Photostimulated Reactions at the Surface of Wide Band-Gap Metal Oxides (ZrO₂ and TiO₂): Interdependence of Rates of Reactions on Pressure–Concentration and on Light Intensity

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In this study we examine photostimulated reactions taking place on the surface of wide band-gap metal oxides such as ZrO₂ and TiO₂. In particular, we explore the photostimulated adsorption (PhA) of oxygen on ZrO₂ upon illumination with UV light ($\lambda < 260$ nm) and its postphotostimulated photoadsorption (PPSPhA) on irradiation with visible light ($\lambda > 400$ nm). The emphasis is on an examination of the decay channels of PhA-active surface centers to rationalize the interdependencies of the rate $r(\rho, p)$ on pressure and light intensity The distinguishing feature of O₂ PhA kinetics, $dp/dt \propto \rho^m p^n$, resides in the dependence of the order of the reaction on the order *m* with respect to photon flow (ρ^m) and on the order *n* with respect to pressure (p^n). In other words, $m \rightarrow 1$ if $n \rightarrow 0$ whereas $n \rightarrow 1$ if $m \rightarrow 0$. The reaction orders *m* and *n* are *interdependent* in the case of PhA of O₂ on ZrO₂. A general mechanism is described for the several stages implicated in both PhA and PPSPhA surface processes. A preliminary consideration is also given to expand the PhA pathway for O₂ on ZrO₂ to processes that take place in the photocatalyzed oxidation of phenol in irradiated TiO₂ aqueous dispersions and the interdependence of the rate of the photoreaction on the concentration of phenol and on the incident light intensity.

Introduction

Photostimulated Adsorption and Photocatalysis. Heterogeneous photocatalysis¹⁻⁴ and photostimulated adsorption of molecules (PhA)^{4,5} are particular cases of photostimulated surface reactions in heterogeneous systems. There are several processes that are common to both photostimulated adsorption and photocatalysis: (i) light absorption, (ii) diffusion and drift of charge carriers toward the surface, (iii) recombination and trapping of charge carriers, (iv) formation of surface-active centers, and (v) interaction of surface carriers with adsorbed molecules. In particular, these common points between PhA and photocatalysis manifest themselves in numerous linear correlations between initial rates of PhA processes and rates of photocatalytic reactions on metal oxides^{6,7} and on alkali halides.⁸ Thus, a study of photostimulated adsorption processes could prove useful in understanding the mechanism of photoexcitation of solids as a first step of surface photochemical processes and photocatalysis. The main goal of the work presented here is a kinetic analysis and experimental verification of the PhA mechanism in which we examine different decay pathways of active surface centers.

Langmuir–Hinshelwood and Eley–Rideal Kinetic Treatments. To describe photostimulated adsorption of molecules at a semiconductor (or insulator) surface, two relevant cases are examined in the framework of the electronic theory of catalysis.⁴ In the first case, PhA is treated as a disturbance of the adsorption equilibrium due to formation of strongly bound species via photocarrier localization by normally weakly bound or poorly adsorbed molecules. In the second case, PhA is considered as the interaction of free or adsorbed molecules with surface-trapped charge carriers (i.e., with photoinduced surfaceactive centers). In both cases, if the heterogeneous system reaches adsorption equilibrium rapidly, the dependence of the steady-state rate r of PhA either on gas pressure p or on the concentration C of molecules and/or ions in a solvent medium can then be expressed as:

$$r = -\frac{\mathrm{d}p}{\mathrm{d}t} = \frac{kKp}{(1+Kp)} \tag{1}$$

$$r = -\frac{\mathrm{d}C}{\mathrm{d}t} = \frac{kKC}{(1+KC)} \tag{2}$$

where k is the apparent rate constant and $K = k_{ads}/k_{des}$ is the adsorption equilibrium constant. Note that when C is the reactant concentration, the dependence expressed by eq 2 resembles the rate of a photocatalytic reaction of the Langmuir–Hinshelwood type (LH).^{2,9}

The experimental dependencies of the initial steady-state PhA rate r(p) of simple molecules (O₂, H₂, CO, CH₄) on gas pressure have been approximated by eq 1 for a number of metal oxides,^{5,10-12} alkali halides,¹³ and other solids.^{14,15} A rather different treatment other than LH of r(p) dependencies for gas/ solid systems is used to interpret the PhA kinetics obtained at relatively low pressure (p < 10 Pa) and at room temperature. The concept of the photoinduced active center is applied in the latter case. To our knowledge, the first and simplest example of such a mechanism was given in the work of Rapoport and co-workers¹⁰ for the PhA of H₂ and CH₄ on TiO₂ particulates.

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In this study¹⁰ (see also the study of Dolgikh et al.¹⁴), generation of a photoinduced surface-active center S* was simplified to S $+ h\nu \rightarrow$ S*. The rate of generation of S* is determined by the absorption cross section k_{abs} of some "potential" surface-active center S. Decay of this active center, S* \rightarrow S, can be described as a spontaneous reaction with first-order kinetics, k_d . Adsorption of a gas molecule M_{gas} : (S* + $M_{gas} \rightarrow M_{ads}$) with the secondorder rate constant (k_a), is represented as the collision of gaseous molecules M (H₂, CH₄) with surface centers S*. Under steadystate conditions for the exited state of the adsorption center (dS*/ dt = 0), the initial PhA rate r(p) is given by

$$r(p) = -\frac{\mathrm{d}p}{\mathrm{d}t_{t\to 0}} = \frac{k_{\mathrm{abs}}\rho S_{\mathrm{o}}k_{a}p}{(k_{d} + k_{a}p)}$$
(3)

where ρ is the photon flow, S_0 is the initial concentration of the light absorbing centers, and p is the initial gas pressure. Equation 3 can be reduced to eq 1 by substituting $k_{abs}\rho S_0$ for k and k_a/k_d for K. This notwithstanding, the physical sense of the constant $K = k_a/k_d$ differs from that in the LH kinetic treatment. The parameter $1/k_d = \tau_d$ in eq 3 refers to the lifetime of the surfaceactive center (S*), whereas the LH reverse constant $1/k_{des} =$ τ_{des} refers to the lifetime of a molecule at the surface in an adsorbed state. Taking k_a as the rate constant for collision between the surface center and a molecule, the lower limit of τ_d can be estimated from approximations of the experimental r(p) dependencies embodied in eq 3. The estimated τ_d values for various systems scale in a wide time range from seconds to microseconds (TiO₂/H₂/CH₄,¹⁰ MgO/O₂, CaO/O₂,¹¹ MgAl₂O₄/ H_2,O_2 ¹² KBr/ O_2 ¹³ and AgBr/ O_2 ¹⁴}. A similar mechanism has been offered for the photooxidation of gaseous hydrogen by oxygen prephotoadsorbed on KBr^{16} and on MF_2 , where M =Mg, Ca, Sr, Ba.¹⁷ Lifetimes τ_d ranging from 10^{-2} to 10^{-4} s have been determined for the spontaneous decay: $O_2^*_{ads} \rightarrow O_2_{ads}$ of excited (presumably singlet ${}^{1}\Delta_{g}$ O₂-like) adsorbed species. Note that the mechanism suggested by eq 3 is of the Eley-Rideal type (ER).^{5,10,14,16,17} The resemblance of the experimental kinetics predicted by LH and ER reaction mechanisms has been discussed earlier.^{2,9,18,19} Whatever the type of mechanism, the dependence of the photocatalytic reaction or the PhA rate on photon flow $r(\rho)$ (eqs 1 and 2) is referenced only by the $k(\rho)$ dependence on photon flow; $k(\rho) = k_{abs}\rho S_o$ in eq 3 is an example. The orders of the rate of reaction or of the PhA process $(r \propto p^n \rho^m)$ on photon flow *m* and on the reagent concentration or gas pressure n are independent of each other in the LH and ER mechanisms. To our knowledge, the only exception is the work of Upadhya and Ollis²⁰ which considered the degradation of TCE (trichloroethylene) over TiO₂ and proposed a mechanism to explain the existence of the interdependence of the reactionrate dependencies on concentration and on light intensity.

The reaction order *m* has been determined for various photoreactions primarily over titania.²¹ Typically, *m* varies between 1 and 0.5. Similar results were obtained for photocatalysts other than TiO₂.^{22,23} The half-order limit of *m* has been ascribed to band-to-band recombination of free electrons and holes or, otherwise, to the recombination of intermediate reaction products (see, for example the studies^{21,24,25}). Reaction orders m < 1/2 have also been reported for photooxidative reactions of organic substrates over titania/solution systems under extremely high photon flow. The diffusion limitation of the reaction in a solvent medium was attributed to a sub-half-order intensity dependence.²¹ A linear dependence of oxygen and hydrogen PhA rates on photon flow has been established for a

number of metal oxides.⁵ In the course of PhA kinetic studies,⁵ measurements of the $r(\rho)$ dependence on photon flow were carried out at high gas pressures ($Kp \gg 1$ in eq 1).

ZrO₂ as a Photocatalyst and Photoadsorbent. Zirconia (ZrO₂; $E_{bg} \approx 5.0$ eV) is an active and typical photoadsorbent and photocatalyst among wide band gap metal oxides in accordance with the empirical correlations between the metal oxide's PhA activity and its band-gap energy E_{bg} .⁵ The red limit of the PhA for O_2 , H_2 , CH_4 , C_2H_6 on powdered $ZrO_2^{6,26,27}$ is at ca. 3.0 eV ($\lambda = 410$ nm) in the *extrinsic* absorption band region. PhA of methane and ethane is the first stage of their photooxidation and conversion to other hydrocarbons.^{26,28} The quantum vield Φ of propene photooxidation over powdered zirconia is ~ 0.03 ;²⁹ Φ of PhA of O₂ reaches 0.02 on irradiation at the red edge of the fundamental absorption band.³⁰ ZrO₂ powder is photocolored under UV excitation due to formation of stable defects (color centers) with trapped electrons (Zr³⁺, F⁺, F) ³¹ and holes (O^{-•}-like V centers).^{6,32} Color centers localized at the surface serve as long-lived PhA centers (i.e. postirradiation adsorption centers) for acceptor (O_2) and donor (H_2, CH_4) molecules, respectively. However, the activity of the PhA of O_2 under UV illumination of ZrO₂ (~90%) has been assigned mostly to shallow trap centers (lifetime $\tau_d \approx 10^{-2}$ to 10^{-3} s).^{7,32}

Prior UV photocoloration of ZrO2 under vacuum shifts the red limit of the PhA of O₂ to ~1.5 eV ($\lambda \approx 830$ nm).^{6,7} PhA of this kind may be described as a postphotostimulated photoadsorption (PPSPhA) effect; it needs two-step photoexcitation: (i) prior UV coloration to produce surface and bulk color centers, and (ii) subsequent photoionization of the bulk color centers by visible radiation to induce further adsorption.^{6,33} Studies of the PPSPhA of O₂ undertaken herein provide additional support for the proposed PhA mechanism. Comparative studies of lightinduced processes in micro- and nanoparticles of zirconia carried out in vacuo and in a solvent medium show similarities between the photophysical and photochemical behavior of zirconia irrespective of the type of heterogeneous system examined.²⁷ We also present a preliminary treatment of photocatalytic processes in a solvent medium: the photooxidation of phenol in aqueous TiO₂ dispersions.

Experimental Section

ZrO₂ Sample. The powdered monoclinic form of ZrO₂ used (high-purity grade, IREA) in this study was prepared from zirconium chloroxide. The major impurity in the sample is Fe (100–120 mg L⁻¹); total content of other metal impurities (Mn, Cu, Co, Cr, Ti) was <100 ppm. The specific surface area of the sample was determined by the BET method with nitrogen gas: ~7 m² g⁻¹. X-ray diffraction structure methods (X-ray diffractometer DRON-2, Co K α line} confirmed that a high-temperature pretreatment and preirradiation of the zirconia samples caused no modifications to the crystalline form.

Sample Pretreatment. Ubiquitous organic impurities and adsorbed molecules on the sample surface were removed by thermal pretreatment (T = 900 K) in an O₂ atmosphere (P = 100 Pa) and in vacuo for a few days. Reproduction of the original state of the samples between experiments was achieved by heating the samples in oxygen for ca. 1 h.

Experimental Setup. Powdered samples were contained in a 5-mm path length quartz cell (illuminated cell area, 6 cm²) connected to a high-vacuum setup equipped with an oil-free pumping system; the final gas pressure in the reaction cell was ca. 10^{-7} Pa. The volume of the reactor occupied by the gas was 40 cm³. The cell was thermostated with air flow at T =

TABLE 1: Coefficients k and K and Lifetime of Active Centers τ_d at Different Relative Light Intensities

light intensity, relative units	coefficient k, Pa s ⁻¹ {mol s ⁻¹ }
0.1	0.00051 ± 0.00001
	$\{(83.8 \pm 1.6) \times 10^{-13}\}$
0.15	0.00075 ± 0.00001
	$\{(123.2 \pm 1.6) \times 10^{-13}\}$
0.3	0.00149 ± 0.00005
	$\{(245 \pm 8) \times 10^{-13}\}$
0.5	0.00263 ± 0.00009
	$\{(43.2 \pm 1.5) \times 10^{-12}\}$
0.78	0.0040 ± 0.0002
	$\{(65.7 \pm 3.3) \times 10^{-12}\}$
1	0.0051 ± 0.0003
	$\{(84 \pm 5) \times 10^{-12}\}$
PPSPhA ($\lambda > 400 \text{ nm}$)	0.00113 ± 0.00003
	$\{(186 \pm 5) \times 10^{-13}\}$

293 K. A Pirani-type manometer (sensitivity, 18 mV Pa⁻¹ for O₂) was used to measure gas pressures under photoadsorption conditions. Analysis of gas composition was obtained using a mass spectrometer MX-7301; it was also used to measure the quantity of postirradiation adsorbed oxygen by means of thermally programmed desorption techniques. Irradiation of powdered ZrO₂ samples was carried out with a 120-W highpressure mercury lamp (DRK-120; MELZ); the light irradiance (6 mW cm⁻²) at wavelengths below 400 nm was measured through a water filter using a thermoelement (IOFI; sensitivity, 1.5 V W⁻¹). The maximum photon flow ρ_0 at wavelengths below 260 nm was about 1×10^{15} photons cm⁻² s⁻¹. Attenuation of ρ_0 was achieved with nonselective "gray" metal-supported quartz filters (Vavilov SOI). Cutoff filters from a standard set of colored glass filters (Vavilov SOI) selected the excitation spectral regions or the mercury spectral lines for the PPSPhA studies (see below). For the latter studies, a 250-W lamp was also used. Any experimental error in the PhA rate measurements that may have been caused by the nonreproducibility of the original state of the ZrO₂ sample does not exceed 10% at, respectively, high oxygen pressure (p > 1 Pa) and at the photon flow used ($\rho = 1 \times 10^{15}$ photons cm⁻² s⁻¹).

TiO₂ Sample. In preliminary experiments to study the dependence of the photooxidation of phenol in aqueous solutions on light intensity and concentration of phenol, we used "Degussa" P25 TiO₂ as the photocatalyst. Experiments were carried out at pH = 3 (HCl). Phenol concentration was measured by liquid chromatography with an HPLC chromatograph (Waters 501 pump and Waters µBondapak C18 column) connected to a Shimadzu flow cell for absorption recording with the Shimadzu UV-265 spectrophotometer interfaced to an IBM PC computer. Recording parameter settings, data collection, and data processing were carried out using the Spectroscopy Interface Software, Version 3 (Shimadzu Scientific Instruments, Inc.). Irradiation of a phenol solution with a TiO₂ loading of $0.3 \text{ g } \text{L}^{-1}$ was carried out with an Oriel 1000-W Hg/Xe lamp in a sphere-like Pyrex reactor. An interference filter selected the 365 nm actinic light. Nonselective gray metal-supported Pyrex filters were used to attenuate the photon flow.

Results

Dependence of the Rate of PhA of O_2 on Pressure and UV Photon Flow. *Extrinsic* absorption of light by ZrO₂ between its red limit ($\lambda \approx 410$ nm) and 260 nm causes a weak PhA of O_2 , whereas band-to-band transitions lead to much stronger PhA at wavelengths <260 nm. *Intrinsic* absorption dominates on illumination of ZrO₂ by the full emitted radiation of the mercury lamp used in the set of experiments described below.

coefficient <i>K</i> , $Pa^{-1} \{mol^{-1}\}$	lifetime τ_d , s
61.1 ± 8.3	0.20 ± 0.03
$ \{ (37.2 \pm 5.0) \times 10^8 \} $ $ 46.2 \pm 5.0 $ $ (29.1 \pm 2.0) = 10^8 \} $	0.150 ± 0.015
$\{(28.1 \pm 3.0) \times 10^{6}\}\$ 23.3 ± 3.6 $\{(14.2 \pm 2.2) \times 10^{8}\}\$	0.075 ± 0.012
$\{(14.2 \pm 2.2) \times 10^{\circ}\}\$ 12.5 ± 1.7	0.040 ± 0.006
$\{(7.6 \pm 1.0) \times 10^8\}$ 9.1 ± 1.6	0.029 ± 0.005
$\{(55.4 \pm 9.7) \times 10^{7}\}\$ 7.3 ± 1.5	0.024 ± 0.004
$ \{(44.4 \pm 9.1) \times 10^7\} 14.7 \pm 0.6 \{(89.5 \pm 3.6) \times 10^7\} $	0.047 ± 0.003



Figure 1. Dependencies of initial rates of oxygen photoadsorption $r_{\rho}(p)$ on pressure *p* at different photon flows ($\rho_0 = 1 \times 10^{15}$ photons cm⁻² s⁻¹): (1) $\rho = \rho_0$; (2) $\rho = 0.78\rho_0$; (3) $\rho = 0.5\rho_0$; (4) $\rho = 0.3\rho_0$; (5) $\rho = 0.1\rho_0$.

PhA O₂ rates r_{ρ} versus initial oxygen pressure *p* at various photon flows are plotted in Figure 1. Initial PhA rates *r* were determined by differentiation of *p*(*t*) curves (dependence of pressure on exposure time, *p*(*t*)). Note that initial PhA rates determined in this manner were the highest for any *p*(*t*) curve recorded. The highest photon flow ($\rho = 1 \times 10^{15}$ photons cm⁻² s⁻¹ at $\lambda < 260$ nm) is taken as a unit of measure. The maximum initial PhA rate at the highest oxygen pressure used (*p* = 2.8 Pa) and maximum photon flow is 0.0047 Pa s⁻¹, i.e., 7.7 × 10⁻¹¹ mol s⁻¹ (or 4.6 × 10¹³ molecule s⁻¹) from the volume of the reactor and the temperature (see Experimental Section). All curves of the set were approximated by eq 1, and values of the constants *k* and *K* are presented in Table 1 and plotted in Figure 2.

The results show that both constants in eq 1 depend on photon flow: *k* depends linearly on photon flow, whereas the constant *K* decreases with an increase in photon flow. In such case, *K* cannot be considered a constant of the adsorption/desorption equilibrium ($K = k_{ads}/k_{des}$) in eq 1. It may be assumed that the desorption constant k_{des} increases with temperature as a result of the heating of the sample by the incident actinic light. To verify this assumption, a few r(p) curves were obtained in the temperature range T = 300-450 °K at the highest photon flow available under our conditions, i.e., for $\rho/\rho_0 = 1$. No significant changes of *K* are evident. For example, *K* (450 K) is 6.7 ± 0.6 Pa⁻¹, close to the value obtained at 300 K (see Table 1).

Comparison of eq 3 and eq 1 shows that *K* can be represented as $K = k_a/k_d = k_a \tau_d$, where τ_d is the lifetime of the surface-



Figure 2. Dependencies of the LH (eq 1) parameters *k* (curve 1) and *K* (curve 2) on photon flow ρ/ρ_0 for $\rho_0 = 1 \times 10^{15}$ photons cm⁻² s⁻¹.



Figure 3. Dependence of the lifetime of surface-active centers τ_d on photon flow ρ/ρ_o with $\rho_o = 1 \times 10^{15}$ photons cm⁻² s⁻¹.

active center (see Introduction). Note that 1/K is also equal to the characteristic pressure p' at which the probability of consumption of the active center in the reaction channel $(k_a p')$ is equal to the probability of its deactivation (k_d) (eq 3). Lower limits of τ_d estimated from K (Table 1) assumed that $k_a = \sigma v/$ $4\kappa T$, where $\sigma \approx 1 \times 10^{-16} \text{ cm}^2$ is the molecule/center collision cross section, $v = 5 \times 10^4$ cm s⁻¹ is the velocity of oxygen molecules in the gas phase, and k is Boltzmann's constant. The dependence of the lifetime of surface-active centers plotted in Figure 3 follows a hyperbolic decay such that both K and τ_d scale with ρ^{-1} . Thus, in contrast with the simplified PhA mechanism, 10,13,14 in the present instance $k_d = 1/\tau_d$, which scales with ρ and cannot be considered as the first-order rate constant of spontaneous decay of the active center. The family of $r(\rho)$ curves at various oxygen pressures p was also obtained in the subsequent set of experiments; they are portrayed in Figure 4. It is clear that the PhA O_2 rate r scales directly with photon flow ρ only at high oxygen pressures (curve 1). Starting from the high-intensity limit, the smaller the pressure, the greater is the deviation of the $r(\rho)$ curve from the straight line. At the lowest initial oxygen pressure, p = 0.028 Pa (curve 5), the $r(\rho)$ dependence becomes extremely sublinear. In fact, it is close to saturation at $\rho > 0.5\rho_0$. In general, all the dependencies can be



Figure 4. Dependencies of initial rates of oxygen photoadsorption $r_p(\rho)$ on photon flow ρ/ρ_0 for $\rho_0 = 1 \times 10^{15}$ photons cm⁻² s⁻¹ at different initial oxygen pressures: (1) p = 2.8 Pa; (2) p = 0.28 Pa; (3) p = 0.11 Pa; (4) p = 0.055 Pa; (5) p = 0.028 Pa.



Figure 5. Dependencies of the parameters a (curve 1) and b (curve 2) on the initial oxygen pressure p (eq 4).

approximated by the function

$$r(\rho) = \frac{ab\rho}{(1+b\rho)} \tag{4}$$

where *a* and *b* are constants at a given oxygen pressure *p*. The dependencies of these constants on oxygen pressure are presented in Figure 5, from which it is evident that the parameter *a* depends linearly on oxygen pressure *p*, whereas *b* decreases with increase in pressure via a hyberbolic decay function. Thus, *a* scales with *p* and *b* scales with p^{-1} . The corresponding values of *a* and *b* are presented in Table 2.

Equation 4 is equivalent to eq 1 provided that a(p) and b(p)in eq 4 satisfy the above-mentioned conditions, i.e., $a \propto p$ and $b \propto p^{-1}$; as well, eq 1 corresponds to eq 4 for $k \propto \rho$ and $K \propto \rho^{-1}$ (see results above). In other words, the functions to describe the experimental $r(\rho,p)$ dependencies for PhA O₂ rates (eqs 1 and 4) are equivalent. The $r(\rho,p)$ dependence can thus be generalized as

$$r(\rho, p) = \frac{A\rho p}{(B\rho + Cp)}$$
(5)

where the coefficients A, B, and C do not depend on light



Figure 6. Dependencies of initial rates of oxygen photoadsorption {as $\ln r_p(\rho)$ } on photon flow ρ {as $\ln(\rho/\rho_0)$ } at different initial oxygen pressures: (1) p = 2.8 Pa; (2) p = 0.28 Pa; (3) p = 0.11 Pa; (4) p = 0.028 Pa. The straight line corresponds to the first-order process dependence on photon flow.

TABLE 2: Coefficients a and b at Different Initial Oxygen Pressures p

initial oxygen pressure, P_{0} [mol m ⁻³]	coefficient <i>a</i> , $\mathbf{P}_{a} = \frac{1}{a} \left[m a \right] a^{-1}$	apafficient h
		coefficient <i>b</i>
0.028	0.00075 ± 0.00002	7.9 ± 0.8
$\{1.15 \times 10^{-5}\}$	$\{(123.2 \pm 3.3) \times 10^{-13}\}$	
0.055	0.00193 ± 0.00001	2.74 ± 0.02
$\{2.26 \times 10^{-5}\}$	$\{(317.1 \pm 1.6) \times 10^{-13}\}$	
0.11	0.00321 ± 0.00015	1.62 ± 0.15
$\{4.52 \times 10^{-5}\}$	$\{(52.7 \pm 2.5) \times 10^{-12}\}$	
0.28	0.0158 ± 0.0004	0.45 ± 0.02
$\{1.15 \times 10^{-4}\}$	$\{(259.6 \pm 6.6) \times 10^{-12}\}$	
1.1	0.083 ± 0.006	0.058 ± 0.002
$\{4.52 \times 10^{-4}\}$	$\{(136.3 \pm 9.9) \times 10^{-11}\}$	
1.6	0.121 ± 0.002	0.0404 ± 0.0005
$\{6.57 \times 10^{-4}\}$	$\{(198.8 \pm 3.3) \times 10^{-11}\}$	
2.8	0.214 ± 0.003	0.0228 ± 0.0005
$\{1.15 \times 10^{-3}\}$	$\{(351.6 \pm 4.9) \times 10^{-11}\}$	

intensity and gas pressure. Note that eq 5 can be cast into the Langmuir–Hinshelwood form (eq 1) when the photon flow ρ is constant.

The PhA O₂ rate can also be described by the function

$$r(\rho, p) = (\text{const})p^n \rho^m \tag{6}$$

where n and m are the orders of the reaction on pressure and photon flow, respectively. The double logarithmic $r(\rho)$ plot for several fixed pressures p is shown in Figure 6. The high-pressure (p = 2.8 Pa) curve 1 has a slope m = 0.98 (correlation coefficient = 0.9999). The remaining curves have variable slopes, e.g., at the higher photon flow and at the smaller pressures the smaller the slope for a given curve. For the lowest pressure examined (p = 0.028 Pa), the slope in the high photon flow region (last four points of curve 4) is 0.16 (correlation coefficient = 0.9986). However, the slope of all curves is close to 1 in the low photon flow region. Slopes estimated using the first few data points (including those not shown for $\rho < 0.1$) place m in the 0.75-1.25 range for the family of curves. The reaction order m in eq 6 varies with pressure in accordance with eq 5; *m* approaches unity as $p \rightarrow \infty$ (i.e., for $Cp \gg B\rho$) and conversely $m \to 0$ if $p \to 0$ (or if $Cp \ll BI$). Similarly, the order *n* approaches unity if $\rho \rightarrow \infty$ at $B\rho \gg Cp$ and conversely $n \to 0$ if $\rho \to 0$ provided that $B\rho \ll Cp$. In other words, $m \to 0$ 1 if $n \to 0$, whereas $n \to 1$ if $m \to 0$. The reaction orders *m* and

n are interdependent in the case of the PhA of O_2 on Zr O_2 . Note that Zr O_2 is a convenient adsorbent for PhA O_2 kinetic studies because the variation of *m* ranges from 0.16 to 1 under moderate (10-fold) changes in photon flow at low pressures (Figure 6, curve 4); m = 1 is observed at high pressures (Figure 6, curve 1).

Spectral Dependence of the Lifetime of PhA Centers in UV-Colored ZrO₂. Pre-excitation of wide band-gap solids in vacuo with UV light leads to their coloration as a result of formation of color centers, i.e., carriers captured by deep traps. The subsequent photoexcitation into the absorption bands of color centers in a gas/solid system causes adsorption of the gas molecules to the solid surface.^{33,34} As in the case of Solonitzin's effect, i.e., postirradiation adsorption in the dark,³⁵ this kind of photoadsorption appears after the preirradiation period but subsequently also needs secondary irradiation. This is what is referred to as the postphotostimulated photoadsorption effect (hereafter referred to as PPSPhA).^{6,33,34} In PPSPhA processes, the charge carriers appear at the surface because of photoionization of the UV-generated color centers. The PPSPhA of O2 has been observed on 10 of 15 wide band-gap metal oxides tested,34 including ZrO2.6 The red limit of PPSPhA of O2 on ZrO_2 is ca. 1.5 eV ($\lambda \approx 830$ nm), in accordance with the position of the red tail of the F center absorption band.³¹ The red limit of the PPSPhA of H₂ places around 2.14 eV ($\lambda \approx 580$ nm), where the hole V center band and electron F⁺ center band overlap.

The dependencies of the initial PPSPhA O₂ rates (r_{PPSPhA}) on initial oxygen pressure *p* satisfy eq 1. The corresponding coefficients *k* and *K* and τ_{PPSPhA} are presented in Table 1 (last row). In this case, pre-UV-excitation of ZrO₂ in vacuo was carried out with the full emitted light of the DRK-120 mercury lamp for 600 s. Illumination of the sample in oxygen was conducted by the same lamp but with a cutoff filter having a transmission threshold of ~400 nm, i.e., in a wide range of both F- and V-color-center absorption bands.

The lifetime τ_{PPSPhA} depends on the wavelength of the incident actinic light within the range of the color centers absorption (260–900 nm) in ZrO₂; $\tau_{\text{PPSPhA}} = 67 \pm 5$ ms from r_{PPSPhA} versus p curve under illumination by blue light ($\lambda = 436$ nm, $\rho_{436} =$ $7.2 \pm 0.1 \times 10^{14}$ photons cm⁻² s⁻¹). By contrast, r_{PPSPhA} does not depend on pressure in the pressure range p = 0.02-5 Pa for a UV-colored sample under illumination by red light ($\lambda >$ 700 nm, $\rho_{700} \approx 5 \times 10^{14}$ photons cm⁻² s⁻¹). In the latter case, the characteristic pressure p' (see above) is less than 0.02 Pa; hence, τ_{PPSPhA} for red light is greater than 1 s. Note that τ_{PPSPhA} for red light can, in principle, be greater than 10⁴ s. The socalled coefficient of postirradiation adsorption ($\Omega = N_a/N_{ph}$, where N_a is the number of post-irradiation adsorbed molecules in vacuo for a given time period and N_{ph} is the number of photoadsorbed molecules during irradiation for the same exposure time,⁵ was near unity for red light irradiation, in contrast to that for blue light illumination ($\Omega_{436} \approx 0.1$). In other words, $N_a = N_{ph}$ for oxygen adsorbed on UV-colored ZrO₂ during a fixed exposure time by red light illumination. Also, no change in $\Omega = 1$ was observed when the delay time between the end of the red light exposure in vacuo and the introduction of oxygen into the reaction cell was changed from 5 to 7×10^3 s. Hence, the delay time of $\sim 10^4$ s can be taken as the lower limit of τ_{PPSPhA} for red light illumination ($\lambda > 700$ nm). Results of PPSPhA O_2 studies on ZrO_2 will be published in some detail elsewhere.36

Only a slight distinction in shape of the dioxygen (m/e = 32) thermally programmed desorption spectra was observed, and



Figure 7. Thermoprogrammed desorption spectra of adsorbed oxygen (m/e = 32) after UV-induced photoadsorption, PhA (1), after postphotostimulated photoadsorption, PPSPhA ($\lambda_{exc} > 400 \text{ nm}$) (2), and after post-irradiated adsorption of oxygen on UV preirradiated (in vacuo) ZrO₂ (3).



Figure 8. Dependence of the rate of phenol photooxidation dC/dt over TiO₂ on phenol concentration *C* at different photon flows {as ρ/ρ_0 }: (1) $\rho = \rho_0 = 1.1 \times 10^{17}$ photons cm⁻² s⁻¹; (2) $\rho = 0.12\rho_0$.

the same desorption peaks were detected at 450, 580–590, and 700 K for PPSPhA under illumination by blue ($\lambda = 436$ nm) and red ($\lambda > 700$ nm) light (see Figure 7). Hence, the types of PPSPhA centers and oxygen species formed on ZrO₂ are independent of the irradiation wavelength. A difference of a few orders of magnitude in the lifetimes of surface-active centers, i.e., between τ_{PPSPhA} for red and blue light illumination, appears because the F centers that absorb the red light produce only electrons whereas electron F⁺ centers and hole V centers excited by blue light generate both free electrons and free holes, respectively, in UV-colored ZrO₂.

Photooxidation of Phenol in Aqueous Dispersions over a Smaller Band-Gap Metal Oxide (TiO₂). The dependencies of the rate of phenol photooxidation on phenol concentration at two different fixed light intensities $\rho = \rho_0 = 1.1 \pm 0.3 \times 10^{17}$ photon cm⁻² s⁻¹ (curve 1) and $\rho = 0.12 \rho_0$ (curve 2) at $\lambda = 365$ nm are presented in Figure 8. The experimental data can be approximated by LH-like kinetics (eq 1) with $k = 6.0 \pm 0.1 \times 10^{-2} \,\mu$ M min⁻¹ and $K = 7.5 \pm 0.6 \times 10^{-2} \,\mu$ M⁻¹ at $\rho = \rho_0$ and $k = 9.9 \pm 0.2 \times 10^{-3} \,\mu$ M min⁻¹ and $K = 1.2 \pm 0.3 \,\mu$ M⁻¹ when $\rho = 0.12 \rho_0$. Clearly, *k* increases with an increase in photon flow, whereas *K* decreases with an increase in incident photon flow. This is similar to the experimental results from

the ZrO_2/O_2 heterogeneous system (compare Figures 1 and 8.). Thus, *K* cannot be considered a LH constant.

In the next set of experiments we assessed the dependencies of the rate of phenol photooxidation on photon flow (Figure 9) on irradiation at $\lambda = 365$ nm for two different phenol concentrations: C = 128 (curve 1) and 4 μ M (curve 2). Both dependencies are approximated by eq 4 with $a = 0.28 \pm 0.09$ μ M min⁻¹ and $b = 0.24 \pm 0.09$ for $C = 128 \mu$ M (curve 1) and $a = 1.76 \pm 0.04 \times 10^{-2} \,\mu\text{M min}^{-1}$ and $b = 7.2 \pm 0.7$ for C =4 μ M (curve 2). Note also that *a* increases with an increase in the concentration of phenol, whereas b decreases with an increase in the phenol concentration. At high phenol concentration, the dependence of the reaction rate on photon flow is nearly linear, albeit the rate dependence approaches saturation; at small phenol concentrations, the rate dependence on photon flow is strongly sublinear (close to saturation) while the rate dependence on concentration is almost linear, again similar to experimental results obtained for the ZrO_2/O_2 heterogeneous system. The existence of an interdependence of reaction orders on phenol concentration and on light intensity can therefore be assumed for the reaction of the phenol photooxidation in TiO₂ aqueous dispersions.

Discussion

General Description of PhA Mechanism for Wide Band-Gap Solids. The mechanism of photostimulated adsorption has been described earlier in connection with the effect of PhA on photoinduced defect formation in metal oxides^{6,27,33,37} and in alkali halides.⁶ Computer simulation of PhA kinetics (i.e. temporal changes of pressure p(t)) at zero reaction order (n = 0) for the r(p) dependence has also been undertaken.^{36,37} The emphasis in the present study is on an examination of the decay channels of PhA active centers to rationalize the $r(\rho,p)$ dependencies for the PhA of O₂ on ZrO₂. We consider the following stages in the PhA mechanism

$$\Lambda + h\nu \rightarrow e + h (k_{abs}; \text{ photoexcitation of lattice } \Lambda)$$
(stage 1)

 $\mathbf{R} + \mathbf{e} \rightarrow \mathbf{R}^{-} (k_{ei}; \text{ trapping of electrons})$ (stage 2a)

 $R^- + h \rightarrow R$ (k_{ht} ; recombination of

trapped e with free hole) (stage 2b)

 $V_a + e \rightarrow F(k_F; \text{ formation of color centers})$ (stage 3a)

 $V_c + h \rightarrow V (k_v; \text{ formation of color center})$ (stage 3b)

 $S + e \rightarrow S^{-}(k_c; \text{ formation of active surface center})$

(stage 4)

 $S^- + h \rightarrow S(k_R;$ recombination decay of active center) (stage 5a)

 $S^- + h\nu \rightarrow S + e(k_{ph}; photoionization decay)$

of active center) (stage 5b)

 $S^- \rightarrow S + e(k_{th}; \text{ thermal decay of active center})$ (stage 5c)

 $S^- + M(gas) \rightarrow M^-(ads) (k_a; adsorption of$

gaseous molecule) (stage 6)

The absorption of photons $(h\nu)$ by the regular crystal lattice (Λ ; note this symbol represents sites on the surface and in the bulk) in the fundamental absorption band (absorption cross section, k_{abs}) creates free electrons (e) and free holes (h) in the conduction and valence bands, respectively (stage 1). The main



Figure 9. Dependencies of the rate of phenol photooxidation over TiO₂ on photon flow ρ/ρ_0 {where $\rho_0 = 1.1 \times 10^{17}$ photons cm⁻² s⁻¹} at different phenol concentrations: (a) $C = 128 \,\mu$ M; (b) $C = 4 \,\mu$ M.

channel of recombination of free carriers is their subsequent trapping by the recombination centers R (stage 2). We presume that electron/hole recombination occurs first by electron capture (stage 2a, k_{et}) and that recombination of holes (stage 2b, k_{ht}) with trapped electrons (R⁻) occurs subsequently. Note that trapping of the hole as a first step followed by recombination with the electron or a consideration of both paths in the mechanism has no influence on the final generalized results. Note also that band-to-band recombination of free carriers (e + h $\rightarrow \Lambda$) has not been included in the mechanism because recombination of charge carriers through defects dominates in very or moderately wide band-gap solids.

The photocoloration of solids is arbitrarily taken to originate from trapping of free electrons and holes by bulk defects, e.g., by anion V_a (stage 3a, k_F) and cation V_c (stage 3b, k_V) vacancies, with formation of F and V color centers, respectively. In fact, a variety of intrinsic and extrinsic lattice defects other than vacancies can serve as deep carrier traps in the formation of color centers. To simplify the quasi-chemical equations, herein we shall adopt the notations valid for alkali halide M⁺X⁻ ionic crystals for which vacancies are singly charged in relation to the lattice and for which F centers $\{V_a^+/e^-\}^0$ and V centers $\{V_c^{-}/h^+\}^0$ are neutral species. In the case of ZrO₂ (see below), the commonly accepted notations for F and F⁺ refer to the neutral state $\{V_a^{2+}/2e^-\}^0$ and the positively charged $\{V_a^{2+}/e^-\}^+$ state, respectively. Similarly, the notation V refers to all kinds of V-type color centers, V $(V_c^{4-}/jh^+)^{j-4}$, where $1 \le j \le 4$ (In reality, $j \le 2$ because of Coulombic repulsions between holes). The V centers, especially those located at the metal oxide surface, have also been described in photocatalysis as O^{-•} species.

Formation of active PhA centers occurs via capture of free electrons and holes by surface traps S. For completeness, creation of electron PhA centers S⁻ are indicated in stage 4 (k_c). The centers interact with gas molecules *M* to yield adsorbed species M^- (stage 6, k_a). For example, M^- can be the O₂^{-•} radical anion in the case of the PhA of O₂ on ZrO₂.³²

Stages 5 describe three possible pathways for the decay of PhA centers: (i) recombination with free carriers of opposite sign (stage 5a, k_R), (ii) photoionization of PhA centers by incident photons (stage 5b, k_{ph}) and (iii) thermal ionization of PhA centers (stage 5c, k_{th}). (A fourth reaction, i.e., recombination

of adjacent trapped carriers by tunneling,^{38,39} is not treated in this work.) To simplify the expression for $r(\rho,p)$ (see below), all three pathways (stages 5a-c) are considered for the same PhA center S⁻, although the probability that all three processes described by stages 5a-c occur is very small since these differ strongly from each other for a given type of center in wide bandgap solids. Which of these three stages predominates will depend on whether the center S^- is a shallow trap in which thermal ionization dominates or a deep trap in which thermal ionization is negligible. In turn, deep traps can be further subdivided into recombination centers (rate of recombination is very high, denoted above as R and R⁻) and color F and V centers (rate of decay by recombination is moderate). Contrary to recombination centers (R⁻), color centers F and V accumulate in the crystal in sufficiently high concentrations and persist for long periods after terminating irradiation. For simplicity, decay of color centers through recombination and photoionization are also not treated in the PhA mechanism described above. Photoionization of color centers will be discussed subsequently in connection with the PPSPhA of O₂ on ZrO₂. Suffice to mention that other types of decay processes may be considered in relation to any quasi-chemical particle or defect that has trapped a carrier; this can include photoadsorbed molecular species. For example, recombination of free holes with M^{-} species (trapped electrons) could break the surface/adsorbate bond. The latter can be associated with indirect thermal or indirect photodesorption (via excitation of the solid) depending on whether thermal or photoliberation of holes takes place. Direct thermal and photodesorption are associated with thermal and photoionization of M^- species, respectively. The simultaneous occurrence of both photoadsorption and photodesorption under irradiation has been demonstrated for metal oxides.⁴⁰ However, the rate of photodesorption was much smaller than the rate of photoadsorption (stage 6) at the beginning of the overall PhA process, i.e., when initial PhA rates were measured.

In the quasi-stationary approximation $(d[S^-]/dt = 0; d[e]/dt = 0; d[h]/dt = 0)$ the photoadsorption rate dp/dt (i.e. d[M]/dt) can be expressed in terms of steady-state concentrations of photoelectrons (e) and photoholes (h):

$$-\frac{\mathrm{d}p}{\mathrm{d}t} = \frac{k_{\mathrm{c}}S[\mathbf{e}]k_{a}p}{(k_{R}[\mathbf{h}] + k_{ph}\rho + k_{th} + k_{a}p)}$$
(7)

Note that in the case of a dielectric, only the photocarriers can be considered. This is also true for semiconductors in the case of sufficiently high photon flow, i.e., when the concentration of photocarriers becomes much greater than the concentration of thermal majority and minority carriers.

The steady-state concentration of photoelectrons and photoholes is given by:

$$[e] = k_{abs} \Lambda \rho \tau_e = \alpha \rho \tau_e = g \tau_e \tag{8}$$

$$[\mathbf{h}] = k_{\rm abs} \Lambda \rho \tau_h = \alpha \rho \tau_h = g \tau_h \tag{9}$$

under conditions that

$$k_{\rm abs}\Lambda\rho \gg [k_{\rm bh}S^-\rho + k_{\rm th}S^-] \tag{10}$$

This condition (eq 10) is reasonable because the rate of electron generation at band-to-band transitions (stage 1) is usually much greater than the corresponding rates of their photo (stage 5b) and thermal (stage 5c) detrapping.

The absorption coefficient α (cm⁻¹) is related to the fundamental band such that $g = \alpha \rho$ (cm⁻³ s⁻¹) is the volume

rate of generation of carriers

$$\tau_e = \frac{1}{k_{et}R + k_F V_a + k_c S} \tag{11}$$

and

$$\tau_h = \frac{1}{k_{ht}R^- + k_V V_c + k_R S^-}$$
(12)

are the lifetimes of free electrons (eq 11) and free holes (eq 12) from the various channels of carrier trapping. In general, τ_e and $\tau_{\rm h}$ are interdependent, vary with time because of carrier trapping by vacancies (see stages 3a and 3b) whose concentration is not stationary, and depend on light intensity. Nevertheless, τ_e and $\tau_{\rm h}$ are taken as constants. This is a realistic assumption in the case of wide band-gap solids irradiated by light of moderate intensity within a narrow variation range. In such a case, when the concentration of recombination centers (ca. 10¹⁷ to 10¹⁹ cm⁻³) is greater than the concentration of free carriers, the lifetime of free carriers is determined by the magnitude of the corresponding trapping cross-sections (also constants) of the recombination centers.⁴¹ We must also point out that the present studies deal with the initial stages of adsorption when the carrier lifetime depends on the initial concentration of defects (see eqs 11, 12), which is the same for each experiment regardless of the conditions used.

On the basis of the above discussion and eqs 7-9, it follows that the initial PhA rate can be described as

$$r = -\frac{\alpha \rho \tau_e k_c S_o k_a p}{\alpha \rho \tau_h k_R + k_{ph} \rho + k_{th} + k_a p}$$
(13)

where *p* is the initial concentration of the molecule *M* in the gas phase and S_0 is the initial concentration of surface traps (stage 4). Equation 13 can be reduced to eq 3 by setting

$$\alpha \tau_e k_c = k_{\rm abs} \tag{14}$$

and

$$(\alpha \rho \tau_h k_R + k_{ph} \rho + k_{th}) = k_d \tag{15}$$

and to eq 1 for

$$k = \alpha \rho \tau_e k_c S_0 \{ \text{i.e.}, k \propto \rho \}$$
(16)

$$K = \frac{k_a}{\alpha \rho \tau_h k_R + k_{ph} \rho + k_{th}} \{ \text{i.e., } K \propto \rho^{-1} \}$$
(17)

or in the form of eq 4, for

$$a = \frac{\alpha \tau_e k_c S_o k_a p}{\tau_b k_a + k_{ab}} \{ \text{i.e., } a \propto p \}$$
(18)

$$b = \frac{\alpha \tau_h k_R + k_{ph}}{k_{th} + k_a p} \{ \text{i.e., } b \propto p^{-1} \}$$
(19)

as well as in the form of eq 5, where $A = \alpha \tau_e k_c S_o k_a$, $B = \alpha \tau_h k_R + k_{ph}$, and $C = k_a p$ with the additional constant k_{th} in the sum of the denominator in eq 5.

Mechanism of Oxygen Photoadsorption on ZrO₂. The experimental dependence $r(\rho,p)$ for oxygen on ZrO₂ (eqs 1, 2, 4, and 5) also satisfy eq 13 obtained from the PhA mechanism described above. However, a few points are worth noting. For simplicity, a single surface center (S, S⁻) is considered in the

mechanism while others might also implicate the PhA O₂ centers on ZrO₂.^{6,27} The sample is assumed to be illuminated uniformly, whereas illumination of the active surface of the sample in the cell used (see Experimental Section) is strongly irregular due to light absorption and light scattering among the sample particulates. Hence, kinetic constants evaluated from the experimental data on the basis of the mechanism proposed represent an average of the relevant constants over several possible surface centers and over a distribution of photon flow.

The estimated lifetime of the PhA centers decreases from 0.2 to 0.02 s as the light intensity increases (Table 1). From eq 13 or 15 and Figure 3 we deduce that the term $(\alpha \tau_h k_R \rho + k_{ph} \rho)$ is greater than k_{th} when $\rho > 1.5 \times 10^{14}$ photons cm⁻² s⁻¹. Moreover, according to the experimental results obtained at different temperatures and at excitation in different spectral regions, we can assume that $k_{th} = 0$ since $k_d = 1/\tau_d$ (see eqs 3) and 15) is independent of temperature and approaches zero during red light irradiation. On the basis of kinetic studies alone, it is difficult to separate the relative contributions of the recombination term $(\alpha \tau_h k_R \rho)$ and photoionization term $(k_{ph} \rho)$ to the decay constant k_d (eq 15). However, the photoionization path is not likely to be responsible for the decay of PhA centers. Using a large k_{ph} or otherwise an ionization cross section of the surface-active centers of $\sigma_{\rm ph} = 1 \times 10^{-16} \, {\rm cm}^2$, we obtain a lower limit of $\tau_d = 10$ s for $\rho = 1 \times 10^{15}$ photons cm⁻² s⁻¹. Thus, the term $k_{ph}\rho$ in eq 13 and in the subsequent expressions can be neglected for the PhA of O₂ on ZrO₂.

In contrast, the decay of PhA centers by a recombination path seems reasonable. Let τ_d equal $1/\sigma_R v[\mathbf{h}_s]$ where σ_R is the recombination cross section of PhA centers (in our notation S⁻), $v \approx 10^7$ cm s⁻¹ is the velocity of carriers, and [h_s] is the concentration of photoholes at the surface. In deducing eq 13 we assumed that the concentration of both charge carriers in the bulk of the solid (see the PhA mechanism, stages 1-3) and at its surface (stages 4 and 5) was the same. In fact, the concentration of photocarriers at the surface may be smaller than in the bulk of the crystal lattice due to surface recombination of the carriers. Thus, although estimation of the hole concentration $[h_s]$ by eq 9 may not reflect the actual concentration, the estimate of the uniform generation of carriers (g = $\alpha \rho$) does give reasonable values. Similarly, the term $(\alpha \tau_h k_R \rho)$ in eq 15 qualitatively describes the rate of decay of PhA centers through recombination and cannot be used for a numerical estimation of τ_d times. The problem of determining the concentration of photocarriers at the crystal surface was solved in earlier studies devoted primarily to the photoconductivity of solids⁴¹⁻⁴³ as well as to photocatalysis.⁴⁴⁻⁴⁷ In the present instance, the characteristic size of the crystalline particle ($d \approx$ 10^{-4} cm) is nearly identical to the inverse of the absorption coefficient α^{-1} (1 × 10⁴ cm⁻¹ at $\lambda = 254$ nm for ZrO₂₄₈). On the basis of the results of earlier studies it can be shown⁴⁹ that in the absence of surface charge and at $d \approx \alpha^{-1}$, the concentration of holes at the surface may be determined from eq 20

$$[h_s] = \frac{\alpha \rho L^2}{D\left(1 + \frac{sL}{D}\right)}$$
(20)

where the diffusion length of the holes *L* is such that $\alpha L < 1$, *D* is the diffusion coefficient for holes, and *s* is the rate of surface recombination. Let *D* equal $\mu \kappa T/e$ (10⁻² cm² s⁻¹) at *T* = 300 K, and the mobility of holes $\mu \approx 1$ cm s⁻¹ V⁻¹, typical of carriers in wide band-gap ionic metal oxides.⁵⁰ Estimated values of *s* (ca. 10⁵ cm s⁻¹) and *L* (ca. 10⁻⁵ cm) are reasonable in the present case. Note that the diffusion length *L* given by $(D\tau_h)^{1/2}$ leads to realistic lifetimes for holes in the bulk of the crystal lattice; namely, $\tau_h \approx 10^{-8}$ s. For these *s*, *D*, and *L* estimates and for a photon flow $\rho = 1 \times 10^{15}$ photons cm⁻² s⁻¹, eq 20 yields $[h_s] \approx 10^9$ cm⁻³ and the lifetime of PhA centers $\tau_d = 1/\sigma_R v[h_s]$ equals the experimentally found $\tau_d = 2.3 \times 10^{-2}$ s at $\rho = 1 \times 10^{15}$ photon cm⁻² s⁻¹ (see Table 1) for $\sigma_R \approx 10^{-14}$ cm². Note that this recombination cross section σ_R is typical for carrier trapping by Coulomb centers in solids. Hence, the measured lifetimes (Table 1) coincide within an order of magnitude with those expected for recombination decay of PhA centers.

Whatever the magnitude of the estimated times τ_d presented above are, results of PPSPhA studies show that decay of PhA– O₂ centers by recombination on ZrO₂ does occur. The difference in the lifetime τ_{PPSPhA} between a few tenths of milliseconds and >10⁴ s depends on whether blue light ($\lambda = 436$ nm) or red light ($\lambda \ge 700$ nm) induced oxygen photoadsorption on UVcolored ZrO₂ occurs. Absorption bands of electron F⁺ and hole V-type centers overlap in the blue region of the UV-induced color in ZrO₂.^{6,27,31} In contrast, only F centers can be excited by red light. To describe the photoexcitation of UV-colored ZrO₂, the set of quasi-chemical processes described by stages 1–6 should be supplemented with

 $F^+ + h\nu$ (436 nm) \rightarrow $V_a + e$ (photoionization of F^+ center) (stage 7a)

V + $h\nu$ (436 nm) → V_c + h (photoionization of V center) (stage 7b)

 $F + h\nu$ (>700 nm) \rightarrow $F^+ + e$ (photoionization of F center) (stage 7c)

where the symbols for F and F⁺ centers and for anion vacancies denote the point defects in the bulk of the crystal lattice because introduction of oxygen into the reaction cell before the secondary irradiation in the visible region leads to the annihilation of the surface centers during the (dark) postirradiation adsorption process. Both electrons and holes become free carriers (stages 7a and 7b) under irradiation with blue light. Carriers liberated from F⁺ and V centers are involved in recombination (stages 2a and 2b), in trapping by bulk defects (stages 3a and 3b), and in the formation of PhA O₂ centers (stage 4). Note that in the case of PPSPhA, the color centers of the same origin play different roles, namely those localized in the bulk lattice absorb light and emit photocarriers whereas those created at the sample surface via capture of photocarriers by the corresponding empty traps serve as PhA centers.^{6,27} Obviously, as occurs under UV irradiation (stage 1), recombination decay of PhA centers occurs (stage 5a) when PPSPhA is stimulated by blue light. As a result, the lifetimes τ_{PPSPhA} measured under irradiation by monochromatic light at $\lambda = 436$ nm (67 ms) or under irradiation with light at $\lambda > 400$ nm (45 ms) are similar to those under UV irradiation (Table 1). Similarly, the coefficients of postirradiation adsorption in the case of UV preirradiation $\Omega \approx 0.1^6$ and $\Omega \approx$ 0.1 for irradiation at $\lambda = 436$ nm are also nearly identical. In contrast, only free electrons are generated under irradiation by light at $\lambda > 700$ nm (stage 7c). Those electrons that avoided trapping in the bulk lattice (stages 2a, 3a, and 7b) can be captured by surface centers (stage 4). In the latter case, recombination decay of PhA centers (stage 5a) does not take place due to the absence of free photoholes. The only possible pathway, namely photoionization, that might lead to decay of

deep PhA centers seems unlikely. As a result, $\tau_{\text{PPSPhA}} > 1$ s from the r(p) dependence on red light irradiation is not in contradiction with reasonable τ_d values for photoionization of PhA centers (see above). For the same reason, the coefficient of postirradiation adsorption Ω is nearly unity for red light illumination.

Our previous view of "short-lived" or "long-lived" PhA centers in ZrO₂⁶ should be reexamined in connection with the recombination decay of PhA centers observed in the present study. Earlier it was thought that O₂ interacts with short-lived active centers primarily when UV light induces PhA of O₂ on ZrO₂. Only 10% of molecules adsorb at long-lived PhA centers in accordance with the coefficient of postadsorption $\Omega \approx 0.1.^6$ The lifetime of these centers is longer than 10^4 s, as judged from the delay time of postirradiation adsorption of oxygen. From the effect of oxygen postadsorption on diffuse reflectance spectra of UV preirradiated ZrO_2 , it was concluded that Zr^{3+} , F^+ , and F centers localized at the surface were responsible for postadsorption of oxygen.⁶ The lifetime of short-lived centers, which scaled in the milliseconds range, was estimated from the r(p) dependence under UV excitation of ZrO₂ by light with a photon flow ρ similar to that applied in this study. The shortlived PhA centers in ZrO₂ were attributed to some electron shallow traps that thermally decay by first-order kinetics. The distinction between short-lived and long-lived PhA centers identical to that made for ZrO2 above was also made for the systems KBr/O₂ and KI/O₂,¹³ MgAl₂O₄/O₂/H₂,¹² and others.⁵ However, present results suggest that deep PhA centers can display a bimodal behavior. Being accumulated at the surface during UV preirradiation in vacuo, such centers persist in an active state for extremely long times (hours to even days⁵) whereas these same centers behave as short-lived adsorption centers under permanent irradiation in a gas/solid system when the decay of these PhA centers takes place by recombination with photocarriers of the opposite sign. Interestingly, PhA centers for H₂ in Sc₂O₃ display a similar behavior.³³

Finally, oxygen adsorption primarily on stable PhA centers $(Zr^{3+}, F^+, and F^{6,31,34})$ determines the rate of the PhA of O₂ on ZrO₂. The decay of PhA centers in an active state occurs via recombination with photogenerated holes. Hence the dependence of the initial rate of PhA of O₂ on oxygen pressure and photon flow can be described by eq 5.

Possible Appearance of Recombination Decay of Active Centers and Intermediates in Photocatalytic Reactions. Photooxidation of organic molecules over illuminated TiO₂ in aqueous media is representative of photocatalysis.¹⁻³ Some workers still maintain that photoholes are the oxidants in these reactions. A few types of interactions between photoholes and organic molecules, RH can be distinguished:

$$h + RH_{ads} \rightarrow products$$
 (21)

$$S^+ + RH_{ads} \rightarrow products$$
 (22)

$$S^+ + RH_{sol} \rightarrow products$$
 (23)

Reaction 21 is of the LH-type where free photoholes (h) are captured by adsorbed molecule (RH_{ads}). In the version of the LH reaction 22, the mobility of adsorbed molecules is presumed when RH interact with the trapped hole S⁺. Reaction 23 is of the ER-type where a "free" molecule in the solvent medium (RH_{sol}) interacts with surface-trapped holes. Reaction 23 may also implicate electron transfer through the solid/liquid interface between the solid catalyst and the reagent molecules. In the

latter case, S^+ can be treated as any localized hole surface state provided that it can recombine with free electrons (see below).

Instead of trapped S⁺ or free holes, surface-adsorbed 'OH radicals have also been taken as the oxidants in the version of photocatalytic oxidation of organic substrates over irradiated TiO₂ particulates.^{18,24,47,51} These 'OH radicals are generated by hole capture by surface OH⁻_s species (or by adsorbed water):

$$OH_{s}^{-} + h \rightarrow OH_{s}$$
 (24)

The PhA mechanism treated earlier (see above) can easily be adopted to these heterogeneous photocatalytic oxidations. Indeed, stages 1 and 2 retain their validity. Stages 3a and 3b are retained for common occurrence. (In addition, from a kinetic point of view, stage 3a can represent the scavenging of electrons by oxygen.) Stage 4 may be replaced by reaction 25:

$$S + h \rightarrow S^+ \tag{25}$$

where S is any surface hole trap including OH_s^- and S^+ is either a hole center (e.g., of the $O^{-\bullet_s}$ -type) or an ${}^{\bullet}OH_s$ radical. Stage 6 in the PhA mechanism is replaced by reactions 22, 23, or 24. It is clear that expressions similar to eq 13 and others can be obtained for the rate of oxidation of RH substrates over an irradiated photocatalyst if the recombination decay of active centers (S⁺) or of ${}^{\bullet}OH_s$ radicals is considered

$$S^+ + e \rightarrow S \tag{26}$$

$$^{\bullet}\mathrm{OH}_{\mathrm{s}} + \mathrm{e} \rightarrow \mathrm{OH}_{\mathrm{s}}^{-} \tag{27}$$

Note that the expressions for the photocatalytic reaction rate $r(\rho, C)$ will coincide with the corresponding $r(\rho, p)$ if the subscripts for electrons and holes in eq 13 are interchanged. In reactions 26 and 27 e denotes free photoelectrons whose concentration depends on the incident photon flow. The latter point distinguishes this mechanism from those discussed earlier where reaction 27 was treated^{47,51} or from those where the ${}^{\bullet}OH_{s}$ radical decay was presented as a first-order reaction.^{18,23} It should be emphasized also that regardless of the LH (in the version presented by reaction 22) or ER (reaction 23) types of reactions, the concept of recombination decay of active centers (localized carriers) or of intermediates remains useful. Of course, the definition of rate constants corresponding to reactions 22 and 23 will differ from each other and from the constant k_a in the PhA mechanism treated above. Nevertheless, the view of photon-flow-dependent lifetimes of active centers or of intermediates also remains valid in photocatalyzed reactions.

Results of preliminary studies on the rate of photooxidation of phenol $r(\rho, C)$ over TiO₂ in aqueous solutions accord with the reaction mechanism outlined above. It is clear that the $r(\rho)$ dependencies for phenol photooxidation over TiO₂ are similar to those for initial rates $r(\rho)$ of the PhA of O₂ on ZrO₂ (compare, e.g., curves 1 and 2 in Figure 9 and curves 1 and 5 in Figure 4). The mechanism proposed will be clarified during further detailed studies of the photooxidation of phenol in solutions over titania. In a preliminary and complementary study of hydrogen photoadsorption on Degussa P-25 TiO₂ particulates, which were heat pretreated in a manner similar to ZrO₂, show that r(p) dependence on pressure is linear up to p = 2 Pa at a photon flow $\rho = \rho_0$ (= 1 × 10¹⁵ photons cm⁻² s⁻¹) whereas at $\rho = 0.1 \rho_0$ the dependence is significantly sublinear (compare, e.g., curves 1 and 2 for $C < 20 \,\mu$ M, Figure 8). Full disclosure of these studies shall be reported elsewhere.

Conclusions

The distinguishing feature of oxygen photoadsorption kinetics, $dp/dt \approx p^n \rho^m$, on ZrO₂ resides in the dependence of the order of the reaction on photon flow ρ^m and in the dependence of the order of reaction on oxygen pressure p^n . Consideration of the photon-flow-dependent pathways of the decay of photoinduced surface centers, e.g., their recombination with photoholes, affords a description of the kinetics of oxygen photoadsorption on ZrO₂. The photoadsorption mechanism proposed can also be expanded to photocatalyzed oxidative reactions of phenol in irradiated aqueous TiO₂ dispersions.

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