

Ni values for  $k_e$  and  $r_e$  have been reported. The bond lengths<sup>15</sup> reported are all 1.15 to 1.16  $\pm$  0.03 to 0.05 Å. Consequently, a distance of 1.16  $\pm$  0.05 Å. has been assumed in each case. Except for Ni(CO)<sub>4</sub><sup>16</sup> no thoroughly reliable CO stretching constants are available. Those reported,<sup>17</sup> however, all lie in the range 15.5–16.5 mdyne/Å. and infrared active CO stretching frequencies in these carbonyls all lie in the range 1950–2050 cm.<sup>-1</sup>. Consequently a  $k_e$  value of 16.0 mdyne/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  $\Delta H_{CO}^*$  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  $\pm$  12 kcal./mole.

The energies,  $\Delta H^*$  (equation 6c) are found to be 87 for Cr(CO)<sub>6</sub>, 89 for Fe(CO)<sub>5</sub> and 77 for Ni(CO)<sub>4</sub>, all in kcal. In Fe(CO)<sub>5</sub> 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 there-

(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)<sub>6</sub> and Mo(CO)<sub>6</sub> see H. Murata and K. Kawai, *ibid.*, **27**, 605 (1957); for Fe(CO)<sub>5</sub> see W. G. Fateley and E. R. Lippincott, *Spectrochim. Acta*, **10**, 8 (1957).

fore 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  $\Delta H^*$  values from the thermochemical data in equations 5, no significance can be attached to the apparent trend in these  $\Delta H^*$  values. The direct thermochemical data themselves do reveal two significant trends. First, it appears that, *per metal-carbon bond*, Ni(CO)<sub>4</sub> is somewhat more stable than Cr(CO)<sub>6</sub> and Fe(CO)<sub>5</sub>. 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)<sub>6</sub>, Mo(CO)<sub>6</sub>, W(CO)<sub>6</sub>. 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.

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

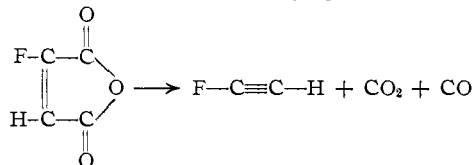
## Fluoroacetylene

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Fluoroacetylene has been prepared in essentially quantitative yield by pyrolysis of fluoromaleic anhydride. Fluoroacetylene is a colorless gas boiling slightly below  $-80^\circ$ . 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,<sup>1</sup> bromoacetylene<sup>2</sup> and iodoacetylene<sup>3</sup> 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

(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).

C<sub>2</sub>HF; by infrared spectrographic analysis (Fig. 1) that indicated the presence of C $\equiv$ C (4.40, 4.54  $\mu$ ), C–F (9.25, 9.50  $\mu$ ) and acetylenic C–H (3.0  $\mu$ ) 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  $-196^\circ$  (liquid nitrogen) and melts to a mobile liquid that boils a little below  $-80^\circ$  (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  $-80^\circ$ .

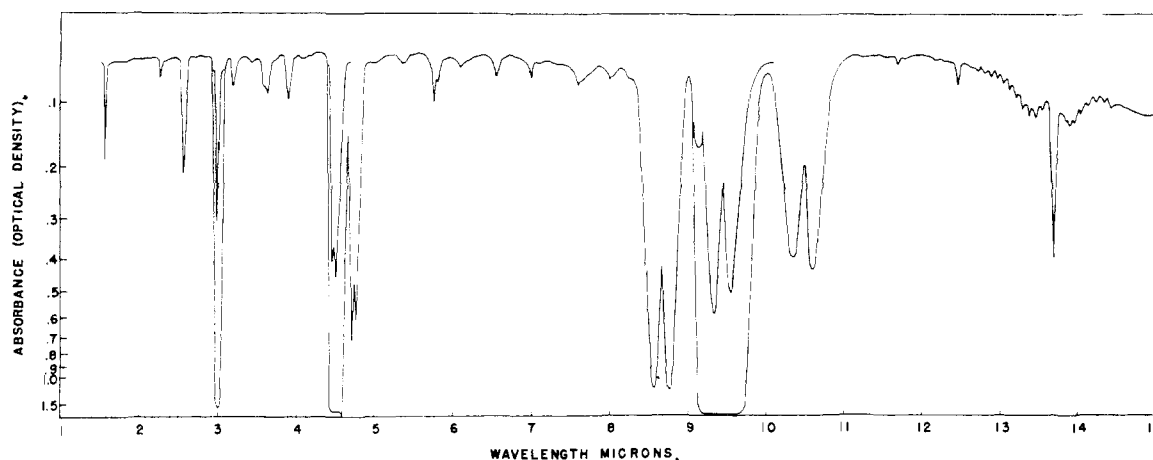


Fig. 1.—Infrared spectrum of fluoroacetylene.

Although liquid samples of fluoroacetylene are treacherously explosive, gaseous fluoroacetylene at atmospheric pressure was handled without incident. A brief examination of gaseous fluoroacetylene showed that it slowly condenses to a trimer, 1,2,4-trifluorobenzene, and a yellow-brown polymer. In contrast to chloroacetylene, fluoroacetylene is not spontaneously inflammable in air. A pyrophoric reaction was observed when fluoroacetylene was bubbled into a solution of bromine in carbon tetrachloride. Mercury and silver salts of fluoroacetylene also have been prepared by passing fluoroacetylene into aqueous solutions of mercury and silver nitrates, respectively.

#### Experimental

**Fluoromaleic Anhydride.**—An intimate mixture of 200 g. of fluorofumaric acid<sup>4</sup> and 200 g. of phosphoric pentoxide was heated in a simple still, and the condensate was redistilled. There was obtained 152 g. of fluoromaleic anhydride as a colorless oil, b.p. 68° (18 mm.),  $n_D^{25}$  1.4436.

*Anal.* Calcd. for  $C_4HFO_3$ : C, 41.40; H, 0.86; F, 16.37. Found: C, 41.27; H, 0.97; F, 16.51.

**Fluoroacetylene.**—A 2.5 cm. "Vycor" tube packed for a length of 25 cm. with quartz rings was connected to a trap cooled with liquid nitrogen and the system was evacuated with an oil pump. The packed tube was heated to 650° by means of an electric muffle furnace and 8.0 g. (0.07 mole) of monofluoromaleic anhydride was added dropwise at such a rate that a pressure of 5 to 7 mm. was maintained in the tube. Carbon dioxide and fluoroacetylene in the effluent gases were condensed to a white solid in the trap. Contents of the trap were passed through a tower of "Ascarite," which removed carbon dioxide quantitatively. There was obtained a quantitative yield of fluoroacetylene as a colorless gas, b.p. < -80°, m.p. > -196°. Infrared and mass spectrometric analysis indicated the presence of traces of vinylidene fluoride and acetylene, which probably were formed from trace impurities in the fluoromaleic anhydride.

Fluoroacetylene is insoluble in water and is unaffected when bubbled through a 10% solution of sodium hydroxide. It is extremely soluble in ether at -80°, but is only slightly soluble in this solvent at room temperature. It is also soluble in acetone, but the solutions obtained slowly become colored.

(4) C. Martius, *Ann.*, **561**, 231 (1949).

#### Nuclear Magnetic Resonance Spectra of Fluoroacetylene.<sup>5</sup>

—The proton resonance of fluoroacetylene was a doublet split by 21 c.p.s. and centered at -157 c.p.s. relative to water at zero. The fluorine resonance was a doublet centered at -7250 c.p.s. relative to trifluoroacetic acid at zero. This is the highest field at which a C-F resonance has ever been noted at this Laboratory. Both the proton and fluorine resonance were calibrated against known hydrogen- and fluorine-containing compounds. Spectra were obtained by means of a Varian<sup>6</sup> High Resolution nuclear magnetic resonance spectrometer and associated electromagnet operating at 40 Mc. and approximately 10,000 gauss. Negative shifts are at higher field relative to the reference. The values reported here must be regarded only as approximate because accurate calibration by the usual sideband techniques was not made.

**Trimerization of Fluoroacetylene.**—A glass, 500-ml. gas sample tube was filled with fluoroacetylene at atmospheric pressure and stored in the dark for two weeks. A yellow-brown polymeric solid deposited on the walls of the tube. The gas remaining in the tube was passed through a trap cooled with solid carbon dioxide in acetone. A small amount of a colorless liquid condensed in the trap. The liquid was identified as 1,2,4-trifluorobenzene by comparison of its infrared spectrum with that of an authentic sample of 1,2,4-trifluorobenzene.<sup>7</sup>

**Salt Formation of Fluoroacetylene.**—Small amounts of a mercuric and a silver salt of fluoroacetylene were prepared by bubbling fluoroacetylene through aqueous solutions of mercuric nitrate and silver nitrate. The mercuric salt was white and the silver salt was light yellow. Both salts appeared to be stable toward shock. The silver salt detonated when warmed. The mercuric salt decomposed violently when warmed but did not detonate.

**Reaction with Bromine.**—Fluoroacetylene was bubbled into a solution of 1 g. of bromine in 35 ml. of carbon tetrachloride. As each bubble entered the solution a flash of light occurred under the liquid level. When the bromine color had disappeared, the carbon tetrachloride was removed by evaporation and the residue was distilled at reduced pressure. A colorless distillate boiling over a wide range of temperatures was obtained. The nuclear magnetic resonance spectrum of this material indicated it to be a mixture of several components in which the tetrabromide of fluoroacetylene appeared to be the predominant product.

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(5) The authors wish to thank Dr. Harlan Foster for the nuclear magnetic resonance determinations.

(6) Varian Associates, Palo Alto, California.

(7) G. Schiemann, *J. prakt. Chem.*, **140**, 97 (1934).