

gen coupled or reduced products (e.g., azines and hydrazines).

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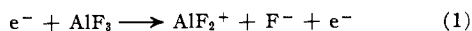
RECEIVED APRIL 18, 1964

### The Heat of Atomization of Aluminum Difluoride

Sir:

Although gaseous AlF and AlF<sub>3</sub> are well-known species, no direct evidence for the existence of AlF<sub>2</sub> has been heretofore presented. We wish to report here mass spectrometric evidence for the existence of AlF<sub>2</sub>(g) and a third law value for its heat of atomization.

Earlier mass spectrometric studies of the aluminum-reduced alkaline earth fluorides<sup>1,2</sup> indicated that only in the Al-MgF<sub>2</sub> system were both AlF<sub>3</sub> and AlF present. Careful re-examination of the species effusing from a heated tantalum Knudsen cell containing magnesium fluoride and aluminum using ordinary mass spectrometric techniques has revealed the presence of AlF<sub>2</sub><sup>+</sup>, the chief ionic species resulting from AlF<sub>3</sub>,<sup>3</sup> below the onset of the pair production process (1), 11.7 e.v., and having an appearance potential of 9 ±



1 e.v. Table I gives the suggested interpretation of the appearance potential data.

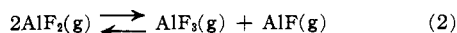
TABLE I

IONIC SPECIES AND THEIR PRECURSORS IN THE MgF<sub>2</sub>-Al SYSTEM

Ion	Appearance potential, e.v. <sup>a</sup>	Probable precursor
Mg <sup>+</sup>	7.6	Mg
MgF <sup>+</sup>	7.8 ± 0.3	MgF
Al <sup>+</sup>	9.2 ± 0.3	AlF
AlF <sup>+</sup>	9.7 ± 0.3	AlF <sup>b</sup>
AlF <sub>2</sub> <sup>+</sup>	9 ± 1	AlF <sub>2</sub>
AlF <sub>2</sub> <sup>+</sup>	15.2 ± 0.3	AlF <sub>3</sub> <sup>b</sup>

<sup>a</sup> Calibration measurements yielded appearance potentials for (Mg<sup>+</sup>) = 6.8 and (Hg<sup>+</sup>) = 9.6 e.v. vs. ionization potentials of 7.6 and 10.4 e.v. for Mg and Hg, respectively, whereby the experimental appearance potential values have been increased by 0.8 e.v.<sup>b</sup> These values agree well with those obtained by R. F. Porter, private communication, 1963.

To obtain  $\Delta H_a[\text{AlF}_2(\text{g})]$ , equilibrium 2 was studied



over the range 1243 to 1301°K. With the JANAF<sup>4</sup> free energy functions and equilibrium constants derived from the ion-current constants, one calculates an average third law heat of -49.5 kcal. mole<sup>-1</sup> with ±1.9 kcal. mole<sup>-1</sup> as the standard deviation. Uncertainties in the experimental quantities and accessory data (for example, whether AlF<sub>2</sub> is linear or bent) bring the uncertainty to about ±4 kcal. mole<sup>-1</sup>. From the known heats of formation of AlF<sub>3</sub>(g),<sup>4,5</sup> AlF(g),<sup>4,5</sup> Al(g),<sup>4</sup> and F(g),<sup>4</sup> one calculates  $\Delta H_a^{\circ}{}_{298}$

(1) G. D. Blue, J. W. Green, T. C. Ehlert, and J. L. Margrave, *Nature*, **199**, 804 (1963).

(2) T. C. Ehlert, G. D. Blue, J. W. Green, and J. L. Margrave, *J. Chem. Phys.*, October, 1964.

(3) R. F. Porter, *ibid.*, **33**, 951 (1960).

(4) "JANAF Interim Thermochemical Tables," D. R. Stull, Ed., The Dow Chemical Company, Midland, Mich., revised through Sept. 30, 1963.

(5) D. Hildenbrand, Ford Motor Co., Aeronutronic Division, Report No. U-2055, March 15, 1963.

$[\text{AlF}_2(\text{g})] = 264.9 \pm 4$  and  $\Delta H_f^{\circ}{}_{298}[\text{AlF}_2(\text{g})] = -149.2 \pm 4$  kcal. mole<sup>-1</sup>.

With these results, the stepwise dissociation energies for AlF<sub>3</sub>(g) are  $D(\text{AlF}_2 - \text{F}) = 156$  (6.8),  $D(\text{AlF} - \text{F}) = 106$  (4.6), and  $D(\text{Al} - \text{F}) = 159$  kcal. mole<sup>-1</sup> (6.9 e.v.), which shows the decreased bond strength in AlF<sub>2</sub>, apparently because of the lack of spin correlation in this "odd-electron" molecule.

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### The Microwave Spectrum, Dipole Moment, and Polarizability of Acetylene-d<sub>1</sub><sup>1</sup>

Sir:

It is well established that substitution of deuterium for ordinary hydrogen causes a change in the electronic distribution in molecules. For example, optical activity has been detected<sup>2</sup> in molecules RR'CHD, proton n.m.r. chemical shifts are found to change upon adjacent deuterium substitution,<sup>3</sup> and the average length for CH bonds has been shown to be longer than for the corresponding CD bonds.<sup>4</sup> It is to be expected, therefore, that molecular dipole moments will show a change when deuterium is substituted for ordinary hydrogen. Studies in this laboratory have shown that a change does occur.<sup>5</sup> A logical extension is to look for a permanent dipole moment in an unsymmetrically deuterated, but otherwise symmetrical, molecule. A permanent dipole moment created by such substitution could be detected by studying the pure rotational spectrum of the molecule.

We have observed the  $J = 0 \rightarrow 1$  transition of HC≡CD at 59,450.6 Mc. In the detection of this transition, we have employed Stark modulation. In order to achieve sufficient modulation, a d.c.-based square wave was employed, providing fields from 82 to 110 kv./cm. In the presence of such large fields, the observed Stark shift is produced by an induced moment, as well as by the permanent dipole moment. However, it should be pointed out that the observation of a  $\Delta J = 1$  transition is unequivocal evidence of a permanent dipole moment. In this case of a  $J = 0 \rightarrow 1$  transition, only one Stark component is observed, and separation of the two contributions to the Stark shift cannot be obtained since both are proportional to the square of the field. However, it has been found<sup>6</sup> that the dipole moment of CH<sub>3</sub>C≡CD is 0.012 D. lower than that of CH<sub>3</sub>C≡CH, and we may assume that the permanent moment of HC≡CD is approximately equal to the

(1) This research was supported by the National Science Foundation and by the Petroleum Research Fund administered by the American Chemical Society.

(2) A. Streitwieser, Jr., J. R. Wolfe, Jr., and W. D. Schaefer, *Tetrahedron*, **6**, 338 (1959).

(3) H. S. Gutowsky, *J. Chem. Phys.*, **31**, 1683 (1959).

(4) V. W. Laurie and D. R. Herschbach, *ibid.*, **37**, 1687, (1962).

(5) Abstracts, 144th National Meeting of the American Chemical Society, Los Angeles, Calif., 1963; and Abstracts, Symposium on Molecular Structure and Spectroscopy, The Ohio State University, Columbus, Ohio, 1964.