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APPROXIMATION OF ELECTRON CAPTURE RESPONSE FACTORS FOR HIGHLY ELECTROPHILIC COMPOUNDS

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SUMMARY

A theoretical upper limit of electron attachment rate constants is derived, based on collision-limited electron interaction with polarizable molecules. This limit is shown to give upper limits for electron capture response factors. Evidence is presented showing that this limit is approached to within a factor of two for a wide variety of highly electrophilic compounds. It is suggested that this limit can be used as an approximation for electron capture response factors for suitable compounds, and that properly chosen derivatizing reagents may allow detection of derivatives with fairly accurate prediction of response factors.

INTRODUCTION

A recent innovation for pulsed electron capture (EC) detectors[1] has raised the promise of more quantitative response. A new mode of operation has been described which entails varying the pulse frequency in such a way that the output current is held constant. The resultant frequency then serves as the output. After suitable conversion to voltage, it is presented on the recorder. Both theory and experiment indicate[2,3] that under suitable conditions, output is linear over a wide dynamic range.

Two suppliers of instrumentation[4,5] for constant current EC claim increased stability of response as well as linearity. This is due to the independence of response factors from the effects of carrier gas impurities and column bleed. This property encourages further inquiry into predicting response factors on the basis of molecular properties.

For the constant current EC, the relationship between output frequency F and sample concentration [A] is

$$F = \frac{1}{K}(k_1[\mathrm{A}]+K_d) \tag{1}$$

where k_1 is the rate constant for electron capture by sample molecules, and K_d is the pseudo first order rate for direct recombination of electrons with positive ions. The K_d term is small—typically, it removes electrons at a rate equivalent to capture by a few picograms per milliliter of lindane. Electron capture by bleed and carrier gas impurities may also be included in K_d without change in the treatment here.

To evaluate the constant of proportionality, K, eqn. 4 from ref. 1 for the output current, I, can be written

$$I = \frac{I_s}{K}[1 - e^{-K}] \tag{2}$$

where I_s is the current produced by the radioactive source, and K has been substituted for $(k_1[A] + K_d)t_p$, according to eqn. 1, since the pulse period, t_p is the inverse of F.

Eqn. 2 allows K to be calculated from the ratio I_s/I by iteration, starting with K equal to the ratio. It follows that the capture rate constant k_1, in ml molecule^{-1} sec^{-1} can be derived from the area response factor Z, in μV·sec/pg

$$k_1 = \frac{KfM \times 10^{12}}{Nr} Z \tag{3}$$

where M is the sample molecular weight, N is Avogadro's number, r is the frequency to voltage conversion factor for the analog output, in μV/Hz. The flow f, in ml/sec, is evaluated at detector temperature.

The relation between response factor and capture rate constant for constant frequency pulsed EC is more complicated. For instance, in the case of sufficiently low frequency and irreversible capture[6], the small sample response factor is proportional to k_1/K_d.

Collision rate theory for electron attachment

The classical theory of kinetics considers bimolecular reaction rates to be composed of three terms: a collision rate term; a steric factor, that is, the fraction of possible orientations over which a molecular collision leads to reaction; and a term exponential in the activation energy. The latter reflects the fraction of colliding species whose relative velocity is sufficient to overcome the activation energy barrier.

Consider now the encounter of a free electron and a highly electrophilic molecule. In most cases, the molecule is surrounded by electronegative groups, or by groups conjugated with electronegative parts of the molecule. Thus, it is not implausible to suggest that the steric factor is close to unity. Similarly, existing data[7–9] suggest that activation energies are often close to thermal energies. For optimum cases, then, the rate constant k_1 can be assumed to be only slightly less than the rate at which electrons collide with sample molecules.

For charged particles, however, the collision rate is not that calculated by the hard, non-reactive sphere model. This is because charges induce a dipole moment in the electron distribution of a molecule, resulting in an attractive force. This leads to a collision rate almost entirely dependent on the electronic polarizability of the molecule[10]. The permanent dipole moment and the atomic polarizability do not have a significant effect, because these mechanisms occur very slowly compared to interaction with the rapidly moving electron[11–14]. This treatment yields an expression for the reaction rate,

$$k_1 = \left(\frac{4\pi^2 q^2 \alpha_E}{m}\right)^{\frac{1}{2}} \tag{4}$$

where q is the electron charge, m is the electron mass and α_E is the electronic contribution to the polarizability of the molecule.

The electronic polarizability is usually treated in terms of the molar refraction, R, which has units in ml,

$$R = \tfrac{4}{3}\pi N\alpha_{E} \tag{5}$$

Substitution in eqn. 4 gives

$$k_1 = 6.29 \times 10^{-8}\sqrt{R} \tag{6}$$

It is interesting that no temperature dependence is predicted for k_1 by this model. The molar refraction can be calculated from the index of refraction, n,

$$R = \left(\frac{n^2-1}{n^2+2}\right)\frac{M}{d} \tag{7}$$

where d is the density. Strictly speaking, n should be extrapolated to infinite wavelength, otherwise α_E may include part of the atomic polarization or the dipole moment, but in practice, only a few percent error is introduced by using light of the sodium D wavelength[15,16].

Fortunately the molar refraction is an approximately additive property, and substantially the same for both liquid and vapor measurements. Many empirical tabulations of coefficients have been published for calculating R from the molecular structure. These fall into two groups, those that add up the contributions from each bond[17–20] and those that mainly add up the contributions of each atom[17,21,22].

For organic compounds, the tabulation of Dreisbach[22] is perhaps the best established, as calculations are compared with the experimental data there for more than 500 compounds, most of them substituted aromatics. The agreement is usually to 1% with the experimental values given. Some representative coefficients are given in Table I.

For elements not included in Dreisbach's work[22], for instance, the metals, Batsanov's values may be used[23], which are also given by Rich[24].

TABLE I

COEFFICIENTS FOR MOLAR REFRACTION

Compound	*Coefficient*	*Compound*	*Coefficient*
Carbon		Nitrogen	
singly bound and alone	2.592	aliphatic primary amine	2.45
singly bound	2.418	aromatic primary amine	3.21
double bond	1.733	primary amide	2.27
triple bond	2.398	Fluorine	
conjugated	1.27	monofluoride	0.95
Hydrogen	1.100	polyfluoride	1.1
Oxygen		Chlorine	5.967
hydroxyl	1.525	Bromine	8.865
ethereal	1.643	Iodine	13.900
ketonic	2.211		
as ester	1.64		

EXPERIMENTAL

A Hewlett-Packard Model 5713A gas chromatograph equipped with a constant current mode EC detector was used. The radioactive source is 15 mCi of ^{63}Ni plated directly on the interior of the cell. For this source, I_s has a value of 8.5 nA at 300°. The electronics holds the output current I, constant at 1.50 nA. These two values give a K of 5.65 according to eqn. 2. The frequency to voltage conversion factor, r, is 3.3 μV/Hz for the integrator tap.

The detector temperature was held at 300° and the flow-rate was 60 ml/min (at room temperature). The columns used were mostly 3 ft. or 6 ft. × 4 mm I.D., OV-1, either 3% or 10%.

Area was measured with a Hewlett-Packard 3370B integrator.

The above parameters give the conversion $k_1 = (5.43 \times 10^{-12}) MZ$.

RESULTS AND DISCUSSION

Motivation for searching for an upper limit to the capture rate constant is seen in the clustering of values at the upper levels of tables of response factors[25,26].

Clemons and Altshuller[25] give data for 35 light hydrocarbons of varying degrees of halogenation. Their response factors span seven decades of range. Yet the highest thirteen values are clustered within one decade.

The work of Zitko *et al.*[26] has the advantage of giving data on a homologous

TABLE II

OBSERVED ELECTRON CAPTURE RATE CONSTANTS COMPARED WITH COLLISION THEORY PREDICTIONS

Compound	*Molecular weight, M*	*Response factor, Z ($\mu V \cdot sec/pg$)*	*Molar refraction, R (ml)*	*Capture rate constant, k_1 (ml molecule^{-1} sec^{-1} × 10^{-7})*	
				Experimental	*Theoretical*
Pesticides					
Lindane	291	228.4	56.91	3.61	4.74
Aldrin	365	229.4	77.08	4.55	5.52
Dieldrin	381	216.9	76.99	4.49	5.52
DDT	354	161.5	83.99	3.10	5.76
TDE	322	168.9	79.12	2.95	5.59
DDE	318	205.8	79.92	3.55	5.62
Mirex	549	153.1	100.2	4.56	6.29
Derivatives					
Trichloroacetylamphetamine	280	188.0	66.84	2.86	5.14
Heptafluorobutyl testosterone	484	27.3	102.1	0.72	6.39
Chromiumtrifluoroacetyl acetate	447	55.0	95.3*	1.33	6.14
Other					
1,2-Dibromo-3-chloropropane	236	100.5	36.45	1.29	3.80
Sulfur hexafluoride	146	—	14.6	2.20**	2.40
Methylmercuric chloride	250	20.4	23.46	0.28	3.05
Decachlorobiphenyl	498	93.4	99.08	4.32	6.26

* From ref. 28.

** From ref. 29.

series, 23 individual polychlorinated biphenyls (PCB). The response factor increases by about a factor of about ten for each chlorine added from one through five. In this range, the exact position of the halogens has a large effect on the capture coefficient. For more than six chlorines, the response factor varies by less than a factor of two through the decachlorobiphenyl.

A series of highly electrophilic compounds were chromatographed and their

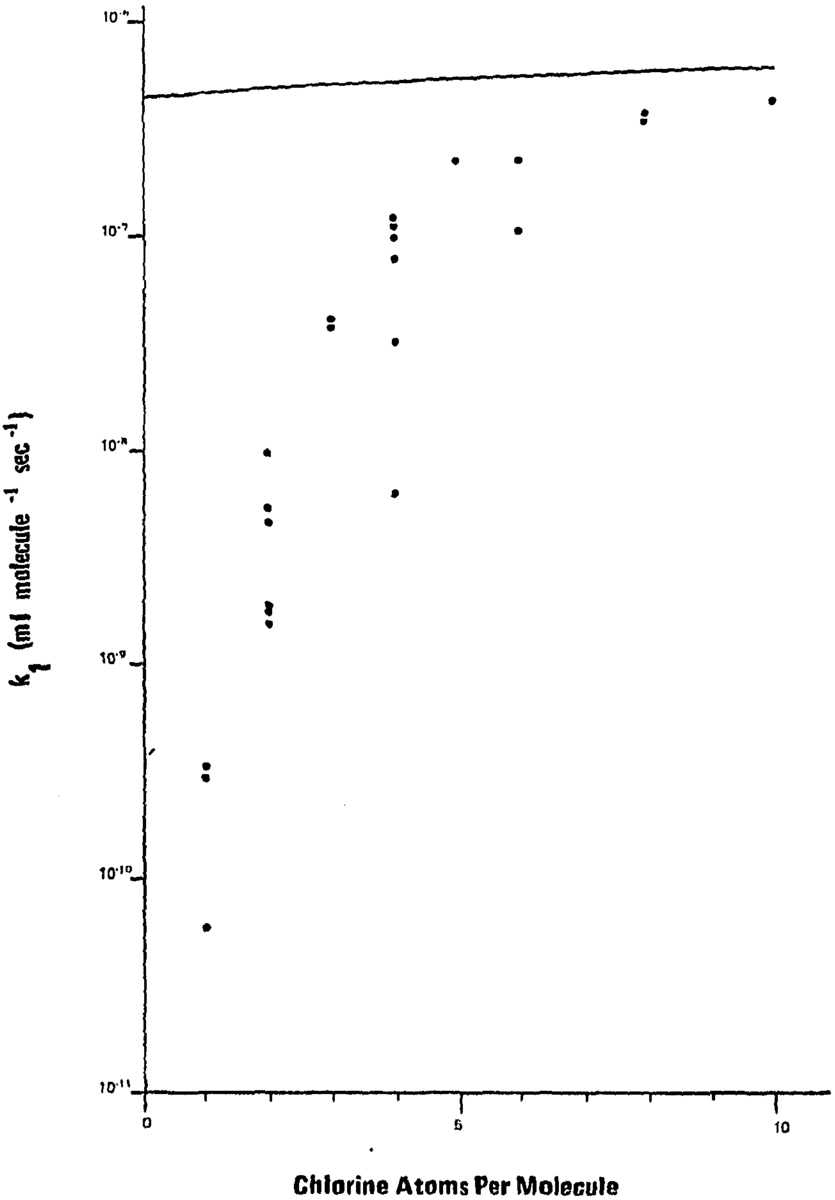

Fig. 1. Experimental capture rate constants for various polychlorinated biphenyls compared with collision theory upper limit (solid line).

response factors were compared with the predicted values from the collision theory. Results are shown in Table II.

The highly chlorinated pesticides fit the theory remarkably well, with the experimental rate constants between 50 and 85% of the theoretical values. The experimental value for SF_6 comes from microwave conductivity measurements.

The somewhat low rate constants for the last two derivatives in the table indicate that searching for more electrophilic derivatizing reagents may be fruitful. For thymol, the pentafluorobenzyl ether and the pentafluorobenzoate are about six times as responsive as the heptafluorobutyl derivative[27]. There is evidence that these derivatives have response factors near the collision theory limit. It seems possible, that in favorable cases, a very good estimate of response may be made for a derivative without calibration.

Zitko's response factors for the PCB's are scaled to the experimental value of k_1 given in Table II and are plotted (Fig. 1) against chlorine number. A smooth approach toward the collision limit with increasing chlorine is observed. The totally chlorinated isomer is 70% of the limiting value.

Cross-section data for electron attachment by 22 halogenated aliphatic hydrocarbons have been measured by the swarm technique[7]. In terms of σ, the cross sectional area of interaction, in cm^2, the rate constant is

$$k_1 = \left(\frac{8RT}{\pi NM}\right)^{\frac{1}{2}} \sigma \tag{8}$$

where R is here the gas constant.

Only the three most capturing compounds are close to their theoretical values (Table III) though several others are less than a factor of ten lower than theory predicts.

One would expect that compounds that approach the limit as closely as CCl_4 would have an unusually low temperature dependence. Such appears to be the case. Wentworth *et al.*[8] give temperature dependence data on CCl_4 and other compounds, several of them not much lower in response. There seems to be a general trend toward lower temperature dependence for higher capturing compounds. The response factor for CCl_4 is approximately the same as that quoted here, but their theory only generates the ratio k_1/K_d under the assumption of irreversible capture, and K_d is not given.

TABLE III

CAPTURE RATE CONSTANTS MEASURED BY THE SWARM TECHNIQUE COMPARED WITH THEORY

Compound	*Cross-section*[7], σ ($cm^2 \times 10^{-16}$)	*Molar refraction, R* (*ml*)	*Capture rate constant*, k_1 (*ml molecule*$^{-1}$ *sec*$^{-1} \times 10^{-7}$)	
			Experimental	*Theoretical*
CCl_4	262	26.46	2.81	3.23
$CFCl_3$	106	21.44	1.14	2.91
CF_2Br_2	243	22.52	2.61	2.98

CONCLUSION

A mechanism has been proposed placing an upper limit on electron capture response factors. Evidence shows that highly electrophilic compounds approach this limit, often within a factor of two.

There are several implications of the collision limit. It may in some cases be used to predict response factors. It can also serve as a guide for what increases in sensitivity are available from different choices of derivatizing reagents.

In the case of the Aroclor series of polychlorinated biphenyls, the following observation can be made. Derivatization by means of total chlorination need not be quantitative for analysis of total PCB by means of total area to be accurate. In fact, the total area analysis of the heavier mixtures, such as Aroclor 1254, which contains an average of 6.3 chlorine atoms per molecule, would appear from Fig. 1 to be rather insensitive to isomeric variations, without further chlorination.

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