LETTERS TO THE EDITOR

COMMUNICATIONS

Observation of a translational energy threshold for a highly exoergic ion–molecule reaction*

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We report the reaction cross sections and product energy distributions for the H-atom abstraction reaction

$$Ar^+ + CH_4 \rightarrow ArH^+ + CH_3 \quad (\Delta H \cong -1.7 \text{ eV}^1) \qquad (1)$$

as a function of collision energy between 0.39 and 25 eV (c.m.). The beam instrument (single beam–collision chamber configuration with product velocity and angular analysis) used in this study has been described.[2] The product velocity vector distributions peak considerably forward of the center of mass, indicating that the reaction is dominated by a direct mechanism over the energy range studied.[3]
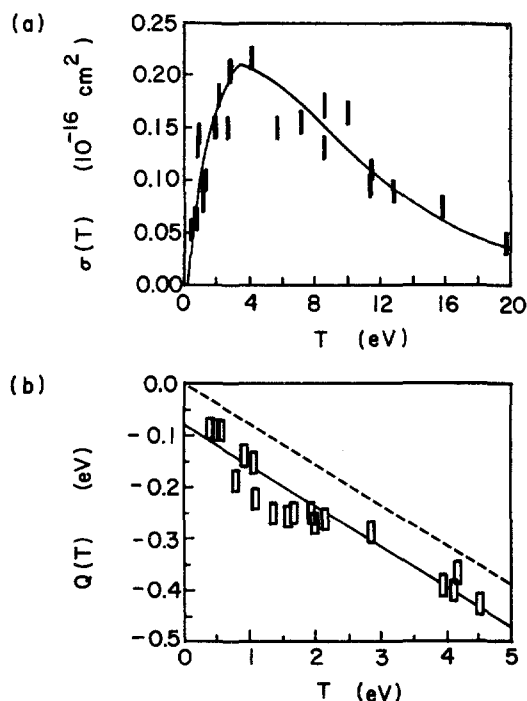

(a)

(b)

FIG. 1. (a) Reaction cross section $\sigma(T)$ vs center-of-mass collision energy T for Reaction (1). (b) Translational exoergicity $Q(T)$ vs center-of-mass collision energy T for Reaction (1). The solid line represents a linear fit to the experimental data by the method of least squares; the broken line indicates the prediction of the spectator stripping model.

The excitation function [reaction cross section $\sigma(T)$ as a function of collision energy T] for Reaction (1) is shown in Fig. 1(a). The cross section is approximately 2 orders of magnitude smaller[4] than that for the similar reaction with molecular hydrogen, $Ar^+(H_2, H)ArH^+$, presumably a result of competition from the very fast dissociative charge transfer reactions occurring in the $Ar^+–CH_4$ system.[5] Moreover, the excitation function maximizes at about 5 eV (c.m.) and decreases at lower collision energies, appearing to possess a threshold at 0.1–0.2 eV. Excitation functions of this shape are normally associated with endoergic ion–molecule reactions, such as $C^+(H_2, H)CH^+$.[6] Consequently, the observation of a threshold for the highly exoergic reaction $Ar^+(CH_4, CH_3)ArH^+$ is most remarkable and provides an exception to the long-established maxim that exoergic reactions of positive ions have no activation energy.[7]

Figure 1(b) illustrates the energy dependence of the translational exoergicity, $Q(T)$, defined as the most probable value of the product translational energy, T'_{MP}, minus the initial collision energy, T. Although the spectator stripping model[8] (shown by the broken line) predicts the energy dependence of $Q(T)$ reasonably well, the experimental values of T'_{MP} are consistently ~0.1 eV *lower* than the value predicted by this model. This observation is quite striking because it is the opposite of the behavior reported for a number of exoergic hydrogenic-transfer ion–molecule reactions studied by molecular beam[9] and high pressure mass spectrometric techniques.[10]

Assuming the linear relation[11] $Q(T) = Q_0 + BT$, a least squares analysis of the data yields $Q_0 = -0.10$ eV and $B = -0.070$. The negative value for Q_0 implies that there is a critical value of the collision energy, $T_c = -Q_0/(1+B)$, below which the products are unable to separate because T'_{MP} would be negative. With the above values for Q_0 and B, T_c for Reaction (1) equals 0.11 eV, a value strikingly similar to the apparent threshold in the excitation function. Hence, it appears that dynamical restrictions rather than competition from other reaction channels cause the cross section for Reaction (1) to go zero.

It is possible to speculate upon the nature of these dynamical restrictions. If product translation is presumed[13] to arise from repulsive energy release as the products separate, the net decrease in translational energy observed for Reaction (1) suggests that the potential energy surface along the $H-CH_3$ coordinate has a positive slope resulting from ArH^+-CH_3 attraction.

This attraction produces a basin in the potential energy hypersurface from which the products can escape only with difficulty, particularly at the lowest collision energies; direct reaction can occur only if the collision energy is high enough or the geometry of the collision such that the products retain sufficient momentum following closest approach to escape from the potential basin and to separate completely.[14]

A more comprehensive account of this work is in preparation.

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Experimental and predicted stability of gaseous ditransition metal dicarbides

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Transition metals are known to form gaseous carbides of the type MC, MC_2, MC_3, and MC_4. Dimetal dicarbides, M_2C_2, have been reported only for aluminum and gallium.[1,2] Knowledge of mixed dimetal dicarbides is limited to the observation of $AlAuC_2$ by Stearns and Kohl.[2] Experimental information concerning the first mixed dimetal dicarbides, ABC_2, containing only transition metal atoms is presented here.

The Knudsen-cell mass spectrometer used in this investigation and the experimental procedure have been described elsewhere.[3,4] The dimetal dicarbide molecules were observed over a Ce-Th-Zr-Rh-Pt-Ir alloy in graphite, following the investigation of certain intermetallic molecules.[5] The molecules identified by their mass to charge ratio, isotope distribution, and appearance potential are $RhCeC_2$, $PtCeC_2$, and $PtThC_2$. The molecule $IrThC_2$ was tentatively observed by measurement of the ion current $^{193}IrThC_2^+$ (M449) near its detection limit.

Information about the stability and molecular structure of these carbides was obtained from the measurement of the third-law reaction enthalpies for the pressure independent reactions shown in Table I. In calculating the equilibrium constants it was assumed that effects of relative ionization cross sections and multiplier gains of the reaction participants cancel.

The free energy functions for the mixed metal dicarbides were estimated in consistency with assumptions used for the molecule Ce_2S_2,[6] and the dicarbides[7,8] and intermetallic compounds[5,9] with cerium and thorium. The free energy functions for the other reaction participants were taken from literature.[10-13] The reaction enthalpies shown in Table I (error terms correspond to standard deviations) were combined with appropriate literature values to yield the atomization energies given. Here the error terms include all other estimated uncertainties. The differences in the enthalpies of the same type of reactions contain considerably smaller errors.

From the data presented in Table I the atomization energies, $\Delta H^0_{0, atm.}$, of the molecules $RhCeC_2$, $PtCeC_2$, $PtThC_2$, and $IrThC_2$ are selected as 400 ± 12, 405 ± 12,