DEUTERATED METHYL CATION REACTIONS WITH ATOMIC OXYGEN

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The rate constants for the reactions between $CD_nH_{1-n}^+$ and O have been measured and found to be fast, independent of isotope. The branching ratio for these reactions has been found to be statistical. Since decay of metastable triplet CD_2HO^+ shows a large isotope effect, it was thought that the present reactions might also do so. The fact that the present experiments do not show this large isotope effect is ascribed to the large exothermicity of reaction $CH_3^+ + O \rightarrow HCO^+ + H_2$, which opens several alternative pathways not involving metastable triplet CD_2HO^+ as the intermediate.

1. Introduction

The reaction

$$CH_3^+ + O \rightarrow HCO^+ + H_2 \tag{1}$$

was studied by Fehsenfeld [1] because of its astrophysical interest. The rate constant at room temperature was determined to be 4.4×10^{-10} cm³ s⁻¹. The structure of the intermediate in this reaction is of interest, i.e. whether it is H₃CO⁺ or the chemically distinct species H₂COH⁺.

Burgers and Holmes [2] have found a large isotope effect in the decay of triplet D_2HCO^+ ions, which are metastable and decay on the microsecond time scale. Metastable triplet H_3CO^+ ions are not produced by dissociative ionization of neutrals, e.g. CH_3ONO or CH_3OCH_3 , but instead the more stable singlet H_2COH^+ ions are produced. The singlet H_3CO^+ ion is not stable but converts to the singlet H_2COH^+ with no potential minimum or maximum on the singlet potential surface. Burgers and Holmes [2] made D_3CO^+ by first producing the negative ion D_3CO^- (or isotopic variants thereof) from deuterated methanol and then using collision-induced charge reversal to produce a small fractional conversion to triplet D_3CO^+ . They were able to establish the existence of a common transition state for the metastable triplet decomposition,

$$D_3CO^+ \rightarrow DCO^+ + D_2, \qquad (2)$$

and for D_2COD^+ produced from dissociative ionization in deuterated methanol. In addition, they demonstrated that the transition state has D_2COD^+ geometry, i.e. its formation from D_3CO^+ involves 1, 2 D shift from C to O. The D_2 elimination involves the D from the O atom and one D atom from the C atom.

The very large isotope effect reported by Burgers and Holmes [2] for decay of the metastable triplet,

$$^{3}[D_{2}HCO]^{+} \rightarrow DCO^{+} + HD$$
, (3a)

$$\rightarrow \text{HCO}^+ + \text{D}_2, \qquad (3b)$$

 $k_{3a}/k_{3b} = 100/(3\pm 2)$, suggested that tunneling through a potential barrier might be occurring in the

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1, 2 H (or 1, 2 D) atom shift, which would favor H atom transfer. Large barriers for 1, 2 H atom transfers are well established theoretically and have been calculated to be in the range of 20-63 kcal mol⁻¹ [3,4].

The present investigation was undertaken to see if the large isotope effect observed by Burgers and Holmes [2] in the triplet D_2HCO^+ unimolecular decay would carry over into the $CH_nD_{3-n}^++O$ reactions, e.g.

$$CH_2D^+ + O \rightarrow HCO^+ + HD, \qquad (4a)$$

$$\rightarrow DCO^+ + H_2 . \tag{4b}$$

These reactions might occur via triplet $H_n D_{3-n} CO^+$, which could be produced in singlet CH_3^+ collisions with $O(^{3}P)$ atoms.

2. Experimental

The measurements were made in a selected ion flow tube previously described [5]. Only details pertaining to the present experiment are discussed. The $CH_n D_{3-n}^+$ ions were made by electron impact on CH_4 , CH_2D_2 , and CD_4 . Oxygen atoms were produced by discharging O_2 in He. The concentration of oxygen atoms was calibrated using the rate constant measured by Fehsenfeld [1] for the reaction of $CH_3^+ + O$. Thus only relative rate constants were measured here. The rate constant for the calibration reaction was measured several times before, during, and after the runs for the isotopic reactants. This rate constant was reproducible within 20%, indicating the accuracy with which we could measure the relative rate constants. The uncertainty in the branching ratios reflects the uncertainty in the individual points of the product determinations, with an additional uncertainty for the CH_2D^+ branching ratio due to the presence of a small impurity of CH_3^+ in the flow tube during the course of the CH_2D^+ experiments.

3. Results

It was found that the rate constants for CH_3^+ , CH_2D^+ , CHD_2^+ , and CD_3^+ reacting with O were the same within experimental error ($\pm 20\%$). As noted

above, the rate constant [1] is 4.4×10^{-10} cm³ s⁻¹. It was also found that the isotopic product ratios were statistical within experimental error, e.g. CD_2H^+ yielded $(70\pm10)\%$ DCO⁺, and CH_2D^+ yielded $(40\pm15)\%$ DCO⁺. A small CH₃⁺ impurity degraded the precision in the latter case.

4. Discussion

We have found that the overall rate constants for $CH_nD_{3-n}^+$ ions reacting with O atoms are independent of the extent of isotopic substitution and that the product isotope ratios are statistical within experimental uncertainty. Thus no marked isotopic dynamic constraints operate, in contrast to the metastable unimolecular decomposition of D₂HCO⁺. This is a result, presumably, of the large exothermicity [6,7], 122 kcal mol⁻¹, of reaction (1) which can affect the reaction in several ways. First, this exothermicity puts the $CH_3^+ + O$ reactant energy 60 kcal mol^{-1} above the energy of ${}^{3}[H_{3}CO]^{+}$ [2]. Hence the magnitudes of possible potential barriers, which might contribute to the metastability (long lifetime) of 3 [H₃CO]⁺, should be exceeded by the CH₃⁺ +O reactant energy.

Alternatively, the large exothermicity may enable an excited triplet state of H_2COH^+ to serve as the transition state. The ground singlet state of H_2COH^+ (protonated formaldehyde) lies 152 kcal mol⁻¹ below the energy of the reactants [2]. Therefore production of a triplet state is energetically plausible.

Another possibility is that the reaction proceeds in steps. In the first step, an intermediate is formed which then decomposes into $H_2CO^+ + H$. This process is exothermic [6,7] by 46 kcal mol⁻¹. The H_2CO^+ may then have enough internal energy to overcome a barrier, allowing it to decay into $HCO^+ + H$. This results in the overall reaction

 $CH_3^+ + O \rightarrow HCO^+ + 2H, \qquad (5)$

which is exothermic [6,7] by 18 kcal mol⁻¹. In the former possibilities, the singlet CH₃⁺ ion and the O(³P) atom presumably produce singlet HCO⁺, i.e. protonated singlet CO, and singlet H₂ molecules. Even though the exothermicity of the reaction of CH₃⁺ with O is sufficient (by 18 kcal mol⁻¹) to produce two H atoms, the exothermicity is far too low to access the lowest H_2 triplet state vertically. The lowest triplet state is strongly repulsive, dissociating into two H atoms. The neutral product identity is unknown experimentally, but dissociation of H_2 could occur only via singlet H_2 , so that a spin-nonconserving reaction appears necessary in that case.

The last mechanism, i.e., reaction (5), enables the reaction to proceed via a path that permits spin conservation. The triplet plus singlet reactants would first produce $H_2CO^+ + H$, which are both doublets. The doublet H_2CO^+ would then decompose into a singlet (HCO⁺) and a doublet (H).

It is not necessary that the reaction proceeds in a manner that allows for spin conservation. There are other fast thermal energy ion-molecule reactions known to violate spin conservation. Examples include the reaction

$$O^{+}({}^{4}S) + CO_{2}({}^{1}\Sigma) \rightarrow O_{2}^{+}({}^{2}\Pi) + CO({}^{1}\Sigma),$$
 (6)

which occurs on every collision [8,9], a number of positive ion charge transfer reactions for which the rate constant exceeds the spin-conserving weighted collision rate constant [10], and a number of hydrocarbon ion reactions with $N(^4S)$ atoms [11].

In conclusion, the reaction of $CD_nH_{3-n}^++O$ proceeds rapidly, independent of isotopic composition, to form $H(D)CO^+$. The product isotopic distribution has been found to be statistical. We initially speculated that the branching ratio might be highly non-statistical, in accord with the experiments of

Burger and Holmes [2], who found a large isotope effect in the decay of CD_2HO^+ , possibly due to tunneling. The fact that the present experiments do not show this large isotope effect may be due to the large exothermicity of reaction (1), which opens several alternative pathways to the tunneling mechanism.

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