$CdSiO_3$:

$D(192/T) + E(246/T) + 2E(630/T) + E(1366/T)$, (0.7%)

The entropy calculations are summarized in Table II.

The entropy of crystalline lead metasilicate is 2.5 units lower than obtained by Kelley[2] for the amorphous substance. Using the entropy values for cadmium oxide and quartz listed by Kelley[2] and that for PbO(red) given by the author,[6] the following entropies of formation from the constituent oxides are obtained for the crystalline silicates: $PbSiO_3$, $\Delta S_{298.15} = 0.6$; Pb_2SiO_4, $\Delta S_{298.15} = 3.4$, and $CdSiO_3$, $\Delta S_{298.15} = 0.2$ cal./deg. mole.

Table II

Entropies at 298.15°K. (cal./deg. mole)

Substance	$S^0_{51} - S^0_0$ (extrap.)	$S^0_{298.15} - S^0_{51}$ (meas.)	$S^0_{298.15}$
$PbSiO_3$	3.40	22.85	26.2 ± 0.3
Pb_2SiO_4	7.80	36.84	44.6 ± .5
$CdSiO_3$	2.02	21.25	23.3 ± .2

Berkeley 4, Cal.

---

[6] E. G. King, This Journal, **80**, 2400 (1958).

[Contribution from the Departments of Chemistry of Massachusetts Institute of Technology, Harvard University and Imperial College, London]

Heats of Combustion and Formation of Metal Carbonyls. III. Iron Pentacarbonyl; The Nature of the Bonding in Metal Carbonyls[1]

By F. A. Cotton, A. K. Fischer and G. Wilkinson

Received May 1, 1958

The heat of combustion of iron pentacarbonyl has been measured by bomb calorimetry and leads to a value of -182.6 ± 1.7 kcal./mole for ΔHf^0_{298} of liquid $Fe(CO)_5$. In the combustion process metallic iron and several iron oxides are produced and each of these was determined analytically. The heat of formation of $Fe(CO)_5$ together with the heats of formation of the carbonyls of Ni, Cr, Mo and W permit calculation of the mean bond dissociation energies in all of these compounds. When these energies are corrected for the valence state promotion energies according to the classical view of the bonding in metal carbonyls, it is found that the energies of dissociation of the metal–carbon bonds to valence states are of reasonable magnitude, thus suggesting that the assumed picture of the bonding is reasonable.

I. Introduction

In previous papers we have reported the heats of combustion and heats of formation of the carbonyls of the group VI[2] elements, *i.e.*, $Cr(CO)_6$, $Mo(CO)_6$ and $W(CO)_6$, and subsequently of $Ni(CO)_4$.[3] In the present paper we report the same quantities for $Fe(CO)_5$. With all of these data it is now possible to draw certain conclusions concerning the nature and strengths of the metal–carbon bonds in these molecules, and this is done in section IV.

Previous efforts to determine the heat of formation of iron pentacarbonyl have also utilized combustion calorimetry. In discussing these previous results and those presented in this paper, the following thermochemical equations are pertinent

$$Fe(CO)_5(l) = Fe(CO)_5(g) \quad \Delta H_v = 8.9 \text{ kcal./mole} \qquad (1)$$

$$Fe(CO)_5(l) + 13/4O_2(g) = 1/2Fe_2O_{3(s)} + 5CO_2(g) \quad (\Delta H_{comb.}) \qquad (2)$$

$$Fe(s) + 5C(s) + 5/2O_2(g) = Fe(CO)_5(l) \ (\Delta Hf^0) \qquad (3)$$

In all cases the temperature is taken to be 298°K. and the substances are in their standard states according to present conventions.[4] The heat of vaporization of $Fe(CO)_5$ has been determined by several workers, the quoted value being that given in the NBS tables,[4] where references to the original papers may be found. About thirty years ago Roth[5] reported some work by Doepke on the heat of combustion of iron pentacarbonyl in which samples sealed in glass were ignited by the burning of Vaseline. It was stated that almost pure Fe_3O_4 was formed; no mention was made of an examination for metallic iron or Fe_2O_3 or of an analysis of the gaseous combustion products. The average heat of combustion from two experiments was reported to be -372.5 kcal./mole, presumably involving liquid $Fe(CO)_5$ and with Fe_3O_4 as the only iron containing product. From this, presumably using the old Berthelot and Thomsen value for the heat of formation of CO, Roth obtained for the reaction, $Fe(\alpha) + 5CO \rightarrow Fe(CO)_5$ (*sic*), an energy of -54.4 kcal., a result stated by him to be in good agreement with Mittasch's value of -54.2 ± 0.7 kcal.[6] Presumably, since Roth makes this comparison and since Mittasch's figure applied to liquid $Fe(CO)_5$, Roth's equation should also specify the liquid state for $Fe(CO)_5$. Mittasch's result appears in the text of a speech and only as an entry in an extensive table of the physical properties of iron pentacarbonyl. It is disconcerting that Mittasch also reports a heat of combustion (states and experimental details unspecified) of -384.5 kcal./mole, 12 kcal./mole higher than Roth's, although their quoted heats of formation agree. From these data the NBS tables[4] derived a value of ΔHf^0_{298} according to equation 3 of -187.8 kcal./mole. The uncertainty and possible error in this value indicated the need for a redetermination before attempting any thermochemical arguments concerning the bonding in this substance.

---

[1] Presented before the Division of Inorganic Chemistry, 133rd Meeting of the American Chemical Society, San Francisco, April, 1958.

[2] F. A. Cotton, A. K. Fischer and G. Wilkinson, This Journal, **78**, 5168 (1956).

[3] A. K. Fischer, F. A. Cotton and G. Wilkinson, *ibid.*, **79**, 2044 (1957).

[4] Selected Values of Chemical Thermodynamic Properties, U. S. National Bureau of Standards Circular 500, U. S. Government Printing Office, Washington, D. C., 1952.

[5] W. A. Roth, *Angew. Chem.*, **42**, 981 (1929).

[6] A. Mittasch, *ibid.*, **41**, 827 (1928).

II. Experimental

Iron pentacarbonyl was obtained from the Antara Division of the General Aniline Corp. and was purified by distillation *in vacuo;* the middle cut was redistilled twice and stored in the vacuum line in a bulb protected from light. From this, sample bulbs of the internally fired type previously described[3] were filled by distillation just prior to use. All operations were performed in the dimmest possible illumination to protect the photosensitive carbonyl. Photochemical decomposition presented its greatest hazard at the moment when the bright blue oxygen-gas flame was applied to the bulb stem; the exposure was slight, however, since most of the bulb was shielded by slotted asbestos paper covering the cooling bath in which the bulb was held. Only at the point of sealing was a slight mirror of metallic iron seen. The weight of this was less than 0.1 mg. and it did not impair the quality of the seal.

In order to facilitate analysis of the combustion products, unglazed Alundum combustion cups were used, and some structural changes were made in the previously used bomb and calorimeter.[2,3] The water equivalent of the bomb and calorimeter was then redetermined; six measurements gave a mean of 411.9 ± 5.0 g. After each run the bomb gases were passed through an absorption train for CO_2 analysis. The large amounts of gas and the long periods of time required for their slow passage through the train made it imperative to reduce leakage to a minimum. This was best achieved by just cracking the bomb valve and drawing the gases through the system with an aspirator and a manostat which kept the pressure at the end of the train 2 cm. below atmospheric pressure rather than by forcing them through under a positive pressure from the bomb. Checks made by generating, under 30 atm. of O_2, comparable amounts of CO_2 from acid and carbonate in the bomb showed that this arrangement gave CO_2 analyses good to 0.2%. The train consisted, in order, of a concentrated sulfuric acid bubbler, a silica gel–anhydrous copper sulfate tube, a Dehydrite–Drierite tube, two Ascarite–Dehydrite tubes in parallel, two more such tubes in series (the last serving as a guard tube) and a mineral oil bubbler. Since no evidence was ever obtained for the presence of unburned carbon, the slight deficits in total CO_2 found in all but one run were attributed to CO. Also it is not likely that in a highly oxidizing atmosphere CO will be reduced to carbon, although, of course, through the agency of the zero valent metal this is not impossible. It was not feasible with the above gas train also to analyze for CO as was done previously for $Ni(CO)_4$.[3] If it should be true that in a given case the CO_2 deficit is due entirely to carbon rather than entirely to CO, a correction greater than that applied by a factor of 1.39 should be used. Thus the average of the fully corrected $\Delta E^0_{298(\text{comb.})}$ values would be raised by 1.71 kcal./mole, if such an extreme revision of the correction were required in all five runs.

Analysis of the solid combustion products was carried out in the following manner. Most of the iron (72 to 96%) appeared as Fe_2O_3 blanketing the inner bomb wall; this oxide was therefore chosen as the final state to which the observed ΔE should be corrected. It was thus unnecessary to recover Fe_2O_3 quantitatively but rather only to recover and determine quantitatively all other iron-containing solids, among which were to be expected Fe, FeO and Fe_3O_4. The bomb was brushed out carefully so as to recover all visible solids except for small amounts of Fe_2O_3. The brushings and the Alundum cup which bore an adherent deposit were ground in an agate mortar under ethanol to inhibit atmospheric oxidation. The crushed mixture was treated with 50 ml. of boiling 5% cupric sulfate solution for 0.5 hr. to dissolve metallic iron.[7] The solids were filtered off and washed; in the filtrate the dissolved metallic iron [as Fe(II)] was separated from the excess Cu(II) by precipitation with ammonia. The hydrochloric acid solution of the filtered, washed and redissolved precipitate of ferric hydroxide was reduced with stannous chloride and titrated with standard dichromate using barium diphenylamine sulfonate indicator.

The filtered residue consisted of glass particles, iron oxides, metallic copper and Alundum. The copper was dissolved by heating overnight with slightly ammoniacal 50% potassium cyanide solution.[7] The washed residue was boiled with 30 ml. of concentrated HCl under an atmosphere of CO_2. After cooling, the solution was diluted to 150 ml. and titrated with dichromate, thus giving a direct measure of Fe(II) dissolved. The correction for Fe(II), Table I, was made on the assumption that all Fe(II) detected here was present in Fe_3O_4. This is acceptable since the amount of Fe(II) was small and the correction would at most raise the average ΔE^0_{298}(comb.) about 0.3 kcal./mole above the values listed were all Fe(II) present as $Fe_{0.95}O$ as the following equations show

$$Fe_{0.95}O(s) + 1.70/8O_2(g) = 1.90/4Fe_2O_3(s) \qquad \Delta H^0_{298} = -29.6 \text{ kcal./mole}$$

$$Fe_3O_4(s) + 1/4O_2(g) = 3/2Fe_2O_3(s) \qquad \Delta H^0_{298} = -27.7 \text{ kcal./mole}$$

The solid residue remaining after this last titration always contained a few black specks which resisted the acid treatment. They were, however, very slowly attacked by prolonged treatment with boiling concentrated HCl. In a preliminary run a few of these specks were collected; they were found to be magnetic and analysis for iron after dissolving them by fusion with sodium carbonate showed an iron content somewhat higher than that of Fe_3O_4. This demonstrated the need for thorough grinding to expose occluded metallic iron to detection in the $CuSO_4$ procedure described above. In all runs reported in Table I the solid residue remaining after titration was fused with carbonate and all iron detected after leaching and acidification of the melt was assumed to have come from Fe_3O_4. In this way, a further increment of about 10% was made to the Fe(II) correction.

TABLE I

DATA ON COMBUSTION OF $Fe(CO)_5(l)$

Vacuum wt. of sample, g.	Cor. temp. rise, °C.	Uncor. ΔE(comb.), kcal./mole
1.8289	1.5243	−377.86
1.7812	1.4689	−373.82
2.6240	2.1553	−372.46
1.9258	1.6081	−378.84
2.3461	1.9348	−373.71

Corrn. for incomplete combustion, kcal./mole			Fuse corrn., kcal./mole	Washburn corrn., kcal./mole	Fully cor. ΔE^0_{298}(comb.), kcal./mole
Fe(0)	Fe(II)	CO			
−2.27	−3.99	− 2.12	0.74	0.58	−384.92
−1.33	−1.25	−11.30	.76	.73	−386.21
−2.96	−6.54	− 4.55	.51	.57	−385.43
−6.62	−3.77	0.00	.70	.57	−388.53
−4.20	−8.73	− 3.75	.58	.60	−389.21

The corrected temperature rise was computed as previously described[2,3] as were the fuse corrections and Washburn corrections.

III. Results for $Fe(CO)_5$

The data on the combustion of $Fe(CO)_5(l)$ are presented in Table I. All runs not known to be unreliable (due, for example, to misfiring, highly atypical appearance of combustion products, etc.) are reported. The average of the five values for ΔE^0_{298}(comb.) is −386.86 kcal./mole with a standard deviation of a single measurement of ±1.7 kcal./mole. The maximum random error, taken as the sum of estimated maximum errors in the various operations, including analyses,[8] was calculated to be ±2.6 kcal./mole. The standard enthalpy of combustion for the process defined in equation 2 is calculated to be −385.9 ± 1.7 kcal./mole. The standard enthalpy of formation of $Fe(CO)_5(l)$ according to equation 3 is found to be −182.6 ± 1.7 kcal./mole, taking all auxiliary data from the NBS tables.[4] With the heat of vaporization given in equation 1, the enthalpy of

---

[7] C. E. Sims and B. M. Larsen, *Ind. Eng. Chem.*, **17**, 86 (1925).

[8] For details see A. K. Fischer, Ph.D. Thesis, Harvard University, 1958.

the following process was calculated

$$Fe(CO)_5(g) = Fe(g) + 5CO(g)$$
$$\Delta H^0_{298} = +138.3 \pm 1.7 \text{ kcal./mole} \qquad (4)$$

IV. Bond Energies in Metal Carbonyls

Using the data for $Fe(CO)_5$ reported above and heats of combustion previously reported[9] for the other carbonyls[2,3] together with other data from the NBS tables,[4] the enthalpies of the following processes have been computed.

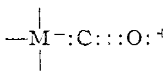
$$1/6Cr(CO)_6(g) = 1/6Cr(g) + CO(g) \quad \Delta^0_{298} = 27.1 \text{ kcal.}$$
$$1/6Mo(Co)_6(g) = 1/6Mo(g) + CO(g) \quad \Delta H^0_{298} = 35.9 \text{ kcal.}$$
$$1/6W(CO)_6(g) = 1/6W(g) + CO(g)$$
$$\Delta H^0_{298} = 42.1 \text{ kcal.} \quad (5)$$
$$1/5Fe(CO)_5(g) = 1/5Fe(g) + CO(g) \quad \Delta H^0_{298} = 27.7 \text{ kcal.}$$
$$1/4Ni(CO)_4(g) = 1/4Ni(g) + CO(g) \quad \Delta H^0_{298} = 35.2 \text{ kcal.}$$

These are the mean thermochemical M–C bond energies with all species in their standard states.

These data provide a means of evaluating the generally accepted theory of the electronic structures of metal carbonyls on the basis of the energetics of bond formation according to that theory. The electronic processes involved in the formation of the metal–carbon bonds may be considered to be the following.[10] The valence electrons of the metal atom, which are *n*d and $(n + 1)$s electrons, are first paired up in the smallest number of d orbitals necessary. This process is represented by equation 6a in which M represents a gaseous metal atom in its ground electronic state and M* represents the same gaseous atom in the excited state described just above which is in fact its valence state. It is then possible for CO molecules to

$$M = M^* \quad (\Delta H_M^*) \qquad (6a)$$

donate unshared electron pairs on the carbon atoms to metal orbitals formed by appropriate hybridization of the remaining, empty *n*d orbitals (if any) with the $(n + 1)$s and the three $(n + 1)$p orbitals. As Pauling remarked, this would lead to a state which could be represented thus



$$-\overset{|}{\underset{|}{M}}{}^{-}:C:::O:^{+} \qquad (I)$$

This electronic structure would be unacceptable because of the large separation of charge required and because of its failure to accord with the short M–C bonds existing in metal carbonyls. These latter considerations led Pauling to propose that the true electronic structure could be represented as a resonance hybrid of I with II. Clearly in neither

$$M::C::\overset{..}{\underset{..}{O}} \qquad (II)$$

of these forms is the electronic state of carbon monoxide very similar to that in the free molecule. It is therefore useful to consider a hypothetical process in which the M–C bond is broken so as to leave the metal atom in the state M* and the carbon monoxide in an excited state, CO*, which is as nearly as possible its state when combined in the metal carbonyl molecule. The conversion of CO in its ground state to the hypothetical CO* in the carbonyl of a given metal, M, is represented in 6b, and the bond breaking process in a metal

$$CO = CO^* \quad (\Delta H^M_{CO}{}^*) \qquad (6b)$$

carbonyl to yield M* and CO*, *i.e.*, "valence state" products is represented in 6c.

$$1/xM(CO)_x(g) = 1/xM^*(g) + CO^*(g) \qquad (\Delta H^*) \quad (6c)$$

We seek to evaluate ΔH^* in order to see if its magnitude is reasonable. It was expected that if the above view of the bonding process were unrealistic it would be so because the high energies of promotion to the required valence states would make ΔH^* too high to be credible. Hence it is important not to overlook any important positive contribution, *e.g.*, 6b, to ΔH^*. Clearly its value in any case is given by the sum of the appropriate one of the equations 5, $1/x$ of equation 6a and equation 6b.

For the metals Ni, Fe and Cr the promotion energies ΔH_{M^*} are available. Ni* represents the nickel atom in the valence state ($3d^{10}$, V_0). This is identical with the observed spectroscopic $3d^{10}$ ^1S state of Ni(I) found at 42.1 kcal. above the ground state.[11] Spectroscopic states corresponding to the required valence states for Fe and Cr have not been observed experimentally. Recently, however, Skinner and Sumner[12] have estimated the energies of these states using Racah parameters evaluated from other observed states. They give for Fe($3d^8$, V_0) 6.62 volts (153 kcal.) and for Cr($3d^6$, V_0) 7.33 volts (169 kcal.).

In order to make some estimate of the energies $\Delta H^M_{CO}{}^*$ a relation between bond energy (strictly, bond dissociation energy) and bond stretching force constant has been used. It would be impossible to justify the use of any very sophisticated treatment in this case; therefore the simple formula of Lippincott and Schroeder,[13] which seems to be empirically valid aside from any *a priori* validity it may have, has been chosen. This relation is of the form

$$D_e = k_e r_e / n \qquad (7)$$

where D_e is the depth of the potential well, k_e the quadratic force constant, r_e the equilibrium bond length and n is a parameter characteristic of the bonding between a particular pair of atoms. We shall ignore the zero point energies and use D_0 for D_e. k_e, r_e and D_0 for CO are 19.02 mdynes/Å., 1.13Å. and 257 kcal./mole, respectively.[14] For the –CO grouping in the carbonyls of Cr, Fe and

---

[9] In reference 3, we quoted Smagina and Ormont as reporting a value of −47.3 kcal./mole for the reaction $Ni(s) + 4CO(g) = Ni(CO)_4(g)$. This was an error on our part; their value refers to the corresponding reaction to produce *liquid* $Ni(CO)_4$. When corrected for the heat of vaporization of $Ni(CO)_4$, it becomes −40.8 kcal./mole, close to what is presumed now to be the correct value.[3] As noted[3] however, the *a priori* reliability of this determination appears to be less than satisfactory.

[10] See L. Pauling, "The Nature of the Chemical Bond," 2nd Ed., Cornell University Press, Ithaca, N. Y., 1945, pp. 251, where the first full exposition of these ideas seems to have been given.

[11] C. E. Moore, "Atomic Energy Levels," Vol. II, Circular No 467, U. S. Natl. Bureau of Standards, Washington, D. C., 1952.

[12] H. A. Skinner and F. H. Sumner, *J. Inorg. Nucl. Chem.*, **4**, 245 (1957).

[13] E. R. Lippincott and R. Schroeder, *J. Chem. Phys.*, **23**, 1131 (1955).

[14] See T. L. Cottrell, "The Strengths of Chemical Bonds," Butterworths, London, 1954. The D_0 value is based on an L_C value of 170.4 kcal./mole, which is now accepted.

Ni values for k_e and r_e have been reported. The bond lengths[15] reported are all 1.15 to 1.16 ± 0.03 to 0.05 Å. Consequently, a distance of 1.16 ± 0.05 Å. has been assumed in each case. Except for $Ni(CO)_4$[16] no thoroughly reliable CO stretching constants are available. Those reported,[17] however, all lie in the range 15.5–16.5 mdynes/Å. and infrared active CO stretching frequencies in these carbonyls all lie in the range 1950–2050 cm.$^{-1}$. Consequently a k_e value of 16.0 mdynes/Å. has been used in each case. Finally it is assumed that the characteristic constant n will be the same for free and bound CO. Since the energy $\Delta H^{\mathrm{M}}_{\mathrm{CO}*}$ is a small fraction of D_{CO}, this is probably not too bad an approximation. D for a CO group in a metal carbonyl can then be estimated by a proportion and it is clear that the available data will only permit us to obtain the same value for all three carbonyls. This value is found to be 225 ± 12 kcal./mole.

The energies, ΔH^* (equation 6c) are found to be 87 for $Cr(CO)_6$, 89 for $Fe(CO)_5$ and 77 for $Ni(CO)_4$, all in kcal. In $Fe(CO)_5$ the bonds are not all equivalent and 89 kcal./mole represents a weighted average. It is our opinion that an energy of dissociation to valence states of approximately 85 kcal./mole is not unbelievably high, and we therefore conclude that the usual view of the bonding, summarized above, is acceptable on the basis of bond energetics.

More detailed conclusions about the nature of the metal–carbon bonding in metal carbonyls might be obtained by consideration of the trends apparent in the thermochemical data. It first must be recognized that because of the uncertainties in the data and procedures used to obtain the ΔH^* values from the thermochemical data in equations 5, no significance can be attached to the apparent trend in these ΔH^* values. The direct thermochemical data themselves do reveal two significant trends. First, it appears that, *per metal–carbon bond*, $Ni(CO)_4$ is somewhat more stable than $Cr(CO)_6$ and $Fe(CO)_5$. This would suggest that the trend in their ordinary chemical and physical stability, which runs roughly in the opposite direction, is due to kinetic factors. The second trend is the regular increase in stability in the series $Cr(CO)_6$, $Mo(CO)_6$, $W(CO)_6$. This order appears quite certain and outside of experimental error and will be discussed in the future in relation to the force constants in these molecules.

Acknowledgments.—The experimental work described was carried out at Harvard University and we are indebted to Professors G. B. Kistiakowsky and L. K. Nash for the loan of equipment, Professor W. Moffit for helpful discussions and the Mallinckrodt Chemical Company for financial support.

CAMBRIDGE, MASSACHUSETTS

[15] For a tabulation, see J. W. Cable and R. K. Sheline, *Chem. Revs.*, **56**, 1 (1956).

[16] H. Murata and K. Kawai, *J. Chem. Phys.*, **26**, 1355 (1957).

[17] For $Cr(CO)_6$ and $Mo(CO)_6$ see H. Murata and K. Kawai, *ibid.*, **27**, 605 (1957); for $Fe(CO)_5$ see W. G. Fateley and E. R. Lippincott, *Spectrochim. Acta*, **10**, 8 (1957).

[CONTRIBUTION NO. 504 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND COMPANY]

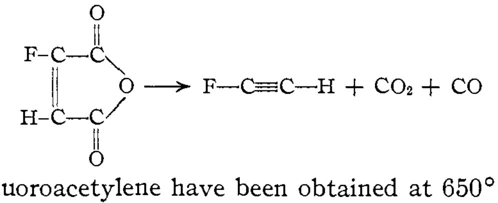
Fluoroacetylene

BY W. J. MIDDLETON AND W. H. SHARKEY

RECEIVED AUGUST 21, 1958

Fluoroacetylene has been prepared in essentially quantitative yield by pyrolysis of fluoromaleic anhydride. Fluoroacetylene is a colorless gas boiling slightly below −80°. It spontaneously trimerizes to 1,2,4-trifluorobenzene, forms metal salts and reacts pyrophorically with bromine. In the liquid state fluoroacetylene is treacherously explosive.

Chloroacetylene,[1] bromoacetylene[2] and iodoacetylene[3] have been studied by several investigators. However, there appears to be no report of attempts to prepare fluoroacetylene. We wish to report a successful synthesis of fluoroacetylene by a new reaction that involves pyrolysis of fluoromaleic anhydride. Essentially quantitative yields



of fluoroacetylene have been obtained at 650° and 5–7 mm. It was identified by mass spectrometric analysis that indicated a molecular formula of C_2HF; by infrared spectrographic analysis (Fig. 1) that indicated the presence of C≡C (4.40, 4.54 μ), C–F (9.25, 9.50 μ) and acetylenic C–H (3.0 μ) bonds; and by proton and fluorine nuclear magnetic resonance spectra (n.m.r.) that are wholly consistent with the expected structure. The fluorine n.m.r. is noteworthy in that the resonance occurred at an extremely high field.

Fluoroacetylene is a colorless gas that freezes to a white solid at −196° (liquid nitrogen) and melts to a mobile liquid that boils a little below −80° (solid carbon dioxide in acetone). Accurate boiling and melting points were not obtained because of the explosive nature of fluoroacetylene. On several occasions, liquid samples have detonated with considerable force. One such sample was mixed with solid carbon dioxide and was boiling at atmospheric pressure. In another case a small sample of the pure liquid had been sealed in a glass tube and allowed to warm slightly above −80°.

[1] O. Wallach, *Ann.*, **203**, 88 (1880); E. H. Ingold, *J. Chem. Soc.*, **125**, 1535 (1924).

[2] K. A. Hoffmann and H. Kirmreuther, *Ber.*, **42**, 4235 (1909).

[3] V. Grignard and K. Tcheoufaki, *Compt. rend.*, **188**, 357 (1929).