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Studies on Characteristics of Electron Capture Responses. VI.[1] A Consideration on the Response Mechanism of the Electron Capture Detector

Masahiro Takeuchi

Tokyo Metropolitan Research Laboratory of Public Health, Hyakunincho, Shinjuku-ku, Tokyo 160

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In order to improve the understanding of the electron capture detector (ECD), a study on the response mechanism has been carried out by using the pulse sampling technique. The ECD currents in the presence and the absence of electron capturing molecules were measured under various pulse conditions. The responses of the ECD probably arise from the current drop based on the slower electron drift velocity in the presence of electron capturing molecules than that in the absence of them.

The electron capture detector (ECD) has been widely used as the most suitable gas chromatographic detector for trace amounts of halogen-containing compounds on account of its high sensitivity and selectivity. Therefore, the ECD is necessary in laboratories concerned with the analysis of environmental contaminations such as organochloro pesticides and polychlorinated biphenyls. However, the response mechanism of the ECD has not completely establised yet, that is, the details of the events which occur within the ECD are not known so well. Several views have been proposed about the ECD.

Wentworth *et al.*[2] have described the behavior of electrons within a pulse-sampled ECD on the basis of the following assumptions:[3] (1) The current measured is due to electrons which are drawn to the positive electrode during the application of pulses. (2) The relatively immobile ions contribute little to the current. (3) The ECD cell is cleared of electrons during each pulse. (4) Positive ions will be in very large excess of electrons because the electrons diffuse quickly to cell boundaries. (5) The charge associated with negative ions formed by electron capture is quickly lost because of the much faster recombination between positive ions and negative ions than that between positive ions and electrons.

Siegel and McKeown,[4] however, criticised assumptions (3), (4), and (5), and insisted that both electrons and positive ions become characterized by a single (ambipolar) diffusion coefficient. According to this view, the current measured from the ECD should be considered to reflect the motion of electrons and positive ions within one Debye length from the positive electrode surface. Though undeniable for the present, this view has not been commonly accepted.

Grimsrud *et al.*[3] have proposed based on the positive space-charge field created by positive ions, and recalled the Wentworth assumption (3). Their modification has the merit that it does not depart so drastically from the Wentworth view, which has become the conventional one because of being strongly supported in many experiments.[2,5—7]

Under the circumstances described above, the author has measured the ECD currents under various pulse conditions in order to understand the behavior of electrons within the ECD and to reveal its response mechanism.

Experimental

A Shimadzu gas chromatograph Model 5A equipped with a Shimadzu ECD Model EDC-5 was used. The ECD has coaxial geometry and contains a 10 mCi ^{63}Ni or a 300 mCi ^{3}H radioactive source. The radius of the electrode is 2.0 mm, and the distance from the center of the electrode to the surface of the radioactive source is 5.0 mm. The carrier gas used (Nihon Sanso, A grade pure gas) was nitrogen of a purity over 99.9995%. Before being introduced into the gas chromatograph, the gas was passed through a Molecular Sieve 13 X column and an oxygen scrubber (Alltech, Oxy-Trap). For the gas chromatographic column, a 1 m×3 mm i.d. glass column packed with 2% Silicone OV-17 on Chromosorb W (AW-DMCS), 60—80 mesh was used at temperatures up to 200 °C. The other conditions were set up as follows: flowrate, 60 ml/min; ECD temperature, 220 °C.

Results and Discussion

Effect of Pulse Conditions on ECD Current. As shown in Fig. 1, the ECD current measured increased with increasing the pulse width (t_W), and finally attained a plateau for each different pulse period (t_P).

According to Wentworth *et al.*[1] the current is due to electrons which are drawn to the positive electrode during the application of pulses. The appearance of the plateau indicates that the number of electrons collected by the positive electrode increases with increasing t_W, and all electrons formed between pulses are collected when t_W becomes sufficiently large. This is because slower electrons can drift to the positive electrode with increasing t_W, without recombination with positive ions.

Electron Drift Velocity. The value of $t_W^{1/2}$, which is denoted by an arrow in Fig. 2 and represents the time required for half the electrons drifting to the positive electrode, is the mean time of the electrons drifting to the electrode. Hence, the reciprocal of $t_W^{1/2}$ is proportional to the electron drift velocity, ω:

$$\omega \propto (t_W^{1/2})^{-1}. \tag{1}$$

As shown in Fig. 2, the value of $(t_W^{1/2})^{-1}$ decreases with decreasing the pulse amplitude (V_a), and finally approaches zero at approximately 2 V in any t_P. These results suggest that the positive ion cloud created within the cell reduces the applied field by about 2 V, *i.e.*, about 2 V of the electrical potential is induced by positive ions.

According to Grimsrud *et al.*,[3] the electrical potential, V, expressed in the form of Eq. 2 is induced by positive

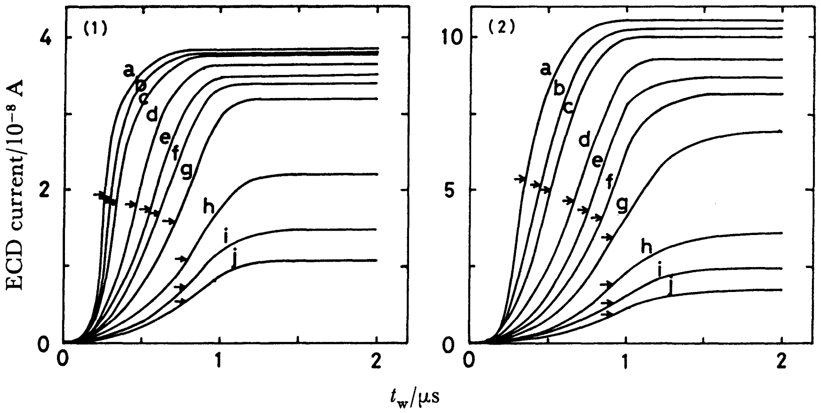

Fig. 1. Effect of t_w on ECD current in various t_p. t_p/µs: a; 10, b; 100, c; 200, d; 400, e; 600, f; 800, g; 1000, h; 2000, i; 3000, j; 4000. ECD: (1); ^{63}Ni, (2); ^{3}H.

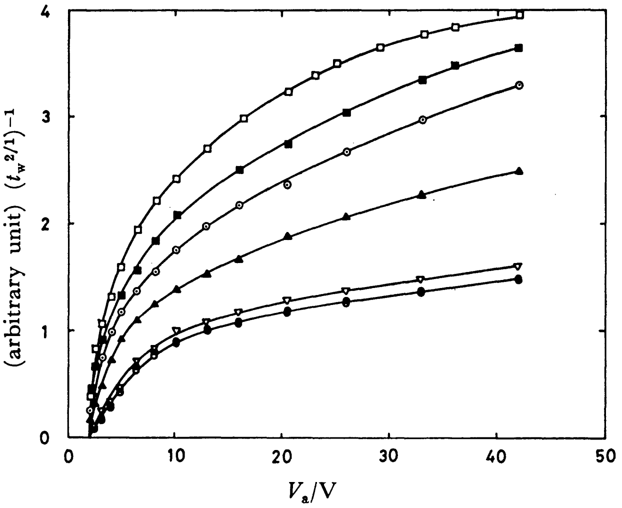

Fig. 2. Effect of V_a on the value of $(_w^{1/2})^{-1}$ in various t_p. t_p/µs: □; 10, ■; 100, ⊙; 200, ▲; 400, ▽; 1000, ●; 2000, ○; 4000. ECD; ^{63}Ni.

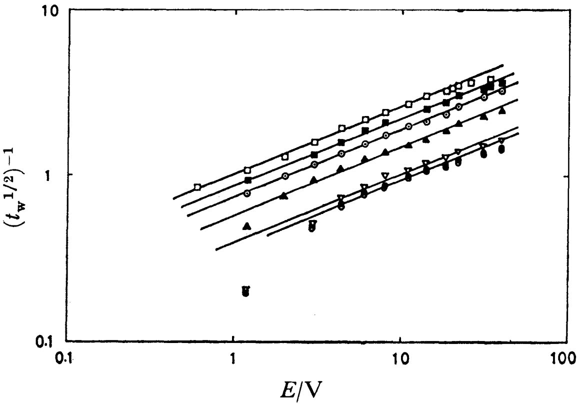

Fig. 3. Plots of ln $(t_w^{1/2})^{-1}$ *versus* E, where $E = V_a - 2.0$. t_p: Same as in Fig. 3.

ions at any point within the cell, if one assumes that the positive ions are uniformly distributed throughout the cell:

$$V = \frac{\rho_o}{4\varepsilon_o}\left\{(b^2-a^2)\frac{\ln(r/b)}{\ln(b/a)}+(b^2-r^2)\right\}. \tag{2}$$

Here ρ_o is the density of the positive ions, ε_o is the permittivity of free space, a is the radious of the electrode, b is the distance from the center of the electrode to the surface of radioactive source, and r is the distance from the center of the electrode to any point within the cell.

The potential calculated from Eq. 2 for the ^{63}Ni ECD used in the present study becomes a maximum value of approximately 10 V at $r = 2.73$ mm. If this value is reasonable, the electrons within the cell will distribute most densely near the middle of the radioactive source and the positive electrode under the field-free, *i.e.*, pulse-free conditions, and then they will drift to the positive electrode against the electrical potential under pulse-sampled conditions. Therefore, the field strength will become lower than that applied to the positive electrode by the maximum value of the induced potential. Consequently, the value of $(t_W^{1/2})^{-1}$ should become zero at approximately 10 V. In practice, however, the value becomes zero at approximately 2 V in any t_P as shown in Fig. 3. This discordance of the theoretical and the observed values suggests the deficiency of Grimsrud's view: The center of the ionization was hitherto considered 1—2 mm for ^{3}H and 6—8 mm for ^{63}Ni, judging from commonly used ECD dimensions.[8,9] Recently, however, Aue *et al.*[9] have reported that the center of ionization is much closer to the radioactive foil than commonly assumed, *i.e.*, at approximately 0.2 mm for ^{3}H and approximately 1 mm for ^{63}Ni in nitrogen at ambient conditions. These experimental facts tend to contradict Grimsrud's view, in which it is assumed that positive ions are uniformly distributed throughout the cell.

The electron drift velocity, ω, in a gas under electric field is expressed in the form of Eq. 3:[10]

$$\omega = \frac{e}{m}\cdot\frac{\lambda}{u}\cdot\frac{E}{p}, \tag{3}$$

where e is the charge, m is the mass, λ is the mean free path, u is the agitation velocity, E is the field strength, and p is the pressure of a gas.

In the ECD used as a gas chromatographic detector, e, m, and p are constant. Hence,

$$\omega \propto \lambda \cdot \frac{E}{u}. \tag{4}$$

On the other hand, electrons which are at thermal equilibrium state under the field-free conditions obtain some kinetic energy proportional to the field strength:

$$\frac{1}{2} \cdot m \cdot u^2 \propto E. \tag{5}$$

Equations 4 and 5 give Eq. 6:

$$\omega \propto \lambda \cdot E^{1/2}. \tag{6}$$

Figure 3 is the ln-ln plots of the curves shown in Fig. 2, where the abscissa is converted into $E = V_a - 2.0$. In any t_P, the plot gives a straight line whose slope is approximately 0.5. This result indicates that ω is proportional to $E^{1/2}$.

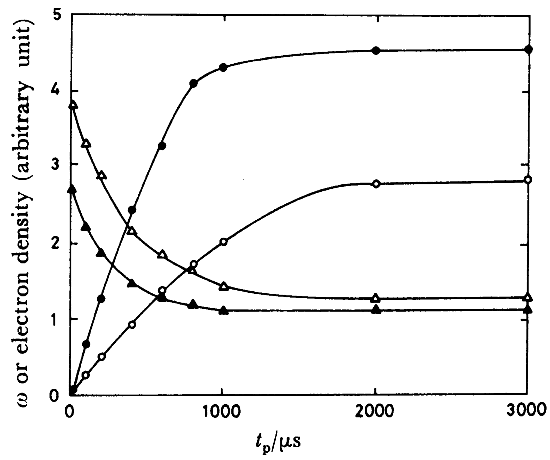

Fig. 4. Variations of ω and electron density with t_p. △: ω (^{63}Ni), ▲: ω (^{3}H), ○: Ion density (^{63}Ni), ●: Ion density (^{3}H). E: 30 V.

Figure 4 shows the variations of ω and the electron density with t_P. The value of ω decreases, and oppositely the electron density increases with increasing t_P for constant E. These results suggest that ω is inversely proportional to the electron density. Since the interaction between electrons and positive ions increases with increasing the electron density, the value of λ should be inversely proportional to the electron density, and consequently ω may be proportional to λ, as in Eq. 5. Therefore, as discussed above, the curves of Fig. 2 are expressed in the form of Eq. 6.

Response Mechanisms. Figure 5 shows the ECD current versus t_w curves in various t_P at 30 °C(a), and 200 °C(b) of column temperatures. In any t_P, the values of $t_W^{1/2}$ increases, *i.e.*, the electron drift velocity decreases, with increasing the column temperature. According to Aue *et al.*,[9] the ECD can simply be considered a non-linear impedance device, whose impedance increases with the introduction of electron capturing molecules. The higher the column temperature is, the more electron capturing molecules which bleed from the column. Consequently, the impedance of the ECD cell increases with the rise of column temperature. The increase of the impedance rusults in the decrease of the electron drift velocity. The curves c, which are the plots for (a—b), correspond to the current drop based on the increase of the impedance. If the drop arises from the increase of the impedance, the curves c should gradually approach zero with increasing t_W. The reason is that even slower electrons can drift to the positive electrode with increasing t_W, and curve b consequently approaches to the corresponding curve a. However, the curves do not practically become zero, but constant in each t_P. These results lead to the probability that the current drop occurs by some other factor rather than the increase of the cell impedance. In the absence of electron capturing molecules, electrons within the ECD attain a thermal equilibrium state through numerous collisions with the carrier gas molecules. In the presence of electron capturing molecules, the thermally equilibrated electrons collide with electron capturing molecules and finally attach to them to form negative ions.[11] Consequently, the value of λ should become smaller than that in the absence of electron capturing molecules. Considered from this view, the curves c correspond to the current drop arising from the decrease of the electron drift velocity, which results from the decrease of λ.

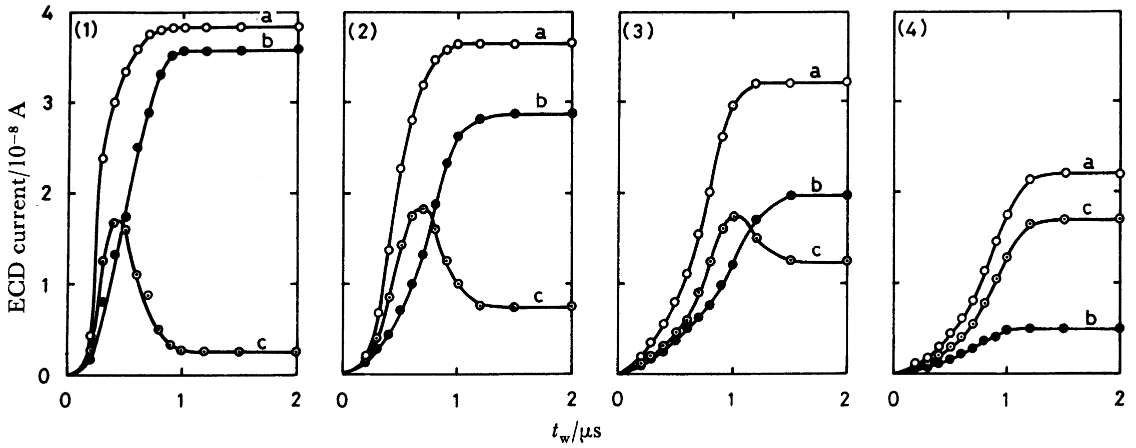

Fig. 5. Effect of t_w on ECD current at column tempertures of 30 °C (a) and 200 °C (b). t_p/μs: (1); 100, (2); 500, (3); 1000, (4); 2000. V_a: 30 V. ECD: ^{63}Ni. Curves c are the plots of (a—b).

The view described above can explain why the curve c does not become zero, but constant, with increasing t_W. So long as the value of λ is not zero, all electrons within the cell can drift to the electrode by applying a sufficiently large t_W of pulses, *i.e.*, the current drop decreases and finally becomes zero with increasing t_w. However, if the value of λ is zero, the electrons can not drift to the electrode even if sufficiently large t_W of pulses are applied, *i.e.*, the current drop approaches a constant value which is proportional to the number of electrons attached to electron capturing molecules. By applying the above discussion for the region where the current drop remains constant, the proposed view recalls the classical mechanism of electron capture detection by Wentworth *et al.*, *i.e.*, attachment to electron capturing molecules, followed by positive ion-negative ion neutralization.

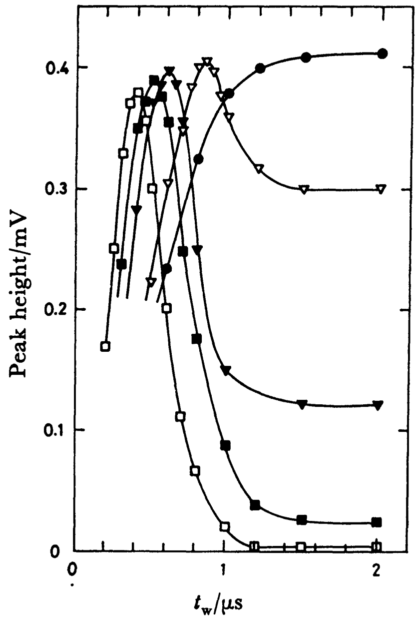

Fig. 6. Effect of t_w on the peak height of γ-BHC.
$t_p/\mu s$: □; 10, ■; 100, ▽; 500, ▼; 1000, ●; 2000.
V_a: 30 V. ECD: ^{63}Ni.

Figure 6 shows the variation of the peak height for γ-BHC with t_W. The profile of the peak height, which represents the sensitivity of the ECD, is in accord with the curves c in Fig. 5. Such a profile is not specific for γ-BHC, but general for the other several samples examined, *e.g.*, α-BhC, β-BHC, δ-BHC, *p,p'*-DDE, aldrin, dieldrin, 2,4,5-trichlorobiphenyl, and 2,2',4,4',6,6'-hexachlorobiphenyl.[12] These results lead to the conclusion that the response of the ECD arises from the current drop due to the decrease of the electron drift velocity resulting from the decrease of λ, and the removal of the electrons whose values of λ become zero as the result of attachment to electron capturing molecules.

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