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Rate Constant of the Gas-Phase Reaction between Fe Atoms and CO_2

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Abstract—The rate constant of the gas-phase reaction $Fe(a^5D_4) + CO_2$ at 1180–2380 K and a total gas density of $(7.0–10.0) \times 10^{-6}$ mol/cm^3 behind incident shock waves is $k(Fe + CO_2) = 1.4 \times 10^{14.0 \pm 0.3}\exp[-(14590 \pm 1100)/T]$ cm^3 mol^{-1} s^{-1}, as determined by resonance atomic absorption photometry. Using thermochemical data available from the literature, the rate constant of the reverse reaction was calculated to be $k(Fe + CO) = 9.2 \times 10^{11.0 \pm 0.3} (T/1000)^{0.57}\exp[-(490 \pm 1100)/T]$ cm^3 mol^{-1} s^{-1}. The results are compared with data reported earlier.

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Gas-phase reactions of transition-metal atoms, which are of considerable interest to researchers engaged in some applied areas, including combustion control [1, 2], and in developing the theory of atomic reactivity [3–5], are being extensively investigated by various experimental methods [4–12].

Earlier [13], we reported the rate constant of the reaction between $Fe(a^5D_4)$ atoms and CO_2 measured at 1300–2380 K, without presenting experimental details or primary data. In a recent study devoted to the same reaction [14], the formation of CO molecules was monitored along with the disappearance of Fe atoms.

In the study reported here, we processed primary experimental data more carefully than we did before [13]. In particular, we more correctly took into account the time resolution of the measuring optical system (~3 μs) and augmented the experimental data array with data for pure CO_2. In addition, the temperature range was extended down to 1180 K.

EXPERIMENTAL

Measurements were made behind incident shock waves using the setup described in [6]. The source of radiation at the resonance wavelength of iron atoms, $\lambda = 344.6$ nm, was a ball-shaped lamp excited with an RF discharge. This wavelength was selected by a DMR-4 double monochromator. The photodetector was an FEU-39A photomultiplier. Gas mixtures consisted of 0.0005% pentacarbonyliron (PCI), which served as the source of iron atoms, and pure CO_2 or 13% CO_2 + Ar (99.999% purity). Measurements were taken between 1180 and 2380 K at a total gas density of $[M] = (7–10) \times 10^{-6}$ mol/cm^3 in the shock wave.

Because CO_2 was in large excess over Fe, experimental data were fitted to the first-order rate equation. Absorbance was represented in terms of the Lambert–Beer equation [15] with $\gamma = 0.7$ [13]. Without an oxidizer, the signal had the shape of a step with a constant-absorbance plateau. This suggested that PCI underwent rapid decomposition and that there was rapid relaxation between a^5D_J states. It was also possible that there was not any relaxation, because the iron atoms might have acquired a Boltzmannian distribution of energy level populations at the instant they resulted from the thermal decomposition of PCI.

According to Simpson et al. [16], the thermal relaxation time for pure CO_2 and the 13% CO_2 + Ar mixture at experimentally possible pressures is shorter than 1 μs. Therefore, the iron atom oxidation reaction, whose characteristic time is at least 10 μs, took place under equilibrium conditions.

RESULTS AND DISCUSSION

The experimental data presented in Fig. 1a and in the table are described by the following expression, which was obtained by least squares fitting using the Student criterion with a confidence probability of 95%:

$$k(Fe + CO_2) = 1.4 \times 10^{14.0 \pm 0.3}$$
$$\times \exp[-(14590 \pm 1100)/T] \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}.$$

This expression is written under the assumption that the only channel of the interaction between Fe and CO_2 is the reaction

$$Fe + CO_2 \longrightarrow FeO + CO. \qquad (I)$$

The other possible reactions, which are

$$Fe + CO_2 \longrightarrow FeCO_2, \qquad (II)$$

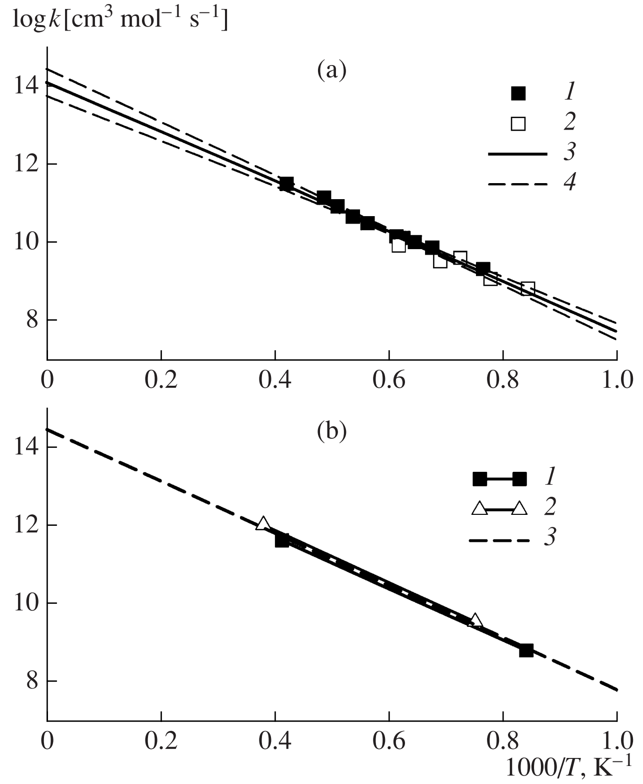

Fig. 1. Temperature dependence of the rate constant of the reaction between Fe and CO_2. (a) Measurements made behind passing shock waves in $Fe(CO)_5 + CO_2 + Ar$ mixtures: (*1*) 0.0005% $Fe(CO)_5$, 13.0% CO_2; (*2*) 0.0005% $Fe(CO)_5$, 100% CO_2; (*3*) linear regression; (*4*) 95% probability confidence interval. (b) Comparison with earlier reported data: (*1*) this work, (*2*) [12], and (*3*) average between *1* and *2*.

$$Fe + CO_2 \longrightarrow FeO_2 + C, \qquad \text{(III)}$$

$$Fe + CO_2 \longrightarrow FeCO + O, \qquad \text{(IV)}$$

$$Fe + CO_2 \longrightarrow FeC + O_2 \qquad \text{(V)}$$

Rate constant ($cm^3\ mol^{-1}\ s^{-1}$) of the gas-phase reaction between $Fe(a^5D_4)$ and CO_2 as a function of temperature for mixtures containing various amounts of CO_2

13% CO_2		100% CO_2	
$1000/T$, K^{-1}	$\log k$ [$cm^3\ mol^{-1}\ s^{-1}$]	$1000/T$, K^{-1}	$\log k$ [$cm^3\ mol^{-1}\ s^{-1}$]
0.765	9.40	0.844	8.89
0.536	10.73	0.778	9.15
0.485	11.20	0.690	9.60
0.419	11.55	0.617	10.01
0.676	9.94	0.725	9.68
0.645	10.08		
0.625	10.19		
0.613	10.23		
0.509	10.98		
0.562	10.56		

are rejected for the following reasons. Concerning reaction (II), to the best of our knowledge, the $FeCO_2$ molecule has never been reported to exist. Moreover, if recombination (II) took place, it would have a zero or negative activation energy, like the other reactions of this class [17]. By contrast, reactions (III)–(V) have exceptionally high activation barriers because their enthalpies are large positive values: $\Delta H^\circ_{3.0}$ = 756.8 kJ/mol (derived from the calculated strength of the Fe–O_2 bond [18] and thermochemical data for CO_2 and C [19]), $\Delta H^\circ_{4.0}$ = 492.2 kJ/mol (derived from the experimental strength of the Fe–CO bond [20, 21] and thermochemical data for CO_2 and O [19]), and $\Delta H^\circ_{5.0}$ = 832.0 kJ/mol (derived from the calculated strength of the Fe–C bond [22] and thermochemical data for CO_2 and O_2 [19]). Another argument in favor of reaction (I) is that the observed activation energy is close to the enthalpy of this reaction ($\Delta H^\circ_{1.0}$ = 117.25 kJ/mol [19]).

Using thermochemical data from [19], we calculated the equilibrium constant of reaction (I). In the temperature range examined (1180–2380 K), it can be represented as

$$K_c(T) = 153.5(1000/T)^{0.57}\exp[-(14100 \pm 1100)/T].$$

Using this constant, we obtained the following expression for the rate constant of the reverse reaction:

$$k(FeO + CO) = 9.2 \times 10^{11.0 \pm 0.3}(T/1000)^{0.57}$$
$$\times \exp[-(490 \pm 1100)/T]\ cm^3\ mol^{-1}\ s^{-1}.$$

In Fig. 1b, we compare our data with data reported in [14]. The average between the expression reported here and in [12] (dashed line) is

$$k(Fe + CO_2) = 2.9 \times 10^{14}\exp(-15155/T)\ cm^3\ mol^{-1}\ s^{-1}.$$

The factors determining the activation energy and the preexponential factor for this reaction and other metal atom–oxidizer reactions remain to be elucidated. As was demonstrated in an earlier publication [10], the resonance model of these processes [23], which is the most developed one, is inconsistent with experimental data in many cases.

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