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A new possibility of photostabilization of polymers by keto-enol tautomerizm of some β-dicarbonyls with fluoro (-CF_3) group

S. K. Wu[1],*, Y. F. Chang[1], Y. Mou[1], and J. F. Rabek[2]

[1]Institute of Photographic Chemistry, Academia Sinica, Beijing 100101, People's Republic of China
[2]Polymer Research Group, Department of Dental Materials and Technology, Karolinska Institute, Box 4064, S-141 04 Huddinge, Stockholm, Sweden and Royal Institute of Technology, S-10044 Stockholm, Sweden

SUMMARY

It has been found that β-dicarbonyl compounds such as 1-phenylbutane-1,3-dione(benzoyl-acetone)and 4,4,4-trifluoro-phenylbutane-1,3-dione (benzoyl-trifluoroacetone) can effectively photostabilize photodegradation of polyisoprene in solutions containing protonic solvents (alcohols). The photostabilization mechanism is due to the photo-enolization reaction,during which absorbed UV radiation is consumed for the proceeding of this reaction. The photostabilization of formulations containing alcohol by β-dicarbonyl compounds,has potential application in the protection of cosmetics against photoageing reaction.

INTRODUCTION

It is well known from very extensive publications and books (1-3), that one of the most important photostabilization mechanism of polymeric materials is based on the keto-enol photoisomerization during which UV energy absorbed is consumed for the proceeding of this reaction. Two important groups of photostabilizers: o-hydroxybenzophenones and o-hydroxy-benzotriazoles stabilize polymers by this mechanism.

Keto-enol conversion of β-dicarbonyl compounds is a well known reaction (4). This gave us an idea that this reaction can be employed for the photostabilization of polymers. However the enol form of these compounds is destroyed in protonic solvents and their photostability is also destroyed,they can be considered as effective photostabilizers. The results presented here by our group are a part of larger study into new photostabilizing agents in protonic solvent system and new types of photostabilizres (5-8).

EXPERIMENTAL

Two of β-dicarbonyl compounds such as benzoyl-acetone (1-phenylbutane-1,3-dione)(Beijing Chemical Works,China) and benzoyl-trifluoroacetone)(4,4,4-trifluoro-1-phenylbutane-1,3-dione)(Tokyo Kasei Co,Japan) have been recrystallized from chloroform-hexane. Polyisoprene,Type IR10 (Koleli Co,Japan) was used for the testing of photostabilization effectiveness of β-dicarbonyl compounds. All samples were irradiated with a low-pressure mercury lamp Type HPK-125 W(264 nm) (Philips). Absorption spectra were recorded with the Hitachi 340 UV/VIS spectrometer.

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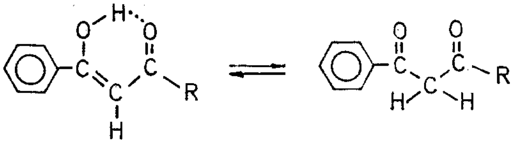
*To whom offprint requests should be sent

RESULTS AND DISCUSSION

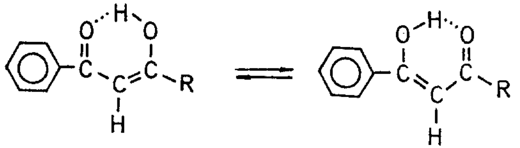
The β-dicarbonyl compound such as benzoyl-acetone (S-1) has strong absorption spectrum in the region 260-360 nm (Fig.1). The interconversion between enol- and keto-tautomers in the pure state or in non-protonic solvents such as cyclohexane (reaction 1) under UV irradiation is very slow (Fig.1):



(enol form) (keto form)

(1)

The enol form of β-dicarbonyl compounds has an absorption band at 320 nm (Fig.1). The enol form of β-dicarbonyl compounds usually exists as the conjugated cis-enol, stabilized by intermolecular hydrogen bonding (9,10). Due to the interconversion reaction which occurs by transfer of an enol proton from one oxygen atom to the other, two different isomeric cis-enols (reaction 2) are distinguishable in the case of unsymmetric β-dicarbonyl compounds:



(cis-enol form I) (cis-enol form II)

(2)

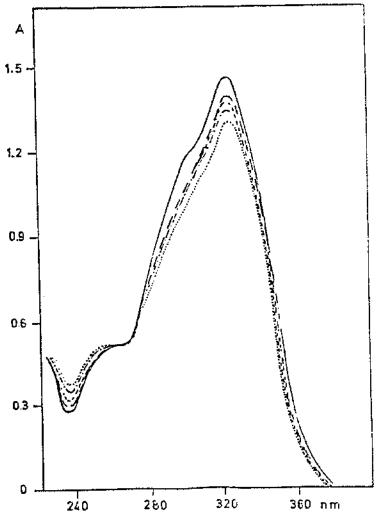


Fig.1 Absorption spectra of benzoyl-acetone (S-1)(1.0×10^{-4}M) in cyclohexane: (—) before and after UV irradiation (254nm): (– –) 5 min;(- -) 10 min; (- • -) 15 min and (•••) 30 min.

Benzoyl-acetone (S-1) in the cyclohexane solution exists as enol-form, however, even by using ^{17}O NMR it is impossible to distinguish between these two different isomeric cis-enols, because the interconversion is very fast at 10^5-10^6 sec^{-1} at room temperature (11).

For the β-dicarbonyl compounds with benzoyl-group in the protonic solvents such as alcohols a new band at 250 nm arises, which belongs to the benzoyl-keto groups formed in the enol-keto interconversion tautomeric reaction (reaction 1)(Fig.2). At the same time a decreasing of a 320 nm band has been observed, which indicate that the intermolecular hydrogen bond in the enol form of β-dicarbonyl compound has been destroyed in the protonic solvents (Fig.2).

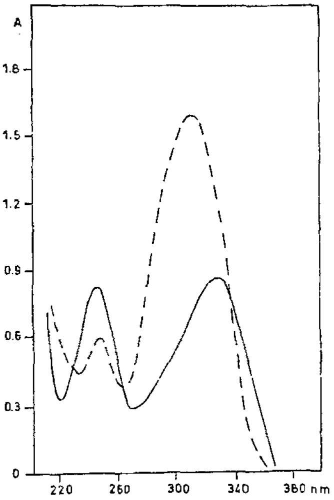
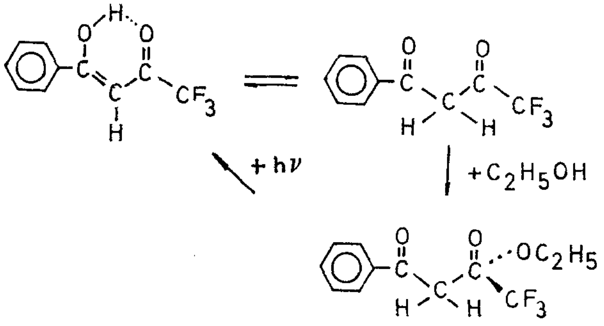


Fig.2. Absorption spectra of:
(—) benzoyl-acetone (S-1) and
(– –) benzoyl-trifluoroacetone
(S-2) both 1.0×10^{-4} M in ethanol.

Under UV irradiation, no change in the absorption spectra of the β-dicarbonyl compound such as benzoylacetone (S-1) has been found. However, an increase in the intensity of 320 nm (enol form) and decrease in the intensity of 250 nm (keto-form) of benzoyl-trifluoroacetone (S-2) have been observed (Fig.3), what indicate for the presence of hydroxyl groups of the β-dicarbonyl compound with $-CF_3$ group in a stabilized hemiacetal intermediate (reaction 3)(9):



(3)

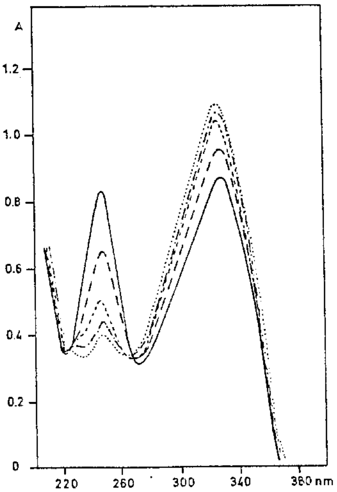


Fig.3 Absorption spectra of benzoyl-trifluoroacetone (S-2) ($1.0x10^{-4}$ M) in ethanol:(—) before and after UV irradiation (254 nm): (– –) 20 sec; (- -) 50 sec; (– • –) 90 sec and (• • •) 150 sec.

The photoenolization reaction consumes UV energy absorbed. In order to see if this reaction can be usefully employed for the stabilization of polydienes,we have measured the change of viscosity of polyisoprene in dichloroethane solution and in the presence of benzoyl-trifluoroacetone (S-2) in dichloroethane and ethanol-dichloroethane (1:9) solutions (Fig.4).

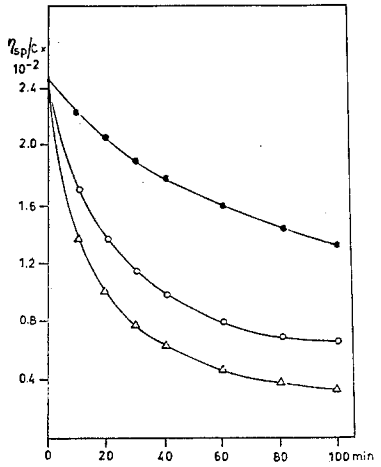


Fig.4 Change of the viscosity of polyisoprene during UV irradiation (254 nm) in: (△) dichloroethane; (o) in the presence of S-2 (1-wt%) in dichloroethane and (●) in the presence of S-2 (1-wt%) in ethanol-dichloroethane (1:9) solutions.

It is well known that viscosity of polydienes decreases rapidly when photodegradation reaction occurs and this process can be partially stopped by addition of photostabilizers (1-3). The results obtained show that β-dicarbonyl compounds containing $-CF_3$ group effectively stop photodegradation reaction of polyisoprene,especially in the presence of protonic solvent (Fig.4). This result also support proposed mechanism for photoenolization reaction. The formation of hemiacetal intermediate in the case of benzoyl-trifluoroacetone (S-2) is due to the presence of the strongly electron-withdrawing fluorine atoms. It is evident from measurements that benzoyl-triflurоroacetone in protonic solvent is more effective that in non-protonic solvent (Fig.4).

A fact that the photoenolization reaction is effective in a photostabilization process, suggests that it can be used in the protecting of cosmetic products (such as sun-screen creems) against photo-ageing. All of these cosmetic formulations contain alcohols as one of many additives, which can participate in the formation of hemiacetals and in photostabilization process. More detailed studies of photostabilization by keto-enol tautomerization reaction are being carried out in our laboratories.

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