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Abstract

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On the Diffusion Theory of the Kinetics of Bimolecular Reactions in Solutions

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In 1936 one of us ([1]) made an attempt to apply the basic propositions of the theory of diffusional quenching of the fluorescence of solutions to explain the dependence of the rate of certain bimolecular reactions on the viscosity of the solvent. It was shown that only the assumption that the rate of diffusion is the principal stage determining the rate of reactions in solutions makes it possible readily to explain the observed, in some admittedly rather rare cases, linear dependence of the reaction rate on the viscosity of the solvent. Without particular difficulty, the diffusion theory can also explain the more frequently encountered case in which the reaction rate decreases considerably more slowly than the fluidity of the solution. For this it is only necessary to take into account the peculiarity in the distribution of collisions between molecules of dissolved substances, or, what is essentially the same thing, to assume a dependence of the reaction rate on the time of interaction of two molecules situated at a given distance from one another; i.e., in this case the decrease in the number of encounters of dissolved molecules in viscous media is compensated by an increase in the effectiveness of each encounter.*

It is possible, however, that there is also a case in which the decrease in the number of encounters per unit time with increasing viscosity of the solution is compensated not only by an increase in the effectiveness of an encounter in viscous solutions, but also by an increase in the duration of existence of the molecule capable of reaction. In this case the possibility is not excluded that independence of the reaction rate from the viscosity of the solution will be observed, despite the fact that the kinetics of the reaction is in many respects determined by the diffusion of the dissolved molecules. Such a phenomenon should be expected, for example, in the case when the excited electronic states of a molecule (singlet or triplet), whose lifetime increases with increasing viscosity of the solvent, are responsible for the reaction.

Since metastable (triplet) states of organic molecules, responsible for their phosphorescence, are at the same time responsible for the most important photochemical and certain chemical reactions, we considered it most expedient, in order to illustrate the above, to investigate the quenching by foreign substances of the phosphorescence of liquid solutions of organic compounds. Known and

convenient objects for such an investigation are solutions of acridine orange, for which, as was shown earlier, the duration of phosphorescence increases as the viscosity of the solution increases ([5]) and decreases sharply upon the addition to the solution of minute amounts of quenchers, for example, aniline and hydroquinone ([6]). In the present work the influence of the viscosity of the solvent on the quenching of the phosphorescence of alcohol–glycerol solutions of the above-mentioned dye by potassium iodide and oxygen was investigated.** The principal characteristic of quenching

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* This peculiarity in the distribution of collisions between molecules of dissolved substances and its significance for the kinetics of bimolecular reactions in solutions was also noted in the papers of Rabinowitch ([2]) and Fowler and Sletter ([3]). They introduced the terms now generally accepted: "encounter" and "collision" (instead of the "primary" and "secondary" collisions adopted in our article).

** We found that the duration of the phosphorescence of acridine-orange solutions increases markedly upon degassing of the solution.

the change in the duration of the phosphorescent state of the molecule; in individual cases the change in the relative yield of phosphorescence upon quenching was also studied.

All the solutions we investigated contained one and the same concentration of dye: $5 \cdot 10^{-5}$ mol/l. The viscosity of the solutions varied from 0.3 to 5 poise. The highest concentration of potassium iodide was $6 \cdot 10^{-5}$ mol/l.

The apparatus consisted of a mercury lamp of ultrahigh pressure, provided with a stabilizer by V. I. Shirokov ([7]), a lens, two light filters: one for absorbing the thermal radiation and the other for isolating the mercury line 436 mμ, a two-disk phosphoroscope rotating from a synchronous motor at a speed of 1500 or 2500 rev/sec, a glass cuvette* with the solution under study, a photomultiplier with its power-supply unit, a cathode follower, and an EO-7 electronic oscillograph. In determining the relative phosphorescence yield, the latter was replaced by a galvanometer possessing considerable inertia.

With an appropriate choice of the apertures in the phosphoroscope disks, a phosphorescence-decay curve corresponding to a considerable change in the initial intensity of the luminescence can be obtained on the oscillograph screen. This curve was recorded by us and then studied. It could be approximated by an exponential, if small portions at the beginning and at the end of the curve, corresponding to the opening and closing of the phosphoroscope aperture, were excluded. The phosphorescence decay constant found in this way agrees well with the constant determined by the usual method, by comparing the luminescence intensity for two positions of the phosphoroscope disks relative to one another.**

An accurate determination of the relative phosphorescence yield by means of the Becquerel phosphoroscope, for the case when the duration of phosphorescence

is comparable with the period of rotation of the phosphoroscope disk, presents considerable difficulties. It is necessary to take into account the decrease in the luminescence intensity during the passage of the aperture in the phosphoroscope disk in front of the photomultiplier window, and also the circumstance that, upon excitation of phosphorescence, a stationary state may not have been reached. It is difficult to carry out a very accurate calculation of the necessary corrections; in our case, however, the problem is simplified by the fact that we are interested not in the exact values of the relative phosphorescence yield as such, but in the exact determination of changes in the relative phosphorescence yield in the course of its quenching.

In Fig. 1 are shown the values we obtained for the duration of the phosphorescent state in deaerated (τ_0) and non-deaerated (τ) solutions of acridine orange as a function of the fluidity of the solution (solid curves). At first glance, from these curves it is difficult to believe that the quenching of phosphorescence by oxygen is governed by diffusion processes. However, if one takes into account that diffusion quenching is proportional to the duration of the excited state of the molecule, and plots a graph of the dependence of quenching on viscosity in which the quenching action is characterized not by the generally accepted quantity $\frac{\tau_0}{\tau} - 1$, but by the quantity $\frac{\tau_0 - \tau}{\tau_0 \tau}$, then the curve obtained in this way (Fig. 2) very much resembles the known curve of the dependence of the yield (duration) of fluorescence on the viscosity of the solvent. An analogous curve is also obtained in studying the influence of viscosity on the quenching by potassium iodide of the phosphorescence of deaerated solutions of the same dye (Fig. 3). At very large values of the viscosity, quenching of phosphorescence is not observed. Thus, the phosphorescence of glycerol–alcohol solutions at the temperature of liquid air decays according to the same law in the absence and upon addition of ($6 \cdot 10^{-5}$ mol/l) potassium iodide.

The assertion that quenching of the phosphorescence of solutions of acridine

* The cuvettes were made of uviol glass, which does not give afterglow.
** In this case the measurements were carried out with the aid of an inertial galvanometer.

orange, like the quenching of the fluorescence of this dye, is due to diffusion processes, is in good agreement with the results of comparing changes in the relative yield and the duration of phosphorescence. From the theory of diffusion quenching [9] it follows that at small quencher concentrations and low efficiency of encounter of the quenching molecule with the excited

Fig. 1
Fig. 1. Duration of the phosphorescence of acridine orange in deoxygenated and non-deoxygenated water–glycerol solutions of different viscosity

Fig. 2
Fig. 2. Effect of the viscosity of the solution on quenching by oxygen of the phosphorescence of acridine orange

(low sphere of action)* changes in the yield and in the duration of luminescence should be strictly proportional to one another. Fig. 4 shows that, in the quenching of the phosphorescence of aqueous-glycerol solutions of acridine orange by potassium iodide, the relative yield and the duration of phosphorescence change in the same way.

Fig. 3
Fig. 3. Effect of the viscosity of the solution on quenching by potassium iodide of the phosphorescence of acridine orange

Fig. 4
Fig. 4. Dependence of the relative yield (B_0/B) and duration τ_0/τ of the phosphorescence of acridine orange on the quencher concentration, a–B_0/B, b –τ_0/τ

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* A comparison of the quencher concentrations required to obtain one and the same effect in the case of phosphorescence and fluorescence, with the durations of the corresponding excited states, shows that the quenching efficiency in the case of phosphorescence is tens and hundreds of times smaller.

Note: Figure translations are in progress. See original paper for figures.