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Abstract

Full Text

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THE ROLE OF $n \to \pi^*$ TRANSITIONS IN THE PROCESSES OF IONIZATION AND DECOMPOSITION OF COMPOUNDS

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It is known that chromophoric groups C=O ↑↓, $>$ N ↓↑, etc., are responsible for long-wave absorption (as a result of the electronic $n \to \pi^*$ transition) and for the luminescence of compounds (^{1}). Depending on the structure of the molecules, they exhibit different degrees of quasiaromaticity, which is manifested in electron-vibrational spectra obtained at low temperature (^{2}).

Fig. 1. Ionization curves of anthraquinone and fluorenone, obtained on a mass spectrometer with automatic recording.

Fig. 2. *a* —scheme of electronic $n \to \pi^*$- and $\pi \to \pi^*$-transitions in a molecule; *b* —scheme of electronic levels for ionization and decomposition of the anthraquinone molecule.

Molecules (derivatives of anthraquinone, acridone, triphenylamine) containing the indicated groups, when in ($n\pi^*$)-states, are capable under certain conditions of passing into a radical state and generating radicals of the matrix (ethanol, etc.) ($^{3-6}$). The decisive role in these processes of radical formation is played by the electronic $n \to \pi^*$ transition, which leads to the appearance of an additional valence of the heteroatom of the chromophoric group; at the same time one of its valences becomes delocalized over the molecule. Excitation of the additional valence of atoms in molecules upon realization of ($n\pi^*$)-states may play an important role not only in the processes of radical generation, but also in many other chemical reactions and, in particular, in the processes of molecular decomposition upon ionization.

In order to clarify the role of $n \to \pi^*$ transitions in the processes of ionization and decomposition of molecules, we studied the ionization curves and ion-appearance potentials of anthraquinone and fluorenone by the electron-impact method.

The studies were carried out on an MX-1303 chemical mass spectrometer, improved for measuring the ionization potentials of molecules by the method of electron quasi-monoenergetization (7).

Amplification of the ion current (the alternating component) was carried out with an 01 ion counter and a selective amplifier U2-6. The signal was detected by an SD-1 synchronous detector at the modulation frequency of the ionizing-electron beam. The ionization curves were recorded automatically on the mass spectrometer recorder

Table 1

Ion appearance potentials

Molecule	Ion	Energy, eV
Anthraquinone	$[C_6H_4(CO)_2C_6H_4]^+$	9.55 ± 0.05 $^*10.24 \pm 0.0510.80 \pm 0.05$
Anthraquinone	$[C_6H_4COC_6H_4]^+$	10.39 ± 0.05
Anthraquinone	$[C_6H_4C_6H_4]^+$	11.02 ± 0.05
Fluorenone	$[C_6H_4COC_6H_4]^+$	$9.42 \pm 0.0710.05 \pm 0.0710.42 \pm 0.07$
Fluorenone	$[C_6H_4C_6H_4]^+$	10.14 ± 0.07

* According to literature data (8), 9.34 ± 0.03 eV (photoionization).

with periodic repetition in time. The electron energy scale was calibrated by the ionization potential of xenon. The vapors of the substances studied were admitted at a constant temperature of the inlet system and the ionization chamber up to 220°.

Figure 1 shows the ionization curves of anthraquinone and fluorenone molecules, recorded automatically on the recorder tape. Table 1 gives the appearance potentials of the molecular and fragment ions of these molecules.

The first ionization potentials of the anthraquinone and fluorenone molecules, I_n, equal respectively to 9.55 ± 0.05 and 9.42 ± 0.07 eV, as follows from the scheme of the electronic levels of molecules containing chromophoric groups with heteroatoms (see Fig. 2a), correspond to the energies of removal of electrons from the lone pair of oxygen atoms, while the second ionization potentials I_π: 10.24 ± 0.07 and 10.05 ± 0.07 eV correspond to the energies of removal of π-electrons. This conclusion agrees with the fact that the first long-wavelength

Scheme 1: proposed fragmentation of anthraquinone molecule involving ionization, spontaneous $n\pi^*$ transition, and loss of CO groups.

Figure 2: Scheme 1: proposed fragmentation of anthraquinone molecule involving ionization, spontaneous $n\pi^*$ transition, and loss of CO groups.

band of the absorption spectrum of the anthraquinone molecule corresponds to an electronic $n \to \pi^*$ transition (promotion of an electron of the lone pair of oxygen to a molecular π^* orbital), while the second band corresponds to a $\pi \to \pi^*$ electronic transition (9). It should be noted that the value $(I_\pi - I_n)$ for anthraquinone (see Fig. 2b), equal to 0.69 eV, is close to the corresponding value of the energy difference between the $\pi \to \pi^*$ and $n \to \pi^*$ transitions $(E_{\pi\pi^*} - E_{n\pi^*})$ of this molecule.

Analysis of the ionization curves of anthraquinone and fluorenone makes it possible to compare the relative probabilities of the processes of removal of n- and π-electrons for these molecules. Thus, in the case of fluorenone, the yield of ions formed by removal of an n-electron of the lone pair of oxygen electrons is 2–3 times smaller than the yield of ions formed by removal of an n-electron for anthraquinone. This fact can be related to the value of the difference between the ionization potentials $(I_\pi - I_n)$ and to the number of π-electrons of the molecules studied per chromophoric group.

The main processes of decomposition of anthraquinone molecules, as shown by analysis of its mass spectrum recorded on a high-resolution mass spectrometer (10, 11) are the processes of elimination of CO groups from the molecule of neutral groups and formation of the ions $C_6H_4COC_6H_4^+$ and $C_6H_4C_6H_4^+$. The appearance potentials of the latter and of the ion $C_6H_4C_6H_4^+$ from fluorenone are given in Table 1. The energy of elimination of the CO group from the anthraquinone molecule with formation of fluorenone, determined as the difference between the appearance potential of the ion $C_6H_4COC_6H_4^+$ from anthraquinone (10.39 eV) and the ionization potential of fluorenone (9.42 eV), is equal to 0.97 eV and agrees well with the value 0.94 eV determined thermochemically (10).

Scheme 1

Scheme 1 shows the proposed decomposition of the anthraquinone molecule. When an anthraquinone molecule absorbs an energy of 10.39 eV, one CO group is eliminated. In the case of absorption of an energy of 11.02 eV, successive cleavage of two carbonyl groups from the anthraquinone molecule is observed. For fluorenone, elimination of one group occurs at an energy of 10.14 eV. In both cases ions of identical structure are formed, corresponding to the cation-radical of *o*-diphenylene.

In this process of molecular decomposition, apparently, the decisive role is played by the electronic $n \to \pi^*_\infty$ transition, which leads to the formation of a cation-radical with primary localization of the unpaired electron on the oxygen atom of the carbonyl group $> C = \overset{+}{O}\uparrow$. As a result of exchange interaction of the unpaired electron of the oxygen atom with the electron of the carbon atom of the neighboring C–C bond, that bond is broken and the CO group is eliminated. The cation-radical formed spontaneously, as a result of an electronic $n \to \pi^*$ transition involving the second carbonyl group, decomposes with formation of the cation-radical of *o*-diphenylene and a CO group.

The case considered is an example of an intramolecular chain process of molecular decomposition in which the principal role is played by $n \to \pi^*$ electronic transitions. From this point of view one should expect a chain process of decomposition of molecules containing a larger number of carbonyl groups. Thus, for example, apparently the following chain transformation is possible:

$$\text{[anthraquinone-type polycarbonyl structure]} + e \longrightarrow 4CO + \left[\text{[fused aromatic cation-radical structure]}\right]^{+} + 2e.$$

Chain decomposition processes of this kind for molecules and molecular systems containing chromophoric groups $> C = O$, $-NO_2$, $> N$, etc. (with participation of electronic $n \to \pi^*$ transitions) are possible in chemical reactions initiated in various ways, complex formation, and adsorption.

The role of $(n \to \pi^*_\infty)$-promotion in the processes under consideration is manifested distinctly in the decomposition of the acetone molecule, observed upon absorption of an energy of 11.06 eV,

$$\mathrm{H_3C{-}C(=O){-}CH_3} \xrightarrow{e} \mathrm{H_3C}{\downarrow}\cdots\mathrm{C(=O^+){-}CH_3} + 2e \longrightarrow \mathrm{H_3C}{\downarrow} + \mathrm{H_3C{-}C{\equiv}O^+} + 2e$$

Formation of the cation-radical under $(n \to \pi^*_\infty)$-promotion requires an energy equal to 10.03 eV. In the case of photoexcitation, the process of formation of a cation-radical of the cation molecule may apparently also proceed by absorption of two quanta:

$$S \xrightarrow{h\nu_1} S^* \rightsquigarrow T \xrightarrow{h\nu_2} T^*.$$

In the case of decomposition of molecules with σ-bonds, the determining role is played by $n \to \sigma^*$ promotion, leading to $(n\sigma^*)$-states and ionization through detachment of an n-electron from the heteroatom. Particles in these states can decompose with formation of radicals and cations by the mechanism described above.

From this point of view, for example, the mechanism of decomposition of alcohols can be explained. The molecules of these compounds, being in the indicated states, decompose as a result of exchange interaction of the unpaired electron of the oxygen atom with the electron of the neighboring carbon atom, which leads to the formation of a new bond between carbon and oxygen and to rupture of the C—H or C—C bond; in this process the corresponding radicals R—CH—OH and cations R—HC=O$^+$—H arise.

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