Time-Resolved Fluorescent Spectroscopy for Determining the Products of Reduction of Aromatic Nitro Compounds

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Abstract

The possibility to apply time-resolved fluorescence spectroscopy to the analysis of mixtures of aromatic amines or nitro compounds after their preliminary reduction to amines is demonstrated.

INTRODUCTION

Luminescent analysis wins increasing importance for solving ecological problems. Previously the possibility was demonstrated to apply sensitive fluorescent method of primary amine determination to the analysis of aromatic (poly)nitro compounds after their preliminary reduction [1]. If separation operations are involved, this allows using the mentioned method also for investigating mixtures of the indicated compounds. For instance, the use of chromatography broadens the possibilities of fluorescent analysis: developments of fluorescent determination of amines in combination with column, thin layer chromatography [2, 3]. However, in spite of reliability, this method of the analysis of mixtures turns out to be rather cumbersome in application to aromatic nitro derivatives. Because of this, it is urgent to search for other mixture investigation methods without separation operations. For this purpose, in the present work we investigated the possibility to use time-resolved fluorescent spectroscopy for analyzing mixtures of aromatic (poly)nitro compounds.

EXPERIMENTAL

Synthesis of luminophores examined in the present work has been described in detail in [1]. Luminescence spectra were recorded with Fluorolog spectrophotometer of Spex Company. Lifetimes of the excited state of the obtained luminophores were determined using the fluorescence spectra recorded with OSP-200 nanosecond fluorometer with N_2 laser excitation source ($\lambda = 337$ nm) and transmission filter with $\lambda > 440$ nm at the outlet. The instrument provides measurement of luminescence lifetime at a level of $\tau > 0.2$ ns.

The data were processed using Fourier transformation of the resulting line into constituents using the program proposed in [4]: the obtained signal is represented as a sum of the signals of components $J = \Sigma J_i \exp(-t/\tau_{oi})$.

RESULTS AND DISCUSSION

The excited states of luminophores formed during the interaction of aromatic nitro derivatives of benzene and toluene, reduced to amines, with fluorescamine [5, 6] as the most

TABLE 1

Lifetimes of excited states of the luminescent adducts of aromatic amines with fluorescamine

Amine	τ, ns
ortho-Aminotoluene	2.0–2.1
para-Aminotoluene	0.5–0.6
2,4-Diaminotoluene	0.5–0.6
2,5-Diaminotoluene	<0.2
2,6-Diaminotoluene	1.6–1.8
3,4-Diaminotoluene	0.9–1.0
2,4,6-Triaminotoluene	0.7–0.9

convenient fluorogenic reagent are investigated. The results of measurements of the lifetime of the excited state of the adducts of the investigated aromatic amines with fluorescamine are shown in Table 1. The obtained values do not depend on the form in which an amine interacts with the fluorogenic reagent: either it was preliminarily isolated as an individual compound or it reacted in reaction mixture obtained by reduction of the corresponding nitro derivative.

The analysis of luminescence decay curves shows that the leading edge of the emission signal fully repeats the shape of laser pulse at the level of time resolution. The time of luminescence increase can be limited by the following processes: transition from one vibrational level to another for the case of fluorescence (its characteristic time is about 10^{-14}–10^{-15} s) or singlet-triplet conversion for the case of phosphorescence (about 10^{-12}–10^{-13} s). As a rule, longer time of luminescence increase characterizes either conformational rearrangement of a molecule or a photochemical process resulting in the formation of an excited luminescent state.

The use of time-resolved fluorescent spectroscopy provides the possibility of rapid analysis of mixtures with the time at a level of pico- and nanoseconds. As it follows from the luminescence spectra, differences between the components of the mixture of nitro compounds reduced to amines in the leading edge of luminescence increase cannot be observed with the nanosecond fluorometer OSP-200. However, luminescence decay times for these substances differ from each other, depending not only on the number of nitro groups but also on their positions in the aromatic ring. This difference provides the possibility to identify separate constituents of mixtures of aromatic amines or the corresponding nitro derivatives after reduction.

CONCLUSION

Investigation of the excited states of luminophores, which are the products formed in the reaction of reduced nitro compounds with fluorogenic reagents, has demonstrated principal possibility of selective registration and analysis of mixtures of aromatic (poly)nitro compounds after their preliminary reduction to amines followed by a fluorogenic reaction. Advantages of the method are fast operation, high (about unity) quantum yield of luminescence, and the absence of any sensitivity to the presence of water and some other components of the air in the mixture to be analyzed.

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