

different solvated complex in the presence of EDTA and excess  $\text{H}_2\text{O}_2$ . Indeed, when EDTA was added to a ferrate solution prepared from the dry solid  $\text{K}_2\text{FeO}_4$  in 9M KOH, the minimum usually occurring at 3900Å. was shifted to 4000Å., and the maximum usually occurring at 5000Å. was shifted to approximately 5500Å. These displacements were somewhat dependent on the concentration of EDTA. In determining the  $\text{FeO}_4^{--}$  concentration spectrophotometrically, it was assumed that the molar extinction coefficient for  $\text{FeO}_4^{--}$  at the 5180 Å. maximum was 1070 l. mole<sup>-1</sup> cm.<sup>-1</sup>, the same as determined by Wood<sup>3</sup> and reproduced by us at 5050Å.

Attempts to prepare  $\text{FeO}_4^{--}$  as described above, in the absence of EDTA, were unsuccessful. When solid  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  was added to the mixture with no EDTA present, purple flashes of color appeared on the crystals and in the immediate area of the crystals but quickly disappeared.

It has been reported by others,<sup>3,4</sup> and observed by us, that addition of  $\text{H}_2\text{O}_2$  to  $\text{FeO}_4^{--}$  in strong alkaline media causes rapid reduction of  $\text{FeO}_4^{--}$  to  $\text{Fe}(\text{OH})_3$ . Likewise, addition of EDTA to an alkaline  $\text{FeO}_4^{--}$  solution prepared from solid  $\text{K}_2\text{FeO}_4$  results in an increase in the rate of thermal decomposition of this solution. We cannot explain the apparent stabilizing effect of EDTA on the formation of  $\text{FeO}_4^{--}$  with  $\text{H}_2\text{O}_2$ . EDTA generally is considered to be a cation complexing agent, but in this strongly alkaline solution, Fe(VI) as  $\text{FeO}_4^{--}$  and Fe(III) as  $\text{FeO}_2^-$  or  $\text{FeO}_3^{---}$  are anionic species. Moreover, as observed by Duke and Haas,<sup>1</sup> addition of EDTA to a  $\text{Fe}(\text{OH})_3$  precipitate in alkaline medium appears to have no effect on the precipitate.

Thanks are due to H. A. Mahlman and J. W. Boyle for suggesting this phase of the work, and to W. F. Vaughan who assisted in the initial preparation of  $\text{FeO}_4^{--}$  by this method. This work was supported by the Oak Ridge Institute of Nuclear Studies in cooperation with Michigan State University and the Oak Ridge National Laboratory.

(4) O. N. Hinsvark, Master's Thesis, Michigan State University, East Lansing, Michigan, 1952.

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RECEIVED APRIL 27, 1961

### SPIN-SPIN COUPLING CONSTANTS BETWEEN NON-BONDED $\text{C}^{13}$ AND PROTON. III.<sup>1,2</sup> ANOMALIES IN $J_{\text{C}^{13}-\text{C}-\text{C}-\text{H}}$

Sir:

It has been shown that a direct correlation exists between the magnitude of either  $J_{\text{C}^{13}-\text{H}}$  or  $J_{\text{C}^{13}-\text{C}-\text{H}}$  and the degree of sp hybridization of the  $\text{C}^{13}$  atomic orbitals.<sup>2,3</sup> This finding, coupled with the fact that calculations based on the assumption

(1) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society.

(2) Previous paper, G. J. Karabatsos, J. D. Graham and F. Vane, *J. Phys. Chem.*, in press.

(3) (a) J. N. Shoolery, *J. Chem. Phys.*, **31**, 1427 (1959); (b) N. Muller and D. E. Pritchard, *ibid.*, **31**, 768, 1471 (1959).

TABLE I

| Compound  | $J_{\text{C}^{13}-\text{C}-\text{C}-\text{H}}$ (c.p.s.) | $J_{\text{H}-\text{C}-\text{C}-\text{H}}$ (c.p.s.) |
|---|---|--|
| $(\text{CH}_3\text{CH}_2)_2\text{C}^{13}=\text{O}$  | $4.7 \pm 0.1$   | $7.5 \pm 0.1$                                      |
| $\text{CH}_3\text{CH}_2\text{C}^{13}\text{O}_2\text{H}$   | $5.5 \pm .2$  | $7.4 \pm .1$                                       |
| $\text{CH}_3\text{CH}_2\text{C}^{13}\text{O}_2\text{CH}_3$  | $5.3 \pm .1$  | $7.4 \pm .1$                                       |
| $\text{CH}_3\text{CH}_2\text{C}^{13}\text{D}_2\text{OH}$  | $6.4 \pm .2$  | $7.3 \pm .2$                                       |
| $(\text{CH}_3\text{CH}_2)_2\text{C}^{13}\text{DOH}$   | $4.0 \pm .2$  | $6.8 \pm .3$                                       |
| $(\text{CH}_3\text{CH}_2)_3\text{C}^{13}\text{OH}$  | $4.5 \pm .1$  | $7.5 \pm .2$                                       |
| $\text{CH}_3\text{CH}_2\text{C}^{13}(\text{OH})(\text{CH}_3)_2$                                       | $4.4 \pm .2$  | $7.3 \pm .2$                                       |
| $\text{CH}_3\text{CH}_2\text{C}^{13}(\text{Cl})(\text{CH}_3)_2$                                       | $5.7 \pm .1$  | $7.5 \pm .2$                                       |
| $\alpha\text{CH}_3$<br> <br>$\text{C}^{13}\text{H}_3-\text{C}(\text{OH})^\beta\text{CH}_2\text{CH}_3$ | ( $\alpha$ ) $3.2 \pm .2$<br>( $\beta$ ) $3.0 \pm .2$   |  |
| $\alpha\text{CH}_3$<br> <br>$\text{C}^{13}\text{H}_2-\text{C}(\text{Cl})^\beta\text{CH}_2\text{CH}_3$ | ( $\alpha$ ) $4.2 \pm .2$<br>( $\beta$ ) $3.2 \pm .2$   |  |

tion that the Fermi contact term is the dominant one predict such a correlation, has led to the conclusion that the contact term is indeed the important term in both  $J_{\text{C}^{13}-\text{H}}$  and  $J_{\text{C}^{13}-\text{C}-\text{H}}$ . We wish to point out that such does not seem to be the case in  $J_{\text{C}^{13}-\text{C}-\text{C}-\text{H}}$ .

Spin-spin coupling constants ( $J_{\text{C}^{13}-\text{C}-\text{C}-\text{H}}$ ) for ten compounds are reported in Table I. The enrichment in the samples varied from 30% to 60% excess  $\text{C}^{13}$ . All spectra were taken with a model V4300D Varian Associates Spectrometer, at 60 Mc.; spin-spin coupling constants were measured by the standard side band technique.<sup>4</sup>

The following observations and conclusions are made: (1)  $J_{\text{C}^{13}-\text{C}-\text{C}-\text{H}}$  varies irregularly and there is no obvious correlation between its magnitude and the hybridization of  $\text{C}^{13}$  atomic orbitals. (2) No correlation is possible involving the electronegativity of the group attached to  $\text{C}^{13}$ . (3) The constancy of the corresponding  $J_{\text{H}-\text{C}-\text{C}-\text{H}}$  excludes the possibility that the variations are due to different populations of rotational isomers; there is no reason to suggest that, in the same compound,  $\text{C}^{13}$  sees the methylene protons in different conformations than the methylene hydrogens do.

Calculations analogous to those reported previously,<sup>2</sup> and based on the assumption that the Fermi contact term is the dominant term, lead to the following results: (1) for  $\text{sp}^3$  hybridized  $\text{C}^{13}$ ,  $J_{\text{C}^{13}-\text{C}-\text{C}-\text{H}} = J_{\text{H}-\text{C}-\text{C}-\text{H}} \times 0.3036$ . (2) For  $\text{sp}^2$  hybridized  $\text{C}^{13}$ ,  $J_{\text{C}^{13}-\text{C}-\text{C}-\text{H}} = J_{\text{H}-\text{C}-\text{C}-\text{H}} \times 0.4046$ . Using the experimental values of  $J_{\text{H}-\text{C}-\text{C}-\text{H}}$  given in Table I, one obtains for  $\text{sp}^3$  hybridized  $\text{C}^{13}$   $J_{\text{C}^{13}-\text{C}-\text{C}-\text{H}} = \sim 2.3$  c.p.s. and for  $\text{sp}^2$  hybridized  $\text{C}^{13}$   $J_{\text{C}^{13}-\text{C}-\text{C}-\text{H}} = \sim 3.0$  c.p.s. The random variation of the experimental  $J_{\text{C}^{13}-\text{C}-\text{C}-\text{H}}$  values suggests that the Fermi contact term is not the only important term. Subtler factors, resulting to higher than predicted values for  $J_{\text{C}^{13}-\text{C}-\text{C}-\text{H}}$ , must be operative. We hope to study the problem further by examining rigid systems where the dihedral angle is fixed, and systematic variations of the hybridization of  $\text{C}^{13}$  and the groups attached to it can be performed.

We wish to comment briefly on the fact that for the same compound  $J_{\text{C}^{13}-\text{C}-\text{C}-\text{H}}$  is occasionally greater than  $J_{\text{C}^{13}-\text{C}-\text{H}}$ . It was shown<sup>2</sup> that  $J_{\text{C}^{13}-\text{C}-\text{H}}$

(4) J. T. Arnold and M. E. Packard, *ibid.*, **19**, 1608 (1951).

for  $sp^3$  hybridized  $C^{13}$  has values of about 4.0 c.p.s. The data presented here show that for  $sp^3$  hybridized  $C^{13}$ ,  $J_{C^{13}-C-C-H}$  is either equal or considerably greater than the corresponding  $J_{C^{13}-C-H}$  in the same compound. Such anomalies—spin-spin coupling constants do not decrease monotonically with the number of bonds separating the interacting nuclei—have been observed in various metal alkyls.<sup>5</sup> The general impression has been that  $J_{M-C-H}$  is abnormally small. We wish to suggest that perhaps, as in the case of  $C^{13}$ ,  $J_{M-C-C-H}$  is abnormally large, and more intensive studies on  $J$ 's between interacting nuclei separated by three bonds may explain decreases which are not monotonic with the number of separating bonds.

(5) (a) P. T. Narasimhan and M. T. Rogers, *J. Am. Chem. Soc.*, **82**, 34 (1960); (b) R. E. Dessy, T. J. Flautt, H. H. Jaffé and G. F. Reynolds, *J. Chem. Phys.*, **30**, 1422 (1959); (c) E. B. Baker, *ibid.*, **26**, 960 (1957).

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RECEIVED APRIL 21, 1961

#### ANOMALOUS HYDROGEN-DEUTERIUM DISTRIBUTION IN STIBINE PREPARED FROM ANTIMONY(III) AND BOROHYDRIDE IN HEAVY WATER

Sir:

We wish to report an unexpected deuterium-hydrogen distribution in the preparation of stibine. This preparation yielded  $SbH_3$  to  $SbD_3$  in a ratio of about 15:1 with no partially deuterated stibine detectable. The synthesis<sup>1</sup> consisted of slowly dropping a heavy water solution containing 2.5*F* NaOD, 0.5*F*  $K_2SbO(C_4H_4O_6)$ , and 0.4*F*  $KBH_4$  into a heavy water solution 2*F* in  $D_2SO_4$  while vigorously bubbling nitrogen through the reaction mixture at 11 cm. total pressure. The total exchangeable hydrogen was 97% deuterium. The gaseous stibine was trapped and purified as recommended by Jolly.

The infrared spectrum of our preparation showed peaks in the rock salt region at 1945, 1882, 1825, 1406, 1362, 1320, 832 and 775  $cm^{-1}$ . These eight peaks, the only peaks in the spectrum of our sample, are in agreement<sup>2</sup> with the four fundamental vibrations of  $SbH_3$  and the two fundamental vibrations of  $SbD_3$  which were in the range of the prism used. Although the intensity<sup>3</sup> measurements could not be used to determine the relative amounts of  $SbH_3$  to  $SbD_3$  it should be mentioned that the relative absorbancy of  $\nu_1$  for  $SbH_3$  to  $SbD_3$  was about 10:1.

Mass spectrometric analysis of the stibine showed a broad peak in the 120–130 region, no oxygen, a little water with  $H_2O$  greatest and  $D_2O$  least, and small amounts of  $H_2$ , HD and  $D_2$  with an H to D ratio of about 15.

The sample was decomposed in the gas phase by an electrical discharge, using an ordinary Tesla coil leak detector external to the glass system. The ratio of H to D was estimated from measure-

(1) W. L. Jolly, *J. Am. Chem. Soc.*, **83**, 335 (1961); S. R. Gunn, W. L. Jolly and L. G. Green, *J. Phys. Chem.*, **64**, 1334 (1960).

(2) W. H. Haynie and H. H. Nielsen, *J. Chem. Phys.*, **21**, 1839 (1953); D. C. Smith, *ibid.*, **19**, 384 (1951); American Petroleum Institute Spectra No. 315.

(3) B. L. Crawford, Jr., *J. Chem. Phys.*, **20**, 977 (1952).

ments of the mass peak heights for  $H_2$ , HD and  $D_2$  in the completely decomposed sample. Assuming the hydrogen originated only from  $SbH_3$  and  $SbD_3$ , our preliminary results gave a ratio of 15:1 for the hydride to the deuteride ratio.

Most of the readily conceivable mechanisms for the reactions producing stibine would be expected to yield  $SbH_3$ ,  $SbH_2D$ ,  $SbHD_2$  and  $SbD_3$  in ratios which would be predicted statistically from the over-all H to D ratio in the stibine. For our experiment, a statistical distribution would correspond to the most abundant deuterated product being  $SbH_2D$ . Hence, it was surprising to find  $SbD_3$  as the only deuterated product. The D in the stibine did not originate from borohydride since the hydrogens of borohydride ion are known not to exchange<sup>4</sup> with the hydrogen of an aqueous solvent.

One possibly is the existence of two independent paths, one resulting in  $SbH_3$  and the other  $SbD_3$ . The path leading to hydride formation would involve reactions only with  $BH_4^-$ . The second path leading to the deuteride would involve reactions of deuteriodiborane with Sb(III). In concentrated sulfuric acid some diborane<sup>5</sup> is formed from borohydride ion; and diborane has exchangeable<sup>6</sup> hydrogens. Such a two-path mechanism can be used to explain the appearance of  $SbD_3$  (without other deuterio species) in addition to the expected  $SbH_3$ .

Work is in progress to elucidate the mechanism of this deuteration and to study the analogous reactions with the corresponding As, Sn and Ge compounds.

We wish to acknowledge assistance of Mr. N. Neunke and thank Dr. H. Papazian for measuring the infrared spectrum.

(4) P. R. Girardot and R. W. Parry, *J. Am. Chem. Soc.*, **73**, 2368 (1951).

(5) H. G. Weiss and I. Shapiro, *ibid.*, **81**, 6167 (1959).

(6) S. Kaye and T. Freund, unpublished results.

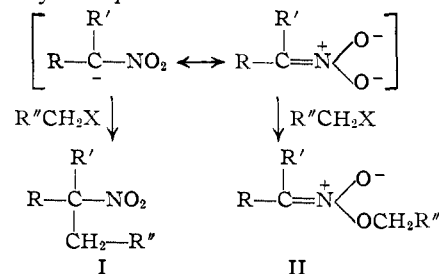
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RECEIVED APRIL 22, 1961

#### THE LEAVING GROUP AS A FACTOR IN THE ALKYLATION OF AMBIDENT ANIONS

Sir:

The reaction of nitroparaffin salts with alkyl halides may occur as carbon-alkylation or as oxygen-alkylation. The latter is productive of nitronic esters (II) which are not isolated; instead the carbonyl compound and oxime are obtained and



it is generally assumed that they arise from the nitronic ester.<sup>1</sup>

(1) L. Weisler and R. W. Helmkamp, *J. Am. Chem. Soc.*, **67**, 1167 (1945); H. B. Hass and M. L. Bender, *ibid.*, **71**, 1767, 3482 (1949).