Status of free radicals

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A survey of the broad-front investigations into methods of isolating free radicals and the prospects for their practical application.

Recent studies by Rice (1, 2) and Broida (3, 4) have suggested that active free radicals might be stabilized and preserved by entrapment in a solid matrix. Although the chemistry of radicals in gases (5) and liquids (6) has been the subject of many investigations, only in recent years has attention been directed toward radicals in solids.

Free radicals, since they have unpaired electrons, have paramagnetic properties. In recent years paramagnetic, or electron spin resonance, properties of radicals have been studied extensively with a view to using such information to elucidate questions of structure and as an analytical device for determining radical concentration (7, 8, 9). Electron spin resonance measurements have been made in the gas phase on such stable free radicals as O_2 (10, 11), NO (12), and NO_2 (12), and on such highly active entities as H(13), N(14), and O(15) atoms which can be generated in fairly high concentrations in the gas phase. Unfortunately, more complex radicals are difficult, if not impossible, to generate in large concentrations in the gas phase, and so measurements of the magnetic properties of gaseous radicals have been limited to these few atomic species.

The problem, then, in studying free radicals is to obtain them in sufficient concentration and at the same time to isolate them from other radicals for a sufficiently long time to permit control and examination. The early studies of Broida (3, 4) and his colleagues suggested how this might be done. In their work they generated an afterglow by passing nitrogen through a discharge and then passing the flowing gas over a surface cooled to 4°K. The gas condensed to a solid which glowed with a brilliant green color. The glow disappeared a few seconds after the electric discharge was discontinued but reappeared upon warming and persisted, with some changes in color, until a temperature of the order of 30 to 35°K was reached. The emission of light and the occasional violent explosions were ample evidence that highly energetic species were present, and the most reasonable interpretation of the results was to attribute this activity principally to nitrogen atoms trapped in the solid. Although this view had to be modified in detail as a result of subsequent studies, it is still essentially the correct one. Stemming from these observations, a great deal of research on the trapping of radicals in solids has been and is being conducted. Broadly, research on trapped radicals