

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

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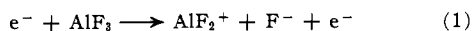
RECEIVED APRIL 18, 1964

The Heat of Atomization of Aluminum Difluoride

Sir:

Although gaseous AlF and AlF₃ are well-known species, no direct evidence for the existence of AlF₂ has been heretofore presented. We wish to report here mass spectrometric evidence for the existence of AlF₂(g) and a third law value for its heat of atomization.

Earlier mass spectrometric studies of the aluminum-reduced alkaline earth fluorides^{1,2} indicated that only in the Al-MgF₂ system were both AlF₃ 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 AlF₂⁺, the chief ionic species resulting from AlF₃,³ 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.

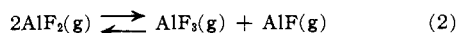
TABLE I

IONIC SPECIES AND THEIR PRECURSORS IN THE MgF₂-Al SYSTEM

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

^a Calibration measurements yielded appearance potentials for (Mg⁺) = 6.8 and (Hg⁺) = 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.^b 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 JANAF⁴ free energy functions and equilibrium constants derived from the ion-current constants, one calculates an average third law heat of -49.5 kcal. mole⁻¹ with ±1.9 kcal. mole⁻¹ as the standard deviation. Uncertainties in the experimental quantities and accessory data (for example, whether AlF₂ is linear or bent) bring the uncertainty to about ±4 kcal. mole⁻¹. From the known heats of formation of AlF₃(g),^{4,5} AlF(g),^{4,5} Al(g),⁴ and F(g),⁴ 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⁻¹.

With these results, the stepwise dissociation energies for AlF₃(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⁻¹ (6.9 e.v.), which shows the decreased bond strength in AlF₂, 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-d₁¹

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 detected² in molecules RR'CHD, proton n.m.r. chemical shifts are found to change upon adjacent deuterium substitution,³ and the average length for CH bonds has been shown to be longer than for the corresponding CD bonds.⁴ 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.⁵ 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 found⁶ that the dipole moment of CH₃C≡CD is 0.012 D. lower than that of CH₃C≡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.

isotope shift in dipole moment of this related molecule. Using this assumption, the polarizability anisotropy, $\alpha_{zz} - \alpha_{xx}$, is calculated to be $1.85 \pm 0.05 \times 10^{-24}$ cm.³. Here z refers to the molecular axis and x to a perpendicular axis. This value may be compared with the result⁶ 2.27×10^{-24} cm.³ obtained rather indirectly from Kerr effect data, refractive indices, etc.

The rotational constant obtained here is $B_0 = 29,725.3 \pm 0.1$ Mc., or $B_0 = 0.991527 \pm 0.000003$ cm.⁻¹. This agrees with the infrared value⁷ of 0.99156 ± 0.00004 cm.⁻¹ within the quoted error.

(6) K. G. Denbigh, *Trans. Faraday Soc.*, **36**, 936 (1940).

(7) W. J. Lafferty, E. K. Plyler, and E. D. Tidwell, *J. Chem. Phys.*, **37**, 1981 (1962).

(8) American Chemical Society-Petroleum Research Fund Fellow, 1963-1964.

(9) Alfred P. Sloan Foundation Fellow, 1964.

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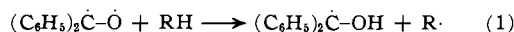
J. S. MUENTER⁸
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RECEIVED JULY 27, 1964

Hydrogen Abstraction by the Triplet State of Benzophenone¹

Sir:

The ability of the triplet stage of benzophenone to abstract hydrogen from suitable substrates is well



known and recognized as a critical step in the photoreduction of benzophenone.² The rate of (1) for various substrates has been estimated by Hammond³ and by Porter⁴ by competitive quenching experiments, although there are some large discrepancies between the two sets of results.

We have been interested in these hydrogen abstraction processes as a method of comparing the reactive properties of triplet states of ketones with those of simple alkoxy radicals. We have employed competitive techniques in which the relative rates of attack on two substrates are compared directly by measuring their relative rates of disappearance when irradiated with benzophenone.

We find that even simple aliphatic hydrocarbons⁵ are readily attacked to yield radicals which undergo their expected reactions. In the presence of cyclohexane benzophenone is reduced to benzpinacol, and the cyclohexyl radicals largely dimerize. If CCl_4 is added, cyclohexyl chloride is produced in high yield, together with C_2Cl_6 , while addition of benzene gives roughly equal quantities of cyclohexylbenzene and bicyclohexyl. Similarly 2,3-dimethylbutane- CCl_4 gives 2-chloro-2,3-dimethylbutane and 1-chloro-2,3-dimethylbutane in a ratio of 50-5000:1.

Competitive experiments, carried out essentially as in our *t*-butyl hypochlorite work,⁶ yield the pre-

(1) Support of this work by a grant from the National Science Foundation is gratefully acknowledged.

(2) For general discussion and references, cf. G. S. Hammond and N. Turro, *Science*, **142**, 1541 (1963).

(3) G. S. Hammond, W. P. Baker, and W. M. Moore, *J. Am. Chem. Soc.*, **83**, 2795 (1961).

(4) A. Beckett and G. Porter, *Trans. Faraday Soc.*, **59**, 2038 (1963).

(5) The photoreduction of acetone in cyclohexane was reported some time ago [N. C. Yang and D. H. Yang, *J. Am. Chem. Soc.*, **80**, 2913 (1958)]. Very recently photoreduction of substituted benzophenones in cyclohexane has also been described [G. Porter and P. Suppan, *Proc. Chem. Soc.*, 191 (1964)].

liminary relative reactivities shown in Table I. Unless indicated, 4 *M* benzophenone solutions in benzene, 0.1-0.4 *M* in each substrate, were irradiated at 20° through a Nonex filter and sampled periodically for gas chromatographic analysis. For comparison, Hammond³ reports a relative reactivity cumene:toluene of 3.5, but Porter⁴ gives 2-propanol:toluene of only 1.2. However, the two groups differ in their rate constant for the toluene reaction by a factor of 50.⁷

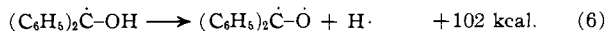
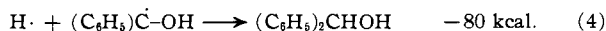
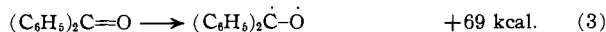
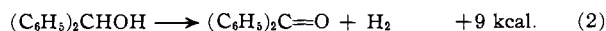
TABLE I
COMPETITIVE HYDROGEN ABSTRACTION EXPERIMENTS

Substrate	Relative reactivity ^a	
	$\text{C}_6\text{H}_5\dot{\text{C}}-\dot{\text{O}}$	$t\text{-C}_4\text{H}_9\dot{\text{O}} (40^\circ)^6$
Toluene (std.)	1.0	1.0
Cyclohexane	2.1 ± 0.06	6.0
Cumene	3.4 ± 0.2	2.8
2-Propanol	9.3 ± 0.4	..
2-Octanol	9.9 ± 0.6	..
Mesitylene	5.5 ± 0.3	4.1
<i>m</i> -Xylene	3.0 ± 0.2	2.34
<i>p</i> -Fluorotoluene	1.15 ± 0.06	..
<i>p</i> -Chlorotoluene	0.97 ± 0.02	0.71
Anisole	0.50 ± 0.03	..

^a Experimental errors indicate spread of several determinations.

Our results indicate a reactivity of the benzophenone triplet qualitatively similar to that of the *t*-butoxy radical. However, the reaction appears somewhat more sensitive to the strength of the R-H bond being attacked since cyclohexane is less reactive relative to toluene and (as noted above) a very high *t:p* selectivity is observed with 2,3-dimethylbutane. The benzophenone triplet also appears to attack selectively points of high electron availability: the substituted toluene data indicate a negative σ -value for the reaction, α -hydrogens of alcohols are particularly reactive, and no photoreduction is produced by solvents such as acetic acid which have weak C-H bonds but strongly electron-withdrawing groups.

An estimate of the energetics of the hydrogen abstraction reaction is of interest and can be obtained from the following thermodynamic cycle which yields the strength of the $(\text{C}_6\text{H}_5)_2\dot{\text{C}}-\text{O}-\text{H}$ bond.



The energetics of (2) and (5) are available from standard thermochemical tables, (3) comes from spectral data,⁸ while (4) is estimated as a maximum value of the exothermicity of the reaction assuming that the resulting bond is no stronger than that for the benzyl hydrogens of toluene.⁹ The resulting bond strength (6) is thus a minimum value. Comparison with $D(t\text{-C}_4\text{H}_9\text{O}-\text{H}) =$

(6) C. Walling and B. B. Jacknow, *J. Am. Chem. Soc.*, **82**, 6108 (1960), and subsequent papers.

(7) Actually, a large part of the difference arises from different assumptions as to the rate of diffusion-controlled quenching in these systems and does not represent an experimental discrepancy.

(8) G. S. Hammond and J. Saltiel, *J. Am. Chem. Soc.*, **84**, 4983 (1962).

(9) $D(\text{benzyl-H})$ is still in question. The value chosen is an arbitrarily weighted average of those reported and is probably uncertain to at least 3 kcal.