Theoret. chim. Acta (Berl.) 4, 265—272 (1966)

Department of Chemistry, Emory University, Atlanta, Ga. 30322, U.S.A.

A Maximum Overlap Orbital Calculation of ^{13}C-H Coupling Constants in the Vinyl Halides

By

V. S. **Watts** and J. H. **Goldstein**

The method of maximum overlap orbitals (MOO) has been employed to calculate all of the $^{13}C - H$ coupling constants in the vinyl halides. The results indicate that values at the β position depend primarily on mesomeric content of each halide, whereas the α couplings are predominately influenced by the nature of the $C - X$ bond. By using only pure p-orbitals for $X = Cl$, Br and I, the observed α couplings are predicted to within one cps, but in the fluoride $\sim 25\%$ s-character is required to obtain satisfactory agreement. The results of these calculations are compared with those obtained for the methyl halides, and are also discussed in relation to relevant bonding inferences derived from microwave data.

Die $^{13}C - H$-Kopplungskonstanten von Vinylhalogeniden wurden mittels der Methode der maximalen Überlappung berechnet, wobei sich ergab, daß diejenigen für β-ständiges H hauptsächlich von der Beteiligung polarer Grenzstrukturen abhängt, wogegen der Wert für α-ständiges H überwiegend durch die $C - H$-Bindung beeinflußt wird. Wenn man für die Halogen-Zustandsfunktionen reine p-Funktionen ansetzt, erhält man die Kopplungskonstanten im Fall von Cl, Br und J bis auf 1 Hz. Beim Fluorid hingegen muß 25% s-Charakter angenommen werden, wenn sich vernünftige Werte ergeben sollen. Die Ergebnisse werden mit Daten aus der Reihe der Methylhalogenide verglichen und außerdem zu Resultaten der Mikrowellenspektroskopie in Beziehung gesetzt.

A l'aide de la méthode des orbitales à recouvrement maximum nous avons calculé toutes les constantes de couplage $^{13}C - H$ pour les halogénures de vinyle. Les résultats indiquent que les valeurs en position β dépendent principalement du poids des formules polaires tandis que celles en α sont influencées prééminemment par la nature de la liaison $C - X$. En n'employant que des orbitales p pures pour $X = Cl$, Br et I, les couplages en α sont prédits à un Hz près. Par contre, il faut admettre $\sim 25\%$ de caractère s pour obtenir un accord satisfaisant pour le fluorure. Les résultats de ces calculs sont comparés à ceux pour les halogénures de méthyle et aux conséquences pour les liaisons que l'on déduit des spectres microondes.

Introduction

An increasing degree of attention has been directed toward the interpretation of $^{13}C — H$ coupling parameters of NMR spectroscopy following the original suggestions by **Shoolery** [*15*] and **Muller** and **Pritchard** [*12*] that this parameter is a linear function of the s-character in the $C — H$ bond. Subsequently, **Malinowski** demonstrated that values of J ($^{13}C — H$) in an extensive series of substituted methanes could be represented to a good approximation as linear combinations of a set of characteristic substituent contributions [*11*]. **Juan** and **Gutowsky** were able to account for this additivity property, using both a potential well model and a valence bond approach, but this work did not predict the magnitudes of the substituent effects [*9*]. **Dreeskamp** and **Sackman** [*4*] have related $^{13}C — H$ couplings to the condition of maximum overlap and **Sackman** [*14*] has used this criterion to predict the couplings in the fluoromethanes in fair agreement with experiment. **Goldstein** and **Hobgood** also used this procedure, modified to include halogen *s*-character (from microwave spectroscopy) and adjusting ionic structures to produce agreement with the $J(^{13}C-H)$ values for twelve halomethanes [*6*]. The ionic contents required were shown to compare reasonably well with the corresponding microwave estimates [*3*]. The MOO approach has also been applied to small ring compounds [*1*].

As yet no similar systematic efforts have been made to interpret the $^{13}C-H$ parameter in unsaturated compounds although in some cases, *e. g.*, the vinyl halides, complete sets of data are now available for all positions. JUAN and GUTOWSKY have suggested that multiplication of α-substituent effects in the alkanes by the factor $\frac{4}{3}$ would convert them into the α-values in the corresponding vinylic derivatives [*9*]. On this basis, and from the available data, the values of J_α for the vinyl halides, C_2H_3X, are expected to be 191, 191.8, 191 and 189.1 cps for $X = F$, Cl, Br, and I, respectively, which do not compare at all well with the corresponding observed values of 200.2, 194.9, 196.6, and 190.8 cps.

In ethylene itself it has been estimated that a π-contribution of ~ 2.5 cps to $J(^{13}C-H)$ should obtain [*9*]. It appears unlikely, however, that this can account for the discrepancies noted above since a comparable contribution should also be included for the vinyl halides.

In this paper we report the results obtained by employing the previously described MOO method for the calculation of all the $^{13}C-H$ coupling constants in the four vinyl halides. The overlap function to be maximized in the present application is the total overlap of the σ-framework alone. The couplings at the β positions are accounted for simply by including mesomeric structures ($^-CH_2$-CHX^+) in amounts roughly consistent with those derived from microwave data. (Although the incorporation of these structures modifies only the π-charge distribution, the accompanying change in the effective charge of the β C atoms affects the values of J_β.)

The values of J_α are understandably much more perturbed by the substituent than are the β couplings, and depend almost entirely upon the nature of the $C-X$ bond. For $X = Cl$, Br and I the values of J_α are predicted to within 1 cps with the use of pure *p*-orbitals for the halogens. In the fluoride, however, 25% *s*-character must be employed to obtain agreement within ~ 3.5 cps. Precise calculations are also possible for Cl, Br and I by using suitable combinations of halogen *s*-character and ionic content (C^+X^-). Such alternatives are discussed and compared with current microwave interpretations of vinylic $C-X$ bonds. The present results are also compared with those previously obtained for saturated (methyl) halides.

Calculations

The bonding orbitals employed are shown in Tab. 1, as the coefficients of the appropriate AO's. In terms of the above coefficients the covalent σ overlap function of any vinyl halide can be formulated as:

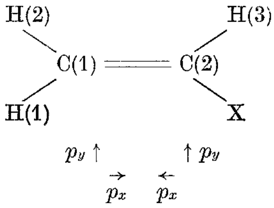
$$\begin{aligned} S = {} & acI_1 + c\,(1-a^2)^{1/2}\,I_2 + a\,(1-c^2)^{1/2}\,I_3 \\ & + (1-a^2)^{1/2}\,(1-c^2)^{1/2}\,I_4 + bI_5 + (1-b^2)^{1/2}\,I_6 \\ & + (1-a^2-b^2)^{1/2}\,I_7 + (a^2+b^2)^{1/2}\,I_8 + (1-c^2-d^2)^{1/2}\,I_9 \\ & + (c^2+d^2)^{1/2}\,I_{10} + d\,(1-k^2)^{1/2}\,I_{11} + (1-d^2)^{1/2}\,(1-k^2)^{1/2}\,I_{12} \\ & + dkI_{13} + k\,(1-d^2)^{1/2}\,I_{14} \end{aligned} \qquad (1)$$

Table 1. *Bonding Orbitals for σ-Frameworks of the Vinyl Halides*

Bond[a]	Coefficients of Atomic Orbitals in Each Bonding Function		
	S	P_x	P_y
C (1) − C (2)	a	$(1 - a^2)^{1/2}$	0
C (1) − H (1)	b	$-ab/(1 - a^2)^{1/2}$	$-(1 - a^2 - b^2)^{1/2}/(1 - a^2)^{1/2}$
C (1) − H (2)	$(1 - a^2 - b^2)^{1/2}$	$-a(1 - a^2 - b^2)^{1/2}/(1 - a^2)^{1/2}$	$b/(1 - a^2)^{1/2}$
C (2) − C (1)	c	$(1 - c^2)^{1/2}$	0
C (2) − X	d	$-cd/(1 - c^2)^{1/2}$	$-(1 - c^2 - d^2)^{1/2}/(1 - c^2)^{1/2}$
C (2) − H (3)	$(1 - c^2 - d^2)^{1/2}$	$-c(1 - c^2 - d^2)^{1/2}/(1 - c^2)^{1/2}$	$\alpha/(1 - c^2)^{1/2}$
H (1) − C (1)	1	0	0
H (2) − C (1)	1	0	0
H (3) − C (2)	1	0	0
X − C (2)	k	$(1 - k^2)^{1/2}$	0

---

[a] Each such function refers to the first atom given in the "Bond" column. The following numbering system was used:



where the symbols, I_i, designate the overlap integrals between the pairs of orbitals shown below:

I_1: $2s_{C(1)}$, $2s_{C(2)}$
I_2: $2s_{C(1)}$, $2p_{C(2)}$
I_3: $2s_{C(2)}$, $2p_{C(1)}$
I_4: $2p_{C(1)}$, $2p_{C(2)}$
I_5: $1s_{H(1)}$, $2s_{C(1)}$
I_6: $1s_{H(1)}$, $2p_{C(1)}$
I_7: $1s_{H(2)}$, $2s_{C(1)}$
I_8: $1s_{H(2)}$, $2p_{C(1)}$
I_9: $1s_{H(3)}$, $2s_{C(2)}$
I_{10}: $1s_{H(3)}$, $2p_{C(2)}$
I_{11}: $2s_{C(2)}$, np_X
I_{12}: $2p_{C(2)}$, np_X
I_{13}: $2s_{C(2)}$, ns_X
I_{14}: $2p_{C(2)}$, ns_X

and $n = 2$, 3, 4 and 5 for F, Cl, Br, and I, respectively. The required overlap values were obtained by interpolation from published tables [*13*]. In the case of vinyl bromide, an additional interpolation between effective quantum numbers of 3 and 5, was required [*8*]. The structural data used in this step has been summarized in Tab. 2.

Table 2. *Vinyl Halide Bond Lengths Used in* MOO *Calculations*

X	C(1)—H(1)	C(1)—H(2)	C(1)—C(2)	C(2)—H(3)	C(2)—X
F[a]	1.087	1.077	1.329	1.082	1.347
Cl[b]	1.090	1.079	1.332	1.079	1.726
Br[c]	1.08	1.08	1.34	1.08	1.89
I[c]	1.08	1.08	1.34	1.08	2.09

---

[a] LIDE Jr., D. R., and D. CHRISTENSEN: Spectrochim. Acta **17**, 665 (1961).

[b] KIVELSON, D., and E. B. WILSON Jr.: J. chem. Physics **32**, 205 (1960).

[c] SUTTON, L. E., Editor, Interatomic Distances, The Chemical Society, London (1958).

The overlap expression, (1), was maximized with respect to only the four hybridization parameters, a, b, c and d. Without some additional restriction, the condition of maximum overlap tends to produce sp hybrids for the halogens, an obviously unrealistic result arising from the fact that rehybridization of the nonbonding halogen orbitals is unconstrained. For this reason the halogen parameter, k, was varied independently as will be described later. The values of $J(^{13}C-H)$ at each position were calculated from the relation [*12*, *15*]

$$J_i = 500\,\alpha_i^2 \text{ (cps)} \tag{2}$$

where α_i is the coefficient of the s-component in the maximum overlap orbital of carbon in the bond, C_i-H.

Using pure p orbitals for the halogens, the calculated values of J_α are very satisfactory, within one cps, for Cl, Br, and I, and about 13 cps too high for F (see entries in Tab. 5 for 0% s-character). It is interesting that the observed reversal of order between Cl and Br is reproduced even at this stage of the computations. The calculated values of J_β (cis and trans) were too large, by 3 — 8 cps, for all four halides. In order to adjust these values, the polar structures, $^-CH_2-CH=X^+$, were introduced in the (unnormalized) wave function

$$\psi = \psi^{(0)} + \lambda\psi^{(m)} \tag{3}$$

where $\psi^{(0)}$ and $\psi^{(m)}$ represent the charge-free and polar structures, respectively. Overlap values for the polar structures were calculated using the same geometry as before, but with new values of Z_{eff} modified by the polar charge distribution and following Slater's rules [*5*].

On the basis of (3) the calculated couplings are expressible as

$$J_{\text{calc}} = \frac{J^{(0)} + 2\,\lambda\,J^{(0m)} + \lambda^2\,J^{(m)}}{1 + 2\,\lambda + \lambda^2} \tag{4}$$

where $J^{(0)}$ is the covalent coupling, $J^{(m)}$ is the coupling in the polar structure, and $J^{(om)}$ is the exchange term between these structures, which is assumed to follow a geometric-mean relationship

$$J^{(0m)} = [J^{(0)}\,J^{(m)}]^{1/2}\ . \tag{5}$$

For the α-position (H_3) $J^{(m)}$ depends only on the s-character of the attached C orbital. However, for the β protons (H_1 and H_2) it is necessary to take account also of the altered effective Z-value at C (1). This was accomplished through the relation

$$J^{(m)} = \left(\frac{Z_{\text{eff}}}{Z_0}\right)^3 \cdot \bar{J}^{(m)} = \left(\frac{2.90}{3.25}\right)^3 \cdot \bar{J}^{(m)} = 0.7501\,\bar{J}^{(m)}\ . \tag{6}$$

The value of $\bar{J}^{(m)}$ was obtained by maximizing the total overlap for the polar structure but using orbital overlap values consistent with new values of Z_{eff}. However, in order to reflect the direct dependence of J on Z_{eff}^3 it was necessary to scale $\bar{J}^{(m)}$ as indicated in eq. (6). After evaluation of the required terms, λ was adjusted to obtain agreement with $J^{(\text{obs})}$ for the β proton in each halide. The per cent polar character

$$M = 100\,\lambda/(1 + \lambda) \tag{7}$$

is shown for each halide in Tab. 3. The polar structures have a pronounced

Table 3. *Lone Pair-π Conjugation in Vinyl Halides*

X	Proton	Value of M required to match $J^{(obs)}$	Average M for β positions	Calc. value of M from quad. data[b]	obs. J_{C-H}[c]
F	1	9.85	10.05	(10)[d]	159.18
	2	10.25			162.16
Cl	1	5.35 (8.80)[a]	9.18	6	162.64
	2	13.00 (9.57)			160.89
Br	1	7.05	10.33	4	163.63
	2	13.61			160.26
I	1	6.04	10.86	3	164.09
	2	15.68			159.20

---

[a] Values in parentheses were obtained by reversing bond lengths C (1) – H (1) and C (1) – H (2).

[b] Goldstein, J. H.: J. chem. Physics **24**, 106 (1956).

[c] Howe, J. A., and J. H. Goldstein: J. chem. Physics **27**, 831 (1957); Mayo, R. E., and J. H. Goldstein: J. Mol. Spect. **14**, 173 (1964).

[d] Estimated.

influence on the values of J_β because of the change produced in Z^3_{eff} at C_1. However, the values of J_α are affected only slightly.

As can be seen from Tab. 3 the values of M obtained here for vinyl chloride, and especially the average for the two β positions is roughly comparable with the microwave value. Since there is no independent estimate of M for the fluoride, this was estimated in advance as 10%, which is almost identical with the contribution required to match both J_β values. The results for the bromide and iodide are in poorer agreement, but are of comparable magnitudes.

In these latter two instances, it should be noted, the structures are less precisely known, and this could introduce errors in the calculation of the total overlap values. Calculations performed for vinyl chloride indicate that errors of ~ 0.01 A in the C — H bond lengths would account for a good part of the discrepancy noted in the values of M. Incidentally, it was observed that exchanging the C — H_1 and C — H_2 bond lengths in vinyl chloride produces better agreement in this case, as shown by the values in parentheses in Tab. 3.

Using the average amounts of polar structures given in Tab. 3, the values of J_α were calculated for the series. Initially, pure p orbitals were employed for the halogens and the results were within $\sim$ 1 cps of the observed values except

Table 4. *Calculated Values of J_α Using Average per Cent Mesomeric Contribution to Match J_β*

X	F	Cl	Br	I
Obs. $J_{C-H\,(3)}$	200.18	194.86	196.58	190.85
%s from X	0	0	0	0
calc. $J_{C-H\,(3)}$	211.85	195.06	195.40	190.86
%s from X	25	15	10	
calc. $J_{C-H\,(3)}$	203.72	188.85	189.85	
%s from X	50			
calc. $J_{C-H\,(3)}$	202.96			

for F, in which case the discrepancy is about 6% or 12 cps (see Tab. 4). The introduction of *s*-character improves the agreement for the fluoride, but worsens it in the other cases. As shown in Tab. 4, approximately 50% *s*-character is required to achieve agreement of ~ 1.5% for the fluoride. For the other halides, the best agreement is obtained with the use of pure *p*-orbitals. It was observed that the modification described above produced virtually no change in the calculated values of J_β. Moreover, the inclusion of ionic forms, of the type $CH_2 = \overset{+}{C}H\ X^-$, tends to compensate for the effects of *s*-character, while also leaving J_β essentially unaffected. It is possible, in principle, therefore, to incorporate both contributions in the chloride, bromide, and iodide in such amounts as to obtain agreement with experiment.

Discussion

In the procedure followed, the calculated values of J_β depend largely on the fractional amount of polar structure in the vinyl halide, whereas J_α depends predominantly on the nature of the $C - X$ bond, that is, on the *s*-character of the halogen orbital and the ionic content of the bond. For sufficiently large magnitudes of polar and ionic content this separation of dependence breaks down. However, for the ranges employed here the opening statement is valid. The subsituent effect on J_β for the vinyl halides is rather small, about 2 — 7 cps, which makes a reliable calculation of polar content by this method correspondingly difficult. Also, for vinyl bromide and iodide the lack of accurate structural data means that all calculated contributions to J will be approximate to the extent of inaccuracy in the bond lengths. Even so, the average polar contributions required for satisfactory agreement with experiment are of the same order of magnitude (~ 10%) as the values derived from nuclear quadrupole coupling (NQC) data from microwave spectroscopy, but generally somewhat higher than the latter results (~ 3 — 6%).

The calculation of J_α is, hopefully, more promising because the halogen substituent effects are now about an order of magnitude greater (~ 33 — 43 cps). It is, thus, gratifying that with the use of pure *p* halogen orbitals not only is the correct order predicted for the series, but with the sole exception of vinyl fluoride agreement to within one cps or better is obtained for J_α (Tab. 4). Incorporation of 25% *s*-character in the fluorine orbital produces an agreement of ~ 3.5 cps, which is quite adequate for present purposes. (In the case of the fluoride, an increase of *s*-character from 25% to 50% decreases J_α by ~ 1.0 cps and values beyond 50% actually reverse the trend in J_α.)

It is instructive to compare the present results for J_α with those obtained previously by the MOO method for the corresponding methyl halides [*6*]. In the latter case, the use of pure *p* orbitals for Cl, Br and I led to calculated values which were too small, by about 6 — 8 cps. In order to obtain agreement it was necessary to introduce ionic character, or some combination of *s*-hybridization and ionic character. The values of *s*-character determined by TOWNES and DAILEY from microwave NQC data were adopted and ionic content was adjusted to obtain agreement of observed and predicted values of $J(^{13}C - H)$. In this way, a unique solution was obtained, and the ionic contents required were reasonably

Table 5. *Vinyl Chloride Parameters Calculated by* MOO

Structure	Charge-free	Charge-free	Polar	Polar	Ionic
% *s* character from halogen	0	15	0	15	
S[a]	3.37288	3.49982	3.48369	3.63266	2.86132
a[a]	.5780	.5783	.5748	.5748	.5436
b[a]	.5751	.5752	.5768	.5769	.5917
c[a]	.6226	.6142	.6667	.6513	.7027
d[a]	.4698	.4926	.4253	.4706	.0000
$J_{C-H\ (1)}$	165.36	165.43	118.21	118.21	175.06
$J_{C-H\ (2)}$	167.57	167.36	119.68	119.68	177.20
$J_{C-H\ (3)}$	195.85	190.05	187.32	117.17	344.23

[a] See eq. (1).

near those employed by Townes and Dailey. Since F has no NQC constant, its *s*-character was estimated at 25%, and only 1.6% ionic character was then required to match J, which is much less than that required for the other halogens. Fluorine is somewhat exceptional in the MOO calculations since in this case the use of a pure *p*-orbital leads to a value of J^{calc} which is already greater than J^{obs}. For this reason, very little of the ionic structure can be employed in methyl fluoride even when 25% *s*-character is introduced, and none at all in vinyl fluoride. (It might be mentioned here that, although ionic content of the CX bond and halogen *s*-character do the same thing in NQC calculations, they produce opposite effects in MOO calculations for the ranges of parameters generally employed, so that in principle, and if *d*-hybridization were unimportant, NQC and ^{13}C — H coupling constants could provide a unique determination of these two parameters.)

Although good agreement with experiment has been obtained in the vinylic series by the use of pure *p* orbitals (except for the fluoride), these results obviously do not provide a unique description of the carbon-halogen bonds in these compounds. (However, we would expect the structures of such bonds to be different in the case of sp^3 and sp^2 carbon in light of the suggestions of Dailey and Townes [*2*] and Jaffe and *co*-workers [*7*] concerning the relationship between hybridization and electronegativity.) In this study we have emphasized primarily calculations based on pure *p* orbitals chiefly because satisfactory results are obtained for J_α without the introduction of any adjustable parameters (except for F).

As judged from previously available data and methods of interpretation, the NQC values of the vinyl halides appear not to be consistent with the choice of pure *p*-orbitals for Cl, Br, and I. From the NQC data for vinyl chloride, Townes and Schawlow have assigned 15% *s*-hybridization and 20% ionic form (C^+Cl^-) to the carbon-chloride bond [*16*]. When contributions of this type are admitted into the MOO calculations, it is found that correct J_α values can be obtained by using 15% and 10% *s*-character for Cl and Br, respectively, adopted from the corresponding methanes in addition to 4% ionic content for each. With this description, the calculated value of the NQC parameter in vinyl chloride becomes 85 Mc as compared with the observed value of 72 Mc [*10*]. Thus, the consistency indicated here is poorer than that obtainable in the methyl halides.

As is well known, the MOO method is largely intuitive in origin, and has no sound theoretical basis. An understanding of its utility and limitations can perhaps best be developed from attempted applications of the type presented here. Considering the complexity of the vinylic structures studied, the results obtained are encouraging and indicate that further applications of the method are warranted.

Acknowledgments. We wish to thank the National Institutes of Health for a Grant in partial support of this work.

References

[*1*] CERTAIN, P. R., V. S. WATTS, and J. H. GOLDSTEIN: Theoret. chim. Acta (Berl.) **2**, 324 (1964).
[*2*] DAILEY, B. P., and C. H. TOWNES: J. chem. Physics **23**, 118 (1955).
[*3*] – J. chem. Physics **33**, 1641 (1960).
[*4*] DREESKAMP, H., and E. SACKMAN: Zeitsch. physik. Chemie [Neue Folge] **34**, 273 (1962).
[*5*] EYRING, H., J. WALTER, and G. E. KIMBALL: Quantum Chemistry, pp. 162 – 163. New York: John Wiley and Sons, Inc. 1944.
[*6*] GOLDSTEIN, J. H., and R. T. HOBGOOD Jr.: J. chem. Physics **40**, 3592 (1964).
[*7*] HINZE, J., and H. H. JAFFE: J. Am. chem. Soc. **84**, 540 (1962).
[*8*] JAFFE, H. H., and G. O. DOAK: J. chem. Physics **21**, 196 (1953).
[*9*] JUAN, C., and H. S. GUTOWSKY: J. chem. Physics **37**, 2198 (1962).
[*10*] KIVELSON, D., and E. B. WILSON Jr.: J. chem. Physics **32**, 205 (1960).
[*11*] MALINOWSKI, E. R.: J. Am. chem. Soc. **83**, 4479 (1961).
[*12*] MULLER, N., and D. E. PRICHARD: J. chem. Physics **31**, 768, 1471 (1959).
[*13*] MULLIKEN, R. S., C. A. RIEKE, D. ORLOFF, and H. ORLOFF: J. chem. Physics **17**, 1248 (1949).
[*14*] SACKMANN, E.: Zeitsch. physik. Chemie [Neue Folge] **34**, 283 (1962).
[*15*] SHOOLERY, J. N.: J. chem. Physics **31**, 1427 (1959).
[*16*] TOWNES, C. H., and A. L. SCHAWLOW: Microwave Spectroscopy, p. 242. New York: McGraw-Hill Book Co., Inc. 1955.

(Received November 26, 1965)