ION CYCLOTRON RESONANCE STUDIES OF SOME REACTIONS OF C^+ IONS[*]

Vincent G. ANICICH[**], Wesley T. HUNTRESS Jr.
Jet Propulsion Laboratory, Pasadena, California, USA

and

Jean H. FUTRELL
Department of Chemistry, University of Utah, Salt Lake City, Utah, USA

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Product distributions and rate constants for the reaction of ground state C^+ ions with O_2, NO, HCl, CO_2, H_2S, H_2O, HCN, NH_3, CH_4, H_2CO, CH_3OH, and CH_3NH_2 have been measured. Rate constants were obtained using ion cyclotron resonance trapped ion methods at JPL, and product distributions were obtained using a tandem (Dempster-ICR) mass spectrometer at the University of Utah. Rapid carbon isotope exchange has also been observed in C^+–CO collisions.

1. Introduction

The reactions of C^+ atomic ions at thermal energies have not been studied extensively due to the fact that C^+ ions are not produced in large quantities by electron impact dissociative ionization of any readily available gaseous molecule. C^+ ions are readily produced, however, by the reaction of He^+ ions with CO.

$$He^+ + CO \rightarrow C^+ + O + He. \qquad (1)$$

Fehsenfeld et al. [1] used this mode of production in a flowing afterglow study of the reaction of thermal energy C^+ ions with O_2 and CO_2, and Bolden and Twiddy [2] also used reaction (1) in flowing afterglow experiments on the reaction of C^+ ions with H_2O. Franklin and Munson [3], and Schildcrout et al. [4] used electron impact ionization of CH_4 and CO_2, respectively, to produce C^+ ions for the study of the reaction of these ions with O_2 and CO_2.

Because of the importance of the reactions of C^+ ions for synthesis of some of the molecules observed in interstellar clouds [5,6], an extensive investigation of the reaction of these ions with some simple molecules was carried out using conventional ICR methods at JPL, and using the tandem-ICR instrument at the University of Utah.

2. Experimental

Both the JPL ICR [7] and Utah tandem-ICR [8] instruments have been described previously, and each has particular advantages for the present study. The JPL ICR was used in the trapped ion mode for measurement of rate constants, and the Utah tandem-ICR was used for measurement of the product distributions. Product distributions for ions produced by secondary reactions, such as C^+ ions formed by reaction (1) in this case, are more easily determined using the tandem-ICR than by conventional ICR ejection experiments. ICR ejection is more appropriate for measuring product distributions for reactions of primary ions produced by electron impact [7], and are less easily interpreted where reactions of secondary ions are concerned.

In the tandem-ICR experiments, He–CO gas mixtures were admitted into the Dempster mass spectrom-

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[**] NASA-NRC Resident Research Associate, 1974–1976.

eter ion source where C^+ ions were produced by reaction (1). The C^+ ions were transmitted into ICR cell where the reactant gas was added, sufficient to insure about 20% conversion to product ions. The relative peaks heights and ion product distribution were measured at constant magnetic field by changing the observing frequency and calibrating for changes in marginal sensitivity using the Q-spoiler device as previously described [9]. The injected ion kinetic energy is close to thermal in these experiments, and certainly less than 0.1 eV as determined by comparison with ICR ejection experiments for reactions sensitive to reactant ion kinetic energy [10].

Rate constants were measured in the trapped ion mode by the decay of C^+ ions at long times in He—CO—reactant gas mixtures. A mixture of gases containing 86% He and 14% CO was admitted to the conventional JPL ICR spectrometer to a total pressure of approximately 8.5×10^{-6} torr (abs.). After a 4 ms ionization pulse, the C^+ ion intensity builds up rapidly with time, becoming constant after about 35 ms and the He^+ ions have all reacted with CO. After recording the C^+ intensity curve versus time, the reactant gas is added in the amount of about 3×10^{-7} torr (abs.) and the C^+ intensity versus time is recorded again. The C^+ ion intensity is no longer constant at long times but turns over and decays exponentially. The rate constant for the reaction of C^+ ions is determined from the slope of a semilogarithmic plot of $\ln([C^+]/[C^+]^0)$ versus time, where $[C^+]^0$ and $[C^+]$ are the measured intensities of C^+ ions before and after adding the reactant gas, respectively. At long times, greater than about 25 ms, the slope of these plots are linear and kinetic analysis shows that the slope of this linear portion is given by the negative of the product of reactant gas number density and rate constant: $S = -nk$. The reactant gas pressure is measured by using a Baratron capacitance manometer as previously described [7]. Kinetic analysis also shows that C^+ ion loss due to reaction of He^+ ions with the added reactant gas does not affect the slope of the semilogarithmic plot of C^+ ion intensity versus time at long times, and therefore does not affect the rate constant obtained from this data.

The rate constant for the exchange reactions

$$^{13}C^+ + {}^{12}CO \rightleftharpoons {}^{12}C^+ + {}^{13}CO \qquad (2)$$

were measured using the technique previously developed for the study of resonant proton transfer reactions [11]. Pure ^{13}CO gas was admitted into the spectrometer via one inlet, pure ^{12}CO gas admitted through a second inlet and pure He gas admitted through a third inlet. The $^{13}C^+$ and $^{12}C^+$ ion signals in trapped ion experiments were recorded versus reaction time well beyond the times at which constant intensity is reached and equilibrium attained. After the equilibrium condition was measured, an rf signal was switched on to selectively and continuously eject either the $^{12}C^+$ or $^{13}C^+$ ions from the ICR cell. The exchange reaction was identified by the exponential decay of the remaining, unejected C^+ ion isotope as it is converted to the alternate isotope and ejected (see fig. 1). The rate constant for the reaction was obtained from the slope of a semilogarithmic plot of the ratio between recorded C^+ ion signals with and without ejection of the other isotope.

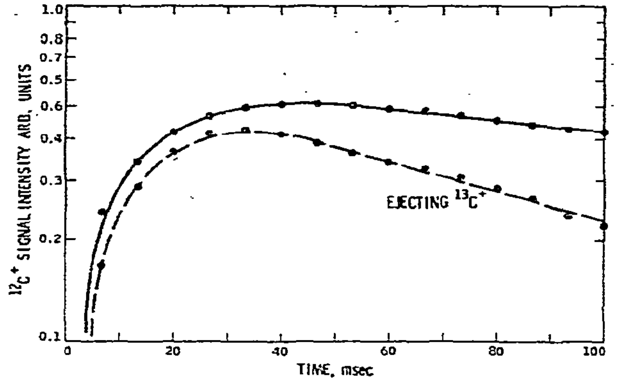

Fig. 1. Plot of $^{12}C^+$ ion intensity in ICR trapped ion experiment in mixture of He, ^{12}CO and ^{13}CO: $n(He) = 2.5 \times 10^{11}/cm^3$, $n(^{12}CO) = 3.6 \times 10^{10}/cm^3$, $n(^{13}CO) = 3.8 \times 10^{10}/cm^3$. For clarity, only the $^{12}C^+$ ion intensity is shown. $^{13}C^+$ ion intensity behavior is similar. Slow fall-off at long times is due to diffusional losses of non-reactive ions from the ICR ion trap. Dashed line shows the result of switching on rf signal to continuously eject $^{13}C^+$ ions at $M/e = 13$. In the absence of ^{13}CO, this rf field has no effect on $^{12}C^+$ ion intensity. Rate constant for the isotope exchange reaction in $^{12}C^+ - {}^{13}CO$ collisions is obtained from a semilogarithmic plot of the ratio between the two plots.

3. Results and discussion

The product distributions and rate constants obtained are given in table 1. The rate constants are compared in table 1 with those calculated from either the

Table 1
Reactions of $\mathrm{C^+}$ ions

Reaction		Product distribution	Rate constants (10^{-9} $\mathrm{cm^3/s}$)		
			experiment	theor.	lit.
$\mathrm{C^+ + O_2}$	$\to \mathrm{O^+ + CO}$	0.36	1.22 ± 0.10	1.01	1.1 a), 0.9 b)
	$\to \mathrm{CO^+ + O}$	0.64			
$\mathrm{C^+ + NO}$	$\to \mathrm{NO^+ + C}$	1.00	0.85 ± 0.10	1.05	
$\mathrm{C^+ + CO_2}$	$\to \mathrm{CO^+ + CO}$	1.00	1.1 ± 0.1	1.25	1.9 a), 1.6 c)
$\mathrm{C^+ + CH_4}$	$\to \mathrm{C_2H_2^+ + H_2}$	0.29	1.45 ± 0.12	1.44	
	$\to \mathrm{C_2H_3^+ + H}$	0.71			
$\mathrm{C^+ + NH_3}$	$\to \mathrm{NH_3^+ + C}$	0.50	2.3 ± 0.2	2.5	2.3 d)
	$\to \mathrm{H_2CN^+ + H}$	0.47			
	$\to \mathrm{HCN^+ + H_2}$	0.03			
$\mathrm{C^+ + H_2O}$	$\to \mathrm{HCO^+ + H}$	1.0	2.7 ± 0.5	2.7	2.0 e)
$\mathrm{C^+ + H_2S}$	$\to \mathrm{H_2S^+ + C}$	0.28	2.0 ± 0.2	2.0	
	$\to \mathrm{HCS^+ + H}$	0.72			
$\mathrm{C^+ + HCN}$	$\to \mathrm{C_2N^+ + H}$	1.0	3.2 ± 0.2	4.2	
$\mathrm{C^+ + HCl}$	$\to \mathrm{CCl^+ + H}$	1.0	fast	1.8	
$\mathrm{C^+ + H_2CO}$	$\to \mathrm{CH_2^+ + CO}$	0.48	4.4 ± 0.4	3.1	1.6 f)
	$\to \mathrm{HCO^+ + CH}$	0.21			
	$\to \mathrm{H_2CO^+ + C}$	0.31			
$\mathrm{C^+ + CH_3OH}$	$\to \mathrm{CH_3OH^+ + C}$	0.33	4.1 ± 0.3	2.6	
	$\to \mathrm{CH_3O^+ + (CH)}$	0.30			
	$\to \mathrm{HCO^+ + CH_3}$	0.08			
	$\to \mathrm{CH_3^+ + (HCO)}$	0.29			
$\mathrm{C^+ + CH_3NH_2}$	$\to \mathrm{CH_3NH_2^+ + C}$	0.73	4.2 ± 0.8	2.3	
	$\to \mathrm{CH_2NH_2^+ + (CH)}$	0.19			
	$\to \mathrm{H_2CN^+ + (CH_3)}$	0.06			
	$\to \mathrm{CH_3^+ + (HCN + H)}$	0.03			
$\mathrm{^{12}C^+ + {}^{13}CO}$	$\to \mathrm{^{13}C^+ + {}^{12}CO}$	1.00	0.20 ± 0.02	1.13	
$\mathrm{^{13}C^+ + {}^{12}CO}$	$\to \mathrm{^{12}C^+ + {}^{13}CO}$	1.00	0.20 ± 0.02	1.13	

a) Ref. [1]. b) Ref. [3]. c) Ref. [4] d) Ref. [15]. e) Ref. [2]. f) Ref. [16], and see text.

Langevin [12] or the ADO theory [13], and with rate constants previously reported in the literature. For reaction with non-polar molecules and with $\mathrm{NH_3}$, $\mathrm{H_2O}$, and $\mathrm{H_2S}$, good agreement is found between experiment and Langevin or ADO calculations. For reaction with HCN, $\mathrm{H_2CO}$, $\mathrm{CH_3OH}$, and $\mathrm{CH_3NH_2}$ the experimental value tends to be higher than the ADO value but this may be due to uncertainties in both the rate constants and in the polarizabilities and dipole moments of the neutrals [14]. An accurate value for the rate constant of the $\mathrm{C^+}$–HCl reaction could not be obtained because of the damaging effect of gaseous HCl on the copper ICR cell plates, but it is clear that the reaction is very fast with a rate constant on the order of the ADO value. Compared to the Langevin value, the rate constant observed for the isotope exchange reaction in $\mathrm{C^+}$–CO collisions indicates that exchange of C atoms occurs for only about one in every six collisions.

The rate constants measured in this work for the reaction of $\mathrm{C^+}$ ions with $\mathrm{O_2}$ and $\mathrm{NH_3}$ are in good agreement with the previous literature values [1,3,15]. The values for the reaction of $\mathrm{C^+}$ ions with $\mathrm{CO_2}$ and $\mathrm{H_2O}$

are not in good agreement with previous flowing afterglow studies [1,2], but are closer to the theoretical collision rate constants than are these earlier values. The literature value [16] quoted for the rate constant of the C^+–H_2CO reaction is an adjustment to the reported value in order to account for the fact that these authors identified only the channel producing CH_2^+ ions in this reaction. The poor agreement with the present value probably suggests that the original data analysis by Karpas and Klein [16], which is based on the assumption of a single product, is faulty.

The product distributions given in table 1 are accurate to about 3% of total distribution. One surprising result is the identification of two channels in the reaction with O_2:

$$C^+ + O_2 \rightarrow CO^+ + O, \qquad (3a)$$

$$\rightarrow O^+ + CO. \qquad (3b)$$

It has been previously assumed that CO^+ ions were the only product of this reaction [1,3]. The tandem-ICR results show, however, that 36% of the products are O^+ and CO. The O^+ product ion would have been difficult to distinguish in the flowing afterglow experiments of Fehsenfeld et al. [1] from O^+ ions produced by direct electron impact ionization of CO in the He–CO mixture used to produce the C^+ reactant ion. Franklin and Munson [3] did not look for the products because of similar difficulties at both $M/e = 16$ and 28, and measured only the decay of the C^+ ion intensity with added O_2. Electronically excited states of the C^+ ions are not permitted by the exothermicity of reaction (1), and excess ion kinetic energy in the present experiments is probably not a factor due to the near-thermal kinetic energies (< 0.1 eV) in the tandem-ICR experiments.

The product distribution measured for the C^+–NH_3 reaction in the tandem-ICR experiment differs substantially from the flowing afterglow experiments reported by Schiff et al. [15]

$$C^+ + NH_3 \rightarrow NH_3^+ + C, \qquad (4a)$$

$$\rightarrow HCN^+ + H, \qquad (4b)$$

$$\rightarrow H_2CN^+ + H_2. \qquad (4c)$$

Schiff et al. [15] did not observe the minor reaction channel producing HCN^+ ions, and reported $k_{4c}/k_{4a} \approx 0.05$. The present results give $k_{4c}/k_{4a} = 0.94$. The large disagreement is most likely due to problems with ion mass discrimination in the flowing afterglow experiment associated with diffusive ion losses, ion sampling, and quadrupole mass spectrometer ion detection. The importance of the reactions of C^+ ions with NH_3, HCN, and H_2O in the synthesis of HCN and HCO^+ in interstellar clouds is described in refs. [5,6]. The C^+–CO isotope exchange reaction may be of significance in explaining the variations in the $^{13}C/^{12}C$ ratio observed in some interstellar molecules [17].

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