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**THE MECHANISM OF THE REACTION  $\text{CH}_4^+ + \text{CH}_4 = \text{CH}_5^+ + \text{CH}_3$   
AS A FUNCTION OF ENERGY: RATE CONSTANTS  
AND PRODUCT DISTRIBUTIONS FOR THE REACTIONS  
OF  $\text{CH}_4^+ + \text{CD}_4$  AND  $\text{CD}_4^+ + \text{CH}_4$  AT 80 AND 300 K \***

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ABSTRACT

The collision mechanism of the reaction  $\text{CH}_4^+ + \text{CH}_4 = \text{CH}_5^+ + \text{CH}_3$  has been investigated as a function of temperature by measuring rate constants and product distributions for the reactant pairs  $\text{CH}_4^+ + \text{CD}_4$  and  $\text{CD}_4^+ + \text{CH}_4$  at 80 and 300 K. At 80 K, both reactions give the same product distribution, which is close to the statistical distribution and consistent with a long-lived complex mechanism. With increasing temperature, the product distributions change dramatically and, at 300 K, they already show strong contributions of the channels which dominate at higher energies ( $\geq 0.15$  eV)—namely the “direct” transfer of protons and hydrogen atoms. Together with results from ICR, tandem mass spectrometry, crossed beams,

\* It is a privilege to be able to honor Frank Field on his retirement. He has changed unmistakably several different areas of science—analytical chemistry, mass spectrometry, reaction kinetics and thermochemistry. We salute him for his tireless energy, his bold innovation and his unyielding commitment to vigorous dialectic. We salute him also as a teacher who taught one of us much during a year at the University of Leeds in 1963–64. For this and a 25-year friendship, M.H. feels particularly blessed.

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photoionization and quantum chemical calculations, the present low-temperature study is able to provide a unified description of the mechanism of this reaction and its energy dependence.

## INTRODUCTION

The reaction



occupies a primordial place in the history of ion/molecule reactions. It has been studied very extensively [1] and it was also the first ion/molecule reaction to be studied—both in the U.S.A. [2] and in the U.S.S.R. [3], where Talrose and Lyubimova began the modern study of the subject in 1952 [4].

The reaction also has a special historical significance for our honoree Frank Field. It was the first ion/molecule reaction that he, Franklin and Lampe studied in 1957 [5], and, nine years later, Field and Munson used the same reaction to launch the technique of chemical ionization [6].

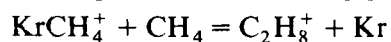
In spite of the extensive attention given to this reaction over the past 35 years, several fundamental questions have remained unanswered. What is the reaction mechanism at the lowest energies? Should the reaction be considered as a proton transfer and/or a hydrogen-atom transfer reaction? What can the collision dynamics reveal? Does reaction proceed exclusively via a long-lived collision complex at the lowest temperatures or energies? What are the principal features of the potential-energy hypersurface that determine how the reaction proceeds?

Very recently, some answers have been provided for several of these questions. For the first time, it has been possible to study the dynamics of reaction (1), using the crossed-beam apparatus EVA II at the Heyrovsky Institute of Physical Chemistry and Electrochemistry in Prague—utilizing the capability of that apparatus for measuring angular distributions for quasi-thermal ions [7]. These experiments have confirmed the role of three different collision mechanisms, competing as follows:

proton transfer > hydrogen-atom transfer  $\gg$  complex formation

and have revealed some of the dynamic characteristics of the complex involved. Complex formation contributed only a few percent in the range of collision energy studied (0.6–2.3 eV) but, even so, the percentage contribution doubled as the collision energy was reduced. Does this suggest that the reaction proceeds exclusively through a long-lived complex at the lowest energies? One requirement for a “complex” mechanism is that the complex itself be sufficiently stable. Recent evidence has demonstrated that the  $\text{C}_2\text{H}_8^+$  ion is indeed a stable species. It has been synthesized in two different

ways, by the photoionization of the van der Waals dimer  $(\text{CD}_4)_2$  [8], and by the displacement reaction [9]



Theory corroborates these findings, predicting  $\text{C}_2\text{H}_8^+$  to be stable, with a dissociation energy estimated to be  $14 \text{ kcal mol}^{-1}$  [10].

All these results point to the reaction proceeding through a long-lived complex at thermal energies. Unfortunately, this conclusion cannot be tested directly, as angular distributions have not been measured at collision energies below 0.6 eV. What experimental information is available comes from isotopic labelling studies and allows only an indirect test. In the labelling studies, a statistical product distribution implies the participation of long-lived collision complexes. The labeling data available for reaction (1) include the very first investigation of any ion/molecule reaction using isotopic labels [11] and they also include one study, identified as having been made at thermal energy [12]. The thermal-energy study produced results that were incompatible with a "long-lived complex" mechanism but that were compatible with a "direct" mechanism, involving both proton transfer and hydrogen-atom transfer.

The dynamical study and the labeling study therefore seem to disagree. In an attempt to resolve this, we have repeated the isotopic labeling experiments, at lower temperatures and controlled temperatures, using a different technique, the Selected Ion Flow Tube (SIFT). The SIFT technique has a proven capability of studying isotope-exchange reactions under isothermal conditions at temperatures as low as 80 K [13].

#### EXPERIMENTAL

The experiments were conducted with the temperature-variable Birmingham SIFT apparatus [14,15], using helium as the carrier gas in the flow tube. Measurements were made at 80 and 300 K, i.e. liquid-nitrogen and room temperature. At both temperatures, two sets of measurements were made. In one set, methane was introduced into a low-pressure ion source to produce the  $\text{CH}_4^+$  ion which was then injected into the flow tube and reacted downstream with  $\text{CD}_4$  (Matheson, containing  $< 1\%$   $\text{CHD}_3$ ). In the second set, the gases were interchanged to study the corresponding "mirror-isotope" reaction  $\text{CD}_4^+ + \text{CH}_4$ . Total rate constants and the product distribution of the various isotopically labelled products were measured using standard procedures [14,15], which have been described in detail for a previous isotopic-labeling study [16].

There was no evidence to suggest that either the  $\text{CH}_4^+$  or the  $\text{CD}_4^+$  reactant ion, injected into the flow tube, was internally excited. This matter is discussed further below.

## RESULTS

For each of the reactant pairs studied,  $\text{CH}_4^+ + \text{CD}_4$  and  $\text{CD}_4^+ + \text{CH}_4$ , the four possible reaction products were measured, as follows:



The channels are labeled systematically by letter according to reaction type. Thus (a) is the hydrogen-atom-transfer channel, transferring D for reaction (2) and H for reaction (3); (d) is the proton-transfer channel, transferring  $\text{H}^+$  for (2) and  $\text{D}^+$  for (3); and so on.

The experimental results, obtained at 80 and 300 K, are presented in the second and third rows of Table 1, as total rate constants and percentage product distributions. The product distributions for (2) and (3) are compared according to channel so that, for example, results for (2a) and (3a) are placed in the same column.

Additional information is also included in Table 1. For each reaction the first row gives, as a reference, the product distribution expected for statistical mixing. The fourth row gives the "thermal energy" distribution reported by Huntress using the ICR technique [12]. [In that study no measurements could be made on reactions (2c) and (3b).] The fifth row gives the distribution measured at  $\sim 0.15$  eV using beam techniques and the sixth row the distribution for  $\sim 1$  eV, using beam data for reaction (2) and ICR data for reaction (3). Finally in the seventh row, there are limited beam data for reaction (3) at even higher energies, 7 eV. In each case, the energy cited is the collision energy. The internal energy content of the reactant ions will be discussed later.

With increasing collision energy, it becomes increasingly difficult to identify reaction channels unambiguously because new channels—collisional dissociation and charge transfer—compete and even dominate. Accordingly, it becomes increasingly difficult to assess quantitatively the relative contributions of channels (a)–(d).

TABLE 1

Rate constants and product distributions for the reactions  $\text{CH}_4^+ + \text{CD}_4 \rightarrow \text{products}$  and  $\text{CD}_4^+ + \text{CH}_4 \rightarrow \text{products}$  at 80 and 300 K, compared with theoretical prediction and other data

Reactants	Source	Temperature or energy <sup>a</sup>	Product distribution (percentage)				Rate constant ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) <sup>b</sup>
			(a)	(b)	(c)	(d)	
$\text{CH}_4^+ + \text{CD}_4$			$\text{CH}_4\text{D}^+$	$\text{CH}_3\text{D}_2^+$	$\text{CH}_2\text{D}_3^+$	$\text{CHD}_4^+$	
	Statistical	—	7	43	43	7	—
	SIFT <sup>c</sup>	80 K	10	45	35	10	1.0(-9)
	SIFT <sup>c</sup>	300 K	10	22	43	25	1.3(-9)
	ICR <sup>d,e</sup>	"Thermal"	28	9	<sup>f,g</sup>	63	<sup>f</sup>
	Beam <sup>h</sup>	0.15 eV	24	12	<sup>f,g</sup>	64	<sup>f</sup>
	Beam <sup>h</sup>	1 eV	18	3	<sup>f,g</sup>	79	<sup>f</sup>
Beam <sup>h</sup>	7 eV	~10	<sup>f</sup>	<sup>f,g</sup>	~90	<sup>f</sup>	
$\text{CD}_4^+ + \text{CH}_4$			$\text{CHD}_4^+$	$\text{CH}_2\text{D}_3^+$	$\text{CH}_3\text{D}_2^+$	$\text{CH}_4\text{D}^+$	
	Statistical	—	7	43	43	7	—
	SIFT <sup>c</sup>	80 K	12	30	48	10	0.95(-9)
	SIFT <sup>c</sup>	300 K	12	24	36	28	1.2(-9)
	ICR <sup>d,e</sup>	"Thermal"	32	<sup>f,g</sup>	9	59	<sup>f</sup>
	Beam <sup>h</sup>	0.15 eV	31	<sup>f,g</sup>	8	61	<sup>f</sup>
	ICR <sup>d</sup>	1 eV	24	<sup>f,g</sup>	4	72	<sup>f</sup>

<sup>a</sup> The SIFT data are thermal. The energy listed for the rest is translational energy, ignoring internal energy of  $\sim 1$  eV. <sup>b</sup> 1.0(-9) means  $1.0 \times 10^{-9}$ . <sup>c</sup> Present study. <sup>d</sup> Ref. 12. <sup>e</sup> See also ref. 17 for limited corroboration. <sup>f</sup> Not measured. <sup>g</sup> Even though the ICR and beam studies cannot measure  $\text{CH}_2\text{D}_3^+$ , the two data sets complement each other. <sup>h</sup> Ref. 18 with corrections for charge exchange and collision-induced dissociation. Energy  $\pm 0.1$  eV.

In Table 1, the assignment of molecular formulas to the mass-to-charge ratios measured for the reaction products requires discussion. Thus  $m/z = 20$  could be either  $\text{CH}_2\text{D}_3^+$  or  $\text{CD}_4^+$ . However, no evidence was found for charge transfer in either reaction. For reaction (3), we simply detected no  $m/z = 16$  at either 80 or 300 K. For reaction (2), we did detect the ion  $m/z = 20$ —it was the major ion at 80 K—but we identify it as  $\text{CH}_2\text{D}_3^+$  from its failure to react further, at a significant rate, at higher flow rates of the  $\text{CD}_4$  reactant [19]. Any  $\text{CD}_4^+$  component of the  $m/z = 20$  ion would have reacted with the  $\text{CD}_4$ , essentially on every collision, and no evidence was found for that behavior. [Finally, charge transfer in reaction (3) is shown later to be endothermic.]

The contribution of reaction (3b) had to be found by kinetic modeling as the product ion has the same mass-to-charge ratio as the reactant ion. The total rate constant was determined from the slope of the semilog plot in the limit of zero conversion. The contribution of the ion  $\text{CH}_2\text{D}_3^+$  to the product

distribution was then obtained by considering the total count rate at  $m/z = 20$  and accounting for the experimental loss of the reactant ion  $CD_4^+$ .

#### DISCUSSION

The results presented in Table 1 provide new insights into the mechanism of reaction (1) and into the energy dependence of the mechanism. A simple mechanism can account for the present data and those available from the other techniques.

Let us consider first the general trends in the product distributions in Table 1. At 80 K, the lowest temperature studied, the distributions for both reactions show a clear similarity to the statistical product distribution. Increasing the temperature from 80 to 300 K changes the distributions significantly away from the statistical, with channels (2d) and (3d) showing a consistent increase in each case. It should be noted that at 300 K and at all higher temperatures and energies, the two product distributions of reactions (2) and (3) appear to be rather similar. At the next higher energy,  $\sim 0.15$  eV, the product distributions have changed dramatically, to be even further from the statistical distribution. At the next higher energy,  $\sim 1$  eV, the systematic change has continued but the change is less marked. At the highest energy, 7 eV, the trend has continued but has tapered off.

The evolution of the product distribution with increasing energy is simply described. Those channels which require no mixing, (a) and (d), are progressively favored at the expense of those, (b) and (c), which do require mixing. At the lowest energy, there is effectively complete mixing and at the highest energy, there is effectively none.

We are now in a position to evaluate the ICR data which have been assigned to thermal kinetic energies. We see in Table 1 that the product distributions for the "thermal" ICR measurements correspond not to the distributions for 300 K but rather to those for  $\sim 0.15$  eV. Because the product distribution is a sensitive function of temperature/energy in this range, an effective temperature of  $\sim 1000$  K can be assigned to the "thermal" ICR experiment [20]. (This is not inconsistent with the reported trapping voltage of 0.2 V [12].) Furthermore, this temperature assignment is compatible with other estimates of effective temperatures for "thermal-energy" ICR measurements in the same laboratory [20].

The original ICR study noted that the product distribution, identified as being "thermal", was essentially identical to that for the beam measurement at a collision energy of 0.3 eV [12]. Furthermore, the beam measurements showed the product distribution not to change much in the energy range 0.15–1 eV, and it was plausible to assume that this would continue down to the lowest energies. With these results and this assumption, it was possible

to identify the ICR experiment at the lowest energy as a "thermal energy" measurement. Our measurements at 80 and 300 K do not challenge the earlier data. Rather, they add the new information that the distribution is indeed a sensitive function of energy in the range 0.03–0.15 eV—permitting a more detailed re-evaluation of this question and modifying the previous interpretation.

All the isotopic labeling experiments provide a consistent picture of the reaction mechanism. At the lowest temperature there is complete mixing and as the energy is increased, the channels that involve mixing progressively disappear. Additionally, Table 1 reveals competition between the two channels that require no mixing. Channel (d) always dominates channel (a), increasingly so with increasing energy.

It should be noted too that the classic early study of Wagner et al. [11] is perfectly consistent with the results summarized in Table 1. These were studies over an energy range; particle transfer, and not isotopic mixing, would be predicted; and that is precisely what was observed.

#### *Comparison with dynamical studies*

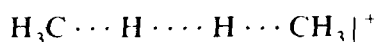
The crossed-beam measurements of reaction (1) produce angular distributions of  $\text{CH}_3^+$  with three distinct maxima—showing strong forward scattering, strong back scattering and scattering at the center of mass [7]. These are interpreted in terms of the following mechanisms: direct hydrogen-atom transfer, direct proton transfer, and complex formation. These dynamical studies of reaction (1) are reconciled with the labeling studies of reactions (2) and (3), as follows: channel (a) involves direct hydrogen-atom transfer, channel (d) direct proton transfer, and channels (b) and (c) complex formation. Both the crossed-beam technique and the rate measurements of isotopically labelled reactants give similar relative contributions for the three mechanisms; and they give a similar temperature/energy dependence for these contributions. The failure of the two methods to give a strict quantitative agreement for the relative contributions [21] does not invalidate our interpretation. First, as already noted above, it is not always possible in the labeling studies to identify a particular ion. Thus, at higher energies,  $m/z = 18$  could be either  $\text{CH}_4\text{D}^+$  [reaction (3d) or  $\text{CD}_3^+$  (by collisional dissociation)]. Second, direct mechanisms do not preclude the possibility of isotope exchange, as shown dramatically by the deuterium-labeling study of the reaction:  $\text{CH}_3^+ + \text{CH}_4 = \text{C}_2\text{H}_5^+ + \text{H}_2$ , where significant isotopic mixing was shown to occur [12,18a] during the course of a "direct" reaction [23]. There is no mystery here. A lower limit to the time scale for isotopic mixing is  $\sim 5 \times 10^{-14}$  s, set by the C–H bond vibrational period, whereas the lifetime of the intermediate for a direct reaction will not exceed  $\sim 5 \times 10^{-12}$

s, the rotational period of the reaction intermediate. Products that show an asymmetric angular distribution may yet have ample opportunity for isotope exchange [23].

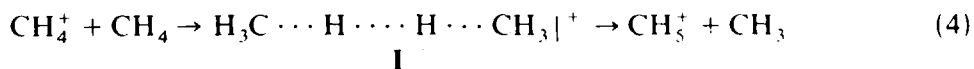
### *Isotopic mixing*

Details of the transition from complete mixing at the lowest temperature to no mixing at the highest collision energy, provide new insight into the mechanism of reaction (1) and into the structure of the reaction intermediates involved.

We first identify the salient features of the hypersurface for reaction (1). The reaction is slightly exothermic, with an enthalpy decrease determined to be  $\Delta H_{298}^{\ominus} = -4 \pm 2 \text{ kcal mol}^{-1}$  [24]. (A subsequent re-determination of the proton affinity of methane [25] would raise this to  $-7 \text{ kcal mol}^{-1}$  but this is not confirmed by other, more recent experiments [26]. The hypersurface appears to be characterized by a single basin,  $18 \text{ kcal mol}^{-1}$  deep with respect to the entering reactants  $\text{CH}_4^+ + \text{CH}_4$  and therefore  $14 \text{ kcal mol}^{-1}$  deep with respect to the products  $\text{CH}_5^+ + \text{CH}_3$ . (The other singularities that have been identified on the hypersurface are local minima that appear to exercise no control over the reaction [27].) How should this basin be characterized in chemical terms? It cannot be  $\text{CH}_4^+$ ,  $\text{CH}_4$  or  $\text{CH}_5^+$ ,  $\text{CH}_3$  because such a simple hypersurface is only found where both partners are filled-shell species [28]. Here one of the partners would necessarily have an unfilled shell so that electron delocalization forces a particular  $\text{C}_2\text{H}_5^+$  structure for the basin in the hypersurface. Two independent quantum chemistry calculations reveal it to have the symmetric structure



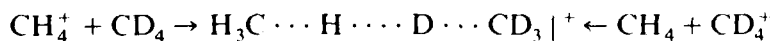
with a  $D_{3d}$  point group [10]. The methyl groups lie in a staggered configuration; however, in the collision experiment there is ample energy available to allow free rotation. If this is the intermediate involved in reaction (1), we write the following mechanism:



I

where **I** is the global minimum corresponding to the stable intermediate [29].

Applying this mechanism (4) to reactions (2) and (3), we see that the same intermediate **II** would be formed for both reactions:



II

↓  
products

and that identical product distributions would be formed for the two reactions. The product distributions would be identical irrespective of the mechanism of hydrogen "mixing" within the intermediate **II** and irrespective of the operation of any isotope effects. (This holds for hydrogen mixing in a long-lived intermediate but not in a "direct" reaction.) The only difference in preparing **II** via reaction (2) or (3) would be the difference in energy content, resulting from zero-point energy differences.

*The mechanism at 80 K*

We now use the data in Table 1 to test mechanism (4) at the optimum temperature, 80 K, where the intermediate lifetime is longest and thus allows the most extensive mixing. We have already made a qualitative comparison of the product distributions of reactions (2) and (3) at 80 K. We noted a clear similarity to the statistical product distribution and we concluded that there was effectively complete mixing. We now make this comparison more quantitative. Both product distributions differ, slightly but measurably, from the statistical distribution, and it is appropriate to examine the significance of the difference.

In Table 2, we compare the product distributions for reactions (2) and (3) in two different ways. In the right-hand column, they are compared according to channel (as in Table 1); in the left-hand column, they are compared according to the identity of the product. We now consider the 30 K data. The comparison according to channel gives good agreement for only two channels; the comparison according to product gives remarkably good agreement for all the products. At 80 K, both reactions give the same products with the same rate constants, independent of the identity of the reactants:  $\text{CH}_4^+ + \text{CD}_4$  or  $\text{CD}_4^+ + \text{CH}_4$ . This symmetry establishes the validity of mechanism (4) and provides independent kinetic evidence for the quantum mechanical identification of **II** as the reaction intermediate [30].

We can eliminate immediately an alternative mechanism involving charge transfer between the reactants prior to the collision. "Prior charge-transfer" would predict a similar result for 300 K; as discussed below, that is not found. Furthermore, as we have shown, there is no evidence for charge transfer for either  $\text{CH}_4^+ + \text{CD}_4$  or  $\text{CD}_4^+ + \text{CH}_4$ .

Although the actual product distribution found at 80 K was close to the statistical distribution, it was not identical to it. Specifically, the  $\text{CH}_2\text{D}_3^+$  product was low by about 10%. (This difference from the statistical distribution has to be significant because the same result was obtained from the two independent experiments.) The result may reveal something about the mechanism of isotopic mixing in **II** and/or the influence of isotope effects. Further discussion of this matter is deferred to the next section.

TABLE 2  
Comparison of the product distributions of reactions (2) and (3) at 80 and 300 K

Reactants	Temperature (K)	Product distribution (%) compared by product				Product distribution (%) compared by channel			
		$\text{CH}_4\text{D}^+$	$\text{CH}_3\text{D}_2^+$	$\text{CH}_2\text{D}_3^+$	$\text{CHD}_4^+$	(a)	(b)	(c)	(d)
$\text{CH}_4^+ + \text{CD}_4$	80	10	45	35	10	10	45	35	10
$\text{CD}_4^+ + \text{CH}_4$	80	10	48	30	12	12	30	48	10
$\text{CH}_4^+ + \text{CD}_4$	300	10	22	43	25	10	22	43	25
$\text{CD}_4^+ + \text{CH}_4$	300	28	36	24	12	12	24	36	28
Statistical		7	43	43	7	7	43	43	7

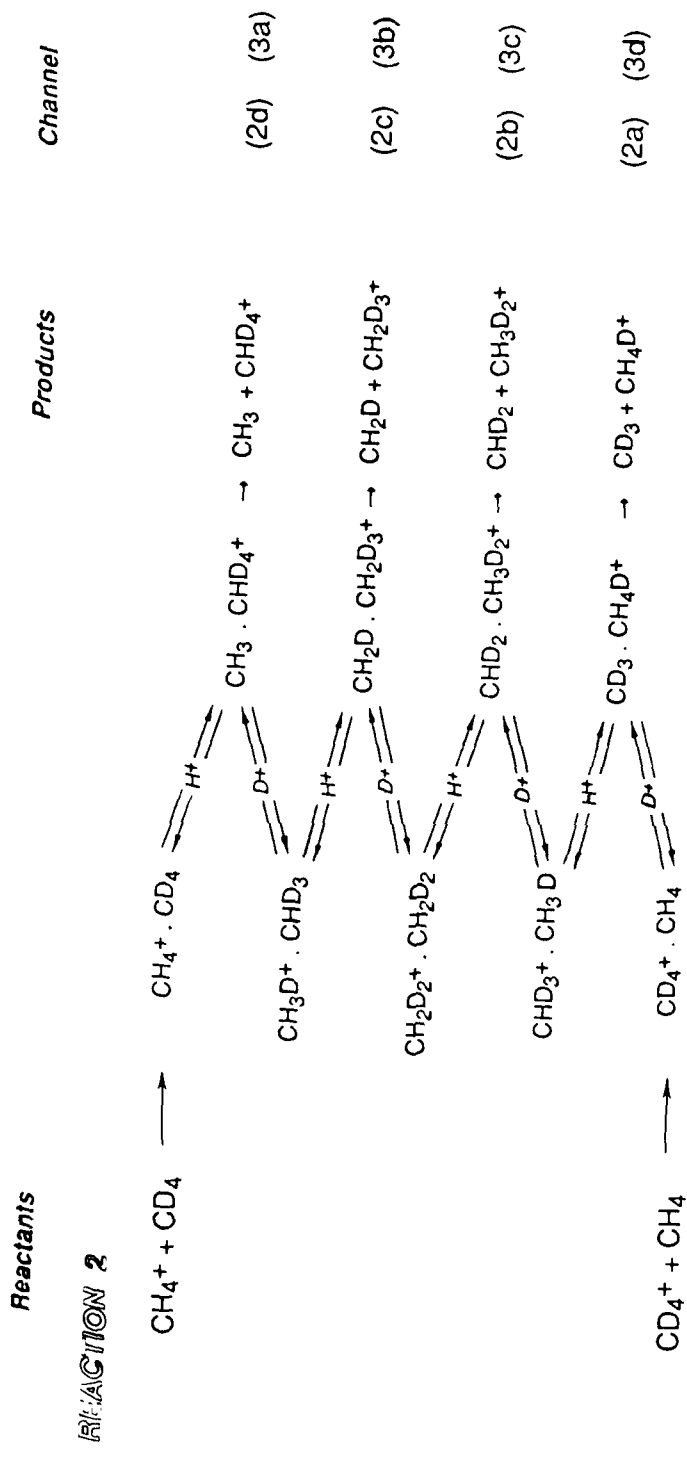
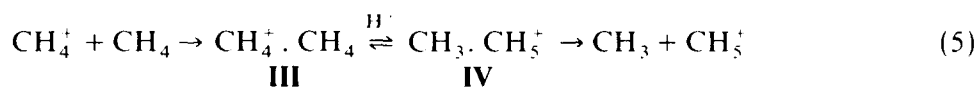


Fig. 1. Mechanistic scheme proposed for isotopic mixing for reactions (2) and (3) involving proton and deuteron transfers.

*The mechanism at 300 K*

A very different result is found at 300 K. Reactions (2) and (3) no longer give an identical product distribution. Indeed, none of the products show even similar yields for the two reactions (Table 2, left-hand column). At 300 K there is no evidence whatsoever for the operation of a common intermediate [mechanism (4)]. However, the product distributions are remarkably similar, if they are compared according to channel (Table 2, right-hand column). Both reactions show the same channels to the same extent but there is no common intermediate **II**. What has changed between 80 and 300 K? Channel (a) has remained constant, at about the statistical value; channel (b) has decreased by 15% (on average) and channel (c) by 2%; and channel (d) has increased by 17% [31]. This is the first step in the process whereby, with increasing excitation, the "unmixed" channels, (a) and (d), supplant the "mixed" channels, (b) and (c). Mixing occurs via the sequence (d) → (c) → (b) and a mechanism can be proposed for this, involving the intermediates **III** and **IV**:



The intermediates **III** and **IV** are reactant like and product like respectively and can interconvert by a simple proton transfer. If free rotation is possible for  $\text{CH}_4^+$  in **III** and for  $\text{CH}_5^+$  in **IV**, a mechanism is provided for isotope exchange, through interchange of  $\text{H}^+$  and  $\text{D}^+$  according to the scheme given in Fig. 1.

Every channel uses the same elementary step—a proton or deuteron jump—which occurs a different number of times for each channel. For channel (d), it occurs once for (c) twice, for (b) thrice and for (a) four times. It is a plausible elementary step because the elementary step itself, channel (d), is observed directly. It is efficient because, at collision energies of 0.15 eV and above, proton transfer [channel (d)] is the major channel; and it is a proton jump, as shown by the crossed-beam studies at collision energies of 0.6 eV and above. It is worth noting, parenthetically, that proton transfer has been invoked as the elementary step for many other isotope-exchange reactions [13,16,19,28,32].

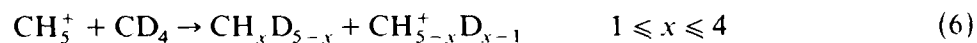
As applied here to reaction (1), the proton-transfer mechanism for isotope exchange differs from our previous applications. Hitherto it has always been possible to define the identity of the intermediate unambiguously, because the proton donor and acceptor within the intermediate were both filled-shell species [28]. Here it is less straightforward because either the proton donor or acceptor ( $\text{CH}_4^+$  or  $\text{CH}_3$ ) has an unfilled shell. Thus, in the filled-shell system  $\text{OH}^- + \text{H}_2 = \text{HO}^- \cdot \text{H}_2 = \text{HOH} \cdot \text{H}^- = \text{H}_2\text{O} + \text{H} \cdot$ , it has been straightforward to define the intermediates [32]; in contrast, here in reaction

(5), it is speculative to identify the intermediates **III** and **IV**. However, there is some encouragement from the quantum chemical calculations. Thus **III** can be identified with structure 4 of Zahradnik's calculation [10a] and complex B of Morokuma's [10b]; similarly **IV** can be identified with structure 9 and complex C of those authors respectively.

Given the failure of mechanism (4) to account for the 300 K data, mechanism (5) is a possible alternative. It accounts qualitatively for the energy dependence of the product distribution, predicting that channel (d) should persist at the highest energies and that channel (b), as the more mixed channel, should decrease at lower energies than channel (c). However, the mechanism fails with channel (a), which it predicts should decrease at even lower energies than channel (b). Actually channel (a) increases with increasing energy, and there is a simple explanation for the disagreement between the data and the prediction of mechanism (5). The crossed-beam results show channel (a) to follow a different mechanism—a direct hydrogen-atom transfer—which is a simpler short-cut to the alternative sequence of four proton jumps, proposed in mechanism (5).

### *Isotope effects*

Where deuterium labeling is used to examine reactions that are effectively thermoneutral, isotope effects can exercise a controlling influence at low temperatures. A dramatic example is provided by the isotope exchange reaction



where the entropy change determines the product distribution at high temperature and where the enthalpy change gives a completely different distribution at low temperatures [19]. It is therefore necessary to estimate the reaction enthalpies for the various channels of reactions (2) and (3). Zero-point energies of all the species involved are listed in Table 3. Few of these are known directly. Consequently, we have been forced to estimate them, using a semi-empirical procedure that we have proposed and tested previously [35,36].

Enthalpies of reaction for the various channels 2(a-d) and 3(a-d) are shown in Fig. 2; the values are tied to that of  $-4 \text{ kcal mol}^{-1}$  for reaction (1). Figure 2 shows that zero-point-energy effects do not alter the reaction enthalpy by more than  $\pm 1 \text{ kcal mol}^{-1}$ . No channel becomes endothermic as a consequence of isotopic substitution [in contrast to reaction (6), for example]. Thus enthalpic restrictions cannot alter the product distribution significantly. This predicts that the product distribution at 80 K should be statistical; and we are therefore unable to invoke zero-point-energy effects to

TABLE 3

Zero-point energies (kcal mol<sup>-1</sup>)

CH <sub>3</sub>	17.6 <sup>a</sup>	CH <sub>4</sub> <sup>+</sup>	22.8 <sup>a</sup>	CH <sub>4</sub>	27.7 <sup>b</sup>	CH <sub>5</sub> <sup>+</sup>	31.6 <sup>a</sup>
CH <sub>2</sub> D	16.0 <sup>d</sup>	CD <sub>4</sub> <sup>+</sup>	16.8 <sup>c</sup>	CD <sub>4</sub>	20.3 <sup>b</sup>	CH <sub>4</sub> D <sup>+</sup>	29.9 <sup>d</sup>
CHD <sub>2</sub>	14.4 <sup>d</sup>					CH <sub>3</sub> D <sub>2</sub> <sup>+</sup>	28.2 <sup>d</sup>
CD <sub>3</sub>	12.8 <sup>c</sup>					CH <sub>2</sub> D <sub>3</sub> <sup>+</sup>	26.5 <sup>d</sup>
						CHD <sub>4</sub> <sup>+</sup>	24.8 <sup>d</sup>
						CD <sub>5</sub> <sup>+</sup>	23.1 <sup>c</sup>

<sup>a</sup> Zero-point energies (CH<sub>3</sub>, 19.4; CH<sub>4</sub><sup>+</sup>, 25.1; CH<sub>4</sub><sup>+</sup>, 34.8) have been calculated at the 3-21 G level for harmonic frequencies [33] but are 10% too high because of the anharmonic correction and because of the neglect of electron correlation [34].

<sup>b</sup> Ref. 35.

<sup>c</sup> Calculated according to the relationship that the zero-point energy ratio of perdeutero- to perproto- (CD<sub>n</sub>/CH<sub>n</sub>) is equal to 0.73 [35].

<sup>d</sup> The zero-point energy of the partially deuterated species is derived by linear interpolation between the values for the completely deuterated and the completely undeuterated species [35].

account for the anomalously low yield of CH<sub>2</sub>D<sub>3</sub><sup>+</sup> at 80 K (Table 2). Although we fail to provide an explanation for this experimental result, the failure is self consistent. The yield of CH<sub>2</sub>D<sub>3</sub><sup>+</sup> at 80 K is the same for reaction (2) and (3); the actual reaction enthalpies (2c) and (3b) differ by 1.4 kcal mol<sup>-1</sup>, and if the low yield were caused by zero-point-energy effects, the yield would have to differ for the two reactions.

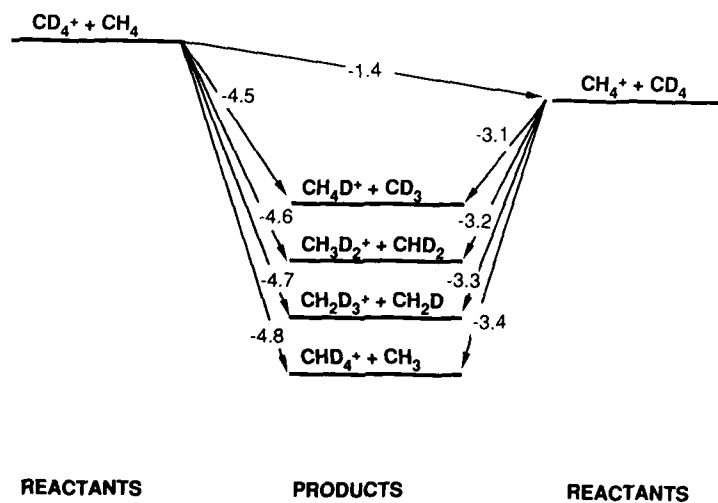


Fig. 2. Schematic enthalpy diagram showing enthalpies of reaction for the possible reaction channels of CH<sub>4</sub><sup>+</sup> + CD<sub>4</sub> [reactions (2) and (7)] and CD<sub>4</sub><sup>+</sup> + CH<sub>4</sub> [reactions (3) and (8)]. Enthalpies in kcal mol<sup>-1</sup>.

Other observations emphasize the irrelevance of enthalpic effects. Of the two products that require extensive "mixing" ( $\text{CH}_3\text{D}_2^+$  and  $\text{CH}_2\text{D}_3^+$ ),  $\text{CH}_3\text{D}_2^+$  occurs in greater yield at 80 K (Table 2); yet the reactions which produce  $\text{CH}_3\text{D}_2^+$  actually have the lower reaction enthalpy, although only by  $0.1 \text{ kcal mol}^{-1}$  (Fig. 2). Again, at collision energies of 0.15 eV and above, proton transfer is the major pathway [(2d) and (3d)]; for reaction (2) this is the most exothermic channel, yet for (3) it is the least.

Having eliminated the possible influence of reaction enthalpy upon the product distributions, we next consider reaction entropy. We start with two sets of reactants,  $\text{CH}_4^+ + \text{CD}_4$  and  $\text{CD}_4^+ + \text{CH}_4$ , and we consider producing the two sets of products  $\text{CH}_3\text{D}_2^+ + \text{CHD}_2$  and  $\text{CH}_2\text{D}_3^+ + \text{CH}_2\text{D}$ . As H and D are interchangeable, the configurational entropy change has to be identical for the four possible reactions (2b), (2c), (3b) and (3c). Therefore, arguments based on entropy cannot account for the diminished yield of  $\text{CH}_2\text{D}_3^+$  at 80 K (Table 2). Similarly, entropic arguments cannot predict the preference for proton transfer over hydrogen-atom transfer [channel (d) over channel (a)] that is observed at higher energies (Table 1).

Isotope effects cannot affect the reaction thermodynamics significantly—but what about dynamic isotope effects? Because of inertial reasons, tunneling, etc., protons can be more easily transferred. Let us consider again  $\text{CH}_2\text{D}_3^+$ , formed in low yield at 80 K. According to the scheme given in Fig. 1, this is formed by reaction (2c) by the sequence of three jumps  $\text{H}^+/\text{D}^+/\text{H}^+$  and by reaction (3b) by the five-jump sequence  $\text{D}^+/\text{H}^+/\text{D}^+/\text{H}^+/\text{D}^+$ , yet the yield is the same. The more favored product  $\text{CH}_3\text{D}_2^+$  is formed by reaction (2b) by the five-jump sequence  $\text{H}^+/\text{D}^+/\text{H}^+/\text{D}^+/\text{H}^+$  and by reaction (3c) by the three-jump sequence  $\text{D}^+/\text{H}^+/\text{D}^+$ ; again the yield is the same for both. If the proton-transfer mechanism given in Fig. 1 is correct, the diminished yield of  $\text{CH}_2\text{D}_3^+$  observed at 80 K cannot be rationalized by dynamic isotope effects.

In summary, neither thermodynamic nor kinetic isotope effects can account for the slight but measurable difference between the product distribution observed at 80 K and the statistical prediction. This result tells us that distributions will not necessarily be statistical. For example, in interpreting the photoionization (TESICO) results on the effect of internal energy on reactions (2) and (3), it was assumed plausibly that the cross sections  $\sigma_{2b} = \sigma_{2c}$  and that  $\sigma_{3b} = \sigma_{3c}$  [37]; yet the results in Table 1 show that this does not hold, at least for reactants without internal energy. It is reassuring that the assumption cannot introduce significant error in the interpretation of the TESICO investigation [37], because the results of that study agree with those of other studies. Thus Table III in the TESICO study [37] showed similar estimates for the contributions of the various channels measured by the photoionization and crossed-beam techniques.

*Charge transfer*

We consider next the possibility of the charge-transfer reactions (7) and (8), competing with reactions (2) and (3) respectively:



(The enthalpy change is derived from experimental and calculated data using our procedures (Table 3 and shown in Fig. 2); an independent estimate  $|\Delta H_0^\ominus| = 1.6 \text{ kcal mol}^{-1}$  has been derived from experimental data alone [37].)

The charge-transfer reactions (7) and (8) have been observed experimentally as follows. In the present SIFT study, neither reaction was observed in the temperature range 80–300 K. [Actually reaction (7) is too endothermic to be observable under those conditions.] In the ICR study also, neither reaction was observed to a significant extent [12]. In the tandem mass spectrometer study, reaction (7) was observed with a significant cross section that was independent of kinetic energy, and a comparable cross section was observed for reaction (8) at the lowest energies [18]. In a photoionization study (the TESICO technique) of the effect of internal energy on reactions (2) and (3), the cross sections of reactions (7) and (8) were observed to decrease with increasing internal energy and to decrease slightly with increasing collision energy [38]. In the crossed-beam experiment, it was not possible to look for reactions (7) and (8).

How are these results to be interpreted? Charge transfer becomes possible when the methane reactant ions are internally excited, and it is impossible when they are not. The important point to note is that all methane ions,  $\text{CH}_4^+$  or  $\text{CD}_4^+$ , produced by electron impact on methane, are formed with considerable internal excitation energy (0.1–1.5 eV, with a mean of about 1 eV [37]. Collision in the ion source cannot remove this energy from the ions because collision (with methane molecules) would remove the ions themselves, by reaction (1). Only in the SIFT experiment can the internal energy be lost, by collisions with the helium bath gas in the flow tube. Thus charge transfer is observed in the photoionization and tandem mass spectrometer experiments but in the SIFT experiment, it is not. We would expect charge transfer to be observed in the crossed-beam experiment, where it was not studied, and in the ICR experiment, where it was studied but not observed. The failure to observe charge transfer in the ICR is hard to understand. The  $\text{CH}_4^+$  ions in the ICR cell have to be internally excited, and further experiments are needed.

We note that wherever exothermic reaction (8) occurs, endothermic reaction (7) also occurs. For charge transfer to occur, the internal excitation of the reactant ion must be large compared to the endothermicity of reaction (7).

The failure to observe charge transfer in this study does have some relevance to the mechanism of reaction (1). Charge transfer between  $\text{CH}_4^+$  and  $\text{CH}_4$  cannot be a step in any mechanism for the competition between proton transfer, hydrogen-atom transfer and complex formation, involving thermal reactants.

*Were the reactant ions internally excited?*

In this study the evidence suggests that the reactant ions possessed no internal excitation in excess of thermal energy.

In our experiments, charge transfer is not observed. This sets the internal energy of the reactant ions below the threshold energy for charge transfer. This threshold energy has not been determined precisely. An upper bound of 0.8 eV comes from the experimental TESICO study [37]. Theory predicts it to be 0.7 eV for the system held under certain restricted symmetry constraints [10b].

Two pieces of circumstantial evidence suggest that the methane reactant ions are completely thermalized in the helium bath gas. First, although several diatomic ions and two triatomic ions ( $\text{N}_2\text{H}^+$  and  $\text{H}_3^+$ ) do not thermalize in the flow tube, all other polyatomic ions are observed to thermalize efficiently [38]. A finding that  $\text{CH}_4^+$  was internally excited would be inconsistent with a large body of data which are themselves self consistent. Second, raising the temperature from 80 to 300 K has a profound effect upon the product distribution (Table 1). It is difficult to imagine how such a small amount of energy could have such a large effect, if the system itself already possessed considerable internal excitation.

*Rate constants*

The SIFT data, reported for reactions (2) and (3) in Table 1, suggest that  $dk/dT > 0$ , a 30% increase in rate constant in the range 80–300 K. No other exothermic ion/molecule reaction shows at 300 K a collisional rate that decreases with decreasing temperature. Indeed, the photoionization study shows that  $dk/dE < 0$ , for both collision energy and total energy (translational plus internal) [37]. (The first dependence is for reactants without internal energy, the second for reactants with internal energy.) Our present assessment of our SIFT data is as follows. It is possible that, at 80 K, some of the methane condensed on the walls of the inlet tube, between the

pressure regulator and the injector. If so, this could account for the apparent drop in rate constant. This needs to be investigated before the 80 K rate constants in Table 1 can be accepted.

#### CONCLUSIONS

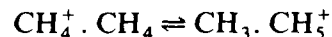
(1) The product distributions for the reactants  $\text{CH}_4^+ + \text{CD}_4$  and  $\text{CD}_4^+ + \text{CH}_4$  have been measured with a variety of techniques throughout a range of temperature and collision energy, from 80 K to 7 eV, giving a consistent account of the temperature/energy dependence of the collision mechanism. This is consistent too with measurements of the angular distribution for the reactant pair  $\text{CH}_4^+ + \text{CH}_4$  in the collision-energy range 0.6–2.3 eV. The present study contributes experimental results for the lowest temperatures 80–300 K.

(2) At the lowest temperature, 80 K, the reaction proceeds via a long-lived collision complex where there is complete mixing of the isotopic labels, both reactant pairs yielding the same product distribution. This distribution differs slightly from the statistical distribution—a difference that cannot be explained by zero-point-energy or dynamic isotope effects. The participation of the long-lived complex  $\text{C}_2\text{H}_8^+$  in the reaction is consistent with the experimental isolation of the complex and with its theoretical characterization as a linear species.

(3) The mechanism changes dramatically between 80 and 300 K, perhaps because the reaction is only slightly exothermic ( $-4 \text{ kcal mol}^{-1}$ ) and the intermediate complex is only weakly bound ( $14 \text{ kcal mol}^{-1}$ ). (Within this temperature range, the product distribution can therefore be used as a sensitive “thermometer” [20].)

(4) The mechanism changes dramatically again between 300 K and 0.15 eV. (This comparison is a little misleading. The 300 K experiment is truly thermal; the 0.15 eV experiment defines the collision energy, but there is also about 1 eV internal energy.) The change is from processes requiring substantial isotopic mixing to those requiring chiefly particle transfer (a proton or a hydrogen atom). There is good reason to infer that, even at this energy, these transfers are “direct” processes, in the dynamical sense. With increasing energy, proton transfer dominates increasingly.

(5) The isotopic mixing can be described qualitatively by a mechanism which involves a sequence of proton (deuteron) exchanges and features the two intermediates



(6) In the temperature range 80–300 K, no isotope effects can be identified within the precision of the data. At collision energies of 0.15 eV

and above, where the reaction consists of the "direct" transfer of protons and hydrogen atoms, a slight, normal isotope effect (not exceeding 10%) favors  $H^+$  transfer over  $D^+$  and  $H$  transfer over  $D$ .

(7) The failure to observe electron transfer as a competing channel is attributed to the reactants not being internally excited. This result excludes, for reaction (1) at thermal energy, mechanisms that invoke electron transfer as a component step.

(8) Isotopic mixing for the reactant pair  $CH_4^+ + CD_4$  [reaction (2)] may be compared with that for  $CH_5^+ + CD_4$  [reaction (6)]... and  $CD_4^+ + CH_4$  with its analog  $CD_5^+ + CH_4$ . For reaction (2) at 80 K, there is complete mixing; for reaction (6), there is not [16]. For (6), the incomplete mixing derives from a shorter complex lifetime; even though the reaction is effectively thermoneutral, the complex is less tightly bound (7 kcal mol<sup>-1</sup>). Additionally for (6), the product distribution is far from being statistical at 80 K; it is determined by zero-point energy effects for an effectively thermoneutral reaction.

(9) The reaction  $CH_4^+ + CH_4$  serves as a prototype for the general reaction type  $X^+ + Y$  where the reactant  $Y$  is a filled-shell species and the reactant  $X^+$  has one less electron than a filled shell. Where  $X = Y$ , as in the system examined here ( $X = Y = CH_4$ ), three mechanisms are possible for one channel—complex formation, proton transfer and hydrogen-atom transfer. Where  $X \neq Y$ , two channels are, in principle, possible (proton and hydrogen-atom transfer) with two mechanisms for each, complex formation and direct particle transfer [39]. Various techniques can be used to study these processes—beam [18] crossed-beam [7,39], ICR [12,40], photoionization [37,41], SIFT and photoionization of van der Waals dimers [43]. This is currently an area of active research.

(10) The broad features of the mechanism of the reaction  $CH_4^+ + CH_4 = CH_5^+ + CH_3$  and its energy dependence are now well understood. Its kinetic interest is that the mechanism consists of three channels which compete down to thermal energy and show a dramatic temperature dependence. Aspects that still await explanation include (a) the energy/temperature dependence of the rate constant and (b) the non-statistical product distribution of the common intermediate, shown by deuterium labeling.

(11) The present study emphasizes that differences are to be expected in the study of mechanism (a) under single-collision conditions, and (b) under multiple-collision conditions. In the former any internal energy of the reactants will not be removed; in the latter it generally will. Crossed-beam studies at the very lowest collision energies can only reveal the thermal mechanism if the reactant ions are not excited. In satisfying this requirement, the present study differs from all previous investigations of reaction (1).

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