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 unsaturated 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.

### References


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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. The C—N bonds are cleaved in this reaction to yield a nitrogen molecule and two radicals: $R—N=N—R \xrightarrow{\Delta} (R—N=N' + R') \rightarrow 2R' + N_2$. 


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Table 1. Thermolysis of azobenzene

<table>
<thead>
<tr>
<th>Run</th>
<th>Solvent</th>
<th>T/°C</th>
<th>Time /h</th>
<th>Conversion of AB (%)</th>
<th>Yield of aniline (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Toluene</td>
<td>250</td>
<td>2.5</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>2</td>
<td>Toluene</td>
<td>280</td>
<td>6.5</td>
<td>33</td>
<td>25</td>
</tr>
<tr>
<td>3</td>
<td>280</td>
<td>4.5</td>
<td>100</td>
<td>24</td>
<td>41</td>
</tr>
<tr>
<td>4</td>
<td>310</td>
<td>25</td>
<td>24</td>
<td>24</td>
<td>41</td>
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<tr>
<td>5</td>
<td>310</td>
<td>45</td>
<td>100</td>
<td>24</td>
<td>41</td>
</tr>
</tbody>
</table>

In asymmetrical azocompounds, the bond cleavage occurs consecutively with the intermediate formation of a diazenyl radical. Symmetrical azocompounds can decompose both with consecutive and synchronous simultaneous cleavage of both bonds.

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.

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):

\[
\text{Ph} = \text{N}=\text{N} = \text{Ph} \xrightarrow{\Delta} \text{PhNH}_2.
\]

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, 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 R--X \rightarrow R + X depends on the energy of the bond dissociation \( E_D(R--X) \) which is equated to the standard enthalpy of the reaction \( \Delta H^0(R--X) \):

\[
E_D(R--X) = \Delta H^0(R--X) = \Delta H^0(R^+) + \Delta H^0(X^-) - \Delta H^0(RX^+),
\]

where \( \Delta H^0(i) \) is the standard entropy of formation of the \( i \)-th particle. 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, \( E_D(\text{PhNH}=\text{N}=\text{NPh}) = 142 \text{ kJ mol}^{-1} \) (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\(^{-1}\)) 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, therefore, the efficiency of this reaction is determined as a whole by the first stage of the process. Let us estimate the value of \( E_D(\text{PhNH}=\text{N}=\text{NPh}) \) from Eq. (1) (at \( R = X = \text{Ph} \)). The values of \( \Delta H^0 \) for AB are 404 and 458 kJ mol\(^{-1}\) for the trans- and cis-forms, respectively. \( \Delta H^0 \) for phenylnitrene can be calculated from (1) using \( \Delta H^0(\text{PhNH}) = 230 \), \( \Delta H^0(\text{H}) = 218 \), and \( E_D(\text{PhNH}--\text{NHPh}) = 385 \text{ kJ mol}^{-1} \). 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-