Volume 54, number 3 CHEMICAL PHYSICS LETTERS 15 March 1978

REACTIONS OF CH_n^+ IONS WITH MOLECULES AT 300 K

N.G. ADAMS and D. SMITH

Department of Space Research, University of Birmingham,
Birmingham B15 2TT, UK

Received 7 October 1977

The rate coefficients and product ion distributions have been obtained for the reactions of the CH_n^+ ions ($n = 0$ to 4) with COS, H_2S, H_2CO, CH_3OH and CH_3NH_2 in a SIFT at 300 K. The reactions are generally fast binary with multiple products except for CH_3^+ for which fast ternary association channels are also observed in parallel with the binary channels.

1. Introduction

As part of a comprehensive study of ion–molecule reactions important in the synthesis of molecules in interstellar clouds [1] and in planetary atmospheres [2,3] we have recently determined the rate coefficients and product ion distributions for the reactions of the CH_n^+ ions ($n = 0$ to 4) with the relatively simple molecules H_2, N_2, O_2, CO, CO_2, H_2O, CH_4 and NH_3 [4–6]. Many other molecules have been observed in interstellar clouds [1] and thus it is pertinent to study the reactions of likely and observed interstellar ions with these molecules. To this end, we report here the rate coefficients and product ion distributions for the reactions of CH_n^+ with COS, H_2S, H_2CO, CH_3OH and CH_3NH_2 at 300 K determined in our SIFT (selected ion flow tube) apparatus [7,8]. This study has also enabled us to more clearly establish trends in the reactivity of the various CH_n^+ ions with molecules and in two cases a comparison has been made between the reactions of oxygen–sulphur analogues, viz. CO_2 and COS and H_2O and H_2S. Such comparisons are of fundamental interest since they give an insight into reaction mechanisms and into the parameters governing these mechanisms.

2. Experimental

The SIFT technique has previously been described in detail [7] and the method of determining product ion distributions reported [8]. The CH_n^+ ions were generated in an electron impact ion source containing CH_4, mass selected using a quadrupole mass filter and injected through a small orifice into flowing helium. The ions were injected at low energy (≈ 6 eV) essentially eliminating collisional fragmentation on the helium and subsequently thermalise in collision and convect down the flow tube. At a point downstream a controlled and monitored flow of reactant gas was added and the reaction observed using a conventional mass filter/ion counting equipment mounted at the downstream end of the flow tube.

The reactant gas CH_3OH was added as an unsaturated mixture with He ($\approx 4\%$ CH_3OH) and monomeric H_2CO gas was produced by thermal decomposition of paraformaldehyde. Rate coefficients were obtained from the exponential decay in the primary ion count rate with reactant gas flow rate. Such a decay is illustrated in fig. 1a for the reaction of CH^+ with H_2CO. Also shown are the variations in the count rates for the primary product ions CH_3^+, HCO^+, H_3CO^+ and $H_2C_2O^+$. This reaction is one of the most complex we have encountered since the product ion CH_3^+ reacts with H_2CO to produce HCO^+ (see also table 1) which itself reacts with H_2CO to produce the terminating ion H_3CO^+ [9]. Only $H_2C_2O^+$ is not involved in further reaction. Thus the product distribution for the primary reaction cannot be obtained directly from fig. 1. This distribution, unaffected by secondary reactions can

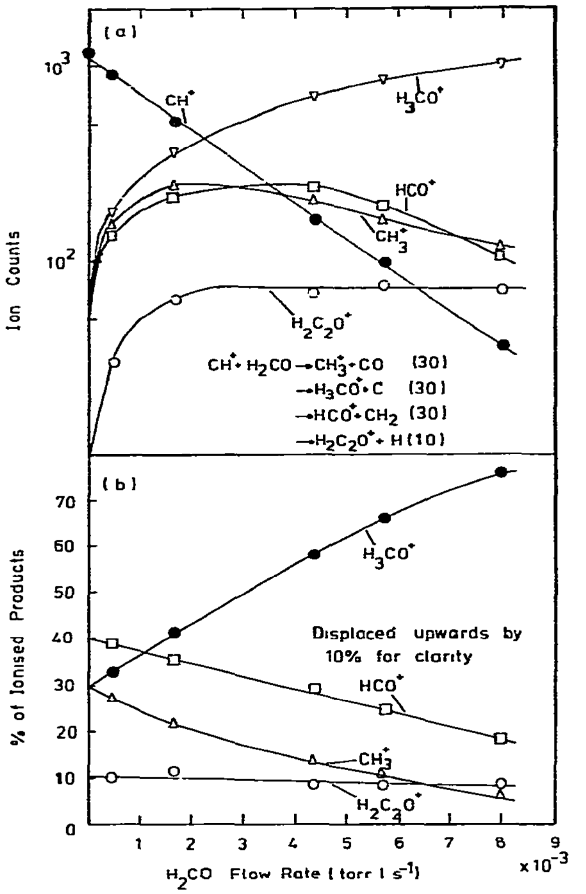

Fig. 1. Variation of (a) the primary ion, CH^+, and product ion counts (10 s sampling period) and (b) the percentages of the ionized products as a function of the H_2CO flow rate for the $CH^+ + H_2CO$ reaction.

readily be obtained by adopting the procedure of plotting the percentages of the various product ions as a function of reactant gas flow rate and extrapolating to zero flow as is illustrated in fig. 1b. Account has been taken of mass discrimination in the detection system by the method described earlier [8].

3. Results

The binary rate coefficients (cm^3 s^{-1}) and percentage product ion distributions (bracketed) for all of the reactions studied are given in table 1. In the case of the CH_3^+ reactions with H_2CO, CH_3OH and CH_3NH_2, in addition to the binary reaction channels, an association channel is observed. The significance of these association channels and their dependence on gas temperature is considered elsewhere [10]. The rate coefficients quoted for the CH_3^+ reactions are for the binary channels only. The rate coefficients are considered to be accurate to ± 20% for COS, H_2S, H_2CO and CH_3NH_2 and ± 30% for CH_3OH.

3.1. COS

The reactions with COS are relatively simple, proceeding by charge transfer (where this is energetically possible), by proton transfer and by S atom abstraction, all of which retain the strong CO bond. The rate coefficients are close to the values predicted by the ADO theory [11].

It is interesting to compare the data for COS with the corresponding data for the analogous CO_2 molecule which we have obtained previously [4]. This data is also given in table 1. It can be seen that for every binary reaction channel observed with CO_2, the analogous channel is observed for COS. Conversely channels observed for COS are not always detected in the CO_2 reactions; however in these latter cases the analogous CO_2 channel is usually endoergic. Also, as for the COS reactions, those with CO_2 proceed at close to the gas kinetic rate (with the exception of CH_3^+).

3.2. H_2S

For these reactions, charge transfer and proton transfer channels are evident and rate coefficients are again close to the ADO values. As in the COS reactions, HCS^+ and H_3CS^+ are common product ions. Also included in table 1 are the corresponding data for H_2O reactions which have been reported previously (although detailed product distributions were not obtained) [4]. Again it can be seen that there are distinct similarities between the two sets of reactions. However in the case of the CH_4^+/H_2O reaction the apparently exoergic direct charge transfer channel is not observed. Charge transfer reactions when exoergic usually proceed rapidly, a feature clearly illustrated by our accumulated data for CH_4^+ reactions given in table 2 which suggests that the Franck–Condon factors may be unfavourable for ionization of H_2O to states resonant with the CH_4 ionization potential. Calculation of the ergicities for

Table 1
Rate coefficients ($cm^3\ s^{-1}$) and percentage product ion distributions (bracketed) for the reactions of CH_n^+ (n = 0 to 4) with several molecules at 300 K. Rate coefficients are expressed as for example 2.0(−9) to represent $2.0 \times 10^{-9}\ cm^3\ s^{-1}$

	C^+	CH^+	CH_2^+	CH_3^+	CH_4^+
COS	$CS^+ + CO$ (80) $COS^+ + C$ (20) 2.0(−9)	$HCS^+ + CO$ (55) $HCOS^+ + C$ (45) 1.9(−9)	$HCS^+ + HCO$ (60) $H_2CS^+ + CO$ (40) 1.8(−9)	$H_3CS^+ + CO$ (100) 1.2(−9)	$HCOS^+ + CH_3$ (70) $COS^+ + CH_4$ (30) 1.4(−9)
H_2S	$HCS^+ + H$ (75) $H_2S^+ + C$ (25) 1.7(−9)	$HCS^+ + H_2$ (70) $H_3S^+ + C$ (30) 2.1(−9)	$H_3CS^+ + H$ (80) $HCS^+ + H_2 + H$ (10) $H_3S^+ + CH$ (10) 2.3(−9)	$H_3CS^+ + H_2$ (100) 1.4(−9)	$H_3S^+ + CH_3$ (55) $H_2S^+ + CH_4$ (45) 2.1(−9)
H_2CO	$CH_2^+ + CO$ (60) $H_2CO^+ + C$ (20) $HCO^+ + CH$ (20) 3.9(−9)	$CH_3^+ + CO$ (30) $H_3CO^+ + C$ (30) $HCO^+ + CH_2$ (30) $H_2C_2O^+ + H$ (10) 3.2(−9)	$HCO^+ + CH_3$ (85) $H_3C_2O^+ + H$ (10) $H_2C_2O^+ + H_2$ (5) 3.3(−9)	$HCO^+ + CH_4$ (100) $CH_3^+ \cdot H_2CO + He$ a) 1.6(−9)	$H_3CO^+ + CH_3$ (55) $H_2CO^+ + CH_4$ (45) 3.6(−9)
CH_3OH	$CH_3^+ + HCO$ (80) $H_3CO^+ + CH$ (20) 2.6(−9)	$CH_3^+ + H_2CO$ (50) $CH_3OH_2^+ + C$ (40) $H_3CO^+ + CH_2$ (10) 2.9(−9)	$CH_3OH_2^+ + CH$ (50) $H_3CO^+ + CH_3$ (50) 2.6(−9)	$H_3CO^+ + CH_4$ (100) $CH_3^+ \cdot CH_3OH + He$ a) 2.3(−9)	$CH_3OH^+ + CH_4$ (60) $CH_3OH_2^+ + CH_3$ (40) 3.0(−9)
CH_3NH_2	$CH_3NH_2^+ + C$ (65) $CH_2NH_2^+ + CH$ (35) 2.2(−9)	$CH_2NH_2^+ + CH_2$ (50) $CH_3NH_3^+ + C$ (40) $CH_3NH_2^+ + CH$ (10) 2.2(−9)	$CH_2NH_2^+ + CH_3$ (55) $CH_3NH_2^+ + CH_2$ (35) $CH_3NH_3^+ + CH$ (10) 2.1(−9)	$CH_3NH_2^+ + CH_3$ (55) $CH_2NH_2^+ + CH_4$ (45) $CH_3^+ \cdot CH_3NH_2 + He$ a) 2.2(−9)	$CH_3NH_2^+ + CH_4$ (60) $CH_2NH_2^+ + CH_4 + H$ (40) 2.2(−9)
CO_2 b)	$CO^+ + CO$ (100) 1.1(−9)	$HCO^+ + CO$ (100) 1.6(−9)	$H_2CO^+ + CO$ (100) 1.6(−9)	$CH_3^+ \cdot CO_2 + He$ a) ternary	$HCO_2^+ + CH_3$ (100) 1.2(−9)
H_2O b)	$HCO^+ + H$ (100) 2.5(−9)	$\underline{HCO^+ + H_2}$ $H_2CO^+ + H$ $H_3O^+ + C$ 2.9(−9)	$\underline{H_3CO^+ + H}$ $H_3O^+ + CH$ 2.9(−9)	$CH_3^+ \cdot H_2O + He$ a) ternary	$H_3O^+ + CH_3$ (100) 2.6(−9)

a) Ternary association product observed. The rate coefficient quoted is that for the binary channels only.
b) Previous data from ref. [4] and included for comparison with the COS and H_2S reactions. For the H_2O reactions a detailed product distribution was not obtained. The major product is underlined.

the CH_2^+/H_2S and CH_2^+/H_2O proton transfer reactions using the available thermochemical data [12] apparently indicates these channels to be endoergic, clearly not possible since proton transfer is a very significant channel in these fast gas kinetic reactions. This then implies that the literature value of the CH proton affinity (7.6 eV) is too large by at least four tenths of an electron volt.

The reactions of the CH_n^+ ions with H_2S have been studied previously by Huntress and co-workers [13, 14]. The rate coefficients and product ion distributions for the C^+ reaction (2.0(−9) $cm^3\ s^{-1}$, HCS^+ (72%), H_2S^+ (28%) [13]) and for the CH_4^+ reaction (1.3(−9) $cm^3\ s^{-1}$, H_3S^+ (55%), H_2S^+ (42%), CH_5^+ (6%) [14]) are similar to the present values except that we do not observe the minor product CH_5^+. For the CH^+, CH_2^+ and CH_3^+ reactions the agreement is not good, the ICR rate coefficients being consistently lower by about a factor of 3. Also the very significant proton transfer to H_2S from CH^+ and CH_2^+ that we observe was not observed in the ICR experiment. However both CH_4 and H_2S were simultaneously present in the ICR cell which must complicate the identification of the products of a given reaction.

Table 2
Percentage product ion distributions and ergicities for the reactions of CH_4^+ with a series of molecules at 300 K. Exoergicities are denoted by the + sign.

Reactant molecule	Percentages of products and ergicities (eV)		
	charge transfer	proton transfer	other channels
H_2 a)	−2.7	−1.1	100%, CH_5^+ + H
N_2 a)	−2.9	−0.4	–
O_2 a)	100%, +0.6	−1.1	–
CO a)	−1.3	100%, +0.7	–
CO_2 a)	−1.1	100%, ≈0	–
COS	30%, +1.5	70%, ≈+1.4	–
H_2O a)	+0.09	100%, +1.7	–
H_2S	45%, +2.3	55%, +1.6	–
NH_3 b)	60%, +2.5	40%, +3.6	–
CH_4 c)	resonant	100%, +0.04	–
H_2CO	45%, +1.8	55%, +1.8	–
CH_3OH	60%, +1.9	40%, +2.5	–
CH_3NH_2	60%, +3.7	+4.0	40%, $CH_2NH_2^+$ + CH_4 + H

Previous data a) ref. [4], b) ref. [5], c) ref. [6].

3.3. H_2CO

The C^+, CH^+ and CH_2^+ reactions are complex with many product channels requiring considerable bond rearrangement. The common product ion HCO^+ cannot result from direct charge or proton transfer to H_2CO followed by unimolecular decomposition of $(H_2CO^+)^*$ or $(H_3CO^+)^*$ respectively since this is energetically unfavourable. This reaction must proceed via an excited association complex. Such a close interaction is likely to produce condensation products with carbon–carbon bonds. That the product ions $H_2C_2O^+$ and $H_3C_2O^+$ are observed supports this deduction. CH_3^+ is also more reactive with H_2CO than with most molecules, exhibiting both fast binary and ternary channels. Consistent with its general behaviour, CH_4^+ reacts by charge and proton transfer (see table 1 and section 4).

The C^+ and CH_3^+ reactions have previously been studied by Anicich et al. [13] and by Huntress [12] respectively. The agreement is good for the C^+ reaction, an ICR rate coefficient of 4.4 (–9) cm^3 s^{-1} and a product distribution H_2CO^+ (31%), CH_2^+ (48%) and HCO^+ (21%) being obtained. In this ICR experiment the product distribution was determined under conditions for which 20% of the primary C^+ ions had reacted. Since the CH_2^+ product rapidly reacts further with H_2CO producing mainly HCO^+ (table 1) and since HCO^+ and H_2CO^+ also react rapidly with H_2CO [9], the ICR product distribution is expected to be somewhat distorted. This could account for the small discrepancy between the product ion distributions obtained in the two experiments. For the CH_3^+ reaction only the binary channel is observed in the low pressure ICR experiment. Detection of the collisionally stabilized association product is not expected at such low pressure (≈ 10^{-6} torr).

3.4. CH_3OH

Reactions of the CH_n^+ ions with this molecule produce the ions CH_3^+, H_3CO^+ and $CH_3OH_2^+$ which are amongst the most stable ions we have observed. H_3CO^+ is regularly observed in H_2CO and CH_3OH chemistry. An association product is again observed in the CH_3^+ reaction in parallel with a fast binary channel and as usual CH_4^+ reacts by charge and proton transfer. As part of a systematic study of C^+ reactions, Anicich et al. [13] have obtained a rate coefficient of 4.1 (–9) cm^3 s^{-1} for the reaction with CH_3OH significantly greater than the present value and observe the product ions CH_3OH^+ (33%) and HCO^+ (8%) in addition to the CH_3^+ and H_3CO^+ products which we observe. However, as discussed earlier the product distribution may be affected by secondary reactions. As in the case of the CH_3^+ reaction with H_2CO, Huntress [12] observes only the binary product in the CH_3OH reaction with a rate coefficient of 1.3(−9) $cm^3\ s^{-1}$.

3.5. CH_3NH_2

These reactions are relatively straightforward. Since CH_3NH_2 has a small ionization potential, direct charge transfer is energetically possible in all cases and is always observed to occur rapidly. Proton transfer to produce $CH_3NH_3^+$, when it occurs, is a minor channel although $CH_3NH_3^+$ is a common product of secondary reactions and is invariably the stable terminating ion. For this particular ion because of these secondary reactions, a very minor proton transfer channel producing $CH_3NH_3^+$ would not be discernable and cannot therefore be ruled out. $CH_2NH_2^+$ is an important product probably resulting from partial unimolecular decomposition of $CH_3NH_2^+$ and $CH_3NH_3^+$ produced by very exoergic direct charge transfer and proton transfer. That $CH_3NH_3^+$ is not observed in the CH_4^+ reaction is surprising since proton transfer from CH_4^+ is usually rapid when energetically possible. In this case it probably occurs, but the large exoergicity of the reaction ($\approx$ 4 eV) is sufficient to fragment the $(CH_3NH_3^+)^*$ thus removing it from the product ion spectrum.

Again Anicich et al. have studied the C^+ reaction obtaining a rate coefficient of 4.2(−9) $cm^3\ s^{-1}$ (a factor of $\approx$ 1.5 greater than the present value) and in addition to $CH_3NH_2^+$ and $CH_2NH_2^+$ they observe two minor products H_2CN^+ (6%) and CH_3^+ (3%) not evident in the present experiments.

4. Summary and conclusions

This study of the reactions of the CH_n^+ ions with triatomic and polyatomic molecules adds to the considerable body of data now available for the reactions of these ions. The reactions are generally fast binary being approximately gas kinetic, often with multiple products. In the present measurements the structure of the product ions is usually obvious, however for the CH^+ and CH_2^+ reactions with H_2CO the structures of the product ions $H_2C_2O^+$ and $H_3C_2O^+$ is not clear. Isotopic labelling may assist in the structural determination.

The CH_4^+ reactions are interesting and worthy of further comment. These reactions are listed in table 2 together with the product ion distributions and reaction energetics. In all of the reactions in this and our previous study [4] (with the exception of H_2O, a special case discussed in section 3), where charge transfer and/or proton transfer are exoergic they are rapid and when these occur no other reaction channel is evident. For the CH_3NH_2 reaction both direct charge transfer and dissociative charge transfer products are observed presumably because of the large exoergicity of the reaction (section 3). In all other cases where both charge transfer and proton transfer are observed, of these two processes the one favoured is that with the lower exoergicity, underlining the principle that to a large extent, thermochemical considerations control the mechanism by which reaction proceeds.

Acknowledgement

Our thanks are due to Professor A.P. Willmore for the provision of laboratory facilities, to the Science Research Council for financial support and to Derek Grief for helpful discussions.

References

[1] A. Dalgarno and J.H. Black, Rept. Progr. Phys. 39 (1976) 573.
[2] W.T. Huntress Jr., Advan. At. Mol. Phys. 10 (1974) 295.
[3] R S. Narcisi, in: Interactions between ions and molecules, ed. P. Ausloos (Plenum Press, New York, 1974) p. 635.
[4] D. Smith and N.G. Adams, Intern. J. Mass Spectrom. Ion Phys. 23 (1977) 123.
[5] D. Smith and N G. Adams, Chem. Phys. Letters 47 (1977) 145.
[6] N.G. Adams and D. Smith, Chem. Phys. Letters 47 (1977) 383.
[7] N.G. Adams and D. Smith, Intern. J. Mass Spectrom. Ion Phys. 21 (1976) 349.
[8] N.G. Adams and D. Smith, J. Phys. B 9 (1976) 1439.
[9] N.G. Adams, D. Smith and D. Grief, Intern. J. Mass Spectrom. Ion Phys., to be published.
[10] D. Smith and N.G. Adams, Chem. Phys. Letters 54 (1978) 535.
[11] T. Su and M.T. Bowers, Intern. J. Mass Spectrom. Ion Phys. 12 (1973) 347.
[12] W.T. Huntress Jr., Astrophys. J. Suppl. (1977), to be published.
[13] V.G. Anicich, W.T. Huntress Jr. and J.H. Futrell, Chem. Phys. Letters 40 (1976) 233.
[14] W.T. Huntress Jr., R.F. Pinizzotto and J.B. Laudenslager, J. Am. Chem. Soc. 95 (1973) 410.