MODEL FOR THE PHOTODISSOCIATION OF ARYL HALIDES

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Summary

A simple localized model has been developed to explain the mechanism of photodissociation of some aryl halides. The results agree with the experimental data. The anomalously long lifetimes of the bromonaphthalenes have been rationalized in terms of unfavourable Franck–Condon factors.

1. Introduction

In the past years some experiments on the photodissociation of the aryl halides have shown interesting differences in the lifetimes of their excited states [1]. The most striking difference has been found between the iodo- and bromo-substituted naphthalenes, their lifetimes differing by two orders of magnitude [2].

In order to explain these discrepancies, we propose in this paper a simple model based on a localized picture of the relevant states involved in the predissociative process. This model is used to calculate the predissociative probability of the S_1 state of iodobenzene and of the S_2 state of iodo- and bromo-substituted naphthalenes. Although more thorough theoretical approaches to the phenomenon of predissociation in small molecules have recently stressed the importance of taking into account all nuclear motions [3], we consider that an approximate localized picture can be useful in the explanation of the photophysical behaviour of relatively large systems.

2. Outline of the treatment

A photodissociation process can occur either directly, with absorption of the light into a dissociative state of antibonding nature, or indirectly. While the alkyl halides undergo direct photodissociation, there is clear evidence that the aryl halides follow a predissociative mechanism [2] according to the reaction

$$Ar—X \rightarrow [Ar—X]^* \rightarrow Ar\cdot + X\cdot \tag{1}$$

In this case the light is first absorbed by a $\pi\pi^*$ state delocalized on the aromatic frame and after a relaxation period the energy is transferred in a radiationless manner to a dissociative state. Experiments on the photodissociation of molecular beams have shown that the excited state involved is S_1 (^1L_b), long axis polarized for the phenyl iodide, and S_2(^1L_a), short axis polarized for the naphthyl halides [2]. The rate of the predissociative process is governed by the "golden rule" expression [4]

$$W = \frac{2\pi}{\hbar} |V_{12}|^2 F \tag{2}$$

where V_{12} represents the matrix element of electronic interaction between the states involved and F is the Franck—Condon (FC) factor between the initial vibrational state and the continuum of vibrational states degenerate with it in the final manifold. While the calculation of V_{12} requires a detailed knowledge of the electronic wavefunctions involved, the evaluation of F can be made on the basis of the corresponding energy curves. Therefore, in order to calculate W we specify the initial and final states as follows.

(1) The initial state is a singlet $\pi\pi^*$ bonding state which is delocalized on the aromatic part of the system (S_2 for naphthyl halides, S_1 for iodobenzene) with energy given by the corresponding 0—0 transition (Table 1). Since the excitation is essentially localized on the aromatic part of the system, the potential curve for C—X may be taken to be identical to that of S_0 and described by a Morse-type potential curve [7]. The use of parameters of the ground state for the excited states is justified by the relatively small variation of charge on the halogen atom and of the C—X bond order during the excitation [5].

(2) The final state is a dissociative triplet $\pi\sigma^*$ state localized on the C—X bond. The description of this potential curve could be given using a valence bond scheme as done in ref. 8 for the C—H bond. However, in view of the difficulties of treating the atomic orbitals of heavy atoms with sufficient accuracy, we have adopted here the simpler and more approximate description obtained from the analysis of the dissociative spectra of the alkyl halides [7]. This approximation is based on the extremely localized character of the C—X bond, which is indicated by the following facts:

(i) the absorption spectra of alkyl halides show very little dependence on the length of the alkyl chain and on the size of the molecule [7];

(ii) the complicated spectrum of phenyl iodide in the zone of the first transition (about $40\,000$ cm^{-1}) has been successfully explained as the superposition of the absorption band of benzene ($^1B_{2u}$) and the diffuse band of the C—I system [9] which is assumed to be the same as that of CH_3I in the same region of the spectrum;

(iii) the results of a calculation based on the molecules in molecules (MIM) scheme [17] show little contribution of charge transfer configurations to the total wavefunction of the S_2 state of the naphthyl halides, as reported later.

TABLE 1

Excited states energies, spin–orbit matrix elements and photodissociative lifetimes of the aryl halides

Compound	Excited state (cm^{-1})	V_{12} (cm^{-1})	τ(calc) (s)	τ(exp)[a] (s)	τ_{Br}/τ_I
Iodobenzene	S_1 38962[b]	1014	0.33×10^{-12}	0.5×10^{-12}	
α-Iodonaphthalene	S_2 33970[c]	580	1.4×10^{-12}	0.9×10^{-12}	
α-Bromonaphthalene	S_2 34634	197	1.1×10^{-9}	about 10^{-10}	783
β-Iodonaphthalene	S_2 35154	209	1.2×10^{-12}	about 10^{-12}	
β-Bromonaphthalene	S_2 35394	121	0.7×10^{-9}	about 10^{-10}	564

[a]Ref. 2; [b]ref. 5; [c]ref. 6.

Analysis of the absorption spectra of the carbon—halogen systems of ref. 7 shows a maximum at about 50 000 cm^{-1} for C—Br, compared with 40 000 cm^{-1} for C—I, and a steeper dissociative curve for C—Br. In the absorption region of the naphthyl halides (about 35 000 cm^{-1}) the initial potential curve crosses the dissociative triplet at different distances from the equilibrium point and this causes large differences in the Franck—Condon factors involved (Fig. 1).

Once the relative position and shape of the states of the composite system have been defined, the FC factors are evaluated using the exact solution of the Morse potential for the initial vibrational states and the delta function approximation for the dissociative triplet state nuclear wavefunctions [8].

3. Evaluation of the electronic matrix element

Owing to the different spin symmetry of the initial and final states involved, the electronic factor V_{12} is expressed as an integral over the spin—orbit operator H_{so} [4] :

$$V_{12} = \langle S_i(\pi\pi^*)|H_{so}|T_f(\pi\sigma^*)\rangle \tag{3}$$

where S_i ($i = 1$, for iodobenzene, $i = 2$ for naphthyl halides) stands for the initial singlet state and T_f for the final dissociative triplet. If we expand the
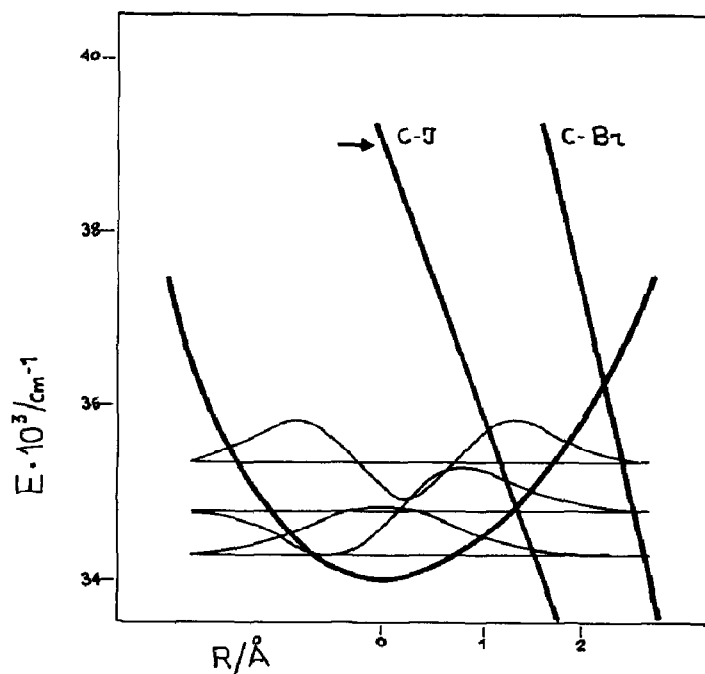

Fig. 1. The Morse potential curve with the first three vibrational wavefunctions for the system C—I and the dissociative curves for C—I and C—Br in the zone of absorption of S_2 for the naphthyl halides. The arrow shows the resonance coordinate for iodobenzene.

relevant states in terms of configurations, restrict ourselves to one-centre terms and assume that the contribution of the halogen atom is much larger than the contributions of the others, we obtain the relationship [10]

$$V_{12} \approx \langle \pi_i^* | H_{so} | \sigma_f^* \rangle \approx c_{i\mu X} \, c_{f\nu X} \, \frac{\zeta(\mu\nu)_X}{2} \tag{4}$$

where $c_{i\mu X}$ and $c_{f\nu X}$ represent the coefficients of the atomic orbitals $\mu(p_z)$ and $\nu(p_z)$ centred on the halogen X (=Br,I) in the initial and final states respectively, and $\zeta(\mu\nu)_X$ is the atomic spin–orbit coupling factor for an electron in atomic orbitals μ and ν on centre X. In order to evaluate these coefficients we specify the electronic states as follows. The σ^* molecular orbital which involves halogen and carbon $p\sigma$ atomic orbitals is assumed to be completely localized and antibonding in nature, i.e. of the form

$$\frac{1}{2^{1/2}}\left(\frac{1}{3^{1/2}} s_C + \frac{2^{1/2}}{3^{1/2}} p_{x\,C} - p_{x\,X} \right) \tag{5}$$

The coefficients of the halogen atom in the π^* orbital, however, can be estimated from the electron density change on excitation and from the population of the highest occupied orbital of the molecule [11]. While several calculations based on the MIM scheme or PPP model have been performed on the substituted benzenes [5, 12], no such calculations are available for the halo-substituted naphthalenes. Therefore a MIM calculation on these molecules has been carried out, adopting the values of ref. 5 for the resonance integrals, the overlap integral S and the C—X distance R. All necessary two-electron integrals have been computed in the point charge approximation and the coefficients of the molecular orbitals for naphthalene in the S_2 state have been calculated with a PPP program with complete configuration interaction over the monoexcited configuration space. The participation of the charge transfer configurations in the S_2 state has been found to be 0.3293 for α-iodonaphthalene, 0.2426 for α-bromonaphthalene and 0.134, 0.1137 for the β-substituted compounds respectively. The analogous figure for iodobenzene in the S_1 state is 0.377 [5]. These results are in qualitative agreement with the larger mesomeric effect which is experimentally found for the iodo-substituted and the α-substituted compounds compared with the bromo- and β-substituted ones [6]. Taking into account the density matrices of refs. 13 and 14 relative to the ground state of the aryl halides, we can finally derive the $c_{p_z X}$ coefficients of eqn. (4). The quantities ζ in eqn. 4 have been taken from ref. 10 and are 5060 cm^{-1} and 2460 cm^{-1} for iodine and bromine respectively. The spin–orbit coupling matrix elements thus evaluated are reported in Table 1.

4. Results and discussion

The results obtained for the photodissociative lifetimes of the aryl halides under consideration are reported in Table 1. Despite the number of

approximations used, the lifetimes are in good agreement with the experimental data, reproducing the right order of magnitude. The large ratio of τ_{Br} to τ_I, which ranges from 564 to 783, depends in part on the ratio of the spin–orbit coupling factors $(\zeta_I/\zeta_{Br})^2 \approx 4$, but principally on the different FC factors because of the different distances and slopes of the dissociative curves for C—I and C—Br. In fact the resonance coordinate R_0 for C—Br is about 1 Å larger than that of C—I and this is responsible for a difference of two orders of magnitude in the relevant FC factors. The short lifetime found for iodobenzene arises from a large spin–orbit coupling element and also from a favourable FC factor, the energy of S_1 (about 39 000 cm^{-1}) corresponding to the maximum overlap of the first vibrational wavefunction with the dissociative continuum of the triplet C—I. For the halonaphthalenes, however, the contribution of the excited vibrational states becomes more important, especially for the bromo-substituted compounds, which must overcome a large energy barrier during the predissociative process. This fact is in agreement with the temperature dependent mechanism proposed for the photodissociation of iodoaromatics in solution [15].

These results indicate that the heavy atom effect, which has been found to be responsible for the different phosphorescence lifetimes of the aryl halides [10], is not the rate-determining factor of the dissociative process. It should be noticed that no account has been taken of the possible different stabilization of the dissociative triplet for the compounds examined. Such a stabilization could reduce the somewhat large ratio found but it should not affect its order of magnitude. In ref. 2, in order to explain the long lifetime of the excited states of the bromo-substituted compounds, a transfer from S_2 to S_1 with subsequent dissociation from S_1 was suggested. However, it has been shown that for naphthalene, β-naphthylamine and β-naphthol in the vapour phase the rate of non-radiative decay of S_2 does not exceed 10^8 s^{-1}, owing to the low density of vibrational states of S_1 corresponding to the zero level of S_2 (the energy gap is about 2100 cm^{-1}) [16]. Moreover, the FC factor from S_1 will be much smaller than that from S_2 and we can conclude that predissociation from S_1 is highly improbable for halonaphthalenes.

Finally we can note that the lifetimes of biphenyl bromide and 9-bromoanthracene, although not quantitatively determined [2], seem to follow the same pattern of the naphthyl bromides and this supports the conclusion of a highly unfavourable FC factor for the bromo-substituted compounds.

Acknowledgment

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