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Organic Chemistry

On a Possible Destruction Mechanism of Spiropyran Solutions

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ABSTRACT. Issues of photo- and autodestruction of spiropyran are considered. Based on literary and the author's experimental data, destruction in the said solutions is found to be generally conditioned by hydrolysis of the colored form of a spirochromene molecule. *© 2008 Bull. Georg. Natl. Acad. Sci.*

Key words: *spiropyrans, destruction, hydrolysis, equilibrium.*

Spiropyrans, one of the classes of photochromes, do not undergo changes in a crystalline state (observation covers over 30 years). Along with repeated colorization/decolorization, irreversible processes also take place in their solutions, leading to their "ageing" [1–7]. Based on this, study of the causes of irreversible processes is of major importance with a view to blocking them.

Solutions of some spiropyrans, in addition to photochemical decomposition, are noted to undergo significant changes without irradiation [8, 9]. In the course of studying almost all the spiropyrans (over 200 compounds) synthesized by the author, it was found that the compounds, whose solutions are colorless or slightly colored in the dark, do not change even over a long-term storage.

Colored solutions of 8-nitro-6-chloro and 6.8-dinitro-substituted spiropyrans undergo drastic spontaneous changes. Return to the initial state under the impact of light or temperature becomes impossible. The disappearance of the absorption maximum in the visible light spectrum does not mean an equilibrium decolorization, because equilibrium in the solutions of dinitro-substituted spiropyrans is almost fully biased towards the colored form and the electronic spectrum of the light-discolored solution differs drastically from the degraded one.

It should be noted that the above-mentioned spiropyrans, whose alcoholic solutions are distinguished for pronounced absorption maximums in the visible spectrum, are colorless in hydrocarbon solvents and non-polar polymer films (6,8-dinitro-substituted being exceptions) and do not change over long time. For example, 6, 8-dinitro-2H-chromen-2-spiro-2'-N-amyl-3',3'-dimethylindoline in the colored film of polymethyl methacrylate did not change over 1.5 years (observation period) [10], and the solution 6-nitro-2H-chromene-2-spiro-2'-N-amyl-3',3'-dimethylindoline in dry benzene, in a sealed ampoule, remained unchanged for 20 years (Fig. 1).

Based on the above, it may be concluded that the more biased is the equilibrium towards the colored form, the easier occurs spontaneous degradation of the solution. Presumably, the colored, merocyanic form of a spiropyran undergoes degradation, which has been experimentally proved [9].

In order to find out the role of oxygen in the irreversible processes, an alcoholic solution of spiropyran was investigated in the medium of oxygen and argon. Following three-day keeping in the dark, changes in both solutions were identical, and after long-term (520-day) keeping, the difference was insignificant. It is indicative

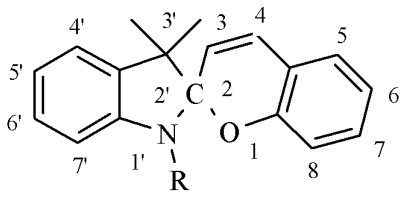


Fig. 1

that oxygen does not take part in irreversible processes, at least at the initial stage.

Upon ultraviolet irradiation of long-kept degraded solution, the characteristic 280 nm maximum disappears to yield the same spectrum as during photodegradation, enabling to suppose that the photodegradation process goes through the colored form [8].

The experimental data by Gautron concerning photodegradation [3] coincide with the author's data regarding spontaneous degradation. Such coincidence calls into question Gautron's opinion that colorless forms undergo degradation. Experiments prove [11] that in general the colored form of spiropyran is degradable.

How does degradation take place and what are the transformation products? In studying a degraded complex mixture together with other products [12], the author found derivatives of oxindole and salicylic aldehyde. The same compounds were also found by Gautron [3] in the photodegraded solution. Noteworthy is the statement [13] according to which in the chromene part of the spiropyran molecule some salicylic aldehyde derivative might be replaced by another derivative of the same aldehyde. This phenomenon has been qualitatively identified by the author as well.

It is known [14] that radical growth in spiropyran at nitrogen atom is accompanied by an increase in their solubility. The first homologues of 8-nitro-6-chlorine derivatives of spiropyran are easily isolated in the alcoholic medium, and beginning from $C_{(5)}$ and above the chromene is not crystallized and the solution does not manifest its thermo- and photochromic qualities. In case cyclohexane is used as a medium, where equilibrium tends towards the colorless form, colorless crystals will be then obtained from the warm mother water, i.e. spiropyran does not spoil if one of the components is excluded from the system. In many cases the use of pyridine as a reaction medium when obtaining spiropyran should be conditioned by retention of one of the reaction products - water.

The mentioned facts and many nuances allow the author to think that both spontaneous and photodegradation are preceded by hydrolysis of the colored form of spiropyran. Hydrolysis is a reversible process. Therefore, in some cases, restoration of the degraded solution is observable. Since Fischer's base, 1, 3, 3-trimethyl-2-methylene indolenine is an unstable compound [15], unstable are also its analogs and they are subject to changes over time [12] in the equilibrium system:

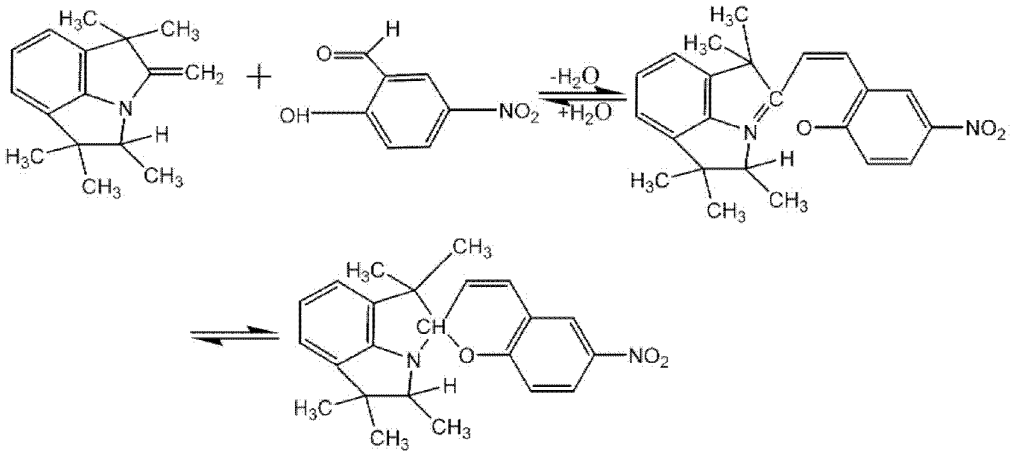
Base + aldehyde D spiropyran + water

Owing to the exclusion of the base, equilibrium fully deviates to the left, causing complete hydrolysis of spiropyran. Certainly, electronic acceptor substitutes facilitate formation of a colored form and consequently degradation.

The earlier voiced supposition [16] of a possible hydrolysis in the solutions of spiropyrans was proved once more with the help of chromatographic control of the course of reaction. Observation with the aid of thin-layer chromatography demonstrated that the reaction medium contains the initial base, aldehyde and spiropyran. If the reaction medium is added with an excess aldehyde, the base will disappear. Upon keeping in the dark or heating up of the alcoholic solution of the chemically pure spiropyran ($C \sim 5 \times 10^{-5}$ mol/l), given below the initial base and aldehyde will be isolated (see the scheme).

It should also be noted that the given base, like Fischer's base and its analogs, does not change when being kept/aged [17]. This enabled the author not only to register its existence in the solution but also to avoid the formation of a complex compound, which accompanies the transformation of the base itself and interaction of the transformation products with the solvents and aldehyde.

If the colored form is poorly soluble (for instance, bromnitro- and dinitro-derivatives), then the colored form will crystallize from the solution and the equilibrium will deviate towards its formation. Hydrolysis does not occur either when there is a medium in which the thermodynamic equilibrium is displaced towards the colorless form (stability in hydrocarbon solvents, supposedly low temperature). If water is excluded from the reaction medium (relative stability in hydrocarbon solvents and polymer films), the stability of spiropyrans in terms of degradation will grow significantly.



Scheme.

Based on the above, it might be concluded that in the said solutions, along with the generally known equilibrium between the colorless and colored forms, there is also the equilibrium between the colored, merocyanic form of the molecule of spiropyran and the basic materials. Since Fischer's base, its analogs and derivatives of the salicylic aldehyde change over time, hydrolysis of the spiropyran molecule gradually takes place, resulting in the "ageing" of liquid and solid solutions of spiropyrans and loss of photochromic properties.

Of course, upon UV irradiation other irreversible processes also take place; however, the author believes that it is hydrolysis of the colored form that creates the basis for the "spoil-ageing" of spiropyrans.

ორგანული ქიმია

სპიროპირანების ხსნარების დესტრუქციის შესაძლო მექანიზმის შესახებ

ჯ. მაისურაძე

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ფოტოქრომული ნაერთების ერთ-ერთი საინტერესო კლასის, სპიროპირანების, ხსნარების სინათლით მრავალჯერადი გაუფერულება-შეფერვის დროს მიმდინარეობს შეუქცევადი პროცესებიც, რაც ზღუდავს მათი გამოყენების სფეროს.

ანალოგიურ პროცესს ადგილი აქვს შეფერილი ხსნარის სიბნელეში ხანგრძლივი დაყოვნების დროსაც. ექსპერიმენტულ მონაცემებზე დაყრდნობით მოვედით დასკვნამდე, რომ გარდა წონასწორობისა შეფერილ და

უფერო ფორმებს შორის, სისტემაში არსებობს კიდევ ერთი წონასწორობა სპიროპირანის შეფერილ ფორმასა და ამოსავალ ნივთიერებებს შორის, რაც იწვევს შეფერილი ფორმის ჰიდროლიზს და ფოტოქრომული ნაერთის დესტრუქციას.

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