ester was complete. All attempts to obtain pure crystals from the yellow glass remaining after working up the mixture and steam distilling failed. Nine tenths of a gram (0.0023 mole) of the glass was refluxed for 90 min. with 8 cc. of acetyl chloride in 20 cc. of anhydrous thiophene-free benzene. The product was treated with decolorizing carbon, filtered, evaporated almost to dryness, crystallized from anhydrous petroleum ether and dried under vacuum at 54°, yielding white crystals melting at 93.5–95°. *Anal.* Calcd. for $C_{29}H_3Cl$: C, 83.1; H, 8.4; Cl, 8.47. Found[24]: C, 82.7; H, 8.6; Cl, 9.2. This product was passed through charcoal in anhydrous petroleum ether, recrystallized from this solvent and dried at 10^{-3} mm. and 56° to give white crystals melting at 95.5–96.0° (uncorr.). *Anal.* Found[11]: hydrolyzable chloride, 8.65.

Crystalline mono-*m*-neopentyltriphenyl carbinol, m.p. 53–56°, was obtained with great difficulty[34] but attempts to convert it to crystalline chloride were not successful.

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[34] *Cf.*, ref. 27, pp. 57–60.

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Potential Method for the Determination of Electron Affinities of Molecules: Application to Some Aromatic Hydrocarbons

BY W. E. WENTWORTH AND RALPH S. BECKER

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One of the principal aims of this investigation is to establish the fundamental nature of the electron capture by molecules occurring in a detector used in gas chromatography. The interpretation is developed in terms of an equilibrium between the neutral molecules and the electrons. The relationship between the electron capture coefficients and the electron affinities of molecules is presented. The results for a series of aromatic hydrocarbons are compared to the half wave reduction potentials. If certain assumptions are made concerning the ratio of the partition functions of the gaseous negative ion of the molecule to the neutral gaseous molecule, the electron affinity of the molecule can be estimated. This has been carried out for anthracene and other aromatic hydrocarbons, and the results compare favorably with recent theoretically calculated values.

Within the past year and a half, an electron capture cell has been developed by Lovelock primarily for use as a sensitive detector in gas chromatography.[1] The detection of a compound is based upon its ability to capture thermal electrons. The relative magnitude of capture of an electron has been expressed in terms of the electron absorption or capture coefficient. The electron absorption coefficients of numerous compounds have been measured by this technique.[2,3] Up to this time, the functional relationship of this parameter with other fundamental physical properties of molecules has not been elucidated. The purpose of this paper is to discuss a relationship between the electron absorption coefficient and the electron affinity of a molecule. The electron affinity is defined here in the usual rigorous way as the energy associated with the process when a gaseous molecule captures an electron to produce a gaseous ion. Previous references to electron capture detectors employing the terminology electron affinity[1–3] have been made relative to the functional nature of the process and not relative to the energy involved in the process.

In general, it has been assumed that a molecule can capture an electron by either of two processes: (1) a nondissociative process whereby a gaseous negative ion of the molecule is formed, or (2) a dissociative process in which a portion of the molecule forms an independent gaseous ion and the remainder of the molecule exists at least temporarily as a radical in the gaseous state. The discussion in this paper will be restricted to the former process.

Heretofore, there has been no accurate and definitive method for the measurement of the electron affinity of complex molecules. The best estimate of this parameter has been accomplished by measurement of the polarographic half wave reduction potential. For example see Matsen[4] and references therein. However, as Matsen has pointed out,[5] in order to obtain the true electron affinity of the molecule from the half wave reduction potential, it is necessary to evaluate the difference in energy of solution of the neutral molecule and the negatively charged molecular ion. Unfortunately, it is difficult to evaluate this difference in energy of solution. For this reason, it is advantageous to work in the gaseous phase where this complication does not exist.

For the experimental details of the technique for measuring electron absorption coefficients, the original references should be consulted.[1,2] Our interpretation of the capturing process of an electron by a molecule is based on the establishment of an equilibrium between the neutral gaseous molecules, the free thermal electrons, and the gaseous negative ions of the molecule

$$AB + e^- = AB^- \qquad (1)$$

where AB represents the neutral molecule. The corresponding ideal gas equilibrium expression would be

$$K = [AB^-]/[AB][e^-] \qquad (2)$$

If the electron absorption coefficient is relatively small, the initial concentration of neutral molecules *a* will not be significantly diminished through

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[1] J. E. Lovelock, *Nature*, **189**, 729 (1961).

[2] J. E. Lovelock and N. L. Gregory, "Proceedings International Gas Chromatography Symposium," Lansing, Michigan, June 1961, Academic Press, Inc., New York, N. Y., p. 151.

[3] J. E. Lovelock, A. Zlatkis and R. S. Becker, *Nature*, **193**, 540 (1962).

[4] F. A. Matsen, in "Proceedings of 1957 Conference on Carbon," Pergamon Press, New York, N. Y., 1957, pp. 21–26.

[5] F. A. Matsen, *J. Chem. Phys.*, **24**, 602 (1955).

the formation of negative ions. If b represents the initial concentration of electrons then

$$[AB^-] = Ka(b - [AB^-]) \qquad (3)$$

In previous publications,[1,2] it was assumed that the concentration of free electrons approximately fit the Beer–Lambert absorption law for monochromatic radiation. A comparison of equation 3 with the exponential absorption law, will reveal that the two expressions reduce to a similar linear form when $b >> [AB^-]$, that is, when the fraction of electrons captured is small. Therefore, in our interpretation of the capturing process the electron absorption coefficients are synonomous with the equilibrium constant defined in equation 2. The electron absorption coefficients which have been published to date are relative to the assignment of unity for chlorobenzene. For this reason, only the relative values of the equilibrium constants are known. Designating the relative experimental values by K', the true equilibrium constant can be expressed as $K = CK'$.

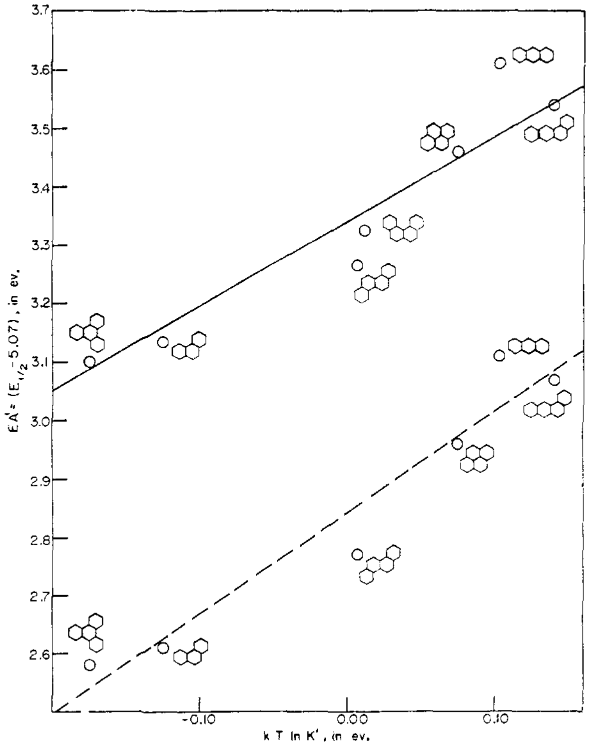

Fig. 1.—EA' *versus* kT ln K' both in e.v.: ———, EA' from $E_{1/2}$ in 2-methoxyethanol and --------, EA' from $E_{1/2}$ in 75% dioxane.

In general, extremely small concentrations of both the gaseous molecules and free electrons are used in these measurements. For this reason, the ideal gas expression can be used to represent the equilibrium. Hence, kT ln K is proportional to the electron affinity where the ratio of partition functions is assumed to remain constant. A similar assumption also must be made in order that the half wave reduction potentials be linearly related to the electron affinity.[6] Since the relative equilibrium constant K' is proportional to K, then kT ln K' will also be related linearly to the electron affinity.

Recently, the electron absorption coefficients for a series of aromatic hydrocarbons were published.[3] The half wave reduction potentials for the compounds in this series have also been measured and the relationship with the theoretically estimated electron affinity has been investigated.[4] It is meaningful to compare the electron absorption coefficients with the reduction potentials for this series of molecules for the following reasons. The aromatic hydrocarbons in general have a high degree of thermal stability, and most certainly the gaseous negative ion is stable relative to bond dissociation. Furthermore, as a consequence of the rigid sigma bonded framework of the aromatic hydrocarbons, the ratio of the partition functions should be nearly constant and hence kT ln K' should be linearly related to the electron affinity. The significance of the error in the latter assumption is further diminished when it is remembered that the logarithm of the expression is used.

In Fig. 1, kT ln K' for the aromatic hydrocarbons is plotted versus the half wave reduction potential corrected for the work function of mercury and the potential of the calomel electrode.[4] Reduction potentials for the hydrocarbons are known in both 75% dioxane solution and 2-methoxyethanol. Both sets of data quite satisfactorily support a linear relationship. A least squares adjustment, assuming the kT ln K' values free of error, yielded the following slopes: 75% dioxane 1.74 ± 0.23, 2-methoxyethanol 1.46 ± 0.23. The estimates of error in the slopes are standard deviations computed on the basis of the deviations of $-(E_{1/2} - 5.07)$ values from the straight line. The error in the slopes is remarkably small, considering the small energy range (~0.4 ev.) in the electron affinity data.

In an ideal situation where there are no complicating terms, such as the energy of solution, the slope should be unity. Most likely the greatest source of deviation results from the variation of the difference in energy of solution among the hydrocarbons and their ions. It would not seem unreasonable that this variation could amount to 0.2 ev. considering a magnitude of the energy of solution on the order of 2.5–3.0 ev.[7]

One referee pointed out that the deviation of the slope from unity suggested a relationship between the electron affinity and the energy of solution. The authors acknowledge that this could possibly arise if the solvation process involved the formation of a charge transfer complex. Considering the neutral hydrocarbon molecule as the acceptor in a solvated complex, and the negative hydrocarbon ion as a donor in a solvated ion complex, the difference in energies of solution would decrease with increasing electron affinity. This correction would increase rather than decrease the observed slope in Fig. 1. Only if the hydrocarbon negative ions are the acceptors in solvated charge transfer

[6] R. Daudel, R. Lefebvre and C. Moser, "Quantum Chemistry," Interscience Publishers, Inc., New York, N. Y., 1959, Ch. 12.

[7] R. M. Hedges and F. A. Matsen, *J. Chem. Phys.*, **28**, 950 (1958).

complexes would agreement be obtained with the observed results. This, however, is probably unlikely since the electron affinity for the second electron would be extremely small.

The deviation of the slope from unity may also be caused by the fact that equilibrium is not truly established in the electron absorption coefficient measurements. However, this would require at least a hundredfold variation in K', which seems unreasonable. The precision of the K' measurements has been estimated as ±24%[3] which propagates to only ± 0.01 in $kT \ln K'$.

Another possible source of discrepancy arises from the neglect of the formation of a double negative gaseous ion in which the neutral molecule has captured two free electrons. In this group of aromatic hydrocarbons, only the second half wave reduction potentials for anthracene and benz[a]-anthracene have been measured.[8] The difference of the second half wave reduction potential from the first is 0.46 and 0.35 ev., respectively. As a consequence, the concentration of doubly charged gaseous ions would be expected to be small. Furthermore, since the concentration of the hydrocarbons is in excess of the concentration of free electrons, the formation of double negative ions is even less favorable.

Previously it was noted that the published electron absorption coefficients are relative to chlorobenzene assigned a value of unity. However, if the actual concentration of the capturing species were known, then the actual equilibrium constant K could be calculated. Since the actual concentration in the cell was not measured, it was necessary to utilize the total amount of sample, the actual elution curve, and the flow rate to calculate the absolute K value. From equation 3 it will be noted that the ratio $[AB^-]/(b - [AB^-])$ is linearly related to the concentration a in the cell at that time. Since only the total amount of sample injected into the column is known, it is necessary to carry out an integration over the elution curve where the ordinate is now $[AB^-]/(b - [AB^-])$. The integration is carried out over the volume of gas passed through the cell which is known from the time axis on the recorder and the flow rate. The ratio of the value of the integration to the total amount of sample injected (assuming it is of 100% purity) will now give the desired K. This has been done for anthracene and a value of $K = 3.5 \times 10^6$ l./mole at $T = 420°$ K. was determined.

From the statistical thermodynamic equilibrium expression for an ideal gas mixture[9] it should be possible to calculate the electron affinity.

$$K = \frac{f_{AB^-}}{f_{AB}f_{e^-}} e^{-EA/kT} \tag{4}$$

If it is assumed that the ratio of the partition functions for the anthracene negative ion and the neutral anthracene remains not only constant, but is equal to two because of the electron spin degeneracy of the ion, then evaluation of f_e- permits an estimate of the electron affinity of anthracene. With this estimated absolute value for anthracene, the electron affinities for the remaining hydrocarbons can be calculated for this series under similar assumptions. These are found in Table I.

TABLE I

ELECTRON AFFINITIES OF HYDROCARBONS

Hydrocarbon	K'	$kT \ln K'$	E.a.[a] (ev.) (experimental)	E.a. (ev.) (Goodman and Hoyland)
Triphenylene	0.015	−0.175	0.14	..
Phenanthrene	0.05	− .125	.20	0.25
Chrysene	1.2	.008	.33	..
Benz[c]phenanthrene	1.3	.011	.33	..
Pyrene	6.0	.074	.39	0.55
Anthracene	12.0	.103	.42	0.61
Benz[a] anthracene	29.0	.140	.46	..

[a] Electron affinity of anthracene was calculated assuming that the ratio of the partition functions of the mononegative ion and neutral gaseous molecule was equal to two. The other values were calculated from the relative electron absorption coefficients, K', and the estimated value for anthracene.

Recently theoretically calculated electron affinities of three of the hydrocarbons in this series have been published.[10] These are also given in Table I. Comparison of the experimental results of this work with the calculated electron affinities reveals a remarkably good agreement between the two sets of data. The estimate of error in the theoretically calculated electron affinity is an average error of ±0.2 − 0.3 ev.[11] These results lend further strong support to the interpretation presented in this paper for the relationship between the electron absorption coefficient and electron affinity.

The most significant advantages of this method for obtaining electron affinity measurements compared with polarographic measurements are: (1) the necessity for the evaluation of energies of solution is eliminated, (2) the extreme precision in $kT \ln K$ if conditions can be standardized to reduce the error in K to less than ±24%, (3) the possibility of obtaining absolute electron affinities through the temperature dependence of K, (4) lack of interference arising from subsequent chemical reactions after reduction in solution.

The concepts considered in this paper are not necessarily restricted to hydrocarbons, but they could also be extended to other molecules. In general, the method is limited to molecules whose vapor pressures are sufficient at temperatures where thermal decomposition does not occur. However, in any extention to the general case, other details may have to be considered. The $kT \ln K'$ as a measure of electron affinity has other implications such as a relation to the energy of the lowest electronic transition, evaluation of the difference in energies of solution of the molecule and its ion for the case of the aromatic hydrocarbons, and relations with parameters within and

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(8) G. J. Hoijtink, *Rec. trav. chem.*, **74**, 1525 (1955).

(9) T. L. Hill, "Introduction to Statistical Thermodynamics," Addison-Wesley Publ. Co., Reading, Massachusetts, 1960, Ch. 10.

(10) J. R. Hoyland and L. Goodman, *J. Chem. Phys.*, **36**, 21 (1962).

(11) J. R. Hoyland, private communication 1962.

calculated from the Hückel theory. Also, it should be possible to establish molecular electronegativities. These considerations are presently being investigated.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE, MASSACHUSETTS]

The Preparation of Organolithium Compounds by the Transmetalation Reaction. V. Perfluorovinyllithium[1-3]

BY DIETMAR SEYFERTH, DEAN E. WELCH AND GUNTER RAAB

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Perfluorovinyllithium has been prepared by the transmetalation reaction occurring between phenyltrisperfluorovinyltin and phenyllithium (1:3 molar ratio) in diethyl ether at *ca.* −40° and between *n*-butyltrisperfluorovinyltin and *n*-butyllithium (1:2 molar ratio) in pentane at *ca.* −40°. In both solvents the stability of perfluorovinyllithium decreases with increasing temperature; the reagent is completely decomposed at 0°. The decomposition of perfluorovinyllithium in ether in the presence of an excess of phenyllithium produced diphenylacetylene in *ca.* 40% yield, a result suggestive of the intermediacy of difluoroacetylene in perfluorovinyllithium decomposition. Reactions of perfluorovinyllithium in ether with organotin halides, trimethylbromosilane and carbon dioxide gave the expected perfluorovinyl derivatives.

The availability of the perfluorovinyl Grignard reagents[4,5] has made possible the synthesis of a large number of perfluorovinylmetal compounds.[6] Of particular interest to us have been perfluorovinyl derivatives of tin,[7] since these possibly could serve as precursors for the hitherto unknown reagent, perfluorovinyllithium.

Efforts to prepare perfluorovinyllithium in solution by the action of perfluorovinyl halides on metallic lithium were unsuccessful. Thus it was reported[8] that a noticeable reaction accompanied by tar formation resulted when iodotrifluoroethylene was added to metallic lithium, but no evidence could be obtained for the presence of perfluorovinyllithium. The use of the transmetalation reaction occurring between vinyltin compounds and organolithium reagents in the synthesis of vinyllithium[9] suggested that this procedure might also be applicable to the preparation of perfluorovinyllithium. Initial experiments showed that such exchange did indeed take place. Treatment of triphenylperfluorovinyltin[7] in diethyl ether with one equivalent of phenyllithium resulted in an immediate precipitate of tetraphenyltin (92% yield) and a dark brown solution. However, no evidence could be obtained for the existence of $CF_2{=}CFLi$ in this solution. The rather limited stability of perfluorovinyl Grignard reagents in ether and in tetrahydrofuran[5] provided an indication that the perfluorovinyllithium reagent might not be very stable. Furthermore, the relatively low stability of perfluoroalkyllithium reagents[10] suggested also that perfluorovinyllithium might be stable only at low temperatures.

Investigation of this factor—the effect of lower temperatures—led to the development of conditions under which the perfluorovinyllithium reagent is quite stable and useful in organic and organometallic syntheses.[3] The reaction of phenyllithium with phenyltrisperfluorovinyltin (3:1 molar ratio) in ether between −40 to −30° proceeded rapidly, giving a precipitate of tetraphenyltin and a brownish solution of perfluorovinyllithium

$$C_6H_5Sn(CF{=}CF_2)_3 + 3C_6H_5Li \xrightarrow{Et_2O} (C_6H_5)_4Sn + 3CF_2{=}CFLi$$

Such solutions were characterized by reaction with trimethyltin bromide, triethyltin chloride and trimethylbromosilane, as well as by carbonation. Trimethylperfluorovinyltin (64% maximum yield), triethylperfluorovinyltin (40%), trimethylperfluorovinylsilane (45%) and perfluoroacrylic acid (37%) were obtained in these reactions. In a separate experiment the perfluorovinyllithium-containing reaction mixture was filtered at −40° to remove tetraphenyltin, which was isolated, after recrystallization, in 92% yield. Optimum conditions for preparing perfluorovinyllithium by this procedure require very slow addition of phenyllithium to the phenyltrisperfluorovinyltin solution and the use of rather dilute solutions. The temperature range over

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(1) Part IV: D. Seyferth and M. A. Weiner, *J. Am. Chem. Soc.*, **84**, 361 (1962).

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