

Routes to the Formation of Association Products in CO₂ from Reactions of CO₂·CO₂⁺ Ions with Several Neutral Molecules

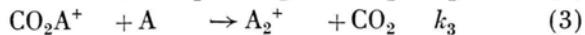
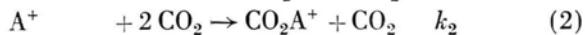
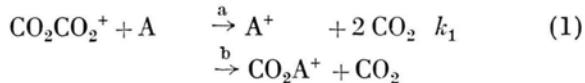
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The reactions of CO₂·CO₂⁺ ions with SO₂, O₂, C₂H₂, COS, NH₃, and CS₂ have been re-investigated to determine the yields of products of the type CO₂·A⁺, where A is the neutral reactant molecule. The same products are also formed by third body attachment of A⁺ to CO₂. In addition, A₂⁺ cluster ions are observed in several cases. Rate coefficients for these reactions are given.

In recent reports [1, 2] we described reactions of CO₂CO₂⁺ cluster ions with a variety of neutral molecules. The study made use of a drift chamber mass spectrometer apparatus featuring selected ion injection [3]. At sufficiently high pressures of CO₂ in the chamber (0.85 Torr) the CO₂⁺ ions formed at the injection point convert rapidly to CO₂·CO₂⁺ via third body attachment so that this ion becomes the predominant primary reactant ion. Many of the reactions investigated were found to proceed exclusively by charge transfer, but several reactions gave in addition association products of the type CO₂A⁺ where A⁺ is the ion of the neutral reactant. Specifically, SO₂, O₂, C₂H₂ and NH₃ behaved in this manner. Unfortunately, the experimental data did not permit a clear-cut decision about the route to CO₂A⁺ formation. These ions could have been formed either directly in a displacement channel of the CO₂CO₂⁺+A reaction, or by the formation of A⁺ via charge transfer followed by the third body assisted attachment of A⁺ to carbon dioxide. The CO₂A⁺ ions were found to react further in some cases and the complete reaction scheme required to explain the observations consists of the reaction sequence



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Stable A₂⁺ ions are observed in the reactions with SO₂, C₂H₂, COS and CS₂, whereas with NH₃ the product is NH₄⁺ and reaction (4) is a bimolecular process. With C₂H₂ one has in addition to reaction (4) the bimolecular formation of the products C₄H₃⁺ and C₄H₅⁺ as discussed previously [1]. Oxygen does not enter into either reaction (3) or (4) at the reactant densities applied.

To clarify the situation concerning CO₂A⁺ formation we have performed additional experiments at lower pressure (0.29 Torr) whereby the influence of the third body reaction (2) is so much reduced that it can be neglected to a first approximation. From the results obtained at low pressure combined with the results obtained at the higher pressure, we have derived a reasonably consistent set of rate coefficients for reactions (1)–(4). The results are presented in this Note.

An example for the type of data obtained under the altered experimental conditions is shown in Fig. 1 for SO₂ as the neutral reactant. The formation of the products SO₂⁺, CO₂SO₂⁺, and (SO₂)⁺ is clearly displayed. The SO₂H⁺ ion results from reaction of SO₂⁺ with water vapour always present as an impurity. Also apparent from the figure is the fact that at the reduced pressure only a fraction of the primary CO₂⁺ ions undergo conversion to CO₂CO₂⁺. A large portion of the SO₂⁺ thus derives from the reaction of CO₂⁺ with SO₂. As a consequence, the evaluation of the experimental data must take into account two further reactions



which occur in addition to reactions (1)–(4). The rate coefficient for reaction (5) is known from our previous work [1, 2]. Rate coefficients for the reactions of CO₂⁺ with several A molecules were obtained from the exponential decay of the CO₂⁺ ion intensity. These data will be presented elsewhere [4] and are not discussed here.

The evaluation of the experimental data and the determination of rate coefficients for the reactions (1)–(4) followed the procedures described in detail previously [1, 3]. Formulae for the normalised intensities of reactant and product ions were obtained by a step-wise integration of the kinetic equations applicable to the mechanism of reactions (1) and

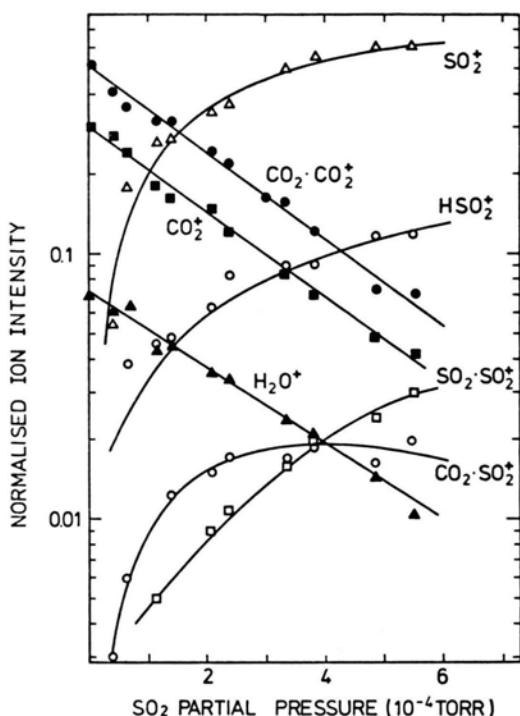


Fig. 1. Semilog plot of normalised ion intensities observed for SO_2 in CO_2 at 0.29 torr total pressure. Solid lines were calculated as outlined in the text, using the rate coefficients given in Table 1.

(3) – (6). The calculated ion intensities are functions of the neutral reactant density, the reaction rate coefficients, and the mobilities of the ions involved. Mobilities for the ions CO_2^+ and CO_2CO_2^+ have been determined experimentally [1], the others were derived by means of a classical scaling procedure if necessary [3, 5]. The unknown rate coefficients were adjusted appropriately until all the calculated

and observed ion intensities converged. In this manner, the rate coefficients k_1 , k_3 , k_4 and the ratio k_{1b}/k_1 were obtained from the experimental results at low pressure. Subsequently, the high pressure data reported previously were evaluated similarly on the basis of the reaction mechanism (1) – (4), employing the values for k_{1b}/k_1 derived from the low pressure data. This evaluation provided again rate coefficients for the reactions (1) through (4).

Rate coefficients obtained in this manner from the two sets of experimental data (low pressure and high pressure) are compiled in Table 1 for comparison. For most of the rate constants given, there exists agreement within a factor of two or better. This is taken as confirmation of the reaction mechanism employed to interpret the experimental observations. A more sizable discrepancy occurs only for the two rate coefficients of reaction (3) when SO_2 is the neutral reactant. The cause for the discrepancy is not readily apparent, particularly in view of the good agreement of the rate coefficients for the other reactants. It is conceivable that in the case of SO_2 the impurity of water vapour is more significant and enters into reactions which are not considered in the mechanism but which are nevertheless important.

The present investigation provides the yields of the displacement products CO_2A^+ from reactions (1b) and we consider this result important. As Table 1 shows, the yields from reaction channel (1b) are small in all cases, comprising 12 percent for SO_2 and less for the other reactants. Thus, most of the CO_2A^+ ions are formed via third body addition of A^+ to CO_2 , reaction (2). The values for k_2 given in Table 1 for the low pressure condition

Table 1. Reactions of CO_2CO_2^+ , CO_2A^+ , and A^+ ions in carbon dioxide. Product distribution for reaction (1) obtained at 0.29 Torr, and comparison of rate coefficients derived at pressures of 0.29 Torr (lp) and 0.85 Torr (hp). Decadic exponents for the rate coefficients are given in parentheses.

Neutral Reactant A	Product Distribution		k_1		k_2		k_3		k_4	
	A^+	CO_2A^+	lp	hp	lp	hp	lp	hp	lp	hp
SO_2	0.88	0.12	2.0(-9)	1.3(-9)	1.5(-29)	2.0(-29)	1.0(-10)	7.0(-10)	7.4(-27)	1.4(-26)
O_2	0.94	0.06	2.0(-10)	1.8(-10)	1.2(-29)	1.2(-29)	—	—	—	—
C_2H_2	0.95	0.05	7.1(-10)	7.0(-10)	9.0(-30)	5.0(-30)	5.0(-10)	7.5(-10)	3.0(-26)	1.6(-26)
CO	1.00	—	1.5(-9)	1.1(-9)	—	2.0(-30)	—	5.0(-10)	7.1(-27)	5.0(-27)
NH_3	0.94	0.06	8.9(-10)	6.0(-10)	1.4(-29)	1.3(-29)	8.5(-10)	8.0(-10)	see text	
CS_2^a	1.00	—	1.2(-9)	1.0(-9)	—	—	—	—	6.3(-27)	6.4(-27)

^a not investigated previously.

are upper limits obtained by setting $k_{1b}/k_1 = 0$. They are entirely consistent with the values derived from the high pressure data and corroborate the low yields for the displacement products in reaction (1). For O_2 , the values obtained for k_{1b}/k_1 and k_2 agree well with our previous more direct determination [1]. The reaction with COS did not lead to the formation of CO_2COS^+ in the low pressure experiments, although this ion was observed at the higher pressures. The CO_2CS_2^+ ion was not observed at all. Both neutral reactants, COS and CS_2 , do lead to the formation of A_2^+ ions via reaction (4). The rate coefficients are comparable to the k_4 values for SO_2 and C_2H_2 as reactants. With NH_3 , reaction (4) does not occur as written since bimolecular proton transfer takes its place. The rate

coefficients obtained for this process are $1.8(-9)$ at low pressure and $1.3(-9)$ at high pressure. These values are in reasonable agreement with each other and with data contained in the literature [6].

The present investigation has aimed at clarifying the reaction mechanism of cluster ion formation in CO_2 . This aim has been accomplished. It has not been possible to determine rate coefficients more precisely than is indicated by the results in Table 1. To improve the rate coefficients requires experimental techniques by which the individual ions can be isolated.

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