

ARAS Measurements on the Thermal Decomposition of CO₂ Behind Shock Waves

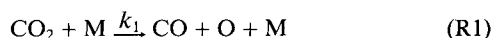
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The dissociation rate coefficient of CO₂ has been measured behind reflected shock waves in the temperature range $2400 \leq T \leq 4400$ K at pressures $1.2 \leq p \leq 2.0$ bar. By the use of the atomic resonance absorption spectroscopy, the formation of O atoms could directly be observed in the postshock reaction zone. The experiments have been performed in mixtures of CO₂ highly diluted in argon. The initial CO₂ concentrations varied from 10 to 5000 ppm. The Arrhenius expression for the thermal decomposition of CO₂, $\text{CO}_2 + \text{M} \xrightarrow{k_1} \text{CO} + \text{O} + \text{M}$ was found to be $k_1 = 3.65 \times 10^{14} \exp(-52,525 \text{ K}/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. The effect of impurities was minimized by keeping background pressures in the shock tube below 5×10^{-7} mbar.

Introduction

IN the past, numerous investigators have studied the decomposition of carbon dioxide



in shock tubes,¹⁻⁷ which is, for example, of interest in hypersonic flows over carbonaceous surfaces or for Mars missions. A review⁸ of these and other studies have shown that the activation energy of this reaction seems anomalously low. The observed activation energies⁸ varied from 300–460 kJ mole⁻¹, whereas the bond dissociation energy is $D = 525$ kJ mole⁻¹ at 3500 K. The obtained rate coefficients and the corresponding experimental conditions and techniques of previous investigations are given in Table 1. Because of the still considerable doubt as to the effect of impurities and the spin-forbidden nature of the dissociation, there is no recommendation made by Baulch et al.⁸

We have reinvestigated the dissociation of CO₂ behind reflected shock waves in the temperature range 2400–4400 K by measuring the reaction product O atoms using the atomic resonance absorption spectroscopy (ARAS). It has been shown that ARAS is a very sensitive and powerful technique to measure atomic species such as O atoms under conditions of high temperature and low reactant concentrations (see, for example, Refs. 9–15). In the present investigation, CO₂ mixtures highly diluted in argon were shock heated and O atoms were monitored in the reaction zone behind reflected shock waves in the temperature range 2400–4400 K. Because of the very high dilution of the reactant in argon, the chemistry can be assumed to be decoupled from transport processes. Simple kinetic interpretation of the measured time-dependent atom concentrations is made possible.

Experiments

The experiments were conducted behind reflected shock waves in a stainless steel shock tube of 79 i.d mm. The internal surface of the tube had been specially prepared for ultrahigh

vacuum purposes. It can be heated and evacuated through a special end plate valve by a forepump, a turbomolecular pump, and a liquid nitrogen-cooled titanium sublimation pump to pressures down to about 10^{-8} mbar. The residual gas, which is practically free of hydrocarbons, is controlled by a quadrupole mass spectrometer. The gas mixing system and the storage cylinder for the gas mixtures are monitored in a similar way. A detailed description of the experimental setup is given in Ref. 10.

Mixtures of CO₂ with argon were prepared in a special stainless steel cylinder by partial pressures using calibrated diaphragm-type pressure gauges. The cylinder could be heated and evacuated using a secondary pumping unit. Because of the high sensitivity of the ARAS detection technique, all gases used were of ultrahigh purity: AR 99.9999% and CO₂ 99.995%. The initial concentration of CO₂ in argon varied between 10 and 5000 ppm.

Prior to each run, the shock tube was evacuated to a pressure of 5.0×10^{-7} mbar or lower. Initial pressures in the test section were in the range of 10–35 mbar. Diaphragms made of aluminum 50 μm thick were ruptured by increasing the driver gas (H₂) pressure. The incident shock velocity was measured with the help of thin film pressure gauges (placed along the test section at known intervals) and a 20-MHz transient recorder with 8 kB storage. Pure compressed N₂ was used for blowing out the diaphragm pieces. The temperature and pressure behind the reflected shock wave were computed from the measured incident shock speed using one-dimensional shock equations, assuming complete vibrational equilibrium. It is expected that the temperature so calculated is close to the real gas temperature immediately behind the reflected shock, since insignificant corrections are needed for the nonideal shock behavior, because of boundary-layer effects at these gas densities and high temperatures. This assumption is supported by direct optical measurements (done at DFVLR, Stuttgart, and in our laboratory) of the temperatures behind reflected shock waves in gas mixtures highly diluted by monoatomic gases.

The optical system for measuring O atom concentrations was based on a line emission—line absorption technique. The optical arrangement¹⁰ consisted of a microwave discharge lamp, two thin LiF windows mounted flush on both shock tube walls, a 1-m McPherson vacuum uv monochromator, and a special solar blind photomultiplier. The O atom spectral line was excited using mixtures of 1% O₂ diluted in helium, passing through the lamp at pressures of about 6 mbar.

The ARAS measurement technique is applied to measure O atom concentrations at OI triplet at $\lambda = 130.5$ nm. Spectral

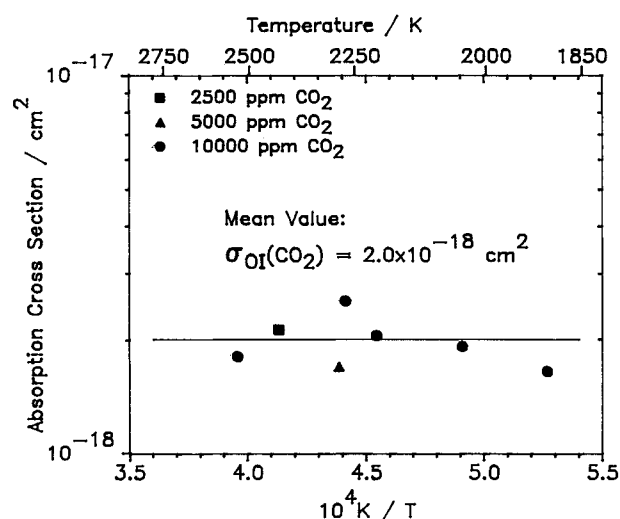
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Table 1 Previous investigations on the thermal decomposition of CO₂

Reference	Conditions	Method	Rate coefficient, cm ³ mol ⁻¹ s ⁻¹
Brabbs et al. ¹	$T = 2550\text{--}2860$ K $p = 11\text{--}21$ bar CO ₂ in argon 3.44–7.02%	UV emission at 351 nm, gas chromatography, reflected shock waves	$3.0 \times 10^{11} T^{0.5} \exp(-43300 \text{ K}/T)$
Davis ²	$T = 3000\text{--}6000$ K $p = 1$ bar CO ₂ in argon 0.5–10%	IR emission at 4.45 μm , incident shock waves	$2.88 \times 10^{11} T^{0.5} \exp(-57600 \text{ K}/T)$
Michel et al. ³	$T = 2800\text{--}4400$ K $p = 2.5\text{--}22.4$ bar CO ₂ in argon 0.19–0.7% CO ₂ in N ₂ 0.2–0.59%	IR emission at 4.4 μm , reflected shock waves	$5.0 \times 10^{14} \exp(-49800 \text{ K}/T)$
Fishburne et al. ⁴	$T = 3000\text{--}5000$ K CO ₂ in argon 1–10%	IR emission at 2.7 and 4.3 μm , incident shock waves	$7.11 \times 10^{11} T^{0.5} \exp(-42500 \text{ K}/T)$
Dean ⁵	$T = 3700\text{--}5000$ K $p = 0.7\text{--}1$ bar	IR emission at 4.22 μm , reflected shock waves	$6.31 \times 10^{13} \exp(-42900 \text{ K}/T)$
Hardy et al. ⁶	$T = 2700\text{--}4300$ K $\rho_t = 0.2\text{--}1.0 \times 10^{-4}$ mole cm ⁻³	IR emission at 4.4 μm and CO + O chemiluminescence at 350 nm, reflected	$4.7 \times 10^{14} \exp(-52840 \text{ K}/T)$
Wagner and Zabel ⁷	$T = 3000\text{--}4000$ K $\rho_t = 0.2\text{--}1.0 \times 10^{-4}$ mole cm ⁻³	shock waves	$5.1 \times 10^{14} \exp(-55560 \text{ K}/T)$

Fig. 1 Measured absorption cross sections of CO₂ for OI-radiation.

shapes of the lines emitted by the resonance lamp are not known precisely as a result of self-absorption, or perhaps self-reversal; therefore, a series of carefully controlled shock wave calibration measurements have been done to relate the measured resonance absorptions to the corresponding O atom concentrations. For O atom calibration, the partial equilibrium of O atoms that can be realized behind reflected shock waves in N₂O/Ar mixtures has been used.¹¹ At temperatures above 2000 K, the N₂O decompose rapidly into N₂ and O, so the measured absorption on the OI triplet at constant level was transformed into the O atom concentration at equilibrium. An O atom

absorption of 50% corresponds to an O atom concentration of 1.6×10^{12} molecules cm⁻³.

Results

Absorption Cross Section of CO₂ for OI-Radiation

The absorption of OI radiation by CO₂ was measured behind reflected shock waves in the temperature range 1900–2530 K at pressures of about 1.85–2.10 bar. Mixtures of 2500, 5000, and 10,000 ppm CO₂ highly diluted in argon were used. All measured absorption cross sections, defined by Lambert-Beer law, are shown in Fig. 1. The best least-squares fit to the data leads to the expression

$$\sigma_{\text{OI}}(\text{CO}_2) = 2.0 \times 10^{-18} \text{ cm}^2 \quad (1)$$

In this temperature range, interference absorption of O atoms, especially at early CO₂ decomposition, is negligible. A concentration and temperature dependence was not observed.

Absorption Measurements in CO₂ Reaction System

The shock tube experiments on CO₂ decomposition were conducted behind reflected shock waves in the temperature range 2400–4000 K at pressures of about 1.2–2.0 bar. A total of 17 individual experiments, with initial mole fractions of CO₂ varied between 10 and 5000 ppm, were conducted and O atom resonance absorptions were measured. The conditions of all of the experiments carried out are listed in Table 2.

The useful temperature range for each investigated mixture was limited at the low-temperature side by the detection limit, and at the high-temperature end by absorption, which had to be less than 85%. A typical absorption profile obtained from O atoms is shown in Fig. 2. The signals are composed of a time-independent part (fast signal increase after incident and

reflected shock wave) that must be referred to the CO_2 absorption and a time-dependent part originated from O atoms produced in the reaction zone.

Using the O atom calibration curve and the absorption cross section of CO_2 , all absorption signals measured can easily be transformed into O atom concentration profiles. Typical examples of O atom concentrations measured behind reflected shock waves in CO_2/Ar mixtures are given in Fig. 3. The experimental uncertainties of O atom concentrations are of the order of $\pm 20\%$. Under the present experimental conditions, O atom concentrations increase in all cases linearly with time, with a tendency to level off due to secondary reactions.

Discussion

The kinetics of the CO_2 reaction system can be described by the reaction mechanism and the corresponding forward rate coefficients given in Table 3. The reverse rate coefficients were obtained from the reaction equilibrium constants, calculated from the JANNAF thermochemical data.¹⁶ A simple analytical solution of the time-dependent O atom concentration in the reaction zone can be derived from the reaction scheme, assuming that reaction R1 is the dominant path for the O atom production at early reaction time. For this reason, the initial slope of the measured O atom profiles was used to determine the rate coefficient of the CO_2 decomposition by using the following expression:

$$k_{\text{CO}_2, \text{M}} = \frac{d[\text{O}]/dt}{[\text{CO}_2]_0[\text{M}]_0} \quad (2)$$

Table 2 Experimental conditions and inferred rate coefficients for the CO_2 decomposition

T/K	p/bar	$[\text{CO}_2]/\text{ppm}$	$k_{\text{CO}_2, \text{M}}/\text{cm}^3 \text{ mole}^{-1} \text{ s}^{-1}$
3689	1.48	10	1.89×10^8
3922	1.32		5.29×10^8
4385	1.21		1.35×10^9
2944	1.49	100	1.95×10^7
3383	1.54		9.88×10^7
3569	1.41		1.76×10^8
2416	1.97	1000	3.26×10^5
2619	1.88		3.02×10^5
2711	1.81		1.08×10^6
2832	1.75		4.50×10^6
2975	1.66		7.83×10^6
2467	1.74	2500	1.59×10^5
2649	1.79		7.10×10^5
2810	1.74		2.92×10^6
2413	2.00	5000	3.57×10^4
2575	1.87		2.64×10^5
2846	1.78		2.27×10^6

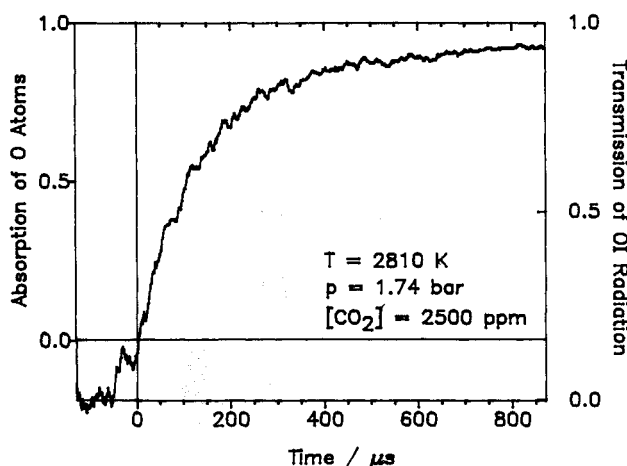


Fig. 2 Typical absorption profile of O atoms at $\lambda = 130.5 \text{ nm}$.

with $\text{M} = \text{argon}$. The example in Fig. 3 shows the nearly linear increase of the measured O atoms. Results of all of the 17 individual experiments are summarized in the last column of Table 2 and in Fig. 4. A least-squares fit to the measured $k_{\text{CO}_2, \text{M}}$ data leads to the Arrhenius expression

$$k_{\text{CO}_2, \text{M}} = 3.65 \times 10^{14} \exp(-52525 \text{ K}/T) \text{ cm}^3 \text{ mole}^{-1} \text{ s}^{-1} \quad (3)$$

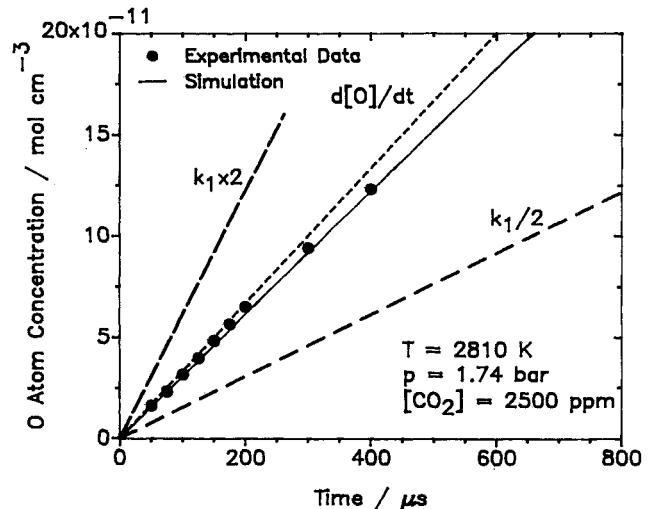


Fig. 3 Example of measured and computed O atom concentrations in shock-heated CO_2/Ar mixtures.

Table 3 Simplified reaction mechanism and kinetic data for the CO_2 reaction system

Reaction	Rate coefficient, $\text{cm}^3 \text{ mole}^{-1} \text{ s}^{-1}$	Ref.
R1 $\text{CO}_2 + \text{M} \rightarrow \text{CO} + \text{O} + \text{M}$	$3.65 \times 10^{14} \exp(-52525 \text{ K}/T)$	see text
R2 $\text{CO}_2 + \text{O} \rightarrow \text{CO} + \text{O}_2$	$1.70 \times 10^{13} \exp(-26500 \text{ K}/T)$	8
R3 $\text{O}_2 + \text{M} \rightarrow \text{O} + \text{O} + \text{M}$	$9.65 \times 10^{14} \exp(-61400 \text{ K}/T)$	14

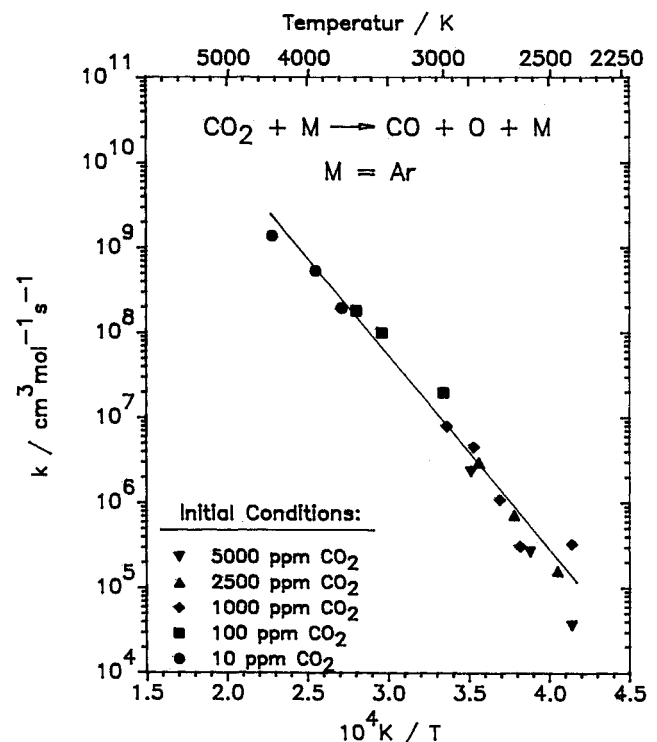


Fig. 4 Arrhenius diagram of the measured rate coefficient for the reaction $\text{CO}_2 + \text{M} \rightarrow \text{CO} + \text{O} + \text{M}$.

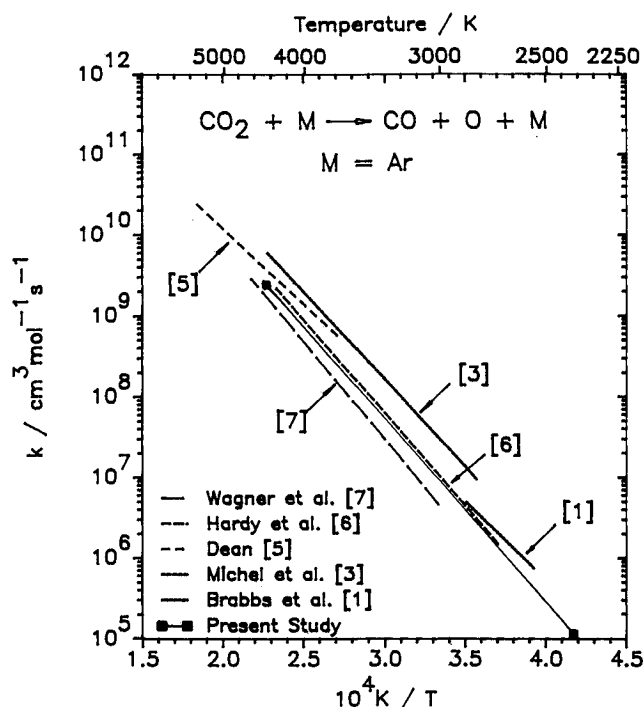


Fig. 5 Comparison of shock tube measurements of the rate coefficient for the CO₂ decomposition.

Table 4 Rate coefficient and weak collision factors for the dissociation of CO₂

T/K	$k_{\text{CO}_2, \text{M}}, \text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$	$k_{\text{CO}_2, \text{M}}^{\text{sc}}, \text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$	β_c
2400	1.14×10^5	1.97×10^6	0.058
2600	6.14×10^5	1.36×10^7	0.045
2800	2.60×10^6	7.04×10^7	0.037
3000	9.09×10^6	2.88×10^8	0.032
3200	2.72×10^7	9.78×10^8	0.028
3400	7.13×10^7	2.84×10^9	0.025
3600	1.68×10^8	7.27×10^9	0.023
3800	3.63×10^8	1.67×10^{10}	0.022
4000	7.24×10^8	3.51×10^{10}	0.021
4200	1.35×10^9	6.81×10^{10}	0.020
4400	2.39×10^9	1.24×10^{11}	0.019

with a percentage standard deviation due to the experimental scatter of about $\pm 15\%$.

Computer simulations of the CO₂ decomposition based on the reaction scheme in Table 3 show in all cases a nearly perfect agreement between calculated and measured O atom profiles during the reaction time of about 800 μs . Figure 3 also shows the sensitivity of reaction R1 to the computed O atom concentrations when the rate coefficient k_1 is multiplied or divided by a factor of two. Figure 5 compares the Arrhenius fit of the carbon dioxide dissociation obtained in this work with those reported by previous investigators (see, for example, Table 1) in the overlapping temperature range.

The present result for k_1 is in agreement with estimates obtained from the weak collision unimolecular reaction rate theory.¹⁷ For the present experimental conditions, reaction R1 is within the low-pressure regime. According to the weak collision theory, the dissociation rate coefficient for this regime can be expressed as

$$k_1 = \beta_c k_1^{\text{sc}} \quad (4)$$

where k_1^{sc} is the strong collision rate coefficient and β_c is the weak collision factor. The strong collision rate coefficients and the weak collision factors were computed for different temperatures in the range of the present study. The values of β_c , listed in Table 4, show that the expected temperature behavior and the absolute quantity seem to be in reasonable agreement with the experimental values for the decomposition of similar molecules.

Acknowledgment

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