

The Increase of the 1,3-dinitrobenzoyleneurea Photochemical Reactivity in the Presence of the H-atom donors

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Summary. The additives influence on the photochemical reactivity of 1,3-dinitrobenzoyleneurea was studied. Amines having different chemical nature, *iso*-propylic alcohol and sodium salt of mandelic acid proved to be efficient additive to activate the title compounds activity. The additive role is electron and/or H-atom transfer ability improving.

Key words. photochemical reactivity, 1,3-dinitrobenzoyleneurea, H-atom transfer, *iso*-propylic alcohol, mandelic acid, photochemical synthesis.

Nitro aromatic compounds photochemistry has collected much attention for the last two decades [1]. A great majority of the unusual peculiarities concerning the nitro aromatics is reasoned by peculiarities of their electronic structures in the excited electronic states [2]. The peculiarities can be listed as

- nitro aromatics have closely situated electronic states (there 2-4 triplet states between S_1 and S_0 singlet states);
- the relative energies of the electronic states can change when a solvent replaces vacuum;
- nitro group has noticeable acceptor character in the excited states.

There were some reports stated that aromatic nitro compounds (NC) could play a role of photochemical oxidants [3]. Just now aromatic nitro compounds and their mixtures found their usage as photochemical initiators of polymerization [4] and as additives to catalysts on the base of TiO_2 [5]. However these oxidations occur with low rates and effectiveness because of large photochemical stabilities of NC and large rates of degradation of the excited states in aromatic nitro compounds. There is one possible way to improve the effectiveness – to add activating substances that can activate the nitro group and/or molecular oxygen if it is present in the reaction mixture.

The aim of our work is to find additives that could increase the photochemical effectiveness of 1,3-dinitrobenzoyleneurea.

Experimental details

1,3-dinitrobenzoyleurea was purified by repeated recrystallization from hot water. The concentration of the working solutions was 10^{-4} M. Due to poor solubility of the title substance in water 10^{-3} M of NaOH was added. A pale-yellow solutions were obtained. Aqueous solutions of 1,3-dinitrobenzoyleurea contained additives (10^{-4} M of amines, isopropyl alcohol or mandelic acid).

The samples were irradiated under DRK-120 Hg-lamp in quartz reactor in the presence of dissolved air (310-380 nm). SF-2000 (Russia) spectrophotometer was used to obtain the UV spectra in the working range from 200 up to 1100 nm.

Results and their discussion

We have tried to improve the 1,3-dinitrobenzoyleurea photochemical effectiveness by means of activators addition into the parent reaction system. Two types of additives were utilized: amines of different chemical nature and the widely known H-atom donors such as isopropyl alcohol [6] and mandelic acid [7]. The combinations of amines and the H-donors were also tried.

An amine addition. Irradiation of the 1,3-dinitrobenzoyleurea aqueous solution by U.V. light (0-20 min) gives progressive decrease of absorbance at 294.0 nm and increase of absorbance at 360.0 nm. The rate constant of the title compound decay is $2.0 \times 10^{-6} \text{ s}^{-1}$ ($R^2=0.9869$). Irradiation of the 1,3-dinitrobenzoyleurea aqueous solution containing 10^{-4} M of amines gives an increase of the decay reactions of the title compound (see Table 1 and Fig.1).

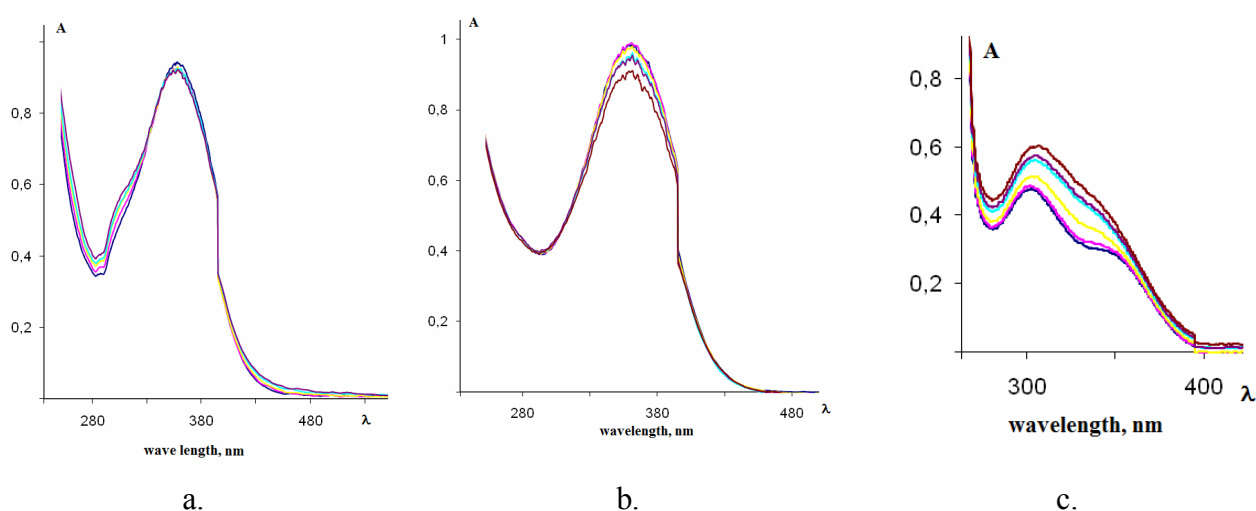


Fig.1. The progressive changes of the U.V. spectra of 1,3-dinitrobenzoyleurea aqueous solution containing 10^{-4} M of amine by U.V. light (0, 1, 5, 10, 15 and 20 min): a – aniline tartrate; b - diethylamine nitrate; c - N,N-dipropylaniline.

The increase of the photochemical decay rate constants of 1,3-dinitrobenzoyleneurea in the presence of amines seems to be connected with formation of complexes between the title nitrocompound and amine. The complexes have greater extinction coefficients than the starting compounds due to more inhomogeneous electron density distributions. The result of the increase should be an increase of the effective rate constants.

In addition there has place mutual polarization and enlightens electron transfer between the amine and nitrocompound molecules.

Some authors assume [8] that such a transfer could be a desirable stage in the nitrocompound photochemical decomposition. Besides, there is an opinion that the photochemical reduction of aromatic nitrocompounds includes an intermolecular electron transfer accompanied by a proton transfer. In the course of the 1,3-dinitrobenzoyleneurea reduction in the presence of amines having different chemical nature the amines play part both as an electron donor and as a proton donor.

It is important to note that the most appropriate scheme includes a hydrogen atom transfer from the carbon atom adjacent to the nitrogen atom towards the nitro group [9]. There is a support of the idea flowing out from the fact that the biggest value of the nitrocompound disappearance rate constant corresponds to the tertiary amine that is to be N,N-dipropylaniline.

To verify the idea we measured kinetics of the nitrocompound disappearance in the system "nitrocompound-amine" with addition of the H-atoms donating molecules, such as isopropyl alcohol and mandelic acid (see Table 1). The results obtained in the series of our experiments gave us a possibility to assume that both an electron transfer and H-atom transfer could take its part in the accelerating of the nitrocompound decay but the latter mechanism is more preferable. It is also interesting to note that the reaction media in our work is water and the greatest effect observed was in the case of tertiary amine having easily abstractable H-atom.

Table 1. Additive influence on the photochemical properties of the 1,3- dinitrobenzoyleneurea

Reaction system	Increasing picks, nm	Decreasing picks, nm	Effective rate constant of decomposition, s ⁻¹
aqueous solution of 1,3-dinitrobenzoyleneurea containing 10 ⁻⁴ M of aniline tartrate	237; 360	290	1.95·10 ⁻⁵ (R ² =0.9872)
aqueous solution of 1,3-dinitrobenzoyleneurea containing 10 ⁻⁴ M of diethylamine nitrate	221; 362	294	5.3·10 ⁻⁵ (R ² =0.9887).
aqueous solution of 1,3-dinitrobenzoyleneurea containing 10 ⁻⁴ M of N,N-dipropylaniline	217; 256; 309	226; 281	1.83·10 ⁻⁴ (R ² =0.9847)
aqueous solution of 1,3-dinitrobenzoyleneurea containing 10 ⁻⁴ M of aniline tartrate and 10 ⁻⁴ M of isopropyl alcohol	360; 237	290	5.2·10 ⁻⁵ (R ² =0.9935).
aqueous solution of 1,3-dinitrobenzoyleneurea containing 10 ⁻⁴ M of diethylamine nitrate and 10 ⁻⁴ M of isopropyl alcohol	362; 234	294	1.0·10 ⁻⁴ (R ² =0.9842)
aqueous solution of 1,3-dinitrobenzoyleneurea containing 10 ⁻⁴ M of N,N-dipropylaniline and 10 ⁻⁴ M of isopropyl alcohol	216; 310; 356	226; 281	2.8·10 ⁻⁴ (R ² =0.9914)
aqueous solution of 1,3-dinitrobenzoyleneurea containing 10 ⁻⁴ M of aniline tartrate and 10 ⁻⁴ M of sodium salt of mandalic acid	350	290	7.9·10 ⁻⁵ (R ² =0.9748)
aqueous solution of 1,3-dinitrobenzoyleneurea containing 10 ⁻⁴ M of diethylamine nitrate and 10 ⁻⁴ M of sodium salt of mandalic acid	206; 358	292	1.38·10 ⁻⁴ (R ² =0.9895)
aqueous solution of 1,3-dinitrobenzoyleneurea containing 10 ⁻⁴ M of N,N-diethylaniline and 10 ⁻⁴ M of sodium salt of mandalic acid	216; 356; 310	226; 281	2.85·10 ⁻⁴ (R ² =0.9957)

Isopropyl alcohol addition. In the next series of our experiments we tried to use the compositions of amine and isopropyl alcohol being an active H-atom donor.

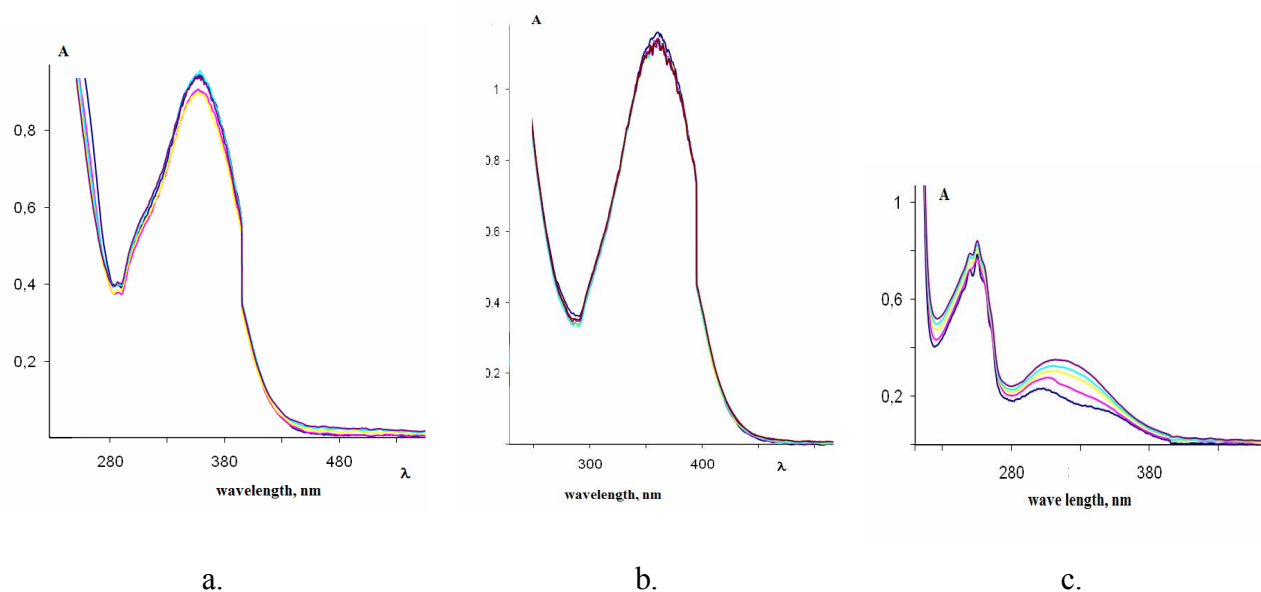


Fig. 2. . The progressive changes of the U.V. spectra of 1,3-dinitrobenzoyleneurea aqueous solution containing 10^{-4} M of amine and 10^{-4} M of isopropyl alcohol by U.V. light (0, 1, 5, 10, 15 and 20 min) a – aniline tartrate; b - diethylamine nitrate; c – N,N-dipropylaniline.

Addition of isopropyl alcohol to solution prepared from the system “1,3-dinitrobenzoyleneurea-aniline tartrate” does not produce any changes in the U.V. spectra. More pronounced effect was observed in the case of addition of diethylamine nitrate. This compound can be poor H-donor and the photochemical activity of the reaction system is slightly improved. However, the activity becomes greatly improved when a tertiary amine used as a component of the reaction system.

Thus it is possible to conclude that a reaction system containing both tertiary amine and isopropyl alcohol is the best activator for photochemical disappearance of 1,3-dinitrobenzoyleneurea in aqueous media. The same conclusion could be made by inspecting of the data presented in Table 1.

Sodium salt of mandelic acid addition. . In the next series of our experiments we tried to use the compositions of amine and sodium salt of mandelic acid being much more active H-atom donor compared with isopropyl alcohol. The results obtained are shown in Table 1 and depicted on Fig. 3.

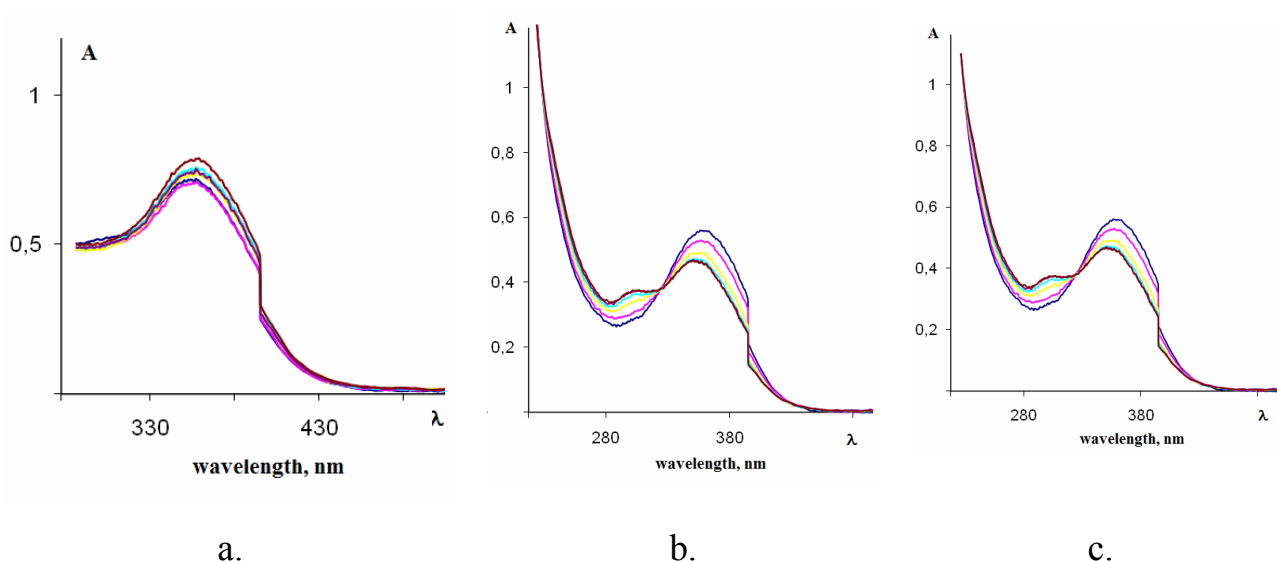
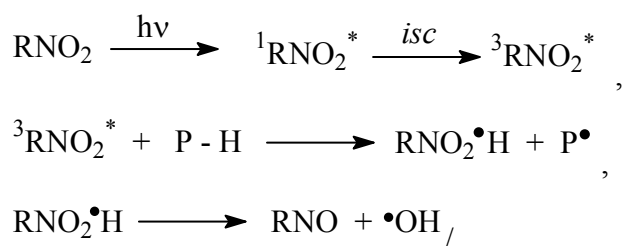


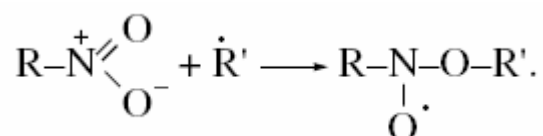
Fig. 3. . The progressive changes of the U.V. spectra of 1,3-dinitrobenzoyleurea aqueous solution containing 10^{-4} M of amine and 10^{-4} M of sodium salt of mandelic acid by U.V. light (0, 1, 5, 10, 15 and 20 min) a – aniline tartrate; b - diethylamine nitrate; c – N,N-dipropylaniline.

The results are quite the same as in the case of the amine-isopropyl alcohol system. It should be noted that even for a primary amine - mandelic acid usage the changes under U.V. irradiation are noticeable. In the cases of a tertiary or secondary amine usage they become much greater.

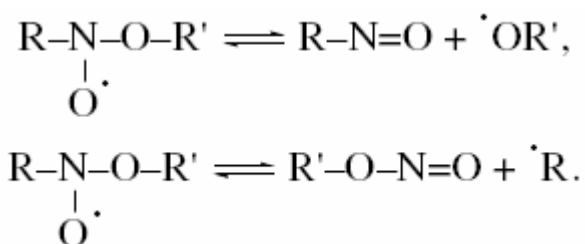
The results obtained in our work we tried to explain on the bases of the following reaction scheme [10,11].



The scheme needs to be modify to account for reaction which existence was assumed in several work (See, for instance [11]).



The radical formed decays in one of the reactions



Conclusion

We have studied an effect of amines and H-donor addition on the photochemical ability of 1,3-dinitrobenzoyleneurea to decompose in aqueous solution. In the conditions of our experiment there observes preferable H-donation and minor contribution from an electron or proton transfer. One of the explanation of the results is the assumption that the radical products formed at the first step of the nitrocompound photochemical reaction could accelerate the nitrocompound decomposition.

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