KINETIC STUDY OF THE SYSTEM NH_2^+ + CH_3OH at 0.046 eV

J. Barassin, R. Thomas and A. Barassin
Laboratoire de Chimionisation, U.E.R. Sciences, Université d'Orléans.
45046 ORLEANS Cedex France.
Centre de Recherches en Physique de l'Environnement Terrestre et Planétaire
(C.R.P.E.) Avenue de la Recherche Scientifique, 45045 ORLEANS Cedex.

ABSTRACT

The kinetics of the reaction NH_2^+ + CH_3OH have been studied with a drift tube mass spectrometer apparatus. A reaction scheme is proposed and the rate coefficient is determined for each step of the mechanism at 0.046 eV(Teff ≈ 350 K) with 0.5 torr of helium as buffer gas.

I. INTRODUCTION

We present a brief summary of the results obtained in the study of the NH_2^+ + CH_3OH reaction.

The experimental details and extensive tabulations of the rate constants over a large temperature range (350 < Teff < 5000 K) will appear in another article |1|, so this paper contains only the essential features which are necessary to support the comments on some of the particular reactions of the reaction scheme which involves a large number of binary and ternary steps occuring in parallel.

2. RESULTS

Experiments were performed in a drift tube mass spectrometer apparatus |2| in the energy range 0.046–0.7 eV with 0.5 torr of helium as buffer gas. Mass spectra of ions of m/e < IOO^+ involved in the reaction, have been recorded as a function of methanol concentration. Ions were detected at m/e = $I6^+$, $I7^+$, $I8^+$, 33^+, 47^+, 65^+, 79^+ and 97^+. The results obtained at Teff = 350 K are reported in Fig.I.

Figure 2 schematically illustrates the conclusions drawn from the analysis of the mass spectra. Based upon this scheme, the profiles of the different ions were computed using the rate coefficients of Table I. The agreement between experiment and calculation (Fig.I) supports the proposed mechanism.

3. COMMENTS ON THE FORMATION OF NH_4^+

We have found, as have Adams and al. |3|, that NH_3^+ and $CH_3OH_2^+$ are the products of two binary reactions between NH_2^+ and CH_3OH ($k_{overall} = 3.0\ IO^{-9}\ cm^3\ s^{-I}$. at 350 K; branching ratio NH_3^+: $CH_3OH_2^+$ ≈ I3:87); moreover NH_4^+ arises in our model (and for a large part) from a transfer of H_2 on NH_2^+. This step is thought to be very exothermic (5.8 ev) and consequently needs an efficient

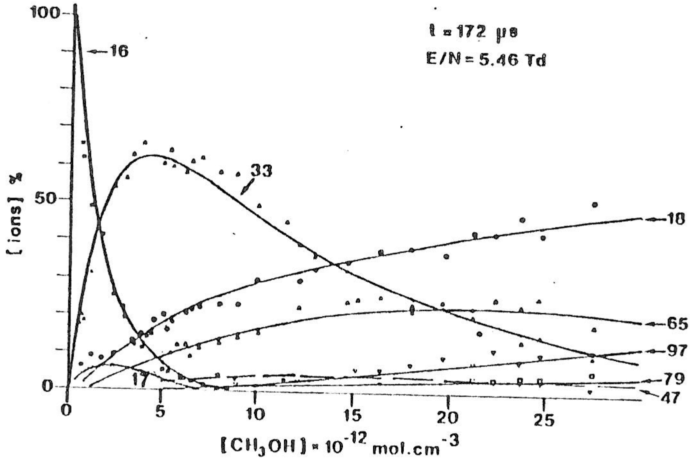

Fig.1: Percentage ion abundance vs methanol concentration. The points are experimental results and the lines are computed fits.

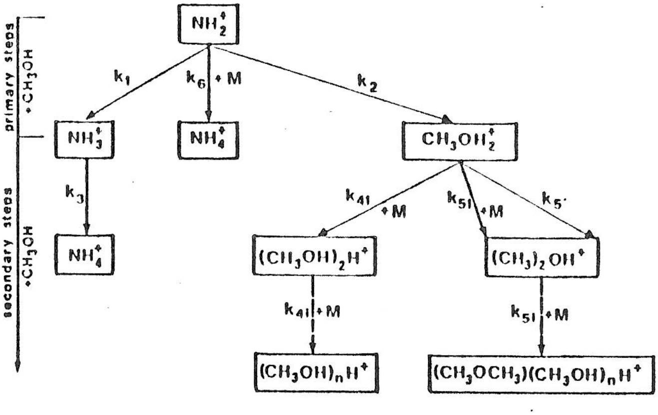

Fig.2: Reaction scheme - The third body M is methanol or helium.

third body to remove energy and stabilize the ion.

Thus the reaction (6) of Fig.I:

$$NH_2^+ + CH_3OH \xrightarrow{M} NH_4^+ + \text{neutral} \qquad (6)$$

is found to be a termolecular reaction.

Surprisingly the molecules of the buffer gas (He) play a minor role in this collisonal process while the reactant CH_3OH whose concentration in helium is about IO^3 ppm plays the major part.

To account for the methanol concentration dependence of $|NH_4^+|$, we found that the rate of formation of this ion via the reaction (6) where $M = CH_3OH$ is unsually fast: $k_6 = 7\ IO^{-23}\ cm^6\ s^{-I}$ at 350 K.

4. COMMENTS ON THE REACTION BETWEEN $CH_3OH_2^+$ AND CH_3OH.

Clustering and water elimination reactions have been observed and reported in earlier works |4-5| and the energetics of these reactions were discussed. Their kinetics were studied to a lesser extent and the order of the two steps was not clearly elucidated.

The mean overall rate constant of the reaction

$$CH_3OH_2^+ + CH_3OH \rightarrow \text{Products}$$

was deduced from the profile of the ion $CH_3OH_2^+$; at 350 K, $k = 3.IO^{-IO}\ cm^3\ s^{-I}$.

The branching ratio $R = \dfrac{|(CH_3OH)_2H^+|}{|(CH_3OH)_2H^+| + |(CH_3OCH_3)H^+|}$ was found to be dependent upon the methanol pressure; it increases with $|CH_3OH|$, then reaches a plateau ($R_\infty = 0.83$ at 350 K). This effect is more marked when the temperature increases.

A similar effect was encountered by MIASEK and al. |6| in the study of the reaction $C_3H_5^+ + C_2H_4$. The ion products formed were $C_5H_7^+$ and $C_5H_9^+$ and to rationalize the pressure dependence of the ion abundances in ethylene these authors proposed a mechanism including both a unimolecular and a collision-induced route to the formation of $C_5H_7^+$ product.

An anologous mechanism was envisaged in our study. It includes a competition between a binary and a ternary route to the dehydration reaction while the association reaction is only collisional:

$$CH_3OH_2^+ + CH_3OH \xrightarrow{M} (CH_3OH)_2H^+ \qquad (4_1)$$

$$\xrightarrow{M} (CH_3)_2OH^+ + H_2O \qquad (5_1)$$

$$\rightarrow (CH_3)_2OH^+ + H_2O \qquad (5')$$

The collisional reactions (4_1) and (5_1) must involve the two different collision partners $M = He$ and $M' = CH_3OH$ to obtain an equation consistent with the experimental curve of R vs $|CH_3OH|$.

The computed profiles of the different ions 33^+, 47^+, 65^+ are not very sensitive to the relative stabilization efficiencies attributed to He and CH_3OH.

Thus for the formation of $(CH_3OH)_2H^+$, a mean rate constant $k_{4_1} = 2.4\ 10^{-10}\ cm^3\ s^{-1}$ leads to a rather good computed profile.

If we split up k_{4_1} into its two terms (M = He and M' = CH_3OH):

$$k_{4_1} = k_{4_1}^{(M)}\ |He| + k_{4_1}^{(M')}\ |CH_3OH|$$

We can obtain the limiting values of $k_{4_1}^{(M)}$ and $k_{4_1}^{(M')}$:

$$k_{4_1}^{(M)} < \frac{2.4\ 10^{-10}}{|He|}\ ;\ k_{4_1}^{(M)} < 1.5\ 10^{-26}\ cm^6\ s^{-1}$$

$$k_{4_1}^{(M')} < \frac{2.4\ 10^{-10}}{|CH_3OH|}\ ;\ k_{4_1}^{(M)} < 1.6\ 10^{-23}\ cm^6\ s^{-1}$$

On the other hand the R function is very dependent on the relative values given to $k^{(M\ )}$ and $k^{(M')}$ but in the region where R shows the greatest variation, the concentrations of 47^+ and 65^+ are low ($47^+ < 2\%$; $65^+ < 6\%$), so the experimental ratio is rather imprecise. Nevertheless a great number of measurements were carried out and the observed variation of R is thought not to be an experimental artefact.

In table I we have shown the mean values of the rate coefficients expressed as second order, the limiting values of the third order rate constants and values leading to a good representation of R and of the ionic concentrations.

The plausibility of the reaction scheme is supported by the results of calculation since we can find a set of parameters which leads to a good agreement with experimental observations. The values obtained for the rate coefficients involving He as third body are in the usual range (10^{-26} - $10^{-27} cm^6 s^{-1}$) and some examples of termolecular reactions involving large molecules as third body and having rate coefficients in the 10^{-24} - 10^{-25} range were previously reported. This is the case of the reaction $C_3H_5^+$ - C_2H_4 studied by MIASEK |6| where the third body is C_2H_4 itself.

Nevertheless a doubt may remain because this representation leads to a stabilization efficiency of methanol, relative to that of He, of $\simeq 10^2$ while a ratio of $\simeq 10$ was expected.

5. A POSSIBLE REACTION PATH FOR THE SYNTHESIS OF DIMETHYL ETHER IN INTERSTELLAR CLOUDS.

The formation of interstellar dimethyl ether via radiative association reactions has been investigated |7| .

The ionic precursor $CH_3OH^+CH_3$ could be formed by reactions involving CH_3^+ or CH_5^+ and methanol or aldehyde.

The binary reaction:

$$CH_3OH_2^+ + CH_3OH \rightarrow (CH_3)_2OH^+ + H_2O \qquad (5')$$

studied in this work has a rate coefficient of about $\approx 1.10^{-11}$ $cm^3\ s^{-1}$ which is not very temperature dependent.

As methanol is a relatively abundant neutral interstellar molecule and as there are many fast proton transfer reactions leading to $CH_3OH_2^+$, reaction (5') could contribute in some degree to the formation of interstellar dimethyl ether.

Table 1

Binary Reactions		Ternary Reactions					
Reaction	k ($cm^3 . s^{-1}$)	Reaction	k($cm^3\ s^{-1}$) mean value $k^{(M)}\|M\|+k^{(M')}\|M'\|$	k($cm^6\ s^{-1}$)			
				M = He		M' = CH_3OH	
				limit	good fit	limit	good fit
1	$3.0\ 10^{-9} \times$ 0.17	4_1	$3.0\ 10^{-10} \times$ 0.83	$<1.5\ 10^{-26}$	$1.3\ 10^{-26}$	$<1.6\ 10^{-23}$	2.10^{-24}
2	0.83	5_1	0.17	$<3.\ 10^{-27}$	$2.5\ 10^{-27}$	$<3\ .10^{-24}$	4.10^{-25}
3	$2.2\ 10^{-9}$	4_2	$1.5\ 10^{-10}$				
5'	$\approx 1.10^{-11}$	5_2	$3\ .10^{-10}$				
		6					7.10^{-23}

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