

# Routes to the Formation of Association Products in $\text{CO}_2$ from Reactions of $\text{CO}_2 \cdot \text{CO}_2^+$ Ions with Several Neutral Molecules

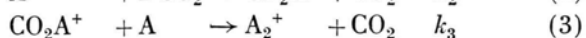
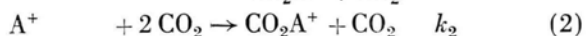
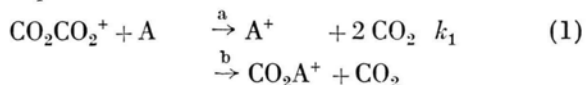
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The reactions of  $\text{CO}_2 \cdot \text{CO}_2^+$  ions with  $\text{SO}_2$ ,  $\text{O}_2$ ,  $\text{C}_2\text{H}_2$ ,  $\text{COS}$ ,  $\text{NH}_3$ , and  $\text{CS}_2$  have been re-investigated to determine the yields of products of the type  $\text{CO}_2 \cdot \text{A}^+$ , where A is the neutral reactant molecule. The same products are also formed by third body attachment of  $\text{A}^+$  to  $\text{CO}_2$ . In addition,  $\text{A}_2^+$  cluster ions are observed in several cases. Rate coefficients for these reactions are given.

In recent reports [1, 2] we described reactions of  $\text{CO}_2 \cdot \text{CO}_2^+$  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  $\text{CO}_2$  in the chamber (0.85 Torr) the  $\text{CO}_2^+$  ions formed at the injection point convert rapidly to  $\text{CO}_2 \cdot \text{CO}_2^+$  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  $\text{CO}_2 \text{A}^+$  where  $\text{A}^+$  is the ion of the neutral reactant. Specifically,  $\text{SO}_2$ ,  $\text{O}_2$ ,  $\text{C}_2\text{H}_2$  and  $\text{NH}_3$  behaved in this manner. Unfortunately, the experimental data did not permit a clear-cut decision about the route to  $\text{CO}_2 \text{A}^+$  formation. These ions could have been formed either directly in a displacement channel of the  $\text{CO}_2 \cdot \text{CO}_2^+ + \text{A}$  reaction, or by the formation of  $\text{A}^+$  via charge transfer followed by the third body assisted attachment of  $\text{A}^+$  to carbon dioxide. The  $\text{CO}_2 \text{A}^+$  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  $\text{A}_2^+$  ions are observed in the reactions with  $\text{SO}_2$ ,  $\text{C}_2\text{H}_2$ ,  $\text{COS}$  and  $\text{CS}_2$ , whereas with  $\text{NH}_3$  the product is  $\text{NH}_4^+$  and reaction (4) is a bimolecular process. With  $\text{C}_2\text{H}_2$  one has in addition to reaction (4) the bimolecular formation of the products  $\text{C}_4\text{H}_3^+$  and  $\text{C}_4\text{H}_3^+$  as discussed previously [1]. Oxygen does not enter into either reaction (3) or (4) at the reactant densities applied.

To clarify the situation concerning  $\text{CO}_2 \text{A}^+$  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  $\text{SO}_2$  as the neutral reactant. The formation of the products  $\text{SO}_2^+$ ,  $\text{CO}_2 \text{SO}_2^+$ , and  $(\text{SO}_2)^+$  is clearly displayed. The  $\text{SO}_2 \text{H}^+$  ion results from reaction of  $\text{SO}_2^+$  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  $\text{CO}_2^+$  ions undergo conversion to  $\text{CO}_2 \cdot \text{CO}_2^+$ . A large portion of the  $\text{SO}_2^+$  thus derives from the reaction of  $\text{CO}_2^+$  with  $\text{SO}_2$ . 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  $\text{CO}_2^+$  with several A molecules were obtained from the exponential decay of the  $\text{CO}_2^+$  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

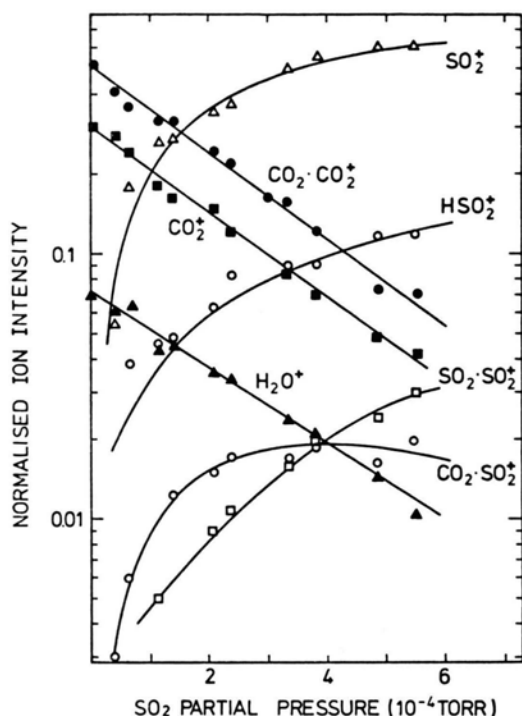


Fig. 1. Semilog plot of normalised ion intensities observed for  $\text{SO}_2$  in  $\text{CO}_2$  at 0.29 torr total pressure. Solid lines were calculated as outlined in the text, using the rate coefficients given in Table 1.

(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  $\text{CO}_2^+$  and  $\text{CO}_2\text{CO}_2^+$  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  $\text{SO}_2$  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  $\text{SO}_2$  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  $\text{CO}_2\text{A}^+$  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  $\text{SO}_2$  and less for the other reactants. Thus, most of the  $\text{CO}_2\text{A}^+$  ions are formed via third body addition of  $\text{A}^+$  to  $\text{CO}_2$ , reaction (2). The values for  $k_2$  given in Table 1 for the low pressure condition

Table 1. Reactions of  $\text{CO}_2\text{CO}_2^+$ ,  $\text{CO}_2\text{A}^+$ , and  $\text{A}^+$  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		$k_1$		$k_2$		$k_3$		$k_4$	
			lp	hp	lp	hp	lp	hp	lp	hp
$\text{SO}_2$	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)
$\text{O}_2$	0.94	0.06	2.0(−10)	1.8(−10)	1.2(−29)	1.2(−29)	—	—	—	—
$\text{C}_2\text{H}_2$	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)
$\text{COS}$	1.00	—	1.5(−9)	1.1(−9)	—	2.0(−30)	—	5.0(−10)	7.1(−27)	5.0(−27)
$\text{NH}_3$	0.94	0.06	8.9(−10)	6.0(−10)	1.4(−29)	1.3(−29)	8.5(−10)	8.0(−10)	see text	
$\text{CS}_2^a$	1.00	—	1.2(−9)	1.0(−9)	—	—	—	—	6.3(−27)	6.4(−27)

<sup>a</sup> 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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