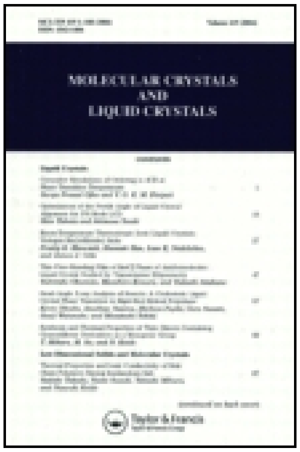

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Electron Phototransfer in the Dichromate - Macromolecule Systems and Photoinduced Changes of Polymer Structure

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Electron Phototransfer in the Dichromate - Macromolecule Systems and Photoinduced Changes of Polymer Structure

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The Dichromated Gelatin (DCG) known as medium for the phase holograms registration and production of special planographic printing plates as well as the solutions of dichromates in alcohols have been studied for chromium compound reactions and phase-conformational transformations of denatured collagen molecules in their own polymer matrix. One- and multielectron transfer schemes are discussed as well as the delocalization of an electron along the macromolecular chains and polypeptide fragments and phase conformational changes in them.

Keywords: dichromated gelatin, chromium (V) compounds, electron phototransfer, conformation-phase transformations.

INTRODUCTION

The dichromated gelatin (DCG) layers are known as excellent media for the phase hologram registration and printing plates which are supposed to be applied for modern computerized printing technologies. The image formation mechanism has become familiar for the last decade for such media. Yet many questions of these are not clear now. The Cr(V), Cr(1V) and Cr (III) compounds which are formed as a result of photochemical and dark redox processes in DCG provide the polymer structurization or its cross-linking.

PARAMAGNETIC PRODUCTS OF ELECTRON PHOTOTRANSFER

The primary photochemical process is supposed to be one-electron reactions resulting in the formation of Cr(V) compounds and radical products which were identified by ESR and electronic absorption spectra.

$Cr_2O_7^{2-}$ and CrO_4^{2-} as Cr(VI) or Cr^{+6}
$[Cr(VI)...HR] \rightarrow Cr^{+5} + HR^{+\cdot}$
$Cr(VI) + HR \rightarrow Cr(V) + HR^{+\cdot}$
$HR^{+\cdot} \rightarrow H^{+} + R^{\cdot}$
$CrO_4^{2-} + H^{+} \rightarrow CrO_4H^{-}$ (also Cr(V))

The products of the reaction in polymer matrixes are paramagnetic ions of five-valent chromium and macroradicals or cation-macroradicals which may be formed from the protein macromolecules .

In many cases especially when the chromium (VI) salt concentration is more than a few percents the single paramagnetic product is chromium (V). The absence of ESR-registrated radical products in some experiments may be interpreted as a result of the interactions of radical products with the active oxidizing particles such as chromium (VI) and chromium (V) oxyanions. As the model systems of DCG we have studied solutions of ammonium dichromate in simplest alcohols and polyvinylalcohol.

The kinetics of the Cr(V) generation is relatively simple only at irradiation of the vacuumed matrixes and liquid alcohol solutions too. Thus photoreduction of oxyanions of Cr(VI) in methanol, ethanol and pentanol (degassed samples) provides singlet ESR spectra ($g=1.969$). Irradiations of none-vacuumed solutions in methanol and ethanol provides two-components spectra or the superposition of a singlet and at last a triplet ESR spectra.

In the presence of peroxides the doublet (superposition of two single lines) ESR spectra were registered. Thus such a nature of registered spectra is considered to be superpositions of the primary Cr(V) compounds and those ones resulted in dark secondary processes. As we have shown the ESR spectra of Cr(V) in DCG are also a superposition of at least two products.

$\mathrm{Cr(VI) + RCH_2OH \rightarrow Cr(V)_1 + RCH_2OH^{+}}$
$\mathrm{Cr(VI) + RCH_2OH^{+} \rightarrow Cr(V)_2 + RCHO}$

Side by side with the last reaction the following reaction can proceed :

$\mathrm{Cr(V)_1 + RCH_2O^{+\cdot} \rightarrow Cr(V)_2 + RCHO}$

E.g., one can interprete sometimes the result of the photoreduction of Cr(VI) in alcohols as two-electron act. That is why exclusively one-electron reactions in the systems studied are not quite evident. Some possibilities of two-and sometimes three - electron transfer reactions can be discussed.

One can suppose fragments of polypeptide chains to be in the state of keton-enol tautomery. Excitations and charges can be spread along the polypeptide chains.

-CR=COHNH-… ← …-CHR-CO-NH-… → …-CH-COH=N-…

An electron in ion-radicals which were formed as a result of electron phototransfer from the peptide chain fragment to chromium (VI) oxyanion is able to transit in the frames of conjugative chain.

…-NH-CHR-CO-NH-CHR-CO-… → … -NH-CR=COH-NH-CHR-CO-
… -1e (hν) → …-NH-CR=COH-$\mathrm{N^{\cdot+}}$H-CR=COH-… - $\mathrm{H^{+}}$ → …-NH-
CR=COH-$\mathrm{N^{\cdot+}}$H-CR-CO-… → …-NH-CR=COH-NH-$\mathrm{C^{\cdot}}$R-CO-… →
…NH-CR=COH-NH-CR=$\mathrm{CO^{\cdot}}$- → …-NH-CR=COH-NH-CR=COH-$\mathrm{N^{\cdot}}$-
CHR-CO-… → …-NH-CR=COH-NH-CRH-CO-NH-$\mathrm{C^{\cdot}}$R-CO-… etc.

That is why the registered chromium(V) compounds may be the product of the photoreduction of initial Cr(VI) ions or the interaction of cation- or free radicals with Cr(VI) or Cr(IV) compounds

PHASE-CONFORMATIONAL TRANSFORMATIONS OF THE MATRIX

One of the main results of the photoredox processes in the studied polymer systems[1] are the phase-conformational interactions in denatured protein molecules. This leads to crystallization-amorphization of the polymer.

The degree of amorphization according to the X-rays diffraction spectra and the degree of chromium (V) generation according to the ESR spectra have similar changes. Thus we can conclude that conformational-phase transformation is due to the phototransfer of electron from the protein molecule. As a result of this is a rearrangement of spiral macromolecules to the despiralized ones.

The main reason of such phase transformation is an electron phototransfer in the complexes Cr(VI)-denatured protein molecules. Only free radical formation do not lead to such conformation. We have registrated radical products in the DCG samples irradiated by light $\lambda = 254$ nm but failed to find any conformational changes.

We suppose the role of chromium compounds in conformational transformation to be the generation of the cation-radical, proton elimination and formation of pentacoordinated complexes with water molecules which may be either nonbonded or bonding ones.

$$ {}^{-}\mathrm{O\text{-}CrO(OH)\text{-}O}^{-} + \mathrm{H}^{+} + \mathrm{H_2O} \rightarrow {}^{-}\mathrm{OCr(OH)_3O}^{-} $$

This leads to destroying the spiral structure and thus to the amorphization of the polymer.

REVERSIBLE TRANSFORMATIONS

We have shown the important role of chromium (V) centers in irradiated DCG when the layers of DCG are vacuumed and then treated by water vapor at low pressure ($2.0 \cdot 10^4$Pa) and irradiated by polarized light of He-CD-laser ($\lambda = 441$nm). When the concentration of Cr(V) reached the maximum value and didn't change, turning light off did not change the Cr(V) concentration, e.g. the intensity of ESR singlet spectrum. But that led to essential change in g-value. A lot of acts of light irradiation (light on) and light off practically didn't change the Cr (V) concentration but g-value of ESR spectra were always g=1.961 without irradiation and g=1.970 during the irradiation. Early we had interpreted this fact by excitation of Cr(V) compounds and alternatively by the formation of ion-radical pairs[2]. Now we can explain the unusual data as a result of changing the conformational surrounding of Cr(V) due to the protonization-deprotonization with the simultaneous hydrotation-dehydrotation which leads to the geometrical (dimensional) changes from tetrahedral to the tetrahedral pyramid.

These features may be the most essential for the image formation in related systems such as phase and relief-phase holograms.

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