sibility of local fluctuations. The positions of energy minima of the whole system and its subsystems are significantly changed, too.

Finally it must be mentioned that the obtained results must be taken carefully because of the restrictions of the CNDO method and the cluster model used. Nevertheless, the calculated trends seem to be correct.

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The Photocatalytic Degradation of Cyclic Acetals in Aqueous Titanium Dioxide Suspension

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The photocatalytic oxidation of 2-ethoxytetrahydropyran in aqueous titanium dioxide suspension in the presence of oxygen was studied. On the basis of quantum-chemical calculations, IR, FTIR, and UV—VIS spectroscopy and GC—MS analysis the reaction mechanism was proposed.
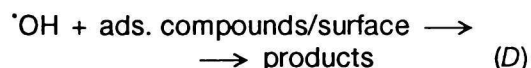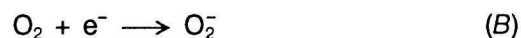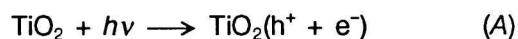
New photocatalytic processes for conversion of carbohydrates, starch and cellulose into hydrogen and carbon dioxide in the irradiated TiO$_2$ suspensions were investigated by *Kawai* and *Sakata* [1—3]. *St. John et al.* studied the photocatalytic degradation of glucose in aqueous suspension of titanium dioxide. Hydrogen and carbon dioxide were determined under inert atmosphere and CO$_2$ alone under oxygen atmosphere [4].

The mechanism of photocatalytic degradation of saccharidic structures was not yet published in detail.

During irradiation in the Pt/TiO$_2$ aqueous suspension the significant changes in the polymerization degree of hydroxyethylcellulose (HEC) and carbon dioxide evolution were observed [5]. The proposed mechanism of HEC polymer chain cleavage includes the attack of the photogenerated hydroxyl radical onto the C-1 atom of the hexopyranose unit [5]. EPR studies confirmed high concentrations of hydroxyl radicals in the irradiated TiO$_2$ aqueous suspensions in the presence of oxygen [6].

The formation of the basic reactive intermediates on the irradiated titanium dioxide surface in aqueous suspension is described by the following equations [7]

$$TiO_2 + h\nu \longrightarrow TiO_2(h^+ + e^-) \qquad (A)$$

$$O_2 + e^- \longrightarrow O_2^- \qquad (B)$$

$$OH^- + h^+ \longrightarrow {}^\cdot OH \qquad (C)$$

$${}^\cdot OH + \text{ads. compounds/surface} \longrightarrow \\ \longrightarrow \text{products} \qquad (D)$$

where h$^+$, e$^-$ are photogenerated hole and electron.

Information on electronic structure (charges) in the molecule implying the possible reaction centra

of the model systems may be obtained by the theoretical tools of the quantum chemistry. The semiempirical INDO/2 method has been used [8, 9]. This method is capable to describe the properties connected with the electronic structure of organic compounds with relatively small molecules. The solvent effect may be partially accounted in Germer model for the known permittivity (ε_r) of the solvent [10].

The main aim of this study is to confirm the primary reaction centre of the model compounds with the basic saccharidic skeleton in the photocatalytic reaction in aqueous titanium dioxide suspension.

EXPERIMENTAL

The photocatalytic reactions of 2-ethoxytetrahydropyran (Et-O-THP) in titanium dioxide aqueous suspensions were studied. For all photocatalytic experiments, the titanium dioxide P25 (Degussa, FRG; predominantly anatase, surface area (50 ± 5) m^2 g^{-1}) was applied. Photocatalytic experiments were carried out in a photochemical immersion well (Applied Photophysics, Surrey, Great Britain) at a temperature of 30 °C as described elsewhere [11]. The reaction suspensions were bubbled by cleaned air (flow rate of 500 cm^3 min^{-1}) and were stirred magnetically. A 125 W medium pressure mercury lamp (Applied Photophysics, Surrey, Great Britain) with Pyrex sleeve was used for irradiation ($\lambda > 290$ nm). The carbon dioxide evolved during irradiation was measured conductometrically. The suspensions were centrifuged before analysis at 6400 g on an ultracentrifuge T24 (Janetzki).

The spectra were recorded on UV—VIS spectrophotometer PU 8800 (Philips), the titanium dioxide powders by IR spectrophotometer 599 (Perkin—Elmer) (KBr pellet technique) and FTIR spectrophotometer PU 9800 (Philips) (diffuse reflectance accessory). Titanium dioxide samples were dried at 60 °C before measuring the IR spectra. The analysis of the products in the irradiated aqueous TiO$_2$ suspensions was carried out by GC—MS head space technique on a 5980A/5790 apparatus (Hewlett—Packard). The capillary column SE (30 μm, length 60 m, inner diameter 0.3 mm) and the carrier gas helium (80 cm^3 min^{-1}) at the temperature range 50 °C—200 °C (temperature gradient of 8 °C min^{-1}) were applied.

All the chemicals used were of anal. grade purity. 2-Ethoxytetrahydropyran was prepared by the addition reaction of ethanol with 2,3-dihydro-4H-pyran (Sigma, USA) in the presence of p-toluenesulfonic acid (Lachema, Brno) [12]. The IR and MS spectra of the prepared Et-O-THP were equal as published in [13, 14].

RESULTS AND DISCUSSION

Quantum-Chemical Calculations

Using semiempirical INDO/2 method the electronic structure of 2-hydroxy- (H-O-THP), 2-ethoxy- (Et-O-THP), 2-isopentoxy- (iPe-O-THP), 2-cyclohexoxytetrahydropyran (cyHe-O-THP) and glucose has been calculated. Because of the negligible dependence of the individual atom charges of the model systems on the geometry variations, the calculations were performed not for the optimized geometries but for the experimental ones [15] only.

Table 1 presents the calculated values of charges for considered carbon and oxygen atoms of the model systems of 2-substituted tetrahydropyrans.
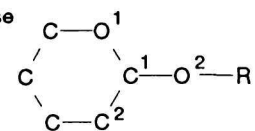
Our results show that introducing the solvent effect of water ($\varepsilon_r = 80$) leads to higher polarization of individual atoms. However, no qualitative changes of atom charges are observed. Moreover, the charge shifts on the relevant atoms are constant within different members of the model series. Consequently, the results obtained for isolated systems ($\varepsilon_r = 1$) are sufficient for our purposes.

The most probable reaction centre for the attack of hydroxyl radical may be deduced from the calculated atomic charges (it is located at the centre of minimal electron density). The highest positive charges are located at C-1 atom and here the reaction starts with much higher probability than at the C-2 atom. The reactivity rises with the polarity of the solvent. On the other hand, the highest negative charges are located at both oxygen atoms; the O-1 and O-2 ones are nearly equal for all the model systems despite the different character of both the atoms.

Blank Experiments

No changes were observed during 90 min of irradiation and/or stirring in the UV spectral set in

Table 1. Calculated Values of Charges for Relevant Carbon and Oxygen Atoms of 2-Substituted Tetrahydropyrans and Glucose

Compound	ε_r	O^1	C^1	C^2	O^2
				Atom charges	
H-O-THP	1	−0.316	0.382	−0.004	−0.321
Et-O-THP	1	−0.311	0.383	−0.009	−0.295
iPe-O-THP	1	−0.316	0.386	0.001	−0.305
cyHe-O-THP	1	−0.318	0.389	0.001	−0.309
Glucose	1	−0.317	0.356	0.144	−0.304
Et-O-THP	80	−0.372	0.490	−0.035	−0.355
Glucose	80	−0.375	0.448	0.162	−0.367

the studied systems (concentration of Et-O-THP 6.4 mmol dm^{-3}, concentration of TiO$_2$ 0.8 g dm^{-3}) when the experiments were carried out either by the irradiation of Et-O-THP solution in the presence of air without TiO$_2$; or by the stirring of the suspension of Et-O-THP and titanium dioxide without irradiation; or by the irradiation of the suspension of Et-O-THP and titanium dioxide in nitrogen atmosphere.

The results of blank experiments show that the presence of TiO$_2$, light and oxygen (electron scavenger) is necessary for the photocatalytic oxidation of Et-O-THP.

Adsorption of 2-Ethoxytetrahydropyran on the TiO$_2$ Surface

The adsorption of Et-O-THP on the TiO$_2$ surface from the aqueous suspension can be studied by IR spectroscopy. Comparison of the IR spectra of neat 2-ethoxytetrahydropyran and on the TiO$_2$ adsorbed one suggests the significant decrease in intensity of the peaks at $\tilde{w}$ = 1040, 1070, and 1080 cm^{-1}, respectively. These peaks are attributed to the skeletal vibrations of C—O—C—O—C bonds in the Et-O-THP molecule [16].

Davydov et al. proved the interaction of diethyl ether with two vicinal hydroxyl groups on the aluminium oxide surface shown in Fig. 1A [17].

On the basis of this information and of the measured IR spectra of Et-O-THP on the TiO$_2$ surface it can be assumed that oxygen atoms in the Et-O-THP molecule interact with hydroxyl groups on the titanium dioxide surface by the way shown in Fig. 1B, C, D. This assertion is in accordance with the oxygen charges values (Table 1) and with the order of basicity of the cyclic ethers [18].

Photocatalytic Degradation of 2-Ethoxytetrahydropyran in the Aqueous TiO$_2$ Suspension

During irradiation of Et-O-THP suspensions the amount of evolved carbon dioxide was continuously measured. Fig. 2 shows the time dependence of the amount of evolved carbon dioxide in the suspensions with different concentrations of TiO$_2$ (concentration of Et-O-THP in all systems was 6.4 mmol dm^{-3}). All kinetic curves of CO$_2$ formation have the induction period of *ca.* 15 min (Fig. 2).

The evolution of carbon dioxide in the system is a consequence of the photocatalytic decarboxylation of carboxylic acids in the irradiated titanium dioxide suspensions [4, 19]. Thus the carboxylic acid must be produced during the photocatalytic degradation of Et-O-THP.

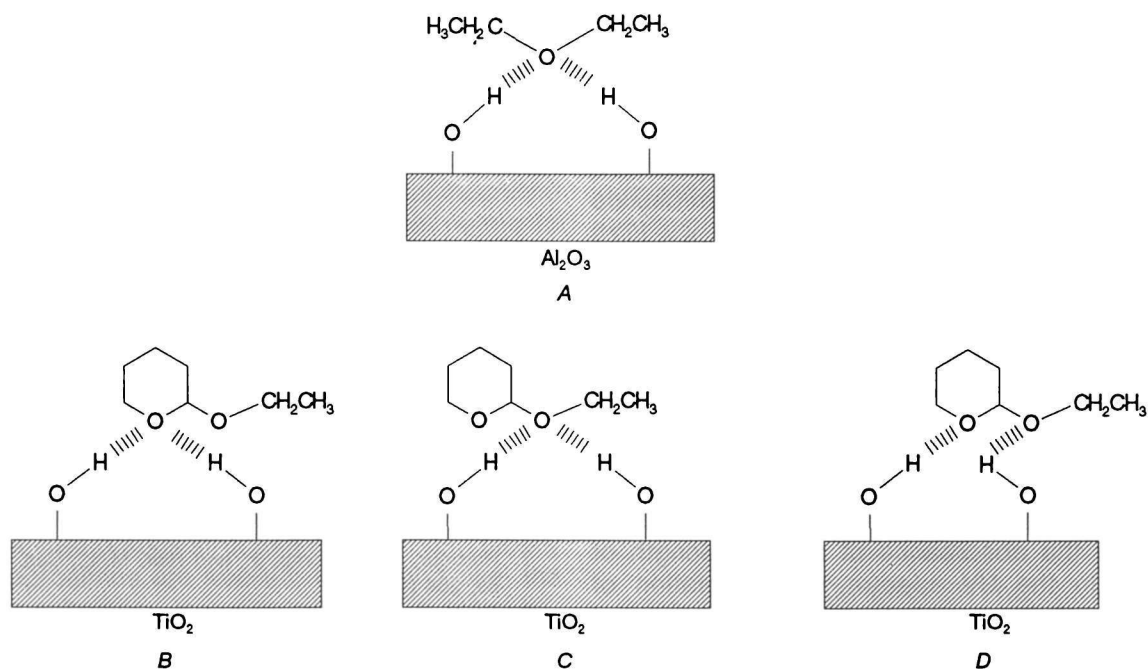Carboxylic acids formation on the irradiated TiO$_2$ surfaces was proved by FTIR spectroscopy. In the

Fig. 1. Interaction of diethyl ether (*A*) and 2-ethoxytetrahydropyran (*B, C, D*) molecule with the hydroxyl groups on the aluminium oxide [17] and TiO$_2$ surface, respectively.
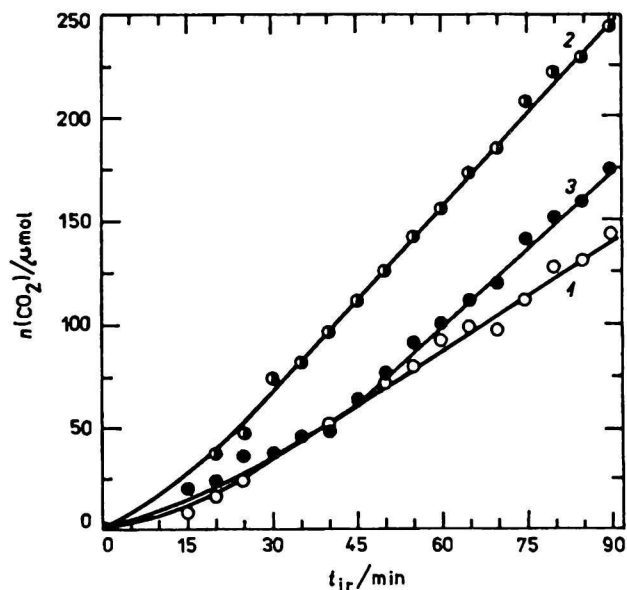
Fig. 2. The formation of CO_2 in the photocatalytic systems $(c(Et-O-THP) = 6.4 \text{ mmol dm}^{-3})$ with different concentrations of TiO_2. $\rho(TiO_2)/(g \text{ dm}^{-3})$: 1. 0.8; 2. 1.6; 3. 2.4.

duction period of the carbon dioxide formation (Fig. 2). Thus 4-pentenoic acid must be the product of the photocatalytic oxidation of 4-pentenal.

CONCLUSION

On the basis of our results the degradation mechanism of 2-ethoxytetrahydropyran in irradiated aqueous TiO_2 suspension shown in Scheme 1 is proposed.

Experimental results confirmed the reaction centre predicted by quantum-chemical calculations. It may be supposed that the reaction mechanism in the photocatalytical reaction of 2-substituted tetrahydropyrans will be analogous as in our study. This problem, however, demands further experimental investigations.
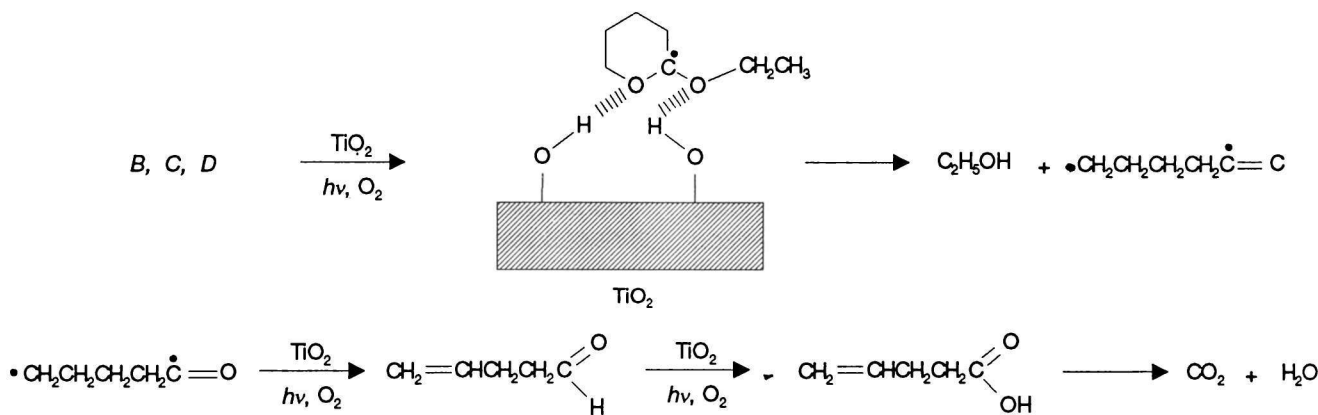
Scheme 1

FTIR diffuse reflectance spectrum of TiO_2 after 60 min of irradiation in the Et-O-THP titanium dioxide suspension the significant strong peak at $\tilde{w} = 1718$ cm^{-1} was observed. This FTIR spectrum can be successfully attributed to the IR spectrum of 4-pentenoic acid [20].

The GC—MS analysis of the irradiated suspensions was carried out by head space technique without centrifugation. Ethanol and 4-pentenal were detected as the major intermediates of the photocatalytic process. The formation of aldehyde structure in the irradiated suspensions confirmed increase of the absorbance at the wavelength of 260 nm in the UV spectra. The formation of 4-pentenal from the photochemically generated biradical ˙$CH_2CH_2CH_2CH_2$ĊO was published by *Srinivasan* [21].

The maximal concentration of the aldehydic products is well correlated with the length of the in-

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Diffusion Coefficients of n-Hexane in Particles of Molecular Sieve NaY Determined by means of Chromatographic Measurements

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The values of effective diffusion coefficients of n-hexane in the presence of nitrogen (1.48—5.60) × 10^{-9} m^2 s^{-1} were determined at 160—240 °C under the assumption that the particle of molecular sieve NaY can be described by a quasi-homogeneous model. Considering a biporous structure in this particle, the determined values of diffusion coefficients D_a/r_0^2 of n-hexane in a molecular sieve crystal in the presence of nitrogen are ranging from 32.4 to 41.4 s^{-1}.

Values of diffusion coefficients in a single particle of adsorbent as well as equilibrium data are a necessary prerequisite for mathematical modelling of the adsorption separation units. With regard to the complexity of the adsorbent structure, a dependence of the diffusion coefficient on the properties of adsorbent, adsorptive, and carrier gas has not been formulated up to now. In characterizing the transport of adsorptive in a single adsorbent particle, experimental values of diffusion coefficients are used in models describing both adsorption and desorption.

In describing the transport of adsorptive in a complicated porous structure of adsorbent, mostly two approaches are applied. In the first one, the porous substance is supposed to be a quasi-homogeneous isotropic medium from the standpoint of mass transport [1, 2]. The second one proposes that the porous structure of the adsorbent particle can be approximated by two kinds of pores, *i.e.*

by the so-called biporous structure [3, 4]. Particles of molecular sieve NaY employed in this study consist of zeolite crystals with dimensions in μm, entrance openings of nm irregularly distributed in a particle of adsorbent and joined by the secondary pores having a most frequent radius of about 120 nm [5]. Therefore, the assumption to describe the mass transfer in a particle of adsorbent also by diffusion in a biporous particle of adsorbent is justified.

The relationships used for the determination of diffusion coefficients are presented in [5].

EXPERIMENTAL

n-Hexane (Lachema, Brno) had the following composition (x/mole %): n-hexane 98.47; 3-methylpentane 1.13; 2-methylpentane 0.40.