

undeuterated ester, and that ionization resulting from transfer of the deuterium is seen at mass 62 in the other spectra. The mass 62 peak in the second spectrum represents only 8% of the total ionization due to this process and shows that the availability of the protons on the terminal methyl group is less than statistical. In the third spectrum the mass 62 peak is more intense; it makes up 37% of the total ionization due to the rearrangement process, indicating that the protons on the carbon  $\delta$  to the carbonyl group are favored. The mass 62 peak in the last spectrum represents only 16% of the total intensity of the mass 61 and mass 62 peaks. This result indicates that direct transfer of a proton to the adjacent oxygen is not highly favored, a result also indicated by the data of McLafferty<sup>4</sup> on deuterated 2-butyl acetate.

**Table III:** Effect of Deuteration on the Acetate Rearrangement Peaks of 1-Butyl Acetate

	$\begin{array}{c} \text{C} \\   \\ \text{C}=\text{O} \\   \\ \text{O} \\   \\ \text{C} \\   \\ \text{C} \\   \\ \text{C} \\   \\ \text{C} \end{array}$	$\begin{array}{c} \text{C} \\   \\ \text{C}=\text{O} \\   \\ \text{O} \\   \\ \text{C} \\   \\ \text{C} \\   \\ \text{C} \\   \\ \text{CD} \end{array}$	$\begin{array}{c} \text{C} \\   \\ \text{C}=\text{O} \\   \\ \text{O} \\   \\ \text{C} \\   \\ \text{C} \\   \\ \text{CD} \\   \\ \text{C} \end{array}$	$\begin{array}{c} \text{C} \\   \\ \text{C}=\text{O} \\   \\ \text{O} \\   \\ \text{CD}_2 \\   \\ \text{C} \\   \\ \text{C} \\   \\ \text{C} \end{array}$
$m/e$	Ionization, %			
59	0.08			
60	0.16	0.14	0.15	0.10
61	5.42	5.09	3.45	5.14
62	0.16	0.48	2.03	1.01
63	0.05	0.08	0.07	0.10

The 2-monodeuterio-1-butyl acetate was not synthesized but the availability of this hydrogen for the rearrangement can be surmised. As shown above, the deuterium on the dideuterated C-1 and the monodeuterated C-3 and C-4 are available for transfer 16, 37, and 8% of the time, respectively, for a total of 61%. The second two values would be considerably greater if each position were fully deuterated (approximately  $37\% \times 2$  and  $8\% \times 3$ ); consequently the transfer of a proton (deuteron) from the C-1 would not seem to be significant. These results indicate that in this rearrangement of the 1-butyl acetate the protons on C-3 of the butyl group participate to a greater extent than do those on the C-1 or C-2, contrary to the observation of Colomb, *et al.*, from the mass spectra of deuterated hexyl butyrate and valerate.<sup>2</sup>

In addition, data exist for deuterated ethyl acetates which indicate that deuteration on the C-1 of the ethanol<sup>5</sup> or the C-2<sup>19</sup> leads to a nearly statistical selection of deuterium in formation of this rearranged ion. Thus, it is possible that for some molecules the two-proton transfer process proceeds by a mechanism different from that proposed by McLafferty.<sup>4</sup> The present data suggest a selective transfer of one proton from C-3 followed by a random selection of the second proton from the other protons in the alcohol moiety. Such a random selection will always occur if the second transfer proceeds at a rate significantly less than the rate of H-D exchange within the alcohol group.

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(19) Unpublished data of authors.

(20) Reference to a company or product name does not imply approval or recommendation of the product by the U. S. Department of Agriculture to the exclusion of others that may be suitable.

## Long-Range Metal-Proton Coupling Constants in Vinyl Metallic Compounds

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Metal-proton spin-spin coupling constants for metals with spin  $1/2$  have shown several interesting features in compounds of the type  $(\text{C}_2\text{H}_5)_n\text{X}$ .<sup>1</sup> In all cases, except the fluoro compound,<sup>1</sup> vicinal coupling constants are of greater magnitude than geminal couplings and are of opposite sign. For ethyl fluoride the absolute magnitudes are reversed with  $J_{\text{CH}_3-\text{F}} > J_{\text{CH}_2-\text{F}}$  and the relative signs are identical.

Several mechanisms, including contributions arising from electron-orbital interaction<sup>2</sup> and involvement of d-electrons in the C-X bond<sup>1</sup> in addition to Fermi contact interaction, have been proposed to account for these coupling constants. Recently Maher and Evans<sup>3</sup> interpreted long-range thallium( $\text{Tl}^{205}$ )-proton coupling constants qualitatively in terms of a Fermi contact interaction arising from a large effective nuclear charge on the thallium atom. A similar coupling mechanism was suggested for other metal alkyls.<sup>3</sup>

(1) S. L. Stafford and J. D. Baldeschwieler [*J. Am. Chem. Soc.*, **83**, 4473 (1961)] gave a summary of metal-proton  $J$  values for ethyl derivatives.

(2) P. T. Narasimhan and M. T. Rogers, *J. Chem. Phys.*, **34**, 1049 (1961).

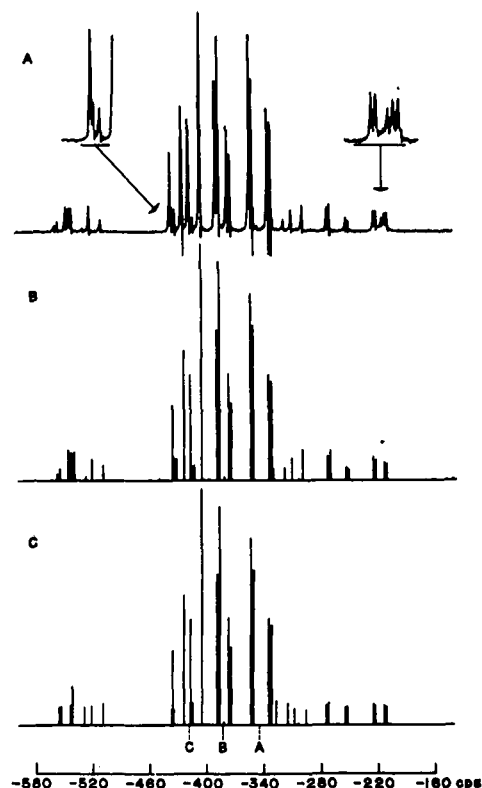
The coupling mechanism for long-range metal-proton coupling constants in vinyl metalics is less certain and in order to clarify this we have measured coupling constants at 60 Mc./sec. for vinyl metalics of the type  $X(\text{CH}=\text{CH}_2)_n$  where  $X = \text{Si}^{29}$ ,  $\text{Sn}^{117}$ ,  $\text{Sn}^{119}$ , or  $\text{Pb}^{207}$ . These results along with data for vinyl fluoride,<sup>4</sup> trivinylphosphine,<sup>5</sup> and thallium vinyl cations<sup>3</sup> are summarized in Table I. Metal-proton coupling constants were obtained from an analysis of satellite multiplets observed in spectra for neat vinyl metalics. For example, the three  $\text{Pb}^{207}$ -proton coupling constants are readily picked out by inspection of the satellites superimposed on the 60 Mc./sec. proton spectrum for tetravinyllead, Fig. 1. Comparison of calculated and observed spectra shows that relative signs for *gem*-, *cis*-, and *trans*- $\text{Pb}^{207}$ -proton couplings are identical (assumed positive, cf. Fig. 1) and of the same sign as the *cis* and *trans* proton-proton coupling constants.<sup>5,6</sup> Similar results have been noted for trivinylphosphine<sup>5</sup> at 60 Mc./sec. and tetravinyltin ( $\text{Sn}^{119}$ ).

**Table I:** Metal-Proton Coupling Constants for Vinyl Metalics  $X(\text{CH}=\text{CH}_2)_n$

Compound	$J_{X-H(cis)}^a$	$J_{X-H(trans)}$	$J_{X-H(gem)}$	Ref.
$\text{F}^{19}(\text{CH}=\text{CH}_2)$	$\pm 19.8^b$	$\pm 52.7$	$\pm 84.6$	4, 8
$\text{Si}^{29}(\text{CH}=\text{CH}_2)_4$	$\pm 8^c$	$\pm 22^c$		6
$\text{P}^{31}(\text{CH}=\text{CH}_2)_3$	$\pm 13.62$	$\pm 30.21$	$\pm 11.74$	5
$\text{Sn}^{117}(\text{CH}=\text{CH}_2)_4$	$\pm 86.1$	$\pm 174.1$	$\pm 91.2$	
$\text{Sn}^{119}(\text{CH}=\text{CH}_2)_4$	$\pm 90.4$	$\pm 183.0$	$\pm 96.0$	
	$\pm 90.4^d$	$\pm 183.1$	$\pm 98.3$	7
$\text{Hg}^{199}(\text{CH}=\text{CH}_2)_2$	$\pm 159.5$	$\pm 296.4$	$\pm 128.3$	
	$\pm 159.6^d$	$\pm 295.5$	$\pm 128.5$	7
$\text{Pb}^{207}(\text{CH}=\text{CH}_2)_4$	$\pm 161.7$	$\pm 330.1$	$\pm 212.4$	
$\text{Tl}^{205}(\text{CH}_2=\text{CH})\text{Tl}^{++}$	$\pm 1806$	$\pm 3750$	$\pm 2004$	3
$(\text{CH}_2=\text{CH})_2\text{Tl}^+$	$\pm 805$	$\pm 1618$	$\pm 842$	3

<sup>a</sup> *cis*, *trans*, and *gem* refer to the orientation of the proton relative to the metal atom. <sup>b</sup> All measurements were made at 60 Mc./sec. unless otherwise stated. <sup>c</sup> Estimated from  $\alpha$ -chlorovinyltrichlorosilane. <sup>d</sup> 40 Mc./sec.

Several features of the vinyl couplings are of interest. The three metal-proton coupling constants each show an increase in magnitude with increasing atomic number although the rates of increase differ, with the *trans* coupling constant showing the largest change. A linear correlation of coupling constants with atomic number was only observed for compounds within a given group of the periodic table, e.g., group IV-B. Somewhat surprisingly the increase in magnitude for  $J_{X-H}$  values in going from group II-B to group IV-B elements within a given period is of the same order as that observed in going from elements in one period



**Figure 1.** Observed and calculated proton magnetic resonance spectra for tetravinyllead ( $\text{Pb}^{207}$ ): A, observed spectrum for neat tetravinyllead at 60 Mc./sec. Tetramethylsilane used as an internal reference. The small signal at 217 c.p.s. is due to a trace impurity of a lead alkyl derivative. B, calculated spectrum with all  $J_{\text{Pb}^{207}-\text{H}}$  coupling constants positive. The letters A, B, and C refer to protons *cis*, *trans*, and *gem* to the metal atom. C, calculated spectrum with  $J_{\text{Pb}^{207}-\text{H}(gem)}$  assumed negative and of opposite sign to the *cis* and *trans* coupling.

to elements in the adjacent period.<sup>7</sup> The increase in  $J_{X-H}$  values within a given period parallels a corresponding increase in effective atomic number,  $Z_e$ .

Of additional interest are the relatively large *gem* metal-proton coupling constants for vinyl groups bonded to heavier elements in groups III to VI.  $J_{X-H(gem)}$  is larger than  $J_{X-H(cis)}$  in the majority of vinyl metalics studied. In contrast, the magnitudes of proton-proton coupling constants for all of the vinyl metalics fit into the normal sequence observed for vinyl groups, i.e.,  $J_{trans} > J_{cis} > J_{gem}$ .

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(6) S. Cawley and S. S. Danyluk, to be published.

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The relative magnitude and signs for proton- $F^{19}$  coupling constants in vinyl fluoride have been interpreted<sup>4,8</sup> in terms of Fermi contact interaction as the predominant coupling mechanism. Considering the other vinyl compounds the contact contribution to the X-H coupling would vary with the electron densities at the X and H nuclei and would be proportional to  $Z_{eX}^3 Z_{eH}^3 \gamma_X \gamma_H$ . The electron densities of  $ns$  valence electrons at the nucleus,  $|\psi_{ns}(0)|^2$ , increase in going from group II-B to group V in any given period and parallel a corresponding increase in  $Z_e$ .<sup>9</sup> An increase of  $|\psi_{ns}(0)|^2$  would also be expected with increasing atomic number within a given family, *i.e.*, group IV-B.<sup>10</sup> Accordingly, the trends in magnitude for metal-proton couplings in vinyl metalics indicate, at least qualitatively, that the contact contribution predominates in these systems also. Additional factors such as changes in hybridization in going from group II to group V compounds and  $d_{\pi}-p_{\pi}$  interaction along the C-X bond would also affect  $J_{X-H}$  although in the case of the latter any effect on the coupling constant would be relatively small.<sup>11</sup>

The reasons for the large *gem* coupling constants in vinyl derivatives of heavier elements are not readily apparent. Although a wide variety of factors (electronegativity, bond angle, substituents) are known to influence the relative signs and magnitudes of geminal and vicinal proton-proton coupling constants<sup>12</sup> these do not change sufficiently within a given family (*e.g.*, group IV-B) to account for the observed changes of  $J_{X-H}(\text{gem})$  and  $J_{X-H}(\text{cis})$ . However, it is of some interest to note that the ratio  $J_{X-H}(\text{gem})/J_{X-H}(\text{cis})$  increases with increasing  $s$ -electron density on the X nucleus. It is possible that an additional contribution to  $J_{\text{gem}}$  results from direct coupling "through space" analogous to the mechanisms proposed for unusually large vicinal couplings in metal alkyls<sup>13</sup> and saturated fluorine compounds.<sup>14</sup> Such an interaction would decrease rapidly with increasing interaction distance and would be less important for *cis* and *trans* couplings.

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### Mechanism of the Dependence of Yields upon pH and Solute Concentration in the $\gamma$ -Irradiation of Water

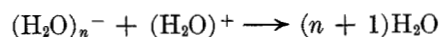
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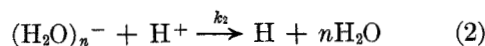
It was shown<sup>1</sup> in the radiolysis of water that the yields of oxidizing and reducing species, as well as the total decomposition of water, increase on going from neutral to acid solutions. Thus the 100-e.v. yield of total reducing species  $G(\text{red.})$  in *dilute* solutions increases from 2.85 at neutral pH to 3.7 at pH 0.5, that is an increase of  $\sim 30\%$ .  $G(\text{red.})$  is equal to  $G(\text{H}_2\text{O})_n^- + G_H$ , the sum of the two reducing entities formed from the water by the action of ionizing radiations. On irradiation of chloro compounds it was suggested,<sup>2</sup> and later shown,<sup>3</sup> that the increase of  $G(\text{red.})$  with  $[\text{H}^+]$  and/or solute concentration is due mainly to an increase of reducing species which are initially produced in the form of electrons  $(\text{H}_2\text{O})_n^-$ . The effect of the acid is to reduce in the spurs (radical scavenging by the solute) the back reaction to form water



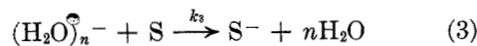
possibly also



and consequently increase the yield as follows



The same increase<sup>3</sup> can be obtained in neutral solution when certain electron-accepting solutes are present in concentrations equivalent to  $[\text{H}^+]$  at low pH



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