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PHOTOLYSIS OF AROMATIC AZOCOMPOUNDS IN ETHYLACETATE SOLUTION

V.Řehák, F.Novák, J.Kunčický, I.Čepčiansky

University of Chemical Technology,Pardubice,Czechoslovakia

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Ethylacetate solutions of monosubstituted derivatives of azobenzene (I,R=H,CH_3,Cl,NO_2,$COCH_3$,COOEt,OCH_3; $c=10^{-3}M$) were irradiated in a quartz reaction vessel by a medium pressure mercury lamp PRK-2. During photolysis dry oxygen-free argon was passed through the solution. After a 1,5 hour irradiation the reaction was completed and the azo-compound had disappeared. During irradiation the samples of photolysed solutions were collected at 15 minute intervals and reaction products analysed by chromatographic methods.

Photolysis of unsubstituted azobenzene was followed especially carefully, in which case hydrazobenzene, aniline and p-acetylazobenzene were found. From the results of chromatographic detection, we also suppose temporary production of N-acetylhydrazobenzene. During the next stages of photolysis o- and p-aminoacetophenone were also found and probably ring diacetylated derivatives of aniline also form during prolonged exposure.

In order to investigate the participation of supposed products in consecutive photoreactions, the photolyses of ethylacetate solutions of N-acetylhydrazobenzene, N,N′-diacetylhydrazobenzene, hydrazobenzene, acetanilide, aniline, o-aminoacetophenone and p-aminoacetophenone were followed. Hydrazobenzene, aniline, o- and p-aminoacetophenone were formed from N-acetylhydrazobenzene. In the products of photolysis of N,N′-diacetylhydrazobenzene, hydrazobenzene was not detected, but aniline, o- and p-aminoacetophenone were detected. Hydrazobenzene undergoes not only the photoreduction but also the photodisproportionation to azobenzene and aniline; o- and p-aminoacetophenone are also formed. Aniline and also o- and p-aminoacetophenone form from acetanilide. In all the cases besides the identified products, unknown products arise, which are the same as the products generated by photolysis of o- and p-aminoacetophenone. Therefore we suppose that these products must be ring diacetylated anilines.

In the photolysis of other substituted azobenzenes(with the exception of nitrosubstituted azocompounds), aniline and substituted anilines were found as the first products. In the photolysis of m-acetylazobenzene, m-acetylhydrazobenzene was also found. In following the course of photolysis the generation of isomeric acetylated and probably also diacetylated derivatives of aniline took place. In the photolysis of some azocompounds (o-, p-chlorazobenzene, p-methylazobenzene, p-acetylazobenzene) the substituent was split off and azobenzene was generated.

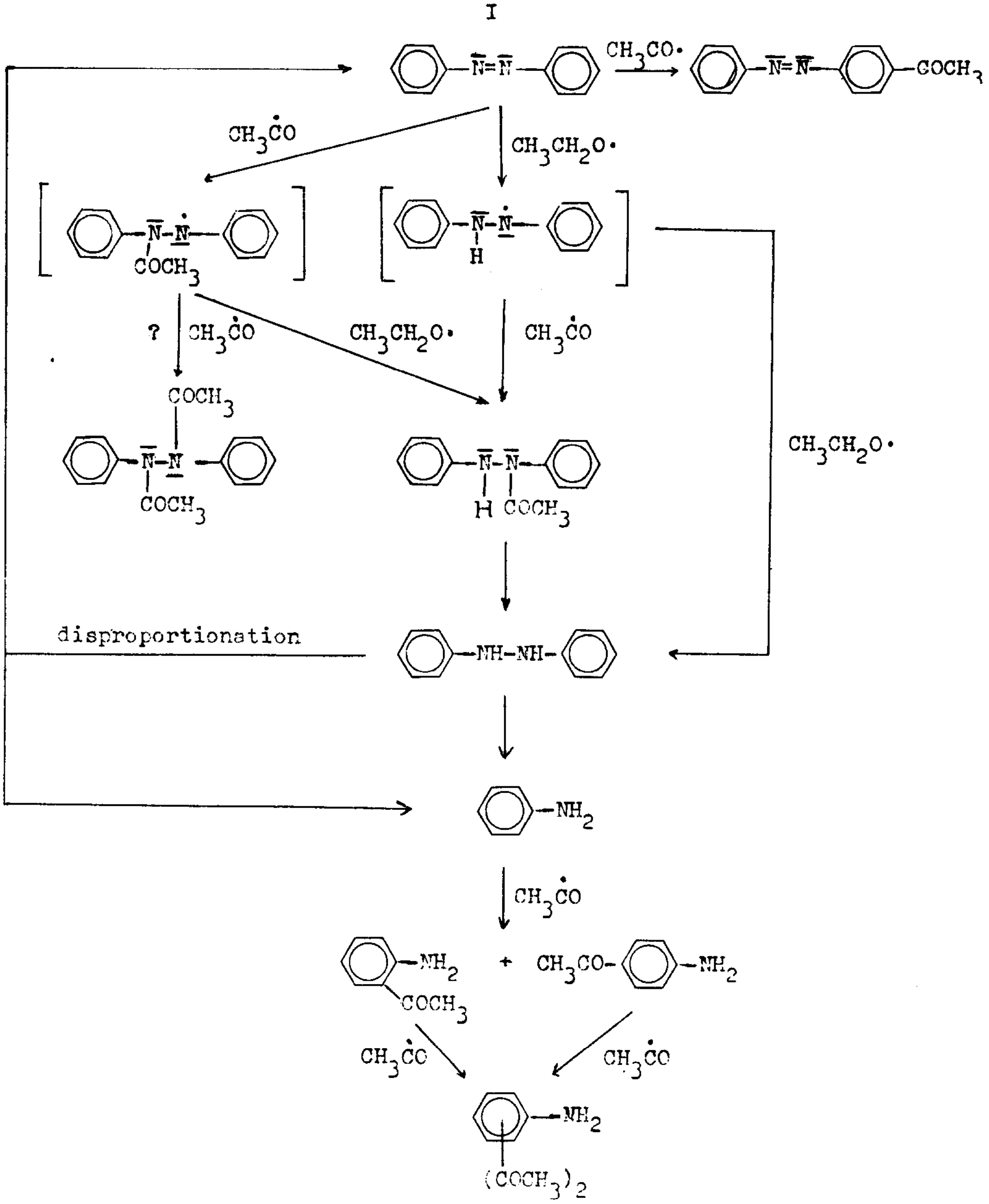
At first the mononitroazobenzenes were reduced to the aminoazocompounds and on further irradiation the concentration of phenylenediamine, aniline and their ring acetylated derivatives were increased. In the case of the photolysis of any isomer of nitroazobenzene the presence of nitroanilines was not proved.

In the gases leaving the reaction mixture, acetaldehyde and carbon monoxide were found.

It is possible to suppose that the photolysis of azocompounds is caused by attack of radicals, generated during photolysis of ethylacetate, on the molecules of the azocompound. The assumption is favoured by the fact that all azobenzenes are photolysed in the same reaction time and the gaseous products generated during irradiation of ethylacetate alone are the same as in the case of photolysis of ethylacetate solutions of azocompounds. When the solution of azocompounds was irradiated by light of wavelength 313 nm (out of the absorption region of ethylacetate) photolysis did not take place.

Ausloos [1-3] proved that during photolysis of ethylacetate in the liquid phase, generation of acetyl and ethoxyradicals is preferred. The acetyl radical is next split into methyl radicals and carbon monoxide. The radicals generated in this way can attack the azomolecules and acetylic-reduction processes take place. The ethoxyradicals can be stabilised by splitting off the hydrogen atom and generating acetaldehyde. This reaction was proved in photoreduction processes in alcohol [4].

It is possible to represent the whole process of photolysis by the following reaction scheme.



All the compounds shown in the reaction scheme, with the exception of unstable intermediates (given in the brackets in the reaction scheme) were found in the reaction mixture.

It is possible to suppose, that the photolysis of monosubstituted derivatives of azobenzene follows roughly the same reaction scheme.

REFERENCES

1. P.Ausloos, Can.J.Chem., 36, 383 (1958)
2. P.Ausloos, J.Am Chem.Soc., 80, 1310 (1958)
3. P.Ausloos, R.E.Rebbert, J.Phys.Chem., 67, 163 (1963)
4. D.N.Shigorin, V.G.Plotnikov, Zh.Fiz.Khim., 40, 295 (1966)