

the interpretation of  $J_{\text{HCOH}}$  in primary alcohols<sup>2</sup> and cyclohexanols.<sup>3</sup>

A reinterpretation of the di-*t*-butylcarbinol (DTBC) results by considering a *cis* (OH and CH eclipsed) conformer to occur for the bonded OH group in a linear DTBC dimer brings the dihedral angle dependence of  $J_{\text{HCOH}}$  into agreement with the Karplus equation and the  $J_{\text{HCOH}}$  measurements of Bauld and Rim,<sup>5</sup> who found that  $J_{\text{HCOH}} = 12.3$  Hz for a conformationally homogeneous diarylcarbinol where intramolecular hydrogen bonding is thought to maintain a *trans*-HCOH conformation, and of Stolow and Gallo,<sup>6</sup> who found that  $J_{\text{HCOH}} = 11.4$  Hz for *cis,cis,cis*-2,5-di-*t*-butyl-4-methoxycyclohexanol where intramolecular hydrogen bonding is expected to cause a  $167 \pm 2^\circ$  H-C-O-H dihedral angle. Combining our previous contention that for monomeric DTBC  $J_{\text{HCOH}} = 5.4$  Hz (which is temperature independent between  $-10$  and  $25^\circ$ ) is  $(1/3)(2J_o + J_i)$  with Bauld and Rim's assignment of  $J_i = 12.3$  Hz gives  $J_o = 1.95$  Hz. As before<sup>1</sup> it is assumed that the free OH group of the DTBC dimer has  $J_{\text{HCOH}} = (1/3)(2J_o + J_i) = 5.4$  Hz as does the monomer. Now if one accounts for the increase of  $J_{\text{HCOH}}$  for DTBC from 5.4 to 8.5 Hz on the basis of the bonded OH group taking up the *cis* conformation,<sup>7</sup> then  $J_{\text{HCOH}}(\text{dimer}) = 8.5$  Hz =  $(1/2)(5.4 + J_{cis})$  gives  $J_{cis} = 11.6$  Hz. Thus  $J_{\text{HCOH}} = 11.6, 1.95,$  and  $12.3$  Hz at dihedral angles of  $0, 60,$  and  $180^\circ$ , respectively, is in accord with the Karplus values<sup>4</sup> of 8.2, 1.7, and 9.2 Hz, respectively, for  $J_{\text{HCOH}}$  and is consistent with the fact that this type of dihedral angle behavior has been reported for  $J_{\text{HCC}^{13}\text{F}},$ <sup>8</sup>  $J_{\text{HC}^{14}\text{NH}},$ <sup>9</sup>  $J_{\text{HCC}^{19}\text{F}},$ <sup>10</sup> and  $J_{\text{HCC}^{13}\text{C}}.$ <sup>11</sup>

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### Trapped Electrons in $\gamma$ -Irradiated Polycrystalline *n*-Hydrocarbons Studied by Electron Spin Resonance Spectroscopy

*Sir:* Using esr spectroscopy and optical measurements, a number of workers recently found the formation of

trapped electrons in several hydrocarbon glasses by ionizing radiations.<sup>1-5</sup> In all of these experiments, it is reported that the glassy state of the samples was the necessary condition for detecting the trapped electrons with sufficient yields. We have, however, found the esr signal due to the trapped electrons in the polycrystalline state of some hydrocarbons  $\gamma$  irradiated at  $77^\circ\text{K}$ , such as *n*-nonane, *n*-decane, and *n*-hexadecane.

Compounds used in the experiments were obtained from Tokyo Kasei Kogyo Co. Ltd. Samples were purified by passing through a 30-cm column of 28-200-mesh silica gels two times at a rate of 1 drop/min. Then, samples were distilled under vacuum into bottles containing metallic sodium and were kept for 24 hr to remove any trace of water. After these treatments samples were distilled again into Spectrosil esr tubes under vacuum and then the tubes were sealed off. The esr tubes were dipped into liquid nitrogen to crystallize the samples. Although nontransparent polycrystalline samples were obtained by shock cooling, the procedure of melting and crystallization near the melting point was repeated several times to avoid the mixing of super-cooled glasses. The samples thus prepared were irradiated at  $77^\circ\text{K}$  in the dark by  $^{60}\text{Co}$   $\gamma$  rays. The total dose was  $7.2 \times 10^4$  R at a dose rate of  $1.44 \times 10^5$  R/hr. The esr measurements were made in the dark with a Japan Electron Optics Model 3BSX spectrometer operated at 9.4 Gcps with 100-keps modulation.

The esr spectra obtained from *n*-decane are shown in Figure 1 as typical examples. The sharp singlet at the center of the spectrum shown in Figure 1a is due to the trapped electrons ( $g = 2.002$  and  $\Delta H_{\text{msl}} = 4$  G). This is confirmed by the strong saturation tendency with low microwave power and by the photobleaching with infrared light. The singlet in Figure 1a became saturated at the microwave power level higher than 0.03 mW. The light illumination was carried out at  $77^\circ\text{K}$  through the quartz lens attached to the sample cavity using a 300-W tungsten lamp located 1.5 m from the samples with a Toshiba filter IR-D1B, which allows the transmission of a 1-3- $\mu$  wavelength. With the above condition, the sharp singlet decayed within 5 sec, leaving the spectrum shown in Figure 1b, which is the same as the background spectrum of Figure 1a. This spectrum is attributable to the alkyl radicals. Although our samples were polycrystallines, the samples seem to be fairly transparent for the infrared light because of its long wavelength. The signal due to the trapped electrons

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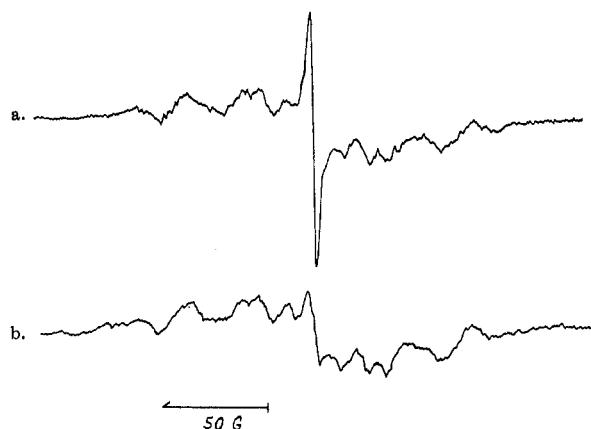


Figure 1. ESR spectra of *n*-decane  $\gamma$  irradiated at 77°K in the dark: (a) immediately after irradiation; (b) after bleaching with a 300-W tungsten lamp using a Toshiba IR-D1B filter. Measurements were made at 77°K in the dark with a microwave power of about 0.03 mW (The wavelength ranged from 1 to 3  $\mu$ .)

was thermally stable at 77°K, and the appreciable decrease of the intensity was not found during 0.5 hr. The yield of the trapped electrons was of comparable order with that for the 3-methylpentane or 3-methylhexane glasses, which were purified by the same procedures and were irradiated at the same condition, but the sensitivity to the infrared light illumination seems higher in the polycrystalline case of *n*-decane, although the quantitative comparison is not made yet. The similar sharp singlet was also observed in *n*-nonane and *n*-hexadecane.

Our experiments strongly suggest that the nonpolar organic crystalline solids are capable of trapping the electrons produced by irradiations, even if the actual reason for the appearance of the signal of the trapped electrons was some impurities in the samples. Nevertheless, our results clearly indicate that the glassy matrix is not always necessary for trapping electrons. The experiments using the crystalline solids may give some other information about the trapping sites of the electrons.

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## Electrogenerated Chemiluminescence. II. The Rotating-Ring-Disk Electrode and the Pyrene-N,N,N',N'-Tetramethyl-*p*- phenylenediamine System<sup>1</sup>

*Sir:* In conventional studies of electrogenerated chemiluminescence (ECL), both anion and cation radi-

cals of an appropriate fluorescer are alternately generated at a single electrode, thereby producing luminescence in the subsequent reaction of these ionic species within the diffusion layer about the electrode. One common method employs an unreference sinusoidal potential as a means of generating ionic species;<sup>2,3</sup> another uses a double (or multiple) potential step between known oxidative and reductive potentials.<sup>4,5</sup> While the former technique is probably the simplest means of observing the electrochemical phenomenon, it is undesirable from an electrochemical standpoint, because accurate potentials are not known; hence it is possible that dianions or dications are formed or that the decomposition of the solvent or supporting electrolyte at unknown potentials forms agents which inhibit the desired chemiluminescent reaction. Even if this difficulty can be eliminated by employing the latter technique, the current-time-intensity behavior obtained is observed to be quite complex because of the diffusional nature of the processes involved so that mathematical description of these processes is extremely difficult. In addition, large nonfaradaic double-layer charging effects inevitably result when a high-frequency alternating potential is applied to a cell having large uncompensated resistance. Most importantly, no alternating-potential process can achieve a true steady state; the intensity of chemiluminescent emission always varies with time.

These problems may be surmounted through the somewhat novel use of the ring-disk electrode<sup>6</sup> for the simultaneous generation of the anionic and cationic precursors of the chemiluminescent product. This type of electrode is particularly convenient for quantitative work because the solutions of the hydrodynamic equations which describe mass transfer as a function of rotation rate are known.<sup>7</sup> Since the steady state may be attained quickly at even moderate rotation rates, the potentials of both the ring and the disk may be set independently, thereby resulting in constant-current levels at both electrodes; this, in turn, results in the steady-state emission of chemiluminescence (unless the bulk concentration of the fluorescer is depleted or sufficient quantities of quenching agents are generated so as to

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