Determination of the rate and order of the reaction from broadening of the ring and butyl lines is straightforward. The reaction is second order with $k = 300\ M^{-1}$ sec.$^{-1}$ at 30°; the activation energy is 1.0 ± 0.5 kcal. per mole.

The principal point of interest is the possibility of detecting properties of an intermediate through the magnetic behavior of the hydroxyl proton. The initial and final magnetic environments of an hydroxyl proton undergoing transfer are identical. Broadening of its resonance would be produced by a sufficiently strong magnetic pulse in transit. Application of the theory of McConnell and Berger,[2] or in the limit of weak impulses of a random walk model,[3] or the appropriate modification of BPP theory[4] lead to the same result. For pulses of duration τ each accompanied by a frequency shift δ the contribution to $1/T_2$ is $kc(2\pi\delta\tau)^2[1 + (2\pi\delta\tau)^2]^{-1}$ where k is the rate constant and c the concentration of radical. Under the previously mentioned assumption, values of $2\pi\delta\tau$ ranging from 0.4 ± 0.1 at 60° to 0.7 ± 0.1 at 27° were obtained. If δ corresponds to a splitting of twenty gauss in the intermediate, the duration of the intermediate is $\tau = 1 \times 10^{-9}$ sec. at 60° and $\tau = 2 \times 10^{-9}$ sec. at 27°.

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(5) Shell Fellow for 1961–1962.

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VALENCE BOND INTERPRETATION OF THE ADDITIVITY RELATION FOR C^{13}-PROTON COUPLING IN SUBSTITUTED METHANES[1]

Sir:

Several additivity relations have been pointed out recently[2–4] for the internuclear coupling constants observed in high resolution n.m.r. spectra. One involves the constancy of the three H–H coupling constants in monosubstituted ethylenes.[2] Another concerns the additivity of substituent effects upon the C^{13}–H coupling in substituted methanes.[4] Such observations are of considerable potential value to valence theory, but thus far detailed interpretations of the results have not appeared. The case of the monosubstituted ethylenes is the least tractable because it includes three H–H coupling constants, which originate in small deviations from the perfect pairing electronic structure. The coupling between directly bonded nuclei, such as C^{13}–H, is simpler to treat inasmuch as it depends almost entirely upon the perfect pairing structure.[5,6] The main purpose of this note is to report that by taking advantage of the latter aspect, and by making certain other reasonable approximations, we have developed a simple interpretation of the additivity relation for J_{CH}.

Malinowski's results[4] for the substituted methanes CHXYZ, may be summarized as

$$J_{CH}\,(CHXYZ) = \zeta_X + \zeta_Y + \zeta_Z \qquad (1)$$

where ζ_X is a numerical constant for substituent X, determined from experiment as

$$\zeta_X = J_{CH}(CH_3X) - (2/3)J_{CH}(CH_4) \qquad (2)$$

Our interpretation is based on the correlation which has been found[6–8] between J_{CH} and the s character of the carbon orbital used in the C–H bond.

For methane, a valence bond adaptation[6] of Ramsey's general formulation[9] has shown that the Fermi contact term governs J_{CH}. Moreover, the calculation made of the C^{13}–H coupling[6] gives J_{CH} to be a function primarily of λ, a parameter related to the C–H bond polarity. Upon extension of this approach to the substituted methanes we find that

$$J_{CH}(CHXYZ) = A\eta^2\alpha_H^2/\Delta E \qquad (3)$$

where A is a collection of constants, ΔE is the average excitation energy,[9] and η is the normalization constant of the perfect pairing ground state wave function

$$u(i,j) = \eta[\phi_C(i)\phi_H(j) + \phi_H(i)\phi_C(j) + \lambda\phi_C(i)\phi_C(j)] \qquad (4)$$

The quantity α_H^2 is the fractional 2s character of the carbon hybrid orbital

$$\phi_C = \alpha s_C + \sqrt{1 - \alpha^2}\, p_{\sigma_C} \qquad (5)$$

used in the C–H bond. To a good approximation, Eq. (3) reduces to

$$J_{CH}(CHXYZ) \approx J_o\alpha_H^2 = 4J_{CH}(CH_4)\alpha_H^2 = 500\alpha_H^2 \text{ c.p.s.} \qquad (6)$$

because ΔE is not very sensitive to substituents and we have found that η, which depends upon α_H and λ, is nearly constant for the ranges of α_H and λ involved.

Two additional assumptions are required. The first is that all of the carbon 2s orbital is used in forming the C–H, C–X, C–Y and C–Z bonds, or

$$\alpha_X^2 + \alpha_Y^2 + \alpha_Z^2 + \alpha_H^2 = 1 \qquad (7)$$

The second concerns the manner in which a substituent perturbs the distribution of the carbon 2s orbital among the four bonds. As a model, consider the latter to be four interconnected potential wells for the 2s electron. In CH_4 the wells are of the same shape and depth and thus contain the same fraction of the 2s electron, $\alpha_H^2(CH_4) = 1/4$. Introduction of a substituent X changes the "depth" of the corresponding well by an effective,

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characteristic (+ or −) amount Δx, which we assume to be independent of the other substituents. In CHXYZ, the resulting difference in the 2s electron content at the bottom of the wells is $\Delta x + \Delta y + \Delta z$, which must be accommodated by a change in the *common level* at the top of each of the four wells. This, by means of Eq. (7), leads to

$$\Delta x + \Delta y + \Delta z = 4[\alpha_H^2(\mathrm{CHXYZ}) - (1/4)] \quad (8)$$

For monosubstituted derivatives, Eq. (8) reduces to

$$\Delta x = 4[\alpha_H^2(\mathrm{CH_3X}) - (1/4)] \quad (9)$$

which enables us to eliminate Δx, Δy, and Δz from Eq. (8) and obtain

$$\alpha_H^2(\mathrm{CHXYZ}) = [\alpha_H^2(\mathrm{CH_3X}) - (2/3)\alpha_H^2(\mathrm{CH_4})] + [\alpha_H^2(\mathrm{CH_3Y}) - (2/3)\alpha_H^2(\mathrm{CH_4})] + [\alpha_H^2(\mathrm{CH_3Z}) - (2/3)\alpha_H^2(\mathrm{CH_4})] \quad (10)$$

And, finally, the relation between J_{CH} and α_H^2, in Eq. (6), converts this to

$$J_{\mathrm{CH}}(\mathrm{CHXYZ}) = \zeta_X + \zeta_Y + \zeta_Z \quad (11)$$

which is exactly the form of additivity observed by Malinowski.[4] A two-center molecular orbital of the form

$$\psi = c_1(1s_H) + c_2(2s_C) + c_3(2p_{\sigma_C}) \quad (12)$$

yields essentially the same equation as Eq. (6), after which the analysis is identical.

The formalism introduced above enables one to use experimental values of J_{CH} to obtain not only α_H^2 but also α_X^2. The relation of these quantities to parameters such as bond angles and lengths is under investigation and will be reported later[10] along with details of the present work. In addition, it appears that substituent parameters obtained from the monosubstituted methanes can be applied to J_{CH} in substituted ethylenes.

The $\mathrm{Si^{29}}$–H coupling has been observed in $\mathrm{SiH_4}$ and in a number of derivatives.[11] However, our inspection of the results shows that the substituent effects are not additive. Nonetheless, the deviations from additivity are systematic in that for the halosilanes, the deviations follow the sequences: $\mathrm{SiHX_3} > \mathrm{SiH_2X_2}$; and F > Cl > Br > I. Several factors can contribute to these effects, of which the most likely appears to be the use by Si of 3d orbitals, the importance of which is suggested also by the dependence of J_{HH} upon the H–Si–H angle.[11,12] The inclusion of 3d orbitals in Eq. (5) may prevent Eq. (6) from applying to J_{SiH}, and also it could affect Eq. (7). This presents the attractive possibility of learning something about the d hybridization from the deviations, to compensate for the more difficult nature of the analysis.

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THE REACTIONS OF ATOMIC CARBON WITH ETHYLENE[1]

Sir:

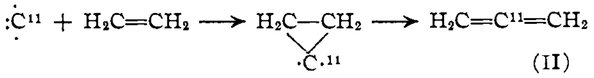
The reactions of atomic carbon with ethylene have been studied. Recoil $\mathrm{C^{11}}$ from a nuclear reaction was introduced into the gaseous reagent, and analysis made for the $\mathrm{C^{11}}$-labeled radioactive products by techniques outlined previously.[2] Results are summarized in Table I. Column I shows products obtained with pure ethylene, column II with oxygen added as a radical scavenger, and column III is representative of runs containing a large excess of neon to thermalize (*i.e.*, remove excess kinetic energy from) the carbon atom before reaction.

As with the alkanes previously reported,[2] the main products are highly unsaturated hydrocarbons. The high yield of acetylene, in particular, probably results largely from the C–H bond insertion process as postulated for the alkanes.

$$\cdot\ddot{\mathrm{C}}\cdot^{11} + \mathrm{H_2C{=}CH_2} \rightarrow \underset{\cdot}{\dot{\mathrm{C}}}\mathrm{H_2} + \mathrm{HC^{11}{\equiv}CH} \quad \text{(I)}$$

However, there are two significant differences between ethylenic hydrocarbons in general and saturated systems: (1) in the presence of $\mathrm{O_2}$ the CO yield is appreciably less with alkenes than with alkanes. This indicates the alkenes are more reactive. (2) The yields of products containing one more carbon atom than the reacting hydrocarbon are considerably higher with alkenes than with alkanes. Thus about twice as much allene and methylacetylene form from ethylene, as do propane and propylene from ethane.

The most obvious and satisfactory explanation of these observations is that the C atom can react directly with the double bond to form a π-bonded species. This intermediate then can rearrange to allene[3]



$$:\!\dot{\underset{\cdot}{\mathrm{C}}}{}^{11} + \mathrm{H_2C{=}CH_2} \longrightarrow \mathrm{H_2C{-}CH_2}\ (\text{bridged by } \cdot\mathrm{C}\cdot^{11}) \longrightarrow \mathrm{H_2C{=}C^{11}{=}CH_2} \quad \text{(II)}$$

(In the case of higher alkenes, the corresponding substituted allene largely isomerizes to a conjugated diene.) We are presently attempting to confirm this mechanism by showing that $\mathrm{C^{11}}$ appears in the central position of allene.[4]

The intermediate formed by this double bond addition also has sufficient energy to decompose with bond rupture. It may thus contribute to the yield of acetylene-$\mathrm{C^{11}}$ from ethylene.

The cyclopropane observed is consistent with the previous hypothesis that a few per cent of the C atoms react by H atom pick-up from hydrocarbons[2] to form $\mathrm{C^{11}H_2}$. This will react in a characteristic

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