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ELECTRON ATTACHMENT SPECTROSCOPY USING A MODIFIED ELECTRON-CAPTURE DETECTOR

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SUMMARY

An electron attachment spectroscopy technique is described, which enables the mean energy of electrons to be varied in the range 0.04–0.5 eV by means of a radiofrequency voltage superimposed on the d.c. voltage of an electron-capture detector. Plotting the electron-capture coefficients against the mean electron energies for each compound yields a characteristic curve which may be helpful for the identification of unknown substances. This method also makes it possible to increase the sensitivity and the specificity of the electron-capture detector. The dependence of the electron-capture coefficient on the mean electron energy for eight compounds (CHCl_3 , CCl_4 , C_2HCl_3 , CCl_2F_2 , $\text{C}_6\text{H}_5\text{Cl}$, O_2 , SO_2 , N_2O) is discussed.

INTRODUCTION

Electron attachment spectroscopy is the name given by Lovelock *et al.*¹ to a procedure which permits a variation of the mean energy of electrons within the ionization region of an electron-capture detector. These authors used a pulse electron-capture detector and accelerated the thermal electrons by use of a radiofrequency voltage during the pulse intervals. Popp *et al.*²⁻⁴ modified this method by superimposing the radiofrequency voltage on the voltage of a d.c. electron-capture detector. Thus, it was possible to vary the mean electron energy between thermal energies and 0.5 eV using nitrogen as carrier gas, and between thermal energies and 2.8 eV with argon–nitrogen mixtures. Because electron-capture processes are dependent on the electron energy, with this method it is possible to increase the sensitivity and the specificity of the electron-capture detector. Our recent investigations with eight substances illustrate the efficiency of electron attachment spectroscopy.

THEORETICAL

Popp *et al.*²⁻⁴ showed that the electron-capture coefficient, K , in the relationship

$$\Delta i/i - \Delta i = KC_{AB}$$

where i = basic ionization current, Δi = decrease of the basic ionization current in

the presence of an electronegative sample AB and C_{AB} = concentration of the electronegative sample AB, is connected with the electron attachment cross-section, $\sigma_{AB}(\varepsilon)$

$$K = N_L \cdot \frac{x}{v_e} \cdot \sqrt{\frac{2}{m_e}} \cdot \int_0^{\infty} \sigma_{AB}(\varepsilon) W(\varepsilon, E/p) \varepsilon^{1/2} d\varepsilon$$

where N_L = Loschmidt's number, x = electrode distance of the electron-capture detector, v_e = drift velocity of the electrons, m_e = mass of an electron, ε = electron energy and $W(\varepsilon, E/p)$ = energy distribution function (E = electric field strength, p = pressure). According to Christophorou⁵ a "mean electron attachment cross-section" can be defined as

$$\langle \sigma_{BC}(\varepsilon) \rangle = \frac{\int_0^{\infty} \sigma_{BC}(\varepsilon) \varepsilon^{1/2} W(\varepsilon, E/p) d\varepsilon}{\int_0^{\infty} \varepsilon^{1/2} W(\varepsilon, E/p) d\varepsilon}$$

and taking into account that

$$\langle \varepsilon^{1/2} \rangle = \int_0^{\infty} \varepsilon^{1/2} W(\varepsilon, E/p) d\varepsilon$$

one obtains:

$$K = N_L \cdot \frac{x}{v_e} \cdot \sqrt{\frac{2}{m_e}} \langle \sigma_{BC}(\varepsilon) \rangle \langle \varepsilon^{1/2} \rangle$$

This means it is possible to calculate the mean attachment cross-section, $\langle \sigma_{BC}(\varepsilon) \rangle$, from the electron attachment coefficient, K , measured at a series of E/p values if the energy distribution function, $W(\varepsilon, E/p)$, and the drift velocity, v_e , are known. The estimation of the mean electron energy is based on the calculations of Phelps and Voshall⁶ for the energy distribution function in nitrogen and of Ritchie and Whitesides⁷ for the energy distribution function in argon which is dependent on the E/p values. A requirement is that small concentrations of electronegative compounds should not have little effect on the energy distribution within the ionization region. While Christophorou and co-workers^{8,10} determined the drift velocity directly, this is not possible under the conditions of electron-capture detection. Due to the space charges within the electron-capture detector^{11,12}, the use of drift velocities determined by other authors results in considerable errors, and a quantitative agreement of the $\langle \sigma_{BC}(\varepsilon) \rangle$ values calculated from experimentally determined K values with the results of other swarm experiments cannot be expected. However, the knowledge of the dependences of the electron attachment coefficients on the mean electron energy makes it possible to increase considerably the sensitivity and the specificity of the electron-capture detector.

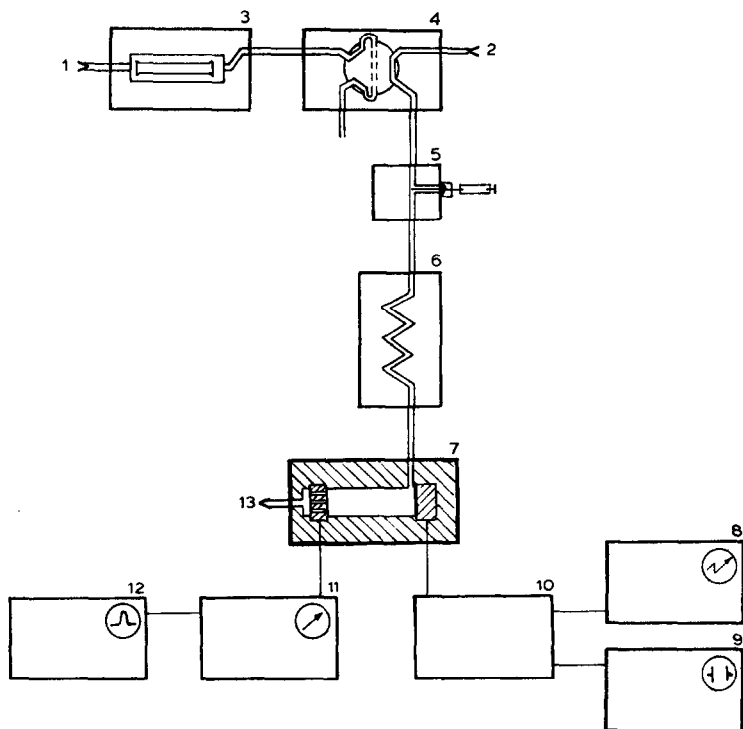


Fig. 1. The experimental arrangement: 1,2 = carrier gas inlet; 3 = permeation tube; 4 = sample loop; 5 = injection port; 6 = GC column; 7 = ^{63}Ni electron-capture detector; 8 = radiofrequency generator; 9 = d.c. voltage source; 10 = superposition of radiofrequency and d.c. voltages; 11 = electrometer; 12 = recorder; 13 = carrier gas outlet.

EXPERIMENTAL

Fig. 1 shows the experimental arrangement. The electronegative compounds are added to a carrier gas by means of a gas-tight syringe (5) or a permeation tube (3) connected with a sample loop (4). The gas chromatographic separation occurs on a column filled with Porapak QS or Chromosorb W + 10% SE-30. The electron-capture detector (7) contains a ^{63}Ni radioactive source and is designed such that the distance between the electrodes (17 mm) is somewhat greater than the range of the β -radiation in nitrogen (15 mm), determined experimentally by variation of the electrode distance. A voltage, $U_{\text{eff}} = 0\text{--}600\text{ V}$, provided by a radiofrequency generator (8) is superimposed on the d.c. voltage $U = 0\text{--}150\text{ V}$, from the power supply (9). The frequency of the alternating voltage is 30 MHz. The ionization current is measured with a vibrating reed electrometer (11) and changes in the current are displayed by a recorder (12).

RESULTS AND DISCUSSION

By varying the amplitude of the radiofrequency voltage, the dependence of the electron-capture coefficient, K , on the mean electron energy, $\langle \epsilon \rangle$, was determined for

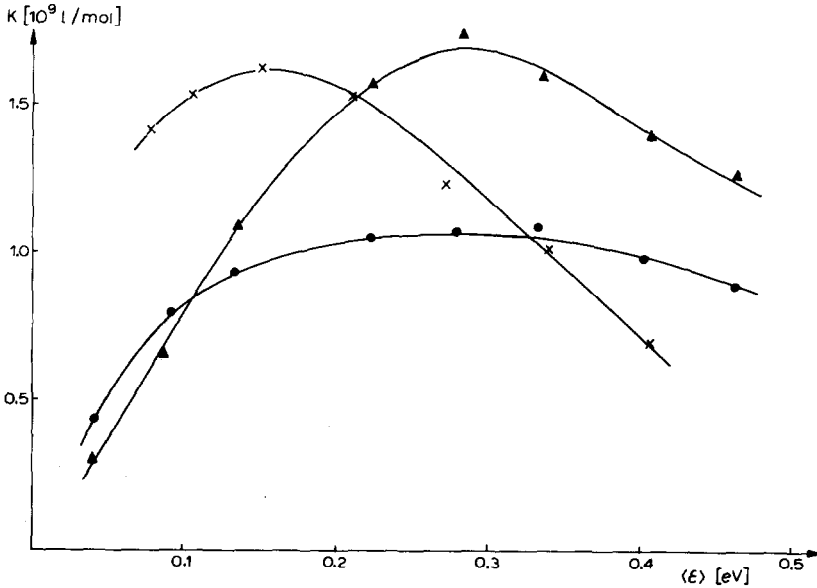


Fig. 2. Dependence of the electron-capture coefficients on the mean electron energy: \blacktriangle , CHCl_3 ; \bullet , C_2HCl_3 ; \times , CCl_2F_2 ($K \cdot 500$).

eight substances. For E/p values between 0.01 and $0.5 \text{ V/cm} \cdot \text{Torr}$ ($7.6 \cdot 10^{-5}$ and $3.8 \cdot 10^{-3} \text{ V/cm} \cdot \text{Pa}$) the mean electron energy in the carrier gas nitrogen varies from 0.04 to 0.5 eV . Figs. 2 and 3 show these dependences for CCl_4 , CHCl_3 , C_2HCl_3 , CCl_2F_2 and $\text{C}_6\text{H}_5\text{Cl}$ and Fig. 4 for O_2 , N_2O and SO_2 . It is seen that the electron-capture coefficients of $\text{C}_6\text{H}_5\text{Cl}$ and N_2O increase by several orders of magnitude

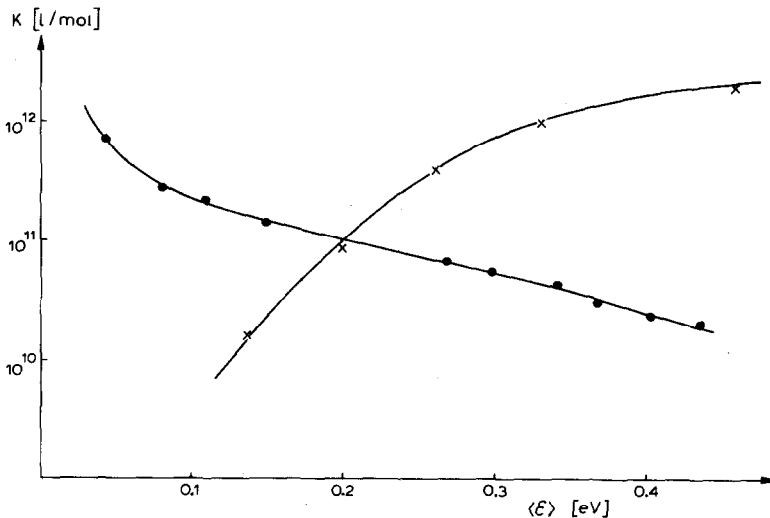


Fig. 3. Dependence of the electron-capture coefficients on the mean electron energy: \bullet , CCl_4 ; \times , $\text{C}_6\text{H}_5\text{Cl}$ ($K \cdot 10^3$).

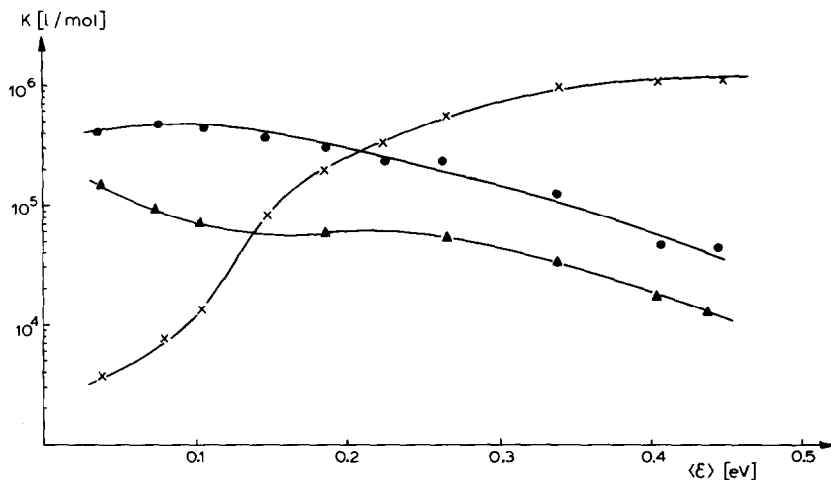


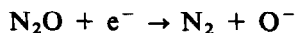
Fig. 4. Dependence of the electron-capture coefficients on the mean electron energy: ●, SO_2 ; ×, N_2O ; ▲, O_2 .

upon increasing the mean electron energy from 0.04 to 0.5 eV. In the case of $\text{C}_6\text{H}_5\text{Cl}$ the formation of negative ions occurs by the dissociative reaction



with a maximum electron-capture cross-section of 0.86 eV^{13} . Due to the negative electron affinity of $\text{C}_6\text{H}_5\text{Cl}$, $\text{EA} = -0.9 \text{ eV}$, the sensitivity of the electron-capture detector at thermal electron energies is very low.

In the case of N_2O the dissociative process



is responsible for the formation of negative ions¹⁴. The appearance potential of O^- is 0.21 eV^{15} . The compounds CCl_4 , CHCl_3 , C_2HCl_3 and CCl_2F_2 also undergo a dissociative process with the formation of Cl^- ions. In these cases, maximum electron attachment cross-sections are reached at thermal energies (CCl_4), at 0.20 eV (CHCl_3) and 0.39 eV (C_2HCl_3)^{16,17}. Fig. 2 shows that the values of 0.20 and 0.39 eV are in good agreement with our measurements. The gases SO_2 and O_2 react according to a non-dissociative process. In these cases the maximum cross-sections lie close to thermal energies.

The dependence of the sensitivity and the detection limit of the electron-capture detector on the mean electron energy for $\text{C}_6\text{H}_5\text{Cl}$ is given in Fig. 5. The energy variation from 0.135 to 0.5 eV results in an increase of the sensitivity and a decrease of the detection limit by about four orders of magnitude.

CONCLUSIONS

The results of these investigations show that electron attachment spectroscopy permits an improvement of the performance of the electron-capture detector. This technique makes it possible:

- (1) to increase the sensitivity and to decrease the detection limit (in several

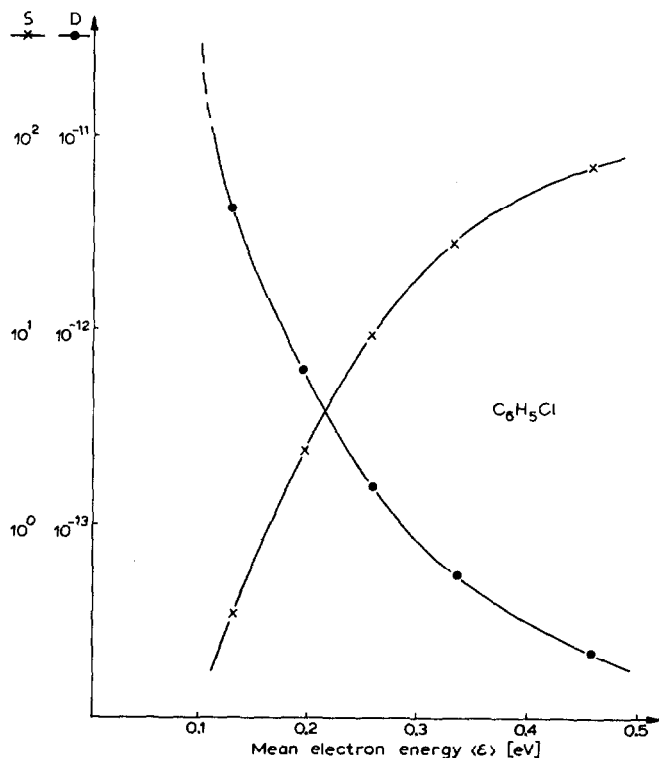


Fig. 5. Dependence of the sensitivity, S , ($\text{A cm}^3/\text{mol}$) (x) and the detection limit, D (mol/m^3) (●), on the mean electron energy for $\text{C}_6\text{H}_5\text{Cl}$.

cases by three to four orders of magnitude),

(2) to identify unknown substances in a gas chromatogram by the characteristic shape of the K versus $\langle \epsilon \rangle$ plots.

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