Stable Radicals obtained by Treatment of Azulene with Periodic Acid and Other Oxidants

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IT has been reported[1] that the action of periodic acid on polycyclic aromatic hydrocarbons can produce coupling products through a radical intermediate, or other cases give quinones by a two-equivalent oxidation.

The action of periodic acid and other oxidants on azulene[2,3] has now been examined; the products isolated were found to be radicals having remarkable stability to air and heat.

A solution of azulene (I) (0·64 g., 0·005 mole) in acetic acid (or acetonitrile) (40 ml.) was stirred with an aqueous solution (10 ml.) of paraperiodic acid (2·3 g., 0·01 mole) at 20° for 30 min. Water (10 ml.) was then added, and the black-green precipitate was collected, washed with water, aqueous acetic acid, and glacial acetic acid, and dried in a vacuum desiccator for 24 hr.; yield 0·85 g. The product was paramagnetic, and gave the symmetrical e.s.r. spectrum shown in the Figure.

Thin-layer chromatography of the crude product showed the presence of two major components [silica gel; 8 : 1 : 1 (v./v.) benzene–*NN*-dimethylformamide (DMF)–glacial acetic acid, 1 hr.] at R_F 0·05 and 0·78, and minor components at R_F 0·91 and 0·94. A sample reprecipitated three times from aqueous DMF and corresponding mainly to the component having R_F 0·05 was used in all analyses and measurements. The dried sample (150°/0·05 mm.)† is a black, glass-like, amorphous (*X*-ray evidence) powder which is strongly paramagnetic, giving an e.s.r. spectrum identical with that of the crude material. Microanalysis indicates that the repeating unit of the product consists of three azulene moieties, one iodine atom, and four oxygen atoms. Magnetic susceptibility measurements (Thorpe–Senftle method, liquid nitrogen) indicate that the number of radicals is about 20% of the number of repeating units. Conductivity measurements in DMF suggest that the product is a weak electrolyte. The conductance of the solvent was $9{\cdot}0 \times 10^{-6}$ ohm^{-1} cm.$^{-1}$, and that of a stock solution (0·5 g./l.) was $94{\cdot}9 \times 10^{-6}$ ohm^{-1} cm.$^{-1}$. The ratio of conductance to concentration decreases rapidly as the concentration increases. The viscosity of a solution of the product (0·06 g.) in DMF (100 ml.) showed an intrinsic viscosity of about 0·53 dl.g.$^{-1}$, which indicates that the degree of polymerization of the product may be of the order of 20—100 repeating units.

This product is not soluble in aqueous base and is little affected on fusion with potassium hydroxide; however, it is somewhat affected by hot 7M-nitric acid. In addition to slight solubility in DMF, the product is only sparingly soluble in dioxan, acetone, or acetic acid, and practically insoluble in benzene, chloroform, or ether. Its u.v. spectrum shows λ_{max} (DMF) at 292, 370 sh, and 590 sh nm., which are spectral shifts of 90—100 nm. as compared to the peaks of azulene [λ_{max} (DMF) 326, 351, 548, 579, 620, and 682 nm.]. A similar hypsochromic shift has been observed on alteration of azulene to the azulenium cation.[4] I.r. maxima (Nujol) were observed at 1700 and also at 1590 and 1700 and also at 1590 and 1570 $cm.^{-1}$ (aromatic C=C stretchings observed also for azulene[5]); but the spectrum showed no significant absorption between 1400 and 625 $cm.^{-1}$ (fingerprint region).

In DMF, the product shows a single-line, symmetrical e.s.r. spectrum; as suggested for triphenylvinylmethyl polyradicals,[7] the absence of spectral fine-structure may be attributed to the high local concentration of radicals in individual units, or to their mutual interaction.

An attempt was made to sublime a sample of the product (0·25 g.) at 395°/0·05 mm. for 1 hr.; the unsublimed residue (0·22 g., 88%) (Found: C, 84·0; H, 2·9; I, 9·9%) was strongly paramagnetic, and gave the same symmetrical e.s.r. spectrum (spectrum A). The dark brown sublimate contained mainly iodine, and a trace of naphthalene. The initial protonation of azulene with periodic acid may afford, as expected,[6] a monomer cation; however, the product isolated is polymeric, as evidenced by its nonvolatility, thermal stability, resistance to fusion with potassium hydroxide, and visible and i.r. spectra.

The stability of this radical is shown by the fact that further heating of a sample (0·05 g. in evacuated ampoule, preheated to 395°) at 485° for 15 min. (evolution of iodine) left a residue (Found: C, 93·5; H, 3·1; I, 2·9%) that was still paramagnetic; however, the intensity of the e.s.r. spectrum of this residue (same amount) had diminished considerably. Similar stability of the radical was observed when heating was conducted in air or in oxygen-enriched air. No appreciable change in the intensity of the peaks in the e.s.r. spectrum was observed with a sample exposed to air for four months at room temperature.

Similarly, treatment of (I) (in acetic acid) with nitric acid produced a dark brown, paramagnetic powder; the e.s.r. spectrum of this radical was asymmetric (Figure, spectrum B). Heating this material under vacuum (140°/0·05 mm.) for 1 hr. or storage at room temperature for one month, results in a product that exhibits an altered e.s.r. spectrum, asymmetrical but without the shoulders seen in spectrum B. Paramagnetic solids were also obtained by treating (I) with iodic acid (width, 9 gauss; g 2·0036 ± 0·0002) and with antimony pentachloride in dichloromethane (width, 7 gauss; g 2·0038 ± 0·0001).

In contrast to the results with the oxidants already mentioned, the product from treatment of

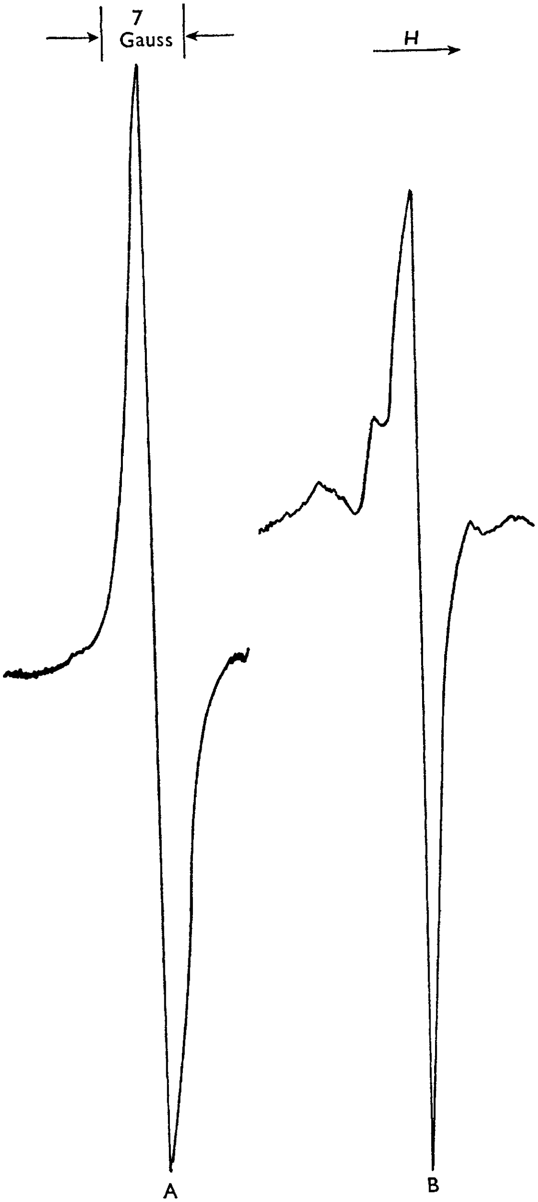

FIGURE. (A) *The e.s.r. spectrum of the powder prepared by treatment of azulene (in acetic acid) with periodic acid,* H_5IO_6, *(in water) at room temperature,* g 2·0034 ± 0·0002; (B) *the e.s.r. spectrum of the freshly prepared powder obtained on treatment of azulene (in acetic acid) with conc. nitric acid at room temperature;* g 2·0087 ± 0·001 (g-*values and indicated error limits, respectively, are average deviations for three determinations*).

(I) with sulphuric acid or perchloric acid showed the presence of only a trace of a paramagnetic species (width, 6—12 gauss; g 2·0033 ± 0·0002); and paramagnetic species were not observed on treatment of (I) with phosphoric, hydrochloric, or trifluoroacetic acids.

The structure of the product obtained on treatment of (I) with periodic acid is not yet clearly understood. Because of its high intrinisc viscosity, it cannot be a small free-radical of the type observed on heating azulene;[8] on the other hand, a linear polymer having unpaired electrons only on the ends of the chain[9] is excluded by the larger ratio of radicals in the polymer, according to its magnetic susceptibility. The product that results after heating at temperatures above 400° may be similar to the well known chars, but such "structures" cannot represent that of the initial product, because of its solubility. A polymeric charge-transfer complex involving iodine remains a possibility.

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