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GAS PHASE ELECTRON ATTACHMENT REACTIONS AND NEGATIVE ION MASS SPECTRA OF
SUBSTITUTED PENTAFLUOROPHENYL COMPOUNDS

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SUMMARY

Compounds of the type $C_6F_5.R$ ($R = F, CH_3, NH_2, OH, SH, OCH_3, COCH_3, CHO, NO_2, CN$) undergo low energy electron attachment reactions in the gas phase under negative chemical ionisation (NCI) conditions which can result in the production of intense negative ion beams. Long-lived molecular negative ions are formed when R is highly electron withdrawing and this correlates in certain cases ($R = F, CN, CHO$) with reported $[M]^-$ autodetachment times. Compounds with $R = COCH_3, CHO, CN$ which exhibit minimal fragmentation of $[M]^-$ are useful negative ion mass calibrants.

INTRODUCTION

While a considerable amount of information is available concerning the chemistry of pentafluorophenyl compounds which form stable carbanion intermediates in the solution phase [1], studies of the gaseous negative ions formed by a number of $C_6F_5.R$ compounds have in the main been restricted to measurements of their negative ion lifetimes and the correlation of these data with their electronic and molecular structures [2,3]. Negative ion mass spectra have been obtained for various series of fluorinated compounds [4] as well as fluorinated β -diketones known to be significant metal derivatising reagents [5], and rationalisations defining various structural requirements for the existence of long-lived organic molecular negative ions

TABLE 1

Principal ions in the negative ion mass spectra^a of substituted pentafluorophenyl compounds C₆F₅-R

Ions	% total ion current ^b									
	R: -F	-CH ₃	-NH ₂	-OH	-SH	-OCH ₃	$\overset{\text{O}}{\parallel}\text{-CCH}_3$	$\overset{\text{O}}{\parallel}\text{-CH}$	-NO ₂	-CN
Number:	I	II	III	IV	V	VI	VII	VIII	IX	X
Adduct ions ^c	-	-	-	5	12	-	-	-	-	-
[M] ⁻	81	7	-	94	86	-	96	97	-	99.6
[M - H] ⁻	-	11	8	-	-	-	0.3	-	-	-
[M - H ₂] ⁻	-	5	0.2	-	-	36	-	-	-	-
[M - CH ₂] ⁻	-	5	-	-	-	-	-	-	-	-
[M - F] ⁻	1	5	2	-	-	-	-	-	-	0.1
[M - HF] ⁻	-	17	85	-	-	-	0.2	-	-	-
[M - CF] ⁻	-	-	-	-	0.3	-	-	-	2	-
[M - F ₂] ⁻	1	7	-	-	-	-	-	-	-	-
[M - CF ₂] ⁻	13	2	-	-	-	-	-	-	3	0.1
[M - 2HF] ⁻	-	11	1	-	-	-	-	-	-	-
[M - R] ⁻	-	-	-	0.5	-	6	0.3	-	92	0.1
[M - RF] ⁻	1	3	-	-	-	2	1	-	-	-
Other ions ^d	3	27	3.8	0.5	1.7	56 ^e	2.2	3	3 ^f	0.1

^aElectron energy moderating gas methane (0.10 Torr); electron energy 50 eV; total emission current 0.50 mA; repeller voltage 0 V (with respect to chamber); accelerating voltage 4.00 kV; ion source temperature 200°C.

^bAll isotopes of all elements are considered. Total ion currents were in the range 1 to 20 nA.

^cIons observed : M+1, M+14, M+15, M+16, M+19, M+28, M+29, M+32.

^dLow mass ions observed were F⁻, CN⁻, OH⁻, NO₂⁻, as well as ions resulting from fragmentation of the C₆F₅ nucleus.

^e[M - CH₂F]⁻, 21%.

^f[NO₂]⁻, 2%.

have been reviewed recently [6]. In this paper we describe results of gas phase electron capture reactions examined under NCI conditions given by a series of compounds of formula $C_6F_5.R$ [R = F (I), CH_3 (II), NH_2 (III), OH (IV), SH (V), OCH_3 (VI), $COCH_3$ (VII), CHO (VIII), NO_2 (IX), CN (X)] which are significant because some are known to be useful derivatising reagents for negative ion mass spectrometric organic analysis [7,8], and can be related to electrophores [2,9] of the type $-C_6F_4.R$ which may be incorporated as substituents into metal derivatising ligands.

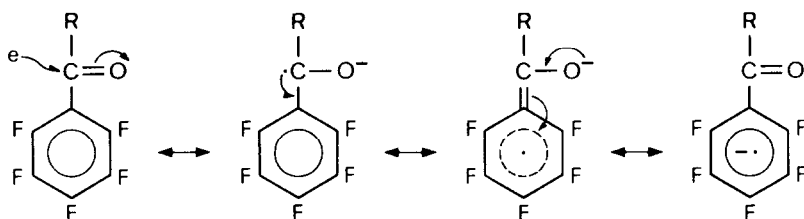
RESULTS and DISCUSSION

The principal ions observed in the negative ion mass spectra of compounds I - X are listed in Table 1 along with their respective percentages of the total ion currents. All of the compounds when ionised gave appreciable total negative ion currents which maximised at 70 nA for VII and VIII with minima of 5 and 2 nA given by I and II, for similar sample sizes and introduction rates into the ion source. Varying degrees of molecular ion fragmentation are apparent in Table 1, but it is possible to classify the compounds into two categories:

- (i) Compounds I, IV, V, VII, VIII and X which form molecular negative ions which undergo a minimal degree of fragmentation;
- (ii) Compounds II, III, VI and IX for which molecular ions were detected in low abundance or not at all.

Higher total ion currents which averaged 40 nA were given by compounds in the first category whereas 10 nA was the average for those in category (ii). Compounds VII and VIII gave the highest ion currents and a very low degree of molecular ion fragmentation. The trend observed in the measured total negative ion currents for I, X, VIII is consistent with reported autodetachment times, Table 2. The apparent stability of the molecular negative ions of VII and VIII towards fragmentation may be related, as is the case with the substituted benzene analogues [2b], to the interaction of the symmetric ring π -orbital in-phase and out-of-phase with the carbonyl π^* -orbital to provide an additional resonance state for the negative ions.

Resonance stabilisation involving delocalisation of the charge in the ions is illustrated in Scheme 1.



Scheme 1

Pentafluorobenzonitrile, X, also formed a molecular negative ion which carried in excess of 99% of the total ion current, which is consistent with the comparative autodetachment data summarised in Table 2. The extended lifetime of X with respect to I has been interpreted in terms of the electron withdrawing ability of the -CN group [2a]. It is also noteworthy that for a number of cyanocarbons, the electron affinity of the molecule increases as the number of -CN substituents increases [10].

TABLE 2

Comparison of total negative ion current^a determined in this work with published autodetachment times.^b

Compound :	C ₆ F ₆	C ₆ F ₅ -CN	C ₆ F ₅ -CHO
Number :	I	X	VIII
Total Negative Ion Current (nA)	5	30	70
Autodetachment Time (μs)	12	17	36

^aMeasured with 2 μL of sample in liquid inlet to give an ionisation gauge reading of 1.0×10^{-5} Torr 10 cm remote from the ion source. Factors have been applied to the ion current arriving as [M]^{-•} at the first dynode of the electron multiplier to take into account the ion current carried by other ions in the spectrum as well as ion current losses in the ion optics of the mass spectrometer. The final figure is thus an approximation of the total negative ion current passing through the ion source exit slit.

^bReference 9.

The mass spectrum of hexafluorobenzene, I, is characterised by fragmentation involving the elimination of a fluorine radical and decomposition of the aromatic ring by the elimination of CF_2 . The latter neutral species has been reported previously as a product of gas phase ion decompositions [11] including those involving molecular negative ions of metal chelates containing fluorinated ligands [12].

In contrast, the negative ion mass spectrum of II is characterised by the presence of a greater degree of fragmentation than was the case with I. The principal fragmentation pathways involved with II can be inferred to involve the loss of $\text{H}\cdot$, $2\text{H}\cdot$ or H_2 , $\text{F}\cdot$ and carbene, CH_2 , from $[\text{M}]^{-\cdot}$. This latter neutral has been inferred previously as a negative ion decomposition product associated with the ions formed by bis- and tris-chelates of transition metals where the ligand was the enolate ion of dipivaloylmethane [13]. The $[\text{M} - \text{HF}]^{-\cdot}$ ion given by II points to an intra-ionic rearrangement involving hydrogen and fluorine atoms, and a similar reaction can account for the major fragmentation route for the molecular ion of pentafluoroaniline, III.

It is interesting that both pentafluorophenol, IV, and pentafluorothiophenol, V, display little fragmentation in their negative ion mass spectra. The solution phase acidity of IV together with the relatively high position of fluorophenols and thiophenol on the gas phase acidity scale [14] suggest that the conjugate base ion, $[\text{M} - \text{H}\cdot]^{-}$ would be relatively stable. However no evidence of such an ion could be found in the spectrum of either IV or V. The loss of $\text{OH}\cdot$ in the case of IV in a qualitative sense is consistent with the reported stability of the pentafluorobenzenide ion [1]. The adduct ions observed for IV and V probably result from either molecule/radical or ion/molecule processes in the ion source, and similar adduct species have been observed in other negative ion mass spectra obtained by the use of hydrocarbon electron energy moderating gases under NCI conditions [15-18]. However, as yet in these latter instances the mechanisms operative for the formation of such adduct species are not resolved [19].

The negative ion mass spectrum of pentafluoroanisole, VI, is characterised by a high degree of fragmentation. The principal pathways for the decomposition of the molecular ion involve the loss of H_2 , $\text{CH}_3\text{O}\cdot$ and CH_3F .

The interaction of thermalised electrons with pentafluoronitrobenzene, IX, under the standardised conditions employed here did not yield a molecular ion with a lifetime sufficiently long for its detection. In this case it is possible that dissociative electron attachment occurred with the cleavage of a C-N bond to produce the pentafluorobenzenide ion and a NO₂ neutral. This is in contrast to nitrobenzene which forms a relatively long-lived molecular negative ion [2,6] where after electron capture the system can resonance stabilise itself via a π -system [6]. The abundance of the [M - NO₂]⁻ and NO₂⁻ ions in the spectrum of IX suggest that the electron affinity of the pentafluorophenyl group is greater than that of the nitro group with charge retention and localisation occurring in the ring π -system of the principal fragment ion.

The compounds which give the most intense negative ion beams and molecular ions which undergo minimal fragmentation show excellent potential as negative ion mass spectrometric calibration compounds. Whereas substances such as perfluorokerosene and perfluorotributylamine are often used as mass calibration compounds because of the number of negative ions which they form and the mass range covered [20,21], the individual ion abundances are relatively low, and a need often arises for an intense and readily recognised calibration peak to be present or introduced into a negative ion mass spectrum. The use of various reference standards including sulphur for the mass range to m/z 256 [22], or phosphonitrile chlorides, polyperfluoropropylene oxide and tris(perfluoroheptyl)-s-triazine to cover higher mass ranges [21,23] has been suggested to provide more intense ion beams, but the need to use solids introduction procedures in some instances can limit the utility of these compounds. However, some of the pentafluorophenyl compounds studied here, notably VII, VIII, X provide intense negative ion beams comprised of one dominant ion, Table 1, with the added advantage that they can readily be introduced into the ion source by a regular liquids inlet system. Furthermore, such compounds which yield long-lived molecular ions are ideally suited to establish routinely the dynamic instrument sensitivity and to tune the mass spectrometer ion source and ion optics in the negative ion mode. Thus, 2 μ L of VII injected into the liquids septum inlet system under standardised NCI conditions, with a methane ion source pressure of 0.1 Torr, produced a molecular ion beam which registered an ion current of 6×10^{-7} A on the FA3 amplifier of the mass spectrometer used in this work. This was established to be an accurate reflection of the optimum sensitivity attainable and thus used as a dynamic sensitivity reference parameter in the negative ion mode.

EXPERIMENTAL

Compounds used in this work were obtained from the Fairfield Chemical Co. Inc., and their purities were checked by reference to their mass spectra. The negative ion mass spectra were obtained on a VG MM-16F single focusing mass spectrometer using conditions which have been described in detail [16,24,25], or specified in Tables 1,2. Methane (Matheson, UHP, 99.97%) was used as the electron energy moderating gas under measured and controlled ion source pressure and temperature conditions to achieve optimum sensitivity for molecular ion signals at the collector. Ion source pressure measurements were referenced to a MKS Baratron system type 170/315BHS-10.

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