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Photocatalytic reduction of nicotinamide coenzymes in the presence of titanium dioxide: The influence of aliphatic aminoacids

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Abstract

Illumination of a TiO_2 dispersion in a weakly alkaline solutions of nicotinamide coenzymes (NMN^+, NAD^+, $NADP^+$) leads in the presence of aminoacids (glycine, lysine, serine and aspargine as well as EDTA and DTT) to one-electron reduction of the coenzymes. The formation of the respective dimers observed in the initial stage of illumination at 365 nm was confirmed by polarographic, spectrophotometric and enzymatic analysis. The relative efficiency of photoreduction strongly depends on the nature of the electron donor. Effects of pH and coenzyme concentration on the efficiency of photoconversion process were investigated. Prolonged irradiation leads to tetrahydroderivatives and/or hydration products of the respective dimers. © 1997 Elsevier Science S.A.

Keywords: Nicotinamide coenzymes; Titanium dioxide; Aminoacids

1. Introduction

Photocatalytic reactions on the surface of semiconductors, such TiO_2, CdS, ZnO, are very important from the point of view of the perspective utilization of these systems for direct conversion of solar energy [1–4] and hydrogen production by photoelectrochemical water cleavage [5,6]. Suspensions of TiO_2 powder have also found prominent use as a photosensitizer for a wide range of redox processes, including non-conventional organic synthesis [7–11] and photodegradation of environment pollutants [12–15].

The use of semiconductors in the construction of a photocontrollable enzyme reaction systems capable of recycling of NAD^+ was achieved successfully by co-immobilization of alcohol dehydrogenase and TiO_2 [16]. This system could be used for continuous oxidation of NADH to NAD^+ on irradiation with UV light.

TiO_2 has also been successfully used to sensitize redox processes of the couple NAD^+/NADH in the excited state. Cuendet and Grätzel [17] reported that illumination of NAD^+ solution in the presence of TiO_2 and rhodium trisbipyridyl complex [$Rh(bipy)_3^{3+}$] led to continuous generation of biologically active NADH.

It is known from our previous study that excitation of the oxidized form of nicotinamide coenzymes at 254 nm in the presence of aminoacids leads to the one-electron reduction of coenzymes [18]. In this study we have investigated the influence of band gap illumination of TiO_2 dispersions on the photoreduction of NAD^+, NMN^+ and $NADP^+$ in the presence of aliphatic aminoacids at different pH values in an attempt to evaluate their properties as electron donors.

2. Experimental details

2.1. Materials

NMN^+, NAD^+, $NADP^+$ (free acids), alcohol dehydrogenase (EC 1.1.1.1), glucose-6-phosphate dehydrogenase (EC 1.1.1.49) and glutathione reductase (EC 1.6.4.2) were purchased from Sigma Co. (USA). Glycine, lysine, aspargine and serine were products of Pierce (Illinois, USA). Catalase (EC 1.11.1.6) was obtained from Serva (Heidelberg, Germany) and lactate dehydrogenase (from chicken heart) was a product of PL Biochemicals (Milwaukee, USA). EDTA-(disodium salt) was obtained from POCh (Poland). TiO_2 (anatase 145 $m^2\ g^{-1}$) was a gift from dr M. Grätzel (Institute of Physical Chemistry, Swiss Federal Institute of Technology, CH-1015 Lausanne, Switzerland).

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2.2. Photochemical experiments

Irradiation at 365 nm in 10 mm path length quartz cuvettes was done with an Osram HQV 125 W Wood's lamp (major emission at 365 nm, virtually negligible at 320 nm). The intensity of the incident light, measured using a ferrioxalate actinometer, was 33 mW cm^{-2}. Before irradiation, solutions were rendered anaerobic by flushing with argon. Cuvettes were maintained at room temperature using a stream of cool air. The concentration of coenzymes in irradiated solutions was 5×10^{-4} M, electron donors (EDTA, DTT, aminoacids) 5×10^{-2} M. TiO_2 powder (6 mg/3 ml) was suspended in solutions containing coenzyme and electron donor and removed after irradiation by centrifugation. Photochemical experiments were done in 0.1 M carbonate buffer (pH 9–10), 0.1 M phosphate buffer (pH 7–8), 0.1 M ammonium buffer (pH 8–12).

2.3. Electrochemical measurements

Direct current polarography was carried out with a Polarographic Analyzer PA42 (Prague, Czech Republic) under conditions described previously [19].

2.4. Spectral measurements

UV and visible absorption spectra were recorded on a Specord M-40 spectrophotometer (Jena, Germany).

2.5. Kinetic of the photochemical processes

To evaluate the efficiency of photochemical transformation of nicotinamide coenzymes, we applied a simple kinetic model for homogenous reaction [20]. The plots of photoreduction rate vs. irradiation time were analysed in terms of formal kinetic yielded formal rate constants which serve as a general measure for the efficiency of the photoreduction process. In heterogenous photocatalysis the term "quantum yield" is elusive since the number of absorbed photons remains experimentally difficult to assess. Recently comprehensive method to standardize and compare processes efficiencies in heterogenous photocatalysis was proposed by Serpone et al. [21,22].

2.6. Enzymatic studies

The enzymatic assay for NADH was performed as follows: sodium pyruvate (2.27 M) and 0.2 units of lactate dehydrogenase was added to 3 ml of an irradiated solution of NAD^+ in 0.1 M phosphate buffer (pH 7.5). The resulting decrease of absorbance at 340 nm gave the amount of NADH.

For the enzymatic assay of NADPH, 20 μl of oxidized glutathione (0.1 M) was added to 3 ml of an irradiated solution. The reaction was initiated by addition of glutathione reductase. The resulting decrease in absorbance at 340 nm, relative to a non-irradiated control, gave the amount of NADPH.

The concentrations of the dimers were calculated from the UV absorbances at 340 nm using the molecular absorption coefficients for $(NMN)_2$, $(NAD)_2$, $(NADP)_2$ [19].

The amount of NAD^+ in the irradiated solution was determined using an yeast alcohol dehydrogenase system. 0.8 μg of the enzyme was added to 3 ml NAD^+ solution at pH 7.0, containing 0.05 M ethanol. The concentration of NAD^+ was determined on the basis of the appearance of 340 nm absorption band characteristic for NADH.

Glucose-6-phosphate dehydrogenase system was employed for determination of $NADP^+$ concentration in irradiated solutions. 2 units of the enzyme were added to 3 ml of irradiated $NADP^+$ solution (pH 7.4) containing 0.04 M glucose-6-phosphate. The increase in absorbance at 340 nm gave the amount of NADPH formed during the enzymatic reduction of $NADP^+$.

Enzymatic assay for H_2O_2 was carried out with catalase by following the disappearance of the respective polarographic wave [19].

3. Results

3.1. Characteristic of the photoreduction products

Irradiation of oxidized forms of nicotinamide coenzymes (NMN^+, NAD^+, $NADP^+$) at 365 nm under anaerobic conditions (pH 9.5), in TiO_2 dispersion and in the presence of lysine leads in the initial stage of irradiation (less than 60 min) to the appearance of an absorption band at 340 nm

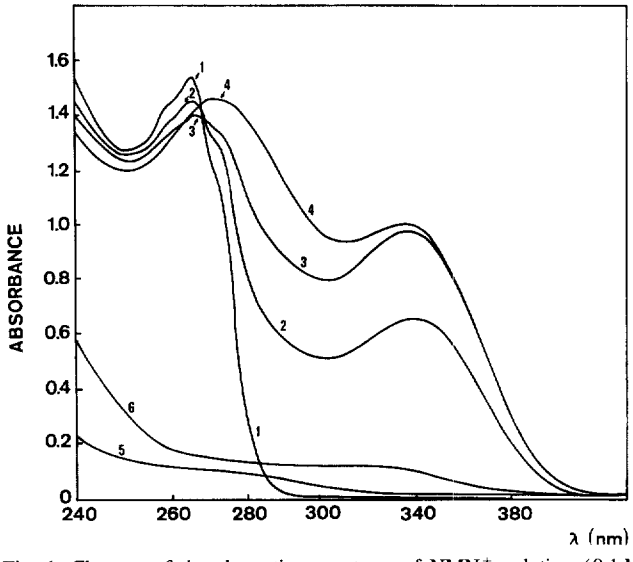

Fig. 1. Changes of the absorption spectrum of NMN^+ solution (0.1 M carbonate buffer, pH 9.5) with time of irradiation at 365 nm in the presence of lysine and TiO_2: (1) before irradiation, (2) after 10 min of irradiation, (3) after 20 min of irradiation, (4) after 40 min of irradiation, (5) lysine irradiated 60 min in the presence of TiO_2, (6) lysine irradiated 120 min in the presence of TiO_2.

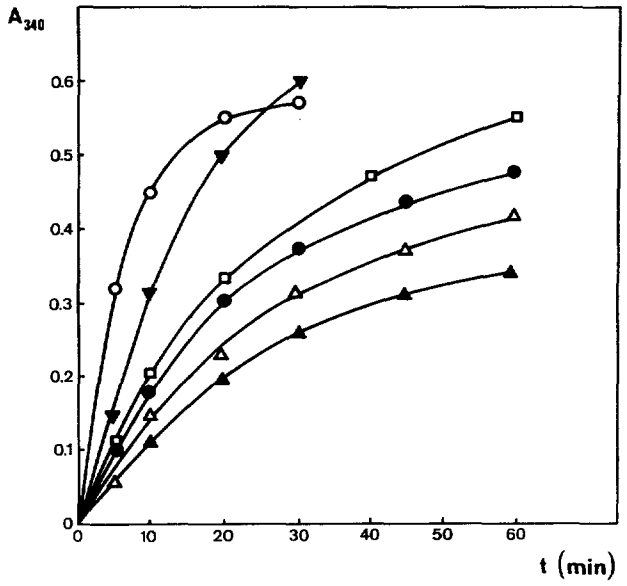

Fig. 2. Changes of the absorption band of NMN^+ solution (5×10^{-4} M) at pH 9.5 with time of irradiation at 365 nm in the presence of TiO_2 (▲); TiO_2 and electron donors: (●) serine, (▼) DTT, (□) lysine, (○) EDTA, (△) glycine.

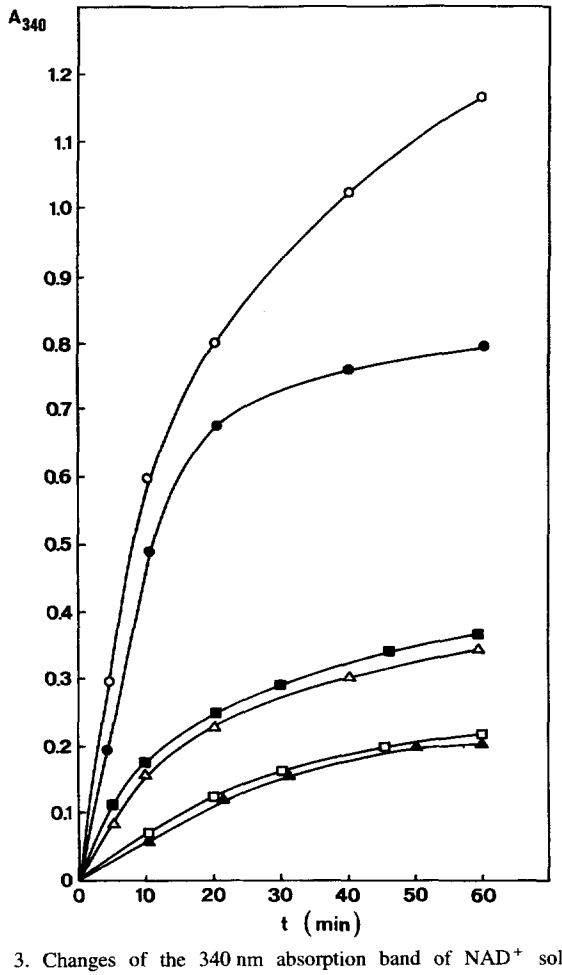

Fig. 3. Changes of the 340 nm absorption band of NAD^+ solution (5×10^{-4} M) at pH 9.5 with time of irradiation at 365 nm in the presence of TiO_2 (▲); TiO_2 and electron donors: (●) serine, (■) asparagine, (□) lysine, (○) EDTA, (△) glycine.

characteristic of the reduced forms of the nicotinamide ring (Fig. 1).

Control experiment with lysine in TiO_2 dispersion irradiated without coenzyme has shown very small changes in the absorption region 315–330 nm (Fig. 1). The same product absorbing in the region 315–325 nm is formed during irradiation of lysine and serine at 254 nm in alkaline solutions (pH 9.5). This compound has been identified as a 4-pyridinoline derivative [2] by comparison with the reported absorption and fluorescence spectra [23,24].

Irradiation of NMN^+, NAD^+ and $NADP^+$ in the presence of TiO_2 and other aliphatic aminoacids also leads to the reduction of the corresponding coenzymes. Changes in the absorption at 340 nm of irradiated solutions of NMN^+, NAD^+ and $NADP^+$, in the presence of different electron donors as a function of irradiated time are shown in Figs. 2–4.

Blank experiments established that only a negligible amount of the reduced forms of coenzymes are produced when coenzymes are subjected to 365 nm irradiation under equivalent conditions in the absence of electron donors (Figs. 2–4).

The reduction products of irradiated coenzymes were identified by UV absorption spectra and polarographic analysis, which revealed the disappearance of the cathodic waves at potentials from −0.9 V to −1.1 V characteristic of the oxidized forms of the coenzymes, and formation of anodic waves in the region of −0.38 V to −0.42 V (Table 1) due to oxidation of the respective dimers [25].

Enzymatic analysis of the reduction products of NAD^+ with lactate dehydrogenase and those of $NADP^+$ with glutathione reductase confirmed that the photochemically generated species were biologically inactive: this result rules out

[2] The complete structure remains to be elucidated. Study is under way.

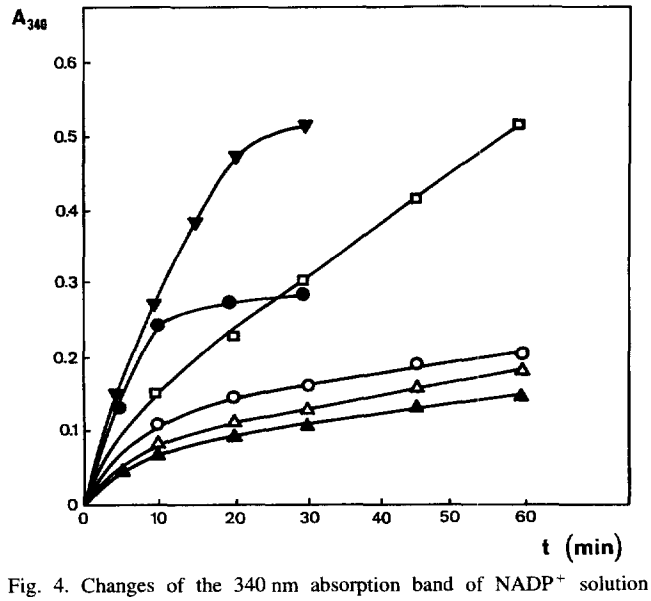

Fig. 4. Changes of the 340 nm absorption band of $NADP^+$ solution (5×10^{-4}) M) at pH 9.5 with time of irradiation in the presence of TiO_2 (▲); TiO_2 and electron donors: (●) serine, (▽) DTT, (□) lysine, (●) EDTA, (△) glycine.

Table 1
Changes of absorption spectra and formation of polarographic anodic waves during irradiation of nicotinamide coenzymes in the presence of aminoacids and TiO_2 (pH 9.5, argon atmosphere)

Electron donor	$(NMN)_2$		$(NAD)_2$		$(NADP)_2$	
	λ_{max} (nm)	$E_{1/2}$ (V)	λ_{max} (nm)	$E_{1/2}$ (V)	λ_{max} (nm)	$E_{1/2}$ (V) [a]
EDTA	338	−0.35	339–340	−0.38	339–340	−0.40
DTT	339	−0.36	338–340	−0.41	338–340	−0.40
Lysine	337	−0.36	337–339	−0.39	338–340	−0.42
Glycine	338	−0.35	337–340	−0.40	337–340	−0.41
Serine	335	−0.35	339–340	−0.42	339–340	−0.42
Aspargine	–	–	339–340	−0.41	–	–

[a] Polarographic waves not well defined.

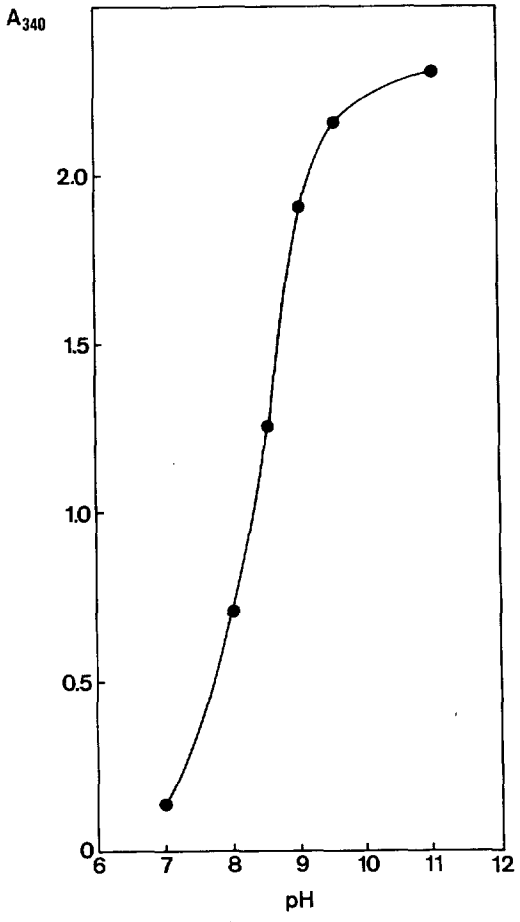

Fig. 5. Photoreduction of NAD^+ as a function of pH in the presence of serine.

the formation of dihydro derivatives (NADH and NADPH respectively) in this system.

The extent of the photochemically induced conversion to the dimers in the presence of electron donors was measured as the ratio of the concentrations of the dimers formed during irradiation to the initial concentration of the respective monomers. The extent of the photoreduction process of $NADP^+$ varies from 5 to 15%, depending on electron donors. The conversion of NMN^+ to the dimer amounts to 10–40% while it increases to 90% for NAD^+.

The photoreduction efficiency strongly depends on the pH of the irradiated solution (Fig. 5). As an example, the photoreduction process of NAD^+ in the presence of TiO_2 and serine in buffered solutions was examined. It was found that the yield of the reduced forms increases steeply in the pH range 7–9 and attains the plateau for alkaline solutions at the pH 9.5–11 similar in carbonate and ammonium buffers. The decrease of the photoreduction rate at pH < 7 is probably due to the less negative flat band potential with decreasing pH (0.059 V per pH unit) [26] and/or a reversible protonation of TiO_2 surface [22].

The plots of photoreduction rate vs. initial concentration of NAD^+ (Fig. 6) were analysed on the basis of a simple kinetic model for homogenous reactions [20]. This model yielded formal rate constants which serve as a general measure for the relative efficiency of photoreduction. The differential rate for homogenous reactions is

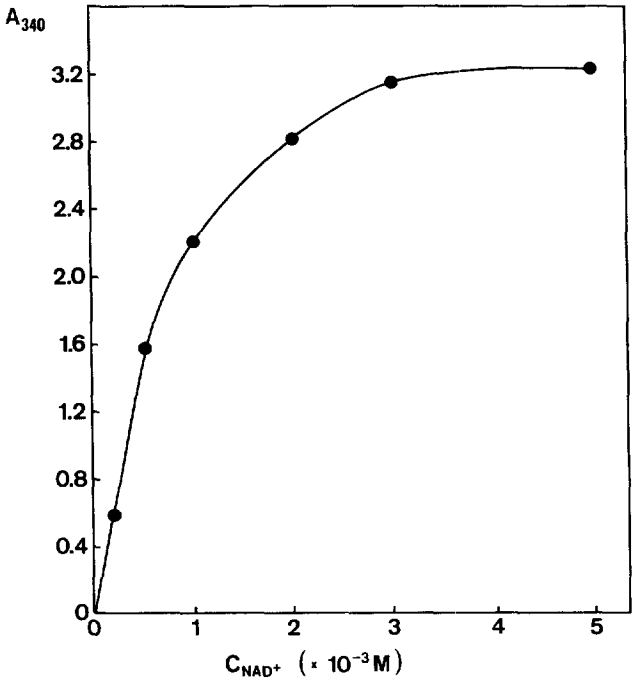

Fig. 6. Photoreduction of NAD^+ as a function of initial concentration during irradiation at pH 9.5 (0.1 M carbonate buffer) in the presence of serine and TiO_2 (irradiation time 15 min).

$$-dc/dt = kc^n \quad (1)$$

where c is the concentration of the coenzyme at irradiation time t, k the reaction constant, and n the reaction order. The analysis of the data revealed two limiting cases. The photoreduction process of NAD^+ in the presence of serine at NAD^+ concentration $c > 3\times10^{-3}$ M proceeds according to zero-order kinetics (slope corresponding to $n=0$) while at concentrations $c < 1\times10^{-3}$ M pseudo first-order kinetics (slope corresponding to $n=1$) have been observed. This means that at high substrate concentration a saturation type kinetic occurs [21]. At low concentrations the number of catalytic sites is not the limiting factor of the photoreduction rate which is proportional to the substrate concentration in accordance with apparent first-order kinetics. The first-order rate constants of photoreduction of NMN^+, NAD^+, $NADP^+$ in the presence of different electron donors are summarized in Table 2. These values may be used for comparison of relative efficiencies of the photoreduction process of the respective compounds, instead of quantum yields [20].

Long lasting irradiation of nicotinamide coenzymes (2–3 h) in the presence of semiconductor and electron donors leads to further photochemical transformations of the dimers. In this case the polarographic analysis of irradiated solutions shows that the anodic waves due to the oxidation of photochemically generated dimers gradually decreases following irradiation. Simultaneously, new cathodic waves at the potential region from −1.3 to −1.5 V (depending on the electron donors) appeared due to the reduction of photochemically transformed aminoacids [18].

The UV absorption spectrum changes during long term irradiation. The two bands at 260 and 340 nm (characteristic for the dimers) are replaced by a new peak at 380–290 nm characteristic of hydrated dimers [27].

3.2. Reversibility of the photoreduction

It was shown previously that the electrochemically generated NAD(P) dimers irradiated at 365 nm under anaerobic conditions revert photochemically to the enzymatically active monomers [18].

To test the reversibility of photochemically produced dimers, TiO_2 was removed from the irradiated solution (60 min at 365 nm) containing 5×10^{-4} M NAD^+ and 5×10^{-2} M serine and the reaction mixture was further irradiated at 365 nm under anaerobic conditions. In a control experiment, the electrochemically generated NAD dimer was irradiated under the same conditions. It was found that both NAD dimers, electrochemically and photochemically generated, were converted to monomers at comparable rates and photoconversion was accompanied by the formation of H_2O_2.

Similar experiments performed with the photochemically generated NAD dimer in the presence of EDTA, and NMN dimers in the presence of lysine and glycine have shown that in all cases the photochemically produced dimers were converted to enzymatically active monomers (under the conditions described above) at the same rate and with the same yield of H_2O_2 formation as was found for the corresponding dimers generated electrochemically.

The reversibility of $(NADP)_2$ was not been examined because of the low efficiency of the $NADP^+$ photoreduction process in a TiO_2 dispersion.

Table 2
First-order rate constants for the catalytic photoreduction process of NMN^+, NAD^+, $NADP^+$ in the presence of TiO_2 and electron donors (irradiation at 365 nm under anaerobic conditions, pH 9.5)

Electron donor	k ($\times10^{-3}$ s^{-1})		
	NMN^+	NAD^+	$NADP^+$
EDTA	1.20	3.30	0.43
DTT	1.33	–	1.95
Lysine	1.18	2.10	0.58
Glycine	2.64	1.60	0.15
Serine	3.70	3.10	1.90
Aspargine	–	0.76	–

3.3. Photooxidation of dimers in the presence of TiO_2

To test the photocatalytic effect of TiO_2, on the photooxidation process of nicotinamide dimers, the electrochemically produced $(NAD)_2$ (2×10^{-4} M) was irradiated at 365 nm (pH 9.5, argon atmosphere) in the presence and absence of TiO_2. In both cases the photooxidation rate was comparable (Fig. 7) but no H_2O_2 generation was observed in the presence of TiO_2.

The absence of H_2O_2 in the photooxidation process of $(NAD)_2$ may be explained by the reaction of H_2O_2 with electrons formed by illumination of TiO_2 as follows [28]:

$$H_2O_2 + e^- \text{ (from } TiO_2) \rightarrow OH^{\bullet} + OH^- \quad (2)$$

In the presence of aminoacids and TiO_2 the photochemical conversion of NAD dimer to monomers was inhibited (Fig. 7), probably due to two redox processes: photooxidation and photoreduction proceeding inversely at comparable efficiencies. Similar results were obtained for electrochemically generated NMN and NADP dimers.

After 60 min of irradiation formation of tetrahydro derivatives or/and hydrated forms of the dimers are observed from the increase of the absorption in the region 280–290 nm, as occurs during long lasting irradiation of the oxidized forms of the nicotinamide coenzymes at 254 nm [18].

4. Discussion

It was reported that band gap illumination of TiO_2 in weakly alkaline solutions of NAD^+ in the presence of rhodium trisbipyridyl complex $[Rh(bipy)_3^{3+}]$ leads to generation of biologically active NADH [17]. According to the results presented above, photoreduction of nicotinamide coenzymes by excited TiO_2 in the presence of aliphatic aminoacids leads to the formation of the respective biologically

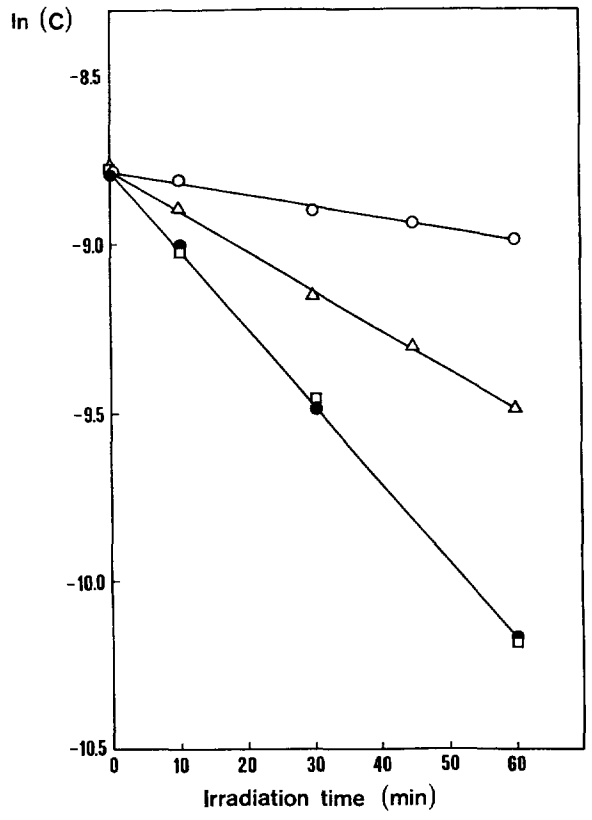

Fig. 7. Plots of the concentration (ln c) of electrochemically generated NAD dimer as a function of irradiation time at 365 nm: (●) without TiO_2 and electron donor, (□) in the presence of TiO_2, (△) in the presence of serine, (○) in the presence of TiO_2 and serine.

inactive dimers. The results are confirmed by enzymatic and polarographic analysis.

The photocatalytic effect of TiO_2 has been explained by excitation with light of wavelength shorter than the band gap resulting in the formation of electron–hole pairs which enable the occurrence of redox reactions at the semiconductor surface [28–30].

In our study, nicotinamide coenzymes have been employed as electron acceptors and aliphatic aminoacids (not absorbing at the wavelength of irradiation) as hole/$OH^{\cdot}$ scavengers [31]. The electrons are transferred from the conduction band to the coenzymes adsorbed on TiO_2 particles, the growth of 340 nm absorption band reflecting the kinetics of this interfacial charge transfer reactions. As illumination of the solutions without TiO_2 caused no dimer formation, this suggests a direct reduction of NMN^+, NAD^+, $NADP^+$ by conduction band electrons, leading to formation of nicotinamide radicals and ultimately to biologically inactive dimers. The rate of reaction of the e_{cb} electrons with coenzyme depends on the coenzyme concentration and pH (Fig. 5) in accord with the dynamics of interfacial electron-transfer process in TiO_2 dispersion [26,32].

The pH effect on the photoreduction of coenzyme NAD^+ (Fig. 5) and other coenzymes arises from the cathodic shift of the Fermi level of the TiO_2 particles with increasing pH [26,32] and coincides with the pH effect on the initial rate on NADH formation in the presence of $[Rh(bipyr)_3^{3+}]$ [17].

The complementary valence band process is the oxidation of aminoacids, which scavenges valence band holes or OH radicals [30,31]. The pre-steady-state photoproduction of hydroxyl radicals from TiO_2 samples was investigated using electron paramagnetic resonance (EPR) [30]. An agent removing the holes from the semiconductor should increase the lifetime of e_{cb} and hence the efficiency of coenzyme reduction [26].

Usually the efficiency of photoreduction is measured as quantum yield; however for heterogenous photoreaction, this is hampered by the high turbidity in the measurements used to evaluate the efficiency of a photoreaction. One-electron photoreduction of nicotinamide coenzymes was observed in the presence of EDTA, glycine, serine and aspargine.

The relative efficiency of coenzyme phototransformation in the presence of aminoacids, summarized in Table 2, was determined as first order rate constants on the basis of a simple kinetic model. In the presence of other aliphatic aminoacids (valine, leucine, isoleucine) and aromatic aminoacids, the reduction of coenzymes did not occur. This is probably due to the different reactivity of various aminoacids and the nature of the products formed from aminoacids irradiated in the presence of TiO_2. It is known that photolysis of aminoacids either by direct irradiation or by the use of photosensitizers leads to generation of radicals [33] which undergo further transformations: cyclization, recombination and decarboxylation [34]. In fact, during the preparation of this manuscript, a report appeared by Nohara at al. [35] on the dependence of formation of NH_4^+ and/or NO_3^- ions on chemical structure during TiO_2-photocatalysed oxidation of amino acids, amides and nitrogen heterocycles. Recently a laser photolysis of aliphatic aminoacids has been reported [36].

Some aliphatic aminoacids undergo peroxidation when exposed in the presence of oxygen to hydroxyl or peroxyl radicals. The efficiency of the peroxidation is surprisingly high, reaching over 40% (in the case of OH radicals) for five aliphatic aminoacids: proline, glutamine, isoleucine, valine and lysine [36]. Additionally, adsorption phenomena of aminoacids may also play an important role in the photoredox process.

It was reported that the first step in the photooxidation of flavin in the presence of EDTA involved also one-electron transfer [37]. However, in most cases the primary and secondary products formed during the photosensitized reactions of aminoacids are not known in details.

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