

Figure 1.

The question of  $^{13}\text{C-H}$  coupling involving a positively charged carbon atom is of particular interest.

In a previous paper<sup>9</sup> we briefly reported that  $^1J_{^{13}\text{C-H}}$  for  $(\text{CH}_3)_2^{13}\text{CH}^+$  is 382 cps. This would imply more than 75% s character for the carbon atomic orbital used in the  $^{13}\text{C-H}$  bond and would not be compatible with the suggested  $\text{sp}^2$  hybridization at the  $^{13}\text{C}$  atom.

It of course could be argued that the symmetry environment of the positively charged carbon atom being different from that of the uncharged carbon atom does not allow any more the application of simple linear relationships. On the other hand the exceptional value of  $J_{^{13}\text{C-H}}$  observed for the isopropyl cation clearly indicated the need for a more detailed investigation of proton- $^{13}\text{C}^+$  spin-spin coupling constants in carbonium ions.

Using improved methods to generate stable carbonium ions in strongly acidic solutions the proton- $^{13}\text{C}^+$  spin-spin coupling in  $(\text{CH}_3)_2^{13}\text{CH}^+$  has now been reinvestigated and the investigation also extended to  $(\text{C}_6\text{H}_5)_2^{13}\text{CH}^+$ . The ions were generated from the corresponding  $^{13}\text{C}$ -enriched chlorides (Merck Sharp and Dohme, Ltd., Montreal, Canada) with antimony pentafluoride (neat at  $+2^\circ$  in the case of the isopropyl and in  $\text{SO}_2\text{-SbF}_5$  solvent at  $-60^\circ$  in the case of the benzyhydril system). Table I summarizes the observed  $^{13}\text{C}$ -proton coupling constants (obtained from  $^{13}\text{C}$  satellite bands of enriched samples on a Varian Model A-60 spectrometer equipped with a variable temperature probe).

**Table I.** Proton- $^{13}\text{C}$  Spin-Spin Coupling Constants of Secondary Carbonium Ions and Their Parent Hydrocarbons

	$^1J_{^{13}\text{C-H}}$ , cps	Calcd s character, %	State of hybridization
$(\text{CH}_3)_2^{13}\text{CH}_2$	128	25.6	$\text{sp}^3$
$(\text{CH}_3)_2^{13}\text{CH}^+\text{SbF}_5\text{Cl}^-$	168	33.6	$\text{sp}^2$
$(\text{C}_6\text{H}_5)_2^{13}\text{CH}_2$	126	25.2	$\text{sp}^3$
$(\text{C}_6\text{H}_5)_2^{13}\text{CH}^+\text{SbF}_5\text{Cl}^-$	164	32.8	$\text{sp}^2$

Normally direct one-bond  $^{13}\text{C-X}$  coupling interactions are well observable ( $\sim \pm 1$  cps) from  $^{13}\text{C}$  satellite spectra. The observation of the couplings in the case of carbonium ions, however, represents difficulties. Figure 1 shows the low-field part of the proton spectrum of the  $(\text{CH}_3)_2^{13}\text{CH}^+$  ion obtained on the high-resolution nmr spectrograph of Baker and Burd.<sup>12</sup> The 382 cps proton- $^{13}\text{C}$  coupling constant reported from this spectrum<sup>9</sup> was based on the observations of the assumed  $^{13}\text{C}$  satellite bands. On reinvestigation of the system with improved technique of preparation of the ion it was now found (Figure 2) that the upfield "satellite band" (191 cps from  $\text{CH}^+$ ) is not a  $^{13}\text{C}$  satellite but is due to a small amount of Brønsted

(12) E. B. Baker and L. W. Burd, *Rev. Sci. Instr.*, **28**, 313 (1957); **34**, 238 (1963).

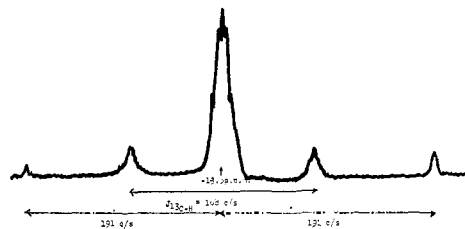


Figure 2.

acid impurity in the antimony pentafluoride. This was not recognized in previous work. Inspection of Figure 1 explains the reason. There is a low-field peak centered at  $-191$  cps from  $\text{CH}^+$ , mistakenly considered the parent  $^{13}\text{C}$  satellite band. The identity of this peak is not established but is considered due to an impurity. The same low-field peak is, however, substantially reduced in intensity in the improved system shown in Figure 2. Addition of water, producing conjugate acid, increases the upfield peak, but has no effect on the low-field peak. The proton- $^{13}\text{C}$  coupling of 168 cps is hardly observable in Figure 1, but is apparent in Figure 2 (all bands were checked to be not spinning side bands).

Having obtained proton- $^{13}\text{C}$  spin-spin coupling constants for the  $(\text{CH}_3)_2^{13}\text{CH}^+$  and  $(\text{C}_6\text{H}_5)_2^{13}\text{CH}^+$  ions it is possible now to state that the linearity between  $J_{^{13}\text{C-H}}$  and fractional s character of the  $^{13}\text{C}$  hybrid atomic orbital is also valid in the case of positively charged carbon atoms. The s character observed is in excellent agreement with the suggested  $\text{sp}^2$  hybridization of the involved carbonium ions.<sup>13</sup>

**Acknowledgment.** This work was supported by the National Science Foundation.

(13) NOTE ADDED IN PROOF. We recently also observed the proton- $^{13}\text{C}$  coupling in a primary carbonium ion: the 2,4-di-*t*-butyl-6-methylphenylcarbonium ion  $^1J_{^{13}\text{C-H}}$  is 169 cps, which corresponds to 33.8% s character.

(14) National Science Foundation predoctoral fellow.

George A. Olah, Melvin B. Comisarow<sup>14</sup>  
Department of Chemistry  
Western Reserve University, Cleveland, Ohio  
Received January 15, 1966

## The Identification of the $\text{P}_2\text{H}_2$ Molecule in the Pyrolysis of Diphosphine

Sir:

The known hydrides of phosphorus consist of  $\text{PH}_3$ ,  $\text{PH}_3$ ,  $\text{P}_2\text{H}_4$ , and some solids which are not well characterized.<sup>1,2</sup> This note reports the production of a new hydride of phosphorus,  $\text{P}_2\text{H}_2$ , by the pyrolytic decomposition of diphosphine,  $\text{P}_2\text{H}_4$ , and its identification by mass spectrometry.

Diphosphine, prepared by hydrolyzing calcium phosphide and purified by trap-to-trap distillation,<sup>2</sup> was pyrolyzed in a 1-mm i.d., 3-cm long, electrically heated, tubular flow reactor of quartz construction. The diphosphine was pumped through the reactor at a pressure

(1) J. R. Van Wazer, "Phosphorus and Its Compounds," Vol. 1, Interscience Publishers, Inc., New York, N. Y., 1958.

(2) E. C. Evers and E. H. Street, Jr., *J. Am. Chem. Soc.*, **78**, 5726 (1956).

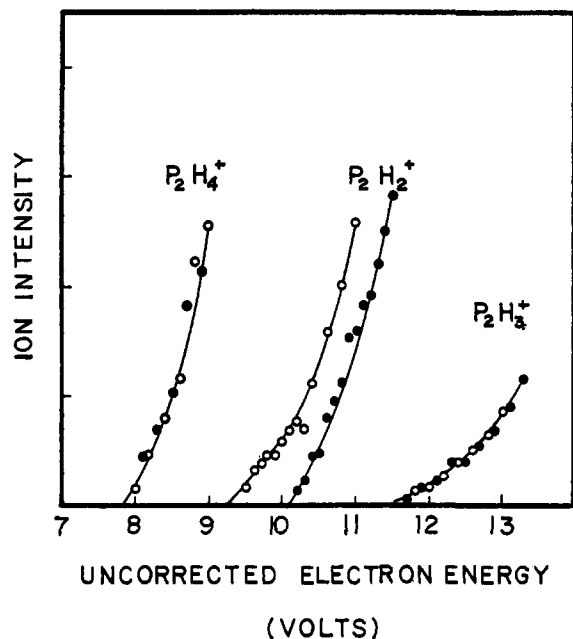


Figure 1. Appearance potential curves of the ions  $P_2H_4^+$ ,  $P_2H_3^+$ , and  $P_2H_2^+$ . The open circles refer to points taken with the reactor at an effective temperature of  $430^\circ K$  while the solid circles refer to points taken with the reactor at  $300^\circ K$ .

of approximately 0.1 torr and a speed of about 0.02 l./sec. The efflux of the reactor was sampled through a 0.3-mm diameter circular hole situated about 2 mm from the downstream end of the furnace. The sampled gas was directed into a mass spectrometer constructed with the following considerations in mind.

The utilization of mass spectrometers employing electron-bombardment sources and conventional sampling<sup>3</sup> in the analysis of thermally unstable compounds can lead to serious problems resulting directly from sample decomposition in the hot source. This problem was recognized, although not eliminated, in one mass spectrometric study of diphosphine<sup>4</sup> but has not been taken into account in other studies.<sup>5,6</sup> A solution to this problem<sup>7</sup> is achieved if the efflux of the sampling orifice is collimated into a beam which is then conventionally ionized, mass analyzed, and detected. By mechanically modulating the molecular beam and amplifying the in-phase part of the total detector response of the mass spectrometer with a narrow-band, lock-in amplifier, strong discrimination against products of decomposition in the source and other background effects is achieved. A mass spectrometer utilizing this type of sampling and detection was employed in this study.

The modulation system alone does not prove that any species found originate in the reactor. However, if the sampling from the reactor is collision free, then the ion intensity for an unreactive molecule should depend on the molecular velocity which in turn will depend on the reactor temperature. As noted below, this is indeed the case here and thus the species described originate from the reactor.

(3) C. A. McDowell, Ed., "Mass Spectrometry," McGraw-Hill Book Co., Inc., New York, N. Y., 1963, pp 72, 342.

(4) Y. Wada and R. W. Kiser, *Inorg. Chem.*, **3**, 174 (1964).

(5) F. E. Saalfeld and H. J. Svec, *ibid.*, **2**, 50 (1963).

(6) F. E. Saalfeld and H. J. Svec, *ibid.*, **3**, 1442 (1964).

(7) S. N. Foner and R. L. Hudson, *J. Chem. Phys.*, **21**, 1374 (1953).

The initial experiments consisted of the examination of the mass spectrum at an electron energy of 50 v with  $P_2H_4$  flowing through the reactor as the effective (*vide infra*) reactor temperature was varied between 300 and  $450^\circ K$ . Ions were identified by previous calibration with added gases and by their dependence on the leak setting. The observed ion intensities were corrected for the decrease in ion intensity to be expected as a result of the increased average velocity of the beam molecules at increased reactor temperatures by using the decrease in signal intensity from a nonreactive internal standard ( $N_2$ ) as a measure of this effect. An effective gas temperature was also calculated from the decrease in ion intensity of the internal standard. This is thought to be a better measure of the temperature of the gas than the thermocouple measurements. By assuming that the spectrum of  $P_2H_4$  is independent of the reactor temperature,<sup>8</sup> the spectrum of undecomposed  $P_2H_4$  could be subtracted from the total spectrum at each reactor temperature. At furnace temperatures greater than  $400^\circ K$  the residual intensities of the ions  $P_2H_2^+$ ,  $P_2H^+$ ,  $P_2^+$ ,  $PH_3^+$ ,  $PH_2^+$ ,  $PH^+$ , and  $P^+$  were appreciable.<sup>9</sup>

Identification of the neutral species producing these ions was achieved by measuring the appearance potentials of the pertinent ions. Figure 1 contains plots of ion intensity vs. electron energy for the ions  $P_2H_4^+$ ,  $P_2H_3^+$ , and  $P_2H_2^+$  with the reactor both activated and inactivated. Although the appearance potentials of  $P_2H_4^+$  and  $P_2H_3^+$  are unaffected, the lowering of the appearance potential of  $P_2H_2^+$  with the reactor on is quite evident. As neither  $P_2H_3$  radicals nor hydrides of higher molecular weight are being produced in detectable quantities, the increase in the  $P_2H_2^+$  ion intensity on activation of the reactor must be due to  $P_2H_2$  molecules, and the appearance potential of the  $P_2H_2^+$  ion with reactor active corresponds to the ionization potential of  $P_2H_2$ .<sup>10</sup>

Simple thermochemical calculations are consistent with this assignment. Using the log matching method<sup>3</sup> and  $P_2H_4^+$  from  $P_2H_4$  as a reference, the shift in the appearance potential of  $P_2H_2^+$  on activating the reactor is 0.9 ev with a precision of  $\pm 0.2$  ev. (If one takes the ionization potential of  $P_2H_4$  as 8.7 ev,<sup>4</sup> the ionization potential of  $P_2H_2$  is 10.0 ev.) Assuming that  $P_2H_2^+$  from  $P_2H_4$  is produced by the process,  $e + P_2H_4 = P_2H_2^+ + H_2 + 2e$ , then the heat of reaction for  $P_2H_4 = P_2H_2 + H_2$  is  $21 \pm 4$  kcal/mole. This gives  $D(P_2H_3-H) + D(P_2H_2-H) = 124 \pm 4$  kcal/mole. If one assumes that  $D(P_2H_3-H)$  equals the average P-H bond energy

(8) This is a weak assumption; however, the main proof for the presence of additional species at high reactor temperatures rests in the appearance potential measurements.

(9) Ions of mass higher than 66 were not observed in these experiments. Examination for the  $H_2^+$  and  $H^+$  ions was not carried out.

(10) It may be argued that the lowering of the  $P_2H_2^+$  appearance potential can be explained by the presence of  $P_2H_3$  and by the assumption that the parent ion intensity of this species is very small. This argument is not tenable on two counts. First the appearance potential of  $P_2H_3^+$  from  $P_2H_4$  has been measured in an instrument employing conventional sampling.<sup>4</sup> A value of  $9.1 \pm 0.3$  ev was obtained, and as this low value was inconsistent with other data obtained, it was assigned to the ionization potential of  $P_2H_3$ , this species presumably being formed by decomposition of  $P_2H_4$  in the source. This assignment is probably correct as the appearance potential of  $P_2H_3^+$  from  $P_2H_4$  obtained in this study is  $2.6 \pm 0.1$  ev higher. This implies a P-H bond energy of  $2.6 \pm 0.4$  ev, a value consistent with that obtained in this study. Consequently, the parent ion intensity from  $P_2H_3$  cannot be negligible. Secondly, the appearance potential of  $P_2H_2^+$  from  $P_2H_3$  should be about  $9.1 + 2.6 = 11.7$  ev, which is about 2 ev higher than that measured with the reactor on.

(77 kcal/mole<sup>11</sup>), then  $D(\text{P}_2\text{H}_2\text{-H}) = 47$  kcal/mole. As the heat of formation of gaseous diphosphine is  $5.0 \pm 1.0$  kcal/mole,<sup>12</sup> the heat of formation of  $\text{P}_2\text{H}_2$  is  $26 \pm 5$  kcal/mole. If one assumes that  $D(\text{P-H})$  equals the average P-H bond energy, one obtains  $D(\text{HP=PH}) = 74$  kcal/mole. This result for the phosphorus-phosphorus double bond energy is between the value for the single bond energy, 48 kcal/mole,<sup>11</sup> and the value for the triple bond energy, 117 kcal/mole.<sup>11</sup>

The residual  $\text{PH}_3^+$  ion intensity is due to the formation of  $\text{PH}_3$  as evidenced by the appearance potential of  $\text{PH}_3^+$  shifting down about 3 eV on activation of the reactor to  $10.4 \pm 0.3$  eV, a value equal to the ionization potential of  $\text{PH}_3$ .<sup>4</sup> The appearance potential of the  $\text{PH}_2^+$  ion with the reactor hot corresponded to that of  $\text{PH}_2^+$  formed by dissociative ionization of  $\text{PH}_3$ .<sup>4</sup>

The contribution of  $\text{PH}_3$  to the residual ion intensities was then subtracted out yielding the approximate mass spectrum of  $\text{P}_2\text{H}_2$  which is given in Table I.

Table I. Relative Abundances of the Principal Ions from  $\text{P}_2\text{H}_2$

Ion	Rel abundance at 50 eV
$\text{P}_2\text{H}_2^+$	24
$\text{P}_2\text{H}^+$	39
$\text{P}_2^+$	100
$\text{PH}_2^+$	0.5 (?)
$\text{PH}^+$	5
$\text{P}^+$	60

The nitrogen analog of this compound has been prepared<sup>13</sup> by the decomposition of hydrazoic acid in an electric discharge and identified by mass spectrometry. It may be noted that the difference between the ionization potentials of  $\text{N}_2\text{H}_4$  (9.00 eV<sup>14</sup>) and  $\text{N}_2\text{H}_2$  (9.85 eV<sup>13</sup>) is in the same direction and is of the same order of magnitude as that between  $\text{P}_2\text{H}_4$  and  $\text{P}_2\text{H}_2$  measured in this work.

**Acknowledgment.** The aid of Mr. Robert B. Callen in the preparation of the diphosphine is gratefully acknowledged. This work was supported by a National Science Foundation grant, NSF-GP-4186.

(11) T. L. Cottrell, "The Strengths of Chemical Bonds," Butterworths and Co. Ltd., London, 1958.

(12) S. R. Gunn and L. G. Green, *J. Phys. Chem.*, **65**, 779 (1961).

(13) S. N. Foner and R. L. Hudson, *J. Chem. Phys.*, **28**, 719 (1958).

(14) V. H. Dibeler, J. L. Franklin, and R. M. Reese, *J. Am. Chem. Soc.*, **81**, 68 (1959).

T. P. Fehlner

Department of Chemistry, University of Notre Dame  
Notre Dame, Indiana 46556

Received February 21, 1966

## Molecular Structures of Triiron Dodecacarbonyl and Tetracobalt Dodecacarbonyl

Sir:

All further speculation concerning the probable structures of  $\text{Fe}_3(\text{CO})_{12}$  and  $\text{Co}_4(\text{CO})_{12}$  in the *solid state* can be laid to rest; the structures of these two important transition metal carbonyls have been *ascertained* from three-dimensional X-ray investigations.

Although a disordered triangular iron structure originally was proposed by Dahl and Rundle<sup>1</sup> for  $\text{Fe}_3$ -

$(\text{CO})_{12}$  as being the only model compatible with their X-ray work, initial interpretations of subsequent Mössbauer resonance and other spectral measurements<sup>2-5</sup> rejected the triangular iron model in favor of ones involving a linear array of iron atoms. From a structural analysis<sup>6</sup> of the  $\text{HFe}_3(\text{CO})_{11}^-$  anion,<sup>7</sup> however, Dahl and Blount<sup>8</sup> proposed a molecular configuration for  $\text{Fe}_3(\text{CO})_{12}$  involving a triangular arrangement of iron atoms which they showed to be in agreement with the X-ray, reinterpreted Mössbauer, and solid-state infrared data of  $\text{Fe}_3(\text{CO})_{12}$ . The same triangular model for  $\text{Fe}_3(\text{CO})_{12}$  independently was suggested by Erickson and Fairhall<sup>9</sup> from their Mössbauer spectrum of  $\text{HFe}_3(\text{CO})_{11}^-$ .

In a vigorous effort to unravel the actual structure of  $\text{Fe}_3(\text{CO})_{12}$ , a new sample was prepared, and three-dimensional photographic data were recollected with Mo  $K\alpha$  radiation from a particularly good crystal which yielded 539 independent intensity maxima. From Patterson and Fourier methods the disordered crystal structure of  $\text{Fe}_3(\text{CO})_{12}$  was elucidated and refined by least squares to  $R_1 = 12.5\%$ .<sup>10</sup>

The idealized molecular configuration of  $\text{C}_{2v}$ -2mm symmetry (Figure 1) is in accord with the molecular model of  $\text{Fe}_3(\text{CO})_{12}$  derived from  $\text{HFe}_3(\text{CO})_{11}^-$ <sup>8</sup> and can be considered as being formed by the insertion of a *cis*- $\text{Fe}(\text{CO})_4$  group at one of the three bridging carbonyl positions of  $\text{Fe}_2(\text{CO})_9$ . The twelve carbonyl groups are approximately disposed toward the vertices of an icosahedron. The two chemically equivalent Fe-Fe distances of 2.69 and 2.68 Å and the third shorter distance of 2.55 Å (individual esd, 0.01 Å) for the isosceles iron

(1) L. F. Dahl and R. E. Rundle, *J. Chem. Phys.*, **26**, 1751 (1957).

(2) M. Kalvius, U. Zahn, P. Kienle, and H. Eicher, *Z. Naturforsch.*, **17a**, 494 (1962).

(3) R. H. Herber, W. R. Kingston, and G. K. Wertheim, *Inorg. Chem.*, **2**, 153 (1963).

(4) E. Fluck, W. Kerler, and W. Neuwirth, *Angew. Chem. Intern. Ed. Engl.*, **2**, 277 (1963).

(5) G. R. Dobson and R. K. Sheline, *Inorg. Chem.*, **2**, 1313 (1963).

(6) J. F. Blount, Ph.D. Thesis, University of Wisconsin, Madison, Wis., 1965; J. F. Blount and L. F. Dahl, to be published.

(7) J. R. Case and M. C. Whiting, *J. Chem. Soc.*, 4632 (1960).

(8) L. F. Dahl and J. F. Blount, *Inorg. Chem.*, **4**, 1373 (1965).

(9) N. E. Erickson and A. W. Fairhall, *ibid.*, **4**, 1320 (1965).

(10) In spite of the crystal disorders in both  $\text{Fe}_3(\text{CO})_{12}$  and  $\text{Co}_4(\text{CO})_{12}$ , the molecular configurations were unambiguously apparent from the electron-density maps, which showed complete resolution of all carbon and oxygen peaks. The crystal-disordered model successfully utilized in the least-squares refinements of the two compounds assumes a random distribution of each molecule in one of two orientations such that on the average one-half of an atom occupies each atomic position. Since the Fourier maps of  $\text{Fe}_3(\text{CO})_{12}$  and  $\text{Co}_4(\text{CO})_{12}$  showed a *near*-superposition of the corresponding half-atom carbon and oxygen peaks for the two orientations, the least-squares analyses were based on a half-atom weighting for only the disordered metal atoms and a whole-atom weighting for each of the light atoms in which each of the refined carbon and oxygen positions in both structures represents the *mean* of two half-atom positions. In  $\text{Co}_4(\text{CO})_{12}$  the twofold crystallographic axis which relates the two orientations of half-molecules to each other is coincident with one of the 15 molecular twofold axes of an *idealized* icosahedron. This twofold axis, which is also coincident with a threefold *localized* axis of the tetrahedron of cobalt atoms, passes through a *basal* cobalt atom and transforms the other three cobalts (*i.e.*, the apical and other two basal cobalt atoms) of a given molecule into a hexagon of six half-cobalt atoms. In  $\text{Fe}_3(\text{CO})_{12}$  a crystallographic center of symmetry located to a first approximation at the centroid of a given triangle of iron atoms relates the two half-molecules to each other and thereby produces a hexagon of six half-iron atoms and *six* crystallographically independent carbonyl groups (with the assumption given above that each light atom in the *idealized* centrosymmetric icosahedron is the *mean* of two half-atoms). The resulting consequence for *each compound* is that either choice of the two possible orientations of the metal framework together with the twelve "whole" carbonyl groups (of which only *six* are crystallographically independent in our calculations) unambiguously yields the same molecular configuration. Details of the structural analyses and order-disorder phenomena for both compounds will be given elsewhere.