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Thermal Generation of Singlet Oxygen on Zeolite ZSM-5

A. N. Romanov, M. Ya. Bykhovskii, Yu. N. Rufov, and V. N. Korchak
Semenov Institute of Chemical Physics, Russian Academy of Sciences, Moscow, 117977 Russia

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Abstract—The thermal generation of equilibrium singlet oxygen in air at $T > 140°C$ and the effect of the nonequilibrium thermal desorption of singlet oxygen from zeolites ZSM-5 substituted by cations of alkaline (Cs) and alkaline-earth (Ca) metals are found. Possible mechanisms of singlet oxygen generation during desorption are discussed.

INTRODUCTION

The participation of singlet oxygen in heterogeneous catalytic hydrocarbon oxidation has already been discussed in the literature [1–3]. Some authors [2, 3] reported the thermal desorption of singlet oxygen from the catalyst surfaces (e.g., the Li–Sn–P–O system and V_2O_5). ESR spectroscopy also provides indirect evidence for the existence of $^1\Delta_gO_2$ on the surface of several transition metal oxides. However, these findings are poorly reproducible, and we know of no example of an oxidation process (either homogeneous or heterogeneous) that occurs via the thermal excitation of oxygen to the singlet state, although the principal possibility of these reactions was mentioned [4].

The thermal generation of singlet oxygen under equilibrium conditions by the reversible reaction

$$O_2 \rightleftarrows {}^1\Delta_gO_2 \qquad \text{(I)}$$

was not observed experimentally (probably due to an insufficient sensitivity of the available methods for measuring the concentration of $^1\Delta_gO_2$). In this work, we present the results of the measurements of the equilibrium generation of singlet oxygen via reaction (I) and the nonequilibrium thermal desorption of $^1\Delta_gO_2$ from the surfaces of ZSM-5 zeolites substituted by the cations of alkaline (Cs) and alkaline-earth (Ca) metals.

EXPERIMENTAL

Singlet oxygen was detected in a flow-type vacuum setup described in Fig. 1. A gas flow (P = 60 torr; the flow rate is 25 cm^3/s; the linear velocity in a flow rate is 260 cm/s) first passed through the heated part of a reactor filled with the test substance and then underwent fast cooling to room temperature in the cooled part (water jacket) of the reactor. Then, the gas was transported to the detector through a short (30 cm) pipe. The average lifetime of singlet oxygen due to heterogeneous deactivation on the walls of the main line is [5]

$$\tau_h = k_h^{-1} = k_k^{-1} + k_d^{-1},$$

where k_h is the heterogeneous deactivation constant, k_k is the kinetic deactivation constant, and k_d is the diffusion deactivation constant.

For a cylindrical reactor and pipelines,

$$k_k = \varepsilon v/d \quad \text{and} \quad k_d = 14.63D/d^2,$$

where ε is the accommodation coefficient (for singlet oxygen on quartz and polyvinyl chloride tubes, $\varepsilon \approx 2 \times 10^{-5}$ [5]), v is the average thermal velocity of the motion of oxygen molecules, $v = 4.25 \times 10^4(T/273)^{1/2}$ cm/s, D is the diffusion coefficient of oxygen in the gaseous medium, and d is the diameter of the reactor (tube). Under our experimental conditions (d < 4 mm, P < 760 torr, and $T = T_{room}$), $k_d \gg k_k$. Hence, we assume that $k_g = k_k = 3$ s^{-1} and $\tau_g = 0.33$ s (independent of the gas pressure).

The average lifetime of singlet oxygen determined by homogeneous deactivation is inversely proportional to the gas pressure in air and equals ~1 s at 60 torr. The presented estimates show that heterogeneous deactivation on the walls of the reactor and tubes under the experimental conditions is a decisive factor of $^1\Delta_gO_2$

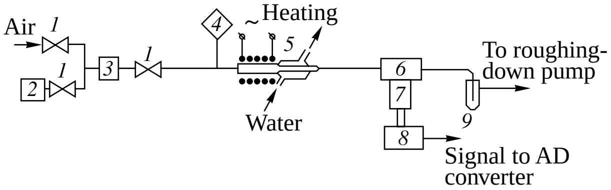

Fig. 1. Experimental setup for studying the thermal generation of singlet oxygen: (*1*) vacuum valve; (*2*) cylinder with helium; (*3*) leak; (*4*) vacuum gauge; (*5*) quartz reactor with electric heating and water cooling; (*6*) chemiluminescence flow-type cell; (*7*) multiplier photocell; (*8*) selective amplifier; and (*9*) trap.

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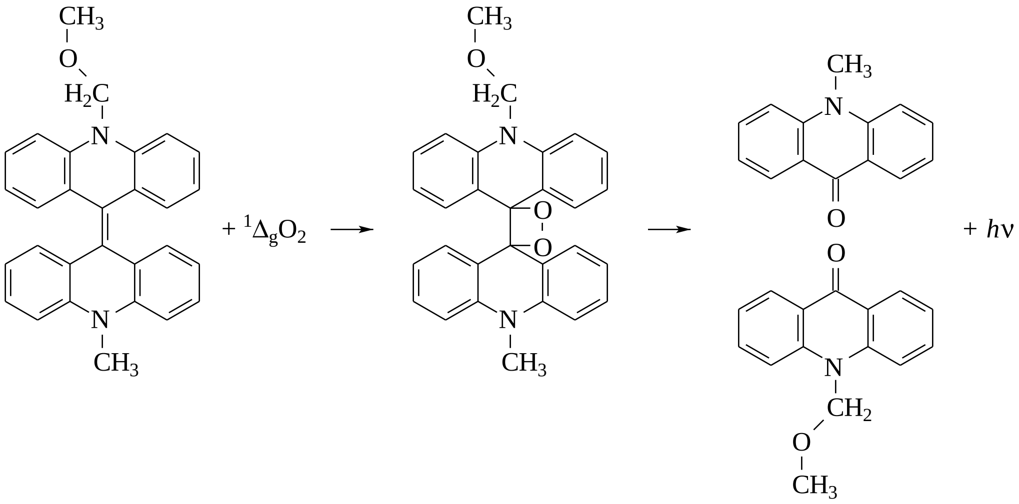
decay, and a pressure of 60 torr is optimal because its further decrease does not lead to a substantial increase in the lifetime of singlet oxygen in the flow. The time of singlet oxygen transportation to the detector is much shorter than τ_g; hence, the loss of $^1\Delta_gO_2$ due to deactivation in the communications can be neglected. As expected, an increase in the time of gas transportation to 1 s results in the experimentally observed disappearance of singlet oxygen at the detector inlet.

The chemiluminescence (CL) detector of singlet oxygen described previously [6] is based on the selective reaction of $^1\Delta_gO_2$ with *N*-methoxymethyl-*N*'-methyl-9,9'-biacridylidene [7] to form dioxetane that decomposes to two molecules of N-substituted acridone, one of which is in the singlet excited state with a high probability:



Deexcitation of substituted acridone molecules is due to luminescence in the visible range as detected by a sensitive photoreceiving system. The system consists of a FEU-79 multiplier photocell working with a load resistor (R_l = 11 kΩ). The signal from the load resistance goes to a selective amplifier tuned to the frequency $f = 1/(R_lC)$ determined by the load resistance and the output capacitance (C) of the multiplier photocell. This regime has several advantages for the detection of small photocurrents over the use of a simple charge amplifier (resistance to noise and stray pick-up and the stability of the zero line). The signal goes from the output of the selective amplifier to the detection system based on a Pentium PC equipped with a multichannel 12-digit AD converter card. The software for collecting and processing information developed by us enables signal collection at every second. The signal at each point is determined by averaging over the 100 separate measurements per 1 s, which decreases noise.

The CL dye used in our study is highly selective to singlet oxygen. However, taking into account the high sensitivity of the CL procedure used to detect singlet oxygen, we studied the influence of possible foreign admixtures in air on the indications of the CL detector. The addition of small amounts of various substances (NO_2, CO, CO_2, CH_4, ethanol, acetone, and octane) to air had virtually no effect on the CL intensity regardless of the pressure and velocity of gas pumping in the system. In addition, in special experiments, we purified air by passing it through a trap filled with anhydrous KOH. No significant difference was observed in the results of the experiments with and without a trap (i.e., for purified and nonpurified air). The experimental results are highly reproducible, which also confirms the absence of influence of such external factors as air contamination.

Thermal desorption of ground-state oxygen was studied in a helium flow (with a flow rate of 35 cm^3/min) in a setup equipped with a oxygen-selective thermochemical detector. A trap cooled with liquid nitrogen was placed before the detector to capture other possible desorption products (water and carbon dioxide). The heating was performed to 220°C for 10 min.

Zeolite samples were prepared from HZSM-5 (module m = 71.5) by ion exchange in solutions of the corresponding nitrates. It is known [8] that almost all hydrogen in Brönsted acid sites of HZSM-5 zeolite can be replaced by cesium cations, whereas for calcium the maximum amount is only 60%. To prevent the formation of free Brönsted acid sites in the sample with introduced calcium ions, it was prepared from CsZSM-5 by exchange in an 0.3 mol/l solution of $Ca(NO_3)_2$. Thus, in the obtained sample, hydrogen was substituted by both calcium and cesium ions, and the fraction of calcium ions was ~60%. After the ion-exchange procedure, the samples were repeatedly washed with water and calcined for 4 h at 700°C.

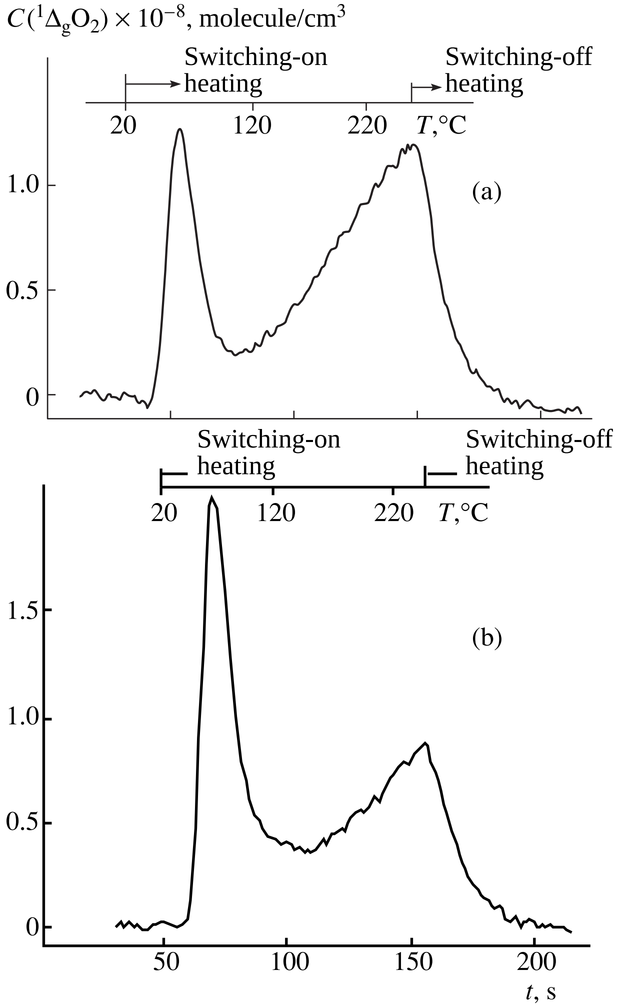


Fig. 2. Nonequilibrium thermal desorption of singlet oxygen from zeolites (a) CsZSM-5 and (b) (Ca–Cs)ZSM-5 under the conditions of the linear heating of the samples in a quartz reactor along with air blowing (60 torr; the linear flow rate is 260 cm/s.

RESULTS AND DISCUSSION

Figures 2 and 3 illustrate experimental results on singlet oxygen generation. Figure 2 shows that singlet oxygen desorbs from zeolite in an air flow (the low-temperature maximum with T_{max} = 65°C) along with the equilibrium thermal generation of singlet oxygen in air at higher temperatures (>140°C) according to reaction (I). In a helium flow (Fig. 3), only the first peak of $^1\Delta_gO_2$ due to thermal desorption from zeolite is observed. The equilibrium thermal generation of singlet oxygen in air is observed with equal intensities on all catalysts and in the empty reactor (Fig. 4). In the latter case, a plot of the $^1\Delta_gO_2$ concentration vs. temperature agrees with a theoretical function (at low temperatures ($RT \ll E$) and $C(^1\Delta_gO_2) \ll C(O_2)$ [9])

$$C(^1\Delta_gO_2) = C(O_2)(g_1/g_2)\exp(-E/RT), \qquad (1)$$

where $C(^1\Delta_gO_2)$ is the equilibrium concentration of singlet oxygen in the gas at temperature T, $C(O_2)$ is the concentration of ground-state oxygen in the gas (oxygen concentration), g_1/g_2 is the statistical weight singlet-to-triplet ratio for oxygen electron states ($g_1/g_2 = 2/3$ [7]), and E is the excitation energy (enthalpy of formation) of the $^1\Delta_gO_2$ state. We obtained 21.5 ± 2.2 kcal/mol for the enthalpy of singlet oxygen formation, which is close to that obtained from the spectroscopic data (22.6 kcal/mol) [10].

Thus, two essentially different mechanisms of singlet oxygen formation are observed: nonequilibrium thermal desorption and equilibrium thermal generation. The former mechanism was observed only on zeolite samples due to oxygen adsorbed on a zeolite, whereas the latter process occurs on any heated surface, but requires oxygen in the gas phase. From this viewpoint, the experimental results in [2, 3] are not completely clear. First, it is unclear what kind of a generation mechanism is discussed. On the one hand, we did not observe any nonequilibrium thermal desorption of singlet oxygen from the substances studied in [2, 3] (Li–Sn–P–O system and V_2O_5). On the other hand, the equilibrium generation of $^1\Delta_gO_2$ does occur on these surfaces in air. The existence of this equilibrium generation directly follows from thermodynamic laws. A more exciting problem is to find an explanation for the phenomenon of the nonequilibrium thermal desorption of singlet oxygen from zeolites. Figure 3 shows that singlet oxygen evolution occurs in parallel with the desorption of most of triplet oxygen. After the end of experiment and 0.5-h exposure of the sample to air, it completely restored its ability to thermally desorb singlet oxygen.

The amounts of desorbed oxygen in the ground and singlet states are compared in the table (two last columns). The amount of desorbed singlet oxygen is much larger than its equilibrium value calculated at the desorption temperature. It should be taken into account that these values are lower estimates, and the amount of desorbed singlet oxygen is in fact higher (evidently due to heterogeneous decay, not all singlet oxygen escapes from the zeolite granule and then detected). Our data suggest that adsorbed molecular oxygen is a precursor of singlet oxygen. Its desorption in the excited rather than thermodynamically more favorable ground state can be explained as follows. The difference between the singlet and ground triplet states of the oxygen molecule is known to be due to different arrangements of two electrons on the antibonding π_g^{x*} - and π_g^{y*} orbitals [1]. These orbitals are degenerate in the gas phase, and the singlet configuration where both electrons occupy the same orbital is energetically less favorable than the triplet configuration where electrons occupy different orthogonal orbitals. However, in strong electrostatic fields inside zeolite channels and near substituent ions (up to 10^{10} V/m), the degeneracy of the orbitals is eliminated, and the singlet state with electrons on the same orbital with a lower energy is stabilized relatively to the

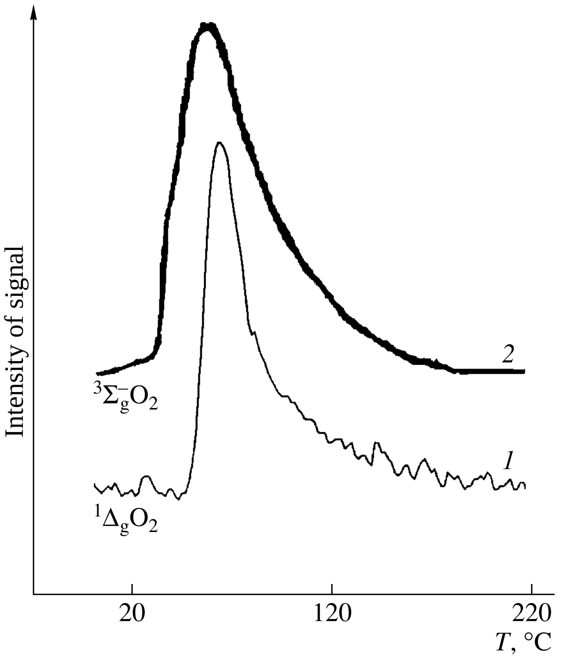


Fig. 3. Thermal desorption of oxygen in (*1*) singlet and (*2*) ground states from zeolite CsZSM-5 in a helium flow. The scales of the curves differ.

gas phase. The value that characterizes the splitting of the energies of the π_g^{x*}- and π_g^{y*} orbitals during the adsorption of an oxygen molecule becomes high (>1 eV according to [1]), and the singlet state of an adsorbed oxygen molecule can be energetically more favorable under these conditions. In this case, the thermal desorption of oxygen in the triplet state to the gas phase is impeded because the corresponding reaction

$$({}^1\Delta_gO_2)_{ads} \longrightarrow ({}^3\Sigma_g^-O_2)_{gas}$$

is spin-forbidden, whereas more endothermic thermal desorption of singlet oxygen

$$({}^1\Delta_gO_2)_{ads} \longrightarrow ({}^1\Delta_gO_2)_{gas}$$

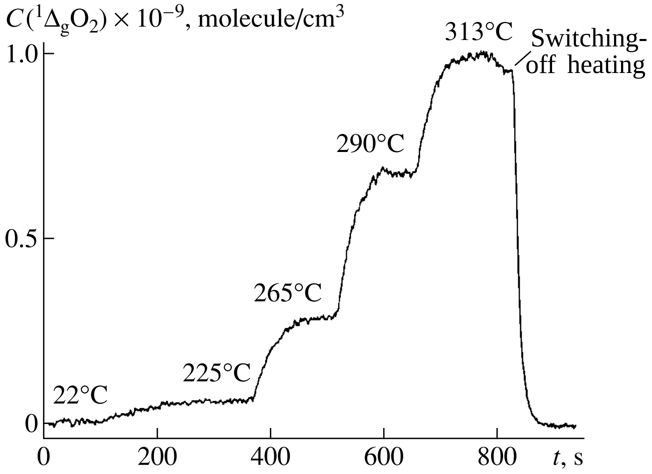


Fig. 4. Thermal generation of equilibrium singlet oxygen in an empty quartz reactor with a stepwise temperature increase. The air was passed through the reactor at *P* = 60 torr with a linear flow rate of 120 cm/s.

is allowed. This is supported by experimental data (see the table), which show that singlet oxygen desorption from the ZSM-5 sample containing calcium ions is more efficient than from the samples containing only cesium ions. This can easily be explained if we take into account that the electrostatic field strength near calcium ions is much stronger that near cesium ions. Therefore, the stabilization of singlet oxygen on calcium-containing zeolite is more efficient. In any case, no explanation can completely be confirmed until the detailed structure and parameters of the molecular oxygen adsorption sites on zeolites become clear. The amount of adsorbed oxygen (10^{17} molecule/g) on both sites is much lower than the concentration of the substituent ions in the sample ($\approx 10^{20}$ ion/g). This indicates that there are few adsorption sites for molecular oxygen. Perhaps these are some defects in the zeolite structure near which especially high strengths of the electrostatic field are achieved.

Desorption of oxygen in the ground and singlet states from CsZSM-5 and (Ca–Cs)ZSM-5

Zeolite	Amount of desorbed oxygen, molecule/g		$C({}^1\Delta_gO_2)/C(O_2)$*	$C_{max}({}^1\Delta_gO_2)/C_{max}(O_2)$**
	$^1\Delta_gO_2$	$^3\Sigma_g^-O_2$		
CsZSM-5	2.8×10^{11}	9.1×10^{16}	3.0×10^{-6}	2×10^{-15}
(Ca–Cs)ZSM-5	4.2×10^{11}	3.7×10^{16}	1.1×10^{-5}	2×10^{-15}

* The average ratio during adsorption.

** The calculated ratio of the equilibrium concentrations at the temperature of the desorption maximum.

CONCLUSIONS

Thus, we present evidence for the equilibrium generation of singlet oxygen in a gas flow at moderate temperatures. In addition, the phenomenon of the nonequilibrium thermal desorption of singlet oxygen from substituted zeolite ZSM-5 samples was observed for the first time.

REFERENCES

1. Che, M. and Tench, A.J., *Adv. Catal.*, 1983, vol. 31, p. 1.
2. Guillory, J.P. and Shiblom, C.M., *J. Catal.*, 1978, vol. 54, no. 1, p. 24.
3. Myasnikov, I.A., Sukharev, V.Ya., Kupriyanov, L.Yu., and Zav'yalov, S.A., *Poluprovodnikovye sensory v fiziko-khimicheskikh issledovaniyakh* (Semiconductor Sensors in Physicochemical Studies), Moscow: Nauka, 1991, p. 307.
4. Turro, N., *Tetrahedron*, 1985, vol. 41, no. 11, p. 2089.
5. Ryskin, M.E., Chernysh, V.I., and Kureneva, T.Ya., *Khim. Fiz.*, 1990, vol. 9, no. 1, p. 163.
6. Romanov, A.N. and Rufov, Yu.N., *Zh. Fiz. Khim.*, 1998, vol. 72, no. 11, p. 2094.
7. Papadopoulos, K. and Nikokavouras, J., *Anal. Chim. Acta*, 1995, vol. 304, no. 1, p. 91.
8. Matthews, D.P., *Chem. Age India*, 1986, vol. 37, no. 5, p. 353.
9. Lewis, B. and Von Elbe, G., *Phys. Rev.*, 1932, vol. 41, p. 678.
10. Okabe, H., *Photochemistry of Small Molecules*, New York: Wiley, 1981.