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Abstract

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ON THE DURATION OF ULTRAVIOLET FLUORESCENCE OF SOME AROMATIC COMPOUNDS

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Many organic compounds that are of scientific interest and important in practical respects possess ultraviolet fluorescence. These include, above all, benzene and its closest derivatives.

Studies of the spectra and yield of fluorescence, as well as of the absorption spectra of the indicated compounds, have made it possible to obtain a number of valuable data on the properties of the excited and unexcited states of the molecules of these compounds and some information on the processes in which excited molecules participate. However, as experience in the study of visible fluorescence shows, investigation of the duration of luminescence gives more direct and often more reliable information on the mechanism of the processes taking place in the excited state of the molecule; in any case, simultaneous measurements of the yield and duration of fluorescence make it possible to judge the energetics of the excited molecule more accurately than measurements of the fluorescence yield alone.

The purpose of the present work was to adapt the optical part of the phase fluorometer developed by A. M. Bonch-Bruevich, V. A. Molchanov, and V. I. Shirokov (^{1}) to measurements of the duration of ultraviolet fluorescence and to determine the values of the fluorescence duration of benzene and some of its derivatives.

To excite the fluorescence of benzene and its methyl-substituted derivatives, a region of the ultraviolet spectrum shorter than 2700 Å is required. All the optics of the modulation unit of the fluorometer developed by the above-mentioned authors was made of quartz and aluminized mirrors; therefore, in this part the possibility of applying the fluorometer for our purposes was limited only by the excitation source—the mercury lamp SVDSh-250.

Because in this lamp the discharge is very far from the walls of the lamp, its emission spectrum lacks the 2500–2600 Å region. We used for excitation of fluorescence a mercury lamp SVD-120, which gives sufficiently intense radiation in the above-mentioned spectral region. At a voltage of 140–160 V the lamp burns steadily on direct current.

A sufficiently pure isolation from the mercury spectrum of the region shorter than 2700 Å presents considerable difficulties. We achieved this by means of an interference filter for the resonance line of mercury and a concave diffraction grating with a radius of curvature of 50 cm, having 1200 lines per 1 mm and giving, in the first order, an energy maximum in the region of 2800 Å*. The entrance slit for the monochromator with the diffraction grating was the slit located at the output of the modulation unit of the fluorometer.

The described device made it possible to separate well the exciting radiation from the adjacent ultraviolet region of the spectrum at 2700 Å, in which the measurements of fluorescence duration were mainly carried out—tions. The small admixture of visible light scattered by the grating and of exciting radiation scattered by the sample was easily removed with a UFS-2 light filter placed in front of the photomultiplier.

For recording the fluorescence under study and the comparison signal, an FEU-18 photomultiplier was used.

In most cases excitation and observation were carried out from one side. The activator concentrations were varied from $1 \cdot 10^{-2}$ mole/l for brightly fluorescing substances to $2 \cdot 10^{-1}$ mole/l for weakly fluorescing ones. Reabsorption of fluorescence was not taken into account.

From the work of Bowen et al. (2) it is known that the fluorescence of most simple aromatic compounds is quenched rather strongly by atmospheric oxygen. In individual cases, along with measurements of the fluorescence lifetime in non-degassed solutions, the emission lifetime was also measured in degassed solutions*, but in the overwhelming majority of cases the measurements were made in non-degassed solutions. The results of our measurements are given in Table 1.

Comparison of the fluorescence lifetimes of benzene, its methyl derivatives, and naphthalene in degassed and non-degassed solutions in hexane and in alcohol shows that the strong decrease in the fluorescence yield of the indicated compounds in the presence of atmospheric oxygen, found by Bowen and Williams, is accompanied by a strong decrease in the fluorescence lifetime.

A detailed consideration of the question of quenching of the fluorescence of aromatic compounds by oxygen was not part of the aim of the present work, and we shall confine ourselves to considering only one case—the quenching of the fluorescence of naphthalene in hexane. If the data obtained for the fluorescence lifetime of naphthalene in degassed and non-degassed solution, the data on the solubility of oxygen in hexane, and the approximate values of the kinetic radii of naphthalene and oxygen molecules** are substituted into the formula for diffusional quenching (3), then, as calculations show, for the quenching probability

* The authors express their deep gratitude to T. N. Krylova for providing the filter and to F. M. Gerasimov for making the grating.

upon encounter we obtain 1.5–1.6, i.e., a value quite close to 1. This result, apparently, may be regarded as good confirmation that the kinetics of quenching is determined by diffusion of the oxygen molecule to the excited naphthalene molecule.

It is seen from Table 1 that the fluorescence lifetime of benzene in degassed hexane is $2.6 \cdot 10^{-8}$ sec. According to Bowen and Williams, the fluorescence yield of a solution of benzene in hexane is 0.1-0.11. Therefore, if one assumes that the cause of the decrease in the fluorescence yield of benzene is some intramolecular quenching processes, proceeding in time and according to such laws that the decrease in yield is proportional to the change in the emission lifetime, one should expect that, in the absence of this quenching, the fluorescence lifetime of benzene would be $2.3 \cdot 10^{-7}$ sec.

On the other hand, according to Sklar' s data (4) the oscillator strength for the first absorption band of benzene is $2.7 \cdot 10^{-3}$***. Hence, from formula (6)

$$\tau = \frac{mc}{8\pi^2 e^2 \nu^2 f n^2}, \tag{1}$$

where c is the speed of light, e the electron charge, m its mass, n the refractive index of the medium, and f the oscillator strength, we find that the fluorescence lifetime of benzene should be $1.8 \cdot 10^{-7}$ sec. For toluene and para-xylene, according to Sklar' s data, the oscillator strengths for the first absorption band are $5.3 \cdot 10^{-3}$ and $12.5 \cdot 10^{-3}$. For naphthalene, according to

* Degassing of the solution was carried out by pumping off the air with a fore-vacuum pump while successively freezing and thawing the solution.

** It should be noted that an error in the values of the kinetic radii of tens of percent has little effect on the result of the calculation.

*** According to McClure' s data (5), the oscillator strength for the first absorption band of benzene is $1.47 \cdot 10^{-3}$.

Table 1

Values of the fluorescence duration of some aromatic compounds

Fluorescing substance	Solvent	$\tau \cdot 10^9$, sec	Fluorescing substance	Solvent	$\tau \cdot 10^9$, sec
Benzene	Hexane	5.7	*n*-Butylbenzene	Hexane	6.8
Benzene	Hexane, degassed	26.0	*n*-Butylbenzene	Alcohol	10.0
Benzene	Alcohol	13.0	Cumene	Hexane	6.0
Toluene	Hexane	5.8	Cumene	Alcohol	10.6
Toluene	Hexane, degassed	26.0	Pentamethylbenzene	Hexane	3.9

Fluorescing substance	Solvent	$\tau \cdot 10^9$, sec	Fluorescing substance	Solvent	$\tau \cdot 10^9$, sec
Toluene	Alcohol	12.4	Pentamethylbenzene	Alcohol	4.3
Toluene	Alcohol, degassed	24.0	Hexamethylbenzene	Hexane	2.0
p-Xylene	Hexane	6.1	Hexamethylbenzene	Hexane, degassed	6.0
p-Xylene	Hexane, degassed	28.0	Pseudocumene	Alcohol	12.6
p-Xylene	Alcohol	13.0	Naphthalene	Hexane	8.3
p-Xylene	Alcohol, degassed	23.0	Naphthalene	Hexane, degassed	103.0
o-Xylene	Hexane	6.0	Aniline	Alcohol	2.7
o-Xylene	Alcohol	12.2	Phenol	Alcohol	4.7
m-Xylene	Hexane	6.0	Hydroquinone	Alcohol	2.0
m-Xylene	Alcohol	12.4	Resorcinol	Alcohol	2.3
Ethylbenzene	Hexane	5.7	Diphenyl	Alcohol	10.0
Ethylbenzene	Alcohol	11.1	Triphenylmethane	Alcohol	9.6
n-Propylbenzene	Hexane	5.2	Toluidine	Alcohol	3.0
n-Propylbenzene	Alcohol	10.0	Phenanthrene	Alcohol	19.0

McClure (5) gives an oscillator strength equal to $2 \cdot 10^{-3}$. Hence the fluorescence durations calculated from (1) will be equal to $1 \cdot 10^{-7}$ sec for toluene, $6.3 \cdot 10^{-8}$ sec for *p*-xylene, and $2.8 \cdot 10^{-7}$ sec for naphthalene. The values of the fluorescence duration measured by us in degassed solutions are, respectively: $2.6 \cdot 10^{-8}$, $2.8 \cdot 10^{-8}$, $1.03 \cdot 10^{-7}$; and the values of the yields of the same solutions, according to Bowen and Williams, are 29.7% for toluene, 41.5% for *p*-xylene, and 37.5% for naphthalene. The values of the luminescence duration in the absence of internal quenching, calculated from the yield measurements and the measured values of the fluorescence duration, will therefore be equal to: $0.9 \cdot 10^{-7}$ sec for toluene, $6.7 \cdot 10^{-8}$ sec for *p*-xylene, and $2.7 \cdot 10^{-7}$ sec for naphthalene; i.e., as in the case of benzene, they are close to the values of the duration calculated by formula (1).

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