=================================== **CATALYSIS** ===================================

Oxidation of I⁻ and S²⁻ Anions by Oxygen in Aqueous Suspensions of Silica Gel

V. N. Pak, C. D. Hanson, and S. R. Coon

Herzen Russian State Pedagogic Institute, St. Petersburg, Russia
University of Northern Iowa, Cedar Falls, Iowa, the United States

Abstract—Oxidation of I⁻ and S²⁻ anions on the silica gel surface by atmospheric oxygen was studied at room temperature. The possibility and rate of oxidation processes are determined by the content of silica gel and oxygen in the systems. Tentative interpretation of the results is based on the assumption that a highly reactive singlet $^1O_2$ species is formed in the oxygen ensemble on the silica surface.

Molecular oxygen can be transferred into an electronically excited singlet $^1\Delta_g$ state in a number of ways, including dye-sensitized photoexcitation in solutions [1–9] and zeolites [10, 11], decomposition of unstable oxygen-containing substances [1, 2, 12], laser evaporation of metal oxides [13, 14], and microwave discharge [2, 15]. The relatively long lifetime $(10^{-3}-10^{-6}$ s in solutions), moderately high excitation energy (22.54 kcal mol^{-1}), and high chemical activity of the singlet form $^1\Delta_g$ of oxygen allow it to be considered as actual oxidizing agent in various processes, including those practically important [1–15].

It is a common knowledge that the solid substance most widely occurring in the nature, silicon dioxide, does not possess under standard conditions any redox properties, at least at the temperature of ambient air. At the same time, it cannot be positively stated that molecules with enhanced reactivity in electronically excited singlet state cannot be present in the oxygen ensemble even at room temperature under conditions of dynamic equilibrium between the SiO_2 surface and the gas phase. The excess amount and the nonuniform distribution of the surface energy may be a reason for conversion of some (presumably only a minor) part of paramagnetic $^3O_2$ molecules into the paired-spin state $^1O_2$. The energy necessary for this to occur is relatively low and, presumably, can be provided by fluctuations of the SiO_2 surface energy.

This hypothesis was the reason for undertaking the present investigation. In choosing a means of verification of the hypothesis, it was necessary to keep in mind not only the low concentration of excited oxygen molecules, but also the high probability of their impact deactivation, drastically impairing the possibility of their direct detection. In this connection, it seemed the most appropriate to assess experimentally the possibility of oxidation of a number of substances at room temperature directly on the silica surface with the aim of ensuring the involvement in the process of a finite fraction of singlet oxygen present on the surface.

Below are presented the results obtained in studying two heterogeneous reactions involving atmospheric oxygen. The first of these is oxidation of the iodide ion to molecular iodine. The choice of this reaction is governed by the reliably established fact that I⁻ is oxidized at room temperature neither by atmospheric nor by pure oxygen, whereas under the action of ozone [16] or singlet oxygen [17] this process occurs. The second reaction, oxidation of the sulfide ion on silica gel, is of particular interest in view of the possibility of occurrence of successive oxidative transformations and the wide variety of the involved charge states of sulfur.

EXPERIMENTAL

The study was performed on ultrapure silica gel S-157 (Fisher) with a specific surface area of 700 m^2 g^{-1}, giving reason to expect that analytically detectable content of oxidation products can be reached. All experiments were carried out at 25°C using a 0.1-mm sieved fraction of silica gel particles.

The rate of I⁻ oxidation in an aqueous suspension of a silica gel of a given type at a constant temperature is determined by the I⁻ and O_2 concentrations. An excess of I⁻ in the working solution can be used, in fact ensuring [I⁻] = const. The concentration of oxy-

gen is determined by the conditions of its supply into the system, i.e., by the intensity of bubbling and stirring. With the number of variable parameters deliberately restricted, the aim was to reveal the very possibility of oxidation and determine the fundamental conditions for its occurrence. For example, in a set of experiments, 50 ml of an aqueous KI solution was added to variable weighed portions of silica gel and stirred with a magnetic stirrer in open vessels in air, with the resulting suspension sampled at regular intervals of time, centrifuged, and analyzed for the content of molecular iodine. In order to ensure additional enrichment of the suspensions with oxygen, air was bubbled at a rate of 30 and 50 $cm^3 min^{-1}$. In some experiments, oxidation of the iodide ion, unhindered by oxygen diffusion, was studied. For this purpose, 0.5-g portions of silica gel were impregnated with 2 ml of 1 M KI solution and exposed to air. After a prescribed time elapsed, the same solution was added to the weighed portions, with the solution volume brought to 50 ml, the suspensions were thoroughly stirred, and samples were taken for analysis.

The appearance and accumulation of molecular iodine in solution was recorded photometrically on a Shimadzu UV-2401 PC automated spectrometer in quartz cells with optical thickness of 1 cm. The enhanced solubility of iodine in solutions containing an excess of I⁻ ions is due to the formation of stable associates $I_2 \cdot I^-$ [17]. The electronic spectrum of I_3^- contains no broad band characteristic of an aqueous solution of iodine, whereas two peaks in the UV are close and furnish an opportunity for direct photometric determination of molecular iodine (Fig. 1). A calibration procedure demonstrated that the Bouguer–Beer law is observed at $\lambda_{max} = 351$ nm with a molar extinction coefficient $\varepsilon = 1.851 \times 10^4$ $l\,mol^{-1}\,cm^{-1}$ in the concentration range 0.01–0.1 mM I_2 in a 1 M solution of KI, which well matched the goal of analytical measurements in the experiments.

The extent of oxidation of the sulfide ion on the silica gel surface and the possibility of formation, in the process, of sulfur oxides SO_2 and SO_3 were determined by Fourier ion-cyclotron resonance mass spectrometry on an IonSpec OMEGA 50 instrument. A glass ampule containing ca. 4 g of silica gel impregnated with a 1 M aqueous solution of $(NH_4)_2S$ and then kept in air was connected to the input for taking gas samples, and all components desorbed into the analyzer chamber by evacuation at room temperature were recorded. In experiments on S^{2-} oxidation in aqueous suspensions, 50 ml of 1 M $(NH_4)_2S$ solution was added to weighed portions of silica gel, and the
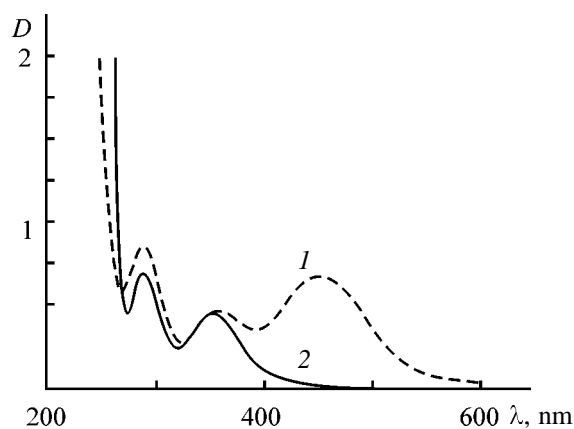

Fig. 1. Electronic spectra of iodine in (*1*) water and (*2*) 1 M solution of potassium iodide. (*D*) Optical density and (λ) wavelength; the same for Fig. 2.

mixture was stirred with a magnetic stirrer in open vessels in air.

Suspension samples taken at certain intervals of time were centrifuged and analyzed on a Dionex DX-100 liquid ion chromatograph equipped with an electrical conductivity detector and a 250-mm-long column packed with an anion-exchange resin containing bound ammonium groups. Preliminary calibration experiments demonstrated that sulfide ions are partially sorbed and/or smeared over the column in analyzing aqueous solutions containing mixtures of S^{2-}, SO_3^{2-}, and SO_4^{2-} anions in concentrations of the order of tens of ppm and, therefore, are not recorded, whereas sulfite and sulfate ions are determined together, without being separated, and are eluted as a single peak with a retention time of 3.7–3.8 min.

Formation of molecular iodine can be reliably established already during the first minutes after placing a weighed portion of silica gel in a starch-containing KI solution by the appearance of a characteristic light blue coloration. The oxidation of the iodide ion can also be observed visually in the absence of starch owing to the fast appearance of yellow coloration, particularly noticeable on the surface of silica particles and passing into solution on stirring. A typical set of spectra illustrating the accumulation of the $I_2 \cdot I^-$ form of molecular iodine are shown in Fig. 2; they completely coincide with the spectra of iodine in 1 M KI solution, taken in the course of calibration (Fig. 1). Thus, the fact of iodide ion oxidation on the silica gel surface is beyond doubt.

The essential role of the rate of oxygen supply to the silica gel surface in the course of oxidation is clearly demonstrated by the dependence in Fig. 3. The noticeable production of molecular oxygen in the ini-
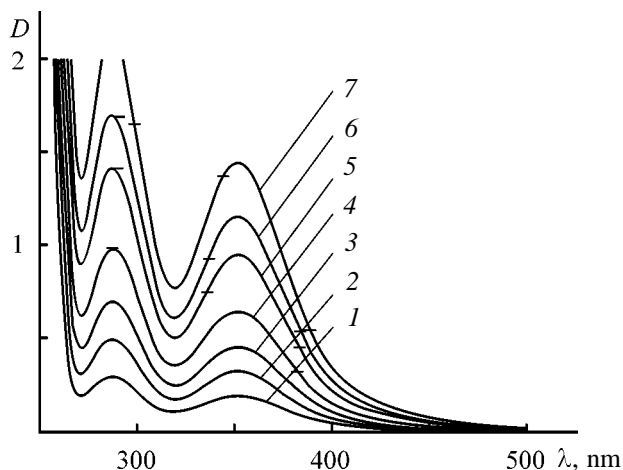
Fig. 2. Electronic spectra characterizing the accumulation of I_3^- in 50 ml of 1 M aqueous KI solution containing 1 g of suspended silica gel. Air bubbling at a rate of 30 $cm^3 min^{-1}$. Time of oxidation (h): (*1*) 0.2, (*2*) 0.4, (*3*) 0.6, (*4*) 1.0, (*5*) 1.5, (*6*) 2.5, and (*7*) 3.5.
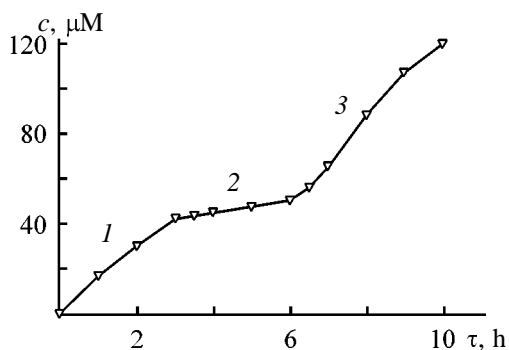

Fig. 3. Iodine concentration *c* vs. time τ of oxidation in 50 ml of 1 M KI solution containing 0.5 g of suspended silica gel. (*1*) Stirring with magnetic stirrer (150 rpm), (*2*) no stirring, and (*3*) stirring with additional bubbling of air (50 $cm^3 min^{-1}$).

tial stage is largely ensured by the amount of oxygen present in silica gel pores and by gas supply into the system, enhanced by stirring. Switching-off the stirrer (portion *2*) lowers the content of oxygen, decelerating the oxidation. In portion *3* of the curve, the process is intensified by bubbling air through the system at a rate of 50 $cm^3 min^{-1}$.

The kinetic curves presented in Fig. 4 furnish additional evidence in favor of the oxygen activation on the silica gel surface. The increase in silica gel mass under conditions of continuous stirring is accompanied by nearly proportional acceleration of molecular iodine formation (curves *1–3*). Air bubbling largely lifts the diffusion limitation on oxygen supply, markedly intensifying the oxidation (curves *4, 5*). The process is accelerated to an even greater extent in the

case of direct access of air to the surface of silica gel impregnated with 1 M KI solution (curve *6*).

In the aggregate, the obtained results suggest that an electronically excited $^1O_2$ species is present in the ensemble of oxygen molecules adsorbed onto the silica gel surface, ensuring the occurrence of the reaction

$$4I^- + {}^1O_2 + 2H_2O \rightarrow 2I_2 + 4OH^-, \qquad (1)$$

$$2I_2 + I^- = I_3^-. \qquad (2)$$
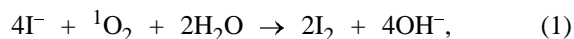
The involvement of just singlet oxygen in I^- oxidation seems to be the most likely, since formation of ozone and, the more so, of atomic oxygen requires gross energy expenditure. Appearance of charged oxygen species on the silica surface under so mild conditions is also hardly possible.

It should be emphasized that the oxidation rate is extremely low and the process can only be recorded because of the high specific surface area of silica gel. The maximum amount of molecular iodine, obtained in 12 h of experiment, is mere $10^{11}–10^{12}$ molecules per 1 cm^2 of SiO_2 surface, i.e., a vanishingly small fraction of a conventional monolayer.

Quantitative monitoring of the oxidation of the sulfide ion on the silica gel surface is hindered by the wide variety of products obtained, reversibility of transformations, and partial removal of gaseous substances from the reaction zone. However, even the results of preliminary qualitative experiments allow rather important conclusions. It is known that solutions containing the sulfide ion gradually become turbid in air because of the liberation of elemental sulfur; however, this process is slow and its consequences can only be observed after a long time. For example, 1 M H_2SO_4 solution remains transparent for many hours. At the same time, placing in this solution a weighed portion of silica gel causes visually observable formation of elemental sulfur on the surface of SiO_2 particles. Such a drastic acceleration of oxidation probably indicates that an active oxygen species is involved in the process:

$$2S^{2-} + {}^1O_2 + 2H_2O \rightarrow 2S + 4OH^-. \qquad (3)$$

However, the oxidation in the system containing S^{2-}, O_2, H_2O, and solid SiO_2 does not terminate at this point and proceeds further with higher oxidation states of sulfur reached. Correspondingly, the mass spectrum of silica gel impregnated with 1 M solution of $(NH_4)_2S$ shows, together with the reliably recorded

components: N_2, O_2, H_2O, and H_2S, also stable weak signals with masses of 64 and 80, undoubtedly belonging to ionized oxides SO_2 and SO_3 (Fig. 5). It is possible, in principle, that SO_2 formation is a result of direct oxidation of sulfide ions by singlet oxygen on the silica gel surface:

$$2S^{2-} + 3\,^1O_2 + 2H_2O \rightarrow 2SO_2 + 4OH^-. \qquad (4)$$
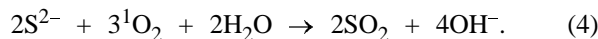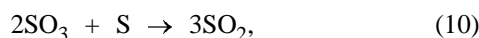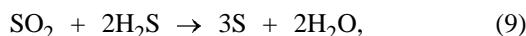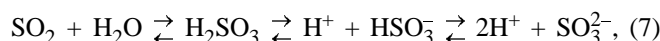
However, even in the case when oxidation proceeds in two successive stages, the occurrence of the reaction (following the liberation of elementary sulfur)

$$S + \,^1O_2 \rightarrow SO_2 \qquad (5)$$
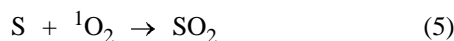
at room temperature seems to be rather uncommon and illustrative. The final stage of oxidation

$$2SO_2 + \,^1O_2 \rightarrow 2SO_3 \qquad (6)$$

again indicates that highly reactive singlet oxygen is present on the silica gel surface. In all probability, along with the above reactions in the suspension, there occur equilibria and transformations typical of charged sulfur species, e.g.:

$$SO_2 + H_2O \rightleftarrows H_2SO_3 \rightleftarrows H^+ + HSO_3^- \rightleftarrows 2H^+ + SO_3^{2-}, \quad (7)$$

$$2SO_3^{2-} + \,^1O_2 \rightarrow 2SO_4^{2-}, \qquad (8)$$

$$SO_2 + 2H_2S \rightarrow 3S + 2H_2O, \qquad (9)$$

$$2SO_3 + S \rightarrow 3SO_2, \qquad (10)$$

and also some others, including those involving unstable polythionic acids. The wide variety of possible reactions, and also partial removal of gaseous products from the system, may give rise to fluctuations in the content of sulfite and sulfate ions being formed. Indeed, these latter can be detected in the suspension soon after the onset of oxidation (Fig. 6), and their concentration changes, on the general background of growth, in a clearly nonmonotonic manner.

Thus, the above examples indirectly confirm the presence of singlet oxygen on the silica surface under standard conditions. It is the chemical activity of singlet oxygen that is presumably responsible for the oxidation on the SiO_2 surface of substances quite stable at the temperature of the ambient air. The large specific surface area of silica gel makes it possible to record oxidative transformations limited by low content of active oxygen under laboratory conditions. Consequently, there is good reason to believe that the
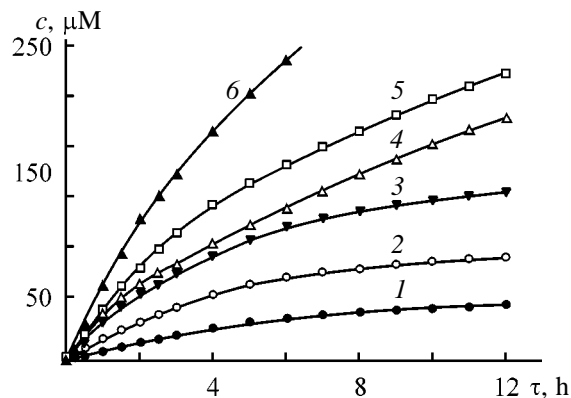
Fig. 4. Kinetic curves describing iodide ion oxidation under varied experimental conditions. (c) Concentration of iodine and (τ) time. (*1–3*) 0.25, 0.5, and 1 g of silica gel, respectively, in 50 ml of 1 M aqueous KI solution (stirring rate 100 rpm); (*4, 5*) the same as (*3*), but with additional bubbling of air at a rate of 30 and 50 cm³ min⁻¹, respectively; (*6*) 0.5 g of silica gel impregnated with 2 ml of 1 M KI solution in oxidation in air.
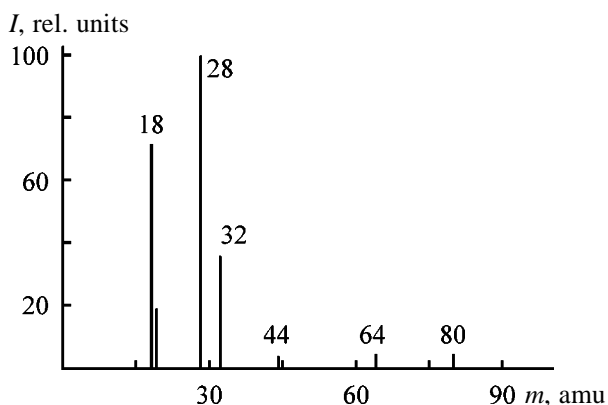
Fig. 5. Mass spectra of desorption products from the surface of silica gel impregnated with 1 M solution of $(NH_4)_2S$ and then kept in air for 20 min. (*I*) Relative signal intensity and (*m*) mass of singly ionized particles.

investigated, and many similar (which is not improbable) processes are of fundamental importance in the nature in view of the overwhelming predominance of silica on the Earth's surface and also in water basins, in suspended and precipitated states.

Finally, it should be noted that the alternative hypothetical reason for "cold" oxidative catalysis on SiO_2, based on the concepts (extensively developed in the 1970–1980s [18, 19]) assuming that coordination-unsaturated electron-acceptor centers are present on the surface of amorphous varieties of silica, is rather unlikely. It is difficult to admit of the possibility of firm adsorption and strong polarization of reagents, necessary for lowering the activation barriers of oxi-
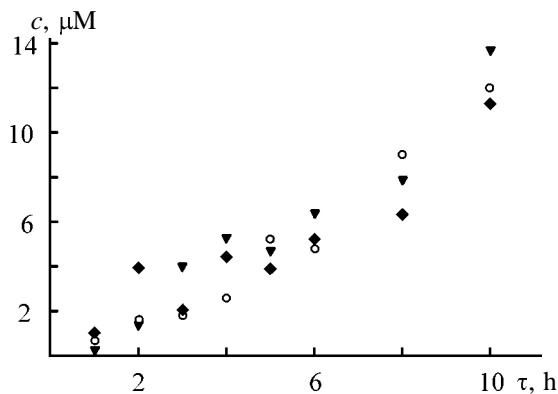
Fig. 6. Total concentration c of sulfite and sulfate ions vs. time τ of oxidation in a suspension of 1 g of SiO_2 in 50 ml of 1 M $(NH_4)_2S$ solution at a stirring rate of 100 rpm (three sets of experiments are represented).

dation processes. Moreover, the probability of reactions (1), (3), and (4) at coordination centers of silica gel is strongly limited by the action of the topochemical factor consisting in the necessity for attachment of several particles of the probable reactants in close proximity to ensure their interaction.

CONCLUSIONS

(1) The iodide ion is oxidized with oxygen at room temperature in suspensions of silica gel in aqueous KI solution to give I_3^- species.

(2) Stepwise oxidation of the sulfide ion with oxygen in suspensions of silica gel in aqueous solution of $(NH_4)_2S$, also proceeding at room temperature, gives elemental sulfur, SO_2, SO_3, and the anions SO_3^{2-} and SO_4^{2-}.

(3) The obtained results suggest that the electronically excited singlet species $^1O_2$ is involved in the oxidation reactions and serve as indirect evidence in favor of the hypothesis that oxygen can be activated on the silica surface.

ACKNOWLEDGMENT

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