Thermochimica Acta
Elsevier Publishing Company, Amsterdam
Printed in Belgium

GASEOUS PHOSPHORUS COMPOUNDS

PART V. THE DISSOCIATION ENERGY AND HEAT OF FORMATION OF CARBON MONOPHOSPHIDE*

KARL A. GINGERICH**
Battelle Memorial Institute, Columbus Laboratories, 505 King Avenue, Columbus, Ohio 43201 (U. S. A.)

(Received August 6th, 1970)

ABSTRACT

The chemical equilibrium $CP(g)+P(g) \rightleftharpoons P_2(g)+C(g)$ has been studied by means of the Knudsen effusion technique combined with mass spectrometric analysis of the vapor. The enthalpy of reaction, ΔH^0_{298}, was determined as 6.3±4.0 kcal/mole. Combined with the literature value for the dissociation energy of P_2, the dissociation energy of gaseous carbon monophosphide was calculated as $D^0_{298} = 123.2 \pm 4.0$ kcal/mole or $D^0_0 = 122.1 \pm 4.0$ kcal/mole. The corresponding value for the standard heat of formation is $\Delta H^0_{f,298} = 127.5 \pm 4.5$ kcal/mole. This compares with the selected JANAF value of 111.7±23.1 kcal/mole.

INTRODUCTION

Band systems that were attributed to the gaseous molecule CP were first reported by Herzberg[1]. A detailed spectroscopic analysis of the CP molecule has been performed by Bärwald *et al.*[2] and its molecular constants determined. These authors give, apparently on the basis of a linear Birge–Sponer extrapolation, a dissociation energy of 58,000 cm^{-1} (6.9 eV) or 159 kcal/mole for the $X^2\Sigma^+$ ground state. They state, however, that these values cannot claim a high degree of accuracy, because of the small number of observed vibrational frequencies. Gaydon[3] confirms this result and states that linear Birge–Sponer extrapolations based on the spectroscopic data by Bärwald *et al.*[2] for the excited states favor a similar value for the dissociation energy of CP. Yet, he estimates that the dissociation energy of the CP molecule, D^0_0 is 6±1 eV or 138±23 kcal/mole, without giving any specific reason for this selection. This value has been adopted by the JANAF Thermochemical Tables[4], while Herzberg[5] gives the approximate value of 6.9 eV the preference.

In view of this apparent uncertainty in the dissociation energy of gaseous CP, a determination from thermal equilibrium measurements appeared to be desirable. In connection with investigations aimed at the thermodynamic properties of gaseous uranium phosphide[6] the CP molecule was observed in the effusing vapor from an

---

*Presented at the 156th National Amer. Chem. Soc. Meeting, Atlantic City, September 8–13, 1968.
**Present address: Department of Chemistry, Texas A and M University, College Station, Texas 77840, U. S. A.

uranium–phosphorus–boron alloy that contained also a small amount of carbon. The results for this molecule and for the gaseous equilibrium $CP + P \rightleftharpoons P_2 + C$ are reported.

EXPERIMENTAL

The design features of the mass spectrometer used as well as the experimental procedure have been described previously[7]. The sample used was the residue from an investigation of the PN and P_2 molecules[8]. The same experimental details were used. The original sample, that consisted of a mixture of UP and BN to which small amounts of graphite and silver were added[8] was at the time of this investigation depleted of its nitrogen and silver and consisted presumably of a ternary U–P–B–C alloy.

The accuracy of the ion-intensity measurements for CP^+ (mass 43) and $^{12}C^+$ was hampered by large relative background contributions. The background contribution to the respective total ion intensity was between 60 and 95% for the mass 12 and >95% for mass 43. The shutter effect for mass 43 could only be measured satisfactorily at the low-mass side of the peak. The measurement was in addition complicated by a slight continuous drift in either accelerating voltage or magnetic field strength. This shutter effect was attributed to the CP^+ ion that was formed by electron impact on the CP molecule in the molecular beam originating from the Knudsen cell. Because of these difficulties and the small absolute observed intensity values no reliable appearance potential measurement could be performed for the CP molecule. The attribution of the measured ion current to other molecules with mass 43 that might be possible, such as BO_2, HBP, or B_3C, is unlikely because no shutter effects could be observed at neighboring peaks, that would fulfill the required isotopic abundance distribution for such boron-containing species. Thus at least a major part of the ion current is attributable to $^{12}C^{31}P$. Furthermore, the chemical composition of the system during the measurements involving the CP molecule, combined with thermodynamic considerations, make the formation of such other primary molecules with mass 43 unlikely under the experimental conditions used. For similar reasons, doubly ionized molecules with mass 86 and of fragment molecules with mass 43 are unlikely.

The ionization efficiency curves and appearance potentials for P^+, P_2^+, and C^+ indicated that these species were primarily formed from the respective parent molecules, P, P_2, and C by direct ionization. An upper limit of 20% of the measured C^+ ion current was estimated for the possible fragment contribution from UC_2 that was also present in the vapor.

RESULTS AND DISCUSSION

The experimentally measured relative ion currents are presented in Table I. The dissociation energy of the CP molecule was obtained by measuring the enthalpy,

TABLE I

ION INTENSITIES AND THIRD-LAW ENTHALPY VALUES FOR THE REACTION $CP(g)+P(g)\rightleftharpoons P_2(g)+C(g)$

T(°K)	*Ion intensities in arbitrary units*				$-\log K_{eq}$	$\Delta[(G^0_T-H^0_{298})/T]$ (*e.u.*)	ΔH^0_{298} (*kcal/mole*)
	$I(CP^+)$	$I(P^+)$	$I(P_2^+)$	$I(C^+)$			
2340	1.0×10^{-11}	6.41×10^{-8}	2.55×10^{-8}	6.0×10^{-12}	0.622	0.271	6.0
2366	1.6×10^{-11}	8.29×10^{-8}	3.49×10^{-8}	8.5×10^{-12}	0.650	0.268	6.3
2364	1.7×10^{-11}	8.08×10^{-8}	3.41×10^{-8}	1.1×10^{-11}	0.564	0.268	6.4
2293	3.2×10^{-12}	2.95×10^{-8}	8.90×10^{-9}	2.5×10^{-12}	0.628	0.275	6.3
2380	$1.4_5\times10^{-11}$	9.66×10^{-8}	3.88×10^{-8}	1.3×10^{-11}	0.444	0.267	6.6
2401	7.0×10^{-12}	2.45×10^{-7}	2.26×10^{-7}	$2.2_5\times10^{-11}$	0.528	0.266	6.4

ΔH^0_{298}, for the chemical reaction $CP(g)+P(g)\rightleftharpoons P_2(g)+C(g)$, using the third law method. In this evaluation, it was assumed that equilibrium was established among the gaseous reactants under the experimental conditions used. The necessary free energy functions were taken from the JANAF tables[4]. The equilibrium constant for this reaction was taken as $K_{eq}=I(P_2^+)\times I(C^+)/I(CP^+)\times I(P^+)$, assuming that the products of the relative ionization cross sections and multiplier gains of the reactants and products cancel each other. This assumption is believed to introduce not more than a 30% error, in view of the similarity of the reaction components on both sides of the equation. The equilibrium constants, free energy function changes and derived third law enthalpies for the reaction $CP(g)+P(g)\rightleftharpoons P_2(g)+C(g)$ are also presented in Table I. The average value for the reaction enthalpy, ΔH^0_{298} is 6.3 ± 0.2 kcal/mole. Combining this value with the dissociation energy $D^0_{298}(P_2)=116.9$[4], results in a value of 123.2 kcal/mole or 5.35 eV for the dissociation energy of CP, D^0_{298}. Correction to 0°K reference temperature, using the JANAF[4] enthalpy functions gives $\Delta H^0_0=6.1$ kcal/mole and with $D^0_0(P_2)=116.0$ kcal/mole (Ref. 4), $D^0_0(CP)=122.1$ kcal/mole or 5.3 eV. Considering all possible errors, the uncertainty in the measurement of the reaction enthalpies represented in Table I is estimated to ±4 kcal/mole and thus the uncertainty in the dissociation energy of CP (neglecting a possible uncertainty in the dissociation energy of P_2) is also ±4 kcal/mole. The derived standard heat of formation for CP(g), using the JANAF ancillary values is $\Delta H^0_{f,298}=127.5\pm4.5$ kcal/

TABLE II

THERMOCHEMISTRY OF GASEOUS CARBON MONOPHOSPHIDE

Reaction	*Enthalpy* (*kcal/mole*)	*Reference*
$CP(g)+P(g)\rightleftharpoons P_2(g)+C(g)$	$\Delta H^0_{298}=6.3\pm4.0$	This investigation
$C(graph.)+P(red)\rightleftharpoons CP(g)$	$\Delta H^0_{f,298}=127.5\pm4.5$	This investigation
	$\Delta H_{f,298}=111.7\pm23.1$	4
$CP(g)\rightleftharpoons C(g)+P(g)$	$D^0_0=122.1\pm4.0$	This investigation
	$D^0_0=\sim159$	2
	$D^0_0=139\pm23$	3

mole, which compares with the value of 111.7±23.1 kcal/mole that was adopted by the JANAF tables[4]. The thermochemistry of the CP molecule is summarized in Table II.

The value for the dissociation energy of CP measured in this investigation is considerably lower than the approximate value given by Herzberg[5] and lower than but within the given uncertainty of the value estimated by Gaydon[3]. This low value is, however, not so unexpected if one assumes the same analogy for the dissociation energies of CP and CS as for those of CN and CO. On the basis of the JANAF[4] values for the dissociation energies of CS, CN, and CO one obtains by equating $D_0^0(\mathrm{CP})/D_0^0(\mathrm{CS}) = D_0^0(\mathrm{CN})/D_0^0(\mathrm{CO})$ a value of 5.3 eV for $D_0^0(\mathrm{CP})$ which coincides with the experimental result of this investigation. The low experimental value also appears reasonable in that it falls between the dissociation energies of the diatomic molecules of the component elements[4] of 6.15 and 5.03 for C_2 and P_2, respectively. As Table III shows it also compares favorably with the dissociation energies of the isoelectronic molecules BeCl, BS, and SiN.

TABLE III

COMPARISON OF DISSOCIATION ENERGIES OF MOLECULES ISOELECTRONIC WITH CARBON MONOPHOSPHIDE

Compound	*Dissociation energie* (D_0^0, *eV*)	*Reference*
BeCl	4.5±0.1	4
BS	5.1±0.8; 6.2±0.3	4; 9
SiN	5.9±0.7	4
CP	5.3±0.2	This investigation
	6.0±1.0	3
	~6.9	5

REFERENCES

1 G. Herzberg, *Nature*, 126 (1930) 131.
2 H. Bärwald, G. Herzberg and L. Herzberg, *Ann. Phys.*, 20 (1934) 569.
3 A. G. Gaydon, *Dissociation Energies and Spectra of Diatomic Molecules*, Chapman and Hall, London, 1968, 3rd ed.
4 D. R. Stull (Ed.), *JANAF Thermochemical Tables*, Dow Chemical Co., Midland, Mich., 1965 and quarterly supplements.
5 G. Herzberg, *Molecular Spectra and Molecular Structure*, Van Nostrand, New York, 1950, 2nd ed., Chapter I.
6 K. A. Gingerich, to be published.
7 K. A. Gingerich, *J. Chem. Phys.*, 49 (1968) 14.
8 K. A. Gingerich, *J. Phys. Chem.*, 73 (1969) 2734.
9 K. A. Gingerich, *Chem. Commun.*, (1970) 580.