The Effect of Substituents Upon The Autodetachment Lifetimes of The Perfluorobenzene and Nitrobenzene Anions

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Summary The autodetachment lifetimes of a number of molecular anions have been measured using a time-of-flight technique and the effect of some electron-attracting and donating groups upon the stability of molecular anions observed; the simple harmonic oscillator model was not capable of explaining these effects in general.

THE existence of a long-lived molecular negative ion of sulphur hexafluoride was reported by Edelson *et al.*[1] who showed that the SF_6^- ion was metastable and subject to autodetachment, the mean lifetime $\tau(SF_6)$ being *ca.* 10 μs.

$$SF_6^{-*} \rightarrow SF_6 + e$$

It was suggested[2] that certain fluorocarbon molecules would form long-lived negative ions and this has been experimentally confirmed.[3] A semi-theoretical model has been advanced to explain this phenomenon in which the ion is regarded as an assembly of weakly coupled harmonic oscillators and the incident electron is considered to share

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its excess energy between the various internal degrees of freedom. Such a model predicts that the negative ion lifetime would increase as the number of atoms in the molecule increases.

By means of a time-of-flight technique and application of a retarding potential to vary the flight time of the ions the relative intensities of the ions and neutrals formed as a result of ion decomposition may be measured as a function of flight time and hence the autodetachment lifetime calculated.

We have measured the autodetachment lifetimes of perfluorobenzene, perfluorotoluene, and perfluoro-*p*-xylene and obtained the following values: 13·3, 37·8, and 450 μs. It is apparent that for this series the lifetime increases as the number of degrees of freedom N increases, the relationship being $\ln\tau \propto N$. Similar behaviour was noted in this laboratory for a series of perfluoromethyl substituted cycloalkanes.

Autodetachment lifetimes of methyl substituted nitrobenzenes

Compound	Autodetachment lifetime (μs)
Nitrobenzene	49
2-Methylnitrobenzene	30
3-Methylnitrobenzene	23
2,3-Dimethylnitrobenzene	21
2,4-Dimethylnitrobenzene	21
2,6-Dimethylnitrobenzene	18

The simple harmonic oscillator model therefore seems applicable to fluorocarbons and related perfluoro-substituted molecules. The effect of electron-donating groups upon the stability of molecular anions has not been studied and it is not known if the oscillator model is similarly capable of explaining, at least semi-quantitatively, these effects.

Nitrobenzene forms a metastable anion and we have examined the autodetachment lifetimes of nitrobenzene and a series of methyl-substituted nitrobenzenes (see Table). In marked contrast to the perfluorocarbons, the autodetachment lifetimes of the nitrobenzenes depend markedly on the number and position of the substituent and, in particular, the lifetime of the anion decreases as the number of degrees of freedom increases. The introduction of an electron donating substituent (methyl group) into the ring reduces the stability of the molecular ion and the introduction of a second such group reinforces this effect.

These observations seem consistent with the following interpretation: the electronegative nitro-group depletes the charge density in the benzene ring and consequently lowers the energy of the two lowest (degenerate) unoccupied π-electron orbitals which are involved in negative ion formation. The unoccupied *p*-orbitals of the nitro-group serve to extend the conjugation and to provide an additional vacant low-lying π-electron orbital which will be strongly influenced by the addition of electropositive substituents into the benzene ring. Such groups, *e.g.* methyl, will serve to replenish electron density and to offset the influence of the nitro-group.

The autodetachment lifetime of 2,4-difluoronitrobenzene was found to be 47 μs. Introduction of fluorine substituents into the benzene ring does not influence the stability of the molecular negative ion to the degree which might be expected from a consideration of its inductive effect alone. It therefore appears that the resonance effect, which has the dominant effect on chemical reactivity and electronic spectra, must cause a strong perturbation on the vacant π-electron orbitals in the substituted nitrobenzene, this effect being reflected in the stability of the parent ion.

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