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Studies on Characteristics of Electron Capture Responses. IV. 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 on several samples in various carrier gas flow-rates at the detector temperatures of 200—320 °C. The effect of the flow-rate on the value of K was considered. The results revealed that the flow-rate dependence of K for each sample was closely related to one of the three electron capture reaction processes. In a sample undergoing the non-dissociative electron capture reaction, the values of K were generally not affected by the flow-rate; they decreased slightly with increasing the flow-rate at higher temperatures. In a sample undergoing the dissociative electron capture reaction, the values of K increased significantly with increasing the flow-rate at all temperatures. In a sample undergoing the dissociative electron capture reaction through an anion radical intermediate, the values of K were slightly or not at all affected by the flow-rate at lower temperatures, but increased gradually with increasing the flow-rate at higher temperatures.

Its high sensitivity and selectivity to halogen-containing compounds have caused the electron capture detector (ECD) to be widely used in the trace analysis of organochloro pesticides, polychlorinated biphenyls, *etc.*, remaining in various environmental samples. Though the practical applications are familiar, the theoretical details of the ECD have not received much study. The author has thus studied the responses of the ECD in order to understand the events occurring within it.

The ECD is a concentration-sensitive detector.[1-3] Its response function, studied by Wentworth *et al.*,[4-6] is given by

$$\frac{I_b - I_e}{I_e} = KC, \tag{1}$$

where I_b is the base current due to pure carrier gas, I_e is the current in the presence of a concentration C of electron capturing vapor, and K is the electron capture coefficient, which expresses the sensitivity of the detector to the vapor. In the practical gas chromatography, K is given by

$$K = \frac{1}{n}\,\frac{F}{S}\int\frac{I_b - I_e}{I_e}\mathrm{d}X, \tag{2}$$

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, and X is the chart distance in cm.

Equation 2 shows that the peak areas, $\int(I_b - I_e)/I_e \mathrm{d}X$, are inversely proportional to F under the constant conditions of S and n: If F increases to 2, 3, 4··· times as much as the initial run, the peak area will decrease to 1/2, 1/3, 1/4···, respectively. Consequently, as long as the response function of Wentworth *et al.* is correct, the value of K for a sample obtained from Eq. 2 is constant at any flow-rate. However, it was reported in the previous paper[7] that there were some samples whose values of K varied with the flow-rate. A similar result has been obtained by Devaux and Guiochon.[2] Therefore, in the present paper, the relation between the electron capture coefficient and the carrier gas flow-rate has been studied. The results have revealed that the carrier gas flow-rate dependence of K is closely related to one of the three electron capture reaction processes.

Experimental

Apparatus and Samples. A Shimadzu GC-5A gas chromatograph equipped with an ECD was used. The ECD was of co-axial geometry and contained a 10 mCi ^{63}Ni radioactive source. Pulses were supplied by a DuMont 404 pulse generator. The pulse conditions were set up as follows in order to collect all of the electrons and to assure a steady state[4,6,8] under which Eq. 1 can be derived: the pulse period, 2000 μs; the pulse width, 2.0 μs; and the pulse amplitude, 30 V. An analog device was used for the conversion of the normal response, $I_b - I_e$, into the Wentworth response, $(I_b - I_e)/I_e$.[9] The carrier gas was pure nitrogen. Before being introduced into the system, the gas was passed through a 40 cm × 5 mm i.d. stainless steel column packed with Molecular Sieve 13 X. The flow-rate was measured at the exit end of the system with a bubble flow meter and a stopwatch. Peak areas were obtained with a Spectra-Physics Autolab System IV integrator. Two different kinds of chromatographic columns were used. One of these was a 1 m × 3 mm i.d. glass column packed with 2% Silicon OV-17 on Chromosorb W, 80—100 mesh (Column I); the other was a 1 m × 3 mm i.d. glass column packed with 2% Silicon OV-275 on Chromosorb W, 60—80 mesh (Column II). The column oven was maintained at temperatures in the range of 140—180 °C on Column I and 100—140 °C on Column II. 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. Aldrin, γ-BHC, *p*, *p′*-DDE, and 2,4,6-trichlorobiphenyl were chromatographed by Column I, and nitrobenzene, azulene, iodobenzene, and 1,2,4-trichlorobenzene were chromatographed by Column II. Solutions of the samples were prepared to give suitable peak sizes, *i.e.*, $(I_b - I_e)/I_e = 1—4$.[9]

Results

Figure 1 shows the variation of I_b with the carrier gas flow-rate. Since I_b is the base current due to pure carrier gas, it ought to be kept constant. In practice, however, I_b decreased with decreasing the flow-rate, owing mainly to column bleed.[4-7] Therefore, a correction factor of I_0/I_b, where I_0 is the base current when no column bleed is observed, was utilized to adjust the value of K: the left side of Eq. 2 was multiplied by this

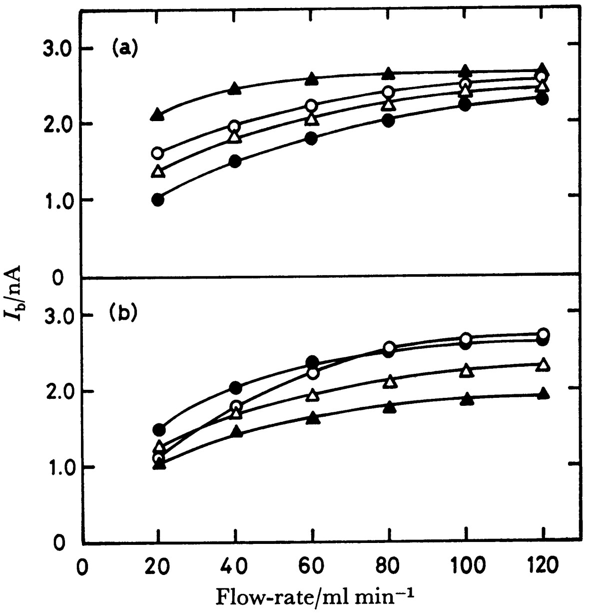

Fig. 1. Variation of base current with carrier gas flow-rate for Column I at 180 °C (a), Column II at 140 °C (b).
ECD temperatures: 200 °C (○), 240 °C (●), 280 °C (△), and 320 °C (▲).

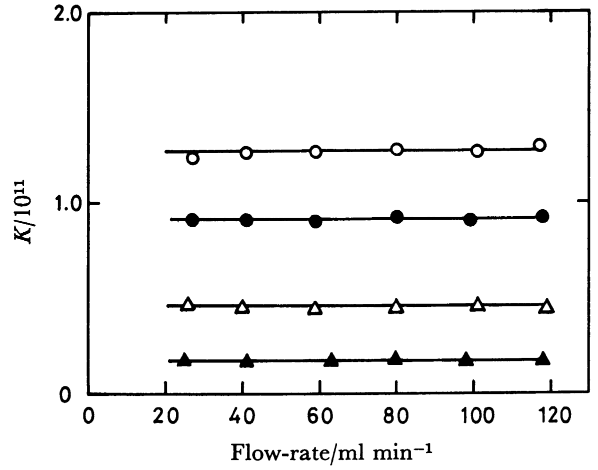

Fig. 2. Values of K for nitrobenzene *vs.* carrier gas flow-rate.
ECD temperatures: 200 °C (○), 240 °C (●), 280 °C (△), and 320 °C (▲).

factor.[4—6] In this paper, I_0 was regarded as I_b when the column oven was cooled to room temperature.

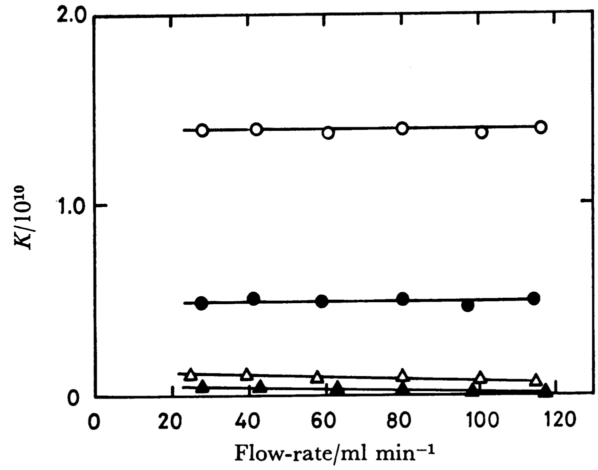

Fig. 3. Values of K for azulene *vs.* carrier gas flow-rate. ECD temperatures: 200 °C (○), 240 °C (●), 280 °C (△), and 320 °C (▲).

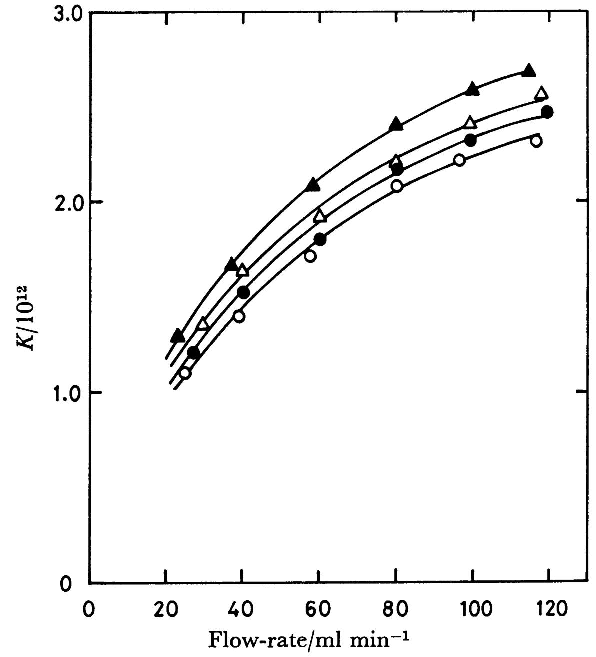

Fig. 4. Values of K for Aldrin *vs.* carrier gas flow-rate. ECD temperatures: 200 °C (○), 240 °C (●), 280 °C (△), and 320 °C (▲).

Figure 2 shows the values of K for nitrobenzene. No variations of K with the carrier gas flow-rate were observed at any temperature. Figure 3 shows the values of K for azulene. At lower temperatures, the values of K were not affected by the flow-rate at all. At higher temperatures, however, the values of K decreased slightly with increasing the flow-rate. Figures 4—6 show the values of K for Aldrin, γ-BHC, and p,p'-DDE, respectively. In these samples, the values of K increased significantly with increasing the flow-rate at all temperatures. Figures 7—9 show the values of K for 1,2,4-trichlorobenzene, 2,4,6-trichlorobiphenyl, and iodobenzene, respectively. In these samples, the values of K were slightly or not at all affected by the flow-rate at lower temperatures, but increased gradually with increasing the flow-rate at higher temperatures.

Discussion

The response of the ECD results from the electron capture reaction, which usually occurs through one of the three following processes:[4—6]

$$\mathrm{AB} + \mathrm{e}^- \rightleftarrows \mathrm{AB}^- \tag{3}$$

$$\mathrm{AB} + \mathrm{e}^- \longrightarrow \mathrm{A}\cdot + \mathrm{B}^- \tag{4}$$

$$\mathrm{AB} + \mathrm{e}^- \rightleftarrows [\mathrm{A}\cdot\mathrm{-B}]^- \longrightarrow \mathrm{A}\cdot + \mathrm{B}^-. \tag{5}$$

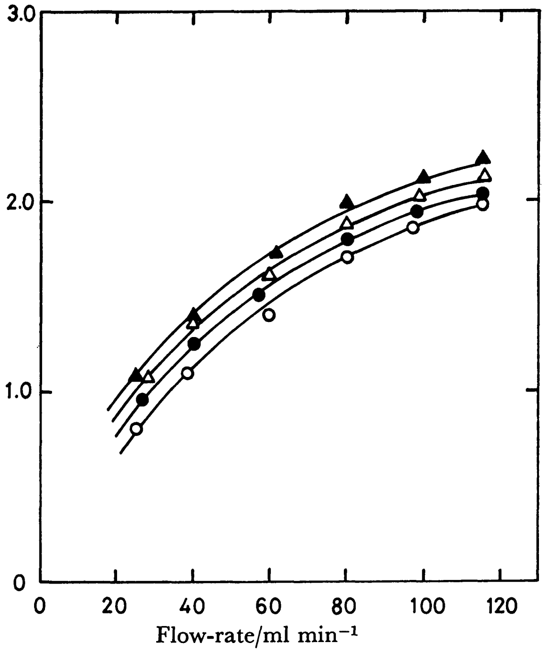

Fig. 5. Values of K for γ-BHC *vs.* carrier gas flow-rate. ECD temperatures: 200 °C (○), 240 °C (●), 280 °C (△), and 320 °C (▲).

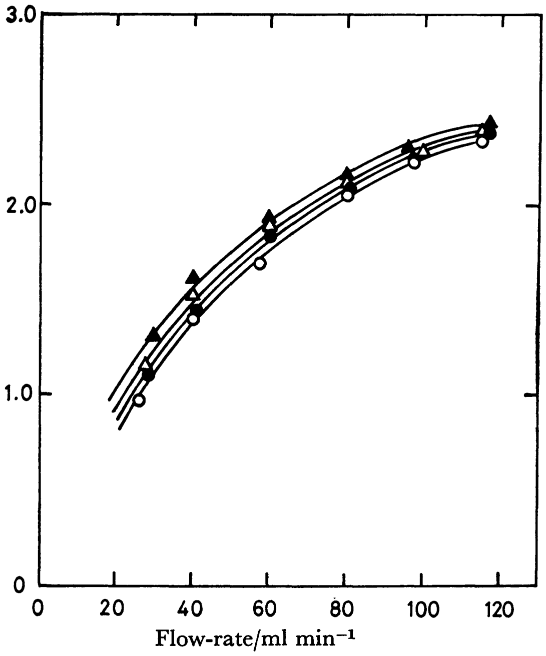

Fig. 6. Values of K for p,p'-DDE *vs.* carrier gas flow-rate. ECD temperatures: 200 °C (○), 240 °C (●), 280 °C (△), and 320 °C (▲).

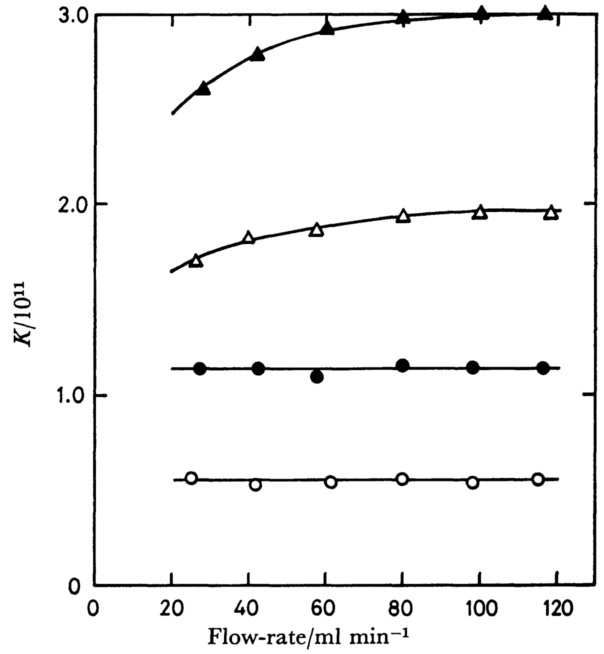

Fig. 7. Values of K for 1,2,4-trichlorobenzene *vs.* carrier gas flow-rate. ECD temperatures: 200 °C (○), 240 °C (●), 280 °C (△), and 320 °C (▲).

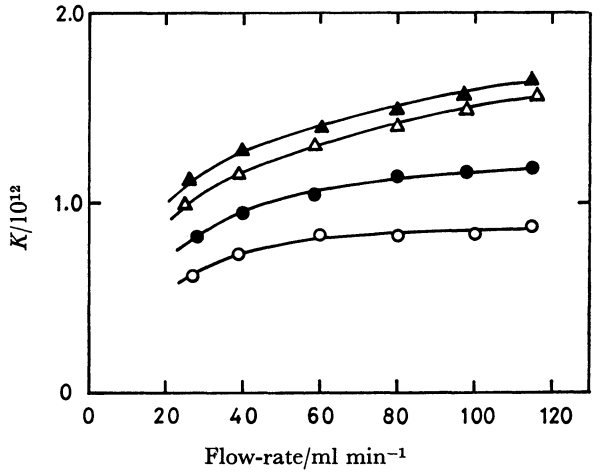

Fig. 8. Values of K for iodobenzene *vs.* carrier gas flow-rate. ECD temperatures: 200 °C (○), 240 °C (●), 280 °C· (△), and 320 °C (▲).

Equation 3, called the non-dissociative electron capture process, represents a reaction in which an electron capturing molecule, AB, reacts with an electron to form a stable molecular anion, AB$^-$. Equation 4, called the dissociative electron capture process, represents a reaction in which an electron capturing molecule dissociates into a radical, A·, and an anion, B$^-$. Equation 5, called the intermediate-dissociative electron capture process,[10] represents a reaction in which an electron capturing molecule dissociates slowly through an anion radical intermediate, [A·—B]$^-$.

These electron capture processes are closely related to the temperature dependence of K.[4-6] In the case of the non-dissociative process, the plot of ln $KT^{3/2}$ *vs.* $1/T$ has a slope of nearly zero at lower temperatures, and/or a positive slope at higher temperatures. In the case of the dissociative process, the plot has a negative slope at higher temperatures. In the case of the intermediate-dissociative process, the slope of the plot changes from zero to either negative through positive or negative directly with the rise of temperature, *i.e.*, the decrease of $1/T$. If we examine Fig. 10 from these points of

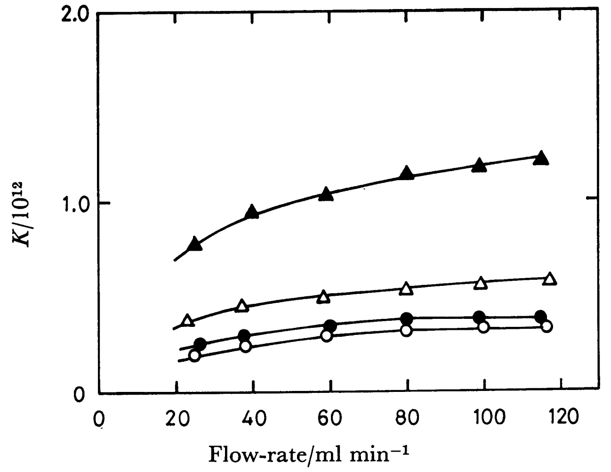

Fig. 9. Values of K for 2,4,6-trichlorobiphenyl *vs.* carrier gas flow-rate.
ECD temperatures: 200 °C (○), 240 °C (●), 280 °C (△), and 320 °C (▲).

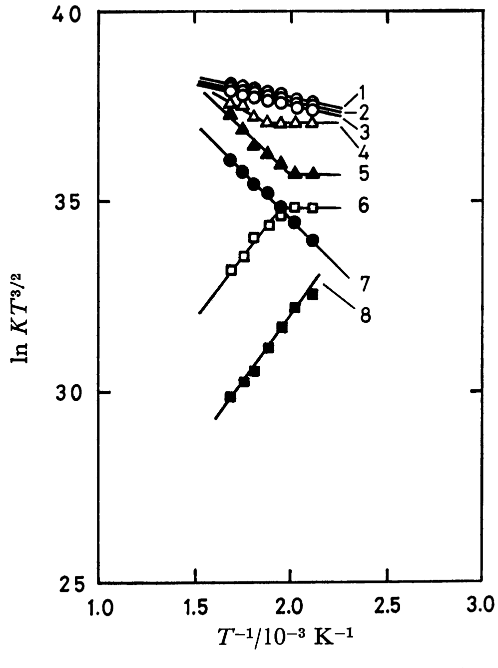

Fig. 10. Plots of ln $KT^{3/2}$ *vs.* $1/T$ for Aldrin (1), *p,p'*-DDE (2), γ-BHC (3), iodobenzene (4), 2,4,6-trichlorobiphenyl (5), nitrobenzene (6), 1,2,4-trichlorobenzene (7), and azulene (8).

view, we recognize that nitrobenzene and azulene are non-dissociative, Aldrin, γ-BHC, *p,p'*-DDE, and 1,2,4-trichlorobenzene are dissociative, and 2,4,6-trichlorobiphenyl and iodobenzene are intermediate-dissociative.

The carrier gas flow-rate dependence of K can also be related to the electron capture processes: The values of K for the samples undergoing the non-dissociative electron capture reaction are either not affected at all by the carrier gas flow-rate at any temperature, or decrease slightly with increasing the flow-rate at higher temperatures. The molecular anion formed within an ECD returns to the original molecule by recombination with a cation and/or progress of the reverse reaction before passing through the exit of the ECD. Therefore, no chemical reaction occurs, that is, the sample is unchanged by the act of detection. In such a case, the ECD acts as a concentration-sensitive detector, and consequently the values of K are either not effected by the carrier gas flow-rate, or decrease with increasing the flow-rate.[11]

The carrier gas flow-rate dependence of K for the samples undergoing the dissociative electron capture reaction are divided into two groups: One is the group whose values of K increase significantly with increasing the flow-rate (Aldrin, γ-BHC, and *p,p'*-DDE), and the other is the group whose values of K are little or not at all affected by the flow-rate at lower temperatures, but increase gradually with increasing the flow-rate at higher temperatures (1,2,4-trichlorobenzene). Each plot of ln $KT^{3/2}$ *vs.* $1/T$ for the samples belonging to the first group has a negative slope of nearly zero. Consequently the activation energy, E^*, which can be calculated from $E^* = -\text{slope} \times R$, where R is the gas constant, is very small. Therefore, it is considered that the samples in this group dissociate perfectly within the ECD. Under these circumstance, the ECD is close to coulometric in response,[12] and acts as a mass-sensitive detector rather than a concentration-sensitive detector.[13] Hence, the values of K calculated from Eq. 2, which represents the response function as the concentration-sensitive detector, increase with increasing the flow-rate. The sample belonging to the second group, *i.e.*, 1,2,4-trichlorobenzene is seemingly dissociative from Fig. 10, because it has a negative slope of the ln $KT^{3/2}$ *vs.* $1/T$ plot at higher temperatures. However, the carrier gas flow-rate dependence of K reveals that the sample is not necessarily dissociative. The values of K are not effected at all by the flow-rate at lower temperatures, although they increase gradually with increasing the flow-rate at higher temperatures. Therefore, it is considered that the reaction occurs non-dissociatively at lower temperatures and dissociatively at higher temperatures, that is, an intermediate-dissociative electron capture reaction occurs. Satouchi and Kojima[14] have pointed out from the values of E^* that the dissociative electron capture reaction for a halobenzene probably proceeds through an anion radical intermediate and that this reaction mechanism is similar to the S_N2 displacement for aromatic compounds. Furthermore, Dzidic *et al.*[15] have actually observed the anion radicals of some polychlorinated benzenes containing 1,2,4-trichlorobenzene by atmospheric pressure ionization mass spectrometry. Recently, Grimsrud and Kim[16] have suggested that the molecular anion resulting from the electron capture reaction of *p*-bromochlorobenzene survives long enough to be stabilized. These descriptions are quite in agreement with the conclusion obtained from the carrier gas flow-rate dependence of K that 1,2,4-trichlorobenzene is practically intermediate-dissociative, although it seems to be dissociative from the temperature dependence of K.

From the temperature dependence of K, iodobenzene and 2,4,6-trichlorobiphenyl should be regarded as intermediate-dissociative. Also, from the carrier gas flow-rate dependence of K, both samples seem to be intermediate-dissociative, since the values of K are not appreciably affected by the flow-rate at lower temperatures, and increase with increasing the flow-rate at higher temperatures.

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10) This process is equivalent to what has been called the intermediate negative ion process in Ref. 5.

11) Whether the values of K are not affected or decrease with decreasing the flow-rate is considered to depend upon the magnitude of the rate constant for the recombination reaction, k_L, and that for the reverse reaction, k_{-1}. The details about this point will be given in the next paper.

$$AB + e^- \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} AB^- \xrightarrow[P^+ \text{ or } R\cdot]{k_L} AB$$

where P^+ and $R\cdot$ represent positive ions and radicals, respectively.

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