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Letter to the Editor

Temperature dependence of electron capture response

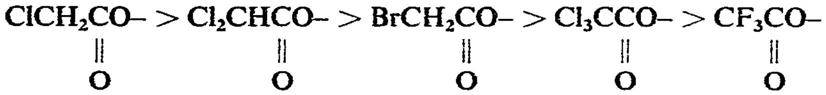
Dear Sir,

The electron capture detector is the most sensitive of all gas chromatographic (GC) detectors for compounds which capture thermal electrons. It has been in use for twenty years or so for this purpose. Our understanding of its mechanism of operation has been greatly advanced by the work of Wentworth and co-workers[1,2], Lovelock[3] and Zlatkis and co-workers[4–6]. A striking result of this work is the temperature dependence of the electron capture response. As a gross simplification a molecule can capture electrons in a non-dissociative manner to form a negative ion or it can dissociate on electron capture to produce a negative ion and a radical (see ref. 1, for a more detailed picture).

$AB \rightleftharpoons AB^-$ Non-dissociative
$AB \rightarrow A^\bullet + B^-$ Dissociative

The non-dissociative mechanism, exhibited by all conjugated electrophores[7], is favoured by low detector oven temperatures, whereas the reverse is true of the dissociative mechanism where bond breaking is favoured by high temperatures. The molar response of a compound can differ by a factor of 1000 over a 100° range of detector oven temperature[1]. As a consequence of this feature the apparent trend to quote detection limits at a single temperature without mention of whether this parameter has been optimized is to be deplored. Further, the comparison of sensitivity of different derivatives of the same molecule is hindered unless one knows the temperature dependence of the detector response to each derivative. It is of little value to compare two derivatives of the same molecule at identical temperatures if one has a much greater response at a different detector oven temperature. The analyst is usually interested in obtaining the maximum response of the compound under study and for this purpose, it is essential that this is made obvious from the literature source, which should include optimum GC conditions, detector operating parameters and optimum detector oven temperature.

The temperature dependence of the electron capture mechanism, usually expressed graphically as a plot of ln $KT^{3/2}$ *versus* $1/T$ (K = capture coefficient and T = detector oven temperature) also provides useful information to aid understanding of the processes occurring within the detector[1]. Unfortunately, this has rarely been taken advantage of when mechanism and position of electron attachment have been discussed. Landowne and Lipsky[8] evaluated the relative molar response of a series of cholesteryl halomethylacetates which they found could be placed in the following order of sensitivity



$$\mathrm{ClCH_2\underset{\underset{O}{\|}}{C}O-} > \mathrm{Cl_2CH\underset{\underset{O}{\|}}{C}O-} > \mathrm{BrCH_2\underset{\underset{O}{\|}}{C}O-} > \mathrm{Cl_3C\underset{\underset{O}{\|}}{C}O-} > \mathrm{CF_3\underset{\underset{O}{\|}}{C}O-}$$

To explain this unpredicted order they assumed that the electron was initially captured at the carbonyl centre and stabilized by a through space interaction with the halogen atom. Implied in their argument is the assumption that the electron capture mechanism is non-dissociative. Zlatkis and co-workers[4–6] have shown that for a series of aliphatic alcohols, amines and phenols, the chloromethylacetates capture electrons in a dissociative manner. Also Landowne and Lipsky[8] predicted on the basis of their arguments that the monofluoroacetate would be the most sensitive of this series of halomethylacetates. This was not found to be the case with the monofluoroacetate of the phenol, thymol, which was much less sensitive than the monochloroacetate derivative[9]. Thus it seems likely that we do not understand the process of electron attachment in the widely used halomethylacetate derivatives and the position is aggravated by a lack of studies on the temperature dependence of the molar response to the electron capture detector.

Another example is the determination of amines as their heptafluorobutyramides or pentafluorobenzamides. The pentafluorobenzamides are invariably more sensitive than the heptafluorobutyramides and this is thought to be due to the ability of these derivatives to stabilize the negative charge through delocalization in a non-dissociative process[10]. This is supported by the few temperature dependence studies that are available[5]. It is also supposed that the heptafluorobutyramides, which cannot resonate, are less sensitive for this reason. However, those temperature studies which are available indicate that a dissociative mechanism is operative so that after the initial electron capture, bond breaking is important[4–6]. The two reagents thus behave differently towards thermal electrons and the simple picture proposed by Martin and Rowland is unlikely to be completely true[10].

The small extra effort expounded in constructing a plot of ln $KT^{3/2}$ *versus* $1/T$ would seem to be very worthwhile in the long run if it enables a more concerted understanding of the electron capture mechanism to be proposed. It will also throw light on some of the mechanisms at present accepted in the literature.

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