

complexes under investigation, with equal or similar concentrations of metal, the maximum luminescence build up is observed during the photolysis of the complex with butyl methacrylate. It seems likely that during the formation of the initial complex, the bulkier substituents of butyl methacrylate produce greater steric hindrance, and a larger number of coordinatively unsaturated structures. As a result, the processes occurring in the polymers during photolysis should proceed more intensely in complexes with a larger number of coordinatively unsaturated structures.

This conclusion is also confirmed by the analysis of the relationship between the luminescence intensity of Eu^{3+} and the time of irradiation of polymeric complexes with different amounts of metal and acrylic acid (Fig. 3). Increasing the amount of AA results in a significant decrease in the efficiency and build-up time of luminescence of Eu^{3+} during the photolysis of Eu-EMAA complexes (compounds 3–5, Table 1, Fig. 3, a).

The efficiency and build-up time of Eu^{3+} luminescence also depend on the metal concentration: in the Eu-BMAA complexes (compounds 6–9, Table 1) with equal amounts of AA the intensity of the Eu^{3+} luminescence build-up noticeably and progressively increases with decreasing metal concentration (Fig. 3, b). Since macromolecular complexes with a low concentration of metal contain more carboxyl groups per Eu atom, the probability of the formation of coordinatively unsatu-

rated structures with low symmetry of the Eu^{3+} environment during photodecomposition of these complexes is higher.

Thus, the efficiency of the luminescence build up of Eu^{3+} during photolysis depends on the composition and structure of the initial macromolecular complex.

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Thermolysis of azobenzene

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Thermolysis of azobenzene in a melt and in solution results in the formation of aniline. The possible directions of the reaction are considered. Comparison of the enthalpies of the reaction proves that the cleavage of a π -bond in the N=N group to form a biradical intermediate is thermodynamically more favorable than that of a C–N π -bond.

Key words: azobenzene, thermolysis, aniline.

Thermolysis of aliphatic azocompounds is well-studied and widely used for practical purposes.^{1,2} The C–N bonds are cleaved in this reaction to yield a nitrogen

molecule and two radicals:

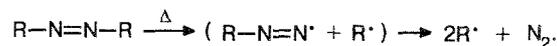


Table 1. Thermolysis of azobenzene

Run	Solvent	T/°C	Time /h	Conversion of AB (%)	Yield of aniline (%)
1	Toluene	250	2.5	—	—
2	Toluene	280	6.5	33	25
3	—	280	4.5	—	—
4	—	310	25	24	41
5	—	310	45	100	39

In asymmetrical azocompounds, the bond cleavage occurs consecutively with the intermediate formation of a diazenyl radical.^{2,3} Symmetrical azocompounds can decompose both with consecutive⁴ and synchronous (simultaneous) cleavage of both bonds.⁵

Aromatic azocompounds have been studied significantly less. They are considered to dissociate similarly, the cleavage of C—N bond occurs heterolytically in the case of azo dyes.^{6–8}

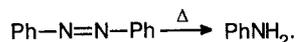
There are contradictory data on the thermolysis of the simplest aromatic azocompound, azobenzene (AB). The decomposition of this compound has not been observed at temperatures of 600–700 °C,⁹ whereas the dissociation of AB at 500 °C in the gaseous phase has been used for the generation of phenyl radicals,¹⁰ *i.e.*, the "usual" direction of the thermolysis reaction with cleavage of the C—N bond occurred.

In the present work it was found that azobenzene decomposes in a melt at 310 °C or in a toluene solution at 280 °C. In both cases aniline is detected as the major reaction product.

Experimental

Azobenzene was twice recrystallized from ethanol; toluene extra pure grade (trade mark 22-5 "for microelectronics") was used. Thermolysis was performed in a sealed glass tube, oxygen was removed from the solution by three freezing-evacuation-thawing cycles. The reaction mixtures were analyzed on a Milichrom liquid chromatograph with a Separon C18 column, 5.0 μm, and methanol-water as the eluent.

The results of the thermolysis of AB are presented in Table 1. As follows from these data, aniline was found in the reaction products in the cases when thermolysis was observed (runs 2, 4, and 5):



This direction of the thermolysis reaction of azocompounds is unusual and is not described in the literature. The known

route of the transformation of azocompounds into amines is the action of reducing agents,¹¹ however, the latter were absent under the conditions used. For example, in the melt, AB was the only substrate in the reaction medium. Apparently, the cleavage of the N=N double bond took place with the retention of the C—N bond.

The ease of the homolytic decomposition $\text{R-X} \rightarrow \text{R} + \text{X}$ depends on the energy of the bond dissociation $E_D(\text{R-X})$ which is equated to the standard enthalpy of the reaction $\Delta H^0(\text{R-X})$:

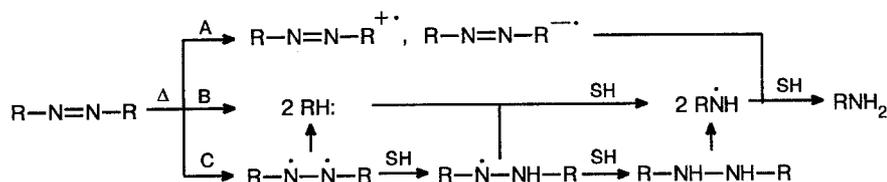
$$E_D(\text{R-X}) = \Delta H^0(\text{R-X}) = \Delta H_f^0(\text{R}^\cdot) + \Delta H_f^0(\text{X}^\cdot) - \Delta H_f^0(\text{RX}^\cdot), \quad (1)$$

where $\Delta H_f^0(i)$ is the standard enthalpy of formation of the i -th particle.¹² Let us consider the possible routes of amine formation during thermolysis of the azocompound (Scheme 1) and estimate the thermochemical parameters of these reaction directions for AB taking into account Eq. (1) (on the basis of the literature data on the enthalpies of formation for gas phase).

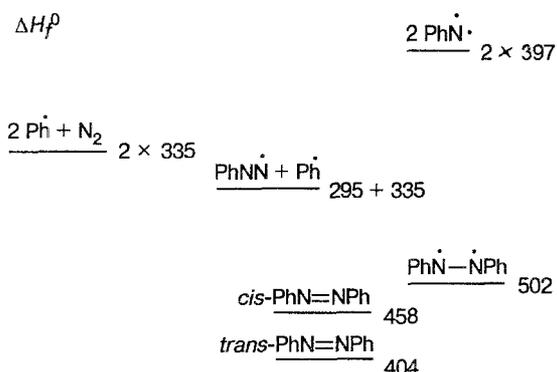
Route A is the oxidative-reductive disproportionation of azobenzene to form hydrazobenzene (HAB), which then dissociates at the N—N bond. This type of dissociation is well known, $E_D(\text{PhNH-NHPh}) = 142 \text{ kJ mol}^{-1}$ (ref. 1). However, by and large this route seems improbable because of the large energy consumption at the first stage, as can be estimated from the ionization potential (866 kJ mol⁻¹) and electron affinity (55 kJ mol⁻¹)¹³ of AB.

Route B is the synchronous cleavage of the N=N bond to form phenylnitrene, which can detach hydrogen atoms from the aromatic ring to transform into the aminyl radical and then into aniline. Detachment of hydrogen atoms from the molecules of the medium is one of the typical properties of aromatic nitrenes,¹⁴ therefore, the efficiency of this reaction is determined as a whole by the first stage of the process. Let us estimate the value of $E_D(\text{PhNH-NHPh})$ from Eq. (1) (at $\text{R} = \text{X} = \text{PhN}$). The values of ΔH_f^0 for AB are 404 and 458 kJ mol⁻¹ for the *trans*- and *cis*-forms, respectively.¹⁵ ΔH_f^0 for phenylnitrene can be calculated from (1) using $\Delta H_f^0(\text{PhNH}) = 230$,¹² $\Delta H_f^0(\text{H}) = 218$,¹⁶ and $E_D(\text{PhN-H}) = 385 \text{ kJ mol}^{-1}$,¹⁷ $\Delta H_f^0(\text{PhN}) = 397 \text{ kJ mol}^{-1}$. Then, the energy of N=N bond dissociation in AB is 390 kJ mol⁻¹ for the *trans*- and 336 kJ mol⁻¹ for the *cis*-form, *i.e.*, the first stage of the reaction is unlikely for route B as also the case is for route A.

Route C is the stepwise dissociation of the N=N bond: cleavage of the π -bond between the nitrogen atoms at the first stage with formation of a biradical which then detaches hydrogen atoms from the molecules of the medium with subsequent dissociation and formation of aniline. Cleavage of the π -bond in the doubly-bound $-\text{X}=\text{Y}-$ fragment occurs in the well-studied *syn-anti*-isomerization of compounds containing a double bond. Therefore, the energy necessary for the formation of a biradical intermediate can be estimated from the activation energy of this reaction. However, it was shown for AB that rotation around the N=N bond is only part of the photo-

Scheme 1

Scheme 2



isomerization during excitation of the molecule the π, π^* absorption band,¹⁸ while thermal isomerization occurs during inversion of the nitrogen atom.¹⁹

Taking into account the difference in the dissociation energies of the first and the second N—H bonds in HAB, the energy of the π -bond in AB was estimated by mass spectroscopy (98 kJ mol⁻¹), and the enthalpy of the formation of the biradical Ph— $\dot{\text{N}}$ — $\dot{\text{N}}$ —Ph was calculated (502 kJ mol⁻¹).¹³

HAB appears after the detachment of a hydrogen atom by the AB biradical. As mentioned above, HAB easily decomposes at the N—N bond. The detachment of a hydrogen atom by a biradical is facilitated by the presence of toluene, which is a better donor of hydrogen than AB and actually serves as a "trap" for the biradical, interfering with its recombination with AB. Therefore, thermolysis in toluene occurs at a lower temperature (see Table 1).

Now let us consider the enthalpy of the reaction for the "classical" direction of AB dissociation at the C—N bond. The enthalpy of the formation of the phenyl radical is known ($\Delta H_f^\circ(\text{Ph}) = 335$ kJ mol⁻¹),¹² which together with the dissociation energy of the phenyldiazenyl radical ($E_D(\text{Ph—NN}) \sim 40$ kJ mol⁻¹)²⁰ gives the enthalpy of formation of the latter ($\Delta H_f^\circ(\text{PhNN}) = 295$ kJ mol⁻¹). Therefore, the dissociation energy $E_D(\text{PhNN—Ph})$ is 226 for *trans*- and 172 kJ mol⁻¹ for *cis*-azobenzene, which is considerably greater than the energy of the π -bond cleavage in the N=N group.

The necessary energy consumptions for the different directions of thermolysis based on a comparison of the standard enthalpies of formation of compounds of the general composition C₁₂H₁₀N₂ are shown in Scheme 2.

It should be mentioned that Eq. (1) is valid assuming barrier-free, reverse radical recombination, when the enthalpy of dissociation is actually equal to the activation enthalpy. This assumption holds true for a series of radical reactions.¹² In the general case, recombination can occur with some activation barrier, which, as a rule, is insignificant for reactions of this type. As in the thermolysis of AB the differences in the enthalpies of the reactions in the different directions are rather large; the existence of a small activation barrier does not affect the relationship between these directions.

Hence, the stepwise dissociation of the N=N-bond with the initial cleavage of the π -bond and biradical intermediate is thermodynamically more favorable than the C—N π -bond dissociation and seems to be the most probable route of amine

formation during thermolysis of the azocompound. Apparently, conjugation of the unpaired electrons with the aromatic π -system in the intermediate stabilizes the latter, *i.e.*, the aromatic character of the azocompound is essential for the successful occurrence of the reaction. Intersystem conversion of the biradical to the triplet state can favor the stabilization of the intermediate, because this conversion hampers electron pair recombination and regeneration of the π -bond.

Thus, the difference in the reaction conditions is a cause of the formation of different reaction products during the thermolysis of azobenzene (10 and the present work). In our opinion, in the condensed phase (melt, solution) the intermediate biradical yields a hydrazobenzene radical in bimolecular reactions with molecules of the medium and then hydrazobenzene itself which easily convert into aniline. In a gas phase under reduced pressure the biradical state of azobenzene can easily be achieved. However, owing to a small probability of bimolecular processes, the monomolecular decomposition with the formation of phenyl radicals becomes predominant.

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