

## Positron Annihilation and Electron Densities in Organic Liquids

B. J. Brown

Department of Nuclear and Radiation Chemistry,  
University of New South Wales, P.O. Box 1, Kensington, N.S.W. 2033;  
present address: School of Chemistry,  
Macquarie University, North Ryde, N.S.W. 2133.

### Abstract

The effective electron density for positron annihilation in substituted aliphatic and aromatic liquid compounds has been determined. For the aliphatic hydrocarbons the molecular electron density  $N_e$  increases linearly with an increase in chain length and is equal to the sum of the partial electron densities of the substituent methyl ( $N_e(\text{CH}_3) = 1.18$ ) and methylene ( $N_e(\text{CH}_2) = 1.28$ ) groups. The values are approximately 10% lower for aromatic systems. The partial electron densities of substituted halogen atoms increase with atomic number and are: fluorine (9.3), chlorine (10.0), bromine (14.4) and iodine (23.0). For the aliphatic alcohols the partial  $N_e(\text{OH})$  value decreases from 1.35 in methanol to 0.86 in octanol.

When a positron enters a medium it will, before annihilation, be slowed to almost thermal energies, where a bound state of an electron-positron pair (positronium) may be formed (see<sup>1</sup> for a review of positron annihilation processes). Positron annihilation in liquid organic compounds has been shown to vary with molecular structure.<sup>2-4</sup> In the aliphatic hydrocarbons the quenching cross-section for annihilation of the positron-electron pair is directly related to the chain length.<sup>4</sup>

The Dirac expression<sup>5</sup> for the mean life of slow positrons  $\tau_2$  in an element of discrete free electron density can be modified for molecular compounds to define the effective molecular electron density for annihilation,  $N_e$ , in terms of the positronium triplet-state quenching cross-section,  $[\sigma_v]_{av}$ :<sup>6</sup>

$$N_e = (c\pi r_0^2 A)^{-1}(M/\rho\tau_2) = [\sigma_v]_{av}(c\pi r_0^2)^{-1}$$

where  $c$  is the velocity of light;  $r_0$ , the classical electron radius;  $A$ , Avogadro's number;  $M$ , molecular weight; and  $\rho$ , the density of the medium.

The annihilation electron densities of a number of de-gassed organic liquids are shown in Table 1. The positron lifetime measurements were made by previously described<sup>6-8</sup> methods. For the homologous series of aliphatic hydrocarbons in Table 1, the electron density is observed to vary linearly with the carbon chain

<sup>1</sup> Brown, B. J., *At. Energy Aust.*, 1973, **16**(3), 2.

<sup>2</sup> Hatcher, C. R., Falconer, T. W., and Millet, W. E., *J. Chem. Phys.*, 1960, **32**, 28.

<sup>3</sup> Bussolati, C., Cora, S., and Zappa, L., *Nuovo Cimento, B*, 1967, **28**, 256.

<sup>4</sup> Gray, P. R., Sturm, G. P., and Cook, C. F., *J. Chem. Phys.*, 1967, **46**, 3487.

<sup>5</sup> Dirac, P. A. M., *Proc. Cambridge Phil. Soc.*, 1930, **26**, 361.

<sup>6</sup> Tao, S. J., Bell, J., and Green, J. H., *Proc. Phys. Soc. (London)*, 1964, **83**, 453.

<sup>7</sup> Bell, J., Green, J. H., and Tao, S. J., *Nucl. Instrum. Methods*, 1965, **36**, 320.

<sup>8</sup> Bell, J., Tao, S. J., and Green, J. H., *Nucl. Instrum. Methods*, 1965, **35**, 213.

length. Good agreement is shown in Fig. 1 between these results and of  $N_e$  values calculated from published estimates of the hydrocarbon quenching cross-section.<sup>4</sup> These compounds consist only of methyl and methylene groups and the slope of the line in Fig. 1 represents that part of the  $N_e$  value which is attributable to the  $\text{CH}_2$  component. This has been estimated to be 1.28 and is taken as the partial electron density for the methylene group. The mean value estimated for the partial electron density of the methyl group is 1.18. Back calculation of the  $N_e$  values by addition of the component elements of the four compounds gives agreement with measured values within 2% and verifies the assumption that the molecular electron density is given by the sum of the partial electron densities of the component groups.

Table 1. Electron densities for positron annihilation in organic liquids

| Compound       | $10^{-9}\tau_2$ (s) | $10^{-14}[\sigma_v]_{\text{av}}$ ( $\text{cm}^3 \text{s}^{-1}$ ) | $N_e$ | Group                        | Partial $N_e$ |
|----------------|---------------------|--|-------|------------------------------|---------------|
| Butane         | 4.60                | 3.65   | 4.9   | $N_e(\text{CH}_3)$           | 1.18          |
| Pentane        | 4.11                | 4.63   | 6.2   | $N_e(\text{CH}_2)$           | 1.28          |
| Hexane         | 3.90                | 5.51   | 7.4   | —                            | —             |
| Octane         | 3.58                | 7.61   | 10.2  | —                            | —             |
| Decane         | 3.42                | 9.31   | 12.5  | —                            | —             |
| 1-Fluorohexane | 3.09                | 6.95   | 9.3   | $N_e(\text{F})$              | 9.30          |
| 1-Chlorohexane | 3.03                | 7.45   | 10.0  | $N_e(\text{Cl})$             | 10.0          |
| 1-Bromohexane  | 2.15                | 10.7   | 14.4  | $N_e(\text{Br})$             | 14.4          |
| 1-Iodohexane   | 1.42                | 17.2   | 23.0  | $N_e(\text{I})$              | 23.0          |
| Methanol       | 3.50                | 1.86   | 2.5   | $N_e(\text{OH})$             | 1.35          |
| Ethanol        | 3.59                | 2.69   | 3.6   | $N_e(\text{OH})$             | 1.14          |
| Octan-1-ol     | 3.20                | 8.12   | 10.9  | $N_e(\text{OH})$             | 0.86          |
| Acetone        | 3.53                | 3.42   | 4.6   | $N_e(\text{C=O})$            | 2.24          |
| Toluene        | 3.24                | 5.35   | 7.2   | $N_e(\text{CH}_3\text{-Ph})$ | 0.95          |
| Benzene        | 3.14                | 4.70   | 6.3   | $N_e(\text{---CH---})$       | 1.05          |

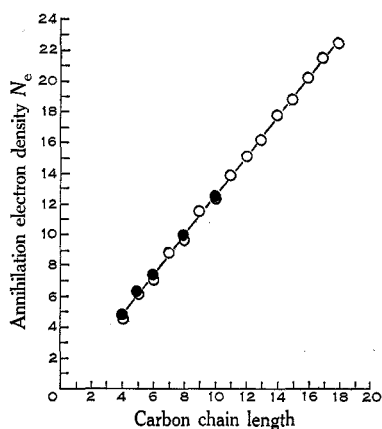


Fig. 1. The annihilation electron density as a function of the carbon chain length for the aliphatic hydrocarbons:

- present study;
- calculated from the positronium triplet-state quenching cross-section<sup>4</sup>  $[\sigma_v]_{\text{av}}$ .

If the partial quenching cross-sections for the methyl and methylene groups are assumed to be the same for substituted alkyl compounds, the partial annihilation electron densities of selected substituent groups are shown in Table 1. For the alkyl halides studied, the partial  $N_e$  value for the respective halides  $N_e(\text{X})$  increases with an increase in the atomic number for fluorine to iodine. The increase in  $N_e(\text{X})$  value

with a decrease in halogen electronegativity suggests that in alkyl halides there is no significant contribution from the alkyl group and that electrons other than those of the outer energy level of the halide may be significant in the triplet state annihilation processes of the positron. For the three alcohols investigated, the partial  $N_e(\text{OH})$  values for the hydroxyl group decrease with an increase in the size of the alkyl group. This result is consistent with a reduction in the polarity of the hydroxyl group with an increase in chain length. The mean value  $N_e(\text{OH}) = 1.1$  for the alcohols is approximately an order of magnitude lower than that for  $N_e(\text{X})$  values in the more polar alkyl halides.

The partial annihilation electron density of the acetone carbonyl group is about double that of the hydroxyl group. A comparison of the  $N_e$  values for toluene and benzene suggests that the partial electron density of the CH component of the phenyl group (1.03), and for a methyl group attached to an aromatic molecule, is slightly lower than for the corresponding values estimated for the aliphatic hydrocarbons.

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