

# Kinetics of the heterogeneous reaction $\text{CO} + \text{O} \rightarrow \text{CO}_2$ on inorganic oxide and water ice surfaces: Implications for the Martian atmosphere

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## **Abstract**

The heterogeneous reaction  $\text{CO} + \text{O} + \text{CO}_2$  on water ice and various inorganic oxide ( $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$ ,  $\text{CaO}$ ,  $\text{MgO}$ , and  $\text{TiO}_2$ ) surfaces has been investigated in order to evaluate the proposition that this heterogeneous reaction may contribute to the  $\text{CO}_2$  stability in the Martian atmosphere. The reaction probabilities were measured at both 196 K and 294 K by using a fast flow-tube reactor coupled to an electron-impact ionization mass spectrometer. The atomic oxygen was generated by passing a mixture of  $\text{O}_2$  and He through a microwave discharge at a side-arm inlet and then allowed to react with CO over these substrates in the reactor. The reaction product,  $\text{CO}_2$ , was monitored as a function of time at the downstream end of the flow-tube reactor. The measured reaction probabilities were determined from the growth rates of  $\text{CO}_2$  signal and were found to range from  $1.6 \times 10^{-7}$  to  $1.0 \times 10^{-5}$ . If we adopt a typical reaction probability of  $5 \times 10^{-7}$  for the heterogeneous  $\text{CO} + \text{O}$  reaction on Martian aerosols at 196 K, a simple calculation suggests that this mechanism plays a negligible role in  $\text{CO}_2$  recycling as compared to that of the homogeneous  $\text{CO} + \text{OH}$  reaction.

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## Introduction

The abundance of atmospheric CO<sub>2</sub> in Mars is known to be about 95.3%, despite continuous photolysis of CO<sub>2</sub>,



The gas-phase associative reaction,

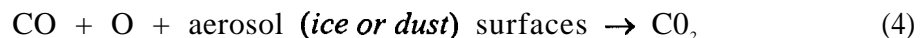


is very slow because it is spin-forbidden. In order to account for the apparent stability of CO<sub>2</sub> in the Martian atmosphere, it has been suggested that OH radicals play a key role in maintaining the balance of CO<sub>2</sub> through the reaction



While two theoretical models developed earlier [*McElroy and Donahue*, 1972; *Parkinson and Hunten*, 1972] are successful in explaining the stability of CO<sub>2</sub> in the atmosphere, they have been criticized for unrealistically high values of the eddy diffusion coefficient ( $K > 10^8 \text{ cm}^2 \text{ S}^{-1}$ ) or water vapor mixing ratio (of the order of 500 ppm), respectively, used in their models.

*Atreya and Blamont* [1990] have proposed that the surface-catalyzed recombination of CO and O atoms on the surfaces of Martian aerosols or water ice clouds,



could significantly contribute to CO<sub>2</sub> recycling in order to resolve the difficulties associated with the previous models. Their suggestion was prompted by the observation of extensive dust aerosols and water ice clouds [*Blamont et al.*, 1989], and a CO hole above Martian volcano regions [*Rosenqvist et al.*, 1990]. Adding to this hypothesis, *Leu*

*et al.* [1992] have reported the adsorption measurements of CO on water ice and inorganic oxide surfaces and suggested that the above heterogeneous process could be a potentially dominant pathway for CO oxidation in the lower Martian atmosphere if the adsorption of CO is the rate-limiting step.

In a recent model study, on the other hand, *Atreya and Gu* [1994] have pointed out that the discrepancy between the photolytic CO<sub>2</sub> loss and the CO<sub>2</sub> reproduction by reaction 3 could be significantly reduced by a factor of 40%. This discrepancy exists in the classical models [McElroy and Donahue, 1972; Parkinson and Hunten, 1972] when *Atreya and Gu* employ the latest revised laboratory data of reaction rate constants and the absorption cross section of CO<sub>2</sub>. According to their model, reaction 4 does not seem to be necessary to meet the balance of CO<sub>2</sub> because the model already overestimates the CO<sub>2</sub> production rate by 40 %. However, being a one-dimensional model for globally and seasonally averaged conditions, their model can not rule out the possible roles of any heterogeneous chemical processes, such as reaction 4. The need for the quantitative evaluation of possible heterogeneous processes is still warranted.

In this article we report the reaction probability ( $\gamma_0$ ) measurements of the heterogeneous CO + O recombination (reaction 4) on water ice and various inorganic oxides substrates, which mimic the Martian aerosol materials, using a fast flow-tube reactor coupled to a quadruple mass spectrometer. First we will present the experimental apparatus and data analysis; then we will discuss the measurement of the  $\gamma_0$  values. Finally, we will compare both homogeneous and heterogeneous processes (reactions 2-4) potentially important for maintaining the stability of CO<sub>2</sub> in the Martian atmosphere.

## Experimental Method

The reaction probability measurements were performed by using a fast flow-tube reactor coupled to an electron-impact ionization mass spectrometer (EIMS). The apparatus has been described in detail elsewhere. [Chu *et al.*, 1993; Leu *et al.*, 1997] Briefly, a Pyrex flow tube of 2.5 cm inside diameter and 40 cm in length was used for inorganic oxide coating. Atomic oxygen was generated by passing O<sub>2</sub> (1-2 % by volume) in a helium carrier through a microwave discharge at a side-inlet of the flow reactor. The reactant CO was admitted into the flow reactor through a movable inlet and allowed to react with the atomic oxygen on the substrate-coated reactor surface. The typical concentrations of CO and O employed in this study were in the range of (1-5) x 10<sup>14</sup> molecules cm<sup>-3</sup> and (0.2- 1.7) x 10<sup>14</sup> atoms cm<sup>-3</sup>, respectively. The flow velocities were measured to be about 800-1200 cm/s which corresponded to a reaction time of 33-50 ms. The total pressure in the flow tube was maintained around 1 Torr throughout the whole experiments. The reaction product, CO<sub>2</sub>, was measured at the downstream end of the flow reactor by the mass spectrometer as a **function** of the CO inlet position. The temperature of the flow reactor was maintained at either 196 K or 294 K for most of the experiments.

Table 1 lists the oxide materials which were coated on the inner wall of the flow reactor in this study. The mass of the coated substrate was determined by weighing the flow tube before and after the coating. The specific surface areas were determined from BET (Brunauer, Emmett, and Teller) analyses of gas adsorption isotherms. The experimental procedures for the preparation of these substrates are given in the footnotes of Table 1.

The first-order rate constants ( $k_o$ ) of the heterogeneous CO + O reaction was determined by using the following equation

$$k_o = \frac{d[\text{CO}_2]/dt}{[\text{O}]} \quad (5)$$

where  $d[\text{CO}_2]/dt$  is the increase of  $\text{CO}_2$  concentration as a function of reaction time and  $[\text{O}]$  is the average concentration of atomic oxygen. The reaction probability was defined as

$$\gamma_o = \frac{4k_o}{\varpi_o \text{ (S/V)}} \quad (6)$$

where  $\varpi_o$  is the average velocity of atomic oxygen and (WV) is the ratio of the reactive surface area to the reactor volume. The geometric area of the flow reactor was assumed to be the reactive surface area in this study. The concentrations of O atoms were determined by monitoring the intensity change of the  $\text{O}_2$  mass signal ( $m/e = 32$ ) upon the discharge,  $[\text{O}] = 2 \{[\text{O}_2]_{\text{discharge off}} - [\text{O}_2]_{\text{discharge on}}\}$ . Typically, the average oxygen dissociation efficiency at the discharge source was about 70%. Since there was an atomic oxygen concentration gradient along the flow tube due to the wall recombination, the average value of  $[\text{O}]$  measured at the end of the discharge tube (upstream end) and  $[\text{O}]$  at the mass spectrometer sampling orifice (downstream end) was used to calculate  $k_o$  in equation 5. The reaction probabilities are expressed in terms of  $\gamma_o$  (not  $\gamma_{\text{CO}}$ ) in this study because the heterogeneous CO+ O reaction is rate limited by the atomic oxygen collision frequency.

## Results and Discussion

A typical set of the data is shown in Figure 1. The  $\text{CO}_2$  signal intensity increase upon exposure of CO over the  $\text{TiO}_2$  substrate is measured as a function of the CO inlet

position, The experimental conditions are  $P = 1.0$  Torr,  $v = 1230$  cm/s,  $[CO] = 3.3 \times 10^{14}$  molecules  $cm^{-3}$ ,  $[O] = 7.2 \times 10^{13}$  atoms  $cm^{-3}$ , and  $T = 294$  K. In this experiment a thin film of  $TiO_2$  (a) is prepared on the inside wall of the flow reactor. The  $CO_2$  production rate,  $d[CO_2]/dt$ , is determined to be  $2.9 \times 10^{12}$  molecules  $cm^{-3} s^{-1}$  and a value of  $\gamma_o = 1.6 \times 10^{-6}$  is then calculated on the basis of eq.(6).

The results of reaction probability measurement for the heterogeneous  $CO + O \rightarrow CO_2$  reaction on water ice and inorganic oxide surfaces are summarized in Table 2. The average values of  $\gamma_o$  range from  $1.6 \times 10^{-7}$  to  $1.0 \times 10^{-5}$ . On the surfaces of  $TiO_2$  (b) substrate the reaction is particularly active and  $\gamma_o$  was found to be as large as  $1 \times 10^{-5}$  at 294 K. This substrate was supplied from **Degussa** Corp. and contains primarily **anatase**. At 196 K,  $\gamma_o$  values are about the same within experimental uncertainties for all substrates. We performed a control experiment which the measurement was conducted over a **halocarbon** grease surface and the enhancement of the  $CO_2$  signals was found to be negligible. In another control experiment we did not find any  $CO_2$  production from the heterogeneous  $CO + O_2$  reaction over any oxide surfaces in the absence of microwave discharge. In the present study we estimate the detection limit for  $\gamma_o$  is about  $1 \times 10^{-7}$ .

We also estimate the production rates of  $CO_2$  from the homogeneous three-body recombination (reaction 3) under the present experimental conditions and find the rates are smaller than  $1 \times 10^9$  molecules  $cm^{-3} s^{-1}$ , which accounts for only 0.1 % of the observed  $CO_2$  production rates from reaction (4). Thus, the contribution from reaction 3 can be ignored.

It should be noted that the present  $\gamma_0$  values are considered to be upper limits since they are calculated on the basis of the geometric area of the flow reactor. If we use the BET surface areas of these substrates listed in Table 1 and the mathematical model of surface reaction and pore diffusion previously developed in our laboratory [Keyser *et al.*, 1991; Keyser *et al.*, 1993], the reaction probabilities could be much smaller than the present values. [Leu, *et al.*, 1992] Furthermore, significant excited molecules  $O_2(a)$  may be generated in the microwave discharge of  $O_2$  in a helium carrier [Simonaitis and Leu, 1985] and could contribute to the production of  $CO_2$  through homogeneous and heterogeneous processes. However, it is well known that the **reactivities** for the reactions of  $O_2(a)$  with many atmospheric molecules are not very efficient [JPL, 1994]. We conclude that this contribution is negligible.

Since the oxide substrates were exposed to air during the preparation, the substrate surface might be covered by water vapor and  $CO_2$  to some extent. The possible effects of surface deactivation on the heterogeneous reaction were investigated by comparing reaction probabilities measured before and **after** a heat treatment (500 K for a few hours) of the oxide coating *in vacuo*. The  $\gamma_0$  values were found to increase by a factor of 3 for  $TiO_2$  and a factor of 6 for  $Fe_2O_3$  after the heat treatment, respectively. However, we observed a rapid decrease of the  $CO_2$  production rates from its initial value in successive measurements. Since similar trends are expected for other oxides, the  $\gamma_0$  values listed in Table 2 would increase by several times for cleaner oxide surfaces. Aerosol surfaces in the Martian atmosphere are subject to continuous adsorption and resorption of water vapor and carbon dioxide, and thus, clean surfaces are not expected to exist.

We believe that the inorganic oxides adopted in the present study may mimic the actual Martian aerosol material; thus, they can be a useful approximation [Leu *et al.*, 1992]. The actual mineralogy of inorganic oxide aerosols is probably more complex. The major elemental compositions of sediments and soils in Mars, which have been determined by the Viking lander X-ray fluorescence spectrometers [Clark *et al.*, 1982] and the Mars 5 and Phobos 2  $\gamma$ -ray spectrometers [Surkov *et al.*, 1989], were O, Si, Fe, Al, Mg, Ca, Ti, and K in the order of abundance. Since the measured  $\gamma_0$  values are quite insensitive to the kind of solid substrates at 196 K, a typical  $\gamma_0$  value of  $5 \times 10^{-7}$  is adopted for all available aerosol surfaces in the Martian atmospheric conditions,

We compare the heterogeneous CO oxidation (reaction 4) rates and the calculated homogeneous CO oxidation (reactions 2 and 3) rates in the Martian atmosphere as a function of altitude [Anbar *et al.*, 1993]. The concentration profiles of CO, O, and OH are taken from modeling results [Yung *et al.*, 1988]. Surface areas are estimated from the data of ice and dust particle concentrations and the mean particle radius in the Martian atmosphere, [Michelangeli *et al.*, 1993] The heterogeneous reaction rates ( $R_{hetero}$ ) for reaction 4 are calculated by using the equation

$$R_{hetero} = 1/4\{[O]\varpi_0\gamma_0(S/V)\} \quad (7)$$

where (S/V) is the total aerosol (ice + dust) surface area per volume. The results are summarized in Table 3. These results show that  $R_{hetero}$  is negligibly small as compared to the homogeneous CO + OH reaction rate (reaction 3). Moreover, it is even smaller than the homogeneous CO + O recombination reaction rate (reaction 2) in the lower atmosphere.



In conclusion, the heterogeneous CO + O recombination reaction studied in this work does not seem to play any significant role in the chemistry of the Martian atmosphere; however, it should be noted that other possible heterogeneous processes remain to be studied. One possible candidate is the **photocatalytic** CO oxidation [*Thevenet et al.*, 1974] on photoactive Martian aerosols (e.g., Fe<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub>) [*Huguenin et al.*, 1977]. A similar calculation to that of Table 3 shows that the rate of the heterogeneous photocatalytic process could be about 10 % of the homogeneous reaction rate in the lower Martian atmosphere by simply assuming that 0.5 % of the available dust aerosol surface area is TiO<sub>2</sub> and that the corresponding reaction probability on photoilluminated TiO<sub>2</sub> is assumed to be  $1 \times 10^{-6}$ . This suggests that the photocatalytic process could be a potentially important mechanism for the oxidation of CO in the Martian atmosphere. Further laboratory work on this reaction mechanism may be necessary.

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**Table 1.** List of solid substrates coated on Pyrex flow reactor.

Substrate	Mass (g)	BET Surface Area (m <sup>2</sup> /g)	Supplier	Notes
Water Ice	14.3			1
SiO <sub>2</sub>	0.82	299	Johnson Matthey Chem.	2
Al <sub>2</sub> O <sub>3</sub> (a)	0.79	9.75	J. T. Baker	2
Al <sub>2</sub> O <sub>3</sub> (b)	0.03	110	Degussa (Alumina C)	2,4
Fe <sub>2</sub> O <sub>3</sub>	0.03	9.14	J. T. Baker	3
Fe <sub>3</sub> O <sub>4</sub>	1.06	2.31	Johnson Matthey Chem.	2
TiO <sub>2</sub> (a)	0.08	7.18	J. T. Baker	3
TiO <sub>2</sub> (b)	0.12	51.6	Degussa (TiO <sub>2</sub> P25)	3,5
MgO	0.10	40.8	Johnson Matthey Chem.	2
CaO	0.43	5.08	Johnson Matthey Chem.	2

## Notes:

1. A flat bed of ice was prepared in a bottom-flattened flow tube. The geometric surface area of ice was 71 cm<sup>2</sup>.
2. Metal oxide powders except Fe<sub>3</sub>O<sub>4</sub> were baked at 250 °C for 3 hr in air. For Fe<sub>3</sub>O<sub>4</sub>, the substrates were deposited on Pyrex surface which was **pre-coated** with **halocarbon** grease. The geometric surface area of the flow-tube reactor was 313 cm<sup>2</sup>. Fe<sub>3</sub>O<sub>4</sub> powder was not subject to heat-treatment due to oxidation in air.
3. Metal oxide coatings were deposited directly on Pyrex surface **from** their concentrated aqueous suspensions (20 g/L), dried, and then baked at 250 °C for 3 hr in air.
4. primarily  $\gamma$ -alumina.
5. primarily anatase.

**Table 2.** Summary of the reaction probability ( $\gamma_0$ ) measurements for the heterogeneous reaction  $\text{CO} + \text{O} + \text{CO}_2$  on water ice and inorganic oxide surfaces.

Surface	$\gamma_0$ (196 K)	$\gamma_0$ (294 K)
Water Ice	$8.9 (\pm 7.0) \times 10^{-7}$	
Pyrex	$4.6 (\pm 2.1) \times 10^{-7}$	$5.2 (\pm 2.9) \times 10^{-7}$
$\text{SiO}_2$	$4.6 (\pm 0.7) \times 10^{-7}$	$4.8 (\pm 1.8) \times 10^{-7}$
$\text{Al}_2\text{O}_3$ (a)	$6.1 (\pm 3.7) \times 10^{-7}$	$1.1 (\pm 0.5) \times 10^{-6}$
$\text{Al}_2\text{O}_3$ (b)		$5.2 (\pm 2.8) \times 10^{-7}$
$\text{Fe}_2\text{O}_3$	$2.9 (\pm 1.3) \times 10^{-7}$	$6.0 (\pm 2.0) \times 10^{-7}$
$\text{Fe}_3\text{O}_4$	$1.6 (\pm 0.3) \times 10^{-7}$	$4.9 (\pm 1.4) \times 10^{-7}$
$\text{TiO}_2$ (a)	$4.0 (\pm 2.5) \times 10^{-7}$	$1.0 (\pm 0.3) \times 10^{-6}$
$\text{TiO}_2$ (b)	$4.3 (\pm 2.6) \times 10^{-7}$	$1.0 (*0.4) \times 10^{-5}$
MgO	$9.2 (\pm 5.5) \times 10^{-7}$	$8.7 (\pm 5.7) \times 10^{-7}$
CaO	$7.7 (\pm 2.3) \times 10^{-7}$	$6.2 (\pm 4.3) \times 10^{-7}$

Notes. These are average values over 3 or more experiments. The error limit represents one standard deviation.

**Table 3.** Comparison of the heterogeneous ( $\text{CO} + \text{O} \rightarrow \text{CO}_2$ ) reaction rates,  $R_{\text{hetero}}$ , and the homogeneous ( $\text{CO} + \text{O} + \text{M} \rightarrow \text{CO}_2$  and  $\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H}$ ) reaction rates,  $R_{\text{homo}}$ , in the Martian atmosphere.

Altitude (km)	[CO] <sup>a</sup> ( $\times 10^{13} \text{ c m}^{-3}$ )	[O] <sup>a</sup> ( $\times 10^9 \text{ c m}^{-3}$ )	[OH] <sup>a</sup> ( $\times 10^4 \text{ c m}^{-3}$ )	Surface Area <sup>b</sup> ( $\times 10^{-6} \text{ cm}^2/\text{cm}^3$ )		$R_{\text{hetero}}$ <sup>a</sup> ( $\text{cm}^{-3} \text{ s}^{-1}$ )		$R_{\text{horn.}}$	<sup>horn.</sup>
				Case I <sup>c</sup>	Case II <sup>c</sup>	Case I <sup>c</sup>	Case II <sup>c</sup>	(CO + O) ( $\text{cm}^{-3} \text{ s}^{-1}$ )	(CO + OH) ( $\text{cm}^{-3} \text{ s}^{-1}$ )
5	9	0.04	2	8.1	10	2	3	90	$3 \times 10^7$
10	5	0.06	3	1.7	2.2	0.7	0.8	40	$2 \times 10^5$
15	3	0.1	5	1.3	4.4	1	4	20	$2 \times 10^5$
20	2	1	30	2.5	25	20	200	60	$1 \times 10^4$
25	1	2	20	0.16	6.3	2	80	30	$3 \times 10^5$
30	0.7	3	10	0.027	7.3	0.5	100	9	$1 \times 10^5$
40	0.2	4	1	0.00002	42	$5 \times 10^4$	$1 \times 10^3$	0.5	$3 \times 10^3$
50	0.05	3	0.07	-	12	-	200	0.01	50
60	0.01	2	0.007	-	3.7	-	50	$2 \times 10^4$	1

Notes:

<sup>a</sup> CO, O, and OH concentration profiles are taken from *Yung et al. [1988]*.

<sup>b</sup> Surface areas are calculated by using the model data of the total (ice+ dust) particle concentrations and the mean particle radii. It is assumed that the dust and ice particles have the same mean radii as a function of altitude. These data are taken from *Michelangelo et al. [1993]*.

<sup>c</sup> Two different cases of the Martian aerosol condition are considered. Case II includes the external flux of meteoritic dust into the Martian atmosphere while Case I does not. For details, refer to *Michelangelo et al. [1993]*.

<sup>d</sup> A typical reaction probability,  $y_o$ , of  $5 \times 10^{-7}$  is adopted for all surfaces (ice+ dust) in this calculation.

Figure 1. The measurement of the  $\text{CO}_2$  production rate from the  $\text{CO} + \text{O}$  reaction on  $\text{TiO}_2$  (a) substrate at 294 K. See text for detailed experimental conditions.

