

Chemical Preparation and Electron Spin Resonance Spectra of Specific Trapped Hydrocarbon Radicals

IN recent years there have been many reports of radicals trapped in solid matrices¹. The radicals have been formed by radiolysis, photolysis, or electrical discharge. We have now succeeded in developing a general method of preparing specific trapped hydrocarbon radicals by simple chemical reaction, using a rotating cryostat previously described by one of us².

The method is to deposit a thin discontinuous film of sodium atoms (far less than a monolayer) on to a freshly prepared moving surface of halogenated hydrocarbon, preferably an iodide, held in a high vacuum at the temperature of liquid nitrogen. The atoms react to form the sodium halide and the hydrocarbon radical. A fresh layer of the halogenated hydrocarbon is then deposited on top of the products of reaction, which thus become embedded and preserved in a matrix. The process is repeated many times to build up an appreciable amount of material. A sample of the deposit is then transferred, still cold and under high vacuum, to an electron spin resonance spectrometer, where the electron spin resonance spectrum of the trapped radical is recorded. A feature of the experimental method is that only a single free radical reaction step $RX + Na \cdot \rightarrow R \cdot + NaX$ ($X = \text{halogen}$) is allowed to take place.

Table 1 summarizes our results listing the radicals formed, the material of preparation (which was also the matrix in which radicals were embedded), some salient features of the electron spin resonance spectrum and, in some instances, the molar concentration of radicals in the samples transferred to the spectrometer. After being warmed to room temperature, some of the samples were analysed by gas liquid chromatography (G.L.C.), with results which are also given in Table 1. The spectra, supported by the analytical results, demonstrate that the radicals formed from the halides were the expected ones.

The electron spin resonance spectra of the radicals *n*-propyl, *n*-butyl, *s*-butyl, isobutyl, *t*-butyl, cyclopentyl and cyclohexyl at 77° K are in good agreement with those reported by Ayscough and Thomson³ while that for allyl is similar to the one reported by Smaller and Matheson⁴. In these other investigations the

radicals were produced by γ -irradiation of parent molecules, so that the preparation described here, by an entirely different method involving simple chemical reaction, is strong confirmation of the identities claimed. The spectra of both phenyl and benzyl radicals exhibit hyperfine structure. Detailed discussion of these and the other spectra will be published later.

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¹ *Formation and Trapping of Free Radicals*, edit. by Bass, A. M., and Broida, H. P. (Academic Press, New York, 1960).

² Thomas, A., *Trans. Farad. Soc.*, **57**, 1679 (1961).

³ Ayscough, P. B., and Thomson, C., *Proc. Chem. Soc.*, 247 (1961).

⁴ Smaller, B., and Matheson, M. S., *J. Chem. Phys.*, **28**, 1169 (1958).

New Evidence for Free AIH

RECENT work in this laboratory on the vapour density of the compound, $AlH_3 \cdot 2N(CH_3)_3$, has indicated that this material dissociates reversibly in two steps. In Table 1, the pressures at various temperatures are presented for a sample of known weight in a volume of approximately 1 litre. The

Table 1. DISSOCIATION PRESSURES OF $AlH_3 \cdot 2N(CH_3)_3$

| (a) (0.1477 gm. sample) | | | (b) (0.07173 gm. sample) | | |
|-------------------------|---------|-------------------|--------------------------|---------|-------------------|
| T (° abs.) | V (l) | P (mm. mercury) | T (° abs.) | V (l) | P (mm. mercury) |
| 333.02 | 0.9752 | 21.00 | 337.48 | 0.9777 | 17.39 |
| 338.06 | 0.9754 | 24.69 | 343.41 | 0.9777 | 18.71 |
| 342.68 | 0.9756 | 27.84 | 347.13 | 0.9778 | 19.37 |
| 348.07 | 0.9759 | 33.81 | 353.18 | 0.9778 | 20.38 |
| 353.15 | 0.9761 | 37.01 | 358.26 | 0.9779 | 21.08 |
| 358.14 | 0.9763 | 40.27 | 362.84 | 0.9779 | 21.86 |
| 363.04 | 0.9765 | 43.30 | 367.78 | 0.9780 | 22.87 |
| 368.16 | 0.9766 | 45.03 | 373.44 | 0.9780 | 23.19 |
| 373.16 | 0.9767 | 46.47 | 377.74 | 0.9780 | 24.10 |
| 400.0 | 0.9769 | 54.34 | 381.10 | 0.9780 | 23.98 |
| | | | 389.36 | 0.9781 | 25.36 |
| | | | 391.22 | 0.9781 | 25.44 |
| | | | 398.19 | 0.9781 | 26.18 |
| | | | 402.79 | 0.9781 | 26.40 |

pressures, measured with a mercury manometer, have been corrected to 0°.

The molecular weights calculated from the ideal gas law and the data in Table 1 are plotted in Fig. 1. The data for the large (0.1477 gm.) sample (curve *a*)

Table 1
Salient features of E.S.R. spectrum at 77° K

| Radical | Material of preparation (also matrix) | No. of lines | Relative intensities (approx.) | Hyperfine splitting observed $\pm 5\%$ | | Concentration of radicals in sample (% molar) | Approximate yield of radicals based on sodium deposited | Substances detected by G.L.C. in warmed-up products |
|------------------|---------------------------------------|--------------|--------------------------------|--|------|---|---|--|
| | | | | Ha | Hb | | | |
| <i>n</i> -propyl | 1-iodopropane | 6 | 1:3:4:4:3:1 | 23.3 | 46.6 | — | — | — |
| <i>n</i> -butyl | 1-iodobutane | 6 | 1:3:4:4:3:1 | 21.9 | 43.8 | — | — | <i>n</i> -butane <i>n</i> -butene <i>n</i> -octane |
| <i>s</i> -butyl | 2-iodobutane | 8 | 1:5:11:15:15:11:5:1* | 23.7 | 41.3 | — | — | — |
| isobutyl | 1-iodo-2-methylpropane | 5 | 1:2:2:2:1 | 20.5 | 40.0 | 0.08 | 10-20% | — |
| <i>t</i> -butyl | 2-iodo-2-methylpropane | 10 | 1:9:36:84:126:126:84:36:9:1 | 22.2 | — | — | — | — |
| <i>n</i> -heptyl | 1-iodoheptane | 6 | 1:3:4:4:3:1 | 22.0 | 44.7 | 0.13 | 10-20% | — |
| cyclopentyl | cyclopentyl bromide | 8† | 1:3:5:7:7:5:3:1 | 24.6 | 46.1 | — | — | cyclopentane + cyclopentene |
| cyclohexyl | cyclohexyl bromide | 6 | 1:1:2:2:1:1 | 20.0 | 40.6 | 0.11 | 30-40% | cyclohexane + cyclohexene |
| allyl | allyl bromide | 5 | 1:4:6:4:1 | 14.4 | — | 0.02 | 1-2% | 1,5-hexadiene |
| phenyl | iodo benzene | 1 | — | 63 (half width) | — | — | — | — |
| benzyl | benzyl chloride | 3 | — | 16.9 ($-CH_2$ protons) | — | about 0.36 | 60-90% | dibenzyl |

* Outermost lines not observed.

† At about 110° K the spectrum changes to one of at least twelve lines; when the sample is cooled back to 77° K the spectrum reverts to the original.