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Competition between Photo-Ionization and Photo-Dissociation of Aromatic Compounds

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Since the pioneering work of Lewis,[1] Porter[2] and their collaborators, it has been widely accepted that the ultraviolet irradiation of substituted aromatics yields their cations or radicals, the latter being formed by the fission of the β-bond of the substituent group. Thus, *p*-phenylenediamine, for instance, forms its cation almost exclusively. Anisole or phenol, on the other hand, forms mainly phenoxyl radical. For some compounds, the assignment of the products by Lewis and Porter was only tentative and lacked conclusive evidence. As far as the author is aware, reasons for such differences in the photo-chemical behaviors of various aromatics do not seem to have been discussed.

We have studied the photo-products of several substituted aromatics irradiated in organic matrices at 77°K.[3-6] In these studies, the assignment of unstable species formed by the ultraviolet irradiation has been reconfirmed using more elaborate techniques. Some new data have also been added.

Some of the results on mono-substituted and *p*-disubstituted benzenes are summarized in Table 1. In the last two columns are indicated the main products formed by the ultraviolet irradiation of these compounds (or ions) in the 77°K matrices. For example, as already mentioned, *p*-phenylenediamines (**1** and **2**) form cations almost exclusively. Hence, for these two compounds, the column headed by "photo-ejection" is marked by + and the column headed by "dissociation" is marded by −, indicating that the main process for these compounds is the photo-ejection of an electron from the parent compound to the matrix.

In the case of *p*-dimethylamino-phenolate anion (**3**), studied in ethanol containing sodium hydroxide, the main process is also the photo-ejection of an electron yielding neutral *p*-dimethylamino-phenoxyl radical. Photo-ejection also prevails in the cases of **4**, **5** and **6**. As for *N*,*N*-dimethylaniline (**7**) and *N*-methylaniline (**8**), our detailed study of the absorption spectra of the photo-products confirmed that both the cation and the β-fission product are formed in the matrix, the former being more abundant in polar matrices such as ethanol. In the case of *p*-dimethoxybenzene (**9**), there is no indication of photo-ionization in ordinary organic solvents. However, we have found that it formed its cation when it is irradiated in a matrix composed of one part acetic acid and one part sulfuric acid at 77°K.[4a] This conclusion was later confirmed by a detailed study of the absorption spectrum of the cation prepared by other methods.[10] In the last three cases, hydroquinone,[4] anisole,[2] and phenol,[2] photo-dissociation is the main process and there was no indication that any cation was formed.

The compounds in the table are tabulated in the order of increasing gas-phase ionization potentials of the parent compounds, I_G. It is evident that the species formed depend strongly on I_G. T shows the (0–0) energy of the lowest triplet level. $I_G - T$ corresponds to the energy necessary for the second step of the photo-ionization. (See next paragraph.) S designates the energy of the first excited singlet state, or, speaking more precisely, gives the approximate absorption edge of the first absorption band. It should be noted that the photo-ejection is prevalent when $S-(I_G-T)$ is positive, and the photo-dissociation prevails when the value is negative. In cases where the value is nearly zero, both processes occur.

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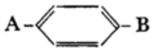
Table 1. Photo-chemical reactions of substituted benzenes*



	A	B	I_G	T	I_G-T	S	$S-(I_G-T)$	Photo-ejection	Dissociation	Reference
1	$N(CH_3)_2$	$N(CH_3)_2$	6.25 7)	2.90	3.35	3.55	+0.20	+	−	3
2	$N(CH_3)_2$	NH_2						+	−	4
3	$N(CH_3)_2$	O^-						+	−	4
4	$N(CH_3)_2$	OCH_3						+	−	4
5	NH_2	OH						+	−	4
6	O^-	OCH_3						+	−	4
7	$N(CH_3)_2$	H	7.14 8)	3.30	3.84	3.82	−0.02	+	+	6
8	$NH(CH_3)$	H	7.35 8)	3.31	4.04	3.87	−0.17	+	+	6
9	OCH_3	OCH_3						−	+	4
10	OH	OH						−	+	4
11	OCH_3	H	8.22 9)	3.61	4.59	4.34	−0.27	−	+	1
12	OH	H	8.52 8)	3.7	4.8	4.4	−0.4	−	+	1

* Energies are given in eV.

It has been established that the photo-ionization of aromatics by the near-ultraviolet light is accomplished by the two-step excitation, with the lowest triplet state as the stepping stone.3,11) The vertical ionization potential of the aromatics in the matrix is only a few tenth eV smaller than I_G, and is almost independent of the polarity of the matrix. Both the photo-ionization and the photo-dissociation processes seem to have small quantum yields, because it takes at least several minutes of strong irradiation to obtain spectra of the products to a measurable amount.

The dissociation energies of the β-bond in the substituted aromatics may be estimated to be about 4 eV, which is about the same order of magnitude as the energies of the S levels and much less than the I_G values. Hence the possibility of one-photon dissociation of aromatics directly from the S states cannot be excluded. Our recent investigation has revealed that in some substituted aromatics, photo-dissociation by ultraviolet light mainly occurs by the two-step biphotonic excitation.12) Anyway it is evident that photo-dissociation needs much less energy per quantum than photo-ionization. That photo-ionization is dominant over photo-dissociation in the compounds with low ionization potentials shows that the latter is a process having much less quantum yields than the former. Thus, only in cases where the former process is energetically forbidden, the products of the latter process will be accumulated.

Based on these arguments, the empirical rule mentioned above concerning the dependence of the products on $S-(I_G-T)$ may be explained in the following way. In the case where $S-(I_G-T)$ is positive, the molecule (or ion) in the triplet state can get ultraviolet light having sufficient energy to excite them to the energy region above the ionization limit. In the case where it is negative, the molecules in the triplet state cannot absorb photons having energies enough to excite them above the ionization limit, because the parent molecule, still abundant in the solution, will screen the light in such regions. In the case where it is almost zero, photoionization may occur to such an extent that it can compete with the photo-dissociation processes.

Validity of the present theory is based on the following facts: 1) the high-pressure mercury lamp used as the light source has considerable intensity even in the wavelength region shorter than 2530 Å (4.8 eV), and 2) the equilibrium concentration of the solute molecules in the triplet state at the time of irradiation is much smaller than that in the ground state. Of course, $S-(I_G-T)$ should be taken as a rough measure, particularly because S is a quantity difficult to define rigorously. More quantitative study is planned in our laboratory for the improvement of the present theory.

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