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Emission Spectra of Toluidines by Controlled Electron Impact

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Synopsis. The spectra of *o*-, *m*-, and *p*-toluidines show an intense band of the S_1-S_0 transition of the parent molecule, and lines and bands of fragment species such as H, CH, C_2, CN, and NH.

Electron impact excitation of molecules is a revised form of the traditional electric discharge method. The aromatic molecules show intense photoemission of the parent molecules in the ultraviolet region.[1,2] These bands are similar with the fluorescence spectra and they have been assigned to the S_1-S_0 transition of the parent molecule. In the present note, the emission spectra of three isomers of toluidines have been measured and their excitation processes have been discussed.

The apparatus consists of a collision chamber, a SPEX 1269 monochromator and a photon counting system; they have been described previously.[2]

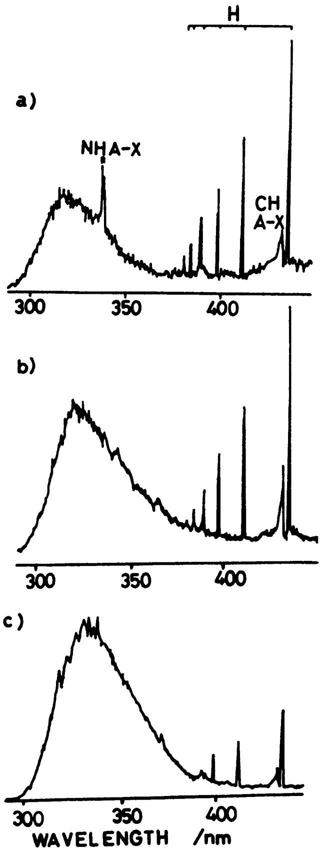

Fig. 1. Emission spectra of (a) *o*-toluidine (100 eV, 500 μ*A*), (b) *m*-toluidine (100 eV, 100 μA), and (c) *p*-toluidine (100 eV, 70 μA) by controlled electron impact.

Typical emission spectra of toluidines by controlled electron impact are shown in Fig. 1. The intense bands observed in the 300—400 nm region are similar to those of aniline[3] and xylenes.[4] The fluorescence spectra of these molecules were measured in ethanol; they have a similar band in the identical region. Therefore, these bands have been assigned to the S_1-S_0 transition of the parent molecules.

There are also many lines and bands of fragment species. They are the Balmer series of the excited hydrogen atom, the 4300 Å system of CH (A-X), the 3360 Å system of NH (A-X) and the Swan system of C_2 (d-a). Their assignments are shown in Fig. 1.

The emission intensities of the parent molecules and such fragments as H* and CH* are proportional to the electron-beam current up to at least 600 μA; this finding indicates that these excited species are produced through a single collision between an electron and a molecule.

The S_1-S_0 band is relatively more intense at lower electron energies than lines and bands of fragments.[2] This is partly due to need of larger excitation energies for the formation of the excited fragments, as is common to most aromatic molecules.[2]

The relative intensity of this band for three toluidines can be estimated from the intensity relative to those of fragments, since the intensity of fragments is expected to be approximately independent of the molecular structure. At an identical electron energy, the band of *p*-toluidine is the most intense, as in the case of xylenes.[4] Furthermore, the band of *p*-toluidine has more vibrational structures. This is due to the higher symmetry of this molecule and, as a result, a higher quantum yield of emission.

Usually a molecule consisted of four atoms or more does not show a band of the parent molecule, unless it is fluorescent. The emission spectra of toluidines have been related with their fluorescence, as have been shown for several aromatic molecules.[1,2]

References

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