Reactions of CO_2^+ , $CO_2CO_2^+$ and H_2O^+ Ions with Various Neutral Molecules

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Received 9th January, 1980

A drift chamber mass spectrometer apparatus was used to determine products and rate coefficients at 300 K for reactions of CO_2^+ , $CO_2CO_2^+$ and H_2O^+ with H_2 , CH_4 , SO_2 , O_2 , C_2H_2 , C_2H_4 , COS, CS_2 , NH_3 , NO₂ and NO. Charge transfer is the predominant reaction channel in most cases. Reaction efficiencies are discussed by comparison with rate coefficients calculated from the capture mechanism according to averaged dipole orientation theory.

In a recent study concerned with reactions of $CO_2CO_2^+$ dimer ions ¹ we wished to compare the rate coefficients obtained with rate data for the corresponding reactions of CO_2^+ ions, but found that only a few such reactions had been treated in the literature. We were particularly interested in reactions of CO_2^+ and $CO_2CO_2^+$ ions with simple sulphur compounds in view of the recent discovery of SO_2 in the atmosphere of Venus ^{2, 3} and the possibility that CS_2 and perhaps even $COS^{-3, 4}$ may also be present. CO_2 is the main constituent of this atmosphere. To obtain the desired information we have performed appropriate measurements and report here rate coefficients for eleven reactions of CO_2^+ ions. A drift chamber mass spectrometer technique was used for these measurements. Due to the presence of impurity water vapour, H_2O^+ ions also occur in the drift chamber in these experiments. From the behaviour of H_2O^+ ion intensities in the presence of additional reactants we have obtained rate coefficients for several H_2O^+ reactions. These will also be presented.

EXPERIMENTAL

The apparatus and experimental techniques have been described previously.^{1, 5}

Briefly, N_2^+ ions are generated by electron impact, mass analysed in a quadrupole filter and then injected into a reaction chamber filled with CO₂ carrier gas. At the injection point, charge transfer produces nearly thermal CO₂⁺ ions. A weak electric field causes these ions to drift towards the rear plate of the chamber. On their way they may interact with the neutral molecules of a reactant gas added in known amounts to the CO₂ flow. Both CO₂⁺ ions and product ions are sampled for mass spectrometric analysis *via* an orifice at the rear plate of the chamber. The residence time of CO₂⁺ ions in the chamber is measured directly as a function of pressure using a double pulse-delay technique.^{1, 5} Methods of CO₂ purification admixing reactant gases and measurements of pressures and flow rates were the same as in our previous study.¹ The determination of rate coefficients for the reactions of CO₂⁺ and H₂O⁺ ions will be described below.

ANALYSIS OF DATA

Experiments were performed at chamber pressures of 38.6 Pa (0.29 Torr). Even at this low pressure the CO_2^+ ions partially attach to CO_2 whereby $CO_2CO_2^+$ dimer ions

are formed. Both CO_2^+ and $CO_2CO_2^+$ react with water vapour which is present as an impurity. As a consequence, the analysis of experimental data must take into account the following reactions

$$\operatorname{CO}_2^+ + 2\operatorname{CO}_2 \longrightarrow \operatorname{CO}_2 \operatorname{CO}_2^+ + \operatorname{CO}_2$$
 (1)

$$\begin{array}{c} \operatorname{CO}_{2}^{+} + \operatorname{H}_{2}\operatorname{O} & \stackrel{a}{\xrightarrow{b}} \operatorname{H}_{2}\operatorname{O}^{+} + \operatorname{CO}_{2} \\ \xrightarrow{b} \operatorname{HCO}_{2}^{+} + \operatorname{OH} \end{array} \right\}$$
(2)

$$\begin{array}{c} \operatorname{CO}_{2}\operatorname{CO}_{2}^{+} + \operatorname{H}_{2}\operatorname{O} \stackrel{a}{\xrightarrow{b}} \operatorname{H}_{2}\operatorname{O}^{+} + 2\operatorname{CO}_{2} \\ \xrightarrow{\rightarrow} \operatorname{CO}_{2}\operatorname{H}_{2}\operatorname{O}^{+} + \operatorname{CO}_{2} \end{array} \right\}$$
(3)

$$H_2O^+ + 2CO_2 \rightarrow CO_2H_2O^+ + CO_2$$
⁽⁴⁾

$$CO_2^+ + R \rightarrow \text{products}$$
 (5)

$$CO_2CO_2^+ + R \rightarrow \text{products}$$
 (6)

$$H_2O^+ + R \rightarrow \text{products}$$
 (7)

where R denotes the reactant admixed to the CO₂ flow. Rate coefficients for the first three reactions are available from previous studies.^{1, 6} The probability for H₂O⁺ formation in reaction (3) is unknown, but this route can be estimated to contribute at the most 35% to the total production of H₂O⁺. Similarly, reaction (3) may produce either most of the observed CO₂H₂O⁺ ions or they derive entirely from reaction (4). In view of these uncertainties we have considered two extreme cases for the analysis of H₂O⁺ intensities. In case (i) it is assumed that CO₂H₂O⁺ formation occurs exclusively via reaction (3b). This requires that $k_{3a} = 0$ and reaction (4) is negligible. In case (ii) we assume alternatively that CO₂H₂O⁺ arises entirely from reaction (4) so that $k_{3b} = 0$. Below we describe, as an example, the treatment of data for case (i). The treatment for case (ii) follows a similar scheme.

The number densities of CO_2 , H_2O and reactant molecules in the drift chamber are denoted by n, n_1 and n_R , respectively. If one neglects losses due to diffusion, the number densities of the reactant ions in the tubular region connecting entrance and exit apertures follow from the kinetic equations

$$v_{44} \frac{\mathrm{d}n_{44}}{\mathrm{d}l} = -(k_1 n^2 + k_2 n_1 + k_5 n_{\mathrm{R}})n_{44}$$
$$v_{88} \frac{\mathrm{d}n_{88}}{\mathrm{d}l} = k_1 n^2 n_{44} - (k_3 n_1 + k_6 n_{\mathrm{R}})n_{88}$$
$$v_{18} \frac{\mathrm{d}n_{18}}{\mathrm{d}l} = k_{2a} n_1 n_{44} - k_7 n_{\mathrm{R}} n_{18}.$$

Here, the individual ion densities n_i and the associated drift velocities are identified by their mass numbers $M(CO_2^+) = 44$, $M(CO_2CO_2^+) = 88$, $M(H_2O^+) = 18$, *l* is the distance from the entrance orifice and the *ks* are the rate coefficients for the reactions involved. Similar equations describe the behaviour of the product ions resulting from reactions (5)-(7).

The neglect of diffusion terms in the kinetic equations is not really justified. Integration of these equations over the entire drift distance l = d will, nevertheless, give the correct individual ion intensities emerging from the chamber exit aperture provided these are normalized to the sum of all ion intensities. A rigorous

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analysis of the motion of ions in the reaction chamber has shown⁵ that even though diffusion losses reduce the total ion intensity, the partitioning among the individual normalized ion intensities remains unaffected. This result is obtained by virtue of the Einstein equation, $D/\mu = kT/e$, which ensures proportionality between the diffusion coefficient D and the mobility $\mu = v/E$ for each ionic species. This relation is strictly valid only in the thermal energy domain but holds approximately in the adjacent range for elevated ion energies, as applies here. Accordingly, the abbreviated kinetic equations given above may serve to simplify the mathematical procedure needed to relate the observed ion intensities with the reactions of ions occurring in the drift chamber.

Integration of the kinetic equations yields the normalized ion intensities for the three reactant ions

$$I_{44} = f e^{-A\tau_4 4} = I_{44}^{\circ} e^{-k_R n_R \tau_{44}}$$
$$I_{88} = f \frac{k_1 n^2}{B - A} (e^{-A\tau_4 4} - e^{-B\tau_4 4})$$
$$I_{18} = f \frac{a k_2 n_1}{C - A} (e^{-A\tau_4 4} - e^{-C\tau_4 4}).$$

The normalized intensities are here represented by $I_{44} = v_{44} n_{44} (l = d) / \Sigma v_i n_i (l = d)$, etc.; f = 0.95 is the fraction of CO₂⁺ ions resulting from the initial charge-transfer process (the remainder is mainly O^{+} which converts to O_{2}^{+}) and $\tau_{44} = d/v_{44} = 5.8$ $\times 10^{-5}$ s is the residence time of CO₂⁺ ions in the chamber for an electric field strength $E = 10 \text{ V cm}^{-1}$ and p = 38.6 Pa. The other abbreviations are:

$$A = k_1 n^2 + k_2 n_1 + k_5 n_R$$

$$B = (k_3 n_1 + k_6 n_R) \mu_{44} / \lambda_{88}$$

$$C = k_7 n_R \mu_{44} / \mu_{18}.$$

Values for k_1 , k_2n_1 and k_{2a}/k_2 are obtained from the ion intensities in the absence of added reactant R. The mobilities for CO_2^+ and $CO_2CO_2^+$ are known from direct measurements. The mobility for H_2O^+ in CO_2 was obtained by a classical scaling procedure, using $\mu(O_2^+) = 1.35 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-18}$ and assuming that intermolecular forces are similar. The rate coefficient k_5 is derived directly from the exponential decay of I_{44} with increasing number density $n_{\rm R}$. The rate coefficients k_6 and k_7 are obtained by fitting the equations for i_{88} and i_{18} to the observed ion intensities as a function of Values for k_6 and k_7 will be less accurate than those for k_5 . We estimate that the n_R. determination of k_5 is accurate within $\pm 20\%$ while the errors associated with k_6 and k_7 may reach \pm 50%. Rate coefficients derived in this manner are then used to calculate the normalized intensities of the product ions resulting from reactions (5)-(7). Comparison with the measured product intensities provides an additional verification of the results. Rate coefficients will be given below in units of cm³ molecule⁻¹ s⁻¹.

RESULTS

From the total set of ion intensities observed in the absence of added reactant we obtain the probability for channel *a* of reaction (2) as $k_{2a}/k_2 = 0.66 \pm 0.04$ in case (i) and $k_{2a}/k_2 = 0.75 \pm 0.03$ when it is assumed that H_2O^+ derives exclusively from reaction (2a). The former value provides a lower limit, the latter an upper limit. The true value will be intermediate between both and we have taken $k_{2a}/k_2 = 0.70$ for the

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purpose of calculating case (ii). All three values are in good agreement with a recent determination, $k_{2a}/k_2 = 0.73$, by Karpas *et al.*⁶ using the ion cyclotron resonance (i.c.r.) technique. Values for k_2n_1 showed a larger variation from day to day. In conjunction with $k_2 = 2.1 \times 10^{-9}$ given previously ^{1, 6} we estimate the H₂O vapour density to lie in the range $(1.6-2.7) \times 10^{12}$ molecules cm⁻³. The rate coefficient for reaction (1) obtained from the measurements of A after substracting k_2n_1 is $k_1 = (2.03 \pm 0.1) \times 10^{-28}$ for case (i) and $\approx 4 \%$ lower for case (ii), in good agreement with our earlier determination $k_1 = 2.1 \times 10^{-28}$.

Ion intensities observed upon the introduction of COS to the reaction chamber are shown in fig. 1 to provide an example of the spread of individual data points. Rate



COS number density/ 10^{13} molecules cm⁻³

FIG. 1.—Normalised ion intensities observed when COS is present in the reaction chamber at the number densities shown. ■, H₂O⁺; ●, COS⁺; ○, CO₂CO₂⁺; △, CO₂⁺; +, (COS)₂⁺.

coefficients derived from the decay of reactant ions for all neutral molecules investigated are compiled in table 1. This table also gives the product distributions and in the case of the $CO_2CO_2^+$ reactions, for comparison, our previous results ¹ obtained at the higher pressure of 113 Pa. At this pressure CO_2^+ converts to $CO_2CO_2^+$ near the injection point, so that $CO_2CO_2^+$ becomes the primary ion. The rate coefficient k_6 is then obtained directly from the exponental decay of I_{88} in the same manner as k_5 is obtained from I_{44} in the present work. The NO₂ used contained $\approx 3\%$ water impurity. The rate coefficients given in table 1 are corrected accordingly.

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		products from CO ₂ ⁺		products from CO ₂ CO ₂ ⁺		k_6^a	products from H_2O^+	
reactant	i.p./eV	%	k_5	%/	k_6	previous	%	k7
H_2	15.43	CO ₂ H ⁺ (100)	4.7 (-10)	$H(CO_2)^+_2$ (100)	2.0 (-11)	$2.8(-11)^{b}$	H ₃ O ⁺ (100)	6.4 (-10)
CH₄	12.70	CO_2H^+ (100)	9.0(-10)	$H(CO_2)_2^+ (\ge 95)$	8.0(-10)	5.8 (-10)	$H_{3}O^{+}(100)$	1.4(-9)
SO_2	12.34	SO_2^+ (100)	1.8(-9)	SO_2^+ (88), $CO_2SO_2^+$ (12)	2.0(-9)	1.3 (-9)	SO_2H^+ (100)	2.6 (-9)
02	12.06	O_2^+ (100)	6.8(-11)	O_2^+ (94), $CO_2O_2^+$ (6)	2.0(-10)	1.8(-10)	$O_2^+(100)$	4.6 (-10)
C_2H_2	11.40	$C_2H_2^+$ (100)	7.3 (-10)	$C_2H_2^+$ (95), $CO_2C_2H_2^+$ (5)	7.0(-10)	7.0(-10)	$C_2H_2^+$ (100)	1.9(-9)
cos	11.17	COS ⁺ (100)	8.5 (-10)	COS (100)	1.5(-9)	1.1 (-9)	COS ⁺ (100)	2.5 (-9)
C_2H_4	10.45	$C_2H_4^+$ (17), $C_2H_3^+$ (27), $C_2H_2^+$ (56)	8.8(-10)	$C_2H_4^+$ (≈ 100)	1.1 (-9)	1.3 (-9)	C ₂ H ⁺ ₄ (100)	1.5 (-9)
NH3	10.17	NH_{3}^{+} (100)	8.9 (-10)	NH_3^+ (94), $CO_2NH_3^+$ (6)	9.0(-10)	6.0(-10)		
CS_2	10.08	CS_2^+ (100)	1.3(-9)	$CS_{2}^{+}(100)$	1.2(-9)	$1.0(-9)^{b}$	CS_2^+ or CS_2H^+	3.0 (-9)
NO_2	9.78	NO ⁺ (100)	2.9(-10)	NO ⁺ (100)	3.3(-11)		1	
NO	9.25	NO^{+} (100)	9.1 (-11)	NO ⁺ (100)	≤4.0(−12)	≤1 (−12)	NO ⁺ (100)	2.7(-10)

In deriving rate coefficients for the reactions of H_2O^+ ions it was found that the two modes of calculation, cases (i) and (ii), gave essentially equivalent results for every neutral reactant studied. The influence of reaction (4) upon the loss of H_2O^+ thus turns out to be of minor importance. Table 1 lists our results for case (i) which assumes that all $CO_2H_2O^+$ derives from reaction (3b). The rate coefficients obtained from case (ii) are slightly but insignificantly higher.

For NH₃ and NO₂ as reactants, H_2O^+ data could not be obtained due to interference with NH₄⁺ in the case of ammonia and H₂O impurity carried into the reaction chamber in the case of NO₂.

DISCUSSION

We compare first the present data with rate coefficients obtained by other experimental techniques. These are summarized in table 2. Our result for the reaction of CO_2^+ with H₂ is in good agreement with the more recent i.c.r. measurements, in acceptable agreement with the value obtained with the space charge trapping technique, but disagrees with the only result available from flowing afterglow This result is now recognized to be too high. The rate coefficient for measurements. the reaction $CO_2^+ + CH_4$ agrees well with data from s.c.t. measurements, while the result from high pressure mass spectrometry is clearly too high. Results for the reactions of CO₂⁺ with O₂ and NO are in good agreement with all flowing afterglow measurements. • The h.p.m.s. result is higher. The fact that the present results are in satisfactory agreement with most of the previous data for the four reactions considered provides further substantiation of the suitability of the drift chamber technique for such measurements. Although the initial charge transfer process produces thermal CO_2^+ ions, the ions acquire some excess energy from the weak electric field in which they We estimate their kinetic energy content to be $\approx 3kT$. It appears from the move.

techniques experimental f.a.ª i.c.r.^b h.p.m.s.^c s.c.t.d reactions $7.0(-10)^{14}$ $1.01(-9)^{10a}$ $CO_{2}^{+} + H_{2}$ $1.4(-9)^9$ $7.2(-10)^{10b}$ $4.0(-10)^{11}$ $5.8(-10)^{12}$ $1.0(-9)^{13}$ $CO_2^+ + CH_4$ $2.3(-9)^{15}$ $1.07(-9)^{16}$ $1.15(-9)^{17}$ $1.1(-9)^{21}$ $CO_{2}^{+}+O_{2}$ $5.6(-11)^{18}$ $6.4(-11)^{19}$ $1.2(-10)^{20}$ $CO_2^+ + NO$ $\approx 1.4 (-9)^9$ $H_2O^+ + H_2$ $H_2O^+ + CH_4$ $1.11(-9)^{22}$ $\approx 2.0 (-10)^9$ $1.29(-9)^{22}$ $H_2O^+ + O_2$

TABLE 2.—Summary of rate coefficients for CO_2^+ and H_2O^+ obtained by various experimental techniques. Units are cm³ molecule⁻¹ s⁻¹ with decadic exponent given in parenthesis.

^{*a*} Flowing afterglow; ^{*b*} ion cyclotron resonance; ^{*c*} high pressure mass spectrometry; ^{*d*} space charge trapped ion source.

 $1.16(-9)^{22}$

 $H_{2}O^{+} + NO$

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good agreement with previous data that this excess energy has little influence on the reaction rates.

There are fewer data available for reactions of H_2O^+ ions and the discrepancies are Although one might call the agreement with the present results still greater. acceptable for the reactions of H_2O^+ with H_2 and CH_4 , there is definite disagreement with the i.c.r. data for O_2 and NO. The reason for this discrepancy is not apparent. Electron impact ionisation of H₂O as used in i.c.r. is known to produce copious amounts of excited H_2O^+ ions.²³ Beam experiments ²³ show that a large fraction of H_2O^+ in the first excited \tilde{A}^2A_1 state survives for several micro-seconds but other data 24 for vibrationally hot H_2O^+ (\tilde{A}) ions indicate radiative lifetimes of only 800 ns. This is much shorter than the residence time of these ions in the i.c.r. cell so excited ions should not influence the measurements. In the present experiments, charge transfer from CO_2^+ produces H_2O^+ ions in the electronic ground Vibrational excitation should be removed by collision with CO₂. state.

Rate coefficients for $CO_2CO_2^+$ reactions are compared in table 1 with our previous results ¹ at higher pressure mainly as a consistency check. The present values are, on average, ≈ 20 % higher. The differences are greatest for the reactions with SO₂ and NH₃ but still within the margin of estimated error. Since the high pressure data are obtained more directly, they should be more accurate and are preferred. The consistency of both sets of data indicates, however, that the present method of data evaluation is useful and since rate coefficients for the H_2O^+ reactions were obtained in the same manner, it lends credence to the latter results.

At thermal energies, collision rates between ions and molecules are thought to be determined by polarisation and dipole forces which lead to mutual spiralling encounters and ion molecule capture under certain conditions.^{25, 26} Only capture is believed to provide the close contact necessary for a reaction to take place, although charge transfer may occur at a greater distance in special cases according to the electron jump mechanism.²⁷ Table 3 lists capture rate coefficients calculated from the

-	reactant	k ₅ (a.d.o.)	k_5/k_5 (a.d.o.)	k ₆ (a.d.o.)	k_6/k_6 (a.d.o.)	k ₇ (a.d.o.)	k_{7}/k_{7} (a.d.o.)		
	H ₂	1.52	0.31	1.50	0.02	1.57	0.41		
	CH₄	1.10	0.82	1.03	0.56	1.29	1.06		
	SO ₂	1.50	1.20	1.26	1.03	2.04	1.27		
	0,	0.69	0.10	0.60	0.30	0.87	0.53		
	$\tilde{C_2H_2}$	1.06	0.69	0.95	0.74	1.31	1.45		
	CŌS	1.24	0.68	1.04	1.05	1.68	1.48		
	C₂H₄	1.17	0.75	1.05	1.23	1.46	1.03		
	NH ₃	1.85	0.48	1.71	0.35	2.19			
	CS ₂	1.26	0.97	1.04	0.96	1.74	1.73		
	NO ₂	0.88	0.33	0.76	0.04	1.16			
	NO	0.72	0.13	0.65	≤0.002	0.91	0.30		

TABLE 3.-- ION-NEUTRAL CAPTURE RATE COEFFICIENTS CALCULATED ACCORDING TO AVERAGED DIPOLE ORIENTATION THEORY (IN UNITS OF 10^{-9} cm³ molecule⁻¹ s⁻¹) and ratios of experi-MENTAL AND THEORETICAL VALUES

averaged dipole orientation (a.d.o.) formulae given by Su and Bowers ²⁶ and ratios of experimental to theoretical rate coefficients. We consider reactions efficient if these

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ratios are greater than 0.3 and inefficient if they are smaller. By this criterion, most of the reactions are efficient, but there are a number of exceptions. When comparing reactions of CO_2^+ and $CO_2CO_2^+$ ions one finds rather similar efficiencies for reactions with CH_4 , SO_2 , C_2H_2 , C_2H_4 , COS, CS_2 and NH_3 . Efficiencies are low for reactions with O_2 and NO in both cases. Replacing CO_2^+ by $CO_2CO_2^+$ increases the efficiency for reaction with O_2 but decreases it drastically for NO. In fact, the low rate of charge transfer to NO from $CO_2CO_2^+$ is comparable with similarly low rates found for the rare gas ions Kr^+ and Xe^+ .²⁸ This finding has been explained on the basis that, on one hand, Kr^+ and Xe^+ ions do not form an intermediate complex with NO and, on the other hand, Franck–Condon factors for electronic transition are small in the available energy range. The reaction of CO_2^+ with H_2 is reasonably efficient while that of $CO_2CO_2^+$ is not. Here, a similar situation has been observed previously for the behaviour of N_4^+ reacting with H_2 .²⁹ This reaction has been shown to require an activation energy. The same may be true for the reaction of $CO_2CO_2^+$ with H_2 .

The reactions of H_2O^+ ions are not only all efficient but several of the ratios of k_7/k_7 (a.d.o.) exceed unity by a considerable margin. The most striking case occurs with CS₂ where the excess is definitely greater than the experimental error. Only a longrange charge transfer process appears capable of explaining this result. From the experimental data, the observed CS₂H⁺ may be a direct product from the reaction of H_2O^+ with CS₂ or it may derive from CS⁺₂ reacting with impurity H_2O . The above argument favours the latter possibility. The proton affinity of CS₂ seems to be unavailable. From the energetics of the former reaction we find PA(CS₂) ≥ 1.15 eV. The second reaction is 2.52 eV more endoergic than the first. A proton affinity of ≥ 3.67 eV is thus required for the second reaction to occur.

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(PAPER 0/041)