

**Table II.** Atomic Charges, Correlation Corrections, and Binding Energies

System	Conformation <sup>a</sup>	Charges on atoms (no. of electrons)	Correlation <sup>b</sup> correction around O or F center, kcal/mol		$\Delta E$ , <sup>c</sup> kcal/mol	
					Calcd <sup>d</sup>	Exptl
HF		F	9.44	21.8		
(HF) <sub>2</sub>		H	0.56			
		F	9.46	45.6	5.3	7 <sup>e</sup>
(HF) <sub>4</sub>	Sym	H	0.54			
		F	9.53	105		
(HF) <sub>6</sub>	Asym	H	0.47			
		F	9.48	95	25	28 <sup>e</sup>
(HF) <sub>6</sub>	Sym	H	0.52			
		F	9.55	163	3-8	
(HF) <sub>6</sub>	Asym	H	0.45			
		F	9.49	146	40	42 <sup>e</sup>
H <sub>2</sub> O		H	0.51			
		O	8.72	33.1		
(H <sub>2</sub> O) <sub>2</sub>		H	0.64			
		O	8.75	69	6.4	5-7 <sup>f</sup>
(H <sub>2</sub> O) <sub>6</sub>	Sym	H <sub>int</sub>	0.61			
		O	8.85	235	11-16	
F-F-				49.5 <sup>g</sup>		
O-O-				46.0 <sup>g</sup>		

<sup>a</sup> All planar, LCAO wave functions. <sup>b</sup> Relative to neutral O or F. <sup>c</sup> Relative to monomers. <sup>d</sup> The numbers in this column give the stabilization energies calculated from our wave functions corrected for both correlation energy and the difference in zero-point energy (zpe) of (HF)<sub>n</sub> and nHF. For example, in the HF hexamer, the original 6H-F stretches are shifted downfield (decrease in zpe) but there are 24 additional vibrations. The additional vibrations are all very low frequency in this weak complex (for example, the F...F stretch has a zpe of roughly 100 cm<sup>-1</sup>). Assuming that the additional zpe is 100 cm<sup>-1</sup> per mode and that the zpe of each HF stretch decreases by 100 cm<sup>-1</sup>, one finds a zero-point correction of 1800 cm<sup>-1</sup> (5.1 kcal). Similar correlations are made for other asymmetric structures. In the symmetric structures, there is a dramatic decrease in H stretching frequency (e.g., the H-F stretching frequency changes from 400 cm<sup>-1</sup> in hydrogen fluoride to 1500 cm<sup>-1</sup> in FHF<sup>-</sup>), but also an increase in frequency for the new vibrations (F...F stretch in FHF<sup>-</sup> is 600 cm<sup>-1</sup>), so that one can crudely estimate the zero-point energy difference between (HF)<sub>6</sub> (symmetric) and 6HF as 5-10 kcal. In infinite two- and three-dimensional solids, the zero-point energy may actually be less than that of the monomers. For additional details on this zero-point energy correction, see E. Clementi and J. N. Gayles, *J. Chem. Phys.*, **47**, 3837 (1967). It is useful to record here computed binding energies when only the correlation correction is added. These are: (HF)<sub>2</sub>, 6.4 kcal/mol; (HF)<sub>4</sub>, 28.8, (HF)<sub>6</sub> sym, 13; (HF)<sub>6</sub> asym, 47; (H<sub>2</sub>O)<sub>2</sub>, 8.1; (H<sub>2</sub>O)<sub>6</sub> sym, 21. <sup>e</sup>E. U. Franck and F. Meyer, *Z. Electrochem.*, **63**, 571 (1959). <sup>f</sup>D. Eisenberg and W. Kauzmann, "The Structure and Properties of Water," Clarendon Press, Oxford, 1969. <sup>g</sup>Correlation energies for the neutral atoms were found from the difference between the nonrelativistic total experimental energies and the calculated Hartree-Fock total energies [A. Veillard and E. Clementi, *J. Chem. Phys.*, **49**, 2415 (1968)]. The known electron affinities [C. W. Scherr, J. W. Silverman, and F. A. Matsen, *Phys. Rev.*, **127**, 830 (1962)] were added to the experimental neutral atom energies to obtain the experimental negative ion energies. Hartree-Fock negative ion total energies are given in E. Clementi, *IBM J. Res. Devel. Suppl.*, **9**, 2 (1965).

buildup around the oxygens (or fluorines) and its values can be estimated by weighting the difference in correlation energy between O and O<sup>-</sup> (or F and F<sup>-</sup>) with the relative charge shifts. A Mulliken population analysis of the LCAO MO wave function was used to obtain the atomic charges. This is a reasonable estimate, valid to first order, because correlation corrections do not change the charge distribution to this order, and because the arbitrary Mulliken charge separation assumption and the several effects tending to

distort a true representation of the charge surrounding an oxygen (or fluorine) center do not significantly modify *relative* charge shifts of monomers and polymers. Correlation corrections computed by the above method are tabulated in Table II. The differential correlation energy between the monomer and cyclic polymer is added to the *ab initio* LC(Hartree-Fock)AO relative energies of Table I. After the further addition of differential zero-point energies (footnote *d*, Table II), the resultant energies of formation can be compared with experimental values (Table II). Assuming the approximations discussed above, we see that cyclic, symmetric, planar water hexamers are predicted to have a lower internal energy than six isolated water molecules. This implies that anomalous water can, in principle, exist as a well-defined entity with its unique and heretofore unrecognized type of chemical binding. However, it is clear that the asymmetric hexamer is considerably more stable than the symmetric hexamer, and it is believed true that symmetric hexamers will have a lower entropy than free water molecules. Thus there remains a very substantial problem in regard to the formation mechanism for a substance like anomalous water that has been in no way elucidated by this work.

**Acknowledgment.** We wish to thank the Chemistry Programs Section of the National Science Foundation (Grant No. GP-8907) for support of this research.

Leland C. Allen and Peter A. Kollman

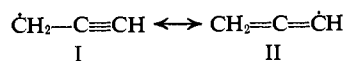
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Received March 7, 1970

### Electron Spin Resonance of Free Radicals from Acetylenes and Allenes

Sir:

A number of studies have been carried out to establish the structure of free radicals derived from acetylenic compounds by hydrogen abstraction.<sup>1,2</sup> The principal C<sub>3</sub>H<sub>3</sub> radical obtained from methylacetylene can be represented by the valence bond structures I and II which are designated propargyl and allenyl, respectively. Chemical studies<sup>3-5</sup> have led to divergent conclusions regarding the structure of the C<sub>3</sub>H<sub>3</sub> radical.



Electron spin resonance (esr) represents the most direct method for the study of the electronic structure of free radicals. An incompletely resolved and broadened esr spectrum of the C<sub>3</sub>H<sub>3</sub> radical trapped in the solid state at 77°K was obtained by direct photolysis

(1) (a) J. Collin and F. P. Lossing, *J. Amer. Chem. Soc.*, **79**, 5848 (1957); *Can. J. Chem.*, **35**, 778 (1957); (b) G. Giacometti, *ibid.*, **37**, 999 (1959).

(2) (a) R. Srinivasan, *J. Amer. Chem. Soc.*, **82**, 5063 (1960); (b) P. Kebarle, *J. Chem. Phys.*, **39**, 2218 (1963).

(3) (a) C. Walling, L. Heaton, and D. D. Tanner, *J. Amer. Chem. Soc.*, **87**, 1715 (1965); (b) M. M. Martin and E. B. Sanders, *ibid.*, **89**, 3977 (1967).

(4) (a) M. L. Poutsma and J. L. Kartch, *Tetrahedron*, **22**, 2167 (1966); (b) R. M. Fantazier and M. L. Poutsma, *J. Amer. Chem. Soc.*, **90**, 5490 (1968); (c) M. L. Poutsma, *Tetrahedron Lett.*, 2925 (1969).

(5) M. C. Caserio and R. E. Pratt, *ibid.*, 91 (1967).

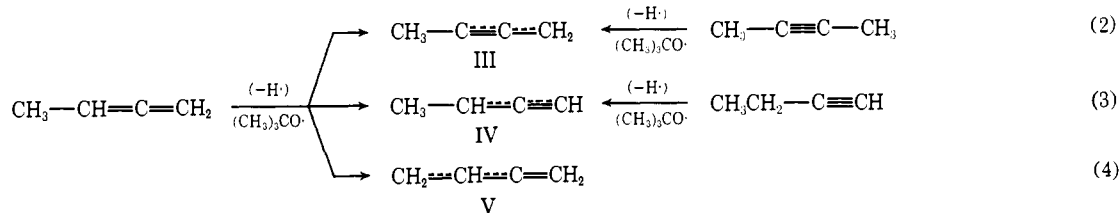
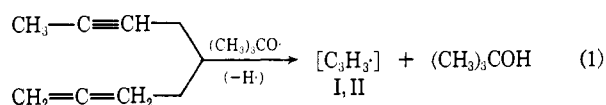
**Table I.** Hyperfine Coupling Constants of Radicals Derived from Acetylenes and Allenes<sup>a</sup>

C <sub>3</sub> H <sub>3</sub> radical and analogs <sup>b</sup>	Temp, °C	Source
$\begin{array}{c} 12.88(d) \\ \text{CH} \equiv \text{C} \cdots \text{CH}_2 \\ 18.92(t) \end{array}$	-120	Propyne, propadiene
$\begin{array}{c} 11.78(d) \\ \text{CH} \equiv \text{C} \cdots \text{CH} \cdots \text{CH}_3 \\ 18.70(d) \quad 19.62(q) \end{array}$	-111	Butyne-1, butadiene-1,2
$\begin{array}{c} 18.54(t) \\ \text{CH}_2 \equiv \text{C} \cdots \text{C} \cdots \text{CH}_3 \\ 12.37(q) \end{array}$	-68	Butyne-2, butadiene-1,2
$\begin{array}{c} 15.67(d) \text{H} \\ \text{C} \cdots \text{CH} \cdots \text{C} = \text{C} \\ 5.04(d) \quad \text{H}_{34,80}(d) \end{array}$	-143	Butadiene-1,2
$\begin{array}{c} 15.19(d) \text{H} \\ 11.88(q) \\ \text{CH}_3 \cdots \text{C} \cdots \text{C} \cdots \text{CH} \cdots \text{CH}_3 \\ 18.44(d) \quad 19.16(q) \end{array}$	-92	Pentyne-2 <sup>c</sup>
$\begin{array}{c} 11.39(d) \\ \text{HC} \equiv \text{C} \cdots \text{C}(\text{CH}_3)_2 \\ 17.82(s) \end{array}$	-150	3-Methylbutyne-1, 3-methylbutadiene-1,2
$\begin{array}{c} 15.11(d) \text{H} \\ \text{C} \cdots \text{C}(\text{CH}_3) \cdots \text{C} = \text{C} \\ 2.91(q) \quad \text{H}_{35,15}(d) \end{array}$	-150	3-Methylbutadiene-1,2
$\begin{array}{c} 14.69(d) \text{H} \\ \text{CH} \equiv \text{C} \cdots \text{CH} \cdots \text{CH}_2 \cdots \text{CH}_2 \cdots \text{C}_3\text{H}_7 \\ 18.6(q)^d \quad 0.51(t) \end{array}$	-73	Octyne-1
$\begin{array}{c} 11.84(d) \\ \text{CH} \equiv \text{C} \cdots \text{CH} \cdots \text{CH}_2 \cdots \text{OC}(\text{CH}_3)_3 \\ 18.7(q)^d \end{array}$	-96	Buten-1-yne-3
$\begin{array}{c} 18.81(t) \\ \text{CH}_2 \equiv \text{C} \cdots \text{C} \cdots \text{CH}_2 \cdots \text{CH}_3 \\ 12.34(t) \end{array}$	-108	Pentadiene-1,2 <sup>c</sup>
$\begin{array}{c} 14.77(d) \text{H} \\ \text{C} \cdots \text{C}(\text{CH}_3) \cdots \text{C} = \text{C}(\text{CH}_3)_2 \\ 2.89(q) \quad 0.67(s) \end{array}$	-79	2,5-Dimethylpentadiene-2,3
$\begin{array}{c} 14.26(d) \text{H} \\ \text{C} \cdots \text{C}(\text{CH}_3) \cdots \text{C} = \text{C}(\text{CH}_3)_2 \\ 0.67(s) \end{array}$		

<sup>a</sup> By reaction with photochemically generated *t*-butoxy radicals in neat hydrocarbon or cyclopropane solutions. <sup>b</sup> Coupling constants in gauss. Letters in parentheses indicate splitting: d = doublet, t = triplet, q = quartet, s = septet. <sup>c</sup> The presence of other paramagnetic species which may have been formed from this source was not scrutinized. <sup>d</sup> Accidentally degenerate.

of methylacetylene<sup>6</sup> or various propargylic and allylic derivatives.<sup>7</sup> A well-resolved esr spectrum of the C<sub>3</sub>H<sub>3</sub> radical was generated during electron radiolysis of a solution of allene in propane by Fessenden and Schuler.<sup>8</sup>

Product analyses indicated that the same C<sub>3</sub>H<sub>3</sub> radical was produced from methylacetylene and allene by reaction with *t*-butoxy radicals during the radical chain chlorination of these hydrocarbons with *t*-butyl hypochlorite.<sup>4c,5</sup>



We find that methylacetylene and allene react with photochemically generated *t*-butoxy radicals<sup>9</sup> (eq 1) to

(6) C. P. Poole, Jr., and R. S. Anderson, *J. Chem. Phys.*, **31**, 346 (1959).

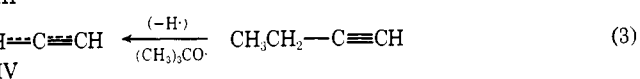
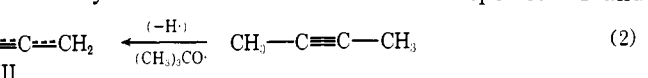
(7) (a) D. H. Volman, K. A. Maas, and J. Wolstenholme, *J. Amer. Chem. Soc.*, **87**, 3041 (1965); (b) T. S. Zhuravleva and I. A. Misurkin, *J. Struct. Chem. USSR*, **5**, 611 (1964); (c) V. I. Smirnova, T. S. Zhuravleva, D. N. Shigorin, E. P. Gracheva, and M. F. Shostakovskii, *Russ. J. Phys. Chem.*, **38**, 246 (1964).

(8) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).

(9) P. J. Krusic and J. K. Kochi, *J. Amer. Chem. Soc.*, **90**, 1755 (1968).

produce the same paramagnetic species. The six-line spectrum is composed of a triplet of doublets (Table I) with the correct intensity ratios.<sup>10</sup> Judging by the same intense esr spectrum of the C<sub>3</sub>H<sub>3</sub> radical obtained from both methylacetylene and allene we conclude qualitatively that these hydrocarbons have approximately the same reactivity toward *t*-butoxy radicals.

The interrelationship between radicals derived from methylacetylene and allene is shown further by the reactions between *t*-butoxy radicals and the isomeric ethylacetylene, dimethylacetylene, and methylallene. Methylallene produces two isomeric radicals III and IV in approximately equal amounts on reaction with *t*-butoxy radicals at -120°. Radical species III and



IV are readily distinguishable by their different behavior toward power saturation. In the spectrum taken at very low microwave powers (Figure 1a) radical species IV predominates. Much higher power levels (Figure 1e) are required to bring out the spectrum of radical species III. The isomeric radicals III and IV can also be generated independently from the reaction of

(10) These values compare with  $a_{\text{CH}_2} = 18.9$  G and  $a_{\text{CH}} = 12.6$  G by Fessenden and Schuler.<sup>8</sup> Volman, *et al.*,<sup>7</sup> assumed values of 17.8 and 13.8 G to reconstruct their incompletely resolved spectrum. The coupling constants reported by Poole and Anderson<sup>6</sup> are incorrect.

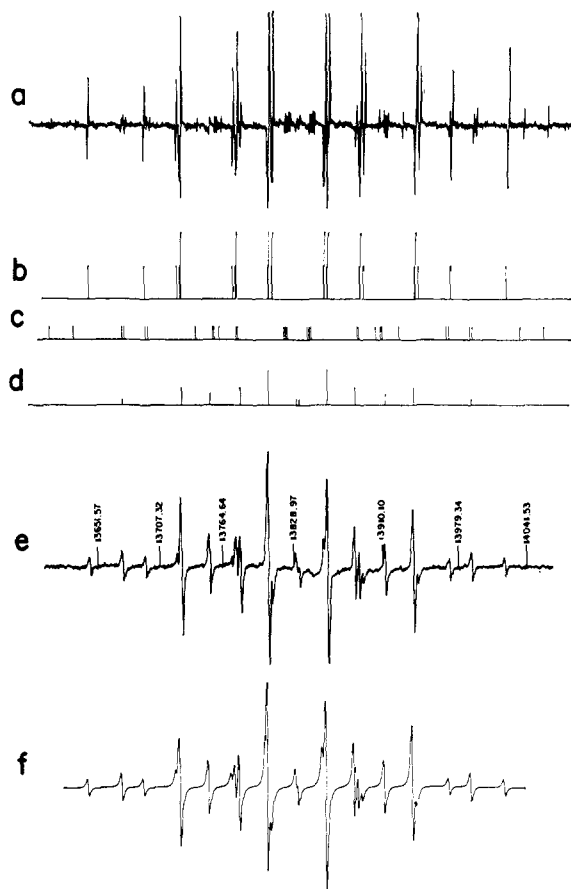
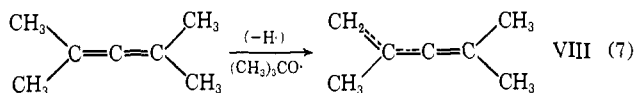
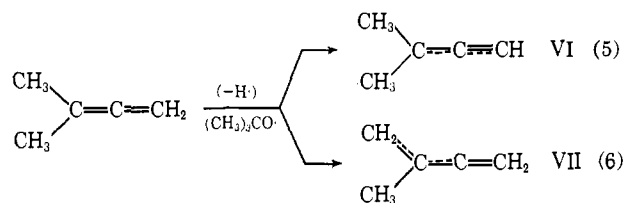
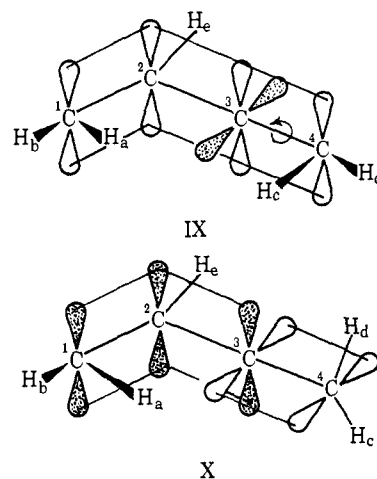


Figure 1. ESR spectra obtained by photolysis of di-*t*-butyl peroxide in methylallene-cyclopropane solution at  $-125^\circ$ . The most prominent lines of the spectrum at low microwave power (a) are due to radical species IV (diagram b including second-order components). The weaker lines are assigned to species V (diagram c) and species III (diagram d). The broader lines of species III do not appear with their correct relative amplitudes. The spectrum at high microwave power (e) is the superposition of the spectra of III and IV in about equal concentrations as substantiated by the calculated spectrum (f). The proton nmr field markers are in kHz.



The related radicals species V, VII, and VIII are neither propargyl nor allenyl. These radicals can be considered in two valence tautomeric forms IX and X which differ by a  $90^\circ$  rotation about the  $\text{C}_3\text{-C}_4$  axis.<sup>11</sup>



The unpaired electron in tautomer IX is, formally speaking, in a *localized* orbital<sup>12</sup> (darkened) associated with a 1,3-butadienyl structure. In tautomer X the electron is in a *delocalized* orbital and it may be considered as a methyleneallyl radical.

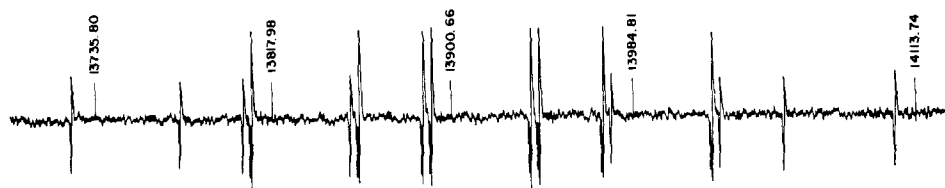


Figure 2. ESR spectrum of radical species IV obtained by photolysis of di-*t*-butyl peroxide in ethylacetylene at  $-112^\circ$  with partially resolved second-order components.

*t*-butoxy radicals with dimethylacetylene and ethylacetylene, respectively.

The ESR spectrum of a third radical species V is also generated from methylallene and can be seen in Figure 1a as the minor component. Radical V, which is formed by abstraction of a hydrogen from the terminal methyl group (eq 4), is not produced from either ethylacetylene (Figure 2) or dimethylacetylene.

Similarly, two radical species VI and VII are formed from 1,1-dimethylallene by abstraction of either an allenyl or a methyl hydrogen, respectively.<sup>4c</sup> The completely substituted tetramethylallene reacted with *t*-butoxy radical to form only radical VIII (Figure 3).

The similarities of the hyperfine coupling constants for  $\text{H}_a$ ,  $\text{H}_b$ , and  $\text{H}_e$  of radical V (see Table I) to those found in the allyl radical<sup>13</sup> [ $\text{H}_a = 13.82$ ,  $\text{H}_b = 14.68$ ,

(11) M. L. Poutsma and P. A. Ibarbia, Preprints, Division Petroleum Chemistry, 159th National Meeting of the American Chemical Society, Houston, Texas, Feb 22, 1970, p E55.

(12) Depending on whether carbon 3 is  $\text{sp}$  or  $\text{sp}^2$  hybridized, carbon atoms 2, 3, and 4 are either collinear or in a bent array. Compare analogous cases in the benzoyl radical [P. J. Krusic and T. A. Rettig, *J. Amer. Chem. Soc.*, **92**, 723 (1970)] and the vinyl radical [R. W. Fessenden, *J. Phys. Chem.*, **71**, 74 (1967)]. See also R. M. Kopchik and J. A. Kampmeir, *J. Amer. Chem. Soc.*, **90**, 6733 (1968).

(13) (a) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963); (b) J. K. Kochi and P. J. Krusic, *J. Amer. Chem. Soc.*, **90**, 7157 (1968).

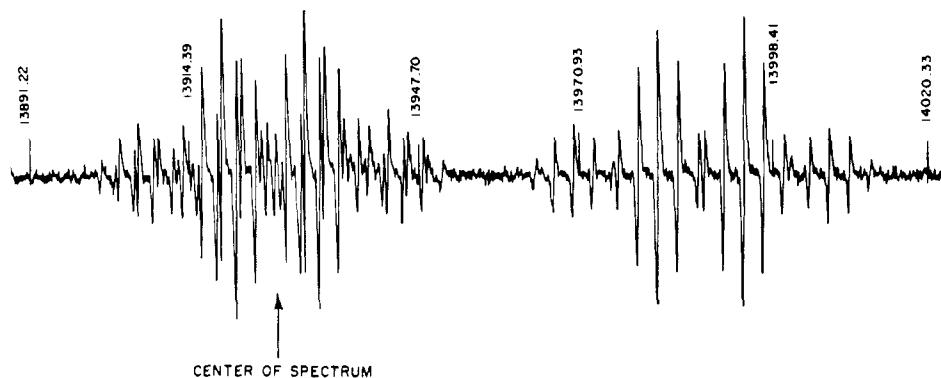


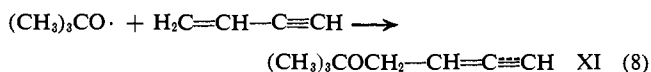
Figure 3. ESR spectrum of radical species VIII obtained by hydrogen abstraction from tetramethylallene at  $-50^\circ$ .

and  $H_e = 3.19$  G] lead us to favor structure X. Hydrogen atoms  $H_c$  and  $H_d$  are  $\beta$  to the allylic system and the rather large values of the hyperfine coupling constants are consistent with their location in the antinode of the  $\pi$ -allyl orbitals.<sup>14</sup> A similar situation pertains to the methylated analogs VII and VIII. INDO-MO calculations also favor structure X.<sup>15,16</sup>

A variety of other substituted acetylenes and allenes were subjected to *t*-butoxy radicals and the hyperfine coupling constants of the resultant propargyl and allenyl radicals are also listed in Table I. It should be noted that in every case we examined, no evidence for the removal of the methinyl ( $\equiv\text{CH}$ ) hydrogen by *t*-butoxy radical was found.

The reactivity of the allenyl hydrogens ( $=\text{C}=\text{CH}-$ ), moreover, was not significantly different from the propargyl hydrogens ( $\equiv\text{C}-\text{CH}$ ) judging by the relative intensities of the ESR spectra.

The reactivity of the allenyl hydrogens appears to be related to the stabilization of the resultant substituted  $\text{C}_3\text{H}_3$  radical since the somewhat related vinylacetylene does not transfer hydrogen to *t*-butoxy radical. Instead it reacts by *addition* to produce the adduct radical XI.<sup>17,18</sup> This is also shown by the removal of *both* allenyl hydrogens in methylallene (*vide supra*) despite



the fact that one hydrogen is attached to a secondary (C-3) and the other to a primary (C-1) carbon center. On the other hand, in pentyne-2 only the radical re-

(14) However,  $H_c$  and  $H_d$  are equivalent in structure X. The slight inequivalence of their hyperfine coupling constants (see Table I) may indicate that the plane formed by  $\text{H}_c\text{C}_1\text{H}_d$  may be tilted slightly from the normal in the equilibrium configuration (*cf.* ref 15).

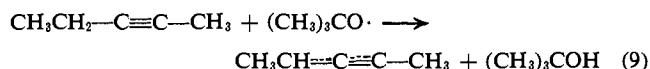
(15) (a) The model employed the following parameters for V:  $\text{C}_1\text{C}_2 = 1.42$ ,  $\text{C}_2\text{C}_3 = 1.35$ ,  $\text{C}_3\text{C}_4 = 1.33$ , all  $\text{CH} = 1.07$  Å, all trigonal angles except at  $\text{C}_3$ .  $\angle \text{C}_2\text{C}_3\text{C}_4 = 180^\circ$ . The hyperfine coupling constants (G) calculated for  $\text{H}_a$ ,  $\text{H}_b$ ,  $\text{H}_c$ ,  $\text{H}_d$ , and  $\text{H}_e$  are: for IX =  $-5.7$ ,  $1.6$ ,  $66.3$ ,  $69.2$ , and  $64.6$ ; for X =  $-15.7$ ,  $-15.2$ ,  $41.3$ ,  $41.3$ , and  $8.0$ ; for X tilted by  $15^\circ$  from the normal =  $-15.6$ ,  $-14.8$ ,  $42.7$ ,  $42.3$ , and  $10.4$ . (b) Thus, the hyperfine coupling constants for  $\text{H}_e$  is particularly revealing since it is (as expected) a sensitive measure of the orientation of the  $\text{C}_4$  methylene group.

(16) (a) J. A. Pople, D. L. Beveridge and P. A. Dobosh, *J. Amer. Chem. Soc.*, **90**, 4201 (1968). (b) A copy of this program was obtained from the Quantum Chemistry Program Exchange, Indiana University.

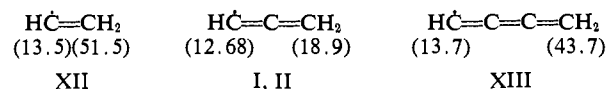
(17) Product studies<sup>11</sup> indicate that attack by *t*-butoxy radical at the acetylenic end is approximately four times less important than addition to the ethylenic site. We have not examined in detail the presence of the former adduct radical (which would be similar to V, VII, and VIII).

(18) Phenylacetylene like *t*-butylacetylene gave only a poor spectrum.

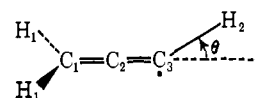
sulting from the loss of a secondary hydrogen is observed.



The proton coupling constants of the  $\text{C}_3\text{H}_3$  radical can be compared to those in the vinyl and butatrienyl radicals. Recent measurements of the  $^{13}\text{C}$  coupling constants<sup>19</sup> for the vinyl radical XII support the trigonal hybridization of the  $\alpha$ -carbon (*i.e.*, bent structure),<sup>20</sup> although in the vinylogous butatrienyl radical XIII a linear hybridization has been assumed.<sup>21</sup>



We have been unable to observe line broadening or other rate effects in the ESR spectrum of the  $\text{C}_3\text{H}_3$  radical down to  $-150^\circ$ . The hybridization of the  $\alpha$ -carbon atom in the  $\text{C}_3\text{H}_3$  radical is still in question. We have carried out INDO molecular orbital calculations<sup>16</sup> for the  $\text{C}_3\text{H}_3$  radical as a function of the most important parameter  $\theta$ , the angle of bend. These calculations



indicate that the magnitudes of neither of the two proton coupling constants depend appreciably on  $\theta$ . Syntheses are in progress to obtain the  $\alpha$ - $^{13}\text{C}$  coupling constant which is a sensitive measure of the angle of bend. Similarly, questions<sup>4</sup> related to the relative electron densities at  $\text{C}_1$  and  $\text{C}_3$  are dependent on a determination of the structure of the  $\text{C}_3\text{H}_3$  radical. However, it is possible to assess the ability of the acetylenic bond to facilitate electron delocalization. Thus, the ESR spectrum of the  $\gamma$ -phenylpropargyl radical XIV<sup>22</sup> shows

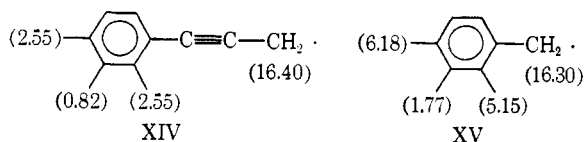
(19) R. W. Fessenden, *J. Phys. Chem.*, **71**, 74 (1967).

(20) F. J. Adrian and E. L. Cochran, 6th International Symposium on Free Radicals, Cambridge, 1963; *J. Chem. Phys.*, **36**, 1939 (1962); *Advan. Chem.*, **36**, 50 (1962); see also, P. H. Kasai and E. B. Whipple, *J. Amer. Chem. Soc.*, **89**, 1033 (1967).

(21) (a) P. H. Kasai, L. Skattebøl, and E. B. Whipple, *ibid.*, **90**, 4509 (1968); (b) compare also the ESR spectrum of the nitrogen analog,  $\text{CH}_2=\text{C}=\text{CN}$ : S. Feinstein, R. Marx, C. Moreau, and J. Serre, *Theor. Chim. Acta*, **14**, 339 (1969).

(22) Previous workers were unable to resolve the aromatic splittings: V. I. Smirnova, *et al.*, *Zh. Fiz. Khim.*, **38**, 469 (1964).

sizable splittings by the aromatic hydrogens in relationship to the benzyl radical XV.<sup>9</sup> Using McConnell's



relationship we estimate that the interposition of two more carbon atoms of an acetylenic group into XV only reduces the spin density in the aromatic nucleus to a value 47% of that in the parent radical.<sup>23</sup>

(23) This conclusion is a variance with an earlier chemical study.<sup>3b</sup>

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Received February 9, 1970

### Solution Structure of Coinage Metal-Phosphine Complexes

Sir:

We report preliminary nmr data that establish solution-state structures of copper-, silver-, and gold(I)-phosphine complexes. Solution behavior has proved to be unexpectedly complex. Many discrete crystalline complexes were found to dissolve in non-polar media to give *several* solution species even at low temperatures. The character and the number of solution species, in some cases, was markedly affected by temperature and by the nature of the solvent. The following structural information pertains to dichloromethane and dichloromethane-toluene solutions at temperatures in the range of  $\sim -100$  to  $-50^\circ$ <sup>1</sup> and to a standard reference phosphine, L, tri-*p*-tolylphosphine.<sup>2</sup>

Solution structures for the phosphine-silver complexes are tetrahedral, trigonal coplanar, or linear with a relatively strong structural dependence on the character of the anion. The tetrahedral  $L_4Ag^+$  ion was the only complex detected by <sup>31</sup>P nmr<sup>3</sup> for a wide range of silver salts<sup>4</sup> in the presence of four or more equivalents of L.<sup>5</sup> The  $J_{107Ag-31P}$  and  $J_{109Ag-31P}$  values were  $227 \pm 3$  and  $258 \pm 3$  Hz, respectively (hereafter only the <sup>107</sup>Ag value will be cited),<sup>6</sup> and the chemical shifts fell in the

(1) Lability of phosphine ligands was kinetically evident from the <sup>31</sup>P nmr spectra. Onset of rapid ligand exchange ranged from  $-70$  to  $0^\circ$  depending on the specific complex.

(2) Structural assignments are based primarily on <sup>31</sup>P coupling constants (silver) and <sup>31</sup>P chemical shift data. Integrity of postulated species was further shown in mixtures of  $L_2MX$  and  $L_{2-1}MX$ , where the characteristic resonances for both species were found. Conductivity data in dichloromethane were also obtained as a function of temperature from  $25$  to  $-78^\circ$  in dichloromethane. Conductivity data are reported for  $0.01 M$  solutions at  $25^\circ$ . Sample reference values are 35, 40, and 35 mhos for the tetraphenylarsonium salts of  $Cl^-$ ,  $B_3H_8^-$ , and  $B_3H_2S^-$ , respectively. Conductivity decreases from  $+25$  to  $-78^\circ$  in the ionic phosphine complexes were proportionate to those found in reference tetraphenylarsonium salts.

(3) Triethylphosphine internal capillary reference and proton noise decoupling.

(4)  $B_3H_8^-$ ,  $S_2PF_2^-$ ,  $OCOCF_3^-$ ,  $NO_3^-$ ,  $PF_6^-$ ,  $ClO_4^-$ ,  $B_3H_2S^-$ ,  $B_9H_4^-$ ,  $B_{10}H_{13}^-$ ,  $B_{11}H_{11}^-$ , and  $BF_4^-$ .

(5) At low temperatures, there is no fast exchange of L between  $L_4Ag^+$  and free L; the <sup>31</sup>P spectrum consisted of the characteristic  $L_4Ag^+$  and L resonances.

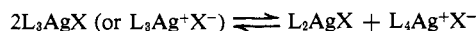
narrow range of  $-25.7$  to  $-25.3$  ppm.<sup>7</sup> Ligand exchange was rapid above  $\sim -50^\circ$  where the lines broadened and then a single resonance emerged. A few strong-field anions effectively competed with L for the silver coordination sphere; these included  $Cl^-$ ,  $Br^-$ ,  $I^-$ , and  $CN^-$ . The equilibrium constant at  $-80^\circ$  for



was  $\sim 10^{-1}$  for  $Br^-$  and  $Cl^-$  and at least  $10^4$  mol/l. for  $I^-$  and  $CN^-$ . No  $L_4Ag^+$  was detected with the latter two counterions nor could  $L_4Ag^+X^-$  solid phases be isolated with these four anions.

In solution, the  $L_3AgX$  species were of two types: pseudotetrahedral molecules and trigonal coplanar cations. The ionic set was based on anions such as  $PF_6^-$ ,  $BF_4^-$ , and  $ClO_4^-$ . The chemical shift for these fell at lowest fields and in a narrow region,  $-30.6 \pm 0.1$  ppm, and the conductivities were high, 45–46 mhos. The observed  $J_{Ag-P}$  values were 316–321 Hz, comparing favorably with the calculated<sup>8</sup> value for  $sp^2$  silver of 303 Hz based on the observed 227-Hz value for  $sp^3$   $L_4Ag^+$ . The halide, cyanate, and cyanide complexes were pseudotetrahedral  $L_3AgX$  aggregates. The  $J_{Ag-P}$  values for this set ranged from 230 to 280 Hz, and essentially no conductivity could be detected in dichloromethane solutions of these complexes. A large group<sup>9</sup> of the  $L_3AgX$  complexes had  $J_{Ag-P}$  values ranging from 300 to 316 Hz and conductivities at  $25^\circ$  as high as 33 mhos. With but one exception, it is impossible at this stage to state whether there is *any binding* of the anion. The exception is the salt based on  $S_2PF_2^-$ . The <sup>19</sup>F and the <sup>31</sup>P data ( $J_{PF}$  and  $\delta$ ) at  $-80^\circ$  for the anion in this salt were comparable to those for bound, unidentate  $S_2PF_2^-$  in transition metal complexes.<sup>10</sup> The conductivity was low, 3.5 mhos at  $25^\circ$ .

In solution, some  $L_3AgX$  complexes disproportionate extensively



This phenomenon was detected for the complexes with the counterions  $NO_3^-$ ,  $B_3H_8^-$ , and  $OCOCF_3^-$ . The equilibrium constant for the nitrate was  $\sim 10^{-2}$  at  $-84^\circ$ . There was also evidence of significant phosphine dissociation at  $25^\circ$  in some of these complexes. For example, <sup>31</sup>P chemical shift data and molecular weight information indicated that  $L_3AgCl$ , a discrete entity at low temperatures, was essentially completely dissociated at room temperature into  $L_2AgCl$  and L.

Linear  $L_2Ag^+$  complexes were observed for the group with the  $PF_6^-$ ,  $BF_4^-$ , and  $ClO_4^-$  counteranions. The coupling constants were about 500 Hz, compared with a calculated value of 452 Hz for  $sp$  linear  $L_2Ag^+$ . Conductivities were high,  $\sim 39$  mhos, and <sup>19</sup>F data in the case of  $PF_6^-$  showed that even at low temperatures

(6) Observed  $J(109)/J(107) = 1.15 \pm 0.1$ ; theory, 1.15.

(7) The conductivities of  $L_4Ag^+X^-$  salts in dichloromethane were high, ranging from 26 to 50 mhos depending on the anion.

(8) This is based on estimation of the amount of s character in the Ag-P bond without any adjustment for changes in the effective nuclear charge on the metal. In those instances where the anion is bound, an electronegativity effect (or strength of the AgX bond) is operating and the coupling constants are not amenable to a simplistic analysis, at least in a quantitative sense. For reference to similar analyses in organic compounds, cf. N. Muller and D. E. Pritchard, *J. Chem. Phys.*, **31**, 768 (1959).

(9) E.g., X =  $SCN^-$ ,  $B_3H_8^-$ ,  $NO_3^-$ ,  $B_9H_2S^-$ ,  $S_2PF_2^-$ ,  $OCOCF_3^-$ .

(10) F. N. Tebbe and E. L. Muettterties, *Inorg. Chem.*, **9**, 629 (1970).