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Electron phototransfer in the initiating systems for the information registration

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Abstract

Electron transfer was shown to be common first stage for photo transformations of different compounds. Free radical formation as a result of electron photo transfer in ferric chloride, chromic acid salts and aromatic carbonyl compounds—benzophenon and its substituted derivatives is discussed. In the presence of vinyl monomers the processes of polymerization initiation, cross-linking and structurization occur. In case of benzophenon and its derivatives the correlations of Hammett's σ-constants with the kinetic characteristics of photo polymerization of vinyl monomers have been found. Investigation of photo polymerization can be an effective tool for studying photo transformations of aromatic carbonyl compounds.

Keywords: Photopolymerization; Information recording; Electron phototransfer

1. Introduction

The first and the last authors of the communication feel a duty to express deep feelings of memory and esteem to the deceased leader of Ukrainian photochemistry professor Iosyph Dilung, the. We also want to memorize the academician Alexander Terenin—one of the founders of the modern photochemistry and photophysics whose books and scientific articles were the fundamentals for several generations of photo chemists.

The photochemistry department in L.V. Pysarzhevsky Institute of Physical Chemistry of the National Academy of Sciences of Ukraine carried out the investigations during more than 50 years period on electron photo transfer and photo dissociation in different systems including chlorophyll and porphyrins, as well as other coordination and different organic and inorganic compounds. Ion radicals and free radicals evolved in the reactions were shown to be effective initiative agents in the photopolymerization and structurization of polymers.

Photopolymerizable layers and compositions were and remain today important functional materials both in writing and treatment of optical information, and in printing engineering. At first, such systems were fruitfully used for preparing printing plates for different kinds of printing—letterpress, screen and offset printing. Now the most important application sphere of such materials is flexographic and screen-printing. Intensive carrying out of technological processes and energy saving are now very important. Thus the problem of printing inks and varnishes development became along with printing plates production one of the actual tasks. The applications of photopolymerizable compositions in holography are well known and remain actual. One of the perspective areas for applications of such materials is the production of constructions by two laser beams.

2. Photo initiating systems

2.1. Ferric chloride

Nano sized systems and nano technologies became a very important direction in modern physics and chemistry of last recent years. One of the interesting results concerning the photo polymerizable systems was photo initiation of polymerization of methacrylates by metal oxides and sulfides nano particles [1].

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Nevertheless the problem of scientific selection of photoactive components for different photo polymerizable compositions and layers remains very important and actual one. The example of the practically important photoinitiating systems and ptotopolymerizable compositions were developed in the L.V. Pysarzhevsky Institute of Physical Chemistry of the National Academy of Sciences of Ukraine on the base of ferric chloride. The compositions had found wide applications for screen-printing.

The principle of using the ferric chloride as a photo initiator is based on its ability to form free radicals in alcohol solutions at their illumination by light into the charge transfer band [2].

Then there was found the free radicals formation in hard layers of the polymer–monomer systems on the base of alcohol solutions (dispersions) of co polyamides (co polymers from adipinic and sebacinic acids with hexamethylendiamine together with ε-kaprolactame) when are exposed to UV light in the presence of ethylenglycoldimethacrylate and ferric(III) chloride [3]. The free radicals initiated polymerization processes in the composed layers. They were especially effective when the layers were previously placed on the nylon screens. The photopolymerization and graft polymerization to the nylon screen surface as well as cross linking of polymer chains leaded to insoluble polymers. The resulted composed material was suited for screen-printing plates making. The unexposed areas of the composition were removed by a solvent (alcohol or water in case of water-soluble start polymers). Thus there were formed printing elements of a screen-printing plate through which printing inks were transfered to the printing material. The produced printing plates had extremely high physical and mechanical properties, grate printability and fine printing technical properties.

At the same time the attempts to use that initiating system on the base of ferric(III) chloride for the bulk photopolymerization of methacrylate monomer and monomer–olygomer systems were unsuccessful. The results recently obtained [1] let us conclude and explain the discussed facts by probable existence of dispersed particles of ferric oxide in the systems "polyamide–olygomer–ferric(III) chloride" on dispersed particles of the polymer. The ferric oxide and hydroxide particles probably contained photoactive nano particles of ferric oxide. These reflections give grounds for the further search of high effective photo initiating systems on the base of ferric complexes and oxides.

2.2. *Chromium compounds (dichromated gelatine)*

Inorganic compounds of polyvalent metals are widely used for the photostructurization and photo cross-linking of different polymers and macromolecular compounds, both synthetic and natural origin.

Probably the most known silverless light sensitive system found were layers of dichromated gelatine and, later, dichromated polyvinyl alcohol. The generally accepted mechanisms of relief and then holographic images after exposition and treatment by water were chromium(III) compounds with polypeptide macromolecules and complexes with hydroxy- and oxo-groups of polymers.

The investigations of such layers and model systems in solutions showed that the photo reduction of oxyanions of chromium(VI) and related compounds can be considered as an electron photo transfer reaction when one of the products of the electron photo transfer is chromium(V) ion that can be protonized [4].

A cation-radical from the oxidised molecule eliminates proton, which adds to the primary chromium(V) compound transforming it from oxo- into hydroxycomplex—a similar product to the known for organic carbonyl compounds ketyl (semipinacol) radicals. Similarly to semipinacol radicals that break off the growing polymer chains, chromium(V) compounds have been shown to be in some extent inhibitors of the polymerization. It is worthy to underline that in the presence of ammonium dichromate the free radicals of growing chain during photo polymerization of methacrylates undergo some transformations. We explain them by stabilization of some possible kinds of the radicals.

The fact of decreasing of the concentration of free radicals and chromium(V) compounds is similar to decreasing of the semipinacol radical concentration. At the other hand, macro radicals as products of photo oxidations by chromate oxo-ions and organic oxo-compounds—aromatic ketones are able to recombine to give cross-linked polymer.

2.3. *Aromatic carbonyl compounds*

We showed that primary processes in such photostructurized systems as dichromated gelatine and photopolymerizable polymer–monomer–olygomer layers containing benzophenones and related compounds as photo initiators have many common features [4]. In both cases the result of primary photochemical reaction is free radical formation from the donor molecule and the photoactive compound.

Thus, aromatic carbonyl compounds were in center of our attention. Two kinds of them are used for the initiation of photo polymerization at all. The first example is photoreducable ketones and benzophenon as well as related compounds. The second is a carbonyl compound for example benzoin or its derivatives, which photo dissociated on Norish II mechanisms.

Aromatic carbonyl compounds are well known to be the initiators of photopolymerization. Photo initiating systems on the base of benzoin and its derivatives—alkoxy (benzoin ethers), dialkoxy (so called ketals), acetophenon and its derivatives were widely used and are applied now in different photo polymerizable materials: compositions for optical writing of information, relief images production—printing plates, photosensitive inks and varnishes and so-called hybrid printing inks.

2.3.1. *Benzophenon and its derivatives*

The most interesting photo initiative systems were those expoiting the phenomena of photo transfer of electron or hydrogen atom. There may open a possibility of search of effective process of the photopolymerization initiation. Indeed, a change of electronic structure of a molecule of substituted benzophenon may be the way for optimisation of the rate of the photopolymerization process.

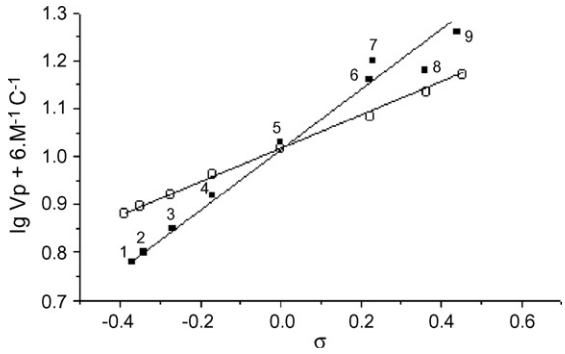

Fig. 1. The influence of substitutes in benzophenon molecule on the photopolymerization rate of buthylmetacrylate in acetonitryl ($\rho = 0.68$) (a) and methylmethacrylate in benzene ($\rho = 0.26$) (b): (1) 4-OH; (2) 4,4′-$(CH_3)_2$; (3) 4-OCH_3; (4) 4-CH_3; (5) B; (6) 4-C1; (7) 4-Br; (8) 4-COOH; (9) 4,4′-$C1_2$.

The systems benzophenon – alcohol, benzophenon – tetrahydrofuran or aromatic keton-amines as donors of electron or hydrogen atom are well known in photochemistry. Benzpinacol or products of recombination of primary semypinacol (ketyl) radical with an isomerized semipinacol radical or other primary radical products (so-called “photoproduct”) are formed as a result of photochemical processes. Other primary photoproducts are alkoxy or hydroxyalkylene radicals in alcohol solutions or tetrahydrofuryl radicals in the tetrahydrofuran solutions. Such systems are known as photo initiators for photo polymerization of vinyl monomers compositions and photo cross-linking of polymer chains.

Molecular photonics of diphenylketyl radicals had been investigated for example in Refs. [5,6]. Thus, a result of photolysis of the radicals is the cleavage of the O–H bond that is a reversible photoreaction. The exited radicals $[Ph_2COH']^*$ had been shown to be stronger acid than those being in the ground state. The life time of substituted diphenylketyl radicals is less than that of unsubstituted ones. The photochemistry of the ketyl radicals is rather complex. That may be a reason under the conclusion about inapplicability of Hammett correlations for chemical reactivity in the molecular photonics of benzophenones [7,8]. The analysis of both the corresponding literature and our experimental results showed no correlations between the kinetic data of the photo reduction process of benzophenones and the Hammett’s σ-constants. The works of many authors suggested similar conclusion [9–11].

2.3.2. Hammett correlations for the systems the benzophenon—a vinyl monomer

We had showed that there existed clear correlations between the photo polymerization rates and the electronic structure of in benzophenon molecules expressed by the Hammett’s σ-constants of the substitutes [9,10].

We obtained many examples of Hammett correlations existence in different systems “benzophenon – electron (hydrogen) donor – vinyl monomer” (Figs. 1–5).

We found that the Hammett correlations for benzophenones reactions hold only in the presence of vinyl monomers. The analogical conclusion was also made in Ref. [11].

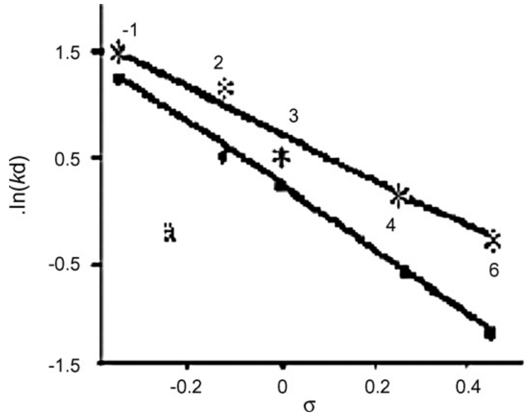

Fig. 2. The dependence of deactivation of the ketyl radical yield from the substitute nature at the interaction of benzophenons with dimethylanilin in benzene (a) (a-s = −2.0) and acetonithryl (*b*) (a-s = −2.7): (1) 4-hydroxy-B; (2) 4-methyl-B; (3) B; (4) 4-chlor-B; (5) 4-brom-B; (6) 4,4-dichlor-B.

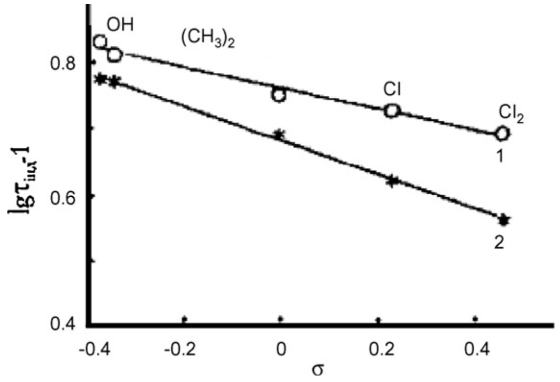

Fig. 3. The correlations of the induction time of photopolymerization of buthylmetacrylate with the Hammett’s σ-constants of *p*, *p*-substitutes in the benzophenon molecules in benzene (1) and acetonithryl (2); $[B] = 5 \times 10^{-4}$ M, [Michler ketone] = 10^{-3} M.

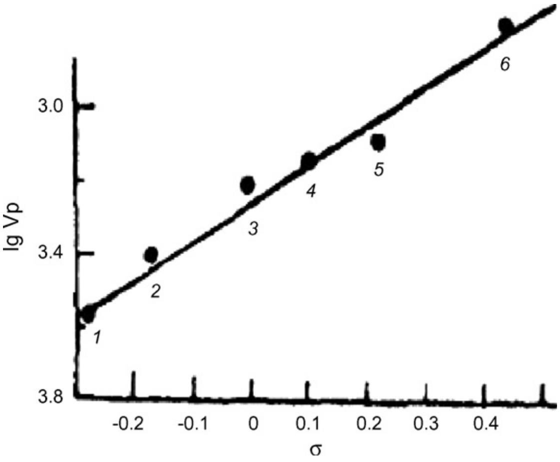

Fig. 4. The dependence of the photopolymeryzation rate of buthylmetacrylate from the Hammett’s σ-constants of substitutes in the benzophenon molecule: (1) 4-OCH_3; (2) 4-CH_3; (3) 4-H; (5) 4-Cl; (6) 4,4″-$(Cl)_2$. The light-absorbing agent ($\lambda = 510$ nm)—2-dimethylphenazin. $\rho = 1.1$.

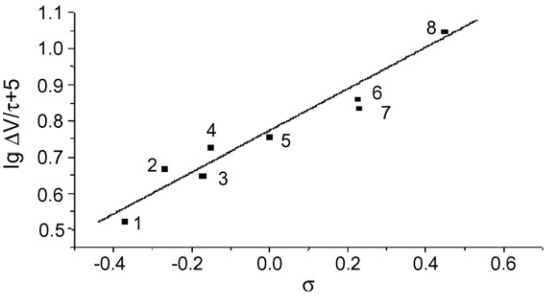

Fig. 5. The correlation between the rate of photo polymerization of dimetacrylates (MDPh-2 + TGM-3) initiated by the system benzophenon–thriethylamine and the Hammett's σ-constants in benzophenon: (1) 4-OH; (2) 4-OCH$_3$; (3) 4-C$_2$H$_5$; (4) 4-CH$_3$; (5) H; (6) 4-Br; (7) 4-C1; (8) 4,4′-(C1)$_2$.

That is why we studied in details the photo reduction of aromatic ketones in the presence of vinyl monomers (methylmethacrylate, buthylmetacrylate) [12]. The interaction of the exited molecules of benzophenon and its derivatives with the monomer molecules decreases an efficiency of the benzpinacol and a “photoproduct” formation. From another side there is a way for the interaction of the primary radicals resulted from molecules-donors of electron (hydrogen atom) with monomer in dark processes of initiation and termination of polymer chains.

We can interpret the photo reduction of ketone groups as the summary process of electron and proton transfers and finally as the hydrogen atom transfer. In some extreme conditions the products of electron photo transfer were registrated. We discussed the Hammett correlations of the photopolymerization rates and some other kinetic constants [4,12].

We had found such correlations for the first time [9,10]. We interpreted them as an evidence of the multistage character of photo reduction of carbonyl groups in benzophenon and organic oxo-compounds. We connect the correlations with protonization–deprotonization processes of the participants of the photochemical and subsequent dark acts. Radical or ion-radical pairs are supposed to be important intermediates of the photo reduction of oxo compounds. So, we can interpret the Hammett's correlations obtained as an evidence of the mechanism of electron photo transfer during photo reduction of aromatic ketones even when the direct registration of the anion-radical is failed.

As we had mentioned no correlations were observed in the absence of the monomer. The correlations suggest electron and proton transfers in the complicate process of the initiation of radical transformations and polymerization of vinyl monomers. From the other side one can claim that study of the process of photo polymerization of vinyl monomers is an effective additional way for investigation of intimate mechanism of photo transformations of aromatic carbonyl compounds as well as inorganic photo reducible oxo compounds such as chromates and dichromates.

Thus, analyzing some features of photostructurization of polymers by aromatic ketones and inorganic oxo compounds we can consider them as related to similar processes which are stimulated by electron transfers.

3. Conclusion

A practical importance of the approaches consists in possible replacement of toxic metal compounds by non-toxic organic ketones in different photostructurized polymer or photopolymerizable systems for the information registration and for digitalized processes of printing and printing plates production.

Early the main applications of photopolymerizable and photostructurized systems in printing technology were in the field of printing plates production. Now the field for applications of photosensitive systems, based in a part on electron photo transfer processes, obtain essential widening. Those include development of light and photo curable inks and varnishes of different kinds, defensive layers, laser sensitive compositions for different spectral areas, digital processes of printing and hologram production. Application of nano sized particles in photopolymerizable compositions and layers opens new possibilities in different practical fields.

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