Properties of Phthalimide Phosphorescence

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The phosphorescence lifetime of phthalimide in boric acid has been studied in the presence of foreign paramagnetic ($NiCl_2$) and diamagnetic (KBr, KI) molecules in solution. It is shown that the intermolecular effects of foreign heavy atoms on the singlet-triplet transitions are negligible.

Studies of the luminescence of many organic compounds in solid solutions have led to the conclusion that besides fluorescence ($S_1 \to S_0$ transition) and α-phosphorescence ($T_1 \rightsquigarrow S_1 \to S_0$ transition) the β-phosphorescence ($T_1 \to S_0$ transition) is at room temperatures particularly efficient in some organic molecules. These phenomena cannot be understood on the basis of classical selection rules forbidding the electron transition in molecules between singlet and triplet states. Another property of the phosphorescent states was investigated by Yuster and Weissman[1], Clementy and Kasha[2] and Pankeeva[3]: diamagnetic foreign molecules enhance the $S_1 \rightsquigarrow T_1$ transition probability, on the other hand paramagnetic foreign molecules enhance the $T_1 \rightsquigarrow S_0$ radiationless transition probability.

The intramolecular heavy-atom effect on the emission of aromatics was also investigated, by McClure[4]. He attributed this effect to the spin-orbit perturbation of the heavy halogen atom on the emitting $\pi\pi^*$ triplet state ($T_{\pi\pi^*}$). The intramolecular mechanism of the heavy-atom effect on the $\pi^* - n$ phosphorescence was examined theoretically by Clementy and Kasha[5] for pyridine, El-Sayed[6] for aza heterocycles and carbonyls and Plotnikov[7] for other molecules with a $C=O$ group.

Intermolecular heavy-atom effects on the triplet-singlet emision of aromatics were observed in ethyl iodide solvent by Kasha[8] and McGlynn with co-workers[9]. It was concluded that the singlet-triplet transitions in carbonyls are negligible (Robinson[10]).

Phthalimides and some of their derivatives exhibit phosphorescence emission in rigid solution at temperatures of 293 °K and 90 °K (Neporent and Iniushin[11], Mokeeva and Sveshnikov[12], Pohoski[13]) but the nature of the phosphorescence state of phthalimides was not investigated.

This paper is concerned with the interaction mechanism of excited phthalimide molecules with foreign diamagnetic (KBr, KI) and paramagnetic ($NiCl_2$) molecules. The presence or absence of interaction of excited phthalimide molecules with foreign admixtures will shed some light on the nature of the phosphorescent state of phthalimides.

Phthalimide dissolved in boric acid exhibits $T \to S_0$ phosphorescence at 293 °K but does not fluoresce. At 90 °K the phosphorescence spectra show vibrational structure (Fig. 1). The average spacing between successive bands of progression is $\sim 1100\ cm^{-1}$ and this frequency cannot be assigned to the totally symmetric $C=0$ stretching vibration with frequency $\sim 1650\ cm^{-1}$ in carbonyls of lowest $n\pi^*$ triplet state. On the other hand the phosphorescence of phthalimide has a longer lifetime ~ 1 sec. It is generally accepted that these facts indicate that the lowest triplet state in this molecule is of $\pi\pi^*$ nature.

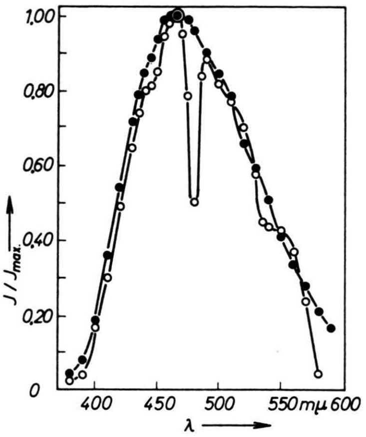

Fig. 1. Phosphorescence spectrum of phthalimide in boric acid ● — at 293 °K, ○ — at 90 °K.

The absence of fluorescence in phthalimide molecules is a result of the great probability of $S_1 \rightsquigarrow T_1$ conversion. Theoretical considerations of the abovementioned authors stated that the probability of $S_1 \rightsquigarrow T_1$ conversion between states of different nature ($S_{n\pi^*} \rightsquigarrow T_{\pi\pi^*}$ and $S_{\pi\pi^*} \rightsquigarrow T_{n\pi^*}$) is $10^2 - 10^3$ times greater than the conversion probability between states of the same nature $S_{n\pi^*} \rightsquigarrow T_{n\pi^*}$ and $S_{\pi\pi^*} \rightsquigarrow T_{\pi\pi^*}$ and greater than the probability $S_1 \to S_0$ of fluores-

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cence transition. These effects arise from strong spin-orbit interaction of $n\pi^*$ and $\pi\pi^*$ states. Therefore in the case investigated in the present paper the $T_1 \rightarrow S_0$ phosphorescence of phthalimide and absence of fluorescence arise from the non-farbidden intramolecular transition $S_{n\pi^*} \rightsquigarrow T_{\pi\pi^*}$, $T_{\pi\pi^*} \rightarrow S_0$ and from the less probable transition $S_{n\pi^*} \rightsquigarrow S_0$, $S_{\pi\pi^*} \rightarrow S_0$.

It can be seen from our measurements of phosphorescence lifetime (Figs. 2 – 4) that the diamagnetic and paramagnetic foreign molecules do not influence the radiative and radiationless processes of phthalimide in boric acid medium. The phosphorescence lifetime of phthalimide molecules in the phosphorescent triplet $T_{\pi\pi^*}$ state is independent of the concentration of foreign molecules. These results show that the intramolecular interaction is greater than the intermolecular one. The intermolecular heavy-atom effects on radiationless transitions $S_{n\pi^*} \rightsquigarrow T_{\pi\pi^*}$ and radiative $T_{\pi\pi^*} \rightarrow S_0$ transitions are thus negligible.

It is worth noting that the phosphorescence intensity of phthalimide in polymethylmethacrylate strongly depends on the presence of oxygen molecules. We think that the oxygen molecules enhance the probabality of $T_1 \rightsquigarrow S_0$ radiationless transitions. Oxygen and $NiCl_2$ molecules are paramagnetic and the different effect of these molecules on the phosphorescence emission of phthalimide is not clear to us.

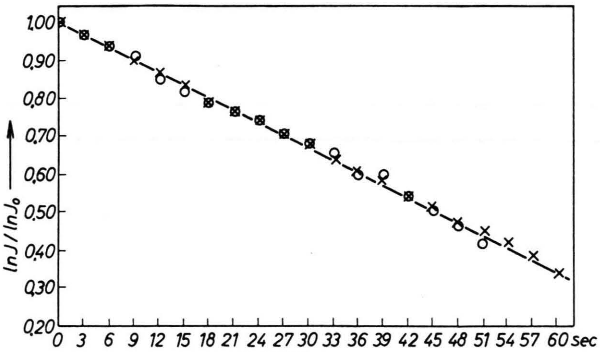

Fig. 2. Decay of phthalimide phosphorescence in boric acid. Concentration of phthalimide in gramme per gramme: × – 5×10^{-4}, ○ – 5×10^{-3}.

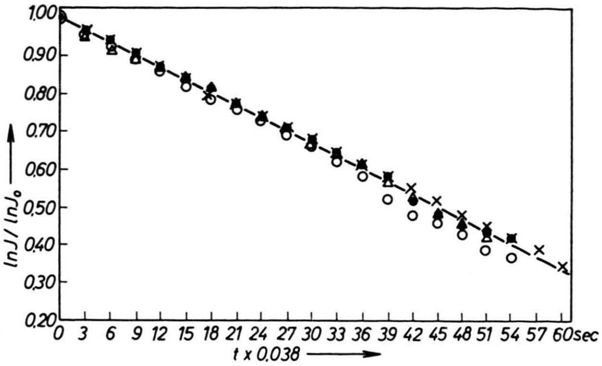

Fig. 3. Decay of phthalimide phosphorescence in boric acid. × – phthalimid concentration $C_0 = 5 \times 10^{-4}$ g/g; ○ – $C_0 + 10^{-2}$ g/g $NiCl_2$; △ – $C_0 + 10^{-2}$ g/g KBr; ● – $C_0 + 10^{-2}$ g/g KI.

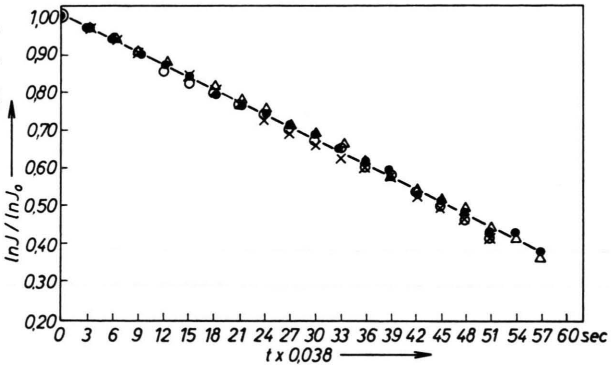

Fig. 4. Decay of phthalimide phosphorescence in boric acid. ○ – phthalimide concentration $C_0 = 5 \times 10^{-3}$ g/g; × – $C_0 + 10^{-2}$ g/g KBr; △ – $C_0 + 3 \times 10^{-2}$ g/g KBr; ● – $C_0 + 5 \times 10^{-2}$ g/g KBr.