Reaction of the Ground and Metastable Excited C^+ and N^+ Ions with C_2H_4, CH_3Cl and SO_2 Gases at 300 K

Asit B. Rakshit

Max-Planck-Institut für Chemie (Otto-Hahn-Institut), Mainz

Z. Naturforsch. **35a**, 1218—1222 (1980); received September 24, 1980

Rate coefficients and product distributions were measured for the reactions of C^+ and N^+ ions with C_2H_4, CH_3Cl and SO_2. The reactant ions were produced by electron impact using electron energies of 30 V and 100 V and then injected into a flow tube. The product ion distributions for these reactions depend significantly on the electron energy at which the reactant ions are formed. Reactions with CH_3Cl and SO_2 of ions formed at 100 V yield product ion distributions with a preference for fragmentation channels. In the case of C_2H_4, the simple charge transfer channel is favoured at high energy. Various new product ions have been identified from these studies, some of which having not been observed previously. Rate coefficients for these reactions at 30 V agree closely with the calculated values using Langevin and ADO theory.

Introduction

In recent publications [1—5], we have reported that ions generated by electron bombartment can contain substantial amounts of excited metastable ions. For such species, generally, rate coefficients and product ions are different from those obtained with ground state ions. Similar results have been obtained previously by Turner et al. [3] from beam experiments. In particular, the additional energy often opens up new reaction channels that are endoergic for the ground state ions. Physical quenching of the excited ion can also occur, and has been observed for $N_2^{+*} + N_2$, $NO^{+*} + NO$ and $O_2^{+*} + O_2$. These results were reported elsewhere [4]. Rate coefficients and product ions for reactions of both ground and metastable states of O^+, O_2^+ and NO^+ [1], C^+, N^+, S^+ and N_2^+ [2] and Cl^+ [5] with several neutral molecules have been reported. We have now extended this work by studying reactions of the ground and metastable C^+ and N^+ ions with C_2H_4, CH_3Cl and SO_2 molecules. The reactions were studied using the Aberystwyth selected ion flow tube (SIFT).

Experimental Results

The SIFT apparatus and the method of evaluating the product ion distributions have been reported in detail previously [1, 2]. The C^+ and N^+ ions were generated by electron bombartment at 30 eV and 100 eV using CO and NO as the source gases. At an electron energy of 30 V the reactant ions are assumed to be ground state ions. This assumption was tested in the following way: since the electron energy scale is not calibrated in absolute units, the reaction rates for $C^+ + O_2$ and $N^+ + O_2$ were measured. The rate coefficients and product ion distributions are well established for ground and excited ions. At 30 V (nominal) electron energy, the rate coefficient obtained for the reaction $C^+ + O_2$ was found to be 7.6(—10) and the product distribution $O^+ = 0.62$, $CO^+ = 0.38$ is in excellent agreement with the values determined by Adams and Smith [6] who obtained $k = 9.9(-10)$ and $O^+ = 0.62$, $CO^+ = 0.38$ using an electron energy of 70 eV in the ionizer. Similarly, for the reaction $N^+ + O_2$, the rate coefficient obtained here was $k = 6.5(-10)$ and the product ion distribution was $O_2^+ = 0.52$, $NO^+ = 0.40$ and $O^+ = 0.08$. The results are again in good agreement with the values $k = 6.1(-10)$ and $O_2^+ = 0.51$, $NO^+ = 0.43$ and $O^+ = 0.06$ reported by Smith et al. [7] who used 40 eV electron energy in the ionizer. McCrumb and Warneck [8] using a drift tube mass spectrometer reported $k = 7.5(-10)$ and $O_2^+ = 0.48$, $NO^+ = 43$ and $O^+ = 0.09$. These results support the above assumption that at 30 V electron energy the reactant ions are predominantly in the ground state. It should be pointed out that 30 eV energy is sufficient for the formation of excited C^+ and N^+ ions from CO and NO, respectively. The results of the tests thus show only that the fraction of excited ions present is small and can be neglected.

Reprint requests to Herrn Asit B. Rakshit, Max-Planck-Institut für Chemie, Saarstr. 23, D-6500 Mainz.

0340-4811 / 80 / 1100-1218 $ 01.00/0. — Please order a reprint rather than making your own copy.

In the previous work [2] the electron impact energy was 100 eV and the fraction of excited metastable ions was 10% for C^+ and 30% for N^+. These percentages were adopted also for the present study when the electron impact energy was 100 eV because the experimental conditions were similar. According to the assignment made previously, the predominant excited states present are ^4P for C^+ and ^1S for N^+ with excitation energies above the ground state of 5.3 and 4.1 eV, respectively.

After mass selection and injection into the flow tube the ions were thermalized by collisions with helium carrier gas before the neutral reactant was entered. The ions spent about 9 ms in the thermalization region and 12 ms in the reaction region. At the end of the reaction region both primary and product ions were sampled and detected by a mass spectrometer. Rate coefficients were determined from the decay of the primary ion counts with reactant flow. For C^+ ions, the same exponential decay was observed at both electron energies. A single exponential decay was found also using 30 V electron energy for N^+ ions. At 100 V electron energy the initial slope of the decay curve at low reactant flows is greater than that at high reactant flows indicating that one of the N^+ species present reacts faster than the others. The observation of two reaction rates do not preclude the existence of more than one metastable states of N^+ in the present experiments. These data have been treated in the manner described in [1, 2].

To illustrate the experimental observation, Figs. 1 and 2 shows the experimental data for the reaction of N^+ and C^+, respectively, with sulphur dioxide. The presence of excited N^+ ions at an electron energy of 100 V is made evident in Fig. 1B by comparison with low energy results in Figure 1A. Both the faster initial decay of the N^+ signal and the different product distribution in Fig. 1B indicate the different reaction behavior of excited N^+ ions. From Fig. 2B, we note that there is no initial curvature at small SO_2 flow, so that C^+ ground and

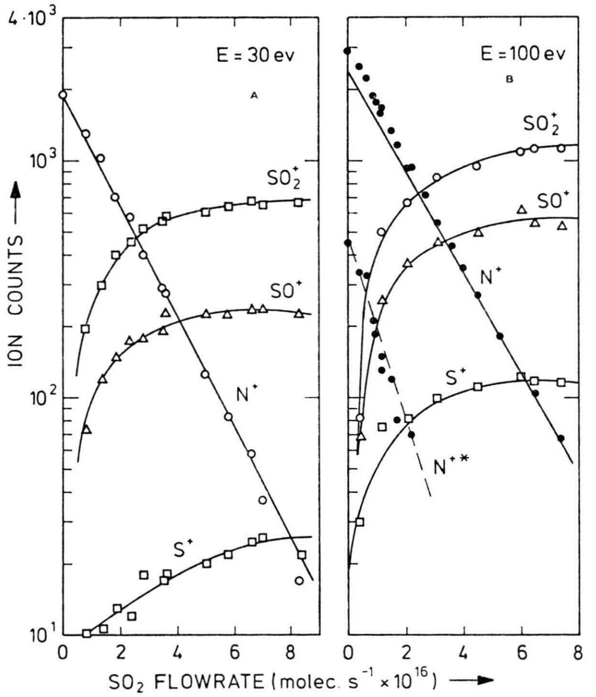

Fig. 1. Variation of the primary and product ion counts with SO_2 flow for the reaction $N^+ + SO_2$, Experimental data obtained at electron impact energy (A) 30 V (sampling period 20 s), (B) 100 V (sampling period 10 s). Other parameters: He pressure, $\bar{p} = 0.71$ Torr, $\bar{v} = 6.04 \cdot 10^3$ cm/sec, $l = 72.2$ cm.

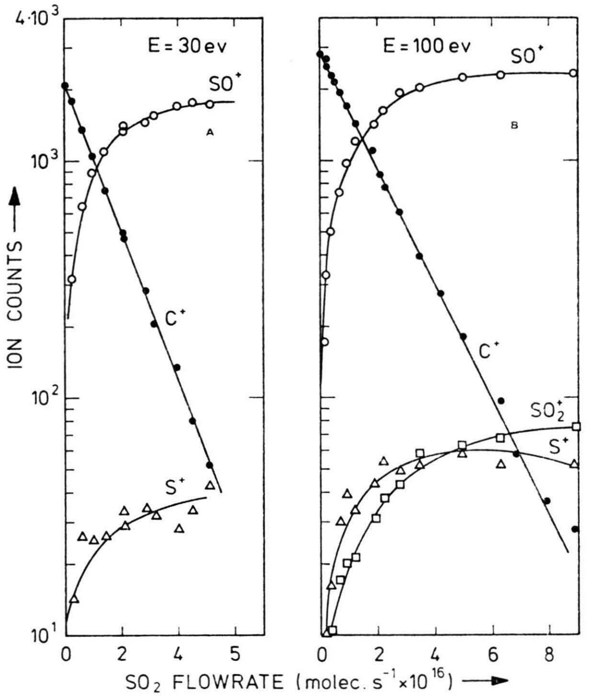

Fig. 2. Variation of the primary and product ion counts with SO_2 flow for the reaction $C^+ + SO_2$, Experimental data obtained at electron energy (A) 30 V (sampling period 20 s), (B) 100 V (sampling period 10 s). Other parameters: He pressure $\bar{p} = 0.71$ Torr, $\bar{v} = 6.04 \cdot 10^3$ cm/sec, $l = 72.2$ cm.

metastable ions apparently react with nearly equal rates. Nevertheless, the different product distributions in Figs. 2A and 2B indicate the presence of excited C^+ ions at high electron energy. For N^+ ions the rate coefficients of excited ions can be distinguished from ground state ions by the difference of the initial and the final slopes of the decay curves, so that the two rate coefficients can be separated. In principle, the excited N^+ ion can undergo both reaction and/or quenching. No distinction can be made here between these two processes. Accordingly, the sum of both rate coefficient $k^* = k_1 + k_2$, where k_1 is the rate coefficient for an excited ion-molecule reaction and k_2 is the rate coefficient for collisional quenching of excited ion, are given in the Table.

Table 1 summarizes the rate coefficients and product ion distributions derived from our measurements and those of other authors (last column), who have used different experimental techniques. Also shown are rate coefficients calculated from the Langevin [9] and ADO theory [10] (column 9). The product ion distributions for metastable ion reactions have been calculated from the data obtained at 100 V electron energy, where the ground and metastable ion reactions occur simultaneously, taking into account the known fractions of metastable to ground state ions and assuming that quenching by reactant gases does not take place. The results are given in column 5. The rate coefficients for metastable C^+ ions were estimated from those product ions observed at 100 V electron

Table 1. Product Ion Distributions and Rate Coefficients for C^+ and N^+ Ions.

Reaction	Product Distribution at 30 V	(%)	$\Delta H^{a,b}$ (ev)	Product Distribution at 100 V	(%)	Inferred metastable Product dist. (%)	Measured Rate Coefficients c			Theoretical	Other
							k (30 V)	k (100 V)	k^* (100 V)^d	k	k
$C^+ + C_2H_4$	$C_3H_4^+$	(85)	− 7.09	$C_3H_4^+$	(30)	50	1.82 (− 9)	1.62 (− 9)	—	1.67 (− 9)	
	$C_2H_4^+ + C$	(15)	− 8.62	$C_2H_4^+ + C$	(70)	50					
$C^+ + CH_3Cl$	$CH_3Cl^+ + C$	(63)	− .09	$CH_3Cl^+ + C$	(51)	20	3.0 (− 9)	2.92 (− 9)	3.2 (− 9)^e	2.8 (− 9)	2.1 − 3 (− 9) [11]
	$C_2H_3^+ + Cl$	(24)	− 4.93	$C_2H_3^+ + Cl$	(15)	10					
	$CH_3^+ + CCl$	(13)	− 1.29	$CH_3^+ + CCl$	(25)	40					
	$CCl^+ + CH_3$	—	+ 1.80	$CCl^+ + CH_3$	(9)	30					
$C^+ + SO_2$	$SO^+ + CO$	(94)	− 6.22	$SO^+ + CO$	(95)	80	2.5 (− 9)	2.1 (− 9)	2.6 (− 9)^e	2.4 (− 9)	2.3 (− 9) [12]
	$S^+ + CO_2$ or	(6)	− 6.34	$S^+ + CO_2$ or	(2)	10					
	$S^+ + CO + O$		− 0.89	$S^+ + CO + O$							
	$SO_2^+ + C$	—	+ 1.07	$SO_2^+ + C$	(3)	10					
$N^+ + C_2H_4$	$C_2H_4^+ + N$	(76)	− 4.1	$C_2H_4^+ + N$	(90)	80	1.54 (− 9)	—	3.8 (− 9)	1.58 (− 9)	
	$C_2H_4N^+$	(24)	− 8.91	$C_2H_4N^+$	(10)	20					
$N^+ + CH_3Cl$	$CH_3^+ + N$ $+ Cl$	(36)	− 1.16	$CH_3^+ + N$ $+ Cl$	(57)	70	2.5 (− 9)	—	3.3 (− 9)	2.6 (− 9)	
	$CH_2Cl^+ + NH$ or $NCl^+ + CH_3$	(40)	− 4.58	$CH_2Cl^+ + NH$ or $NCl^+ + CH_3$	(36)	10					
	$CH_3Cl^+ + N$	(24)	− 3.33	$CH_3Cl^+ + N$	(7)	20					
$N^+ + SO_2$	$SO_2^+ + N$	(59)	− 2.17	$SO_2^+ + N$	(43)	20	1.8 (− 9)	—	3.3 (− 9)	2.3 (− 9)	
	$SO^+ + NO$	(39)	− 4.88	$SO^+ + NO$	(42)	40					
	$S^+ + NO_2$	(2)	− 2.74	$S^+ + NO_2$	(15)	40					

[a] A positive sign indicates an endoergic channel. [b] Heat of formation taken from Ref. [13]

[c] Rate coefficients are given $a(-b)$ to represent $a + 10^{-b}$ in units of $cm^3\ s^{-1}$. [d] For detail see text.

[e] Calculated from the growth curve of the productions.

energy which were not observed at 30 V. For C_2H_4, such an estimation was not possible because the same products were observed at both electron energies. These results are presented in column 8. In column 3 of 1, the reaction enthapies for the ground state ion (30 V) are listed. The estimated accuracy for the rate coefficients is $\pm 20\%$. For the reaction of N^+ ions produced at 100 V electron energy the accuracy is not better than $\pm 30\%$ due to the errors involved in the extrapolation and substration procedure required in the analysis. The product distributions for excited ions are subject to greater error than those for the ground state ion because the contribution due to quenching is not known.

Discussion

The rate coefficients for the reaction of C^+ ions are in good agreement with those reported by others [11, 12]. For the N^+ reactions no data presently are available for comparison. The most interesting features lie in the different product distributions obtained for the two electron energies used. The results indicate that the rate coefficients for ground states C^+ ions are close to the Langevin or ADO values and that the rate coefficients for the metastable excited C^+ ions are similarly higher. This conclusion is supported by a rate coefficient $k = 3.2(-9)$ obtained from the growth curve of the CCl^+ product ion from the reaction $C^+ + CH_3Cl$, which can occur only with excited C^+ ions. The decay of C^+ gives $k = 3.0(-9)$ and $2.92(-9)$ at 30 V and 100 V electron energy, respectively. The endothermicity of CCl^+ formation from ground state C^+ ions is 1.8 eV. Another example, for the difference of reactions of excited and ground state ions is the reaction $C^+ + SO_2$, where SO_2^+ product ions were observed only at 100 V electron energy. The growth curve of SO_2^+ ions gives a rate value $k = 2.6(-9)$, which is close to the rate coefficient $k = 2.5(-9)$ for the reaction of ground state C^+ ions. The formation of SO_2^+ is also endoergic by 1.07 eV for ground state C^+ ions. The measured rate coefficient for the reaction $C^+ + SO_2$ is in good agreement with $k = 2.3(-9)$ reported by Liddy et al. [12] who used the flowing afterglow technique. These authors observed SO^+ ion as the only product ion. We have observed S^+ as an additional ion along with SO^+. This reaction channel is exoergic by 6.34 or 0.89 eV depending upon the neutral products (CO_2 or $CO + O$) formed. It is evident from Table 1 that product distributions are significantly different to the two electron energies used. It appears that metastable ions react through channels which are endoergic for the ground state ions but become favoured with increasing recombination energy of the ion opening fragmentation channels for the charge transfer products.

For the reaction of N^+, the observed product ions are the same at both electron energies but their distributions differ. For example, in the reaction with CH_3Cl and SO_2, the dissociative charge transfer channels are preferred at 100 V electron energy compared with 30 V. In case of C_2H_4, the charge transfer channels are the dominant process at both ground and metastable excited ion reactions. In the reaction with CH_3Cl, the product ion CH_2Cl^+ and NCl^+ are indistinguishable because they occur at the same $m/e = 49$ a.m.u. and their yields are nearly equal at both electron energies. It is quite probable that this ion is mainly NCl^+ because in the reaction $C^+ + CH_3Cl$, CCl^+ is formed instead of CH_2Cl^+ even though the formation of CH_2Cl^+ would be exoergic by 1.1 eV.

Conclusion

This work illustrates that for C^+, though the metastable rate coefficients were not determined, it was still possible to obtain information concerning the reactions of excited C^+ ions from the differences between the total product ion distributions and those for ground state C^+. This study shows also as previously [2] that when charge transfer is possible for the ground state ions the metastable state ions appear to react predominantly into channels with the greatest fragmentation.

Acknowledgements

The author is grateful to Professor Peter Warneck, Max-Planck-Institut for Chemistry, Mainz (F.R.G.), for stimulating discussions. The author is indebted to Professor N. D. Twiddy, Dept. of Physics, University College of Wales, Aberystwyth, U.K., for making available his SIFT appatatus.

[1] J. Glosik, A. B. Rakshit, N. D. Twiddy, N. G. Adams, and D. Smith, J. Phys. B **11**, 3365 (1978).

[2] M. Tichy, A. B. Rakshit, D. Lister, N. D. Twiddy, N. G. Adams, and D. Smith, Int. J. Mass Spectrom. Ion Phys. **29**, 231 (1979).

[3] B. R. Turner, J. A. Rutherford, and D. M. J. Compton, J. Chem. Phys. **48**, 1602 (1968).

[4] A. B. Rakshit, Int. J. Mass Spectrom. Ion Phys. **36**, 31 (1980).

[5] A. B. Rakshit, Chem. Phys. Lett. **75**, 283 (1980),

[6] N. G. Adams and D. Smith, J. Phys. B **9**, 1439 (1976).

[7] D. Smith, N. G. Adams, and T. M. Miller, J. Chem. Phys. **69**, 308 (1978).

[8] J. L. McCrumb and P. Warneck, J. Chem. Phys. **66**, 5416 (1977).

[9] G. Gioumousis and D. P. Stevenson, J. Chem. Phys. **29**, 294 (1958).

[10] T. Su and M. T. Bowers, Int. J. Mass Spectrom. Ion Phys. **12**, 347 (1973).

[11] A. A. Herod, A. G. Harrison, and McAskill, Cand. J. Chem. **49**, 2217 (1971).

[12] J. P. Liddy, C. G. Freeman, and M. J. McEwan, Astrophys. Lett. **16**, 155 (1975).

[13] H. M. Rosenstock, K. Draxl, B. W. Steiner, and J. T. Herron, Energetics of Gaseous Ions, J. Phys. Chem. Ref. Data **6**, Suppl. 1 (1977).