The Potential Curve of ArH$^+$ and the Heats of the Reactions Ar$^+$ + H_2 → ArH$^+$ + H and Ar + H_2^+ → ArH$^+$ + H

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Summary Exothermicities in excess of 30 kcal/mole are calculated for the above ion–molecule reactions.

To obtain some idea of the nature of the potential-energy surface governing the ion–molecule reactions $Ar^+ + H_2 \rightarrow ArH^+ + H$ and $Ar + H_2^+ \rightarrow ArH^+ + H$, we have performed a diatomics-in-molecules[1] calculation of the energy of the system ArH_2^+ in many different geometries.[2] For this calculation the ground- and excited-state potential curves of ArH$^+$ are required, and we report here initially a calculation of the ground-state curve, from which we estimate the heats of the above reactions.

We used an SCFMO method, which should be particularly accurate in this case as no new pair-correlations are introduced on bond formation. (ArH$^+$ dissociates to Ar + H$^+$).

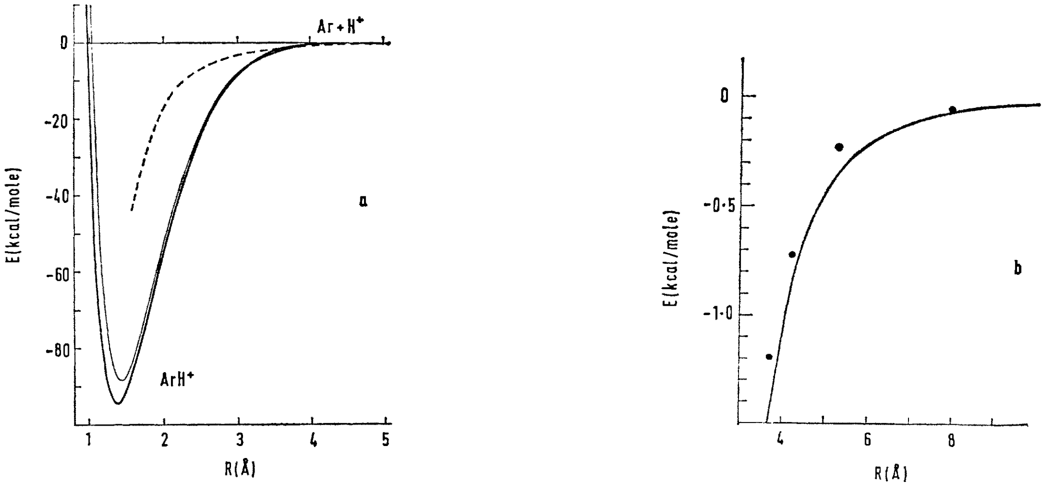

FIGURE. (a) *Potential curve for* ArH$^+$: *extended basis* ——; *minimal basis* ——; *ion-induced dipole curve with experimental polarizability* – – –. (b) *Long-range potential curve for* ArH$^+$: *extended basis* ●; *ion-induced dipole curve* ——.

Calculations were carried out with a minimal and an extended basis set. In the minimal basis, 1*s*, 2*s*, 2*p*, 3*s*, and $3p$ Slater-type atomic orbitals on Ar and a $1s$ orbital on H (with exponents recommended by Clementi and Raimondi[3]) were each represented by an optimized expansion of three gaussians[4] before using the ATMOL program of Hillier and Saunders.[4] In the extended basis, an additional polarization function, consisting of a single gaussian, was added for each of the five valence orbitals. Thus the $3s$, $3p_x$, $3p_y$, and $3p_z$ Ar orbitals were polarized, respectively, by p_z, d_{xz}, d_{yz}, and d_{zz} gaussians on Ar, and the $1s$ H-orbital by a p_z gaussian on H. These additional functions were constrained to have the same mean radii as the AO's they each polarized, thus fixing their exponents.

The resulting potential curves are shown in the Figure (a). The heavy solid curve is for the extended basis calculation; the light curve for the minimal basis calculation. Both curves are adjusted to approach zero for $\mathrm{Ar} + \mathrm{H}^+$. (The extended basis calculation for the argon atom gave an absolute energy 0·03609 a.u. below that of the minimal basis calculation, due mainly to its better description of the core orbitals.) The smallness of the divergence between the minimal and extended basis curves is striking; it gives us confidence that the latter is a close representation of the true shape of the curve.

The broken line is a calculation of the long-range ion-induced dipole interaction $-\alpha e^2/2R^4$ using the experimental[5] polarizability $\alpha_{\mathrm{Ar}} = 1{\cdot}64\,\mathrm{Å}^3$. The solid curve in the Figure (b) is this same function on a larger scale; the dots are the *ab initio* extended basis calculations. It is clear that the ion-induced dipole force alone gives an inadequate description of the interaction for $R < 3$Å.

The calculated equilibrium geometry is at a distance $R_e = 1{\cdot}38$ Å and the dissociation energy, *De*, is 94·4 kcal/mole. Although the experimental dissociation energy of ArH^+ is not known accurately, it has been estimated[6] to be probably greater than 78·3 kcal/mole, which is consistent with this work. The theoretical value when combined with the dissociation energies of H_2 and $\mathrm{H}_2{}^+$ and the ionization potentials of Ar and H gives the following values for the heats of reaction, ignoring the zero-point vibrational contribution:

$$\mathrm{Ar} + \mathrm{H}_2^+ \rightarrow \mathrm{ArH}^+ + \mathrm{H} + 30{\cdot}0\ \mathrm{kcal/mole};$$

$$\mathrm{Ar}^+ + \mathrm{H}_2 \rightarrow \mathrm{ArH}^+ + \mathrm{H} + 34{\cdot}4\ \mathrm{kcal/mole}.$$

(*Received, August 14th*, 1970; *Com.* 1371.)

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