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1960

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

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LUMINESCENCE SPECTRA OF HALOGEN DERIVATIVES OF ANTHRAQUINONE IN FROZEN SOLUTIONS

(Presented by Academician A. N. Terenin, February 11, 1960)

The present work is devoted to the study of the structure and mutual influence of atoms and groups of excited molecules from their luminescence spectra. We have shown ([1]) that, for solving these problems, the method of frozen solutions of E. V. Shpolskii ([2]) can be successfully used, making it possible to obtain electronic-vibrational spectra with fine vibrational structure.

In the present work, for the stated purpose, we studied the luminescence spectra of α- and β-halogen derivatives (F, Cl, Br, and I) of anthraquinone in solutions of n-paraffins at 77°K ($C = 10^{-4} \div 10^{-5}$ mol $\cdot$ l^{-1}) under excitation with $\lambda_{\mathrm{Hg}} = 313$ m . Taking into account the structural features of α- and β-halogen derivatives of anthraquinone, one should expect substantial differences in their spectra. α-Substitution of a hydrogen atom by a halogen atom leads to a substantial nonequivalence of the two carbonyl groups of the anthraquinone ring, since one of the groups C = O and > C − −Hal can noticeably influence the other through π-electron interaction, because they simultaneously interact with the same carbon atom. This is not the case for β-derivatives; therefore their carbonyl groups are almost equivalent. It is also necessary to take into account the influence of the nature of the halogen atom on the spectra of α- and β-substituted anthraquinone. It is known that the electronegativity of atoms decreases in going from fluorine ($E = 4$) to iodine ($E = 2.4$). The electronegativities of iodine and carbon ($E = 2.5$) are close. In this connection, the probability of participation of the unshared electron pairs of the halogens in the π-electron interaction will increase in going from fluorine to iodine, which is consistent with the energy expenditure for their excitation.

Thus, for the F atom a strong inductive effect is characteristic, which may lead to a certain deformation of the π-electron density at the nearest carbon atoms, equivalent to some shortening of the conjugated chain. Therefore the introduction of fluorine may lead to a shift of bands into the short-wavelength region of the spectrum. For atoms Cl, Br, and especially I, participation of unshared electron pairs in the π-electron interaction of the molecule is characteristic, which may lead to lengthening of the conjugation chain and, consequently, to a shift of bands toward longer wavelengths. The indicated differences in the behavior

of halogen atoms should be especially strongly manifested in the excited state of the molecules.

The substantially different sizes of the halogen atoms may also lead to their unequal influence on the luminescence spectra of α-halogen derivatives of anthraquinone. If the F atom, by virtue of its size ($R_b = 1.35$ Å), cannot exert a steric deforming influence on the C = O group, then the atoms Cl and especially Br and I ($R_b = 2.15$ Å) will exert such an influence. Between the halogen atoms (Cl, Br, and especially I), which have large atomic radii, and the oxygen atom of the C = O group, repulsive forces arise, leading to distortion of the valence angles of the bonds $>$ C = O and $>$ C $-$ –Hal

and to some change in the electronic state of the group. This indeed occurs in analogous molecules. It should also be expected that the nature and position of the halogen atoms in the anthraquinone ring should influence the intensity and the character of its change in the electronic-vibrational spectra of the molecules.

The experimental study carried out on the luminescence spectra of halogen derivatives of anthraquinone confirmed the assumptions stated above. Fine vibrational structure was obtained for all α- and β-monohalogen derivatives.

Table 1

Position (ν cm^{-1}) of components in the principal maxima of the spectra of monohalogen-substituted anthraquinone in heptane. $T = 77$°K (ISP-67)

Maximum No.	Component No.	α-F anthraquinone	β-F anthraquinone	Anthraquinone	β-Cl anthraquinone	β-Br anthraquinone	β-I anthraquinone
Initial band	1	–	22064 weak	22075 weak	–	21804 very int.	21730 very int.
Initial band	2	–	21991 med.	21963 weak	21809 very weak	21732 very int.	21659 very int.
Initial band	3	–	21893 weak	21826 weak	21746 weak	21648 med.	–
1	1	20915 med.	20413 very weak	20296 weak	20188 med.	20131 int.	20053 int.
1	2	20797 int.	20317 int.	20198 int.	20131 int.	20050 int.	19982 int.
1	3	20598 med.	20206 int.	20082 int.	20059 int.	19970 weak	–
2	1	19257 weak	18759 very weak	18611 weak	18523 med.	18466 med.	18390 int.

Maximum No.	Component No.	α-F anthraquinone	β-F anthraquinone	Anthraquinone	β-Cl anthraquinone	β-Br anthraquinone	β-I anthraquinone
2	2	19132 int.	18667 int.	18538 int.	18469 med.	18396 med.	18319 int.
2	3	18929 int.	18561 int.	18419 int.	18402 med.	18305 weak	–
3	1	17598 weak	17076 very weak	16962 weak	16886 med.	16822 med.	16744 med.
3	2	17458 int.	17010 med.	16887 int.	16823 med.	16747 med.	16670 med.
3	3	17269 int.	16912 med.	16771 very int.	16752 med.	16663 weak	–

The corresponding components of the electronic-vibrational bands (as also in the spectra of other anthraquinone derivatives with fine vibrational structure) are separated from one another on average by a distance of 1665 cm^{-1}, which characterizes the frequency of the valence vibration of the C=O group in the ground electronic state. However, the spectra of α-chloro-, α-bromo-, and α-iodoanthraquinone were less rich in lines and had a continuous background in the long-wavelength part of the spectrum (Table 1, Fig. 1). The spectra of these α-halogen derivatives are similar to one another and in many respects resemble the spectra of anthraquinone.

The spectrum of α-fluoroanthraquinone differs sharply from the spectra of the other α-halogen derivatives of anthraquinone. The diffuseness of the bands increases on going from octane to hexane, whereas for other α-halogen derivatives and for anthraquinone the opposite pattern is observed. In an octane solution, a doublet splitting of the most intense components of the principal maxima is found. In contrast to other α-monohalogen-substituted compounds, the spectra of α-fluoroanthraquinone show a considerable shift, into the short-wavelength region, of the positions of the principal maxima of the spectrum in comparison with the principal maxima of the anthraquinone spectrum ($\Delta\nu$ = 480–630 cm^{-1}).

In the spectrum of α-fluoroanthraquinone, in addition to the intense principal maxima shifted toward shorter wavelengths relative to the corresponding maxima of anthraquinone, less intense bands are also observed which, in structure and position, coincide with the principal bands of anthraquinone.

It was further found that in the spectrum of the 1,5-difluoro derivative the weak maxima characteristic of anthraquinone disappear.

On the other hand, in the spectra of 1,5-dichloro-, 1,5-dibromo-, and 1,5-diiodo

derivatives, fine vibrational structure is not observed. The spectra of these compounds become similar to the diffuse region of the spectra of α-Cl-, α-Br-, and α-I derivatives of anthraquinone. These facts can be explained on the basis of the assumption that there exist two electronic ($n \rightarrow \pi^*$) transitions for α-monohalogen derivatives of anthraquinone, associated with the presence in these compounds of two nonequivalent carbonyl groups. The values of the probabilities (intensities) of these $n \rightarrow \pi^*$ transitions depend strongly

from the state of the C=O groups. In the case of the α-Cl-, α-Br-, and α-I-monoderivatives of anthraquinone, the spectrum with fine vibrational structure, similar to the spectrum of anthraquinone, is apparently due to a transition in the free C=O group, while the transition associated with the other C=O group has a low probability and appears as a continuous spectrum, which is probably connected with strong deformation of the C=O bond as a result of the steric factor and the participation of the unshared electron pair of the halogen atom, as discussed above. From this point of view one can explain the absence of a spectrum with fine vibrational structure in the dihalogen derivatives (Cl; Br, I).

In the spectrum of the α-fluoro derivative of anthraquinone both electronic transitions appear, the $n \rightarrow \pi^*$ transition in the nonfree C=O group appearing with considerably greater probability.

This is evidently explained by the fact that the fluorine atom, having a small radius, does not exert a deforming steric influence on the carbonyl group (located in the α position), and, in accordance with its nature, acts as an electronegative atom (inductive effect), while its unshared electron pairs do not participate in the π-electron interaction of the system.

This promotes an increase of the electronic charge on the oxygen atom of the C=O group, which apparently leads to an increase in the probability of the $n \rightarrow \pi^*$ transition in it.

The luminescence spectra of the β-halogen derivatives of anthraquinone exhibit fine vibrational structure (Table 1, Fig. 1). The influence of the solvent is manifested in the different multiplicity of the principal electron-vibrational bands and in a change in the relative intensity of their components. The influence of the nature of the halogen atom located in the β position appears in the luminescence spectra in the fact that, on passing from fluorine to chlorine, bromine, and iodine, the position of all components of the principal maxima is shifted regularly to the long-wavelength side by (100—150 cm^{-1}). Anthraquinone occupies an intermediate position between β-fluoroanthraquinone and β-chloroanthraquinone (Table 1), which is in complete agreement with the assumptions made above. The participation of the unshared electron pairs of iodine and bromine atoms in the π-electron interaction of the system at the moment the molecule emits light leads to a different law of distribution of band intensities in the spectra, one different from the law of their distribution in the spectra of anthraquinone and other α- and β-derivatives of anthraquinone having spectra with fine vibrational structure. If in the latter cases, on going from the violet to the red region of

Luminescence spectra

Figure 1: Luminescence spectra

the spectrum, the band intensity first increases and, after reaching a certain maximum, again decreases, then in the spectra of the β-bromo- and especially the β-iodo derivatives a gradual decrease in band intensity is observed (Fig. 1).

In the spectra of β-bromo- and β-iodoanthraquinone the most intense bands are the short-wavelength bands, which, in accordance with the Franck–Condon principle, can be explained by a small change in the internuclear equilibrium distance for the excited electronic level. Therefore, in the case of the β-bromo- and β-iodo derivatives of anthraquinone, the O''—O' transition is allowed as a consequence of the Franck–Condon principle. For an exact determination of the frequency of the O''—O' transition it is necessary to know the absorption spectra of the compounds under the same conditions, but this has not yet been possible. If the first, most intense short-wavelength bands in the spectra of the β-bromo- and β-iodo derivatives are taken as the O''—O' transition, then the frequency values corresponding to the purely electronic transitions will be 21730 cm^{-1} (β-I) and 21804 cm^{-1} (β-Br). Thus, in the excited molecules of the β-bromo- and especially β-iodo derivatives of anthraquinone, owing to the effective participation of the unshared electron pairs of the halogen atoms, no substantial changes occur in the distribution of electron density in the C=O groups, in contrast to anthraquinone and its other derivatives.

Fig. 1. Luminescence spectra of anthraquinone and its halogen derivatives in heptane at 77°K, $\lambda = 313$ mμ.
1 –α-fluoroanthraquinone; 2 –β-fluoroanthraquinone; 3 –anthraquinone; 4 –β-chloroanthraquinone; 5 –β-bromoanthraquinone; 6 –β-iodoanthraquinone.

This, apparently, is associated with the increase in the relative luminescence yield for the β-bromo and β-iodo derivatives. For most monohalogen derivatives of anthraquinone, phosphorescence is observed (with an afterglow duration from 2 to 10 sec.). This question requires special investigation.

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Received
10 I 1960

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