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## ELECTRON-CAPTURE DETECTION OF AROMATIC HYDROCARBONS

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### SUMMARY

The detectabilities and some parameters of electron + aromatic hydrocarbon reactions were investigated in a constant-current, variable-frequency electron-capture detector. It was found that lower alkylbenzenes give weak signals in the detector, polymethylbenzenes, styrene, indene, naphthalenes and biphenyl exhibit medium responses, whereas the response factors of aromatics with three rings and those of diphenylethylene, diphenylacetylene and azulene are relatively high. On the basis of the temperature dependence of the response factors the electron affinities and the electron absorption and desorption rate constants were determined for many aromatics, and the magnitudes of the response factors are discussed.

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### INTRODUCTION

In the last few years there has been increasing interest in the analysis and structures of aromatic hydrocarbons<sup>1–4</sup>. This interest is connected with environmental problems (*e.g.*, trace analysis of aromatics in waste waters) and with energy problems (coal industry), and is underlined by the fact that some polynuclear aromatic hydrocarbons are highly carcinogenic<sup>4,5</sup>, a property that seems to be related to the distribution of electron charge density on the rings.

It was shown 15–20 years ago<sup>6–9</sup> that polynuclear aromatic hydrocarbon molecules (AB) capture thermal electrons in a non-dissociative mechanism:



and exhibit high responses in the electron-capture detector (ECD). The temperature dependence of the equilibrium constant:

$$K_{\text{eq}} = k_1/k_{-1} = AT^{-3/2} \exp(\text{EA}/kT) \quad (2)$$

where  $A$  is a fundamental constant, provides a unique means for the reliable determination of absolute electron affinity (EA)<sup>6–10</sup>.

According to the supposition often mentioned in the literature<sup>8,11,12</sup>, the rate constants  $k_1$  of thermal electron attachment to aromatic molecules with considerable

positive electron affinities are virtually independent of temperature in the range 300–500°K. Therefore, the temperature dependence of the equilibrium constant reflects the temperature dependence of the detachment rate constant.

In this paper we report our investigations on the response factors and response mechanism of aromatic hydrocarbons in the ECD. During our studies we also determined some parameters of electron + aromatic hydrocarbon reactions.

## EXPERIMENTAL

All measurements were carried out on a Packard-Becker Model 419 gas chromatograph equipped with a Model 714 constant-current (400 MBq)  $^{63}\text{Ni}$  electron-capture detector, a Model 736 linearizer and a pulsed power supply. A current of 500 pA was selected. The separations were carried out on a 1.2-m stainless-steel column packed with 20% Apiezon L on Chromosorb P. The column was conditioned before use at 550°K for 24 h without the detector; conditioning was also carried out with the detector at a lower temperature while the detector was heated at 630°K.

The carrier gas was extremely pure nitrogen or argon–5% methane. No meaningful differences were found between the results with the carrier gases, although the peak areas obtained with argon–methane were higher than those obtained with nitrogen. This finding is in agreement with the observations of other workers<sup>13</sup>. The flow-rate of 40 cm<sup>3</sup> min<sup>-1</sup> was maintained by applying a by-pass line. The separations were performed under isothermal conditions. The column temperatures varied between 370 and 500°K, depending on the retention behaviour of the compounds under investigation.

At the beginning of our investigations a few milligrams of a mixture of three or four aromatic hydrocarbons, one of which was always naphthalene, were dissolved in 10 cm<sup>3</sup> of cyclohexane or benzene and 0.1–10 mm<sup>3</sup> of the solution was injected into the chromatograph to check the linearity between the sample size and response. For the temperature dependence investigations, in all instances we chose sample concentrations on the linear part of the sample size *versus* response graph. The peak areas were measured by integration and the response factors were normalized to naphthalene, to which a molar response value of unity at 393°K was arbitrarily assigned. These relative molar responses (*R*) express how many times the number of extra pulses is higher when a unit amount (in moles) of the compound investigated passes through the detector (at temperature *T*) than the number of extra pulses observed for a unit amount of naphthalene when the detector temperature is kept at 393°K.

The aromatic hydrocarbons investigated were obtained from Fluka (Buchs, Switzerland) in the highest purity available.

## RESULTS AND DISCUSSION

### *Relative response factors (R)*

The relative response factors of 23 aromatics are given in Table I for temperatures of 393, 453 and 493°K. We also performed experiments with benzene, methyl-, ethyl-, propyl-, butyl-, dimethyl- and trimethylbenzene and styrene. These compounds, however, except for styrene, exhibit very weak signals in the detector; the *R* values

TABLE I

RELATIVE RESPONSE FACTORS (*R*) AND ELECTRON AFFINITIES (EA) OF AROMATIC HYDROCARBONS

No.	Aromatic hydrocarbon	<i>R</i>			EA (eV), unfixed intercept, $\pm\sigma$	EA (eV), fixed intercept, $\pm\sigma$
		393°K	453°K	493°K		
1	1,2,4,5-Tetramethylbenzene (durene)	0.12	0.09	0.04	0.0462 $\pm$ 0.16	0.067 $\pm$ 0.015
2	1,2,3,5-Tetramethylbenzene (isodurene)	0.42	0.23	0.09	0.064 $\pm$ 0.093	0.108 $\pm$ 0.013
3	Pentamethylbenzene	3.9	1.4	0.73	0.207 $\pm$ 0.033	0.180 $\pm$ 0.013
4	Hexamethylbenzene	0.44	0.22		0.121 $\pm$ 0.091	0.107 $\pm$ 0.014
5	Biphenyl	1.4	0.77	0.42	0.130 $\pm$ 0.033	0.151 $\pm$ 0.013
6	Diphenylmethane (ditan)		0.70	0.43	0.154 $\pm$ 0.042	0.149 $\pm$ 0.014
7	Naphthalene	1.0	0.55	0.37	0.135 $\pm$ 0.042	0.140 $\pm$ 0.013
8	1-Methylnaphthalene	1.2	0.4	0.3	0.161 $\pm$ 0.117	0.132 $\pm$ 0.014
9	2-Methylnaphthalene	2.1	1.2	0.55	0.142 $\pm$ 0.069	0.161 $\pm$ 0.017
10	1-Ethylnaphthalene		1.18	0.8	0.149 $\pm$ 0.056	0.175 $\pm$ 0.015
11	2-Ethylnaphthalene		1.7	1.0	0.194 $\pm$ 0.062	0.186 $\pm$ 0.015
12	1,4-Dimethylnaphthalene		2.4	1.6	0.246 $\pm$ 0.080	0.207 $\pm$ 0.017
13	2,3-Dimethylnaphthalene		0.9	0.8	0.175 $\pm$ 0.13	0.174 $\pm$ 0.016
14	2,6-Dimethylnaphthalene		0.8	0.5	0.160 $\pm$ 0.072	0.159 $\pm$ 0.014
15	Indene	2.3	0.95		0.172 $\pm$ 0.026	0.164 $\pm$ 0.013
16	Acenaphthylene		390	337	0.405 $\pm$ 0.025	0.455 $\pm$ 0.005
17	Azulene		13,250	9840	0.519 $\pm$ 0.011	0.596 $\pm$ 0.004
18	Fluorene	6.6	4.7	2.2	0.279 $\pm$ 0.027	0.223 $\pm$ 0.009
19	Phenanthrene		13.7	13.0	0.270 $\pm$ 0.033	0.305 $\pm$ 0.005
20	Anthracene		1323	898	0.48 $\pm$ 0.040	0.520 $\pm$ 0.010
21	<i>trans</i> -Stilbene		290	104	0.352 $\pm$ 0.051	0.381 $\pm$ 0.007
22	Diphenylacetylene (tolan)		27	20.4	0.323 $\pm$ 0.073	0.308 $\pm$ 0.017
23	1,1-Diphenylethylene		84	76	0.392 $\pm$ 0.061	0.363 $\pm$ 0.010

were 0.04–0.09. The response factor of styrene was approximately equal to that of naphthalene at 393 K.

The relative response factors for aromatics cover a wide range (at least  $10^6$ -fold). The response factors of polymethylbenzenes, alkylnaphthalenes, biphenyl, diphenylmethane (ditan) and indene are much higher than those of benzene and the lower alkylbenzenes, and are close to that of naphthalene (Table I). The *R* values of aromatics containing three rings, azulene, *trans*-stilbene, diphenylacetylene (tolane) and 1,1-diphenylethylene are much higher than those of the above-mentioned aromatics.

The detector signal was found to decrease with increasing gas flow-rate passing through the detector and also with increasing retention time; this behaviour is typical of concentration-dependent detectors<sup>14</sup>. The linear ranges were about 3 and 1.5–2.5 orders of magnitude for aromatics with lower and higher *R* values, respectively.

With the optimal experimental conditions the detection limits for alkylaromatics possessing low *R* values were  $10^{-8}$ – $10^{-10}$  mol, for naphthalenes  $10^{-10}$ – $10^{-12}$  mol and for compounds that exhibit high responses about  $10^{-12}$ – $10^{-15}$  mol. With a flame-ionization detector (FID) the detection limits for aromatics are of the order of

$10^{-12}$  mol, so the sensitivity of our ECD exceeds that of the FID only for aromatics that possess high  $R$  values. Against the low sensitivity of the ECD for most of the compounds investigated, the selectivity of the ECD for aromatics can be an advantage in the analysis of hydrocarbon mixtures.

#### Temperature dependence of $R$ values; electron affinity

The temperature dependence of the  $R$  values for compounds that have relatively low values was measured in the temperature range 373–473°K, and that of aromatics with large values in the range 433–593°K (Fig. 1). The  $R$  values, at least in a certain range, decreased with increasing temperature, which means that the aromatics involved capture thermal electrons non-dissociatively. At higher temperatures (>593°K), for most of the compounds a tendency for the  $R$  values to increase was observed, which may reflect a change in electron-capture mechanism from non-dissociative to dissociative, or the thermal- or radiation-induced thermal decomposition of the hydrocarbons at higher temperatures. For styrene and indene the tendency for  $R$  to increase was observed at lower temperatures (at *ca.* 433 and *ca.* 493°K, respectively); this can be attributed to the low thermal stabilities of these aromatics.

On decreasing the detector temperature to below 473°K we found that the  $R$  values of compounds that have higher ECD responses usually levelled off at a constant value. To understand this behaviour we have to consider the mechanism of

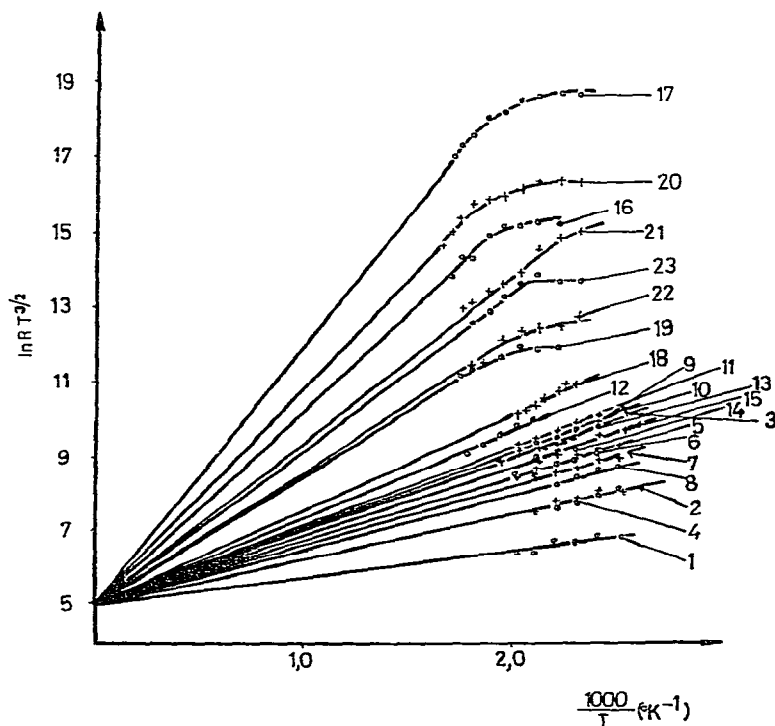


Fig. 1. Variation of  $\ln RT^{3/2}$  with the reciprocal temperature. For identification of numbers, see Table I.

signal formation in the ECD when aromatic hydrocarbons are present. On the basis of studies on the mathematical formulation of detector signals<sup>8,13</sup>, the following equation can be derived for our  $R$  values:

$$R(T) = \frac{k_{L,i} \cdot \frac{k_{1,i}}{k_{L,i} + k_{-1,i}}}{k_{L,n} \cdot \frac{k_{1,n}}{k_{L,n} + k_{-1,n}}} \quad (3)$$

where  $k_L$  is the pseudo rate constant for  $AB^-$  ions with positive charges and radicals present (for details, see ref. 8) and the subscripts  $i$  and  $n$  refer to the compound investigated (at temperature  $T$ ) and to naphthalene (at 393 K), respectively.

As  $k_L$  (and also  $k_1$ ) is assumed to be only slightly temperature dependent<sup>8</sup>, the considerable decrease in  $R$  with increasing temperature (at higher  $T$ , in the so-called  $\alpha$  region<sup>8</sup>) reflects the relationship  $k_{L,i} \ll k_{-1,i}$ , while the plateaux observed for some compounds at lower temperatures ( $\beta$  region) must be the result of a change in the above relationship to  $k_{L,i} \gg k_{-1,i}$ .

On the basis of eqns. 2 and 3, at temperatures in the  $\alpha$  region ( $k_{L,i} \ll k_{-1,i}$ ) there is a linear relationship between the  $\ln(RT^{3/2})$  values and the reciprocal temperature:

$$\ln [R(T)T^{3/2}] = \ln \left( \frac{k_{L,i}}{k_{L,n}} \right) + \ln A - \ln \left( \frac{k_{1,n}}{k_{L,n} + k_{-1,n}} \right) + \frac{EA}{kT} \quad (4)$$

where the slope gives the electron affinity divided by the Boltzmann constant ( $EA/k$ ).

To handle the points in the  $\alpha$  region we developed a computer procedure that permitted us to calculate the slopes for the individual compounds independently of each other and also by using all compounds and all of the experimental points (more than 150) to determine the slopes of the best fit lines that have a common intercept on the ordinate. The latter method assumes that  $k_{L,i} \approx k_{L,n}$  in eqn. 4 for all aromatics investigated, which seems to be a reasonable supposition for compounds that have similar structures and chemical properties. The least-squares treatment yielded a common intercept at  $4.90 \pm 0.34$  (Fig. 1).

In most instances the results of the two determinations (fixed and unfixed intercepts, Table I) coincided. However, for compounds that have high or very low  $R$  values larger differences between the two values were observed. These differences are probably caused by the relatively narrow  $\alpha$  regions in the first case and by the very low temperature variation of the  $R$  values in the second, these factors leading to poorly defined slopes. The common intercept method is, without doubt, the better one, as the common intercept is determined by a large number of measurements, thereby increasing the accuracy of the determinations.

The electron affinities for naphthalene, azulene, phenanthrene and anthracene agree well with the data from other measurements utilizing the ECD method<sup>8,15</sup>, and generally there is fairly good agreement with the data determined in the last 10–15 years by other methods<sup>12,16</sup> also.

The electron affinities in Table I can be divided more or less into three groups: low values (*ca.* 0.1 eV) for polymethylated benzenes (with the exception of penta-methylbenzene), medium values (0.1–0.2 eV) for naphthalenes, biphenyl, biphenyl-

methane, indene and pentamethylbenzene, and higher values (0.2–0.6 eV) for the remaining hydrocarbons. The relatively high electron affinity of pentamethylbenzene compared with that of hexamethylbenzene can be attributed to the shielding effect of the  $\pi$ -orbital system by the substituent methyl groups on the benzene rings. A similar phenomenon has been observed for penta- and hexachlorobenzenes<sup>17,18</sup>.

#### *Electron absorption and desorption rate constants*

As was mentioned before, the response factor *versus* temperature relationship of higher electron affinity aromatics at low temperature levelled off at constant maximum values ( $R^0$ ). By combining eqns. 2 and 3, the following relationship can be derived:

$$\ln \left[ \left( \frac{R^0}{R} - 1 \right) T^{-3/2} \right] = \ln \left( \frac{k_1}{Ak_L} \right) - \frac{EA}{kT} \quad (5)$$

which makes it possible to establish the  $k_1/Ak_L$  values of compounds of higher electron affinity (Nos. 16–23), for which we could perform measurements in the transitional interval between the  $\alpha$  and  $\beta$  regions in our apparatus; by this means we had the possibility of determining the  $R^0$  value. As the estimation of the correct  $R^0$  value from the direct measurements for most compounds listed in Table II was very difficult, the determinations were usually carried out with eqn. 5 also, taking the electron affinity value from Table I as determined by the fixed intercept method. The dependence of the  $\ln[(R^0/R-1)T^{-3/2}]$  values on  $1/T$  for azulene, phenanthrene and *trans*-stilbene is shown in Fig. 2 and the  $k_1/Ak_L$  and  $R^0$  values are given in Table II. Because in the  $\beta$ -region  $k_{L,i} \gg k_{-1,i}$ , the ratio of the  $R^0$  values for two aromatics equals the ratio of the rate constants of the electron-capture reactions:

$$\frac{R_1^0}{R_2^0} = \frac{k_{1,1}}{k_{1,2}} \quad (6)$$

The rate constant  $k_1$  for anthracene has been well established by measurements applying the ECD [ $2.7 \cdot 10^{12}$  l mol<sup>-1</sup> sec<sup>-1</sup> (ref. 8)] and the electron swarm technique [ $2.8 \cdot 10^{12}$  l mol<sup>-1</sup> sec<sup>-1</sup> (ref. 11)]. In view of this, we took the  $k_1$  value of anthracene as the basis for our rate constant calculations. The  $k_1$  values calculated with the help of eqn. 6 and the expressions for  $k_{-1}$  are also given in Table II. Figs. 3 and 4 show the relationship between the electron affinities and the  $k_1$  and  $k_{-1}$  (at 453°K) values. (In the figures, in addition to our own values we also give the data for some compounds taken from the work of Wentworth *et al.*<sup>8</sup>; 24, pyrene, electron affinity = 0.591 eV; 25, benzo(c)phenanthrene, 0.545; 26, benzanthracene, 0.63; 27, triphenylene, 0.285; 28, crysene, 0.397.)

Our  $k_1$  values in Table II for azulene and phenanthrene agree fairly well with the data found in the electron swarm experiments of Christophorou and Blaunstein<sup>11</sup> ( $1.9 \cdot 10^{13}$  and  $1.3 \cdot 10^{10}$  l mol<sup>-1</sup> sec<sup>-1</sup>). On the basis of the  $k_1/Ak_L$  and the  $k_1$  values in Table II, we estimated a  $k_L$  value for our detector of  $1.2 \pm 0.3 \cdot 10^6$  sec<sup>-1</sup>.

#### *Interpretation of response factors on the basis of electron absorption and desorption rates*

In Fig. 3,  $k_1$  increases with increasing electron affinity of the molecules. In

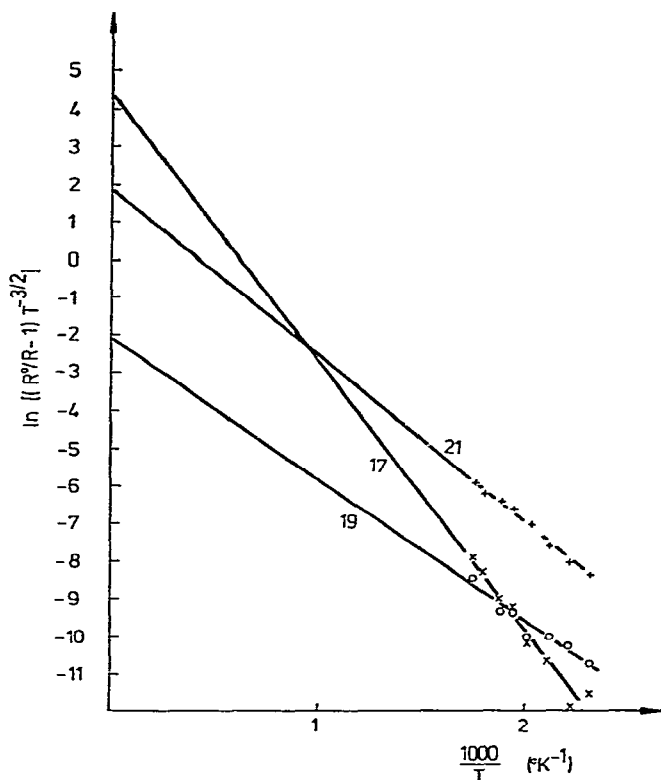


Fig. 2. Variation of  $\ln [(R^0/R - 1) T^{-3/2}]$  with the reciprocal temperature for compounds 17 (azulene), 19 (phenanthrene) and 21 (*trans*-stilbene).

TABLE II  
DETERMINATION OF RATE CONSTANTS

No.	Aromatic hydrocarbon	EA (eV)	$\frac{k_1}{Ak_L}$	$R^0$	$k_1$ ( $l \text{ mol}^{-1} \text{ sec}^{-1}$ )	$k_{-1}$ ( $\text{sec}^{-1}$ )
16	Acenaphthylene	0.46	2.8	470	$9.2 \cdot 10^{11}$	$3.4 \cdot 10^5 T^{3/2} \exp(-0.46/kT)$
17	Azulene	0.60	74.0	13,500	$2.6 \cdot 10^{13}$	$9.7 \cdot 10^7 T^{3/2} \exp(-0.60/kT)$
18	Fluorene	0.22	$\sim 0.1$	$\sim 20$	$\sim 4 \cdot 10^{10}$	$\sim 1.5 \cdot 10^5 T^{3/2} \exp(-0.22/kT)$
19	Phenanthrene	0.30	0.11	18	$3.5 \cdot 10^{10}$	$1.3 \cdot 10^5 T^{3/2} \exp(-0.30/kT)$
20	Anthracene	0.52	8.4	1410	$2.75 \cdot 10^{12}$	$1.0 \cdot 10^7 T^{3/2} \exp(-0.52/kT)$
21	<i>trans</i> -Stilbene	0.38	6.5	1100	$2.2 \cdot 10^{12}$	$8.2 \cdot 10^5 T^{3/2} \exp(-0.38/kT)$
22	Diphenylacetylene (tolan)	0.31	0.27	45	$8.8 \cdot 10^{10}$	$3.3 \cdot 10^5 T^{3/2} \exp(-0.31/kT)$
23	1,1-Diphenylethylene	0.36	0.73	116	$2.3 \cdot 10^{11}$	$8.6 \cdot 10^5 T^{3/2} \exp(-0.36/kT)$

contrast, at lower temperatures [for instance at 453°K (Fig. 4)]  $k_{-1}$  decreases as the electron affinity increases.

It follows from Figs. 3 and 4 that the high sensitivity of the ECD at lower temperatures for the polynuclear aromatic hydrocarbons that have large electron affinity can be attributed to two causes: first, the high electron-capture rate constant,

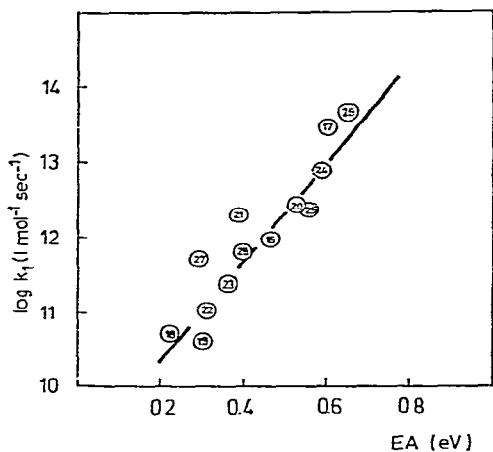


Fig. 3. Variation of  $k_1$  with electron affinity.

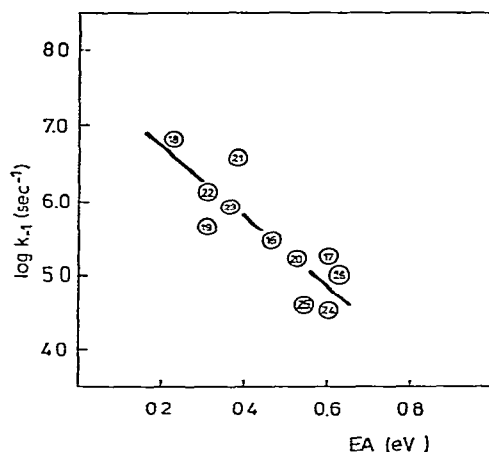


Fig. 4. Variation of  $k_{-1}$  with electron affinity at 453°K.

and second, the relatively slow dissociation of the  $AB^-$  ion. The lifetime ( $\tau$ ) of this ion can be estimated from the relationship  $\tau \approx 1/k_{-1}$ . The latter value for the aromatics listed in Table II was found to be of the order of  $10^{-5}$ – $10^{-7}$  sec at 453°K, *i.e.*, much lower than the residence time of the molecules in the detector (*ca.* 1 sec). Consequently, while a molecule is passing through the detector it may enter a series of electron absorption and desorption reactions. It was for this reason that we established the concentration sensitivity for our detector during the analysis of aromatics.

The response factors in Table I decrease with decreasing electron affinity of the molecules. This decrease also has two causes, *viz.*, the decrease in the absorption and the increase in the desorption rates. The latter can be suppressed by decreasing the detector temperature and trying to approach the  $\beta$  region. However, as the temperature dependence of  $k_{-1}$  in the case of low electron affinities is also low (eqn. 2), the decrease in temperature hardly enhances the response factors.

The exact electron affinities of benzene and lower alkylbenzenes are not known; in the opinion of Christophorou and co-workers they are in the vicinity of zero; on the basis of short-living negative ions observed in the gas phase, for instance for benzene (*ca.*  $10^{-12}$  sec), the electron affinities are very slightly positive<sup>3,19</sup>. The formation of temporary negative ions decreases the drift velocity and also the number of electrons collected during the pulse period. This idea may give an answer to why we can detect these compounds by an ECD only when they are present in the gas flow at higher concentrations ( $10^{-6}$ – $10^{-7}$  M).

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