

THERMALLY STABLE CYCLOHEXADIENYL RADICALS
PRODUCED IN THE BENZENE CLATHRATES WITH METAL COMPLEX HOST LATTICES

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The cyclohexadienyl radicals in the γ -irradiated benzene clathrates
 $\text{Cd}(\text{diam})\text{M}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$ (diam = $(\text{NH}_3)_2$, $\text{NH}_2(\text{CH}_2)_2\text{NH}_2$, or $\text{NH}_2(\text{CH}_2)_3\text{NH}_2$;
M = Cd or Hg) are stable up to 423 K.

The benzene molecules enclathrated in Hofmann type and the analogous clathrates are kept separate one from the other, and the individual molecule appears to be an isolated gaseous molecule imprisoned in a molecular space of a very small volume without any significant chemical bonds with the host lattice constituents.^{1,2)} Thus, the molecular space can be expected to be a good reservoir of chemically unstable species.

The polycrystalline samples of $\text{Cd}(\text{tn})\text{Hg}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$ (tn = $\text{NH}_2(\text{CH}_2)_3\text{NH}_2$), $\text{Cd}(\text{en})\text{Hg}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$ (en = $\text{NH}_2(\text{CH}_2)_2\text{NH}_2$), $\text{Cd}(\text{en})\text{Cd}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$, and $\text{Cd}(\text{NH}_3)_2\text{Hg}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$ were sealed in silica ampoules at 1.3×10^{-3} N m⁻² and at 195 K. The sealed specimens were irradiated with 6.5×10^5 rad ⁶⁰Co γ -rays at liquid nitrogen temperature. The e.s.r. spectra were recorded on a JEOL-JES-PE-3X spectrometer with an X-band frequency and a field modulation of 100 kHz in a temperature range from 77 to 423 K. A typical example of the spectra at different temperatures is shown in Fig. 1 for the irradiated $\text{Cd}(\text{en})\text{Hg}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$. At 113 K the 48.0 G triplet with a 10.8 G quartet substructures due to $\text{C}_6\text{H}_7\cdot$ radical^{3,4)} is evidently distinguished from those signals due to thermally unstable unidentified radicals produced from the host lattice constituents. The intensity ratio of the main triplet is 1:2:1, indicating no significant formation of $\text{C}_6\text{H}_5\cdot$ radical. By increasing temperature, the spectral band widths are getting narrower owing to the reorientational motion of the $\text{C}_6\text{H}_7\cdot$ radical, and each line of the sub-quartet components exhibits clearly further splitting into a 3.0 G triplet. The signal intensities are almost constant from 200 K to 423 K until the clathrate decomposes thermally. The e.s.r. spectra of the other irradiated

benzene clathrates gave the band structures and temperature dependency similar to those shown in Fig. 1.

In contrast with the decay of cyclohexadienyl radical in γ -irradiated neat benzene at 241 K,³⁾ the thermal stabilities of cyclohexadienyl radicals in the clathrates may be due to the absence of any considerable chemical interactions after the irradiation between the imprisoned radical and the host lattice constituents, and between the radicals themselves. Therefore, these clathrates will be useful as the media in which one can study electronic states of isolated unstable radicals at room or higher temperatures.

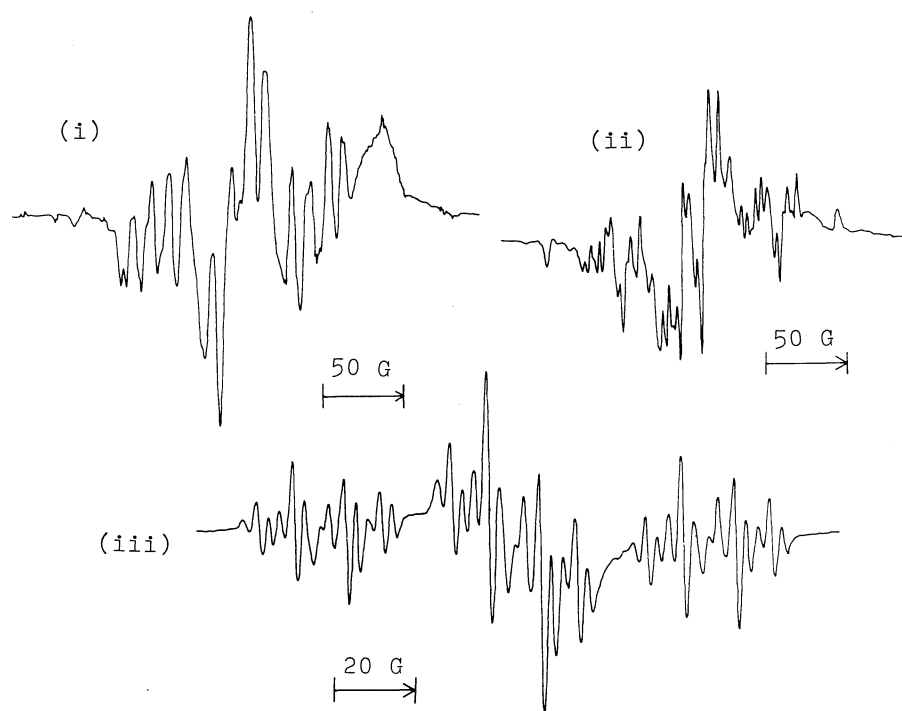


Fig. 1. Temperature dependency of the e.s.r. spectra observed for the γ -irradiated $\text{Cd(en)Hg(CN)}_4 \cdot 2\text{C}_6\text{H}_6$: (i) at 113 K, (ii) at 223 K, and (iii) at 423 K.

References and footnote

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