

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

has tried to answer the questions how to generate trapped radicals, how to identify the active species present, how to measure their concentration, and how to recover them from the solid. None of these questions has been completely answered at this time.

Generation of trapped radicals

In general, trapped radicals can be prepared in two ways: by generating the radicals in the gas phase and suddenly freezing them in a solid matrix at low temperatures or; by irradiating the appropriate solid with either ultraviolet light or ionizing radiation. Both methods have been used extensively. The generation of radicals in the gas phase has usually (and more successfully) been done by electric discharge although both photolysis and pyrolysis of the gases have been employed. Both methods give similar results although each presents problems. When an activated gas is condensed, even at very low temperature, it is almost impossible to remove the energy from the gas completely at each collision of a gas molecule with the wall. The result is that the radicals strike the wall many times before being trapped in the solid, and a large number of them will be removed by chemical reaction. Further, diffusion may occur within the matrix or on the surface with resulting loss of radicals by recombination.

Radicals are usually formed by breaking chemical bonds, and thus they will normally be formed in pairs. If the radicals are formed by irradiation or photolysis of a solid, they will be trapped in pairs in a cage and will recombine immediately. It is only when there is an opportunity for diffusion so that some radicals can escape from the cage, but without enough energy to reach a second radical, that radiation can successfully produce stabilized radicals. In both methods, wherever two radicals recombine a great deal of heat is liberated and the matrix in the neighborhood will be softened and melted. If other radicals are close by, they will have an opportunity to diffuse together and react. In this way an energy chain can be initiated causing the entire system to react very rapidly. Thus, as will be discussed later, the problem of trapping radicals in high concentrations is a very difficult one and has not yet been solved.

Identification

The identification of trapped radicals presents many serious problems, and, as a consequence, only a few have been convincingly identified. The difficulties are obvious. First, one can

never be certain that only one active species is present and, in fact, one can imagine few systems where this would be true. Second, almost no data exist on the effect of the crystal field upon the radical trapped in it. The principal means of identifying radicals trapped in solids have been emission, infrared absorption, and electron spin resonance spectra. Chemical evidence has also been employed, but not always successfully.

The free radical systems that have been subjected to the most extensive investigations have been hydrogen, nitrogen, oxygen, NH, and methyl. When hydrogen gas containing H atoms is condensed at 4°K only a very weak glow is observed in the gas near the solid and none in the solid itself (16). No absorption bands can be detected in the near infrared. Thus, there is no spectral evidence for trapped H atoms. H atoms have

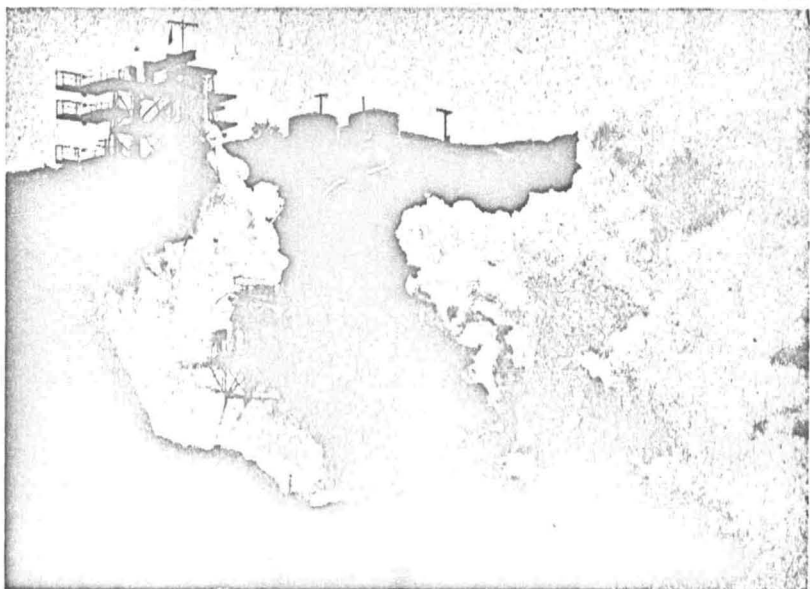
(22). Livingston irradiated solidified aqueous solutions of several acids with gamma rays from cobalt-60 at 77°K, and Matheson and Smaller performed similar experiments with ice. Both groups measured the electron spin resonance of the irradiated solid and found spectra characteristic of hydrogen atoms, Table 1. The measurements on ice, however, gave line

Table 1. Identification of trapped hydrogen atoms.

RADICAL	MATRIX	T°K	METHOD
H, D	H ₂	4	esr
H	Ice ?	77	esr
H, D	H ₂ O-H ₂ SO ₄	77	esr
H	CH ₄	4	esr

separations much smaller than those in the gas phase or in the acid-water mixture. The discrepancy has not been satisfactorily explained.

Nitrogen atoms have undoubtedly been the most intensively investigated



Rocketdyne photo

Remote at present, free radicals may yet be used for future propulsion.

been trapped in very low concentration in a hydrogen lattice and have been positively identified by Jen *et al.* (17, 18) using electron spin resonance. Hydrogen atoms gave a typical doublet and deuterium a triplet, similar to the spectra obtained in the gas phase. There has also been considerable speculation as to whether the hydrogen and deuterium atoms were trapped as H₃ or D₃. Some electron spin resonance data (18) suggest this possibility but are inconclusive. Attempts to predict the spectrum of H₃ from *a priori* theoretical considerations have also been inconclusive (19).

Some interesting measurements have been made by Livingston (20, 21) and by Matheson and Smaller

of any trapped radical. Unfortunately, some of the published material is conflicting, and final explanations of most of the phenomena have not as yet been adduced. The principal energetic species present in the nitrogen afterglow is atomic nitrogen in the ground (⁴S) state (23), and in most of the studies discussed here the N atom concentration is in the order of 2% (23, 24, 25). However, small amounts of nitrogen in both the ²D and ²P states are present (26), their concentrations being, perhaps, 1% of that of the ground state N. The principal spectrum observed in the nitrogen afterglow is due to the B³Π_g—

—A³Σ_u⁺ transition of molecular nitrogen which in turn arises somewhat

indirectly from the recombination of nitrogen atoms.

When the glowing nitrogen gas is condensed at liquid helium temperature, the principal emission spectrum arises from ${}^2D-{}^4S$ transition of atomic nitrogen although many other bands are observed (4). The ${}^2P-{}^2D$ transition of atomic nitrogen has been found in the near infrared emission spectrum (27). It is interesting that the $B^3\Pi_g-{}^+A^3\Sigma_u$ transition which dominates the gas phase afterglow is not observed. Unfortunately, impurities account for much of the spectrum observed, and several false starts toward interpretation of the results are attributable to this fact. Thus, one of the principal sets of bands originally attributed to one of the nitrogen transitions was later definitely proved to be due to the ${}^1S_0-{}^1D_2$ transition of atomic oxygen present as an impurity (28). It is significant that the emission spectra of trapped N and O were shifted slightly toward lower energies, suggesting some kind of stabilizing interaction with the solid lattice. Milligan *et al.* (29) obtained infrared absorption spectra on the glowing solid and attributed certain bands to the radical, N_3 . However, both energy and spin orbital correlation considerations cast some doubt upon N_3 as an important method of stabilizing N atoms. Thus, we have no spectral observations on the most important free radical species presumably present in the solid—namely N^4S —and must rely on other methods for its detection.

Perhaps the most positive identification of trapped nitrogen atoms has been made by electron spin resonance. Both Cole *et al.* (30) and Foner *et al.* (31) measured the electron spin resonance spectrum of the condensed nitrogen afterglow, Table 2. Both obtained a triplet similar to that of N^4S in the gas. Foner *et al.* also studied the effect of hydrogen and methane as the trapping matrix and found a small shift in the hyperfine splitting, the shift increasing as the binding strength of the matrix increased. All of the investigators found satellite lines which have not yet been satisfactorily explained.

Oxygen atoms, NH, NH_2 , HO_2 , and OH radicals have been the subject for numerous investigations, but unfortunately the evidence bearing on all of them is incomplete. Thus, as was mentioned above, O atoms have been found as impurities in the glowing nitrogen solid but as yet they have not been identified in oxygen that has been condensed after passing

through a discharge. Ozone is evolved in copious quantities when the solid is warmed (32, 33), indicating that O atoms were present at some time but there is no convincing evidence that they are trapped in the solid. The NH radical has been tentatively proposed (1, 2) to explain the blue color of the solid obtained when hydrazoic acid vapors are partially decomposed and immediately condensed at 77°K. However, its presence has not yet been proved although it now seems definite that, at most, it can be present only in small concentrations (34, 35). However, Robinson and McCarty (36) have detected both NH and NH_2 by the absorption spectra of the products of a discharge through hydrazine and argon condensed at 4°K. The OH and, especially, the HO_2 radicals have been sought as explanations for the behavior of the solid obtained by freezing the gases leaving an electric discharge in water vapor or hydrogen-oxygen mixtures. Electron spin resonance data on such solids (37) might be attributed to OH or HO_2 , but the assignment is not definite and the data do not agree with electron spin resonance measurements on gamma-irradiated ice (22, 38) which have also been attributed to these radicals. Iodine atoms, CS, ClO, and benzyl have been trapped in hydrocarbon glasses irradiated with ultraviolet light at 77°K, and their presence identified spectroscopically, Table 3 (39, 40).

Several studies have been made in an effort to trap and identify organic radicals in various matrices. Unfortunately, few of these are completely convincing and, in fact, the only satisfactory studies have been of the methyl and benzyl radicals. In all cases except benzyl, attempts at identification have consisted of measurement of the electron spin resonance spectrum of a solid at low temperatures. In most instances the solid is first irradiated with gamma rays to bring about dissociation and the formation of radicals.

When protons are present in a free radical, they will couple or resonate with the spin of the unpaired electron. If all of the protons couple equally, the spectrum will show one line more than the total number of protons in

Table 3. Identification of various trapped inorganic radicals.

RADICAL	MATRIX	T°K	METHOD
O	N_2	4	emission spectra
I	glass	77	absorption spectra
ClO	glass	77	absorption spectra
$N_3(?)$	N_2	20	absorption spectra
NH	A	4	absorption spectra
NH_2	A	4	absorption spectra

the radical. Thus, the spectrum of hydrogen atoms is a doublet and of methyl, a quartet. With equal coupling the relative intensities of the lines are also predictable, the ratios being those of the coefficients of the binomial expansion to the power of the number of protons involved. These considerations form the basis for most of the identifications of organic free radicals entrapped in various matrices. Thus, Gordy and McCormick (41) found a quartet in the electron spin resonance spectrum of zinc dimethyl irradiated with x-rays at 77°K. Smaller and Matheson (42) and Wall *et al.* (43) irradiated solid methane with gamma rays and found a quartet with intensities of the expected order, namely in the ratio 1:3:3:1. Jen *et al.* (18) passed methane through a mild discharge and trapped the products at 4°K. They similarly irradiated methyl iodide with ultraviolet at 4°K. In both cases they obtained a quartet in the electron spin resonance spectrum. The data thus show rather conclusively a methyl radical as the species trapped, Table 4.

Several investigators have studied more complex systems and have attributed the resulting spectra to various possible individual free radicals. Thus, Gordy and McCormick (41) obtained a symmetrical sextet from irradiated mercury diethyl which they attributed to the ethyl radical. Smaller and Matheson (42) obtained a quartet of triplets on irradiation of ethane, ethylene, and ethyl chloride at low temperatures, and decided that their results were similar to those of Gordy and McCormick, except that the latter's spectra involved line broadening due to the influence of the matrix. They also attributed their spectrum to the ethyl radical. It is not clear why other radicals would not also be formed in a system of this kind. Smaller and Matheson (42) have irradiated several hydrocarbons in this way and Luck and Gordy (44) have irradiated various alcohols, amines, and mercaptans. In each case, the spin resonance spectra were attributed

Table 2. Identification of trapped nitrogen atoms.

STATE	MATRIX	T°K	METHOD
4S	H_2, N_2, CH_4	4	esr
2D	N_2	4	emission spectra
2P	N_2	4	emission spectra

to a single free radical. Gibson *et al.* (45) and Ingram and Symons (46) have irradiated several alcohols fixed in a water-H₂O₂ glass with 2537 Å mercury radiation. Apparently the hydrogen peroxide was decomposed to OH radicals which then abstracted hydrogen from the alcohol leaving a free radical which was identified by its spin resonance spectrum.

Concentration in the matrix

It is evident from the above that the problem of identifying trapped free radicals with certainty is a complex one which has been solved satisfactorily in only a very limited number of cases. The problem of determining the number or concentration of trapped radicals is even more difficult since it involves not only identification, but measurement of the numbers involved. The most satisfactory methods for measuring concentration have been magnetic, employing either spin resonance or magnetic susceptibility. In his studies of hydrogen atoms, Livingston (47) estimated the hydrogen atom content of the irradiated frozen aqueous solutions of acids to be in the order of 0.1%. He also collected the hydrogen evolved upon warming the mixture and got satisfactory agreement with the spin resonance measurements. Matheson and Smaller (22) estimated the hydrogen atom content of irradiated ice to be of the order of 0.05 mole %, and from dipolar broadening, Jen *et al.* (18) estimated that the hydrogen atom content of the lattice was about 0.01%. In neither case were efforts made to maximize the hydrogen atom content and so the results given are not necessarily limiting.

Perhaps the most convincing measurement of the concentration of nitrogen atoms in a solid deposited from the nitrogen afterglow has been made by Fontana (48) who measured the magnetic susceptibility of the solid during deposition. He found that the nitrogen atom content built up slowly to concentrations as high as about 0.5%. Near this concentration the situation became unstable and a characteristic yellow flash occurred, at which point the temperature rose and the nitrogen atom content dropped precipitously. The atom content would then slowly build up until the unstable situation was again reached. Wall *et al.* (43) have estimated the nitrogen atom content of gamma irradiated solid nitrogen to be about 0.1%. Other, and much less reliable methods, have led to values as high as 4 to 6% (49). However, these higher values came from meas-

urements of total heat release. Because this heat might have come from excited molecular species, the analysis should be taken with serious reservations.

Estimates of oxygen atom content in the solid condensed after passing oxygen through an electric discharge have led to values as high as 11%. It must be emphasized, however, that oxygen atoms have never been positively identified in the solid and the methods used for estimating their concentration are indirect and extremely doubtful. Thus, calorimetric methods (49) lead to oxygen atom contents of the order of 6%, and interpretations based upon the formation of ozone (33) have led to values in the order of 11%. The calorimetric method is questionable because of the possibility that the heat released came from sources other than atomic oxygen, and the high value of 11% obtained by inference from chemical reaction is probably of no value since infrared spectra have shown that no change in ozone content occurred during warming of the solid (50).

Wall *et al.* (43) found both methyl radicals and hydrogen atoms upon irradiating methane with gamma rays from cobalt-60 at 4°K. The total radical content of the solid was estimated, by electron spin resonance methods, to be of the order of 0.08%. Upon warming, the hydrogen atoms disappeared more quickly than the methyl.

From the above it is evident that the best data uniformly point to very low free radical contents. This is especially disappointing to those interested in the use of trapped radicals as jet fuels. It should not be surprising since it is necessary that the radicals be separated by a rigid matrix if they are to be prevented from recombining and since any recombination is probably sufficient to set off a chain reaction, resulting in the disappearance of essentially all of the radicals. Statistical



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studies have been made by Jackson and Montroll (51) and Golden (52) in an effort to ascertain the probability of laying down an array of radicals on sites that would be sufficiently isolated from other radicals to be stable. The results have shown a maximum of about 10-15% radicals in the solid. A more sophisticated treatment by Jackson (53), employing a model based on autoignition, has deduced a maximum nitrogen atom content of about 0.3%, in good agreement with the value obtained experimentally by Fontana (48). Thus, it seems doubtful at this time that there are any reasonable prospects of obtaining high concentrations of radicals in the near future.

The effect of matrix material upon the stabilization of radicals has not been established although there have been small advances made in this field. In general, the higher the melting point, or the higher the energy of vaporization of the matrix material, the more effective is the matrix in stabilizing radicals. This was indicated above in the effect of hydrogen, nitrogen, and methane on the hyperfine splitting of nitrogen atoms (17, 18). It has also been observed by Pimentel and his colleagues (54, 55) who found that stabilization increases in the order nitrogen, argon, krypton, and xenon as would be expected from their melting points and heats of vaporization. However, there are essentially no data on the stabilization of radicals in strongly-bound matrices such as might be expected of water. An exception has been noted in the studies of irradiation of ice and aqueous solutions of acids at 77°K, where small concentrations of hydrogen atoms were trapped. It is interesting that in Wall's studies of irradiation of methane, the hydrogen atoms disappeared at temperatures far below 77°K. Glasses have been used in several studies and have been found to be effective in trapping radicals, but no systematic study of their effectiveness has been made. It is evident that much work still needs to be done to define the effect and mode of action of the matrix in trapping radicals.

Recovery of trapped radicals. Very little has been done to develop methods of recovering radicals from a matrix. In fact, the author knows of only one brief paper on this subject. Broida and Peyron (56) collected the glowing nitrogen solid at 20°K then let the solid warm slightly and distill to an adjacent surface at about 1.2°K. The redistilled solid, collected at the lower temperature, showed the characteristic spectral lines of the ²D-

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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