric effect in the halides, strictly speaking, should not have been expected, since, in order to explain the properties of carbon-halogen bonds (interatomic distances, dipole moments), the resonance-mesomerism theory is forced to adopt the physically unfounded assumption of an increase in the mesomeric effect in the series $F > Cl > Br > J$, i.e., the ability of the halides to assume a divalent-positive state increases with increasing ionization potential.

Institute of Organic Chemistry
Academy of Sciences of the USSR

Received
6 XI 1964

REFERENCES

1. M. Dewar, H. Schmeising, *Tetrahedron*, **5**, 166 (1959).
2. M. Dewar, H. Schmeising, *Tetrahedron*, **11**, 96 (1960).
3. B. M. Mikhailov, *Izv. AN SSSR, OKhN*, 1960, 1379.
4. M. Brown, *Trans. Farad. Soc.*, **55**, 694 (1959).

5. W. Orville-Thomas, *Quart. Rev.*, **11**, 162 (1957).
6. J. Wilmshurst, *J. Chem. Phys.*, **30**, 561 (1959).
7. J. Hinze, H. Jaffé, *J. Am. Chem. Soc.*, **84**, 540 (1962).
8. J. Hinze, M. Whitehead, H. Jaffé, *J. Am. Chem. Soc.*, **85**, 148 (1963).
9. J. Hinze, H. Jaffé, *J. Phys. Chem.*, **67**, 1501 (1963).
10. C. Coulson, Victor Henri, Memorial Dessoer Liege, 1948, p. 15.
11. B. Dailes, C. Townes, *J. Chem. Phys.*, **23**, 118 (1955).
12. *Tables of Interatomic Distances and Confer. in Mol. and Ions*, Sp. Publ. No. 11, London, 1958.
13. D. Kivelson, E. Wilson, D. Lide, *J. Chem. Phys.*, **32**, 205 (1960).
14. R. Poynter, *Shem. Phys.*, **39**, 1962 (1963).
15. B. Tordi, V. Smit, R. Trambarulo, *Radiospectroscopy*, Moscow, 1955.
16. J. Simons, *Phys. Rev.*, **76**, 689 (1949).
17. B. M. Mikhailov, *Tetrahedron*, **21** (1965).

* In the presence of several halide atoms at one carbon, a spatial effect may influence the bond length.

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.