but there is room for improvement in the details, and work is continuing.[13]

It may be noted that our results have been obtained using an essentially sinusoidal potential function for the twisting motion. This seems to indicate that it is not necessary to use the physically unreal parabolic potential function with cusps, proposed by McDiarmid and Charney,[4] in order to explain the spectra. In their interpretation, McDiarmid and Charney neglected the expected stretching of the C–C bond; we have shown that, if this is not neglected, a more realistic explanation of the spectrum can be found. Ogilvie's assignment which effectively disregards the twisting of the molecule as well[14] is clearly wrong.

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# Notes

## Photoionization of the Cycloheptatrienyl Radical*

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The recent measurement of the ionization potential of the cycloheptatrienyl radical by Thrush and Zwolenik[1] using a flash-photolysis technique indicates a value of 6.237 eV. An earlier measurement by Lossing *et al.*[2] using electron-impact techniques gave a value of 6.6 eV. This discrepancy is larger than would be expected.

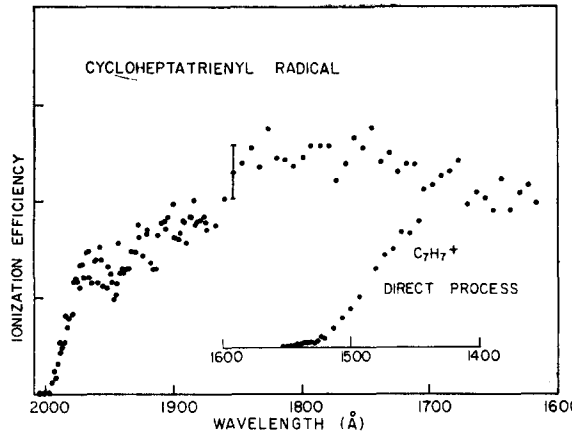


Fig. 1. Ionization efficiency curve for the cycloheptatrienyl radical. The inset curve is the threshold region of the ionization efficiency curve for direct formation of $C_7H_7^+$.

This study was undertaken in an attempt to remove this ambiguity because of the importance of this ionization potential in the interpretation of the fragmentation of toluene and cycloheptatriene.[3] This Note describes a measurement of the ionizational potential of the cycloheptatrienyl radical using photon-impact techniques.

The apparatus used has been described.[4,5] The radical was produced by pyrolysis of ditropenyl in a furnace located adjacent to the ion source. The hydrogen molecular continuum was used as the source of ionizing radiation. The bandpass (full width at half-maximum) was 2.5 Å (0.01 eV at 7 eV). The direct experimental results from this study are shown in Fig. 1.

A survey of the ionization efficiency curve for the radical ion shows an initial rise from zero without significant structure, followed by a leveling off and a second structureless rise, followed by an essentially horizontal region continuing to the upper energy limit of this study.

The initial rise and horizontal region are attributed to photoionization of the cycloheptatrienyl radical to the lowest electronic state of the radical ion. The appearance potential, A.P. ($C_7H_7^+$), for the direct fragmentation of ditropenyl, Fig. 1, shows that the second rise is not due to fragmentation of the unpyrolized molecule. Therefore, the second rise is ascribed to transitions to an upper electronic state of the ion. Within the statistical scatter of the data, the rising sections of the ionization efficiency curve appear to be structureless. This indicates that the vibrational levels of the radical ion are unresolved in the present study. The horizontal regions apparently result from the inaccessibility of further vibrational levels in the respective electronic states of the ion, within the Franck–Condon region. Unfortunately, the rather weak ion currents observed precluded a definitive search for possible fragmentation of the parent radical ion.

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The initial threshold of the ionization efficiency curve from the cycloheptatrienyl radical is of the shape expected for an adiabatic transitation.[3,6–9] The threshold, so interpreted, gives an adiabatic ionization potential, I.P. ($C_7H_7^{\cdot}$), of 6.236±0.005 eV, confirming the value of Thrush and Zwolenik.[1] The onset for the second process is approximately 6.6 eV. The fact that there is a clear-cut difference between the ionization potentials of the radical species observed in this study and the ionization potential of benzyl radical (7.63 eV)[3] shows that the radical observed here has not rearranged to the benzyl structure and indicates that structural integrity is retained during the pyrolysis process.

The equation

$$D_0(C_7H_7\text{–}C_7H_7) = \text{A.P. } (C_7H_7^+)\text{–I.P. } (C_7H_7^{\cdot}) \pm \Delta,$$

where $\Delta$ includes the kinetic shift and the temperature shift, relates the dissociation energy of the molecule to the appearance potential of the fragment ion and the ionization potential of the radical. In a molecule of this type the kinetic shift and the temperature shift should be approximately equal but of opposite sign, hence $\Delta$ would be essentially zero. Within the validity of the above assumption we can determine the dissociation energy of the central carbon–carbon bond in ditropenyl. Substituting the values for the A.P. ($C_7H_7^+$) (8.09± 0.05 eV) and the I.P. ($C_7H_7^{\cdot}$) (6.236±0.005 eV), we calculate $D_0(C_7H_7\text{–}C_7H_7)$ to be 1.85±0.05 eV. This value is to be compared with the value of 1.5 eV given by Lossing *et al.*[2]

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## High-Temperature Dependence of Electron and Hole Mobilities in Anthracene Crystal

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Temperature dependence of hole and electron mobilities in an anthracene crystal have already been measured for almost all principal crystallographic directions (except the $b$ direction for the holes).[1,2] The common result, which all authors agree upon, is a small temperature dependence: $\mu \propto T^{-n}$ with $n$ close or equal to 1—as long as a trap-controlled mobility is avoided.[3] The only well-known exception is the electron mobility in the $c'$ direction ($\perp$ a, b) which increases with temperature. Temperature ranges usually extend from −100° to 140°C.

This kind of temperature dependence has led several authors to increasing complexity calculations of absolute values of the mobility tensor. The most sophisticated calculations have been performed recently by Gosar and Choi,[4] who used the rigorous method of linear response theory and a justified approximation of the correlation function. They showed that mobility exhibits two parts, one ($\mu_1$) which is usual and gives the most important contribution, and the other one ($\mu_2$) which is due to phonon assisted tunneling and whose contribution is not negligible (approximately from $\frac{1}{3}$ to $\frac{1}{5}$ of the whole mobility).[4,5] Obviously, temperature dependence of the two parts are different, and for temperature larger than Debye temperature, one has $\mu_2/\mu_1 \propto T$.

We therefore looked carefully at the temperature dependence $\mu(T) = \mu_1(T) + \mu_2(T)$ in order to detect any possible change of regime which would permit an experimental evaluation of $\mu_1(T)$ and $\mu_2(T)$. From theoretical predictions we expected a less rapidly decreasing mobility in the higher-temperature region. Such a change, if any, can also be produced by space-

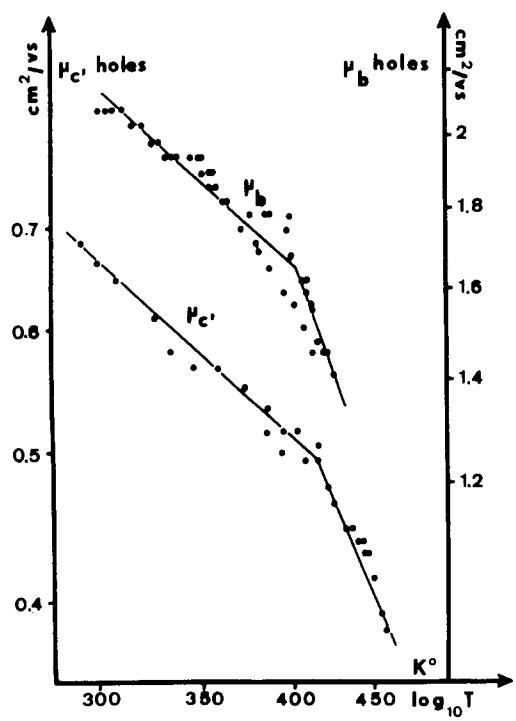


Fig. 1. Temperature dependence for hole mobility.

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