

Figure 1.

expected. In copper acetate dihydrate³ and π -allyl-palladium acetate⁶ the adoption of this oxygen covalent radius taken with the mean values of the metal-oxygen bond lengths predicts metal-metal bond lengths of 2.64 Å. for Cu-Cu (observed 2.64 Å.) and 2.92 Å. for Pd-Pd (observed 2.94 Å.) so that in these binuclear systems there is no significant shortening of the metal-metal bond. The decrease of 0.8 Å. from the sum of the σ -bonded covalent radius of Mo²⁺ in the molybdenum acetate structure is similar to that reported by Cotton and Bratton⁷ for the bonding between technetium atoms in an octachloroditechnate ion and adds credence to the view that, in contrast to the d⁹-binuclear complexes mentioned above, multiple bonding between d⁴-transition metal ions of the second and third row may be of fairly general occurrence.

Details of the crystallography of molybdenum(II) acetate will be reported elsewhere when further X-ray data have been added to the refinement scheme in order to increase the accuracy of the observed ligand bond lengths.

Acknowledgment. We are grateful to the Department of Scientific and Industrial Research for support of these studies.

(6) M. R. Churchill and R. Mason, *Nature*, **204**, 777 (1964).

(7) F. A. Cotton and W. K. Bratton, *J. Am. Chem. Soc.*, **87**, 921 (1965).

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The Ionization Potential of Carbon Tetrafluoride

Sir:

The ionization and dissociation of CF₄ has been studied by both electron impact¹⁻⁵ and spectroscopic^{6,7}

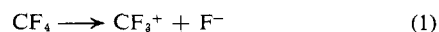
(1) L. Goldstein, *Ann. Phys. (Paris)*, [11] **9**, 723 (1938).

(2) V. H. Dibeler, R. M. Reese, and F. L. Mohler, *J. Res. Natl. Bur. Std.*, **57**, 113 (1956).

methods. The CF₄⁺ ion is usually not detected in the mass spectrum of CF₄.³⁻⁵ However, Dibeler, Reese, and Mohler² have detected a very small amount of the CF₄⁺ ion (<0.01%) but reported no energetic measurements for this ion. Only one value for $I(\text{CF}_4)$, equal to 17.8 e.v.,¹ has been reported in the literature. This value is noted to be surprisingly high in view of the value of $A(\text{CF}_3^+)$ determined from CF₄ (16.0,² 15.44,³ 15.20,⁴ and 15.40 e.v.⁵). It is difficult to understand this high literature value for the ionization potential of CF₄, since the various appearance potential measurements of CF₃⁺ from CF₄ are consistent and are considerably lower than the reported $I(\text{CF}_4)$.

The work of Goldstein¹ on the ionization potential of CF₄ was done by electron impact without mass analysis. CF₃⁺ is known to be the most abundant ion in the mass spectrum of CF₄ and we believe that it is likely that the measurement of $I(\text{CF}_4) = 17.8$ e.v. was actually an approximate determination of $A(\text{CF}_3^+)$ from CF₄. This value was determined by linear extrapolation¹ and is not in extreme disagreement with our linear extrapolation value for $A(\text{CF}_3^+) = 16.4$ e.v.⁴ Cook and Ching⁵ have found using photoionization techniques that the first appearance of an ion current occurs at 15.56 ± 0.01 e.v. This also suggests that the ion current is due to CF₃⁺ and not CF₄⁺.

Zobel and Duncan⁶ observed the beginning of continuous absorption in CF₄ at 120,900 cm.⁻¹ and attributed this to the ion-pair production process



They also estimated $I(\text{CF}_4) = 14.21$ e.v. from thermochemical calculations. Later, Stokes and Duncan⁷ listed $I(\text{CF}_4) = 17.8$ e.v. However, we wish to employ the interpretation that the 120,900-cm.⁻¹ (15.0 e.v.) beginning of continuous absorption is, in fact, an upper limit to the first ionization potential of CF₄, even as the beginning of continuous absorption in CH₂F₂ at 107,000 cm.⁻¹⁹ was assigned to the second ionization potential of CH₂F₂.⁷ In order to corroborate this value by other methods, we have made two separate thermochemical calculations. The first is based on an estimate of $\Delta H_f(\text{CF}_4^+)$, and the second uses both an estimate of $[\Delta H_f(\text{CF}_4^+) - \Delta H_f(\text{CF}_3^+)]$ and the measured value of $A(\text{CF}_3^+)$.

The heats of formation of several different ions, arranged in regular series, are presented in Table I. One notes that the heat of formation of the CX₄⁺ species is 13 to 23 kcal./mole greater than $\Delta H_f(\text{CX}_3^+)$, and that this difference appears to decrease with the value of $\Delta H_f(\text{CX}_3^+)$. Thus, $\Delta H_f(\text{CF}_4^+)$ is estimated to be only some 12 ± 5 kcal./mole greater than $\Delta H_f(\text{CF}_3^+)$; therefore $\Delta H_f(\text{CF}_4^+) = 109 + 12 = (121 \pm 5)$ kcal./mole. The ionization potential of CF₄ is then calculated to be (14.7 ± 0.3) e.v. by using ΔH_f

(3) J. W. Warren and J. D. Craggs in "Mass Spectrometry," Institute of Petroleum, London, 1952, p. 36.

(4) D. L. Hobrock and R. W. Kiser, to be submitted for publication. In this paper, a mass spectrometric study of eight tetrahalomethanes, including CF₄, is reported. We were unable to observe any CF₄⁺ and therefore $I(\text{CF}_4)$ could not be determined directly.

(5) R. I. Reed and W. Snedden, *Trans. Faraday Soc.*, **54**, 301 (1958).

(6) C. R. Zobel and A. B. F. Duncan, *J. Am. Chem. Soc.*, **77**, 2611 (1955).

(7) S. Stokes and A. B. F. Duncan, *ibid.*, **80**, 6177 (1958).

(8) G. R. Cook and B. K. Ching, private communication.

(9) P. Wagner and A. B. F. Duncan, *J. Am. Chem. Soc.*, **77**, 2609 (1955).

$(CF_4) = -217.8 \text{ kcal./mole}^{10}$ along with our estimated $\Delta H_f(CF_4^+)$.

An upper limit for $I(CF_4)$ can also be determined in the following manner. Assume that the CF_3^+ ion from CF_4 is formed as indicated in reaction 2. Then



Then $I(CF_4) = A(CF_3^+) - \Delta H_f(F) + [\Delta H_f(CF_4^+) - \Delta H_f(CF_3^+)]$ neglecting any excess kinetic energy considerations. Using the range of $A(CF_3^+)$ values of 15.2 to 15.4 e.v., as determined by the various workers, one may estimate that $I(CF_4) = 14.9$ to 15.1 e.v.

Table I. Heats of Formation of Various Ions

Ion	$-\Delta H_f$, kcal./mole				
	X = H ^a	X = CH ₃ ¹⁴	X = Br ^b	X = Cl ^b	X = F ^b
CX ₄ ⁺	285	198	265	230 ^c	(121) ^d
CX ₃ ⁺	262	185	244	216	109
CX ₂ ⁺	333	230	309	293	260
CX ⁺	360	285	338	350	321

^a F. H. Field and J. L. Franklin, "Electron Impact Phenomena and the Properties of Gaseous Ions," Academic Press, Inc., New York, N. Y., 1957. ^b See ref. 4. ^c Calculated using $I(CCl_4) = 11.47$ e.v., as determined by K. Watanabe, *J. Chem. Phys.*, **26**, 542 (1957). ^d Estimated; see text.

A completely independent approach may be taken employing the quasi-equilibrium theory of mass spectra.¹¹ From the simpler expression, it can be determined that in order to explain the absence (or a very minute presence) of the parent ion in the mass spectrum of CF_4 , $[A(CF_3^+) - I(CF_4)]$ could not be much greater than a few tenths of an electron volt. This strongly suggests that $I(CF_4) \approx 15.0$ e.v.

These estimates are in agreement with the observation that the ionization potential of a molecule is less than the appearance potential of any fragment ion from that molecule and thus indicates that $I(CF_4) = 17.8$ e.v. is much too high. A similar conclusion has been reached by Melton and Joy, who have recently employed their energy calibrated molecular orbital method¹² to calculate $I(CF_4)$ and obtain a value of 14.36 e.v.¹³ Our present calculations indicate $I(CF_4) = 14.7$ to 15.1 e.v. and lead us to conclude that the 120,900-cm.⁻¹ (15.0 e.v.) beginning of continuous absorption in CF_4 is to be attributed to an ionization process. It is also obvious that this problem should be studied by means other than electron impact. Hopefully, a study by photoionization techniques with mass analysis of the ionic products will provide additional conclusive information about the threshold formation of CF_3^+ or CF_4^+ ions.

(10) W. M. D. Bryant, *J. Polymer Sci.*, **56**, 277 (1962); Supplement No. 15 of the JANAF Thermochemical Data Tables lists $\Delta H_f(CF_4) = -(220.5 \pm 2.5) \text{ kcal./mole}$; this will cause $I(CF_4)$ to change by only 0.1 e.v.

(11) H. M. Rosenstock, M. B. Wallenstein, A. L. Wahrhaftig, and H. Eyring, *Proc. Natl. Acad. Sci. U. S.*, **38**, 667 (1952).

(12) C. E. Melton and H. W. Joy, *J. Chem. Phys.*, in press.

(13) C. E. Melton, private communication.

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Direct Observation of the Charge Neutralization Reaction in a γ -Irradiated Organic Glassy Solid

Sir:

Recently, the formation of trapped ionic intermediates in γ -irradiated organic glasses at low temperatures has been demonstrated in spectrophotometric observation¹⁻⁵ and by electron spin resonance measurements.⁶ It has also been shown that these ionic intermediates including trapped electrons may play an important role in radiation chemistry.

Light irradiation ejects electrons from trap centers and some of these electrons recombine with positive holes. It may be significant to observe directly such charge neutralization processes for the study of the elementary processes in radiation chemistry.

We have observed the charge neutralization processes in both pure 3-methylpentane and a mixture of 3-methylpentane and vinyl acetate, γ -irradiated at 77°K., using the electron spin resonance technique. Figures 1a and 1b show the e.s.r. spectrum of an unbleached pure 3-methylpentane sample and that of the same sample bleached by visible light, respectively. Figures 2a and 2b show the e.s.r. spectrum of an unbleached mixture of 3-methylpentane and 20 mole % vinyl

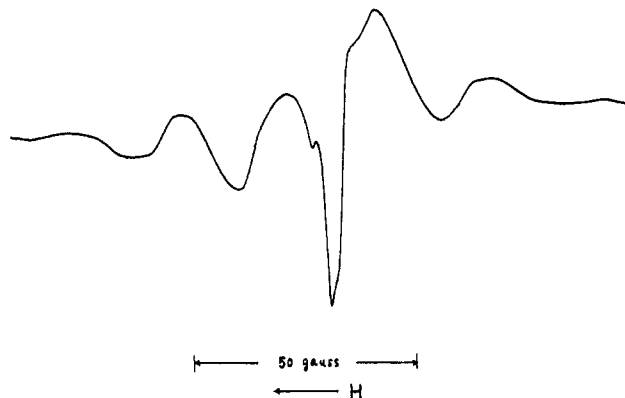


Figure 1a. Unbleached pure 3-methylpentane. The sample was irradiated and measured at 77°K. (radiation dose, 6×10^6 rads).

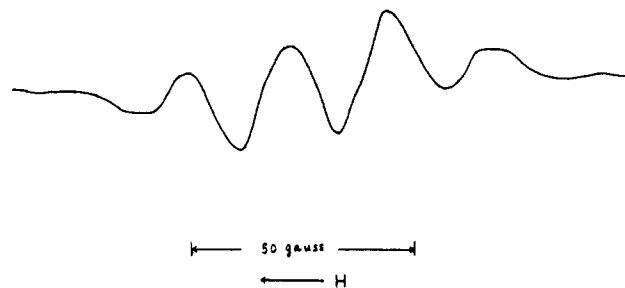


Figure 1b. Bleached pure 3-methylpentane. The sample was irradiated and measured at 77°K. (radiation dose, 6×10^6 rads).

(1) M. R. Ronayne, P. J. Guarino, and W. H. Hamill, *J. Am. Chem. Soc.*, **84**, 4230 (1962).

(2) J. P. Guarino, M. R. Ronayne, and W. H. Hamill, *Radiation Res.*, **17**, 379 (1962).

(3) W. H. Hamill, J. P. Guarino, M. R. Ronayne, and J. A. Ward, *Discussions Faraday Soc.*, **36**, 169 (1963).

(4) M. Kondo, M. R. Ronayne, J. P. Guarino, and W. H. Hamill, *J. Am. Chem. Soc.*, **86**, 1297 (1964).

(5) E. P. Bertin and W. H. Hamill, *ibid.*, **86**, 1301 (1964).

(6) D. R. Smith and J. J. Pieroni, *Can. J. Chem.*, **42**, 2209 (1964).