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Studies on Characteristics of Electron Capture Responses. V. Estimation of Electron Attachment Mechanisms from Carrier Gas Flow-rate Dependence of Electron Capture Coefficients

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The electron capture coefficients, *K*, defined by Wentworth *et al.* were measured for several samples in various carrier gas flow-rates, *F*, by a pulse sampled electron capture detector (ECD). The carrier gas flow-rate dependence of *K*, *i.e.*, the plot of *K versus F*, is discussed from the viewpoint of the kinetic theory. The results reveal that the flow-rate dependence of *K* can be used for estimating the electron attachment mechanisms.

In their early studies on the responses of the ECD, Wentworth *et al.*[1—4] theorized about the electron attachment mechanisms on the basis of kinetic derivations using steady-state approximations. According to their theory, the electron attachment phenomena can be classified into four different mechanisms which can be determined from the temperature dependence of *K*, *i. e.*, the plot of $\ln KT^{3/2}$ *versus* $1/T$.

The author reported[5] that the carrier gas flow-rate dependence of K[6] was also closely related to the electron attachment mechanisms: The values of *K* for samples undergoing a non-dissociative electron capture reaction were little affected by the flow-rate, those for samples undergoing a dissociative electron capture reaction increased significantly with increasing the flow-rate, and those for samples undergoing an electron capture reaction through an anion radical intermediate were little affected with the flow-rate at lower temperatures, but the values increased gradually with increasing the flow-rate at higher temperatures. In the present paper, these relations have been discussed from the viewpoint of the kinetic theory proposed by Wentworth *et al.*

Experimental

Apparatus and Samples. A Shimadzu GC-5A gas chromatograph equipped with a pulse sampled ECD was used. The ECD was of co-axial geometry and contained a 10 mCi ^{63}Ni radioactive source. Pulses were supplied with a DuMont 404 pulse generator. The pulse conditions were set up as follows in order to collect all of the electrons formed during a pulse period and to assure a steady-state for kinetic equations derived from the reactions postulated within the ECD: the pulse period, 2000 μs; the pulse width, 2.0 μs; the pulse amplitude, 30 V. An analog device was used for the calculation of *K* from the equation:

$$Kn = \frac{F}{S}\int \frac{I_b - I_e}{I_e}\,dX, \qquad (1)$$

where n is the number of moles injected, F is the carrier gas flow-rate in l/min, S is the chart speed in cm/min, X is the chart distance in cm, I_b is the base current due to pure carrier gas, and I_e is the current in the presence of electron capturing vapor. Practically, *K* was obtained from the slope of the *n versus* peak area plot under constant conditions of *F* and *S*, and corrected in the same manner as in the proceeding paper.[5] The carrier gas used (Nihon Sanso, A Grade) was specified to contain more than 99.9995% of nitrogen and less than 0.5 ppm of oxygen. Before being introduced into the system, the gas was passed through a Molecular Sieve 13X filter and an oxygen scrubber (Alltech, Oxy-Trap). The flow-rate was measured at the exit end of the system with a bubble flow meter and a stopwatch. Peak areas were calculated with a Spectra-Physics Autolab System IV integrator. Two different kinds of chromatographic columns were used. One was a 1 m×3 mm i.d. glass column packed with 2% Silicone OV-17 on Chromosorb W (80—100 mesh), and the other was a 1 m×3 mm i.d. glass column packed with 2% Silicone OV-275 on Chromosorb W (60—80 mesh). The ECD temperature was measured with a thermometer inserted into the detector oven rather than with the thermocouple provided.

The samples used in the present study were commercially available reagents. Solutions of the samples were prepared to give suitable peak heights, *i.e.*, $(I_b-I_e)/I_e=1$—4.[7]

Results and Discussion

Figures 1, 2, and 3 show the flow-rate dependences of *K* for nitrobenzene, acetophenone, and Aldrin. The flow-rate dependences of *K* for these samples are quite different. The values of *K* for nitrobenzene are constant, *i. e.*, not affected with the flow-rate at all, those for acetophenone decrease in nearly inverse proportion to the increase of the flow-rate, and those for Aldrin increase in nearly direct proportion to the increase of the flow-rate. The differences among these samples are explained below.

According to Wentworth *et al.*,[2] *K* is represented in the form of Eq. 2 by using the rate constants attached to Eqs. 3—6:

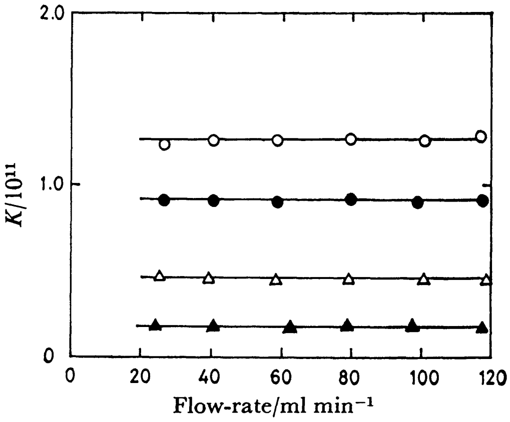

Fig. 1. Carrier gas flow-rate dependence of *K* for nitrobenzene at 200 °C (○), 240 °C (●), 280 °C (△), and 320 °C (▲).

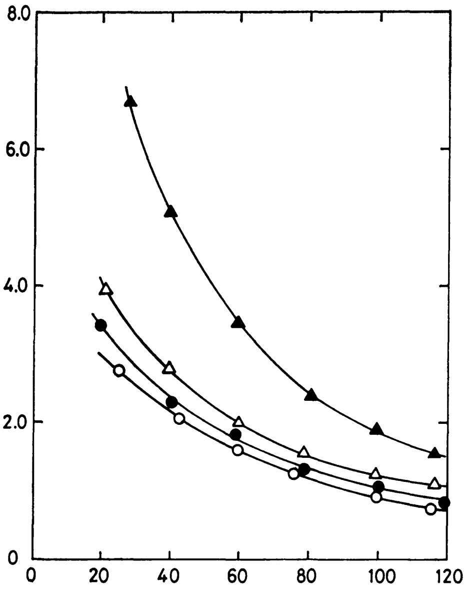

Fig. 2. Carrier gas flow-rate dependence of K for acetophenone at 200 °C (○), 240 °C (●), 280 °C (△), and 320 °C (▲).

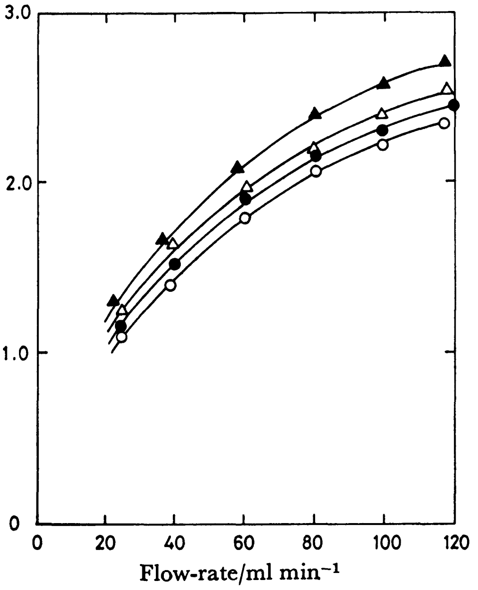

Fig. 3. Carrier gas flow-rate dependence of K for Aldrin at 200 °C (○), 240 °C (●), 280 °C (△), and 320 °C (▲).

$$K = \frac{k_{12}}{k_N + k_R} + \frac{k_1 k_2}{(k_N + k_R)\Sigma k} + \frac{(k_{N1} + k_{R1})k_1}{(k_N + k_R)\Sigma k}, \tag{2}$$

where $k_N + k_R = k'_N[P^+] + k'_R[R\cdot]$, $k_{N1} + k_{R1} = k'_{R1}[P^+] + k_{R1}[R\cdot]$, and $\sum k = k_{-1} + k_2 + k_{N1} + k_{R1}$.

$$AB + e^- \xrightarrow{k_{12}} A\cdot + B^- \tag{3}$$

$$\begin{tikzcd} AB + e^- \arrow[r, shift left, "k_1"] & AB^- \arrow[l, shift left, "k_{-1}"] \arrow[r, "k_{N1} + k_{R1}"] \arrow[d, "k_2"] & AB \\ & A\cdot + B^- & \end{tikzcd} \tag{4}$$

$$P^+ + e^- \xrightarrow{k'_N} R\cdot \tag{5}$$

$$R\cdot + e^- \xrightarrow{k'_R} R^-, \tag{6}$$

where AB is an electron capturing molecule, AB^- is a negative ion, $A\cdot$ and B^- are fragments of dissociation, and P^+ and $R\cdot$ are symbols to designate any of the positive ions and radicals.

It can be seen that K is a sum of three terms, and that the first term of Eq. 2 corresponds to the situation in which Eq. 3 predominates. Such a situation, however, is considered to be the same as the situation where $k_2 \gg k_{-1} + k_{N1} + k_{R1}$ is satisfied in Eq. 4 to which the second and the third terms in Eq. 2 correspond. Consequently, the first term of Eq. 2 can be abbreviated. Hence,

$$K = \frac{k_1(k_2 + k_{N1} + k_{R1})}{(k_N + k_R)\Sigma k}. \tag{7}$$

Equation 7 can be further simplified as follows, according to the relative magnitude of each rate constant in $\sum k$.

(I) When $k_{N1} + k_{R1} \gg k_{-1} + k_2$, the expression for K becomes

$$K = \frac{k_1}{k_N + k_R}. \tag{8}$$

In this situation, K is not affected by the flow-rate. In other words, K for a given sample is constant at any flow-rate. A typical sample belonging to this group is nitrobenzene (Fig. 1).

(II) When $k_{-1} \gg k_2 + k_{N1} + k_{R1}$, the expression for K becomes

$$K = \frac{k_2 + k_{N1} + k_{R1}}{k_N + k_R} \times \frac{k_1}{k_{-1}}. \tag{9}$$

The part of k_1/k_{-1} of Eq. 9 is equal to the equilibrium constant, K_{eq}, of the reaction between AB and an electron in Eq. 4. The concentration of AB^- is negligible in comparison with that of AB in Eq. 4, since K_{eq} is very small in this situation. Therefore, K_{eq} is expressed in the form of Eq. 10 by using the ionization efficiency, p, and the initial concentration of AB, a:

$$K_{eq} = \frac{k_1}{k_{-1}} = \frac{[AB^-]}{[AB][e^-]} = \frac{p}{a(1-p)}. \tag{10}$$

On the other hand, p is expressed in the form of Eq. 11:[8]

$$p = \frac{c}{c + F}, \tag{11}$$

where c is a constant, and F is the carrier gas flow-rate. Combination of Eqs. 10 and 11 gives

$$K_{eq} = \frac{k_1}{k_{-1}} = \frac{c}{a} \times \frac{1}{F}. \tag{12}$$

Equation 12 means that K_{eq} is in inverse proportion to the carrier gas flow-rate. Therefore, if the part of $(k_2 + k_{N1} + k_{R1})/(k_N + k_R)$ is not affected by the carrier gas flow-rate, K expressed by Eq. 9 will also be in inverse proportion to the flow-rate. A typical sample satisfying Situation II is acetophenone (Fig. 2). Another sample belonging to this group was benzonitrile. The flow-rate dependence of K for benzonitrile was similar to that for acetophenone.

(III) When $k_2 \gg k_{-1} + k_{N1} + k_{R1}$, the expression for K becomes

$$K = \frac{k_1}{k_N + k_R}.$$

The values of K in this situation are expected to be constant in any flow-rate, since K is expressed in the same form as in Situation I. In practice, however, K is approximately proportional to the flow-rate. This is because a molecule AB dissociates spontaneously to give A· and B$^-$ on entering into the ECD. Under such a situation, the ECD is considered to be coulometric in response and to act as a mass-sensitive detector.[9–11] Therefore, the values of K calculated from Eq. 1, which is derived by assuming that the ECD is concentration-sensitive,[9,10] are not kept constant but become proportional to the flow-rate. Aldrin is a typical sample which satisfies Situation III (Fig. 3). In fact, Aldrin has a very small activation energy for dissociation, which is calculated from the slope of the ln $KT^{3/2}$ *versus* $1/T$ plot shown in Fig. 4 and the gas constant ($-$slope$\times R$). Consequently, all of the molecules of Aldrin dissociate within the ECD. Therefore, it is reasonable that the ECD acts as a mass-sensitive device rather than a concentration-sensitive one, for detection of Aldrin. Other samples belonging to this group were *p,p'*-DDE, *p,p'*-DDT, and γ-BHC. Their flow-rate dependences of K were similar to that for Aldrin.

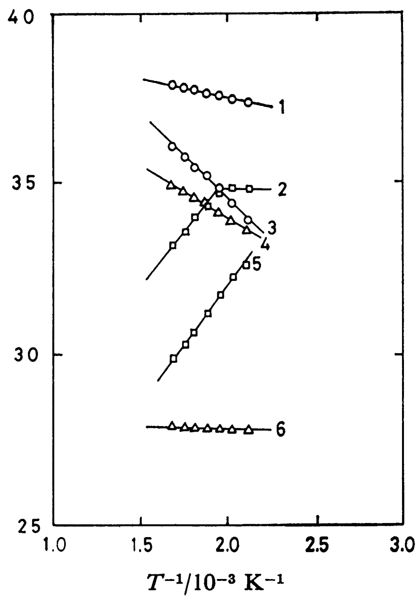

Fig. 4. Temperature dependence of K for Aldrin (1), nitrobenzene (2), 1,2,4-trichlorobenzene (3), dodecyl bromide (4), azulene (5), and acetophenone (6).

On the basis of the flow-rate dependence of K for the three situations described above, those shown in Fig. 5—7 can be considered as follows:

In the case of azulene (Fig. 5), the values of K are not affected at all by the flow-rate at lower temperatures, but decrease slightly with increasing the flow-rate at higher temperatures. Therefore, it is likely that $k_{N1}+k_{R1} \gg k_{-1}+k_2$, *i. e.*, Situation I, is satisfied at lower temperatures, but $k_{-1}+k_2$ becomes almost equal to $k_{N1}+k_{R1}$ at higher temperatures, since k_{-1} becomes larger with the rise of temperature. Although acetophenone,

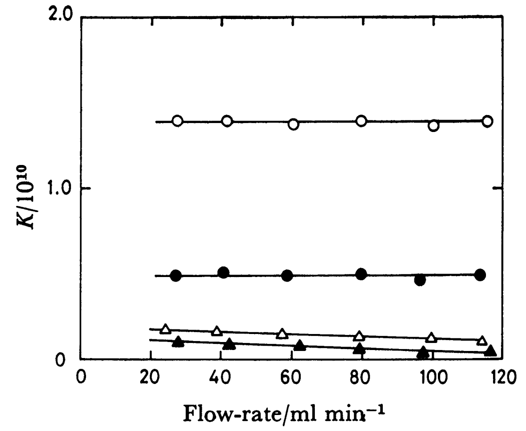

Fig. 5. Carrier gas flow-rate dependence of K for azulene at 200 °C (○), 240 °C (●), 280 °C (△), and 320 °C (▲).

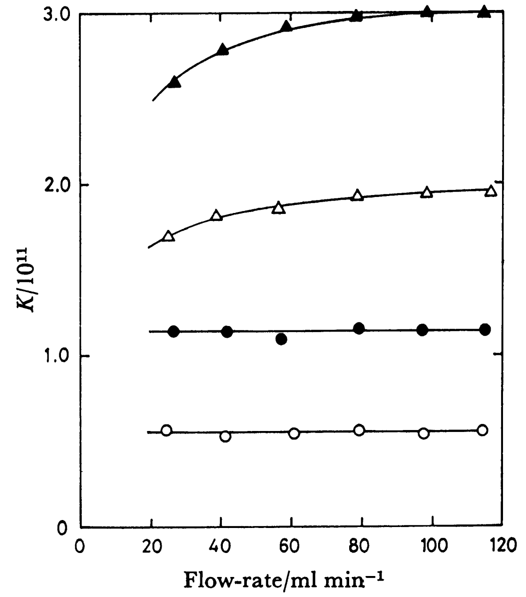

Fig. 6. Carrier gas flow-rate dependence of K for 1,2,4-trichlorobenzene at 200 °C (○), 240 °C (●), 280 °C (△), and 320 °C (▲).

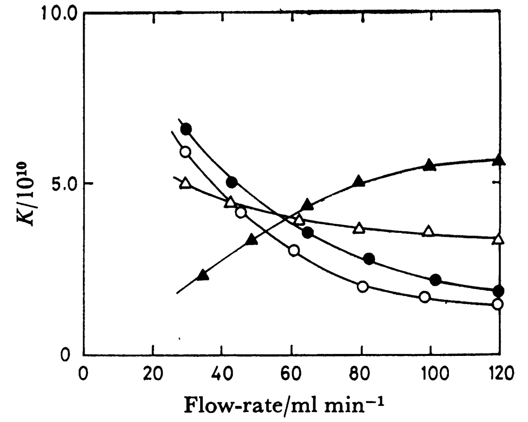

Fig. 7. Carrier gas flow-rate dependence of K for dodecyl bromide at 200 °C (○), 240 °C (●), 280 °C (△), and 320 °C (▲).

nitrobenzene, and azulene are all regarded as nondissociative samples from the plots of ln $KT^{3/2}$ *versus* $1/T$, *i. e.*, a positive slope at higher temperatures and/or a negative slope nearly zero at lower temperatures (Fig. 4), the flow-rate dependences of K show that they are not necessarily in the same situation. This is owing to the difference of the electron affinities: 5.5, 14.7, and 15.2 kcal/mol, for benzonitrile, azulene, and nitrobenzene, respectively.[4,12]

In the case of 1,2,4-trichlorobenzene (Fig. 6), the values of K are constant at lower temperatures, but increased gradually with increasing the flow-rate at higher temperatures. Therefore, the electron capture reaction of 1,2,4-trichlorobenzene occurs nondissociatively under Situation I, *i. e.*, $k_{\rm N1}+k_{\rm R1} \gg k_{-1}+k_2$, at lower temperatures, but dissociatively under Situation III, *i. e.*, $k_2 \gg k_{-1}+k_{\rm N1}+k_{\rm R1}$, at higher temperatures. Although 1,2,4-trichlorobenzene apparently belongs to the dissociative sample, considering the plot of ln $KT^{3/2}$ *versus* $1/T$ (Fig. 4), it is really a sample which dissociates through an anion radical intermediate.[5,12–14]

In the case of dodecyl bromide (Fig. 7), which is regarded as one of the dissociative samples from the negative slope of the ln $KT^{3/2}$ *versus* $1/T$ plot, the values of K decrease with increasing the flow-rate at lower temperatures, but increase at higher temperatures. This flow-rate dependence of K suggests that the electron capture reaction of dodecyl bromide occurs under Situation II, *i. e.*, $k_{-1} \gg k_2+k_{\rm N1}+k_{\rm R1}$, at lower temperatures, but occurs under Situation III, *i. e.*, $k_2 \gg k_{-1}+k_{\rm N1}+k_{\rm R1}$, at higher temperatures. The change from Situation II to III with the rise of temperature reveals that the dissociative electron capture reaction of dodecyl bromide proceeds by a mechanism similar to bimolecular nucleophilic substitution ($S_{\rm N}2$), as shown in Fig. 8. This mechanism is supported by Kojima *et al.*,[15] who have concluded on the basis of the activation energy that the electron capture reaction of alkyl halide is a kind of $S_{\rm N}2$.

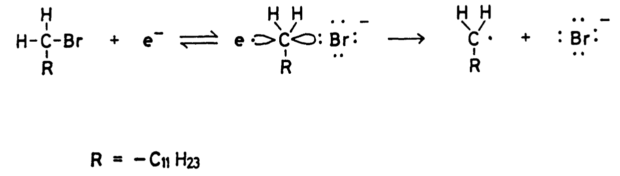

Fig. 8. Electron attachment mechanism of dodecyl bromide.

Conclusion

The carrier gas flow-rate dependence of K was considered from the viewpoint of the kinetic theory proposed by Wentworth *et al.* The results revealed that the electron capture reaction could be divided into three situations by the relative magnitude of the rate constants of elementary reactions postulated within the ECD, and that each situation is related to the carrier gas flow-rate:

(I) When $k_{\rm N1}+k_{\rm R1} \gg k_{-1}+k_2$, K is not affected by the flow-rate.

(II) When $k_{-1} \gg k_2+k_{\rm N1}+k_{\rm R1}$, K is inversely proportional to the flow-rate.

(III) When $k_2 \gg k_{-1}+k_{\rm N1}+k_{\rm R1}$, K is approximately proportional to the flow-rate.

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