

A New Way to Separate Isotopes

Minute magnetic moment of many isotopes of odd atomic weight can influence the course of free radical reactions

The separation of a specific isotope from the mixture normally present in nature is generally an expensive process that requires large amounts of energy. Separations based on the small difference in mass between two isotopes of the same element require massive installations to perform diffusion or centrifugation. Newer techniques rely on slight differences in the frequencies of light absorbed by different isotopes to achieve a selective excitation or ionization of a specific isotope so that it can be collected on the basis of its changed physical or chemical properties. This approach has not been proved in a commercial application.

An unusual new way to separate isotopes has been developed by Nicholas J. Turro and his colleagues at Columbia University. This process makes use of the fact that most isotopes with an odd atomic weight—including carbon-13, oxygen-17, and uranium-235—have a slight magnetic moment, whereas most common isotopes have none. Most investigators had previously thought that this magnetic moment is too small to provide any useful advantage, but Turro has found that it can interact strongly with the odd electron of the free radical species in which it resides to influence the course of a reaction. This interaction can be used to provide substantial increases in the concentration of the desired isotope.

Turro's first experiments were conducted with dibenzyl ketone (DBK) containing the normal abundance of carbon-13, about 1 percent. DBK is relatively insoluble in water, but dissolves readily in micelles formed in aqueous solutions of such detergents as hexadecylammonium chloride. When DBK is partially photolyzed or broken apart by light in such micelles, Turro found, the isotopic composition of the remaining DBK is different from that remaining when the reaction is conducted in an organic solvent.

When DBK undergoes photolysis, it breaks apart into a pair of free radicals that, together, are in the triplet state—that is, the spins of the two odd electrons are parallel. Because the radical pair is in the triplet state, the two radicals do not readily recombine to re-form the parent compound. If the photolysis is carried

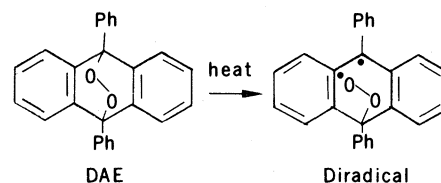
out in benzene, for example, the two radicals diffuse away from one another until the radical containing the carbonyl moiety splits out carbon monoxide. In this process, the triplet radical pair is converted into a singlet radical pair, which can eventually recombine to form diphenylethane.

If the carbonyl carbon happens to be carbon-13, its magnetic moment interacts with the odd electron of the radical and increases its natural tendency to change from a triplet to a singlet state; this process is known as hyperfine coupling and is relatively slow compared to diffusion of the two radicals apart. Even in benzene, though, a small proportion of the radicals containing carbon-13 will recombine and, if only part of the solution is photolyzed, the remaining DBK will be very slightly enriched in carbon-13. If the DBK is photolyzed in the micelle, however, the two radicals cannot separate by diffusion nearly as rapidly: In the 1 out of 100 molecules in which the carbonyl carbon is a carbon-13, the conversion of the radical from the triplet to the singlet state will have time to occur before the radicals diffuse apart; and the parent DBK molecule will re-form. The radicals that have a carbon-12 carbonyl will undergo the conversion to singlet much less frequently and will eventually diffuse into the aqueous phase, where they can be trapped by a scavenger such as copper chloride. The net effect is that DBK molecules containing a carbon-12 carbonyl are destroyed while those containing a carbon-13 carbonyl remain intact. The amount of enrichment depends on the length of time the reaction is conducted and the extent of photolysis. In practice, Turro has obtained DBK in which 10 percent of the carbonyls are carbon-13, a 1000 percent enrichment; but he says that an enrichment of 5000 percent or more should be obtainable with a much longer reaction time.

That the enrichment is due to the magnetic influence of the carbon-13 can be demonstrated by carrying the reaction out in a strong magnetic field. Such a field impedes conversion of the triplet state to the singlet, and much less enrichment is observed.

Turro's system for obtaining oxygen-17 is somewhat simpler, but at present

not yet as efficient. He has been working with a series of anthracene endoperoxides, of which the most useful so far has been 9,10-diphenylanthracene endoperoxide (DAE) (see diagram). When DAE is heated, it decomposes, through a reaction involving a diradical, into 9,10-diphenylanthracene and a mixture of about 30 percent singlet oxygen and 70 percent triplet oxygen. In this case, the magnetic moment of an oxygen-17 atom in the diradical intermediate interacts with the odd electron of the radical to increase its tendency to become a triplet radical.



To take advantage of this situation, Turro adds to the reaction mixture a chemical, such as tetramethylethylene, that is an efficient singlet oxygen trap. It removes from the system all the singlet oxygen, which now contains only oxygen-16 and oxygen-18 atoms, leaving behind free oxygen that is enriched in oxygen-17. The enrichment is small but it is important, Turro says, because there is presently no other way to obtain oxygen-17 enrichment selectively. He is searching for endoperoxides that are decomposed exclusively through a free radical reaction that produces singlet oxygen. If such a compound can be found, then a much greater enrichment of oxygen-17 could be obtained.

The same principle can be applied to any other magnetic isotope, including, presumably, uranium-235, if an appropriate chemical reaction can be found. Isotopes produced in this fashion could be much cheaper than those now available, since little energy is required for the separations and the chemicals used are relatively inexpensive. And, as is the case with oxygen-17, the new method may open the way to obtaining isotopes that have not been available previously. All it will take is a little ingenuity in designing reactions systems.

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