KINETIC MODEL FOR THE PHOTOREACTIONS OF d\(^0\)-OXO-COMPLEXES APPLIED TO SiO\(_2\)

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Based on literature data a kinetic model has been devised for the photoreactions of d\(^0\)-oxo-complexes (Ti\(^{4+}\), V\(^{5+}\), Cr\(^{6+}\), Mo\(^{6+}\), and W\(^{6+}\)) with H\(_2\), alkanes, CO and alkenes, fixed on supports. Equations have been obtained for the rate and quantum yields of the reactions and photosphorescence.

Photoexcited oxo-complexes of metal ions with unoccupied d-shells (d\(^0\)-complexes) react with two types of substrates: H-atom donors (RH) and O-atom acceptors (S). So far, the excited complexes of Ti\(^{4+}\), V\(^{5+}\), Cr\(^{6+}\), Mo\(^{6+}\), and W\(^{6+}\) have been studied in detail [1-5] and their reactions on the surface of supports (the products [2-3, 6, 7], kinetics [4, 7, 8], and mechanisms [2-4, 6, 7, 9]) with H\(_2\) [2, 6], alkanes [2, 3, 9], CO [4, 6-9], and alkenes [6, 9, 10]), which lead to the reduction of the complexes. The main results were obtained by dynamic luminescence [2, 4, 7, 8], EPR [2, 6], and electron [1, 2] spectroscopy. At 77 K the photoprocesses take place as bimolecular reactions of the excited complexes with the substrates, diffusing on the surface [4, 7, 9].

In the present study these results have been employed to develop a general kinetic model which includes photophysical stages, common to all above-mentioned complexes, and substrates, preceding the rupture and formation of chemical bonds, as well as two types of chemical stages. The equations for the rate and the quantum yields of the reactions and luminescence, obtained by means of the kinetic model, make it possible to interpret in detail the concrete experimental results and the general picture of the photoprocesses of the d\(^0\)-oxo complexes with the substrates, acting as reducing agents.

The electron structure of the oxygen and halide complexes of Ti\(^{4+}\), V\(^{5+}\), Mo\(^{6+}\), W\(^{6+}\), etc. (symmetry Td, C\(_{3v}\), C\(_{2v}\)) has been studied by different physical [1-4] and mathematical [1, 2, 5] methods. The main contributors to the upper occupied molecular orbitals (MO) of such complexes are the 2p-atomic orbitals of the ligands (O\(^2-\), Cl\(^-\), etc.) [1, 5]. In the lower unoccupied MO the d-atomic orbitals of the metal and the 2p-orbitals of the ligands participate approximately to the same extent [1, 5]. When the d\(^0\)-complexes are excited by visible or near-UV light, the electrons in the complexes pass from the virtually uncombining upper occupied MO (\(t^2, t^1\)) to the lower unoccupied antibonding MO (\(e^*, t^2*\)) [1, 2, 5]. In this case electron vacancies appear on the ligands (for instance, O\(^2-\) \rightarrow O\(^-\)) [1-5] and the metal-to-ligand bond lengthsens (weakens). In the redox reactions of such complexes with reducing substrates the ligands with electron vacancies as radical centers detach hydrogen atoms from the H-atom donors (H\(_2\), alkanes) [2, 3, 9]; the weakened bonds between the metal and ligand are easily ruptured by acceptors of anion-radicals O\(^-\) or O-atom acceptors (CO, alkenes) [6-9].

The photoexcited d\(^0\)-oxo complexes show strong luminescence [2, 4, 7, 8], whereby the wavelength of the emitted light differs from the frequency of the absorbed radiation. For instance [4], the Mo\(^{6+}\) oxo complexes, applied to SiO\(_2\), absorb at 298 K at the frequency \(\nu_m = 34000\) cm\(^{-1}\) (singlet-singlet transition \(S_0 \rightarrow S_1\)) and emit in a singlet-singlet (\(S_1' \rightarrow S_0\), \(\nu_m = 29,000\) cm\(^{-1}\)) and in a triplet-singlet transition (\(T_1 \rightarrow S_0\), \(\nu_m = 23,000\) cm\(^{-1}\)). The intensity of fluorescence (\(S_1' \rightarrow S_0\)) remains sharply on account of the decreased probability of nonradiating transitions [8].

A correlation exists [7] between the lifetimes \(\tau\) (300 K) of excited complexes on a substrate (218 \times 10\(^{-6}\) (V\(^{5+}\)), 63 \times 10\(^{-6}\) (Mo\(^{6+}\)), 2.9 \times 10\(^{-6}\) sec\(^{-1}\) (W\(^{6+}\)) \rightarrow triplet state [7] and (0.1 \pm 1.0) \times 10\(^{-8}\) sec\(^{-1}\) \→ singlet state [2]) and their reaction rates with the substrates. Due to low values of \(\tau\) the complexes in the singlet excited state do not participate in the chemical conversions. In fact, in distinction from phosphorescence, the fluorescence is not quenched by carbon monoxide [8].

At certain conditions (for instance, 77 K, molybdenum compounds covering about 0.1% of the SiO₂ surface, carbon monoxide up to 10%) the quantum yield of phosphorescence \( Q \) decreases with the increasing concentration of the substrate-quenching agent \( S \) according to the equation of Stern and Volmer [4]

\[
\frac{Q_0}{Q} = 1 + \tau k_q S \cdot \tau
\]

where \( Q_0 \) and \( \tau \) are the quantum yield of phosphorescence and the lifetime of the excited state in the absence of a quenching agent and \( k_q \) is the rate constant of quenching. Satisfying the linear correlation (1) suggests a bimolecular mechanism of the reaction of the photoexcited complexes with the molecules, diffusing on the surface [4].

EPR detected \( V^{4+} \) and \( Mo^{5+} \), and adsorbed free radicals, formed by the detachment of an H atom from RH by the excited oxo complexes, as the products of the photoreaction at 77 K of the \( V^{5+} \) and \( Mo^{6+} \) complexes with alkanes (\( CH_4, C_2H_6, C_3H_8 \)) [2, 3, 9]. The scheme of the conversion of the complexes (\( O^{2-} = M^n \)) and RH substrates [2, 3, 9]

\[
(O^{2-} = M^n) \xrightarrow{hv} (O^+-M^{n+})^* + RH
\]

\[
\rightarrow (HO^--M^{n-}) + \hat{R}_H
\]

is also confirmed by the observed formation of \( C_3H_6 \) as the product of the oxidation of \( CH_4 \) [3, 9]. In the presence of \( O_2 \) and with increasing temperature the yield of the oxidation products of \( CH_4 (C_2H_6, C_3H_8, H_2O, H_2CO, CO, CO_2) \) increases and their composition changes due to regeneration of the complexes, oxidized with oxygen, and the participation of \( O_2 \) in the oxidation of alkyl radicals [3]. The photooxidation of \( H_2 \) at 77 K satisfies a scheme analogous to (2) [2, 9]. EPR detected the formation of the ions \( V^{4+}, Cr^{5+}, \) and \( Mo^{5+} \) and of hydrogen atoms in the reactions of \( V^{5+} / SiO_2, Cr^{5+} / SiO_2, \) and \( Mo^{6+} / SiO_2 \) with \( H_2 \), as well as a hyperfine doublet splitting of the EPR signals of \( Mo^{5+} \) on \( OH^- \) protons [2, 9]. The formation of \( OH^- \) was also established by IR spectroscopy [2].

The photoreaction of the d⁺-oxo complexes, fixed on the surface, with CO

\[
(O^{2-} = M^n) \xrightarrow{hv} (O^+-M^{n+})^* \xrightarrow{CO} \rightarrow CO_2 + (CO \cdot M^{n-2})
\]

includes the formation of \( CO_2 \) and the photoadsorption of \( CO \) [2, 4, 6-9]. At 77 K both products of reaction 93) are accumulated, with the activation energies of ~1.7 and ~2.2 kcal/mole respectively [7].

The reaction scheme of the initial photooxidation stages of alkenes by the systems Ti⁺⁺/SiO₂ [10] and \( V^{5+} / SiO_2 \) [9] is probably similar to (3) and includes the transfer of an O atom or of an \( O^- \) anion from the excited complex to the substrate. EPR showed the formation of the radical \( CH_2-CH_2-O^- \) [9] as the primary product of the photoreaction of \( C_2H_4 \) with \( V^{5+} / SiO_2 \).

The presented facts and conclusions permit us to propose the following general scheme for the photoreactions of the d⁺-oxo complexes, fixed on the support, with two types of substrates (S and RH), diffusing on the surface:

\[
\begin{align*}
(O^{2-} = M^n) \xrightarrow{hv} (O^+-M^{n+})^* & \xrightarrow{k_{s}} (O^- M^{n+})^* \xrightarrow{k_e} (O^- M^{n+})_e \xrightarrow{k_d(S,RH)} (O^- M^{n+})^* \xrightarrow{k_{p}} RH (O^- M^{n+})^* \xrightarrow{k_e} (O^- M^{n+})_e
\end{align*}
\]

\[
\frac{k_d(S,RH)}{k_p} = \frac{S (O^- M^{n+})^*}{RH (O^- M^{n+})^*}
\]

\[
(4)
\]

231