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Note

Dissociation energy of the NaAg molecule

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For a series of mass spectrometric determinations of the bond energy of some diatomic intermetallic compounds between silver and group IA or IIA metals, the following independent reactions are proposed

$$NaX_{(g)} + Ag_{(g)} \rightarrow NaAg_{(g)} + X_{(g)}$$

where X is a group IA or IIA metal of the analysed molecule.

The error associated with the dissociation energy of the NaX molecule is naturally dependent on the uncertainties associated with the D_0^0(NaAg) value. In a previous investigation of the Na–Ag system[1], a dissociation energy of the NaAg molecule ($D_0^0 = 31.8 \pm 3.0$ kcal mole^{-1}) was obtained, unexpectedly lower by about 19 kcal than that derived from the Pauling model[2]. In order to confirm the value, a new experiment on the Ag–Na system was carried out.

EXPERIMENTAL AND RESULTS

A Bendix time-of-flight mass spectrometer combined with a double-oven Knudsen source, similar to that described elsewhere[1, 3], was employed for this study. The general characteristic of the method and the procedure used have been previously described[4]. Because of the limitation in the Knudsen condition, only a limited set of data has been obtained for the NaAg molecule. The ions Na^+, Ag^+, Ag_2^+ and $NaAg^+$ observed at about 1550 K were identified as originating from the corresponding neutral species. The appearence potential of NaAg and Ag_2 were measured as 8.5 ± 2.0 and 9.5 ± 2.0 eV, referred to that of Ag = 7.57 eV[5].

The reaction

$$NaAg_{(g)} \rightarrow Na_{(g)} + Ag_{(g)} \quad (1)$$

and the independent pressure reaction

TABLE 1

RELATIVE ION INTENSITIES OVER Na–Ag SYSTEM AND THIRD-LAW ENTHALPIES (IN KCAL MOLE^{-1}) OF THE REACTIONS

$NaAg_{(g)} \rightarrow Na_{(g)} + Ag_{(g)}$ (1)
$Na_{(g)} + Ag_{2(g)} \rightarrow NaAg_{(g)} + Ag_{(g)}$ (2)

T (°K)	$I^{107}Ag^+$ ($\times 10^7$)	$I^{23}Na^+$ ($\times 10^7$)	$I^{216}Ag_2^+$ ($\times 10^{10}$)	$I^{130}NaAg^+$ ($\times 10^{10}$)	$\log K_p$ (atm) Reaction (1)	Reaction (2)	$-\Delta[(G_T^0 - H_0^0)/T]$ (1) (e.u.)	$-\Delta[(G_T^0 - H_0^0)/T]$ (2) (e.u.)	ΔH_0^0 Reaction (1)	Reaction (2)
1540	10	31	32	20	0.364	0.049	19.83	1.88	33.10	3.24
1540	10	46	32	30	0.335	0.159	19.83	1.88	32.90	4.00
1545	10	26	33	17.5	0.392	0.196	19.83	1.88	33.41	4.29
1560	11	57	32	35	0.303	0.185	19.83	1.87	33.10	4.24
1560	11	61	33	37.5	0.308	0.166	19.83	1.87	33.14	4.10
									33.1 ± 0.1[a]	4.0 ± 0.3[a]

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[a] Standard deviation.

$$Na_{(g)} + Ag_{2(g)} \rightarrow NaAg_{(g)} + Ag_{(g)} \qquad (2)$$

were taken into account.

To convert the ionic intensities into pressures[6], the necessary sensitivity constant was determined from the silver vapor pressure[7] and assuming that in the initial part of the vaporization at lower temperatures silver was at unit activity. The ionization cross-section for atoms were taken from Mann[8] and for the molecules they were estimated as 0.75 times the sum of the atomic cross-sections[9]. For all the ions the multiplier gains were taken as proportional to the inverse of the square root of the mass.

The enthalpies of reactions (1) and (2) were evaluated by third-law method using the relation

$$\Delta H_0^0/T = -R\ln K_p - \Delta[(G_T^0 - H_0^0)T]$$

The necessary free energy functions, $(G_T^0 - H_0^0)/T$, were taken from the literature for Na[7], Ag[7], Ag_2[10] and NaAg[1].

The relative ion intensities, log K_p and the third-law ΔH_0^0 values at each experimental temperature for reactions (1) and (2) are listed in Table 1.

ΔH_0^0 for reaction (1) gives the dissociation energy of the NaAg molecule D_0^0 (NaAg) $= 33.1 \pm 2.0$ kcal mole^{-1}; ΔH_0^0 for reaction (2) combined with D_0^0 $(Ag_2) = 38.0 \pm 1.5$ kcal mole^{-1} [11] yields D_0^0(NaAg) $= 34 \pm 3$ kcal mole^{-1}. The error terms reflect the estimated uncertainties in the temperature measurement, the calibration constant, the free energy and the relative ionization cross-section and multiplier gains.

CONCLUSION

The dissociation energies derived from reaction (1) and the independent pressure reaction (2) are in good agreement and agree also with the value previously determined[1], D_0^0(NaAg) $= 31.8 \pm 3.0$ kcal mole^{-1}.

Giving equal weights to the present and previous values, a selected value of D_0^0(NaAg) $= 33 \pm 2$ kcal mole^{-1} or 138 ± 8 kJ mole^{-1} is recommended, therefore the experimental dissociation value is lower than the bond energy calculated using the Pauling model of polar single bond (51 kcal mole^{-1})[2].

Other experimental dissociation energies of group IA and IB diatomic molecules[12, 13] have shown similar discrepancies, therefore the bond energy values derived from the Pauling model[2] should be considered as upper limit values, as predicted by Gingerich and Finkbeiner[14].

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