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Reactions of Cr Atoms with NO, N_2O, CO_2, NO_2, and SO_2 Molecules

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Abstract—Experimental results on the interaction of Cr atoms with various oxygen-containing molecules (NO, N_2O, CO_2, NO_2, and SO_2) at high temperatures (>1000 K) are presented. It is demonstrated that activation barrier for spin-forbidden reactions is higher, all other things being equal. For the reaction of Cr atoms with N_2O, an interpolated temperature dependence of the rate constant, based on the high-temperature measurements conducted in the present work and the published low-temperature data, is proposed.

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Interest in the oxidation of metals stems from the role they play in natural and technological processes: in atmospheric chemistry, homogeneous and heterogeneous catalysis, production of structures and nanoparticles of oxides, and thermal processing of waste [1–4]. These applications stimulated extensive studies of the reactions of transition metals with oxidizers by various experimental methods [5–7].

One of such metals is chromium. Previously, in a short communication [8], we reported, without giving experimental details and primary data, the rate constants of the interaction of chromium atoms with various oxidizers at high temperatures, which were measured behind shock waves by using atomic absorption spectroscopy. At the time of publication of [8], there were virtually no other measurements, even at low temperatures. In recent years, such measurements, although scarce, have been reported, which makes it possible to examine the mechanism of these reactions more thoroughly and obtain reliable values of their kinetic characteristics. Note that an extension of the temperature range in which an elementary chemical reaction is experimentally investigated is highly important for gaining deeper insights into its mechanism.

These circumstances prompted us to jointly interpret our high-temperature data and the recently published results on the reactions of Cr atoms with various oxidizers, NO [9], N_2O [9–12], CO_2 [9], and SO_2 [13], at low and medium temperatures. While performing this analysis, we more carefully processed the primary experimental data than it was done in our previous study [8], in particular, made an allowance for a finite time resolution of the data acquisition system (~2–3 μs).

In the present work, we measured the kinetic characteristics of the interaction of Cr with NO, N_2O, CO_2, NO_2, and SO_2 and analyzed them together with the available literature data.

EXPERIMENTAL

Measurements were taken behind incident shock waves in a shock tube equipped with means of atomic absorption measurements [5]. Chromium atoms were monitored using the resonance transition at λ = 452.4 nm. The compositions of the mixtures and the temperatures and total densities of the shocked gas are listed in the table. The source of metal atoms was a fast

Experimental conditions of the oxidation of Cr atoms by various oxidizers (OX)*

Mixture	OX, %	Total density $\times 10^6$, mol/cm^3	T, K
		Cr + NO	
1	5.0	1.3–5.3	2220–3150
		Cr + N_2O	
2	0.20	2.5–3.0	1130–2570
		Cr + CO_2	
3	10.0	1.5–3.5	1429–3020
4	30.0		926–2200
5	50.0		940–2080
		Cr + NO_2	
6	0.01	1.4–2.6	1130–2700
		Cr + SO_2	
7	0.20	1.5–2.7	1080–2920
8	0.54		

* The concentration of $Cr(CO)_6$ was 3.0×10^{-4}% in all experiments.

decomposition of chromium hexacarbonyl: over the temperature range covered, it decomposes within 1 μs [14].

One particular feature of atomic absorption measurements is that the optical density generally does not obey the Beer–Lambert law. The reason is that the width of the line emitted by the source is comparable with the absorbing line width, or even exceeds it [15].

It turned out, however, that, at medium values of the optical density, the generally complex relationship between the concentration of atoms (absorbing layer thickness) and the optical density D can be described by the modified Beer–Lambert law [16]:

$$D = \ln(I_0/I) = (\varepsilon[\mathrm{A}]l)^{\gamma}, \qquad (1)$$

where I and I_0 are the intensities of probing light beam before and after passing the absorbing layer, ε is the absorption coefficient, [A] is the concentration of atoms (Cr atoms in our case), l is the optical path length, γ is a dimensionless exponent, ~0.5–1.0. Based on the calibrations conducted in [5], the value of γ was set at 0.73.

Given that the oxidizer molecules are present in a large excess compared to chromium atoms and are not consumed during the experiment and that the atoms are formed virtually instantaneously, the reaction rate can be closely described by the first-order kinetic equation:

$$-(1/[\mathrm{Cr}]) \times (d[\mathrm{Cr}]/dt) = k_{\mathrm{obs}} = k[\mathrm{OX}], \qquad (2)$$

where k_{obs} is the observed first-order rate; k, constant for the bimolecular reaction between the Cr atom and oxidizer OX and [OX] is the oxidizer concentration. Substituting expression (1) into (2) yields a working formula for determining k:

$$k = -(\gamma[\mathrm{OK}])^{-1} \times \{d[\ln\ln(I_0/I)]/dt\}. \qquad (3)$$

RESULTS AND DISCUSSION

Interaction of Cr Atoms with NO

Interest in this reaction is motivated by that the NO molecule is a stable radical and that this process constitutes one of the steps in the transformations of chromium-containing species during incineration of metal-containing waste. The tabulated bond dissociation energies of the NO and CrO molecules, D_0(N–O) = 627 kJ/mol [17] and D_0(Cr–O) = 457 ± 7 kJ/mol [18], suggest that the reaction

$$\mathrm{Cr(a^7S_3) + NO(X^2\Pi_r) \longrightarrow CrO(X^5\Pi_{-1}) + N(^4}S_0) \quad \mathrm{(I)}$$

is endothermic by 169.8 kJ/mol. Since the dissociation energy of the Cr–N bond (D_0(Cr–N) = 361.5 kJ/mol [19]) is substantially lower than that of the Cr–O bond, the reaction

$$\mathrm{Cr(a^7S_3) + NO(X^2\Pi_r) \longrightarrow CrN(X^4\Sigma^-) + O(^3P)} \quad \mathrm{(II)}$$

is even more endothermic and can hardly compete with reaction (I).

There is a large body of publications concerning the interaction of metal atoms with the NO molecule, but, as far as we know, the interaction of metal atoms with NO has been studied only at room temperature or somewhat higher temperatures. In all the metal–NO systems studied, the interaction occurs by the recombination mechanism if the N–O bond is stronger than the metal–O bond, or by the exchange mechanism in the opposite case.

After the publication of our work [8], the interaction of Cr atoms with NO has been studied only in [9], at a temperature of 298 K and pressures from 1 to 700 Torr. It was revealed that the rate constant nearly linearly depends on the pressure, a behavior typical of recombination reactions. Using a simplified method for constructing falloff curves, the authors determined the values of the rate constant in the low- and high-pressure limits.

In the present work, the interaction of chromium atoms was studied at temperatures high enough to ensure the occurrence of reaction (I).

Processing the primary experimental data by formula (3) yielded the temperature dependence of the rate constant displayed in Fig. 1a, which can be presented by the expression (activation energy in kJ/mol)

$$k_1 = 7.1 \times 10^{14}\exp(-166.1/RT)\ \mathrm{cm^3\ mol^{-1}\ s^{-1}}. \qquad (4)$$

The monotonically positive character of the Arrhenius dependence at high temperatures, characterized by a high activation energy, suggests that the interaction between the chromium atoms and nitrogen oxide occurs by the exchange mechanism (Eq. (I)).

Figure 1b compares our results with those from [9] at the same total pressure. This comparison clearly shows that, in the present work and in [9], different processes were studied: exchange reaction and recombination, respectively.

According to [20], the observed activation energy is related to the reaction barrier (which equals the enthalpy change for this reaction, since it is spin-allowed) as

$$E_0 = E_{\mathrm{a}} - nRT_{\mathrm{m}}, \qquad (5)$$

where n is the exponent in the generalized Arrhenius law and T_{m} is the mean temperature. The value of n is normally set at 0.5, whereas T_{m} is defined as $T_{\mathrm{m}} = (T_1T_2)^{0.5}$ (T_1 and T_2 are the boundaries of the temperature range covered) [21]. In this case, $E_{0.1} = \Delta H_1(0\ \mathrm{K})$ = 155 kJ/mol, whence, given that D_0(N–O) = 627 kJ/mol [17], D_0(Cr–O) = 472 kJ/mol.

This quantity is somewhat higher than the value presented in the databases [18] and [19], which is based on the mass-spectrometric measurements of the Cr + AlO = CrO + Al equilibrium (see refs. in [18]): D_0(Cr–O) = 457 ± 7 kJ/mol. A nearly identical value D_0(Cr–O) = 457 ± 9 kJ/mol was obtained in a study of the interaction of chromium atoms with oxygen molecules in crossed molecular beams [22]. A close value can be derived from our experimental results. Indeed, taking into account the remark made in [20] that n can differ from 0.5 because of the contribution from the internal degrees of freedom and setting n = 0, we obtained D_0(Cr–O) = 460.1 kJ/mol, a value close to

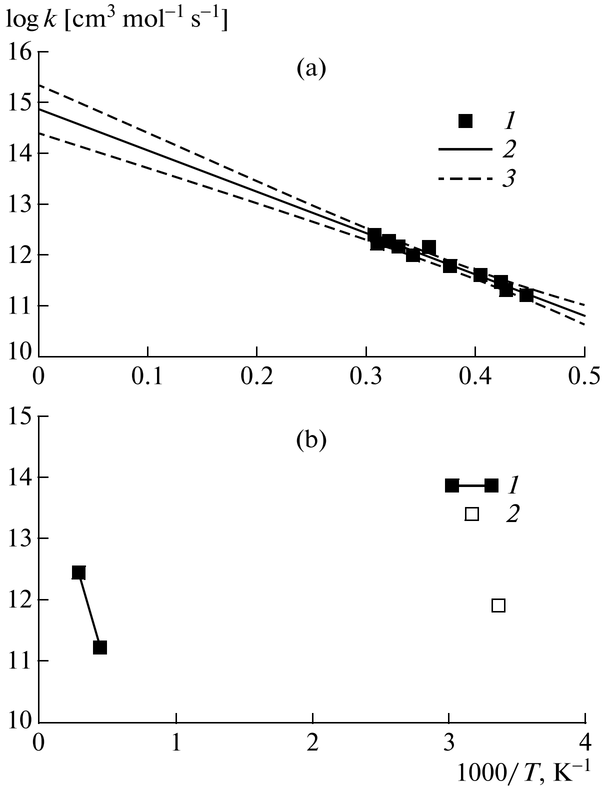

Fig. 1. (a) Temperature dependence of the rate constant for the interaction of Cr atoms with NO: (*1*) measurements behind incident shock waves in a 0.0003% $Cr(CO)_6$ + 5% NO + Ar mixture, (*2*) linear regression, and (*3*) 95% confidence interval; (b) comparison with the published data: (*1*) present work and (*2*) [9].

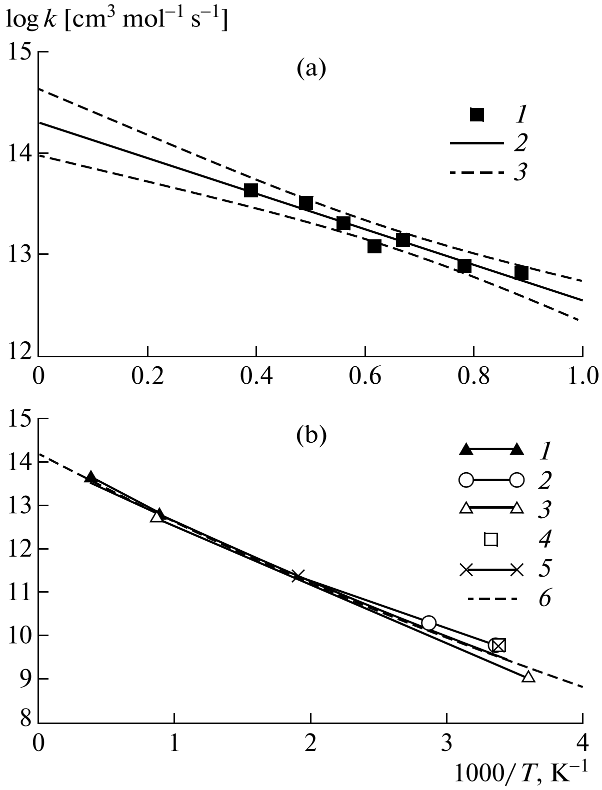

Fig. 2. (a) Temperature dependence of the rate constant for the interaction of Cr atoms with N_2O: (*1*) measurements behind incident shock waves in a 0.0003% $Cr(CO)_6$ + 0.2% N_2O + Ar mixture, (*2*) linear regression, and (*3*) 95% confidence interval; (b) comparison with the published data: (*1*) present work, (*2*) [9], (*3*) [10], (*4*) [11], (*5*) [12], and (*6*) dependence obtained by averaging data (*1*)–(*5*).

the value reported in the above handbooks. In a review paper [2], $D_0(\mathrm{Cr–O}) = 464.0$ kJ/mol was given.

A lower value, $D_0(\mathrm{Cr–O}) = 436.2 \pm 8.9$ kJ/mol, was determined based on an analysis of high-temperature mass-spectrometric data on the composition of the vapor in the europium–chromium–phosphorus–oxygen system [24].

Thus, the obtained characteristics of the interaction of chromium atoms with nitrogen oxide are in close agreement with the available thermochemical data for this reaction.

Interaction of Cr Atoms with N_2O and CO_2

The reaction of chromium atoms with nitrous oxide,

$$\mathrm{Cr}(a^7S_3) + N_2O(X^1\Sigma^+) \longrightarrow \mathrm{CrO}(X^5\Pi_{-1}) + N_2(X^1\Sigma_g^+) \qquad \text{(III)}$$

is spin-forbidden, but, at the same time, it is exothermic, $\Delta H_3^{\circ}(0\ \mathrm{K}) = -295.2$ kJ/mol [17, 18]. This reaction was first investigated in our previous study [8]. Later, this reaction was studied at medium and low temperatures [9–12]. The results of our measurements and a comparison thereof with the published data are presented in Fig. 2. The linear regression of the temperature dependence of the experimental values obtained in the present work yielded the following expression for the rate constant of this reaction:

$$k_3 = 2.0 \times 10^{14.0 \pm 0.3} \times \exp[-(33.5 \pm 9.0)/RT]\ \mathrm{cm^3\ mol^{-1}\ s^{-1}}. \qquad (6)$$

Considered together, the available measurements (Fig. 2b) demonstrate a non-Arrhenius behavior, which can be described by the expression

$$k_3 = 1.4 \times 10^{14} \times \exp(155000/T^2 - 3690/T)\ \mathrm{cm^3\ mol^{-1}\ s^{-1}}. \qquad (7)$$

The observed activation energy at the middle of the temperature range covered was found to be

$$E_{\mathrm{obs}} = R\mathrm{d}(\ln k_3)/\mathrm{d}(1/T) = 25.5\ \mathrm{kJ/mol}. \qquad (8)$$

This value is markedly higher than that predicted by the quantum-chemical calculations performed in [25] (15.5 kJ/mol), but markedly lower than the value obtained from the quantum-chemical calculations carried out in [26] (33 kJ/mol). Nevertheless, one can claim that the experimental data are in satisfactory

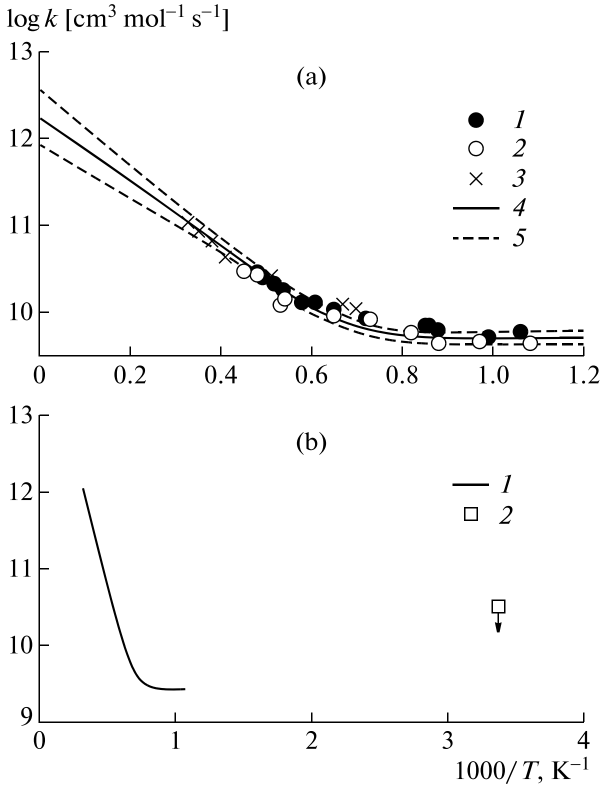

Fig. 3. (a) Temperature dependence of the rate constant for the interaction of Cr atoms with CO_2 measured behind incident shock waves in 0.0003% $Cr(CO)_6 + CO_2 + Ar$ mixtures with various CO_2 concentrations: (*1*) 50, (*2*) 30 and (*3*) 10%; (*4*) regression and (*5*) 95% confidence interval. (b) Comparison with the published data: (*1*) present work and (*2*) upper estimate [9].

agreement with the theoretical predictions, although the accuracy of such predictions remains insufficient. That the calculations performed in [25] gave a substantially lower value can be tentatively explained by that the authors used only one potential energy surface, without regard for the intersection of the quintet and septet terms.

The interaction of chromium atoms with carbon dioxide is similar to their reaction with nitrous oxide:

$$\mathrm{Cr}(a^7S_3) + \mathrm{CO_2}(X^1\Sigma_g^+) \longrightarrow \mathrm{CrO}(X^5\Pi_{-1}) + \mathrm{CO}(X^1\Sigma^+). \qquad \text{(IV)}$$

Note, however, that, in contrast to (III), this reaction is endothermic, with $\Delta H_4^\circ(0\ \mathrm{K}) = 69.1$ kJ/mol [17, 18].

The results of our measurements are displayed in Fig. 3. Apart from our data, there is only one upper estimate of the rate constant of the interaction of chromium atoms with carbon dioxide [9]. As can be seen, in the lower part of the temperature range used in the present work, the rate constant is virtually temperature-independent. Such a behavior can be explained by either the recombination of chromium atoms with CO_2 molecules to form complexes or by the presence of small admixtures of oxygen in the test mixture, since the rate of the interaction of molecular oxygen with chromium atoms is fairly high [27]. We favor the latter possibility, because quantum-chemical calculations [28] and experiments on the interaction of transition metal atoms with carbon dioxide in cryogenic matrices suggest that such complexes, having a bonding energy below 100 kJ/mol [28–30], cannot exist at temperatures above 1000 K. In addition, the rate constant of the formation of such a complex in the low-pressure limit estimated from the data presented in Fig. 3a is approximately 2–3 orders of magnitude lower than the values typical of atom–triatomic molecule recombination reactions [31], making implausible the assumption that Cr and CO_2 recombine.

Subtracting the contribution from admixed oxygen (the concentration of which was estimated as 0.002%) gives the following expression for the rate constant of reaction (IV):

$$k_4 = 2.8 \times 10^{14.0 \pm 0.6} \times \exp[-(140.7 \pm 23.0)/RT)]\ \mathrm{cm^3\ mol^{-1}\ s^{-1}}. \qquad (9)$$

As can be seen, this expression is characterized by a normal preexponential factor and an activation energy substantially higher than the endothermicity of the reaction (69.1 kJ/mol). Such a behavior is likely due to this reaction being spin-forbidden, since an analogous reaction of iron atoms with CO_2 (spin-allowed) has an activation energy close to its endothermicity.

Interaction of Cr Atoms with NO_2 and SO_2

Unlike CO_2 and N_2O, the NO_2 and SO_2 molecules form rather stable complexes with transition metal atoms [13, 26, 32]. According to [26, 32], one of the factors responsible for a high reactivity of NO_2 and SO_2 compared to CO_2 and N_2O is that their electron affinities (2.273 ± 0.005 eV for NO_2 [33] and 1.1 eV for SO_2 [17]) are substantially higher than those of N_2O (0.15 eV [34]) and CO_2 (<0 [35]). The NO_2 and SO_2 molecules have a similar geometric structure, differing in the strength of the bond between the central atom and the oxygen atoms and in the electronic structure. For this reason, it is interesting to examine the reactivity of these molecules with respect to chromium, a typical representative of the transition metal atoms.

To our knowledge, there are no published data on the interaction of chromium atoms with nitrogen dioxide, whereas the data on the reaction with sulfur dioxide have been obtained only at low temperatures (297–534 K) [13].

Quantum-chemical calculations within the framework of density functional theory [26] showed that, except for the Ti atom, which forms a complex with the NO_2 molecule by bonding to the N and O atoms ($\eta^2_{\mathrm{N,O}}$ complex), the rest of the transition metal atoms bond to each of the two oxygen atoms ($\eta^2_{\mathrm{O,O}}$ complex).

The complex then rearranges by passing over a barrier, the height of which does not exceed, however, the energy of the starting reactants, a factor that allows these reactions to occur without an appreciable barrier. Finally, an oxo-nitrosyl complex forms with a bond strength of ~120 kJ/mol. Note that the stability of similar complexes of transition metal atoms with nitrous oxide does not exceed 10 kJ/mol.

The results of the calculations performed in [13, 32] show that the interaction of transition metal atoms with SO_2 also occurs through an $\eta^2_{O,O}$ complex, but its further transformations were not considered.

To our knowledge, measurements of the rate constants of the interaction of NO_2 with transition metal atoms have been conducted only for the iron [36, 37], copper [38], and titanium [39] atoms. In all cases, the rate constant of the reaction was weakly dependent on the temperature and independent of the pressure, a behavior indicative of the reaction occurring by the exchange mechanism.

The interaction of sulfur dioxide with transition metal atoms was studied Cr [13], Ni [40], and V, Fe, Co [32]. All these reactions, except for the reaction with vanadium atoms, are endothermic and, therefore, proceed by the association mechanism. The interaction of V atoms with SO_2 occurs by the exchange mechanism [32].

The primary experimental data on the interaction of Cr with NO_2 were processed on the assumption that the consumption of atoms obeys the first-order kinetic equation in Cr concentration (since the oxidizer is present in a large excess). Based on the data from [41], we concluded that nitrogen dioxide does not decompose to an appreciable extent at temperatures used in [8] and the present work, except for the highest temperature. In this case, the oscillogram was processed within a time interval shorter than the characteristic time NO_2 decomposition at this temperature, ~11 μs.

As in the case of interaction of other transition metals with NO_2, no pressure dependence of the rate constant for the interaction of Cr with NO_2 was observed; therefore, it makes sense to assume that the main pathway of this interaction is the exchange reaction

$$\begin{aligned}&Cr(a^7S_3) + NO_2(X^2A_1)\\ &\longrightarrow CrO(X^5\Pi_{-1}) + NO(X^2\Pi_r),\end{aligned} \tag{V}$$

which is exothermic: $\Delta H^\circ_5(0\ K) = -156.8$ kJ/mol [17, 18]. The reaction involving the abstraction of the nitrogen atom,

$$\begin{aligned}&Cr(a^7S_3) + NO_2(X^2A_1)\\ &\longrightarrow CrN(X^4\Sigma^-) + O_2(X^3\Sigma^-_g),\end{aligned} \tag{VI}$$

is endothermic: $\Delta H^\circ_6(0\ K) = 72.3$ kJ/mol [17–19]. Another possible reaction is

$$Cr(a^7S_3) + NO_2(X^2A_1) \longrightarrow CrNO(X) + O(^3P_J), \tag{VII}$$

which is also likely to be endothermic. As far as we know, there are no experimental data on the stability of the CrNO molecule. As to theoretical treatment, we managed to find only one work in which the value of D_0(Cr–NO) was calculated by quantum-chemical methods [42]. It turned out that this value depends on the accepted spin multiplicity, reaching 259 kJ/mol at the lowest multiplicity ($S = 2$). Comparing the measured rate constant of the Cr + NO recombination with that calculated using the RRKM theory at various values of D_0(Cr–NO), the authors of [42] concluded that CrNO is formed in a high-spin state ($S = 6$ or 8) and that the dissociation energy of the Cr–NO bond is 140 kJ/mol. Using this estimates and the tabulated thermochemical data from [17, 18], we concluded that reaction (VII) is essentially endothermic (by 45–165 kJ/mol), and, therefore, it should be characterized by a high activation energy and, correspondingly, a low rate.

The temperature dependence of the rate constant for reaction (V), displayed in Fig. 4, can be presented by the following Arrhenius expression (activation energy in kJ/mol):

$$\begin{aligned}&k_5 = 6.3 \times 10^{14 \pm 0.3}\\ &\times \exp[-(18.3 \pm 4.0)/RT],\ cm^3\ mol^{-1}\ s^{-1}.\end{aligned} \tag{10}$$

As can be seen, the rate constant k_5 has a normal preexponential factor and an activation energy substantially lower than the enthalpy change for reactions (VI) and (VII). Thus, most likely, reaction (V) is the predominant pathway of the interaction of chromium atoms with nitrogen dioxide.

The primarily experimental data on the interaction of Cr with SO_2 were also processed using the first-order kinetic equation in Cr concentration.

Judging from the data reported in [43], sulfur dioxide shows no appreciable decomposition within the temperature range covered in our experiments, except for the highest temperature.

The reaction of chromium atoms with SO_2 is endothermic and, as discussed above, occurs only by the association mechanism at low temperatures [13]. The exchange reaction

$$\begin{aligned}&Cr(a^7S_3) + SO_2(X^1A_1)\\ &\longrightarrow CrO(X^5\Pi_{-1}) + SO(X^4\Sigma^-)\end{aligned} \tag{VIII}$$

is endothermic, with $\Delta H^\circ_8(0\ K) = 88.6$ kJ/mol, and, therefore, it cannot proceed at a noticeable rate at low temperatures.

The measured temperature dependence of the rate constant for reaction (VIII) is displayed in Fig. 5. As is seen, it exhibits a well-pronounced non-Arrhenius behavior: at low temperatures, the rate constant is virtually temperature-independent and even shows a negative slope. At higher temperatures, the activation energy becomes positive. The rate constant of the interaction can be presented as the sum of two components, low- and high-temperature ones (solid line in Fig. 5):

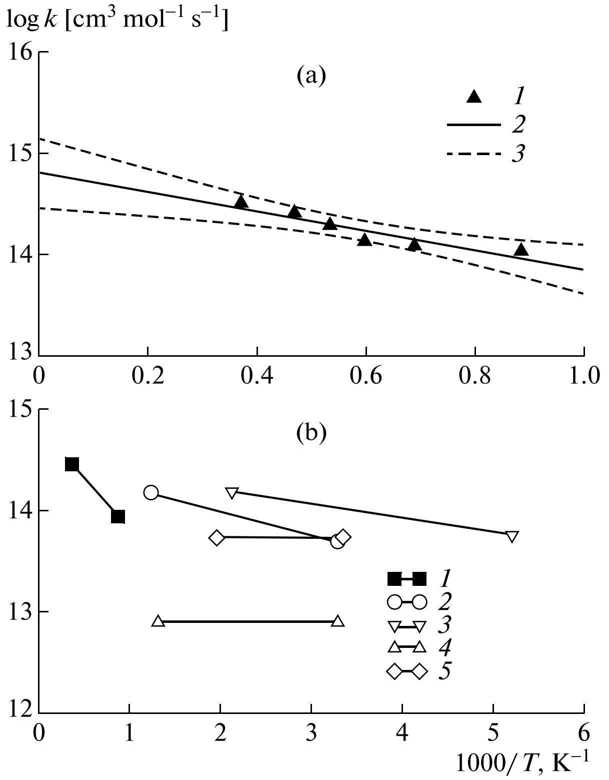

Fig. 4. (a) Temperature dependence of the rate constant for the interaction of Cr atoms with NO_2: (*1*) measurements behind incident shock waves in a 0.0003% $Cr(CO)_6$ + 0.01% NO_2 + Ar mixture, (*2*) linear regression, and (*3*) 95% confidence interval; (b) comparison with the published data on the interaction of various transition metal atoms with NO_2: (*1*) Cr, present work, (*2*) Fe [36], (*3*) Fe [37], (*4*) Cu [38], and (*5*) Ti [39].

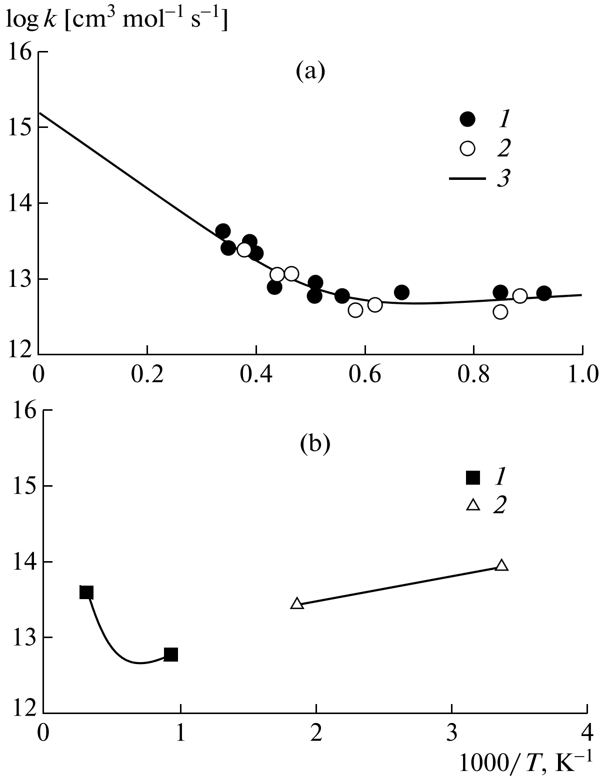

Fig. 5. (a) Temperature dependence of the rate constant for the interaction of Cr atoms with SO_2 measured behind incident shock waves in 0.0003% $Cr(CO)_6$ + SO_2 + Ar mixtures with various SO_2 concentrations: (*1*) 0.2 and (*2*) 0.54%; (*3*) regression. (b) Comparison with the published data: (*1*) present work and (*2*) [13].

$$k_\Sigma = 1.6 \times 10^{15}\exp(-95.4/RT) + 6.5 \times 10^{12}(1000/T),\ \text{cm}^3\,\text{mol}^{-1}\,\text{s}^{-1}. \quad (11)$$

Clearly, the high-temperature component, with positive activation energy,

$$k_8 = 1.6 \times 10^{15}\exp(-95.4/RT),\ \text{cm}^3\,\text{mol}^{-1}\,\text{s}^{-1}, \quad (12)$$

is associated with the exchange reaction.

As can be seen, the preexponential factor is substantially higher than the collision frequency factor, whereas the activation energy somewhat exceeds the endothermic effect of the reaction.

Such a behavior can be interpreted within the framework of the transition state theory on the assumption that the statistical weight (partition function) of the transition state increases at high temperature (~2000 K) faster than the product of the partition functions of the starting reactants [44].

The component of the rate constant of the interaction of chromium atoms with sulfur dioxide, which dominates at high temperatures can be associated with the $Cr(a^7S_3) + SO_2(X^1A_1)$ recombination or with the presence of small admixtures of a very reactive oxidizer, for example, SO_3. The nature of this component can be greatly elucidated by performing experiments at various pressures of the bath-gas. If this component proved to be strongly dependent on the pressure (total density), it would signify that it characterizes recombination.

Thus, in the present work, the rate constants of the interaction of Cr atoms with NO, N_2O, CO_2, NO_2, and SO_2 molecules at high temperatures were measured, which proved to be in close agreement with the available low-temperature data. A qualitative interpretation of the results was made, and approximations of the temperature dependences of the rate constants for some of the studied reactions over a wide temperature range were proposed.

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