ISSN 0023-1584, Kinetics and Catalysis, 2012, Vol. 53, No. 5, pp. 543–553. © Pleiades Publishing, Ltd., 2012.
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Thermochemical Parameters and Rate Constants of the Reactions $Fe + O_2 + M \leftrightarrow FeO_2 + M$ and $FeO + O_2 \leftrightarrow FeO_2 + O$

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Received December 26, 2011

Abstract—The thermochemical and kinetic characteristics of the reactions $Fe + O_2 + M \leftrightarrow FeO_2 + M$ (I) and $FeO + O_2 \leftrightarrow FeO_2 + O$ (II) are determined by analyzing experimental data within the framework of a model based on the Rice–Ramsperger–Kassel–Marcus theory with consideration given to excited electronic states of the three isomeric forms of the FeO_2 molecule. A new method for determining the dissociation energy and the height of the energy barrier for the reverse recombination reaction is proposed. The enthalpy of formation of FeO_2, $\Delta_f H°(FeO_2, 0) = 72 \pm 15$ kJ/mol, and the Gibbs energy function of FeO_2, $\Phi°(FeO_2, T)$, J mol^{-1} K^{-1} $= 421.4552 + 59.9779\ln x - 0.0073327x^{-2} + 0.9598x^{-1}$ ($x = T \times 10^{-4}$; $250 < T < 3000$ K), are obtained. The best description of the measured rate constants of reactions (I) and (–I) in the framework of the model was achieved at $k_{0,\,1}(250 < T/\mathrm{K} < 3000) = 3.2 \times 10^{18}(T/1000)^{-2.6}\exp(-3169/T)$ cm^6 mol^{-2} s^{-1} and $k_{0,\,-1}(1000 < T/\mathrm{K} < 3000) = 4.0 \times 10^{19}(T/1000)^{-4.0}\exp(-45162/T)$ cm^3 mol^{-1} s^{-1}. Using the published data on the rate constant of reaction (–II) and the calculated equilibrium constants, the rate constant of reaction (II), $k_2(1000 < T/\mathrm{K} < 3000) = 10^{13 \pm 0.2}(T/1000)^{0.4}\exp(-8200 \pm 1320/T)$ cm^3 mol^{-1} s^{-1}, is obtained. It is shown that the available experimental data on the rate constants of reactions (I) and (–I) cannot be described without taking into account electronically excited states of the FeO_2 molecule. New estimates of the dissociation energy $D_0(Fe–O_2)$, based on a number of published data for reactions involving the FeO_2 molecule, are presented.

DOI: 10.1134/S0023158412050138

The interaction of iron atoms and gaseous iron oxides with molecular oxygen is of considerable interest for both fundamental studies of reactivity and a variety of applications. In particular, a strong catalytic effect of small additives of iron pentacarbonyl on the oxidation of carbon monoxide CO by molecular oxygen O_2 was observed in shock-wave experiments, and a mechanism of the catalytic action was proposed [1], which involved the formation of iron oxides in the reaction with molecular oxygen and their subsequent reduction in the reaction with carbon monoxide. Small additives of volatile iron compounds show a marked soot-suppressing effect [2] and a strong inhibitory action on the combustion of hydrocarbon fuels [3, 4]. On the other hand, these additives promote the spontaneous ignition of $CH_4–O_2–Ar$ mixtures [5]. The authors of [6] reported a significant reduction in the formation of nitrogen oxides NO_x at industrial power plants in the presence of various iron additives.

The behavior of iron atoms and gaseous iron oxides is of considerable interest to atmospheric chemistry (in particular, their impact on the ozone layer [7]) and for developing the mechanisms of the formation of cosmic dust clouds [8].

This paper deals with an analysis of the thermochemical and kinetic characteristics of the reactions

$$Fe + O_2 + M \leftrightarrow FeO_2 + M, \qquad \text{(I)}$$

$$FeO + O_2 \leftrightarrow FeO_2 + O. \qquad \text{(II)}$$

These reactions play a key role in the aforementioned processes, in particular in the oxygen cycle of transformations of iron in reactive oxygen-containing gas-phase systems.

The rate constant of reaction (I) in the forward direction was measured in [9–13], whereas in the reverse direction, in [14]. In [12, 14], the experimental data were interpreted within the framework of simplified unimolecular dissociation models. For the rate constant of reaction (II) in the forward direction, only an estimate [13] was reported. The rate constant for reaction (II) in the reverse direction was measured in [15] over a temperature range from 209 to 381 K.

The aim of the present work was to conduct a joint analysis of the kinetic and thermochemical parameters of these reactions on the basis of our own and literature experimental data, published results of quantum-chemical calculations, and calculations in the framework of the Rice–Ramsperger–Kassel–Marcus (RRKM) theory, with consideration given to the excited electronic states of the FeO_2 molecule.

MODEL FOR CALCULATING THE RATE CONSTANTS OF REACTIONS (I) AND (–I)

Calculation of the rate constants of FeO_2 dissociation and reverse reaction of recombination is an extremely challenging problem because of the difficulties associated with constructing an adequate model and the absence of reliable molecular parameters for FeO_2. The experimental information on the molecular parameters of FeO_2 is very limited: only the frequencies of the antisymmetric and symmetric vibrations and valence angle of the iron dioxide molecule (OFeO) measured in cryogenic matrices were reported [16]. On the other hand, quantum-chemical calculations show that the FeO_2 molecule has three isomers: oxo (OFeO), peroxo (Fe(O_2), a cyclic structure), and superperoxo (FeOO) forms, each of which has a complex system of excited electronic states [17–20].

The need to take into account the excited electronic states was demonstrated in calculating the rate constants of the reactions $NO + O \rightarrow NO_2$ [21] and $SO + O \rightarrow SO_2$ [22]. The NO_2 and SO_2 molecules have several excited electronic states, and if only the ground state is taken into consideration, a comparison of the rate constants calculated within the framework of the RRKM theory with the experimental data leads to a contradiction: the collisional energy transfer efficiency turns out to be unrealistically large (even greater than unity at low temperatures) [23, 24]. As regards the recombination of metal atoms with an oxygen molecule, the possible contribution of electronically excited states to the reaction rate constant was discussed in [10, 12, 14, 25].

In the present work, we developed and tested a simple additive model for calculating the rate constants of the thermal dissociation of the FeO_2 molecule in the low-pressure limit, since, at moderate pressures (≤1 atm), the dissociation of triatomic molecules, and the reverse reaction of recombination occur in this mode [23, 24]. For reaction (I), this was demonstrated in [12], although at the lowest temperature used in [12], one can expect some degree of falloff behavior, but this issue is beyond the scope of the present paper.

The rate constant in the low-pressure limit is calculated by the formula [23]

$$k_{d,0}(T) = \beta_c k_{d,sc}(T), \tag{1}$$

where $k_{d,\,sc}$ is the dissociation rate constant in the strong-collision limit, and β_c is the collisional energy transfer efficiency (a value not greater than 1). By definition, the rate constant in the strong-collision limit is the product of the collision frequency factor and the statistical weight of the states with energies above the reaction barrier, i.e., capable of dissociating [23]. We hypothesized that the total concentration n^* of molecules capable of dissociation is the sum of the concentrations n_i^* of molecules capable of dissociation in each of the considered electronic states:

$$n^* = \sum_{i=1}^{m} n_i^*, \tag{2}$$

where m is the number of the considered electronic states. Thus, the expression for the dissociation rate constant in the strong-collision limit reads as

$$k_{sc}(T) = Z_{LJ}\frac{\sum_{i=1}^{m} n_i^*}{n}, \tag{3}$$

where n is the total concentration of dissociable molecules and Z_{LJ} is the collision frequency factor. The concentration n_i^* can be represented as

$$n_i^* = n_i f_i = nG_i f_i, \tag{4}$$

where f_i is the fraction of molecules in the ith electronic state capable of dissociating and G_i is the statistical weight of the ith electronic state.

As in the case of one electronic term, the fraction of molecules capable of dissociating can be approximately represented as [23]

$$f_i = \frac{RT\rho_{v,i}(E_0 - E_i)F_{r,i}(T)F_{E,i}(T)F_{anh}}{Q_{v,i}(T)} \times \exp\left[-(E_0 - E_i)/RT\right], \tag{5}$$

where R is the universal gas constant, T is the temperature, $\rho_{v,i}(E_0 - E_i)$ is the density of vibrational states near the dissociation barrier, $F_{r,\,i}(T)$ is the rotational factor, $F_{E,\,i}$ is the energy dependence factor, $Q_{v,i}(T)$ is the vibrational partition function in the harmonic approximation for the ith electronic state, E_0 is the dissociation barrier for the ground electronic state, E_i is the energy of the ith electronic state, and F_{anh} is the anharmonicity factor. The energy of the excited electronic terms is measured from the ground-state energy, which is assumed to be zero ($E_1 = 0$). The dissociation barrier height equals the sum of the dissociation energy D_0 and the barrier height for the reverse recombination reaction E_b: $E_0 = D_0 + E_b$. The density of vibrational states, vibrational partition function, anharmonicity factor, rotational factor, and energy dependence factor were calculated by the formulas presented in [23]. In the expressions for the density of states, rotational factor, and energy dependence factor, E_0 is replaced by $(E_0 - E_i)$, the dissociation barriers for the individual electronically excited states.

The statistical weight of the ith electronic state can be written as [26]

$$G_i = \frac{M_i Q_{v,i}(T)Q_{r,i}(T)\exp(-E_i/RT)}{\sum_{i=1}^{m} M_i Q_{v,i}(T)Q_{r,i}(T)\exp(-E_i/RT)}, \tag{6}$$

where M_i is the multiplicity, $Q_{v,i}(T)$ is the vibrational partition function in the harmonic approximation, and $Q_{r,i}(T)$ is the rotational partition function for the ith electronic state. The partition functions $Q_{v,i}(T)$ and $Q_{r,i}(T)$ were calculated in the standard way [26]. Thus,

$$k_{d,sc} = Z_{LJ} \frac{\sum_{i=1}^{m} M_i Q_{r,i}(T) RT \rho_{v,i}(E_0 - E_i) F_{r,i}(T) F_{E,i}(T) F_{anh}}{\sum_{i=1}^{m} M_i Q_{v,i}(T) Q_{r,i}(T) \exp(-E_i/RT)} \times \exp(-E_0/RT). \quad (7)$$

The collision frequency factor Z_{LJ} was calculated by the formula [23]

$$Z_{LJ} = N_A \pi \sigma^2 \left(\frac{8RT}{\mu}\right)^{0.5} \left[0.7 + 0.52\log(RT/\varepsilon)\right]^{-1}. \quad (8)$$

The parameters of the Lennard–Jones potential were chosen by analogy with CrO_2, a molecule having a structure similar to that of FeO_2 [27]. The collisional energy transfer efficiency was calculated using the formula derived from the expression presented in [23]:

$$\beta_c = \left(\sqrt{\left(\frac{\Delta E}{2RTF_E}\right)^2 + \frac{\Delta E}{RTF_E}} - \frac{\Delta E}{2RTF_E}\right)^2, \quad (9)$$

where $\langle \Delta E \rangle$ is the mean portion of energy transferred in all collisional transitions (upward and downward), while the other designations are given above. The value of $\langle \Delta E \rangle$ was chosen to be 3.3 kJ/mol, so as to obtain $\beta_c = 0.4$ at 350 K, as recommended in [12]. The energy dependence factor F_E was calculated as the weighted average of the relative contributions from the energy dependence factors for the electronic states included in the model for calculating the dissociation rate constant in the strong collision limit:

$$F_E = \frac{\sum_{i=1}^{m} F_{E,i} G_i f_i}{\sum_{i=1}^{m} G_i f_i}. \quad (10)$$

Note that this model should be considered as a first approximation, since it remains unclear how the various isomers of FeO_2 and their electronic states interact with each other at high excitation energies, in particular near the dissociation barrier, and what is the resulting structure of energy levels in this region. In addition, as noted above, most of the molecular parameters, specifically, all the parameters of the electronically excited states are obtained from calculations, with the result being essentially dependent on the quantum-chemical method and on the basis set.

The rate constants of the forward and reverse reactions are related through the equilibrium constant, which can be written as [28]

$$K_c(T) = (R_p T)^{-\Delta n} \exp\left(\frac{\Delta_r \Phi^\circ(T)}{R} - \frac{\Delta_r H^\circ(0)}{RT}\right), \quad (11)$$

where $\Delta_r\Phi^\circ(T)$ and $\Delta_r H^\circ(0)$ are, respectively, the Gibbs energy function change at temperature T and the standard enthalpy change for the reaction at 0 K, R_p is the universal gas constant in pressure units (R_p = 82.057 cm^3 atm mol^{-1} K^{-1}), and Δn is the change in the number of moles in the reaction.

The Gibbs energy function change for reaction (I) can be presented as $\Delta_{r1}\Phi^\circ(T) = \Phi^\circ(FeO_2, T) - \Phi^\circ(Fe, T) - \Phi^\circ(O_2, T)$. The values of $\Phi^\circ(Fe, T)$ and $\Phi^\circ(O_2, T)$ were taken from [29] and [28], respectively. The temperature dependence of $\Phi^\circ(FeO_2, T)$ was calculated by the formula [28]

$$\Phi^\circ(FeO_2, T) = R\ln\left(\frac{R_p T Q(T)}{N_A}\right), \quad (12)$$

where N_A is Avogadro's number, and $Q(T)$ is the total partition function per unit volume (the rest of the designations were specified above). The partition function $Q(T)$ was calculated in the of rigid rotator–harmonic oscillator approximation by summing over all electronic states:

$$Q(T) = Q_{tr}(T) \sum_{i=1}^{m} M_i Q_{v,i}(T) Q_{r,i}(T) \exp(-E_i/RT), \quad (13)$$

where $Q_{tr}(T)$ is the translational partition function.

The molecular parameters of FeO_2 needed to calculate the density of states in (7) and the partition functions in (7) and (13) are listed in the table. To our knowledge, the most detailed calculations of molecular parameters of iron dioxide (OFeO) were performed in [30]. The parameters for the peroxo (cyclic structure $Fe(O_2)$) and superperoxo species (FeOO) were taken from [17]. Additional parameters required for RRKM calculations are presented below:

– the Lennard–Jones collision diameter and well depth, $\sigma(FeO_2\text{–}Ar) = 5.0$ Å and $\varepsilon(FeO_2\text{–}Ar)/k = 400$ K, respectively;

– the total number of oscillators, $S = 3$;

– the numbers of Morse oscillators and the respective anharmonicity factors, $m = 3$ ($F_{anh} = 2.37$) for OFeO and $m = 2$ ($F_{anh} = 1.72$) for $Fe(O_2)$ and FeOO;

– the average energy transferred per collision, $\langle \Delta E \rangle$ = 3.3 kJ/mol.

The temperature dependence of $\Phi^\circ(FeO_2, T)$ was approximated by the standard polynomial for the Gibbs energy function [28] (the coefficients at x, x^2, and x^3 turned out to be negligibly small):

$$\Phi^\circ(FeO_2, T), \text{ J mol}^{-1}\text{ K}^{-1} = 421.4552 + 59.9779\ln x - 0.0073327x^{-2} + 0.9598x^{-1}$$

$$(x = T \times 10^{-4};\ 250 < T < 3000 \text{ K}). \quad (14)$$

Molecular parameters of FeO_2: the electronic states, their energies E_i, the products of the moments of inertia $(I_1I_2I_3)^{0.5}$, and the vibrational frequencies

State	E_i, kJ/mol	$(I_1I_2I_3)^{0.5}$, amu$^{1.5}$ Å^3	ν_1, cm^{-1}	ν_2, cm^{-1}	ν_3, cm^{-1}
			OFeO^{a}		
1^3B_1	0	190.1	205.6	918.8	1025.9
1^3A_1	2.9	183.3	219.5	906.7	1009.3
1^5B_2	5.8	254.4	300.4	904.0	942.6
1^1A_1	30.9	168.8	201.7	933.1	1039.5
1^1B_1	43.4	199.7	216.7	938.2	1035.8
1^3B_2	59.8	244.0	262.6	908.2	946.7
1^3A_2	79.1	229.0	238.4	906.5	964.7
1^1B_2	91.7	244.0	266.5	912.8	964.7
1^5A_2	95.5	195.0	222.2	807.3	886.8
1^1A_2	108.1	233.3	251.2	919.6	968.4
1^5A_1	167.9	300.0	165.2	504.3	846.4
1^7B_2	169.8	303.7	149.5	456.1	721.9
1^7B_1	172.7	146.0	144.2	328.4	689.4
			$Fe(O_2)^{b}$		
T	180.7	251.4	433.7	500.9	985.7
Q	155.2	149.0	462.1	509.7	842.9
S	149.0	299.2	398.0	401.0	1157.0
			FeOO^{b}		
T	195.0	294.8	134.7	472.7	1159.8
Q	203.8	290.1	147.1	476.3	1176.3

[a, b] Calculated in [30] and [17], respectively, using the density functional theory method.

RESULTS AND DISCUSSION

The analysis was carried out as follows. A set of experimental data on the rate constants of reactions (I) and (–I) were described within the framework of the above model. As the fitting parameters, the enthalpy change of reaction (I) $\Delta_{r1}H°(0)$ and the energy barrier height E_b for reverse reaction (–I) were used. It is obvious that $-\Delta_{r1}H°(0)$ is equal to the energy of dissociation of FeO_2 to Fe and O_2, $-\Delta_{r1}H°(0) = D_0(Fe–O_2)$, so in view of its obvious physical meaning, we used the quantity $D_0(Fe–O_2)$.

The set of experimental data for modeling (Fig. 1) included (1) the low-pressure rate constant of reaction (I) measured in [12] at the lower end of the temperature range covered (289 K), (2) the low-pressure rate constant of reaction (I) obtained in the present work by co-processing the data from [9, 10] using the method of falloff curves for 1150 K (the mean temperature of the range in which the measurements were performed in [9, 10]), and (3) the low-pressure rate constant for reaction (–I) [14] at the midrange temperature of the measurement interval (2100 K). The data from [13] were not taken into consideration, since the authors presented an expression for the apparent rate constant, consisting of the contributions from reaction (I) and the reaction

$$Fe + O_2 \rightarrow FeO + O, \qquad (III)$$

which occurs concurrently with reaction (I). However, the rate constant at the lower end the temperature range (950 K) covered in [13], where the contribution of reaction (III) is minimal, is presented in the summary plot for comparison. An upper estimate of the rate constant for reaction (I) at $T = 296$ K [11] was also excluded from the simulation set, although this estimate, as seen from Fig. 1, is close to the rate constant of reaction (I) measured in [12]. Note that, although the rate constant of reaction (I) [12] was measured in an atmosphere of nitrogen, not argon, as in all other studies, the low-pressure rate constants for $Cr + O_2 + M \rightarrow CrO_2 + M$, a similar reaction, measured in argon and nitrogen are practically identical [27]. For this reason, the RRKM calculations for all the experimental data were performed on the assumption that the third body in reaction (I) is argon.

Figure 2 shows an approximation of the experimental data from [9, 10] by a calculated falloff curve to obtain the rate constants of reactions (I) in the low- and high-pressure limits at 1150 K, $k_{0,\,1}(1150)$ and $k_{\infty,\,1}(1150)$. We used a simple expression for the falloff curve (equations (4)–(8) and (13)–(15) in [31]). The calculations were based on the assumption that the electronic states can be considered as an additional active degree of freedom, so that the number of active degrees of freedom was $S = 4.5$: the sum of the contributions from the electronic states (1.0), vibrations (3.0), and active rotation (0.5). The effective number of degrees of freedom was calculated by the formula [31]

$$S_K = \frac{1}{RT}\left[-RT^2\frac{\partial \ln Q(T)}{\partial T} - \frac{5}{2}RT\right] + 1, \qquad (1)$$

where $Q(T)$ is the total partition function for the FeO_2 molecule (the same as in (13)); the expression in brackets represents the energy of the active degrees of freedom: the difference between the total energy of the molecule (first term) and the energy of the inactive degrees of freedom (two rotational and three translational, second term).

The effective activation energy B_K was initially calculated using the barrier for FeO_2 dissociation from [14], $E_0 = 357.7$ kJ/mol, where it was obtained by simulating experimental data on FeO_2 dissociation within the framework of a simplified model (with one electronically excited state). After determining $D_0(Fe{-}O_2)$ and E_b, we substituted the new value of $E_0 = D_0(Fe{-}O_2) + E_b = 363.5$ kJ/mol (see below), and repeated the procedure of fitting the calculated falloff curve to the experimental data, which however, did not lead to noticeable changes in the values of $k_{0,\,1}(1150)$ and $k_{\infty,\,1}(1150)$. The parameters used to calculate the falloff curve are given below:

– the number of active degrees of freedom, $S = 4.5$;

– the effective number of active degrees of freedom, $S_K = 3.94$;

– the effective activation energy, $B_K = 32.8$;

– the collisional energy transfer efficiency, $\beta_c = 0.18$.

The best approximation of the experimental data from [9, 10] by the calculated falloff curve was achieved at $k_{0,\,1}(1150) = 10^{17.3 \pm 0.2}$ cm^6 mol^{-2} s^{-1}, and $k_{\infty,\,1}(1150) = 10^{13.2 \pm 0.4}$ cm^3 mol^{-1} s^{-1}.

Judging by the falloff curve for 1150 K (Fig. 2), the rate constant for reaction (–I) measured in [14] at a total concentration of $[M] \approx 7 \times 10^{-6}$ mol/cm^3 should belong to the falloff region. However, due to the fact that the ratio $k_{0,\,-1}/k_{\infty,\,-1}$ decreases significantly with increasing temperature, the experimental value of the dissociation rate constant FeO_2 is substantially shifted to lower pressures, so that the low-pressure rate constant can be obtained simply by dividing the apparent rate constant by the total concentration [M] of the gas mixture.

The procedure for determining the values of $D_0(Fe{-}O_2)$ and E_b that provide the best agreement between measured and calculated rate constants was as follows. Preliminary calculations showed that, within certain limits, a given value of the rate constant for FeO_2 dissociation or $Fe + O_2$ recombination at a fixed temperature can be obtained at different pairs of

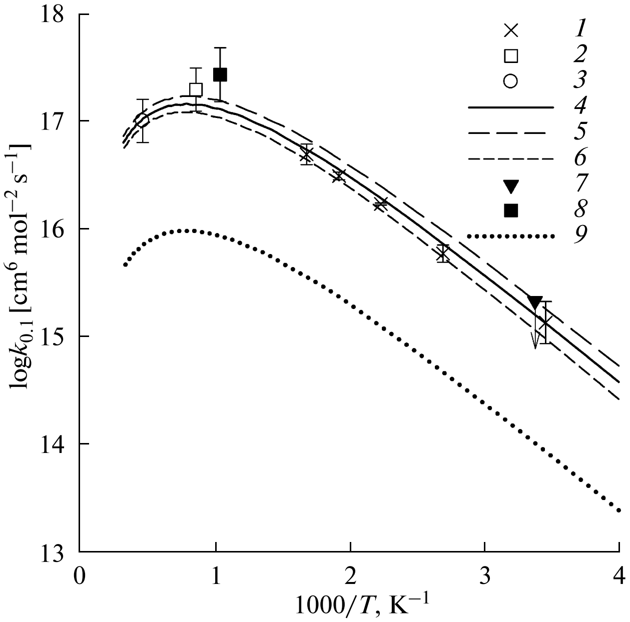

Fig. 1. Temperature dependence of the rate constants of reaction (I): (*1*) experimental data from [12], (*2*) the value determined from the best fit of the falloff curve to the data from [9, 10] at 1150 K (see the text and Fig. 2), (*3*) the value calculated from the rate constant of reaction (–I) at 2100 K by multiplying it by the equilibrium constant; (*4–6*) calculated in the framework of the RRKM model at the (*4*) optimal and (*5, 6*) limiting values of $D_0(Fe{-}O_2)$ and E_b (see the text and Fig. 3); (*7, 8*) estimates of $k_{0,\,1}$ at (*7*) 296 K [11] and (*8*) 950 K [13]; (*9*) $k_{0,\,1}(T)$ calculated at $D_0(Fe{-}O_2) = 340$ kJ/mol and $E_b = 23.5$ kJ/mol by taking into account only the ground electronic state of the oxo form (OFeO).

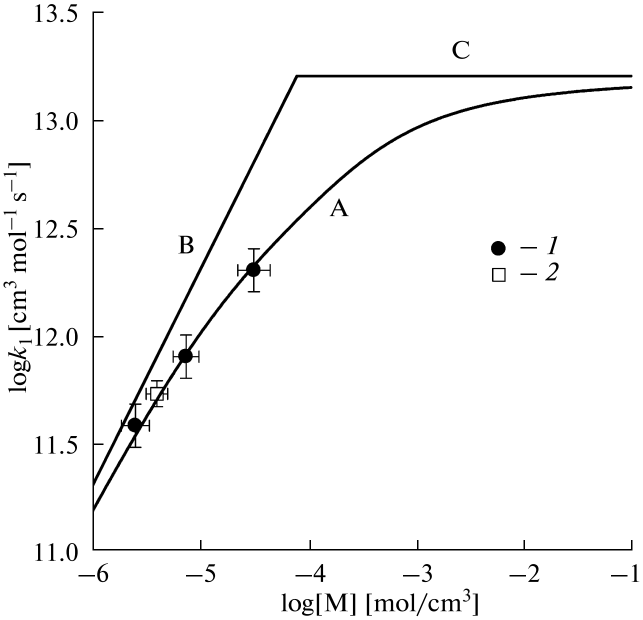

Fig. 2. Falloff curve for describing the experimental data on reaction (I) from (*1*) [9] and (*2*) [10] at 1150 K (the mean temperature of measurements in these studies); (A) falloff curve and (B, C) asymptotics in the low- and high-pressure limits, respectively.

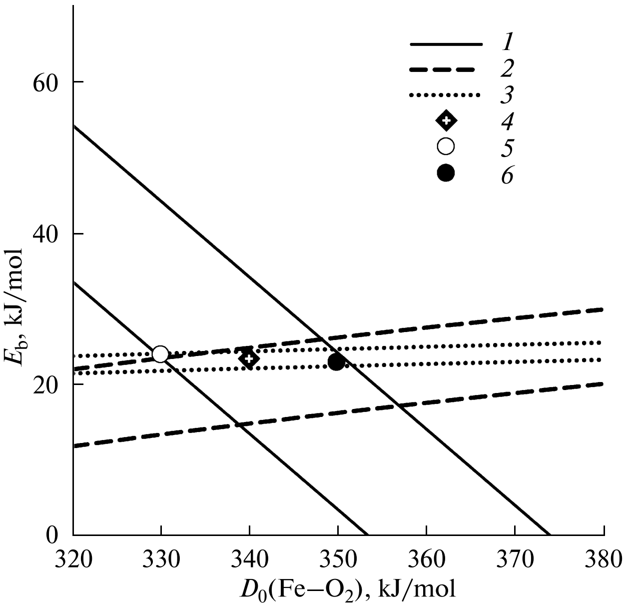

Fig. 3. Determination of the optimal values of D_0(Fe–O_2) and E_b. Lines *1*, *2*, and *3* represent the set of points {D_0(Fe–O_2), E_b} corresponding to the lower (upper line) and upper (lower line) limits of (*1*) $k_{0,\,-1}$ at 2100 K [14], (*2*) $k_{0,\,1}$ at 1150 K (this work), and (*3*) $k_{0,\,1}$ at 289 K [12] (see the text); points *4* and *5*, *6* represent, respectively, the optimal and limiting values of D_0(Fe–O_2) and E_b (see the text).

D_0(Fe–O_2) and E_b values. In other words, for a given value of D_0(Fe–O_2) within a certain range, it is possible to find a value of E_b that provides the coincidence of the rate constant calculated using the above model with the experimental value. Based on this result, we calculated the dependences $E_b = f[D_0(\mathrm{Fe{-}O_2})]$ corresponding to the lower (subscript l) and upper (subscript u) error limits for each experimental point included in the procedure of determining the optimal values of D_0(Fe–O_2) and E_b ($k_{0,\,1}(T)$ and $k_{0,\,-1}(T)$ are in cm^6 mol^{-2} s^{-1} and cm^3 mol^{-1} s^{-1}, respectively): $\log k_{0,\,1l}(289) = 14.95$, $\log k_{0,\,1u}(289) = 15.34$; $\log k_{0,\,1l}(1150) = 17.1$ and $\log k_{0,\,1u}(1150) = 17.5$; $\log k_{0,\,-1l}(2100) = 8.75$, $\log k_{0,\,-1u}(2100) = 9.15$. The $E_b = f[D_0(\mathrm{Fe{-}O_2})]$ dependences for the upper and lower error limits of each experimental value form E_b versus D_0(Fe–O_2) bands (Fig. 3) inside which the calculated rate constants lie within the error limits for the given experimental value. Point *4* at the center, with coordinates $E_b = 23.5$ kJ/mol and $D_0(\mathrm{Fe{-}O_2}) = 340$ kJ/mol, corresponds to the best agreement between the calculated and measured rate constants of reactions (I) and (–I) for the indicated experimental conditions. The limiting values that still provide the agreement within the experimental error bars (points *5* and *6* in Fig. 3) are $E_b = 24.0$ kJ/mol, $D_0(\mathrm{Fe{-}O_2}) = 330$ kJ/mol and $E_b = 23.0$ kJ/mol, $D_0(\mathrm{Fe{-}O_2}) = 350$ kJ/mol, so the errors in E_b and D_0(Fe–O_2) can be estimated as ±0.5 and ±10.0 kJ/mol, while in reality they are apparently somewhat larger because of the simplifications underlying the model and the uncertainties in the input parameters. The corresponding enthalpy of formation of FeO_2 at 0 K is $\Delta_f H°(\mathrm{FeO_2}, 0) = \Delta_f H°(\mathrm{Fe}, 0) - D_0(\mathrm{Fe{-}O_2}) = 411.7 - 340.0 = 71.7$ kJ/mol; the value of $\Delta_f H°(\mathrm{Fe}, 0)$ was taken from [29].

Figure 1 compares the measured and calculated temperature dependences of the rate constant of reaction (I). The rate constant of reaction (I) at 2100 K was obtained by multiplying the rate constant of reaction (–I) by the equilibrium constant calculated by formula (11). As can be seen, there is good agreement between the experimental and calculation results. The dashed curves represent the temperature dependence of $k_{0,\,1}(T)$ calculated at the limiting values of E_b and D_0(Fe–O_2). On the other hand, without regard for electronically excited states, no satisfactory agreement between the calculated and experimental values can be achieved at any values of E_b and D_0(Fe–O_2).

The standard non-Arrhenius approximations of the temperature dependence of the rate constants $k_{0,\,1}(T)$ and $k_{0,\,-1}(T)$ calculated at the optimum values of E_b and D_0(Fe–O_2) read as

$$k_{0,\,1}(250 < T/\mathrm{K} < 3000) = 3.2 \times 10^{18}(T/1000)^{-2.6}\exp(-3169/T)\ \mathrm{cm^6\ mol^{-2}\ s^{-1}}, \qquad (16)$$

$$k_{0,\,-1}(1000 < T/\mathrm{K} < 3000) = 4.0 \times 10^{19}(T/1000)^{-4.0}\exp(-45162/T)\ \mathrm{cm^3\ mol^{-1}\ s^{-1}}. \qquad (17)$$

Reaction (II) can be regarded as the abstraction of the O atom from the FeO molecule followed by the addition of the Fe atom to the O_2 molecule, so the enthalpy change can be written as $\Delta_{r2}H°(0) = D_0(\mathrm{Fe{-}O}) - D_0(\mathrm{Fe{-}O_2})$. Since the dissociation energy of FeO is well known, $D_0(\mathrm{Fe{-}O}) = 403.3 \pm 1.0$ kJ/mol [32, 33], substituting the obtained value of $D_0(\mathrm{Fe{-}O_2}) = 340 \pm 10$ kJ/mol yields $\Delta_{r2}H°(0) = 63.3 \pm 11$ kJ/mol. Using the Gibbs energy function of FeO_2 calculated by (14) and Gibbs energy functions of FeO from [29] and O and O_2 from [28], we calculated the equilibrium constant for reaction (II) and, multiplying it by the rate constant for the reverse reaction (–II) from [15], obtained

$$k_2(1000 < T/\mathrm{K} < 3000) = 10^{13 \pm 0.2}(T/1000)^{0.4} \times \exp(-8200 \pm 1320/T)\ \mathrm{cm^3\ mol^{-1}\ s^{-1}}. \qquad (18)$$

The indicated errors correspond to the sum of the uncertainty in the $\Delta_{r2}H°(0)$, which is mainly associated with the uncertainty in D_0(Fe–O_2), and the errors of measurement of $k_{-2}(T)$ specified in [15]. Figure 4 compares expression (18) with the estimated temperature dependence of $k_2(T)$ [13]. As can be seen, a good agreement is observed. This result is a further evidence for the correctness of the obtained value of D_0(Fe–O_2). In other words, if D_0(Fe–O_2) were estimated based on the equilibrium constant for reaction (II) calculated as the ratio of the rate constants in the forward (from [13]) and reverse (from [15]) directions, a value of $D_0(\text{Fe—O}_2)$ = 340 kJ/mol would be derived (see below).

Let us compare the value of $D_0(\text{Fe—O}_2)$ and the corresponding enthalpy of formation of FeO_2 $\Delta_f H°(FeO_2, 0)$ obtained in the present work with the available measurements and consider a number of experimental data that can be used to evaluate $D_0(\text{Fe—O}_2)$, but, as far as we know, have not been considered from this point of view. The existing theoretical and experimental evaluations of $D_0(\text{Fe—O}_2)$ ($\Delta_f H°(FeO_2, 0)$) are few and contradictory [34] and, apparently, in need of significant refinement.

There are several experimental studies, the data of which can be used to estimate $D_0(\text{Fe—O}_2)$. In particular, the measurement [35] of the equilibrium concentrations of the reactants of the reaction

$$Fe + FeO_2 = FeO + FeO \qquad (IV)$$

during the sublimation of Fe_2O_3 in an effusion cell made it possible to determine the equilibrium constant and then, with an expression similar to (11), to calculate the enthalpy change (the third law of thermodynamics) for this reaction. Further, based on the known enthalpies of the other reactants, the enthalpy of formation of the FeO_2 molecule and, consequently, its energy of dissociation into atoms, $D_0(\text{O—Fe—O}) = 833 \pm 21$ kJ/mol, were determined. This quantity is related to $D_0(\text{Fe—O}_2)$ as $D_0(\text{O—Fe—O}) = D_0(\text{Fe—O}_2) + D_0(\text{O—O})$, whence, given that $D_0(\text{O—O})$ = 493.566 kJ/mol [28], $D_0(\text{Fe—O}_2) = 339 \pm 21$ kJ/mol. It should be noted, however, that the Gibbs energy function change used in [35] was estimated based on data for other metal oxides, which, in turn, were also obtained from assessments.

An alternative interpretation of the experimental data on the equilibrium constant for reaction (IV) reported in [35] was proposed in [36]. Using the analogy with the CrF_2, MnO_2, and MnF_2 molecules, the authors of [36] suggested that the FeO_2 molecule has a linear configuration, and assessing its molecular parameters, calculated the Gibbs energy function. Using this value, they treated the experimental data from [35] for the equilibrium constant of reaction (IV) within the framework of the third-law method (equation (11)) to determine the enthalpy change of reaction (IV) and, consequently, the energy of abstraction of an oxygen atom from the FeO_2 molecule: $D_0(\text{OFe—O})$ = 442.2 kJ/mol. This value is related to the energy of abstraction of the oxygen molecule from FeO_2 as

$$D_0(\text{Fe—O}_2) = D_0(\text{OFe—O}) + D_0(\text{Fe—O}) - D_0(\text{O—O}), \qquad (19)$$

whence $D_0(\text{Fe—O}_2) = 442.2 + 403.3 - 493.6 =$ 351.9 kJ/mol. The corresponding enthalpy of formation of FeO_2 for the accepted enthalpy of formation of the iron atom ($\Delta_f H°(Fe, 0)$ = 411.656 kJ/mol [29]) is $\Delta_f H°(FeO_2, 0) = \Delta_f H°(Fe, 0) - D_0(\text{Fe—O}_2) = 60 \pm 21$ kJ/mol.

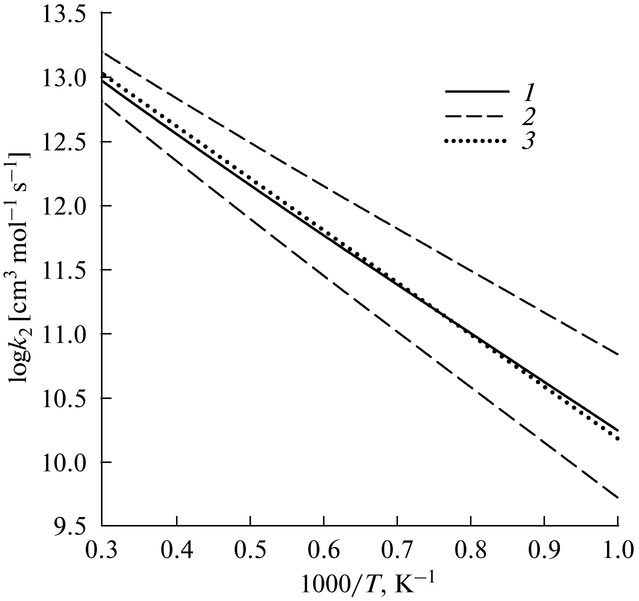

Fig. 4. Comparison of the expressions for $k_2(T)$ obtained in the present study (*1*) (lines *2* are the error limits) with that calculated by the formula proposed in [13] (*3*).

As can be seen from the presented analysis, the enthalpy of formation of FeO_2 obtained from the experimental data [35] depends on the Gibbs energy function, which was obtained in [35] and [36] based on very rough estimates of the molecular parameters of FeO_2. This prompted us to conduct a new analysis of experimental data for the equilibrium constant of reaction (IV) from [35] using the Gibbs energy function of the FeO_2 molecule calculated in the present work based on the molecular parameters listed in Table 1 (formula (14)).

The Gibbs energy functions for the Fe atom and FeO molecule were taken from [29]. Calculation by formula (11) gave an enthalpy change of reaction (IV) of $\Delta_{r4}H°(0) = 11 \pm 21$ kJ/mol (the error was assumed to be the same as in the original paper [35]). Since reaction (IV) can be interpreted as the dissociation of the FeO_2 molecule to Fe and O_2, followed by the dissociation of O_2 to two O atoms and the association of these atoms with two Fe atoms (the original and formed from the FeO_2 molecule), the enthalpy change for this reaction can be written as $\Delta_{r4}H°(0) = D_0(\text{Fe—O}_2) + D_0(\text{O—O}) - 2D_0(\text{Fe—O})$, from where, using the above values of $D_0(\text{Fe—O})$ [32, 33] and $D_0(\text{O—O})$ [28], we obtain $D_0(\text{Fe—O}_2) = 11.0 + 2 \times 403.3 - 493.6 = 324(\pm 21)$ kJ/mol (this error is identical to that reported in the original paper [35]). The corresponding enthalpy of formation of FeO_2 for the adopted enthalpy of formation of the iron atom ($\Delta_f H(Fe, 0)$ = 411.656 kJ/mol [29]) is $\Delta_f H°(FeO_2, 0) = \Delta_f H°(Fe, 0) - D_0(\text{Fe—O}_2) = 88 \pm 21$ kJ/mol. Thus, our estimate of $D_0(\text{Fe—O}_2)$ is about 15 and 28 kJ/mol lower than the values calculated on the basis of the results presented in [35] and [36], respectively, due to the use of a higher value of the Gibbs energy function in the present work, which was calculated by taking into account a large number of low-lying electronic levels.

Another frequently cited estimate of D_0(Fe–O$_2$) ($\Delta_f H°$(FeO$_2$, 0)) is based on measuring the equilibrium constant of the reaction

$$\frac{1}{3}\mathrm{Fe_3O_4(s)} + \frac{11}{6}\mathrm{CrO_3^-} = \frac{1}{2}\mathrm{Cr_2O_3(s)} + \mathrm{FeO_2^-} + \frac{5}{6}\mathrm{CrO_4^-}, \quad \text{(V)}$$

at temperatures near 1400 K [37]. Processing the experimental data within the framework of the third-law method at a Gibbs energy function of $\Phi°$(FeO$_2^-$, 1400 K) = 302.5 J mol^{-1} K^{-1}, the authors of [37] obtained an enthalpy of formation of the FeO$_2^-$ anion equal to $\Delta_f H°$(FeO$_2^-$, 0) = –164 ± 13 kJ/mol. Since $\Delta_f H°$(FeO$_2$, 0) = $\Delta_f H°$(FeO$_2^-$, 0) + EA(FeO$_2$) = –164 ± 13 + 227.5 = 64 ± 13 kJ/mol (the electron affinity of FeO$_2$ was taken from [38]), then D_0(Fe–O$_2$) = 348 ± 13 kJ/mol. The value of $\Phi°$(FeO$_2^-$,1400 K) = 302.5 kJ/mol was obtained from the Gibbs energy function of the FeO$_2$ molecule (calculated from estimated molecular parameters [29] for the ground electronic state, without taking into account the excited states) by increasing its value by Rln2. This correction was introduced on the assumption that, in passing from the neutral molecule to the anion, the degree of degeneracy is doubled due to the appearance of an unpaired electron. In the light of modern quantum-chemical calculations, the latter assumption, as well as molecular parameters used to calculate the Gibbs energy function of FeO$_2$, appears to be unsubstantiated.

Note, however, that despite the serious efforts having been undertaken to determine the structure and molecular parameters of the FeO$_2^-$ anion, the picture remains quite controversial. On the one hand, the authors [38], based on an analysis of the structure of photoelectron spectra of FeO$_2^-$, came to the conclusion that the anion and neutral molecule FeO$_2$ have a similar structure and nearly the same valence angle. Since the neutral FeO$_2$ molecule was demonstrated to have a bent structure, one might conclude that FeO$_2^-$ has a similar structure. On the other hand, recent measurements [39] of the frequency of the antisymmetric vibrations of the Fe^{16}O$_2^-$ and Fe^{18}O$_2^-$ isotopically substituted anions in a cryogenic argon matrix showed that the FeO$_2^-$ molecule is linear. Quantum-chemical calculations are also contradictory. A number of quantum chemical methods predict a linear structure, while the other methods, based on density functional theory, give nonlinear structures [20, 39, 40].

For this reason, we calculated the reduced Gibbs energy of the FeO$_2^-$ anion using the molecular parameters for the linear structure calculated by the multireference configuration interaction (MRCI) method [39] and the parameters for the nonlinear structure obtained within the framework of density functional theory (BPW91 functional) in [40].

In the first case, the calculations were performed for a set of electronic states including two $^2\Delta_{5/2}$ ($E = 0$) states, two $^2\Delta_{3/2}$ (E = 800 cm^{-1}) states, and two sets of $^4\Pi$ states (a total of 16 Π-states) with energies of ~2000 cm^{-1} (the energies of all these states were set at 2000 cm^{-1}). The frequencies for all states were chosen to be 870, 150 (2), and 650 cm^{-1}. The first frequency (asymmetric vibration) was measured in [39], the remaining frequencies were chosen so as to match the proportions between the frequencies of NiF$_2$, a similar linear molecule [29]. The interatomic distance needed to calculate the moment of inertia was obtained in [39] on the basis of quantum-chemical calculations: r(Fe–O) = 1.644 Å. The Gibbs energy function calculated with the use of these molecular parameters was found to be $\Phi°$(FeO$_2^-$, 1400 K) = 297.0 J mol^{-1} K^{-1}. As noted above, the value of $\Phi°$(FeO$_2^-$, 1400 K) used by the authors of [37] to calculate $\Delta_f H°$(FeO$_2^-$, 0) was 302.5 J mol^{-1} K^{-1}. Therefore, at constant values of the equilibrium constant for reaction (V) and thermodynamic functions of the rest of the reactants, the reduction of the Gibbs energy function of FeO$_2^-$ by 5.5 J mol^{-1} K^{-1} (from 302.5 to 297.0 J mol^{-1} K^{-1}) must be accompanied by (in accordance with formula (11)) by a decrease in the enthalpy of formation of the FeO$_2^-$ anion by 1400 × 5.5 = 7.7 kJ/mol: from $\Delta_f H°$(FeO$_2^-$, 0) = –164 ± 13 kJ/mol (in [37]) to $\Delta_f H°$(FeO$_2^-$, 0) = –172 ± 13 kJ/mol. The value of $\Delta_f H°$(FeO$_2$, 0) = $\Delta_f H°$(FeO$_2^-$, 0) + EA(FeO$_2$) = –172 ± 13+ 227.5 = 56 ± 13 kJ/mol (EA(FeO$_2$) from [38]) corresponds to D_0(Fe–O$_2$) = 356 ± 13 kJ/mol (the error is assumed to be identical to the specified in the original paper [39]).

The Gibbs energy function for the nonlinear FeO$_2$ anion calculated based on the molecular parameters from Table 2 in [40] led to $\Phi°$(FeO$_2^-$, 1400 K) = 306.9 J mol^{-1} K^{-1} and, respectively, $\Delta_f H°$(FeO$_2$, 0) = 70 ± 13 kJ/mol and D_0(Fe–O$_2$) = 342 ± 13 kJ/mol.

Let us examine a number of experimental data that can be used to evaluate D_0(Fe–O$_2$) ($\Delta_f H°$(FeO$_2$, 0)), but, as far as we know, have not yet been analyzed from this point of view.

The fact that the FeO$_2^+$ cation effectively abstracts an electron from the hexafluorobenzene molecule [34], which has an ionization energy of 9.9 eV (955.3 kJ/mol), means that the ionization energy of FeO$_2$ is at least not less than this value, i.e., IE(FeO_2) > 955.3 kJ/mol. Since the dissociation energy of the FeO_2^+ cation to Fe^+ and O_2 is known ($D_0(Fe^+{-}O_2)$ = 116.8 kJ/mol [41]), $D_0(Fe{-}O_2)$ can be estimated by using the obvious relation $D_0(Fe{-}O_2) = D_0(Fe^+{-}O_2) + IE(FeO_2) - IE(Fe) > 116.8 + 955.3 - 762.5 = 309.6$ kJ/mol.

In a recent study [42], it was found that the FeO_2^- anion is quickly reduced by carbon monoxide: $FeO_2^- + CO = FeO^- + CO_2$. This suggests that the reaction is exothermic, or at least thermoneutral. Quantum-chemical calculations performed in [42] predicted an exothermic effect of 0.26 eV (25.1 kJ/mol). This means that the energy of abstraction of an O atom from FeO_2^- is less than the energy of addition of the O atom to the CO molecule with the formation of CO_2 (526 kJ/mol): $D_0(OFe^-{-}O) < 526$ kJ/mol. Since the energy of abstraction of an O atom from the neutral molecule $D_0(OFe{-}O)$ is related to $D_0(OFe^-{-}O)$ as $D_0(OFe{-}O) = D_0(OFe^-{-}O) + EA(FeO) - EA(FeO_2)$, where EA(FeO) and EA($FeO_2$) are the electron affinities of FeO and FeO_2, respectively (EA(FeO) = 144.3 kJ/mol [43] and EA(FeO_2) = 227.5 kJ/mol [38]), $D_0(OFe{-}O) < (526 + 144.3 - 227.5) = 442.8$ kJ/mol, and relation (19) yields $D_0(Fe{-}O_2) < 352.5$ kJ/mol.

Another opportunity to evaluate the dissociation energy $D_0(Fe{-}O_2)$ is offered by data on the rate constants for the reaction

$$FeO + CO_2 = FeO_2 + CO \qquad (VI)$$

in the forward and reverse directions. The rate constant in the forward direction was estimated from the simulation of experimental results on the interaction of Fe atoms with CO_2 at 1650–2650 K [44]. In our opinion, the most reliable values of this rate constant were obtained near the upper end of the temperature range, where the rate constant is high and, therefore, has a significant effect on the observed behavior of the reactants (CO and Fe). For this reason, we chose the temperature 2500 K. According to the expression presented in [44], $k_6(2500) = 3.9 \times 10^{11}$ cm^3 mol^{-1} s^{-1}. The cross section for the reverse reaction was estimated in [45] as 3.4×10^{-17} cm^2; multiplying this value by the average relative velocity of the FeO_2 and CO molecules at 2500 K and changing to molar units, we obtain $k_{-6}(2500) = 3.2 \times 10^{12}$ cm^3 mol^{-1} s^{-1}. Consequently, the equilibrium constant for reaction (VI) at 2500 K is $K_{c,6}(2500) = k_6(2500)/k_{-6}(2500) = 0.12$. Substituting into (11) this value and the Gibbs energy function change for reaction (VI) at 2500 K $\Delta_{r6}\Phi°(2500)$ ($\Delta_{r6}\Phi°(2500) = \Phi°(FeO_2, 2500) + \Phi°(CO, 2500) - \Phi°(FeO, 2500) - \Phi°(CO_2, 2500) = 21.1$ J mol^{-1} K^{-1}; the values of $\Phi°(2500)$ for CO and CO_2 were taken from [28], for FeO from [29], and $\Phi°(FeO_2, 2500)$ was calculated in this paper by formula (14)) yields an enthalpy change of reaction (6) equal to $\Delta_{r6}H°(0) = 96.8$ kJ/mol. Since reaction (VI) can be thought of as the abstraction of an oxygen atom from the CO_2 molecule followed by the addition of it to the FeO molecule, the enthalpy change of reaction (VI) is $\Delta_{r6}H°(0) = D_0(OC{-}O) - D_0(OFe{-}O)$ and, consequently, $D_0(OFe{-}O) = 526.1 - 96.8 = 429.3$ kJ/mol ($D_0(OC{-}O)$ is calculated based on the data from [28]). Substituting this value in (19) gives $D_0(Fe{-}O_2)$ = 339 kJ/mol. According to our estimates, the uncertainty in the equilibrium constant is a factor of 2, which is equivalent to an uncertainty in $D_0(Fe{-}O_2)$ of $RT\ln 2$ = 15 kJ/mol and, thus, $D_0(Fe{-}O_2) = 339 \pm 15$ kJ/mol.

The dissociation energy of $D_0(Fe{-}O_2)$ can also be estimated on the basis of the measured rate constant for the reaction [46]

$$C_6H_6Fe^+ + O_2 \rightarrow C_6H_6^+ + FeO_2 . \qquad (VII)$$

The total rate constant of the interaction of the complex ion with molecular oxygen at 295 K was estimated by the authors of [46] as $\geq 1.1 \times 10^{14}$ cm^3 mol^{-1} s^{-1}, with the contribution from reaction (VII) being 0.025. The relatively low rate constant of reaction (VII) may be because this channel is endothermic and/or because, even if exothermic (or at least thermoneutral), it is depleted due to competition with the other three channels. In the first limiting case, the calculation shows that the enthalpy change of reaction (VII) does not exceed 10 kJ/mol. In the second case, the enthalpy change should be set less than or equal to zero. Reaction (VII) can be represented as a sequence of three processes:

(1) the abstraction of the iron ion from the $C_6H_6Fe^+$ ion complex (with an energy input of $D_0(C_6H_6{-}Fe^+)$ = 207.5 kJ/mol [47]),

(2) electron transfer from the formed benzene molecule to the iron ion to produce a neutral iron atom (with an energy input of $IE(C_6H_6) - IE(Fe)$ = 129.5 kJ/mol; the values of IE(C_6H_6) and IE(Fe) were taken from [48] and [49], respectively), and

(3) recombination of the iron atom with the oxygen molecule (with an energy release of $D_0(Fe{-}O_2)$). Thus, the enthalpy changes are $\Delta_{r7}H°(0) = D_0(C_6H_6{-}Fe^+) + IE(C_6H_6) - IE(Fe) - D_0(Fe{-}O_2) \leq 10$ kJ/mol (in the first case) and ≤ 0 kJ/mol (in the second), which lead, respectively, to $D_0(Fe{-}O_2) \geq 327$ kJ/mol and $D_0(Fe{-}O_2) \geq 337$ kJ/mol.

The values of $D_0(Fe{-}O_2)$ estimated based on the published data and obtained in the current work are presented in Fig. 5. As can be seen, the mean value is $D_0(Fe{-}O_2)$ = 340 kJ/mol, with the narrowest corridor of $D_0(Fe{-}O_2)$ values that contains all the points being ±15 kJ/mol. Thus, as an estimate of the dissociation energy $D_0(Fe{-}O_2)$, a value of 340 ± 15 kJ/mol can be recommended. The corresponding enthalpy of formation of FeO_2 is $\Delta_f H°(FeO_2, 0) = 72 \pm 15$ kJ/mol.

The fact that the processing of mass spectrometric data from [35] performed in the present study gave $D_0(Fe{-}O_2)$ significantly below its mean value (340 kJ/mol) is apparently due to uncertainties in the

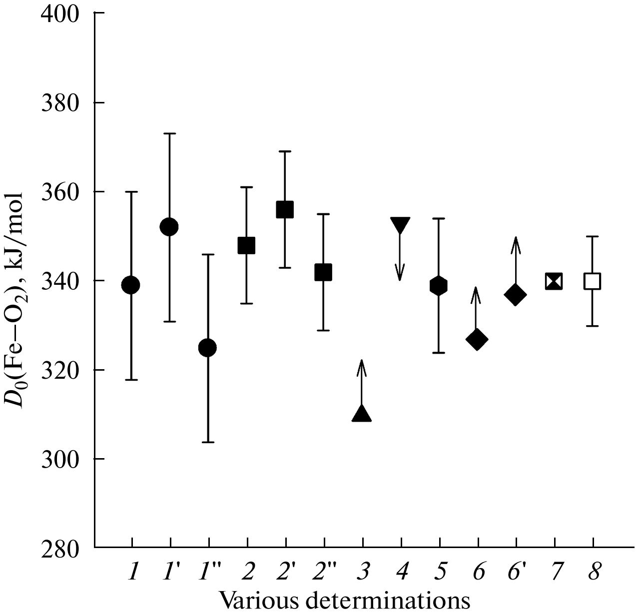

Fig. 5. Comparison of the value of D_0(Fe–O_2) obtained in the present study with those derived from a number of published experimental data: (*1*, *1*', *1*'') calculated based on the third law of thermodynamics from the results of mass spectrometric measurements [35] using the values of the Gibbs energy function Φ°(FeO_2, *T*) from (*1*) [35], (*1*') [36], and (*1*'') the present work (formula (14)); (*2*, *2*', *2*'') determined based on the third law of thermodynamics from the data [37] using the values of Φ°(FeO_2^-, *T*) (*2*) from [37] and calculated by us for the (*2*') linear [39] and (*2*'') nonlinear [40] configurations of the FeO_2^- anion (see the text); (*3*) calculated using the dissociation energy of the FeO_2^+ cation [41] and an evaluation of the ionization energy of FeO_2 from [34]; (*4*) estimated based on the rate constant of the reaction $FeO_2^- + CO = FeO^- + CO_2$ [42] (which indicates that this reaction is exothermic or at least thermoneutral) and the electron affinity of FeO_2; (*5*) assessed using the equilibrium constant (third-law method) for the reaction $FeO + CO_2 = FeO_2 + CO$ defined as the ratio of rate constants in the forward [44] and reverse [45] directions; (*6*, *6*') estimated based on the observation that the reaction $C_6H_6Fe^+ + O_2 \rightarrow C_6H_6^+ + FeO_2$ is fast [46] under the two alternative assumptions that this reaction competes (*6*) and does not compete (*6*') with the other channels of interaction of the reagents; (*7*) determined as in the case of (5) for the reaction $FeO + O_2 = FeO_2 + O$ with the rate constants in the forward [13] and reverse [15] directions; and (*8*) the present work (see the text).

measured concentrations of the species involved in reaction (IV). An indirect evidence of this is, as noted in [34], a substantially underestimated value of the ionization energy of FeO_2 reported in [35]. Therefore, a reliable determination of the ionization energy of FeO_2 is the key element for a more accurate determination of D_0(Fe–O_2), since the dissociation energy of the FeO_2^+ cation D_0(Fe^+–O_2) is well known [41].

The resulting value of the energy barrier for the recombination (reaction (–I)), $E_b = 23.5$ kJ/mol, is in good agreement with the value obtained in [12], $E_b = 21.3$ kJ/mol. An independent assessment based on the assumption that the difference in the rate constants of the reactions $Fe + O_2 + M \rightarrow FeO_2 + M$ and $Cr + O_2 + M \rightarrow CrO_2 + M$ is determined only by the presence of a barrier in the case of the first gives the following estimate of E_b at $T = 289$ K: $E_b = -RT\ln(1.36 \times 10^{15}/2.65 \times 10^{19}) = 23.7$ kJ/mol, where the expression in parentheses is the ratio of rate constants of these reactions at 289 K from [12] and [27], respectively.

CONCLUSIONS

Thus, in the present work, we proposed an additive RRKM model for calculating the low-pressure rate constants of dissociation and recombination, with consideration given to the different isomeric forms of molecules and their excited electronic states. A new method for determining the dissociation energy and the height of the energy barrier for the reverse reaction of recombination on the basis of measured rate constants of dissociation and recombination was developed. Using these tools, we determined the equilibrium constants and rate constants of the reactions $Fe + O_2 + M = FeO_2 + M$, and $FeO + O_2 = FeO_2 + O$ in the forward and reverse directions. Taking into account excited electronic states was demonstrated to be vital for adequately describing the thermochemical and kinetic parameters of these reactions. Note, however, that the obtained parameters need further refinement on the basis of new theoretical and experimental data. In particular, it would be highly desirable to carry out detailed quantum-chemical calculations of the molecular parameters of all isomers of FeO_2.

ACKNOWLEDGMENTS

The author is grateful to Dr. F. Grein for kindly providing additional information to the results published in his paper [30].

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