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Abstract

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THE INFLUENCE OF HEAVY HALOGENS ON THE PROBABILITY OF TRANSITION TO THE METASTABLE STATE AND ON THE PROBABILITIES OF DEACTIVATION OF THIS STATE

(Presented by Academician A. A. Lebedev on 26 X 1959)

In works ($^{1-5}$) there is an indication that halogens increase the probabilities of intercombination transitions. In (^{6}) it was shown that the presence of salts of hydroiodic acid in solid alcoholic solutions of certain luminescent compounds leads to a sharp increase in the absolute yields of phosphorescence (q_{phosph}). This fact was interpreted as direct evidence for the previously expressed assumptions (^{7,8}) that quenching of fluorescence by iodides is reduced to an increase in the probability of transition of excited molecules to the metastable state.

The purpose of the present work is, on the one hand, to show by more striking examples that the action of quenchers of the halide type on the fluorescence of organic compounds is reduced to an increase in the probability of transition of excited molecules to the metastable state (r), and, on the other hand, to investigate the influence of these quenchers on the probabilities of transitions from the metastable state to the ground state without emission (q_2) and with emission (π).

As was indicated in (^{6}), an increase in q_{phosph} under the action of iodides is possible in those compounds for which the increase in r under the action of iodine sufficiently strongly exceeds the increase in q_2. In the present work, in addition to salts of hydroiodic acid, bromides were used as quenchers—it could be assumed that bromides, being weaker quenchers, would increase q_2 less, as a result of which the change in r would be less masked by quenching at the metastable level, and the action of the quencher on π would be more evident. In addition, in order to achieve higher q_{phosph} in some cases and more conspicuous quenching of fluorescence in other cases, concentrations of iodides higher than in (^{6}) were used in the present investigation.

Table 1 gives the values of the absolute yields of fluorescence q_{fl} and phosphorescence q_{phosph} and of the phosphorescence decay rates v^* for

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* In the presence of quenching impurities the law of phosphorescence decay deviates appreciably from an exponential one, and the relative rate of change of intensity with time decreases. As McClure already noted ([1]), this experimental fact cannot be considered unexpected. In the presence in the solution of foreign impurities the probability of deactivation of excited molecules located at different distances from impurity molecules is, generally speaking, different. Since in the initial stages of afterglow the molecules deactivated are mainly those located near the quencher, the decay rate in the initial stages is greater than in the later stages. Since the decay law in the presence of impurities is nonexponential, the afterglow rate cannot be characterized by means of the phosphorescence τ. In the present work the change in the duration of phosphorescence is characterized by the relative decay rate

$$v = -\frac{dI}{dt} \cdot \frac{1}{I}$$

and τ_{phosph}, obtained as a result of approximating a section of the curve by an exponential, at the moment of afterglow corresponding to 0.03–0.04 sec after the cessation of excitation.

at definite concentrations of the salts of hydroiodic and hydrobromic acids in solutions of organic substances in methyl alcohol. The data given are the result of averaging 3–10 independent measurements.

Table 1

Substance No.	Impurity composition	Impurity conc., mol/l	$q_{\text{sum. rad}}$	q_{fl}	q_{phosph}	ν, sec^{-1}	τ, sec.
I	–	–	0.75	0.68	0.07	0.77	1.30
I	C_1	0.60	0.34	0.16	0.18	4.35	0.25
I	C_2	2.35	0.35	0.02	0.30	9.0	0.11
I	C_3	3.15	0.40	0.00	0.40	10.0	0.10
I	C_4	4.3	0.78	0.50	0.28	8.3	0.12
II	–	–	0.06	0.03	0.03	0.77	0.30
II	C_1	0.60	–	–	–	5.0	0.20
II	C_2	2.35	0.16	0.00	0.16	5.0	0.20
II	C_3	3.15	0.31	0.00	0.31	6.3	0.16
II	C_4	4.3	0.27	0.01	0.26	7.7	0.13
III	–	–	0.41	0.10	0.30	0.97	1.03
III	C_2	2.35	0.11	0.01	0.10	–	–
III	C_4	4.3	0.71	0.01	0.70	4.76	0.21
IV	–	–	0.52	0.22	0.30	1.64	0.61
IV	$C_2/2$	1.65	–	–	–	5.0	0.20

Substance No.	Impurity composition	Impurity conc., mol/l	$q_{\text{sum. rad}}$	q_{fl}	q_{phosph}	ν, sec^{-1}	τ, sec.
IV	C_2	2.35	0.08	0.005	0.075	5.0	0.20
IV	C_4	4.3	0.50	0.03	0.47	10	0.10
V	–	–	0.52	0.40	0.12	1.64	0.61
V	$C_2/4$	0.59	0.39	0.16	0.23	–	–
V	$C_2/2$	1.2	0.34	0.04	0.30	2.2	0.45
V	$C_2 \cdot 3/4$	1.8	0.45	0.03	0.42	–	–
V	C_2	2.35	0.55	0.020	0.43	6.3	0.16
V	C_3	3.15	0.51	0.00	0.51	12.5	0.08
V	C_4	4.3	0.52	0.17	0.35	5.8	0.17
VI	–	–	0.70	0.00	0.70		$1.3 \cdot 10^{-4}$
VI	–	–	0.63	0.03	0.60		$1.4 \cdot 10^{-3}$
VII	–	–	0.50	0.40	0.10	–	–
VIII	$C_1/2$	0.60	–	–	0.20	–	–
VIII	C_2	2.35	0.085	0.02	0.065	–	–
VIII	C_3	3.15	0.02	0.00	0.02	–	–
IX	–	–	0.45	0.42	0.03	9.0	1.1
IX	C_1*	0.60	–	–	0.09	2.8	0.35
IX	C_2	2.35	–	–	0.125	5.0	0.2
IX	C_3	3.15	–	–	–	7.7	0.13
IX	C_4	4.3	0.25	0.17	0.08	4.3	0.22
X	–	–	0.65	0.00	0.65	2.1	0.48
X	C_2	2.35	0.66	0.00	0.66	–	–
X	C_3	3.15	–	–	–	6.7	0.15
X	C_4	4.3	0.82	0.00	0.82	3.7	0.27

* A misprint was allowed in work (6).

Note. I –4-acetylamino-N-methylphthalimide; II –4-acetylamino-N-phenylphthalimide; III –3-acetylamino-N-methylphthalimide; IV –3-methylacetylamino-6-acetylamino-N-methylphthalimide; V –3,6-diacetylamino-N-methylphthalimide; VI –3-acetylamino-6-iodo-N-methylphthalimide; VII –3-acetylamino-6-bromo-N-methylphthalimide; VIII –β-acetylaminonaphthalene; IX –β-naphthylamine; X –Michler’ s ketone.

Designation for impurity composition: $C_1 = 0.1$ g/cm^3; $C_2 = 0.4$ g/cm^3 KJ + 0.25 g/cm^3 NaJ; C_3 –0.1 g/cm^3 KJ + 0.25 g/cm^3 NaJ + 0.20 g/cm^3 iodohydrogen cyclohexylamine; $C_4 = 0.15$ g/cm^3 LiBr + 0.15 g/cm^3 NaBr + 0.20 g/cm^3 bromohydrogen cyclohexylamine.

The method used for measuring the absolute yields of luminescence at −180° is described in (6). The study of phosphorescence decay was carried out on the apparatus of B. Ya. Sveshnikov and P. I. Kudryashov, and short durations were measured on the taumeter of N. A. Tolstoi and P. P. Feofilov*.

The use of high concentrations of salts of hydroiodic and hydrobromic acids required the simultaneous introduction into the solutions of several salts of each of the acids. A preliminary control experiment showed that different salts of the same hydrohalic acid produce an identical effect: at the same molar concentration they lead to exactly the same action on the luminescence yields and on the phosphorescence lifetimes. For example, for substance (I), potassium iodide and sodium iodide at a concentration $C = 0.6$ mole/liter lead to a decrease in $q_{\text{sum. rad}}$ to 0.34 and to an increase in q_{phosph} to 0.18. In both cases the phosphorescence lifetime at the initial stage of decay falls to 0.25 sec.

The absence of additional measurement errors and of complicating circumstances associated with the introduction of large concentrations of halides into the solutions is demonstrated by the following experiment. For nonphosphorescent 4-amino-*N*-methylphthalimide, q_{fl} in alcohol at 180° is equal to 1. Addition of bromides to a solution of this substance does not cause phosphorescence to appear, and q_{fl} remains equal to 1. That is, if the fraction of molecules passing into the metastable state is not changed by the action of halides, then the value of the measured luminescence yield also does not change.

The use of salts of hydrobromic acid and of iodide concentrations higher than those used in (6) made it possible, first of all, to reveal more pronounced cases of increase in q_{phosph} under the influence of quenchers. With a bromide content in solid alcoholic solutions at $C = 4.3$ mole/liter, an increase in q_{phosph} was observed in all the cases studied. For substance (IV), q_{phosph} increased by more than a factor of 1.5; for substances (V) and (IX), by almost a factor of 3; for (I), by a factor of 4; and for (II), by almost an order of magnitude. In a number of cases q_{phosph} reaches high absolute values (for example, 0.82 for (X) and 0.70 for (III)).

A decrease in $q_{\text{sum. rad}}$ is observed only for substance (IX). On the contrary, in three cases there is an increase in $q_{\text{sum. rad}}$ (by a factor of 1.7 for (III), by a factor of 1.25 for (X), and by a factor of 4.5 for (II)). In several cases $q_{\text{sum. rad}}$ remains unchanged upon introduction of bromides (for (I), (IV), and (V)).

When salts of hydroiodic acid are introduced into solutions of organic substances, an increase in q_{phosph} was found in four cases out of the eight studied. For (I) and (II), as the concentration of the quencher is increased, q_{phosph} increases,

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and at $C = 3.15$ mole/liter q_{phosph} becomes equal to 0.40 for (I) and 0.31 for (II), thus increasing by factors of 6 and 10, respectively. An increase in $q_{\text{sum. rad}}$ in the presence of iodides was obtained only for (II).

In all cases, simultaneously with the increase in q_{phosph}, a strong decrease in the phosphorescence lifetime is observed. At the high q_{phosph} and $q_{\text{sum. rad}}$ values observed for many substances in the presence of bromine, the shortening of the phosphorescence lifetime cannot be ascribed to quenching of the metastable state. Evidently, the shortening of the lifetime is determined by an increase in the probability of a radiative transition from the metastable level to the ground π.

A quantitative comparison of the luminescence yields and phosphorescence lifetimes makes it possible to verify in a number of cases that the presence of iodine in the solution also leads to a sharp increase in π: the decrease in lifetime under the action of iodine is considerably greater than that which would be observed if one assumed that the deficit of $q_{\text{sum. rad}}$ to 1 were due to quenching at the metastable level.

The influence of halogens on π is especially pronounced when bromine and iodine are present directly in the luminescing molecule. Thus, in the case of 3-acetylamino-6-iodo-*N*-methylphthalimide (VI), the phosphorescence has a lifetime of $1.3 \cdot 10^{-4}$ sec, while $q_{\text{sum. rad}} = q_{\text{phosph}} = 0.7$. Thus, deactivation by nonradiative processes accounts for only 30% of all absorbing molecules. It is therefore clear that the decrease in τ_{phosph} for (VI), relative to that for 3-acetylamino-*N*-methylphthalimide (1.05 sec), cannot be explained by the appearance of strong quenching at the metastable level in the iodine-derivative compound.

It remains to accept that the introduction of iodine into the molecule of the luminescent substance significantly increases π. An identical conclusion can be drawn from the example of 3-acetylamino-*N*-methylphthalimide.

High absolute values of $q_{\text{sum. rad}}$ in the presence of bromine in the medium indicate that q_2, as a rule, is smaller than π.

On the contrary, the introduction of iodine into the solution in most cases leads to such a strong increase in q_2 that quenching at the metastable level leads to a decrease not only in $q_{\text{sum. rad}}$, but also in q_{phosph}. Since iodine acts much more strongly on q_{fl} than bromine, while quenching by halides is determined only by an increase in r, it may be concluded that iodine increases r more strongly than bromine.

The greatest decrease in $q_{\text{sum. rad}}$ (by more than a factor of 20) is observed for (VIII). The decrease in $q_{\text{sum. rad}}$ is accompanied by a fivefold decrease in q_{phosph}. A decrease in $q_{\text{sum. rad}}$ with a simultaneous fall in q_{phosph}, although less pronounced than in (VIII), is also found for (III) and (IV). Only in the case of the weakest decrease in $q_{\text{sum. rad}}$, for (I), is a simultaneous increase in q_{phosph} observed.

Thus, the use of the less active quencher—bromine—and of high concentrations of iodine has made it possible to obtain a number of very clear examples of an increase, under the action of a quencher, both in q_{phosph} and, as a result of this, in $q_{\text{sum. rad}}$. These examples unequivocally show that the quenching action of halides consists in the transfer of excited molecules into the metastable state. The increase in $q_{\text{sum. rad}}$ in several cases is explained by the fact that, at an increased probability of transitions to the metastable state, these transitions successfully compete with radiationless transitions from the labile level to the ground level, on whose probability iodine and bromine evidently have no effect. That the quenching of fluorescence under the action of halides is determined only by an increase in the probability of transition to the metastable state is indicated by a number of observed cases in which $q_{\text{sum. rad}}$ rises to high absolute values, as well as by the aforementioned example of 4-amino-*N*-methylphthalimide, in which there is no transition of excited molecules to the metastable state and, as a result, q_{fl}, equal to 1, does not change when halides are introduced into the solution.

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