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Abstract

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SPECTRAL STUDY OF REVERSIBLE PHOTOTRANSFER OF A PROTON IN TWO-COMPONENT SUBLIMED LAYERS OF ORGANIC COMPOUNDS AT LOW TEMPERATURES

Proton phototransfer was first discovered from a reversible change in the luminescence spectrum of an acridine layer sublimed together with solid acids (^1). Short-wavelength UV light deprotonated, in vacuum at $T = 90^\circ$ K, the acridine cation, which was regenerated by heating the layer to $T = 298^\circ$ K in the dark. Subsequently, under analogous conditions, we detected phototransfer of a proton between "amphoteric" molecules having both proton-donor and proton-acceptor groups at their ends (^2). There are also publications on intramolecular proton phototransfer in the solid phase (^3). In works ($^{4-}$6), changes in the affinity for a proton of excited acceptors and donors, compared with their unexcited state, were found in liquid and frozen solutions, and the rate constants of protolytic reactions were determined.

The results of the latter of the above-mentioned reports indicate an increase in the basic properties of acridine in the singlet-excited state, which excludes the possibility of photodetachment of a proton from the acridine cation. The nevertheless observed phototransfer from the acridine cation (^1) was explained by deprotonation due to the excess vibrational energy of the cation molecule immediately after the act of emission of luminescence light (^2).

The present work pursued the aim of further developing the line connected with the distinctive technique of vacuum deposition of donor–acceptor mixtures, with the involvement of a broader range of objects.

Method

As bases, i.e., proton acceptors, 3,6-diaminoacridine and 3-aminoacridine were taken; on the other hand, 2-naphthol, oxalic acid, and salicylic acid were used as proton donors. The method of joint sublimation distillation of both components in vacuum was used predominantly.

Changes in the position of the proton in the donor–acceptor system were recorded, analogously to solutions (^4), from the position of the acceptor

Figure 1

Figure 1: Figure 1

fluorescence spectra, which in the systems studied are located in the visible region and do not overlap with possible fluorescence spectra of the donors and their anions.

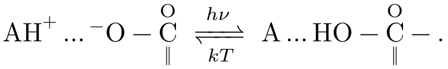
Measurement Results

Figure 1a shows the fluorescence spectra of a sublimed two-component layer of 3-aminoacridine and oxalic acid at 90° K; after sublimation the layer was kept for 15 min without illumination.

Fig. 1. a –fluorescence spectra of a layer of 3-aminoacridine with oxalic acid, deposited in vacuum, 90°K: **1** –spectrum of the initial sample; **2** –after irradiation for 15 min with the light of an SVDSh-250 lamp; **3** –after 3-hour storage of the irradiated sample in the dark at 298°K. **b: 1** –fluorescence spectrum of 3,6-diaminoacridine deposited in vacuum, 90°K; **2** –the same, with oxalic acid, deposited in vacuum, 90°K; **3** –luminescence spectrum of a layer of 3,6-diaminoacridine with oxalic acid after 20 min irradiation with the light of an SVDSh-250 lamp (recovery of the long-wavelength luminescence after thawing of the irradiated sample is not shown). **c** –fluorescence spectra of a layer of 3,6-diaminoacridine with 2-naphthol in vacuum: **1** –spectrum of the initial sample, 298°K; **2** –the same, 90°K; **3** –after irradiation for 30 min with the light of an SVDSh-250 lamp, 90°K.

at 298°K. The initial sample exhibited yellow-green fluorescence with spectrum (1), characteristic of the protonated form of 3-aminoacridine, with a maximum at 550 nm. Protonation occurred as a result of keeping the layer at 298°K and consisted in the transfer of a proton to the base–3-aminoacridine–from oxalic acid within the limits of the hydrogen bond.

Irradiation with the full light of a mercury lamp SVDSh-250 (or with the selected region of the spectrum with $\lambda = 300$ nm) for 15-30 min led to the appearance and subsequent enhancement of a fluorescence maximum located at 480 nm (curve 2). This maximum, as additional measurements showed, corresponds to the emission of the neutral form of 3-aminoacridine at 90°K in condensed layers. Heating the layer to 298°K and refreezing led to restoration of the luminescence of the protonated form (curve 3). An analogous result was obtained with the system 3,6-diaminoacridine + oxalic acid (Fig. 1b). The reactions observed, as in the case of acridine (1), can be represented by the following scheme:



$$\mathrm{AH}^{+}\ldots{}^{-}\mathrm{O}-\overset{\mathrm{O}}{\underset{\|}{\mathrm{C}}}\;\underset{kT}{\overset{h\nu}{\rightleftharpoons}}\;\mathrm{A}\ldots\mathrm{HO}-\overset{\mathrm{O}}{\underset{\|}{\mathrm{C}}}-\,.$$

Experiments carried out with mixtures containing aromatic acids–3,6-

diaminoacridine + salicylic acid and 3,6-diaminoacridine + 2-naphthol—led to a result different from the preceding one.

Figure 1c shows the fluorescence spectra of a binary layer with 2-naphthol sublimed in vacuum. In the initial state, luminescence of the molecular form of 3,6-diaminoacridine appears. Irradiation of the layer with the full light of a mercury lamp at 90°K causes the appearance of a fluorescence-spectrum maximum at 590 nm, due to formation of the protonated form. Brief heating led to regeneration of the initial spectral maximum of fluorescence at 510 nm. The maximum at 450 nm appearing after irradiation evidently belongs to deprotonated 2-naphthol molecules. Indeed, according to the data of (4), the fluorescence spectrum of the 2-naphthol anion in aqueous solution is observed at 425 nm. Changes in the fluorescence spectra reversible in a manner analogous to the latter are also observed upon irradiation of a layer of 3,6-diaminoacridine + salicylic acid.

The stages of the process of hydrogen-bond formation upon cooling and of proton transfer under irradiation from salicylic acid and 2-naphthol to 3,6-diaminoacridine were successfully traced in nonpolar solvents.

(Fig. 2). In such frozen solutions the shift of the fluorescence-spectrum maximum of the base as a result of protonation is smaller than in the solid state (cf. Fig. 1).

Discussion of the results

The thermal energy at room temperature, as follows from the experiments, is sufficient for transfer of a proton from a strong acid to the acridine base. At 90°K, in a rigid sublimed layer, excess vibrational energy concentrated in the hydrogen bond

$$-\mathrm{O}^{-} \ldots \mathrm{H}^{+} - \mathrm{A},$$

is required for transfer of the proton to the anion.

Stabilization of the molecular forms of the acid and base formed as a result of irradiation is due to the low temperature. In choosing proton donors—organic acids—the acid strength, pK, determined from dissociative equilibrium in aqueous solutions, may be used approximately as a parameter for estimating the behavior of these acids in the crystalline state. The validity of this assumption was checked by observations of changes in the fluorescence spectrum of one and the same proton acceptor in mixtures with various crystalline acids in an equimolecular ratio. This made it possible to establish that the gradation of acid strength is preserved in the solid state. However, in a number of cases a change in acidity may be caused by the formation of hydrogen-bonded dimers, whose predominant existence for oxalic acid in the solid state has been found from IR absorption spectra ([8]).

Fig. 2. Fluorescence spectra of donor–acceptor mixtures in benzene: 1 — 3,6-diaminoacridine, $C = 1 \cdot 10^{-4}\,M$, 298°K; 2 —3,6-diaminoacridine, $C = 1 \cdot 10^{-4}\,M$, salicylic acid added (saturated solution), 77°K; 3 —frozen solution irradiated for 20 min with an SVDSh-250 lamp; 4 — 3,6-diaminoacridine, $C = 1 \cdot 10^{-4}\,M$, 2-naphthol $C = 10^{-1}\,M$ added, 77°K; 5 — frozen solution irradiated for 20 min with an SVDSh-250 lamp

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3 —frozen solution irradiated for 20 min with an SVDSh-250 lamp;
4 —3,6-diaminoacridine, $C = 1 \cdot 10^{-4}\,M$, 2-naphthol $C = 10^{-1}\,M$ added, 77°K;
5 —frozen solution irradiated for 20 min with an SVDSh-250 lamp.

Taking the foregoing into account and on the basis of the experimental data presented, the position of the proton within the hydrogen bond between donor and acceptor can be represented qualitatively with the aid of potential curves. Fig. 3 shows such potential curves explaining proton transitions. Positions I and II correspond to the location of the proton at the nitrogen of the heterocycle (cationic form) and in the hydroxyl of the acid (molecular form). The relative position and magnitude of the barrier separating the stable proton states in the unexcited system depend on the acidity and basicity of the interacting components, as well as on temperature. At 90°K the proton is located in the minimum of the dashed curve D_0. At 298°K this curve is shifted upward to the position D_0'.

The change in the position of the potential energy of the proton in the H—O group of the acid molecule at 298°K compared with the position at 90°K, indicated in Fig. 3a, is caused by a process analogous to the phenomenon of solvation in solutions and is due to thermal mobility in the system. This leads to a decrease of the potential barrier to values comparable with the mean value of the thermal energy in the participating vibrational degrees of freedom, which promotes thermal transfer of the proton between donor and acceptor. Thus, for the case of oxalic acid

at room temperature cations of the acceptor molecules are observed, i.e., equilibrium position 1 for the proton on the curve A_0.

According to the scheme in Fig. 3a, the reverse phototransfer of a proton from

Fig. 3. Potential curves for the position of the proton in a hydrogen-bonded donor–acceptor system

Figure 3: Fig. 3. Potential curves for the position of the proton in a hydrogen-bonded donor–acceptor system

AH^+ to O^- can proceed by two routes: in the ground state, immediately after the act of emission of a photon $h\nu'$ by the protonated acceptor, owing to the excess vibrational energy, or in the excited state of the protonated acceptor, owing to the excess vibrational energy upon excitation by photons of high energy.

Fig. 3. Potential curves for the position of the proton in a hydrogen-bonded donor–acceptor system

Since the transitions occur through nonequilibrium vibrational states, the reaction must have a small quantum yield. Indeed, the considerable exposure times (10–30 min) for all the systems investigated indirectly confirm this assumption.

The scheme in Fig. 3b illustrates proton transfer in systems with weak acids in the solid state at 298° K, which do not form a cation of the acceptor molecule. For 2-naphthol and salicylic acid, the molecular form of the proton acceptor is observed (since these are rather weak acids in the unexcited state). In the singlet excited state of donor II, the magnitude of the barrier between forms I and II (Fig. 3b) is somewhat reduced as a result of an increase in the equilibrium distances (9) and a flattening of the potential-energy minimum. But the decrease in the potential barrier occurs mainly because of a strong increase in the acidic properties of 2-naphthol (and salicylic acid) in the excited singlet state, which determines the direction of proton transfer in the excited state (along the curved arrow).

It follows from this, in the general case, that the direction of the phototransfer reaction of a proton depends on the ratio of the acidic and basic properties of the interacting molecules in the ground and excited states and is determined by two processes: the use of excess vibrational energy in the ground or excited states to overcome the barrier, and a change in the donor–acceptor properties of the molecules in the excited state.

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CITED LITERATURE

1. A. N. Terenin, A. V. Kariakin, *Nature*, **159**, 1151 (1947); A. N. Terenin, A. V. Kariakin, DAN, **8**, 425 (1947).

2. A. V. Shablya, A. N. Terenin, *Optics and Spectroscopy*, **10**, No. 5, 617 (1961); A. N. Terenin, E. Putzeiko, L. Akimov, *Disc. Farad. Soc.*, **27**, 90

(1959); A. N. Terenin, **27**, 109 (1959).

3. D. N. Shigorin, *Izv. Akad. Nauk SSSR, Ser. Fiz.*, **14**, 956 (1953); R. N. Nurmukhametov, D. N. Shigorin et al., *Optics and Spectroscopy*, **11**, 606 (1961); R. N. Nurmukhametov, Yu. N. Kozlov et al., DAN, **143**, 1145 (1962).

4. a) T. Förster, *Naturwiss.*, **36**, 186 (1949). b) A. Weller, *Zs. Elektrochem.*, **56**, 662 (1952). c) A. Weller, *Zs. Elektrochem.*, **60**, 1144 (1956); **61**, 956 (1957). d) H. Kokubun, *Naturwiss.*, **44**, 233 (1957).

5. G. Jackson, G. Porter, *Proc. Roy. Soc.*, **A 260**, 13 (1961).

6. N. Mataga, J. Kaifu, *J. Chem. Phys.*, **36**, 2804 (1962).

7. R. H. Acheson, *Acridines*, 1956.

8. L. Bellamy, *Infrared Spectra of Molecules*, IL, 1957.

9. G. Pimentel, *J. Am. Chem. Soc.*, **79**, 3323 (1957).

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