

point with regard to the interpretation of electron capture measurements and their use in chemical or biological correlations. For example, in a recent paper by Briegleb⁹ all the electron capture coefficients were interpreted as involving the formation of a stable negative ion and the electron affinities were calculated accordingly. In our earlier publication³ the existence of two types of capture was emphasized, and it was pointed out that only the non-dissociative case was considered in that paper.

The most direct way of distinguishing these processes is to examine the products of the reaction as did Stockdale *et al.*¹ in the case of chloro- and bromo-benzene. Similar work is planned in our laboratories; however, a mass spectrometer will not necessarily be used. On the other hand, even without this direct information one can distinguish between the two cases with reasonable certainty for many compounds. First, one can rely on a general chemical and structural knowledge of a compound. This includes rough estimates of the bond energies and the electron affinities of possible products, for example, atoms such as the halogens and hydrogen and many of the radicals such as $\text{NH}_2\cdot$ and phenyl. From this, one can see if dissociation would be exothermic or endothermic. Secondly, one could assume the non-dissociative model for a series of compounds and make correlations with other experimental information or theoretical predictions. If the correlation were reasonable, the original assumption can probably be taken as valid. For example, in the case of the three- and four-membered polycyclic aromatic hydrocarbons we feel the correlations lend strong support to the premise that there is formation of a stable negative ion. Thirdly, one can observe the temperature dependence of the equilibrium constant (within certain limitations) and if the results are in agreement with the equilibrium expression³ this should serve as adequate support for formation of a stable negative ion.

The negative molecular ions might also undergo molecular rearrangement. This case was not mentioned by Stockdale *et al.*¹. If this situation arises, possibly only the direct observation of products will distinguish it from the case of electron addition with no rearrangement.

In conclusion we feel that the pulse sampling technique developed by Lovelock yields information involving the interaction of thermal electrons with molecules. Further, if the results are properly interpreted^{3,4,7} they can be correlated with chemical and biological properties and phenomena. Within certain limitations the method can also be used to obtain molecular electron affinities³. As in any new technique a detailed investigation of the processes should be carried out. Many of these have been done and will be submitted for publication shortly⁴.

RALPH S. BECKER
W. E. WENTWORTH

Department of Chemistry,
University of Houston,
Texas.

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³ Wentworth, W. E., and Becker, R. S., *J. Amer. Chem. Soc.*, **84**, 4263 (1962).

⁴ Lovelock, J. E., Chen, E., and Lovelock, J. E. (in preparation).

⁵ Slifkin, M. A., *Nature*, **200**, 877 (1963).

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⁷ Becker, R. S., and Wentworth, W. E., *J. Amer. Chem. Soc.*, **85**, 2210 (1963).

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how this may be done. A number of other workers⁵⁻⁷ have used the results of these three papers¹⁻³ to support various arguments. We are not antagonistic to the 'pulse sampling' method, but it appeared at the time our paper was written that its 'preliminary' results were gaining fairly wide usage before sufficient attention had been directed to their physical basis. We do not wish to debate the individual detailed points raised by Lovelock and Wentworth since their arguments appear to us to be circumstantial. We will welcome a rigorous support of the physical basis of their method, as they promise. However, we do wish to comment at this time on certain important points.

Uman⁸ (as mentioned in our paper, but neglected by Lovelock) and Engelhardt and Phelps⁹ have recently published calculations of the electron energy distribution in Ar-H₂ mixtures and have compared these calculations with the available experimental data. Their results support our estimate that in the cases of C₆H₅Cl and C₆H₅Br almost all the effect observed by Lovelock and his co-workers was that due to dissociative capture at about 0.7 eV. This will hold whether 0.3 per cent¹ or 1 per cent² hydrogen is added to the argon carrier gas. So far as we know there are no published calculations or measurements of electron energy distributions in Ar-CH₄ mixtures. Assuming that the energy distribution changes when the pulse is applied, which certainly appears to be the case at least in the work reported in the first two papers^{8,9}, it is incorrect to state that the maximum error involved is in the ratio of the pulse time to the field free time, whether or not the cross-section for interaction with 'hyperthermal' electrons is less than that with thermal electrons.

We were in error not to state the temperature (22.2° C or 72° F) at which our measurements were made and are indebted to Lovelock for pointing this out. While it may be true that temperature (or pressure) variation may allow dissociative capture to be distinguished from non-dissociative capture with a low stabilization probability, it is not clear to us that temperature variation will necessarily allow dissociative capture to be distinguished from non-dissociative with a high probability of stabilization—the process mentioned in our paper. It might be noted that in the first paper on the pulse sampling method¹ it is simply stated that the "affinities of different substances were observed using electrons in thermal equilibrium with gas mixtures at temperatures of 20°–200° C".

Finally, we wish to say that we find it very difficult to understand Lovelock's argument about dissociative electron capture at thermal electron energies. Dissociative electron capture by a molecule AX can occur even with thermal electrons if X has an electron affinity, EA(X), which is $\geq D(AX)$ [$D(AX)$ = dissociation energy of molecule AX]. Our more recent results indicate this strongly and C₆H₅NO₂ is a representative molecule dissociating with pure thermal electrons.

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J. A. STOCKDALE*
G. S. HURST
L. G. CHRISTOPHOROU

Health Physics Division,
Oak Ridge National Laboratory,
Oak Ridge, Tennessee.

* Australian Atomic Energy Commission, Research Establishment, Lucas Heights, Sydney.

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DR. LOVELOCK *et al.* have published three papers¹⁻³ describing the capture of 'thermal' electrons by a variety of organic compounds. In the first paper¹ the quantity measured is described as the electron affinity of the compounds; in the second² it is stated that the quantity measured may be directly related to the electron affinity, and colleagues of Lovelock⁴ have published an account of