and $g_\perp$. Unfortunately Δ_1 and Δ_2 are not known since the optical absorption spectra of the ring pi electrons probably masks the Δ_1 and Δ_2 transitions. A transition corresponding to Δ_2 would be weak in any case. However graphs of β *vs.* Δ_1 and β_1 *vs.* Δ_2 are given in Figs. 5a and 5b.

The values obtained for A and B are, using the value obtained for a′

$$A = \pm 1.88 \times 10^{-2} \text{ cm.}^{-1}$$
$$B = \pm 0.39 \times 10^{-2} \text{ cm.}^{-1}$$

The sign of A is taken as negative; apparently all copper compounds studied so far have negative A's. For $\beta_1 = 1$, equations 13 solve to give $P = 0.030$ cm.$^{-1}$ and $K = 0.36$.

If, in equation 14, we replace $\Phi_1(0)\Phi_3(0)$ by $\gamma^2|S(0)|^2$ and take

$$|S(0)|^2 = 23 \times 10^{24} \text{ cm.}^{-3}$$

along with $\gamma_{Cu} = 1.53$, $K = 0.36$ and $P = 0.030$ cm.$^{-1}$ we obtain the result that

$$f\gamma^2 = -0.048$$

This shows that only a small admixture of Ψ_2 is necessary to explain the copper hyperfine structure. The negative sign obtained for f is due to the promotion of an electron from a bonding orbital to an antibonding orbital.

Conclusions

Some insight has been gained on the nature of the molecular orbital which involves the odd electron. Since this bond has a fair amount of covalent character it is expected that the other sigma orbitals involving electrons from lower copper d orbitals are also appreciably covalent in character. This is in agreement with the fact that Cu Etio II, as well as other metallo etioporphyrins, is very stable toward acids.[19]

Although knowledge of β and β_1 cannot be obtained without prior knowledge of Δ_1 and Δ_2, we can do some speculating. As is pointed out by Gouterman[20] the similarity of the pi spectra of the metal porphyrins seems to indicate that d orbitals do not appreciably affect the pi spectrum. This is equivalent to saying that the d orbitals of π symmetry do not interact with the ring π orbitals. It seems then that the conclusion that $\beta_1 \approx 1$ can be drawn. For $\beta_1 = 1$ the expression for $g_\perp$ is satisfied if Δ_2 is taken to be 20,700 cm.$^{-1}$. The optical spectrum of Cu Etio II[19] suggests taking 18,950 cm.$^{-1}$ for Δ_2 which leads to $\beta_1 = 0.99$. If we further suppose that the probability of an electron being found near the nitrogens is the same for the excited B_{2g} and E_g states then

$$\beta^2 = 2\beta_1^2 - 1$$

For $\beta_1 = 0.99$ we obtain the results that $\beta = 0.98$ and $\Delta_1 = 27{,}000$ cm.$^{-1}$ [21,22]

The authors are indebted to Professor A. H. Corwin for the high purity sample of copper etioporphyrin II.

(19) W. S. Caughey and A. H. Corwin, THIS JOURNAL, **77**, 1509 (1955).

(20) M. Gouterman, Thesis, The University of Chicago, 1958.

(21) J. G. Erdman and A. H. Corwin, THIS JOURNAL, **68**, 1885 (1946).

(22) J. E. Bennett, J. F. Gibson and D. J. E. Ingram, *Proc. Roy. Soc.* (*London*), **A240**, 68 (1957).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, EMORY UNIVERSITY, ATLANTA, GEORGIA]

Proton Magnetic Resonance in Substituted Propenes. I. 2-Substituted Propenes

BY E. B. WHIPPLE, J. H. GOLDSTEIN AND LEON MANDELL

RECEIVED OCTOBER 26, 1959

The 40-megacycle n.m.r. spectrum of 2-chloropropene is described in detail, medium effects being used to effect a complete analysis including the vinyl proton assignments. Chemical shifts and spin-coupling constants are then reported and discussed for a series of ten 2-substituted propenes in dilute tetramethylsilane solutions.

In earlier work we have studied the effects of chemical substitution on the proton magnetic resonance shifts and couplings in the propargylic system $H{-}C{\equiv}C{-}CH_2X$, and the allenic system $H_2C{=}C{=}CHX$.[1-3] In these studies, the chemical shifts were measured in dilute cyclohexane (CH) or tetramethylsilane (TMS) solutions in order to minimize differences in environmental "medium effects," and the results were standardized in terms of the former solvent with respect to an external H_2O (liq.) reference.[1] The present work extends these methods to the substituted propenyl system, beginning with the 2-substituted propenes, $H_2C{=}CY{-}CH_3$.

Analysis of Spectra

Assuming effective averaging of the methyl group protons by internal motions, the appropriate general class[4] of the spectra is ABX_3 since negligible mixing occurs between the spin states for the vinyl (AB) and methyl (X_3) hydrogens. To these approximations, the 32×32 secular equation for the 5-spin systems can be factorized into blocks no larger than 2×2^5 and general solutions for the observed spectrum written in terms of the usual trigonometric parameters.[4] The essential results are summarized in Table I. In the limit where mixing between the vinyl states is also small ($\Delta\omega_{AB} >> J_{AB}$), the analysis may proceed

---

(1) E. B. Whipple, J. H. Goldstein, Leon Mandell, G. S. Reddy and C. R. McClure, THIS JOURNAL, **81**, 1321 (1959).

(2) E. B. Whipple, J. H. Goldstein and Leon Mandell, *J. Chem. Phys.*, **30**, 1109 (1959).

(3) E. B. Whipple, J. H. Goldstein and W. E. Stewart, THIS JOURNAL, **81**, 4761 (1959).

(4) J. A. Pople, W. G. Schneider and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Company, Inc., New York, N. Y., 1959, Ch. 6.

(5) R. W. Fessenden and J. S. Waugh, *J. Chem. Phys.*, **30**, 944 (1949).

TABLE I

STATIONARY STATES AND ALLOWED TRANSITIONS FOR 5-SPIN ($I = {}^1/_2$) SYSTEMS, TYPE ABX_3

State	Spin eigenfunction	Energy[a]
${}^1(\Gamma)_M$	$\alpha\alpha(\Gamma)_M$	$E_X + {}^1/_2(\omega_A + \omega_B) + {}^1/_4 J_{AB} + {}^1/_2 M(J_{AX} + J_{BX})$
${}^0(\Gamma)_M$	$(\cos\theta_M\alpha\beta + \sin\theta_M\beta\alpha)(\Gamma)_M$	$E_X - {}^1/_4 J_{AB} + C_M$
${}^{-1}(\Gamma)_M$	$\beta\beta(\Gamma)_M$	$E_X - {}^1/_2(\omega_A + \omega_B) + {}^1/_4 J_{AB} - {}^1/_2 M(J_{AX} + J_{BX})$

Transition	Frequency	Relative intensity
${}^1(\Gamma)_M - {}^0(\Gamma)_M$	${}^1/_2(\omega_A + \omega_B) + {}^1/_2 J_{AB} + {}^1/_2 M(J_{AX} + J_{BX}) \mp C_M$	$1 \pm \sin 2\theta_M$
${}^0(\Gamma)_M - {}^{-1}(\Gamma)_M$	${}^1/_2(\omega_A + \omega_B) - {}^1/_2 J_{AB} + {}^1/_2 M(J_{AX} + J_{BX}) \pm C_M$	$1 \pm \sin 2\theta_M$
${}^1(\Gamma)_{M+1} - {}^1(\Gamma)_M$	$\omega_X + {}^1/_2(J_{AX} + J_{BX})$	N
${}^{-1}(\Gamma)_{M+1} - {}^{-1}(\Gamma)_M$	$\omega_X - {}^1/_2(J_{AX} + J_{BX})$	N
${}^0(\Gamma)_{M+1} - {}^0(\Gamma)_M$	$\omega_X \pm (C_{M+1} - C_M)$	$N(\cos\theta_{M+1}\cos\theta_M + \sin\theta_{M+1}\sin\theta_M)^2$
	$\omega_X \pm (C_{M+1} + C_M)$	$N(\cos\theta_{M+1}\sin\theta_M - \sin\theta_{M+1}\cos\theta_M)^2$

$$C_M = {}^1/_2\{[(\omega_A - \omega_B) + M(J_{AX} - J_{BX})]^2 + J_{AB}^2\}^{1/2}$$

$$M = M_X$$

$$C_M \sin 2\theta_M = {}^1/_2 J_{AB}$$

$$N = \begin{cases} 3 \text{ for } A_1 \text{ transitions involving } |M| = {}^3/_2 \\ 4 \text{ for } A_1 \text{ transitions involving } |M| = {}^1/_2 \text{ only} \\ 2 \text{ for } E \text{ transitions involving } |M| = {}^1/_2 \text{ only} \end{cases}$$

[a] In units of h.

directly by simple multiplet rules[6] with due allowances for overlap in the AB patterns. This can be seen by expanding the general expression for C_M in Table I and neglecting terms higher than first order. Most of the systems reported here approach this limit.

A more complex situation occurs when the AB shifts are nearly degenerate and due to the relatively small couplings the spectrum tends to be poorly resolved. This is illustrated in the 2-chloropropene (TMS) spectrum shown in Fig. 1.[7] Since the X group lines are still symmetrical about ω_X, the center of gravity of the methyl group spectrum gives directly its shift, and the quantity $|J_{AX}+J_{BX}| = 2.08$ c.p.s. is determined directly from the splitting of the two most intense lines. It is difficult to assign precise values to the remaining variables, however. Advantage can be taken of the fact that chemical shifts are as a rule much more sensitive to the environment than are nuclear spin couplings, which may allow one to obtain an independent measurement of the latter in solvents which through intermolecular effects largely remove the AB degeneracies.[3] Thus the 2-chloropropene spectrum in benzene solution has the appearance in Fig. 2, which approaches the simple multiplet limit where the analysis is straightforward. From the outer lines in the methyl group spectrum, the value $|J_{AX}+J_{BX}| = 2.03$ agrees within the error of the measurements with the previous value, supporting the assumption that the couplings do not change. From the splitting of the inner pair of methyl group lines, the value $|J_{AX}-J_{BX}| = 0.73$ gives $J_{AX} = 1.38$ and $J_{BX} = 0.65$, the A proton having been labelled by the stronger methyl group coupling. From the five high-field vinyl lines it is apparent that $J_{AX} \cong J_{AB}$, and this also accounts for the qualitative appearance of the B group spectrum to lower field. The best over-all fit occurs with $J_{AB} = 1.3$ c.p.s. Using these values for the couplings, the spectrum in TMS can then be treated in terms of the single variable $\Delta\omega = \omega_A - \omega_B$, the indicated value being $\Delta\omega = 1.2$ c.p.s., which gives the results shown in Fig. 3.

Fig. 1.—Spectrum of 2-chloropropene in tetramethylsilane solution.

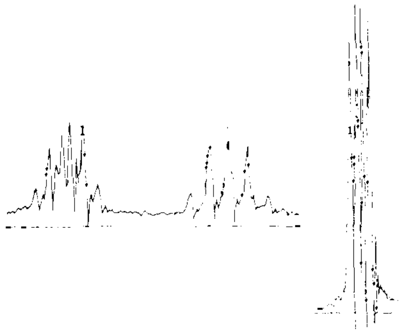


Fig. 2.—Spectrum of 2-chloropropene in benzene solution. (Vinyl group is at left.)

Experimental values for the shifts and couplings in a variety of 2-substituted propenes are summarized in Table II. In most cases the spectra could be analyzed directly by a procedure similar to that for 2-chloropropene (B). The methallyl halide spectra, Fig. 4, were further complicated by methylene group interactions but the patterns were otherwise straightforward. The A and B assignments in Table II are made on the basis of $|J_{AX}|>|J_{BX}|$ rather than on the basis of chemical shifts. The uncertainties in the J_{AB} couplings are generally greater than for the long-range interactions, J_{AX} and J_{BX}.

---

(6) H. S. Gutowsky, D. W. McCall and C. P. Slichter, *Phys. Rev.*, **84**, 589 (1951). E. L. Hahn and D. E. Maxwell, *ibid.*, **84**, 1286 (1951).

(7) Spectra were measured at 40 megacycles on the Varian Model 4300B High-Resolution System. ω refers to the chemical shifts in c.p.s. at the operating frequency and δ to the shifts in p.p.m.

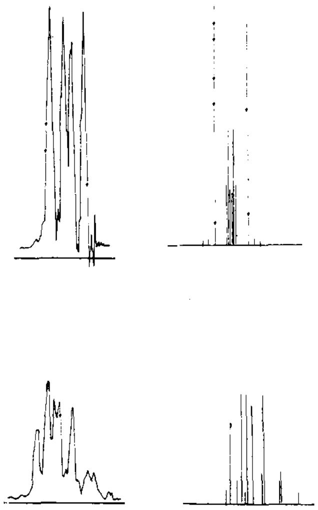


Fig. 3.—Observed and calculated spectra for 2-chloropropene. (Upper figure is methyl group.)

Discussion of Results

The first question that arises concerning the data in Table II is the geometrical assignment of the vinyl protons. It is assumed for this purpose that the relative magnitudes of the couplings will be consistent for the series. This is suggested by the rather constant difference of 0.6 c.p.s. between the J_{AX} and J_{BX} couplings over the range of Y substituents.

Table II

Chemical Shifts[a] and Coupling Constants in 2-Substituted Propenes, $H_2C{=}CY{-}CH_3$[b]

Y Subst.	$\delta_A{}^\infty$	$\delta_B{}^\infty$	$\delta_X{}^\infty$	J_{AX}	J_{BX}	J_{AB}
$-Br$	−0.42	−0.24	2.82	1.4	0.8	2.0
$-Cl$	.03	.00	2.99	1.38	.65	1.25
$-OCOCH_3$	.53	.45	3.19	1.2	.6	1.0
$-OCH_3$	1.3	1.3	3.31	..	..	..
$-CHO$	−1.08	−0.78	3.27	1.6	1.0	1.1
$-CN$	−0.58	− .47	3.15	1.7	1.15	1.0
$-CH_3$	.42	.42	3.36	1.25	1.25	..
$-CH_2Cl$	.20	.05	3.24	1.5	0.85	1.6
$-CH_2Br$	.20	.01	3.21	1.5	.8	1.5
$-CH_2I$	.24	− .09	3.17	1.5	.8	1.5

[a] Relative to H_2O (liq.) external reference for dilute solution in cyclohexane. [b] Parameters listed according to ABX_3 notation with A defined by $|J_{AX}| > |J_{BX}|$.

From the chemical shifts of 2-chloropropene in TMS and benzene solutions, the "specific medium effects," $\beta_n{}^1$, can be approximated[8] for the three proton types, the results being summarized in Table III. Similar effects in acetone solutions are also recorded, the small values in this solvent indicating that association shifts are relatively unimportant. The medium effects in benzene solution are thus by inference primarily anisotropic.[9] The comparable effects in the later solvent on the vinyl proton "A" and the methyl protons suggest that these lie on the same side of the solute molecule. The differences probably are due to a tendency on the part of the solute to be oriented with its dipole moment pointing away from the region of high π-electron density above and below the plane of the solvent molecule (Fig. 5). This reasoning would assign the greater long-range coupling to the vinyl hydrogen *cis* to the methyl group. To confirm the assignment, similar measurements were performed on vinyl chloride solutions, where the assignments are known,[10] and the data recorded in Table III compares favorably with the assigned results in 2-chloropropene. A similar trend was observed, but not measured, in 2-bromopropene solutions.

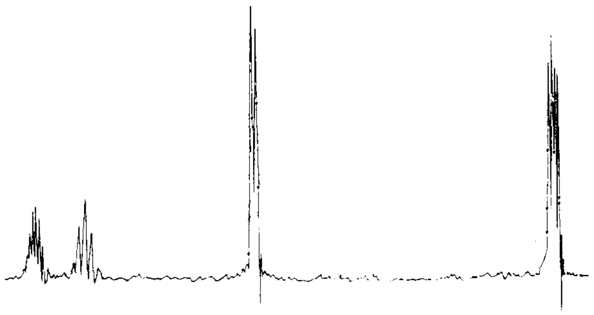
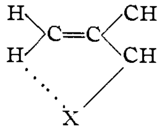


Fig. 4.—Spectrum of methallyl iodide in tetramethylsilane solution.

The assigned order of couplings, *cis* > *trans*, is consistent with results reported by Alexander[11] in butene-1, and by Pople, Schneider and Bernstein[12] in α-methylstyrene. It is also interesting to note at this point that the "A" shifts in methallyl halides are affected less by the allylic substituent than are the corresponding "B" shifts, which could be explained on the basis of direct interactions of the type indicated by I.



I

While the data reported here give little information concerning the relative signs of the various couplings, some tentative conclusions can be drawn by analogy with other systems. The 2-chloropropene spectrum requires that the long-range couplings have the same relative signs. Results by Waugh and Fessenden[6] and by Mortimer[13] on related systems indicates that these signs differ from the larger couplings between protons separated by two carbon atoms, however, and unpublished data obtained in this Laboratory for *cis* and *trans* 1-bromopropene point to the same conclusion.[14] Since the larger couplings are probably positive,[15] a negative value is indicated for the long-range couplings in 2-substituted propenes. The *gem* couplings, J_{AB}, are more uncertain

---

(8) More precise values are obtained by extrapolation to infinite dilution in the various solvents.

(9) A. A. Bothner-By and R. E. Glick, *J. Chem. Phys.*, **26**, 1651 (1957).

(10) E. B. Whipple and J. H. Goldstein (unpublished results).

(11) S. Alexander, *J. Chem. Phys.*, **28**, 358 (1958).

(12) J. A. Pople, W. G. Schneider and J. H. Bernstein, ref. 4, pp. 238–246.

(13) F. S. Mortimer, *J. Mol. Spec.* (to be published).

(14) E. B. Whipple, J. H. Goldstein and J. P. Kokko (unpublished results).

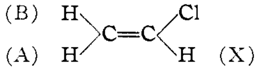
(15) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).

TABLE III

MEDIUM EFFECTS[a] ON CHEMICAL SHIFTS IN 2-CHLOROPROPENE AND VINYL CHLORIDE

Solute	Solvent	δ_A	δ_B	δ_X	$10(2\pi/3)(K - K_S)$[b]	β_A	β_B	β_X
2-Chloropropene[c]	Cyclohexane	0.03	0.00	2.99	...	..	..	..
2-Chloropropene	Acetone	.22	.33	..	−0.312	−0.12	0.02	..
2-Chloropropene	Benzene	.73	.49	3.79	.010	.71	.50	0.80
Vinyl chloride[d]	Cyclohexane	− .23	− .35	−1.15	...	..	..	..
Vinyl chloride	Benzene	.61	.30	−0.36	.01	.85	.66	0.80

[a] Approximate values determined from single measurements in dilute solutions. [b] See ref. 1 for susceptibility data. [c] ABX_3 notation with A proton specified by $|J_{AX}| > |J_{BX}|$. [d] Notation:



since theoretical calculations point to positive, negative or zero values depending on the HCH bond angle.[16] The 2-chloropropene and 2-bromopropene couplings probably are negative by analogy with closely corresponding values in the vinyl; greater electronegativity of the 2-substituent tends to enhance slightly the 1,3 couplings in this series. Opposite trends have been observed in a number of different systems where substitution occurs in a terminal position.[1,2,17]

The vinyl proton shifts show a greater sensitivity to the Y substituent than do the methyl shifts over the series in Table II, and the trends are qualitatively consistent with inductive and mesomeric effects attributable to the 2-substituents. This is particularly apparent in the extreme cases, isopropenyl ether and 2-methylacrolein. No precise correlation is obtained, on the other hand, between the vinyl shifts and Hammett constants[18] for the substituent, so that either these constants are not appropriate in these systems or more probably that other considerations are important in the vinyl proton shieldings. For example, the previously mentioned behavior in methallyl halides points to direct interactions similar to I with nonlinear Y substituents, and long-range anisotropic shieldings may be appreciable even when steric interactions are unimportant.[19] In the case of linear 2-substituents, for example, an anisotropy $\Delta\chi = \chi_{\parallel} - \chi_{\perp}$ in the magnetic susceptibility of Y would affect the various protons in approximate proportion to the value of $\Delta\chi r_i^{-3}$ $(3 \cos^2 \alpha_i - 1)$ measured from the center of the group and relative to an axis along the $=C-Y$ bond. Choosing $Y = -C \equiv N$ as a case in point, and approximating the bond-lengths and angles from structural data by Lide[20] and Costain,[21] the effect is predicted to be greater at the vinyl proton *trans* to the substituent than at the *cis* proton, due of course to the angle term. The calculated anisotropic effect is somewhat greater in the methyl group than at either vinyl proton.

The authors wish to acknowledge their sincere appreciation for the support extended to this work by the National Institutes of Health [Research Grant A-2397(C2)] and Schering Corporation, Bloomfield, N. J.

---

(16) H. S. Gutowsky, M. Karplus and D. M. Grant, private communication.

(17) A. A. Bothner-By and R. E. Glick, *J. Chem. Phys.*, **25**, 360 (1956).

(18) R. W. Taft, Jr., THIS JOURNAL, **79**, 1045 (1957).

(19) H. M. McConnell, *J. Chem. Phys.*, **27**, 226 (1957).

(20) D. R. Lide, Jr., and D. E. Mann, *ibid.*, **27**, 868 (1957).

(21) C. C. Costain and B. P. Stoicheff, *ibid.*, **30**, 777 (1959); W. S. Wilcox and J. H. Goldstein, *ibid.*, **22**, 516 (1954).

[CONTRIBUTION FROM THE PIONEERING RESEARCH DIVISION, QUARTERMASTER RESEARCH AND ENGINEERING CENTER, U. S. ARMY, NATICK, MASSACHUSETTS]

Equilibrium Constant of Benzaldehyde Sodium Bisulfite

BY JOHN A. SOUSA AND J. DAVID MARGERUM

RECEIVED SEPTEMBER 21, 1959

The ultraviolet spectra of the sodium bisulfite addition complex of benzaldehyde are measured in water as a function of concentration at 13, 23 and 33°. The ultraviolet spectrum of the undissociated complex and the equilibrium constants for the dissociation of the complex in water are calculated. Values for the ΔH, ΔF and ΔS of dissociation are reported. The equilibrium constants are an order of magnitude smaller than those previously reported. The rate of dissociation of the complex is measured at 13° and the rate constants for dissociation and association are calculated. The solid bisulfite complex is found to exist as $C_6H_5CHO \cdot HSO_3Na \cdot {}^1/_2H_2O$.

A previous investigation[1] had determined the equilibrium constant for the formation of the sodium bisulfite complex of benzaldehyde by iodimetric titration of the compound, which was assumed not to be subjected to rapid dissociation as a result of the removal of sodium bisulfite. We have found that the rate of dissociation is fairly rapid. Therefore, the values of the equilibrium constant and the thermodynamic changes involved in the dissociation of benzaldehyde sodium bisulfite which were reported by Gubareva[1] would be expected to be incorrect.

The results of a spectrophotometric procedure for redetermining this thermodynamic data are reported here. It has the advantage that the measurements are made directly on the system without disturbing the equilibrium.

---

(1) M. A. Gubareva, *J. Gen. Chem.* (*U.S.S.R.*), **17**, 2259 (1947).