

⁴S_g transition of nitrogen atoms, thus indicating that nitrogen atoms can be vaporized from a solid and recondensed. The second solid also exhibited a faint glow indicating that other active species were probably transferred also.

Chemical Reactions

A few studies of chemical reactions of trapped radicals (other than simple recombinations) have been made. Klein and Scheer (57, 58) have studied the chemical reactions occurring when H or D atoms from the gas phase impinge upon and diffuse into thin layers of solid olefins at 77°K. With propylene and 1-butene they found that the atom added to the terminal carbon yielding a secondary radical which could then add a second H atom, dimerize, or disproportionate. Both the structure and molecular weight of the olefin affected the results significantly.

Using the matrix isolation technique, Pimentel (59) has studied the cis-trans isomerization of HNO₂ at 20°K, and at the same conditions Brown and Pimentel (60) studied the photolysis of nitromethane and methyl nitrate. They concluded that the nitromethane isomerized to methyl nitrite which then decomposed giving formaldehyde and HNO₂ as principal products.

It was mentioned earlier that oxygen gas containing O atoms produces ozone in large yields at low temperatures, although it is not certain that this reaction occurs in the solid phase. Similarly, water vapor or hydrogen-oxygen mixtures when passed through a discharge and condensed at 77°K produce considerable amounts of hydrogen peroxide, but we are not certain that the reaction occurs in the solid. It is evident, however, that at very low temperatures only those reactions which involve very low activation energies can occur at significant rates. Thus, the techniques of carrying out chemical reactions at very low temperatures offer an opportunity, in some instances, to obtain very high selectivities with low yields of undesirable by-products. But, much remains to be done before practical applications can be expected.

Table 4. Identification of some trapped organic radicals.

RADICAL	MATRIX	T°K
CH ₃	Zn(CH ₃) ₂	77
CH ₃	CH ₄	4
CH ₂ OH	glass	77
(CH ₃) ₂ COH	glass	77
CH ₂ = CH-CHOH	glass	77

Table 5. Concentration of trapped radicals.

RADICAL	MATRIX	T°K	CONCENTRATION, %
H, D	H ₂	4	0.01
	CH ₄	4	0.05
	H ₂ O	77	0.05
	H ₂ O-H ₂ SO ₄	77	0.10
N	N ₂	4	0.1
	N ₂	4	0.5
	N ₂	4	6.0
CH ₃	CH ₄	4	0.032

Practical applications

The advantage of using free radicals as rocket fuel arises from the possibility of obtaining high thrust. Thrust depends primarily upon the energy release per unit of mass and consideration of the various radicals that might be used reveals that only hydrogen atoms or helium in the triplet (or higher) excited state would have any large thrust advantage over more conventional fuels. The very low concentrations of trapped radicals obtained to date make this application very remote although, of course, some unexpected discovery might improve the prospects.

If trapped radicals are ever considered for commercial chemical process applications, several problems will demand serious consideration. Among the most serious of these are the very low temperatures involved and the accompanying problems of heat economy. Most of the successful trapping of radicals so far has been at 4-20°K, a temperature very difficult and expensive to achieve. The trapping agents employed have been characterized by rather weak matrix binding forces. In a few instances radicals have been stabilized at higher temperatures (77-125°K) in ice or certain glasses. It seems probable then, that by proper choice of matrix, higher, and hence more economic, temperatures can be employed. No serious study of this problem has been made, however, and a systematic investigation would seem to be both desirable and necessary if any commercial application is to be achieved.

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