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# HIGH ENERGY REACTIONS OF CARBON

Richard M. Lemmon and Wallace R. Erwin

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# HIGH ENERGY REACTIONS OF CARBON

Much of the universe's carbon chemistry takes place at high energies. Since carbon is a key element in living processes, its high energy reactions are of broad interest as they may have been involved in the emergence of life.

by Richard M. Lemmon and Wallace R. Erwin

Of all the elements, none is more important to life than carbon. Aside from water, living cells are almost entirely an assemblage of carbon compounds. For generations chemists have studied these compounds, and have called their studies "organic chemistry" because the chemistry of carbon is so associated with that of life. Life's chemical processes take place at very modest temperatures, which is another way of saying that they take place at very modest energies. Even in laboratory studies of carbon compounds, the chemist rarely employs temperatures above 300° centigrade. However, during the past few years there has developed considerable interest in carbon reactions at much higher energies, for it is now apparent that the carbon chemistry of our universe is almost entirely high-energy chemistry.

The radio astronomers have shown that carbon compounds, formed in high-energy reactions, are present in vast quantities in interstellar space. The "solar wind", the energetic atoms streaming from the sun's corona, are constantly bombarding the Earth with high-energy carbon, and we know that these atoms have played an important role in determining

the properties of the moon's surface [see "The Carbon Chemistry of the Moon," by Geoffrey Eglinton, James R. Maxwell, and Colin T. Pillinger; SCIENTIFIC AMERICAN, October 1972]. The recent Apollo missions have given us a good estimate of the density of solar-wind carbon atoms that strike the moon: approximately 100,000 per square centimeter per second. The corresponding number reaching the Earth would be much lower because of the shielding effect of the Earth's magnetic field. However, if even one-tenth the lunar density reached our atmosphere, our planet would receive over 30 tons of solar-wind carbon per year. Multiplied by the age of the Earth (4.5 billion years), the total weight of solar-wind carbon that has reached our planet is a very large amount, and may be roughly equivalent to the total carbon in all living cells on the contemporary Earth. In part, therefore, studies of carbon reactions at high energies are attempts to add to our understanding of the processes that may have been important for the emergence of life itself.

Whether or not high-energy carbon reactions were necessary for the emergence of life, it is clear why our biology and, very likely, any other that may exist in the universe, is based on carbon. This element is unique in its ability to form an almost unlimited number of compounds. This uniqueness results from its special position in the Periodic Table (see illustration 1). It is the smallest atom of those in Group IV, the group of elements halfway between the "electropositive" elements (those that give up electrons to form chemical bonds) and the "electronegative" elements (those that take up electrons in the process of bond formation). Carbon has an equal tendency to gain or lose its four outer, or bond-forming, electrons, and can form stable compounds by sharing these

| | "Electropositive" elements | | | | "Electronegative" elements | | | |
|---|---|---|---|---|---|---|---|---|
| 0 | I | II | III | IV | V | VI | VII | 0 |
| | H 1 | | | | | | | He 2 |
| He 2 | Li 3 | Be 4 | B 5 | C 6 | N 7 | O 8 | F 9 | Ne 10 |
| Ne 10 | Na 11 | Mg 12 | Al 13 | Si 14 | P 15 | S 16 | Cl 17 | A 18 |

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Illustration 1.

FIRST TWO ROWS of the Periodic Table. The Roman numerals designate groups of elements with similar chemical properties. The Arabic numerals designate both the atomic number of the element and the number of electrons circulating about the atom's nucleus. Carbon is the smallest atom of those in the "central" Group IV. (In order to emphasize carbon's central position, the Group 0, or "noble gas", elements are placed at both sides of the table.)

electrons with either of these major groups of elements. Thus, it forms stable compounds with fluorine and chlorine (electronegative) and with lithium and sodium (electropositive).

As the smallest atom of the Periodic Table's Group IV, carbon is also first among those particular elements in the strengths of its bonds. In general, the closer the electron cloud around one atom can approach the positively-charged nucleus of another, the stronger are the bonds that are formed. Thus, the combination of two properties--small size and electrical "halfway-ness"--have conferred unique bond-forming abilities on carbon. One result is that carbon not only forms strong, electron-sharing bonds with many elements, but also with itself. Carbon atoms can form chains thousands of atoms long; these chains can be joined at the ends to form rings of almost any size. The chains and rings can have carbon-atom branches on them, and carbon-atom links between them, with scarcely any restriction on the number of carbon atoms in the chains, rings, branches, and links. Add to this the ease with which the carbons can include other atoms into these numerous shapes and forms (such as the life-important hydrogen, oxygen, nitrogen, phosphorus, and sulfur atoms) and one can see the virtually limitless possibilities for carbon compounds. Thus, living systems gained their marvelous complexity from the enormous number of carbon compounds available for their construction, and it is difficult for the modern chemist to envisage life based on any element but carbon. As life has evolved, it has constantly experimented in the production of new carbon compounds. Although over a million carbon compounds, both natural and synthetic, are known, billions are possible, and our universe probably contains billions.

For over a century chemists have been synthesizing new carbon compounds that, to our limited knowledge, do not exist in nature (at least not on our own planet). These efforts have had such success that we now have available hundreds of thousands of new carbon compounds. Many of these synthetic compounds, although not without troublesome side effects, have brought great comfort and convenience to humankind. Obvious examples are medicines, plastics, and pesticides.

Although a single, isolated carbon atom is very reactive, a mass of carbon atoms, such as lamp black, is not particularly reactive because they are already combined with each other. The principal means that chemists use to induce chemical reactivity is to apply heat, and thus we have the mental image of the alchemist as a fellow in a sooty cell applying a fire to his retort. To this day, the chemist, in his far more comfortable and sophisticated laboratory, usually promotes a reaction by the application of heat. He does this because he knows that the higher the temperature, the faster a molecule will move, and the faster its atoms will vibrate. If the temperature is high enough, the molecule will move fast enough so that, when it strikes another molecule, the excess kinetic energy will promote reaction between the two molecules. Or, the high temperature may cause a molecule to vibrate so fast that its atoms may fly apart, giving the released, individual atoms the chance to enter into new combinations (that is, new compounds). At room temperature, lamp black is inert. But if one heats it hot enough one jostles the carbon atoms apart; in that state they readily combine with the oxygen in air to become carbon dioxide, $CO_2$.

Another form of energy that the chemist uses to promote reactions

is light, and it has been known for a long time that sunlight promotes reactions such as bleaching or tanning, although little or no warming may be involved. We now know that light consists of packets of energy ("quanta") and that the absorption of this energy by a molecule may be even more effective than heat in putting the molecule in a more reactive, energy-rich state. The application of heat to a molecule causes the weakest bonds to break first. In contrast, the absorption of light quanta may cause the breakage of a molecule's stronger bonds because the light may have been selectively absorbed by those bonds.

In the last two decades chemists have been promoting reactions of carbon (and of other elements) at energies much higher than those achievable by heat or light, that is, at energies that are more closely related to cosmic-ray and solar wind energies. One way they have done this is to take advantage of the very high velocity, or energy, in an atom that is created in a nuclear reaction. A typical example in nature is the process that takes place when a radioactive atom of carbon, $^{14}C$, is born in the Earth's upper atmosphere. A result of this particular nuclear reaction is that a small component of radioactive carbon is put into all living things (whether for their overall betterment or detriment we are not sure). This radioactivity is the basis for the widely used radiocarbon dating method. After a living entity dies it no longer absorbs this radioactive carbon by the eating of food (animals) or the absorption of $CO_2$ (plants), and the radioactivity slowly fades away. The residual radioactivity gives the time elapsed since the death of the organism.

The radioactive $^{14}C$ is formed when neutrons, which are components

of the cosmic rays that constantly strike the Earth, react with atmospheric nitrogen. When a neutron enters the nucleus of a nitrogen atom, $^{14}N$, the resulting transient complex is unstable. It ejects a proton, which is a charged hydrogen atom, and a charged $^{14}C$ atom. A simplified representation of the process is shown in the illustration . . . . When the complex ejects the proton in one direction, the $^{14}C$ recoils in the opposite direction--in accord with Newton's 3rd Law ("action and reaction"). The $^{14}C$ recoils with an energy of 45,000 electron volts, the energy that any singly-charged species (such as the proton, $H^+$) would acquire if it moved from an electrode at ground potential to an electrode that had a 45,000-volt negative charge. The energy of an ordinary ("covalent") carbon-carbon bond is about 2-1/2 electron volts. Consequently, a 45,000-volt atom is capable of breaking 45,000/2.5 = 18,000 carbon bonds before all of its velocity is lost.

The enormous energy of the same recoiling-carbon process has been used many times in the laboratory to study the reactions of energetic carbon. In this case, the high energy end of a reaction scale is being examined. In simple heating, the molecule's bonds slowly acquire energy until some minimum, reaction-promoting, energy is absorbed. In the recoil case, the energetic atom is slowed down, or "cooled", to the point where it can react with a molecule without merely tearing it apart. Recoil reactions therefore have the possibility of causing reaction of the strongest bonds of a struck molecule; no bond is immune. Consequently, these reactions give us possilities of preparing compounds that could not arise from the application of heat or light.

The general technique for recoil studies is simple. If one wants to know how recoiling carbon reacts with a given compound, one puts that

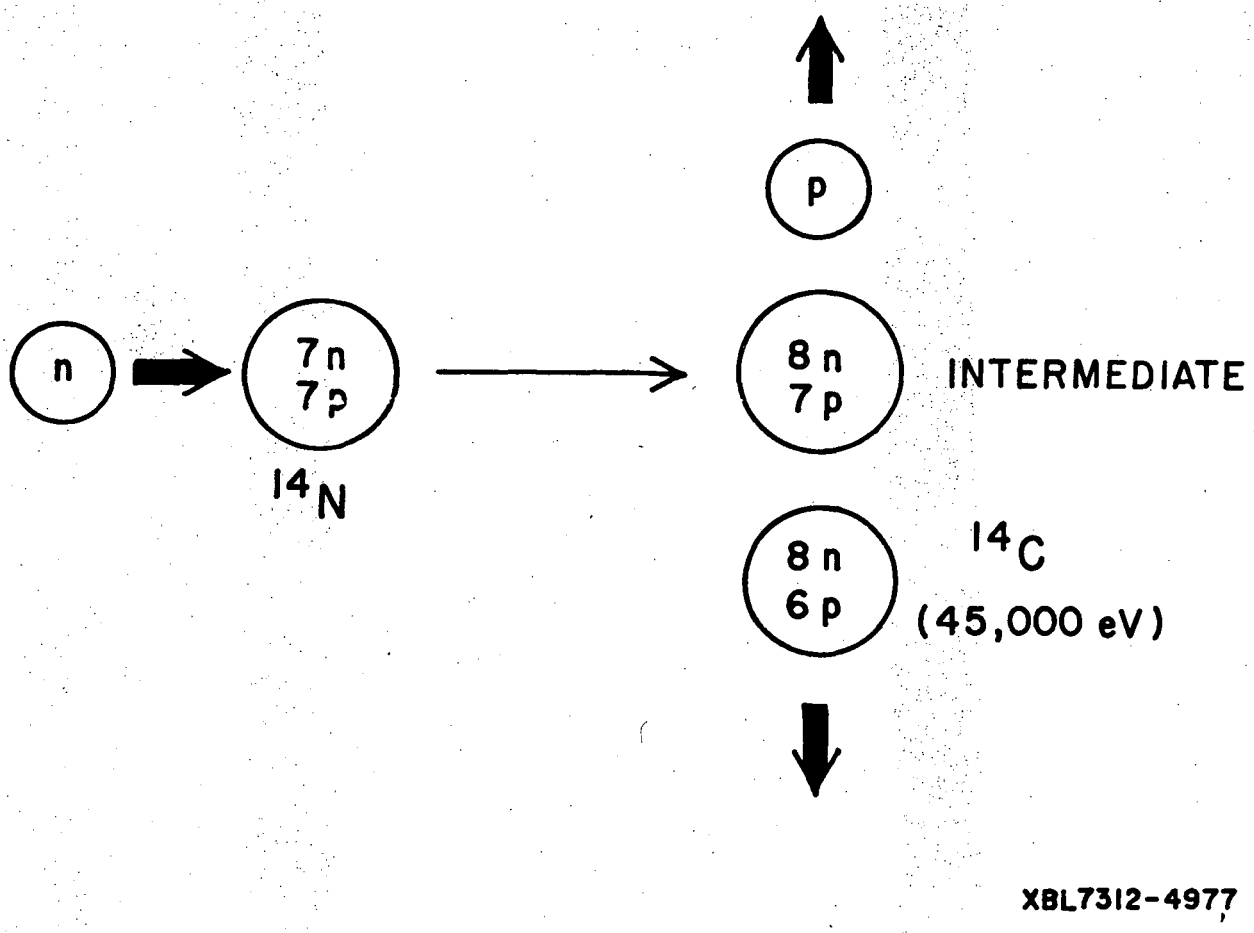



Illustration 2.

THE FORMATION OF RADIOACTIVE CARBON, $^{14}C$, takes place in the Earth's upper atmosphere, and in the laboratory, by this nuclear reaction. A cosmic ray (or nuclear reactor) neutron, n, enters the nucleus of an ordinary nitrogen atom, $^{14}N$, which contains 7 neutrons and 7 protons, p. The resultant transient intermediate nucleus, consisting of 8 neutrons and 7 protons, quickly disintegrates by ejecting, at high velocities, a proton in one direction and a radioactive carbon atom, $^{14}C$, in the opposite direction. Ultimately (with an average lifetime of about 5700 years) the $^{14}C$ disintegrates into an electron and $^{14}N$.

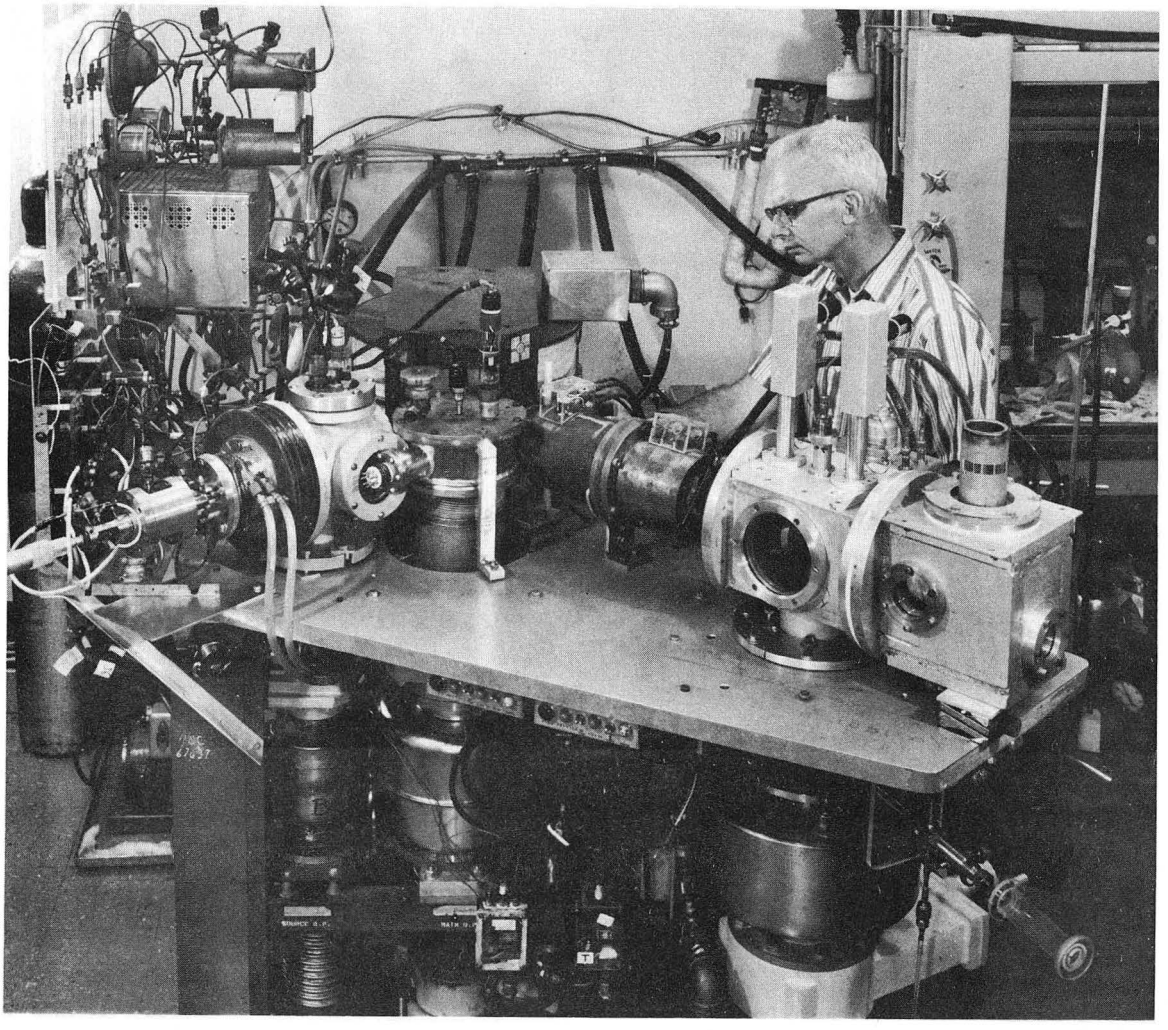
compound in a nuclear reactor, in an intimate mixture with any nitrogen-containing compound. The reactor-supplied neutrons react with the nitrogen atoms, and the resultant $^{14}C$ recoils through the mass of the compound under study until it finally slows down to a sufficiently low velocity or energy where it can form new chemical bonds. That energy, at most only a few tens of electron volts (eV), is low compared to its initial energy, 45,000 eV; however, it is very high in comparison with chemical bond energies, and with the maximum energies that chemists can give to organic compounds by the application of heat (less than 0.1 eV per atom). Since the recoiling carbon atoms are radioactive, the products into which they are formed are also radioactive. This is helpful to the chemist, both for finding the new products, and also for finding the exact position in a new product molecule where the $^{14}C$ has been localized. (In the carbon beam studies outlined below, $^{14}C$ is also used for these helpful "tracer" qualities.) Other carbon nuclear reactions have also been used as a source of high energy carbon atoms. Studies of the reactions of such high energy atoms, carbon as well as other elements, form what is known as "hot atom" chemistry.

Another way of imparting high energies to atoms is to use some kind of an accelerator, such as a cyclotron. The physicist has used this technique for several decades to accelerate nuclear particles and ions (charged atoms or molecules) to energies where nuclear reactions can take place. These energies are in the millions or billions of electron volts. More recently, chemists have been constructing accelerating devices that enable them to study the reactions of atoms at more modest energies where chemical interactions (new compound-forming processes) may take place

[see "Chemical Accelerators," by Richard Wolfgang; SCIENTIFIC AMERICAN, October 1968]. Such devices enable the experimenter to choose the energy, down to a few electron volts, with which an energetic atom will strike a target. The random destruction of the target molecules, during the slowing down ("cooling") of a recoiling atom, may thus be avoided. One such device is in use in our laboratory, and we shall describe our research with it as an illustration of the information that can be obtained from energetic carbon reactions. For the progress of this work we are indebted to many former collaborators and to our current co-worker, Mr. Glenn A. Fisher.

We form a beam of $^{14}C^{+}$ ions in the device pictured and illustrated ③ & ④ . . . . Either $^{14}C$-containing carbon dioxide ($^{14}CO_2$) or methane ($^{14}CH_4$) is admitted into the ion source. Here, between the anode and cathode, an "arc plasma", a cloud of charged molecules (ions), is formed. The ions are expelled out of the area of their formation by an electric field of 5,000 volts. To control an ion beam, one uses electrostatic "lenses"--metal plates of various forms onto which electric charges are placed. These lenses shape, magnify, and demagnify an ion beam in ways quite analogous to the effects of optical lenses on beams of light. Thus, extraction, focusing, refocusing, and deceleration lenses are shown in the accompanying figure.

The beam that emerges from the ion source has many different kinds of carbon- and oxygen-containing ions. These are separated from one another as they travel through the magnetic field. Heavier ions, such as $CO_2^{+}$, are bent less during passage through the field than are lighter ions such as $^{14}C^{+}$. By setting the strength of the magnetic field at the



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THE CARBON-ION ACCELERATOR in use in the authors' laboratory at the University of California, Berkeley. The ion source is in the left center of the photograph; the deceleration lenses and target section are at the right (see accompanying diagram).

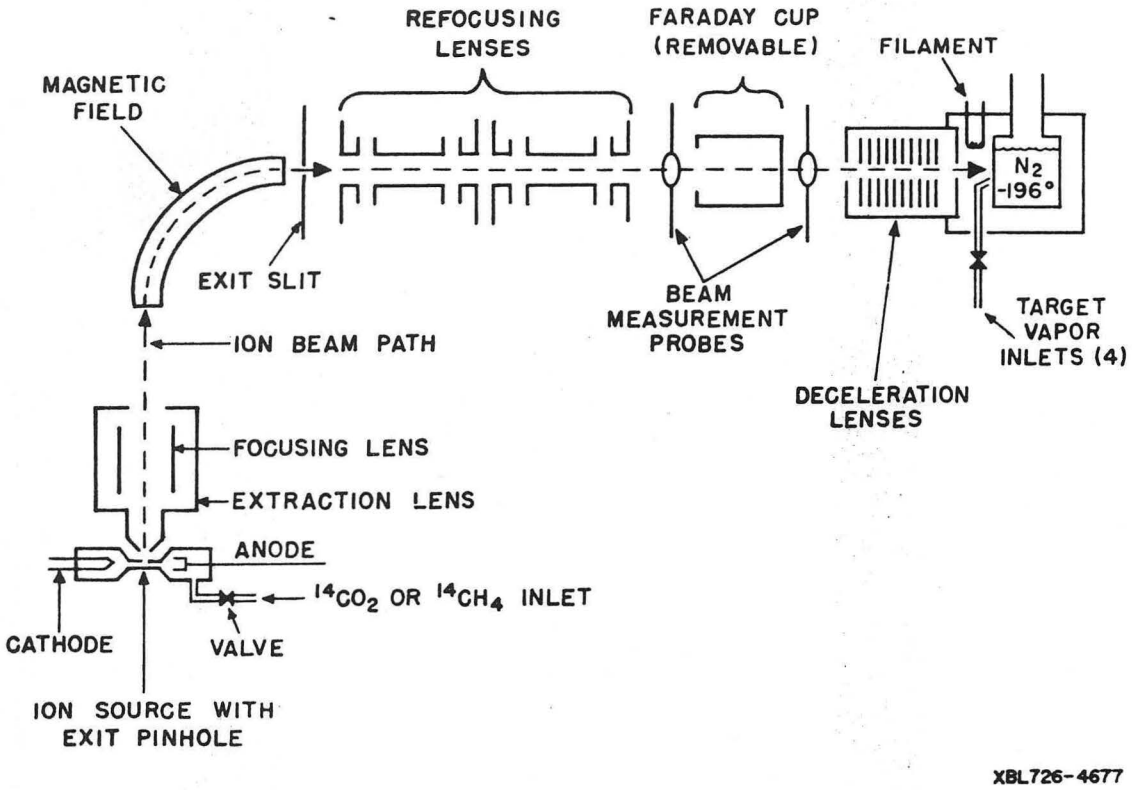
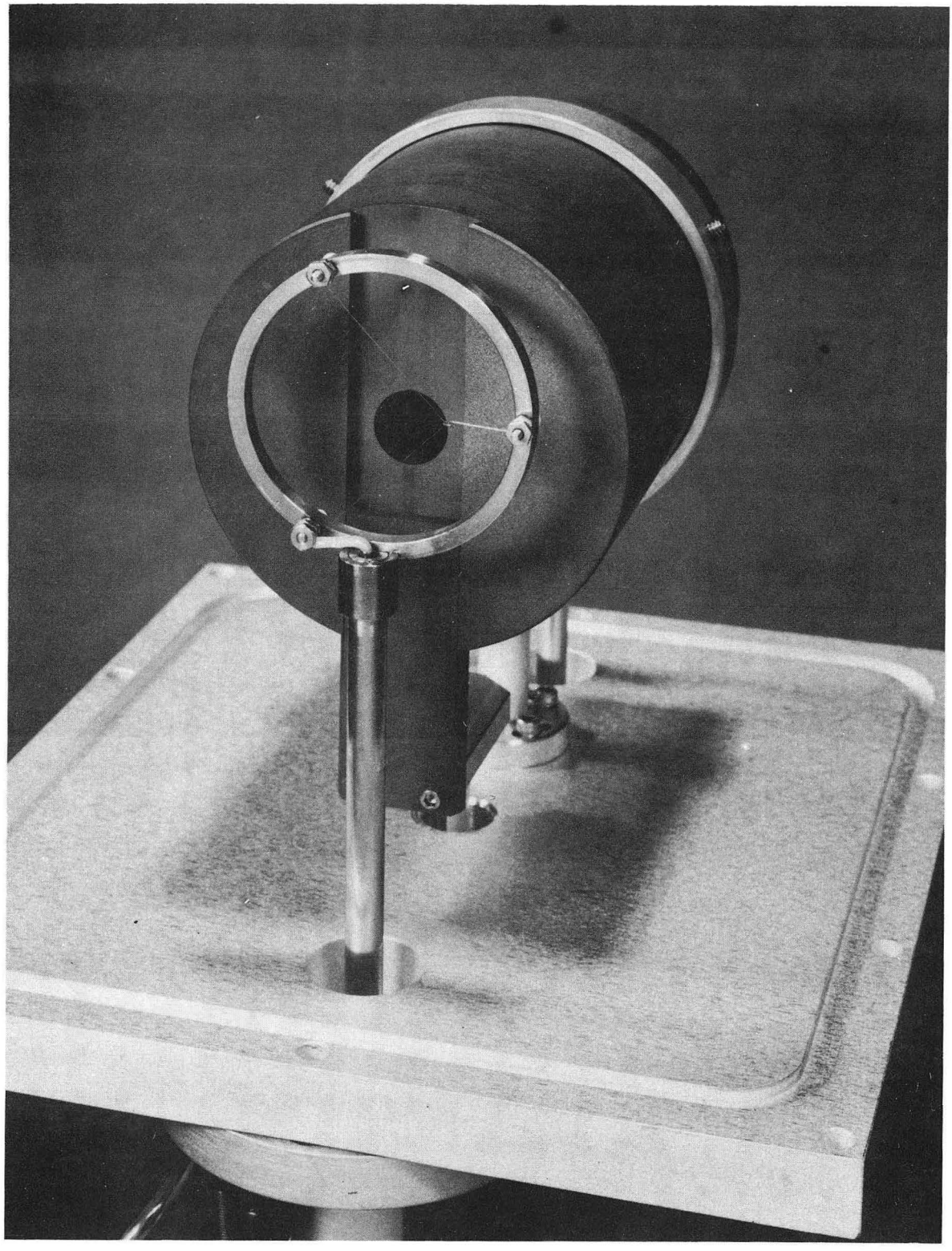



Illustration 4.

DETAILS OF AUTHORS' CARBON-ION ACCELERATOR. $^{14}C$ ions, from $^{14}C$-containing carbon dioxide or methane, are formed between the cathode and anode at the lower left. They are accelerated by an electric field, separated from other ions by the magnet at the upper left, and pass through ion-beam controlling and measuring devices to the target section at the right. Here the energetic carbons impinge on a solid target, formed at liquid nitrogen temperature (-196° centigrade) by condensing vapors of the target molecules on a surface maintained at that temperature.

right value, only the $^{14}C^{+}$ ions emerge from the magnet, and it is with these ions that we have done most of our studies. The intensity of the $^{14}C^{+}$ is measured by the device labeled "Faraday cup", and is usually about 1 microampere, or one-millionth of an ampere. (An ampere is approximately the current that passes through a 100-watt electric light bulb.) Although a microampere doesn't sound like much of a current, it is about $6 \times 10^{12}$, or 6 million million, ions per second. Then, the beam passes through a series of decelerating lenses, doughnut-shaped plates onto which suitable positive, that is, $^{14}C^{+}$ ion-decelerating, voltages are applied. These lenses enable us to set the energy with which the ions strike our target at anything from their initial 5,000 eV down to about 2 eV.

To determine the electric potentials that we need to apply to the lenses in order to achieve the best shape and position of the beam, we use the measurement probes shown in the photograph . . . 5 . and illustrated . . . 6 . Each of these probes consists of a $\succ$ shaped wire that moves up and down so that one arm at a time intercepts the beam. When such an interception is made, a current is induced in the probe and is recorded. In the ideal case of a beam whose cross section is circular, we get a tracing like the full line at the bottom of the illustration. Thus, if the probe is being moved upwards, at position 1 neither arm has yet reached the beam and no current is measured. At position 2, as the upper arm passes through the beam the current reaches a maximum--just as it does at position 4 when the lower arm passes through. Positions 3 and 5 would also give zero current measurements. However, if the beam was not circular in cross section, but was ellipsoidal as indicated by the



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BRANCHED WIRE PROBE that gives a cross-section profile of the $^{14}C$ beam. The probe may be moved up and down, giving the relative intensities as one or the other arm of the probe passes through the beam (see accompanying illustration). The object behind the probe is the Faraday cup, which the beam enters through the round opening.

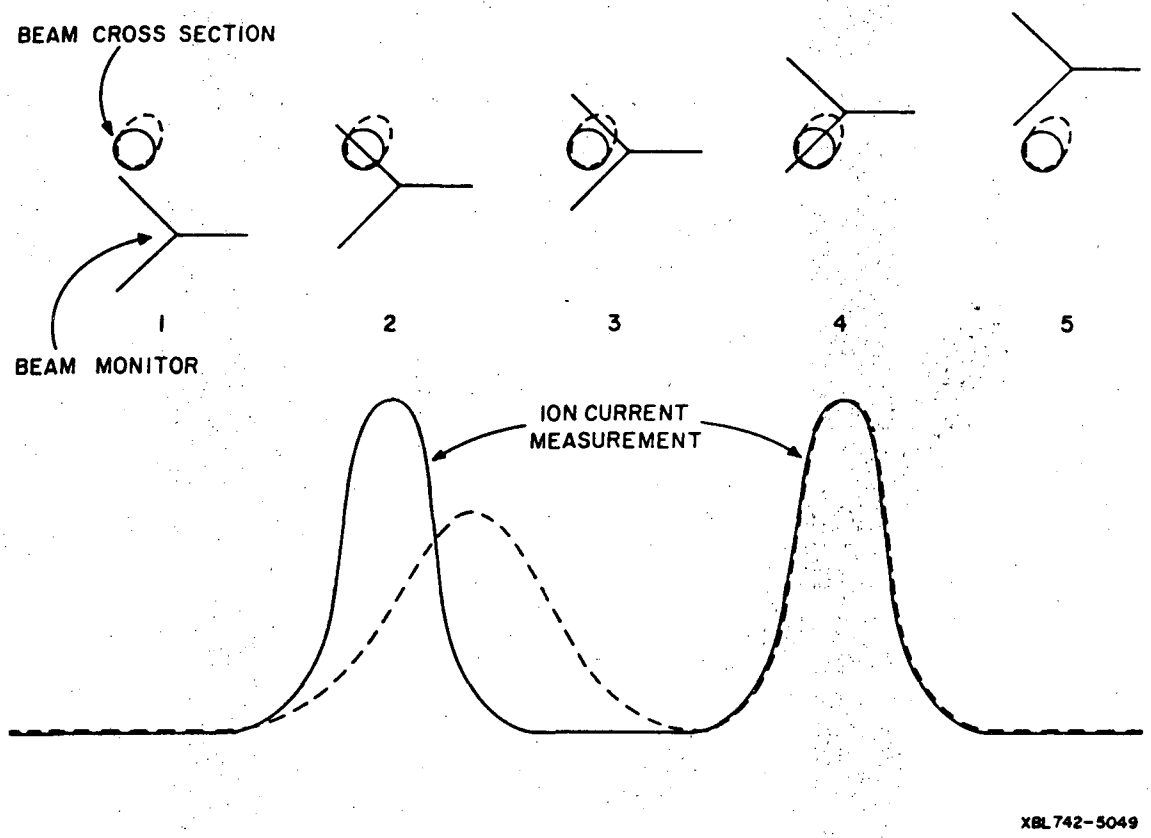



Illustration 6.

CROSS-SECTION OF THE $^{14}C$ BEAM is measured by the current induced in a Y shaped wire probe that may be raised or lowered through the beam (flowing perpendicular to the plane of the page). The ion current measurements for a circular cross-section beam are shown by the full line (below) for corresponding positions of the probe. Ion current measurements for an ellipsoidal cross-section beam (dotted line) are shown by the dotted line for the ion current measurements.

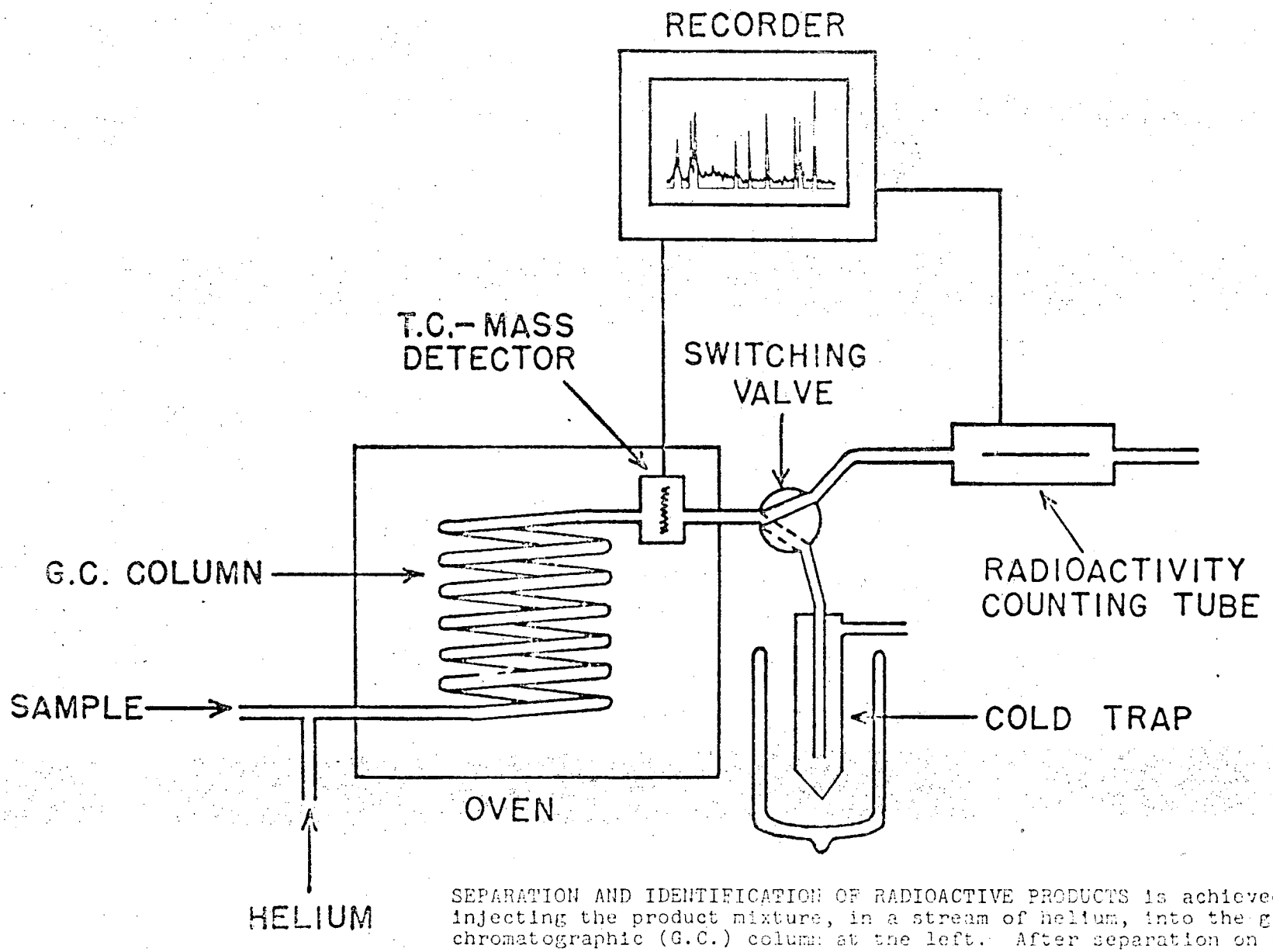
dashed lines, the resulting current would be different through positions 2 and 3 as shown by the corresponding dashed line below. In this way we know our beam's profile and position, and we can optimize these by suitable alterations of the voltages on our lenses through which the beam passes.

Our ion accelerator is operated under high vacuum. Without such a vacuum, the $^{14}C^{+}$ ions would strike, and be scattered by, gas molecules in their path. To keep the pressure in the accelerator low, the molecules of any material we are subjecting to the $^{14}C^{+}$ beam must be kept at a very low temperature. One convenient way to do this is to steadily "bleed in" a vapor of the target material, and to freeze the material on a surface maintained at liquid nitrogen temperature (-196°C.). This procedure has the added advantage of presenting a constantly fresh supply of target molecules to the incoming $^{14}C^{+}$ ions. A new product, once formed, is not likely to react with additional carbon ions; it is quickly "buried" under the incoming vapor that is steadily being transformed into a solid at the -196°C. surface.

The steady impinging of our positively-charged $^{14}C^{+}$ ions on the target surface could lead to a build-up of a positive charge, and thus to the repelling of additional incoming carbon ions. We avoid this undesirable situation by placing a small, hot tungsten filament, which carries an electrical current, near our target area. The filament provides electrons (that is, negative charges) at a rate sufficient to balance the $^{14}C^{+}$ positive charges and keep the surface electrically neutral.

We learn what has happened to our energetic $^{14}C^{+}$ ions by determining what kinds of radioactive (that is, $^{14}C$-containing) products are formed.

To do this, we separate and identify our products by the simple and powerful technique of gas chromatography [see "Gas Chromatography," by Roy A. Keller; SCIENTIFIC AMERICAN, October 1961], combined with a radioactivity detector. The essentials of our system are shown in the illustration . . . 7 Our radioactive products are introduced, usually as a solution in benzene, into the G.C. (for "gas chromatography") column shown at the left. This is a metal tube of about 1/4 inch in diameter and several feet in length. It is filled with an inert solid that is coated with an oily liquid. The column is heated to some temperature that experience has shown to give the best separations. Samples are carried through the column by a stream of helium gas and, depending upon their affinity for, or solubility in, the oily liquid, individual compounds move through the column at varying rates. As individual compounds emerge from the column, their presence is recorded by a T.C. ("thermal conductivity") detector. This device records the difference in heat loss between a filament bathed in pure helium, and another filament which is exposed to the helium stream emerging from the column. Helium is a better conductor of heat than is any gaseous organic compound; consequently, the presence of any quantity, or mass, of such compound in the helium stream reduces the rate of heat loss from the filament. The hotter filament is a poorer conductor of electricity, and this greater resistance is converted to an electrical signal that is displayed as the black line on the advancing paper strip of the recorder shown at the top of the illustration. The helium stream may then be led into the radioactivity counting tube, shown at the left. Any radioactivity is also recorded, by a separate pen, as the red line shown in the illustration.



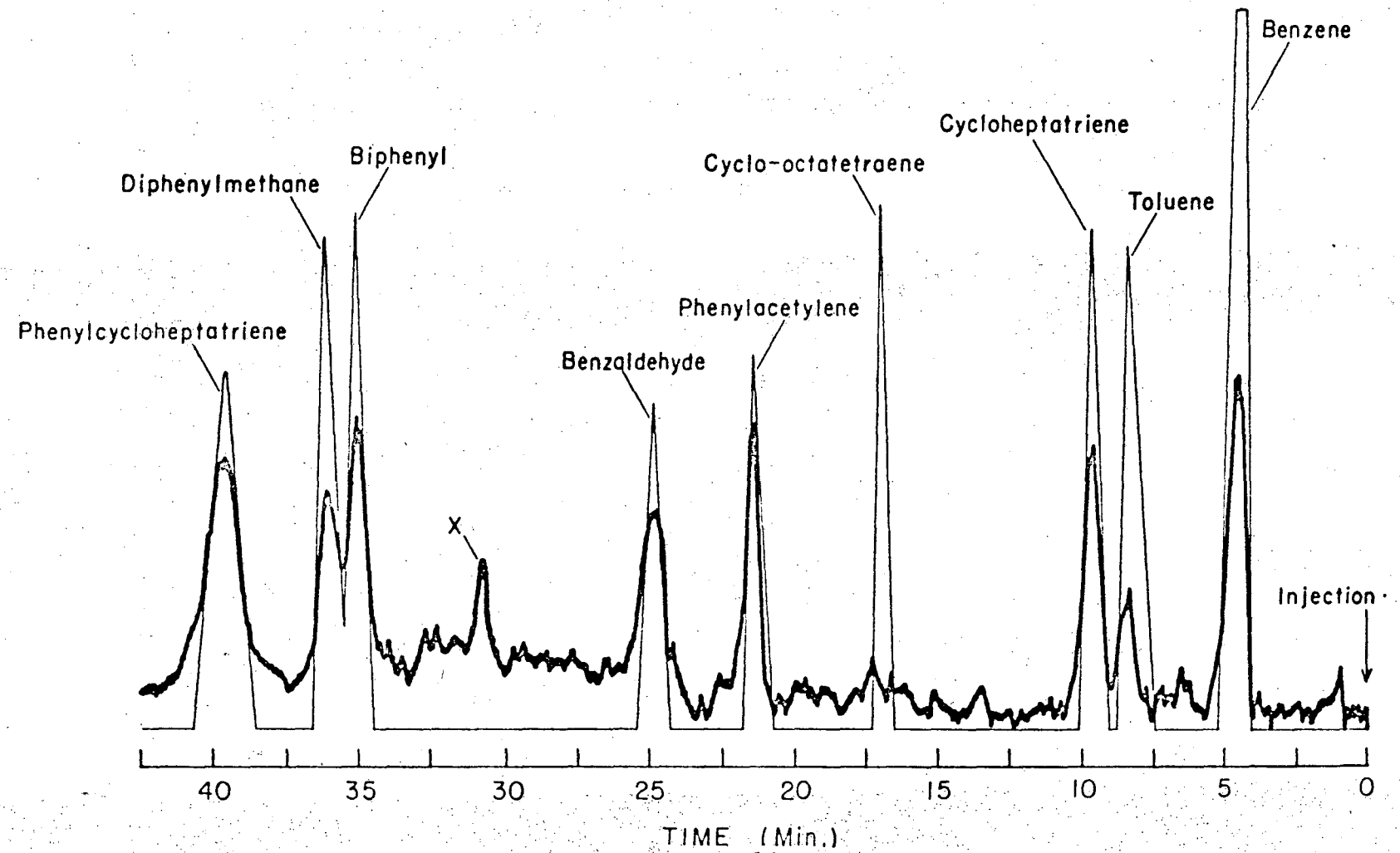

SEPARATION AND IDENTIFICATION OF RADIOACTIVE PRODUCTS is achieved by injecting the product mixture, in a stream of helium, into the gas chromatographic (G.C.) column at the left. After separation on the column, the total amounts of emerging products, and their total radioactivity, are detected and recorded. The products may also be retained in a cold trap for further investigations.

Illustration 7.

From chemical knowledge or intuition we may believe that a certain compound will be formed when carbon ions strike a particular target. To determine if this is so, we need but add a known sample of the suspected compound to the target at the conclusion of a $^{14}C$-ion irradiation. The added sample would not be radioactive but would give a mass (T.C.) detection, and would appear as a peak in the black line. However, if the same compound had been formed in the target during the irradiation, it would contain $^{14}C$ and would be radioactive. Not enough mass of the product would have been formed for it to give a peak in the mass detection (black line) but it would give a peak in the red line. Consequently, if we get a coincidence of a red peak with the black peak of a known added compound, we have provisionally identified the radioactive product--that is, shown it to be identical with the added compound. This procedure becomes very reliable if the coincidence of red and black peaks is repeated on other columns that are packed with other kinds of oily liquids.

Finally, by means of the switching valve we may direct the gas stream from the G.C. column into a cold trap--a glass tube constructed as shown, and immersed in liquid nitrogen or dry ice. The cold freezes and traps the organic compounds, but allows the helium to flow on out as a gas. The frozen compounds may then be recovered and subjected to chemical tests and/or further gas chromatography. The chemical tests may be directed not only to the question of the identity of the product, but also to the location, within the product, of the $^{14}C$ that caused the product's formation.

A typical gas chromatographic tracing, from a $^{14}C$ irradiation of benzene (see below), is shown in the illustration . . . . The peaks on




GAS CHROMATOGRAPHIC DETECTION of products from $^{14}C^{+}$ irradiated benzene. The red line records the emergence from the chromatogram of radioactive, $^{14}C$-containing products. The black line is a record of the emergence of benzene and of added "carrier" compounds. Coincidence of the radioactive (red) peaks with the mass (black) peaks establishes the identity of the $^{14}C$-containing products. One major radioactive product (marked X), and many minor ones, are as yet unidentifed. The cyclo-octatetratriene peak (black peak) is accompanied by little, if any, radioactivity (no corresponding red peak); consequently we know that this particular compound is not formed to any detectable extent when benzene is irradiated with energetic carbons.

Illustration 8.

the black line are the detector's response to known carrier compounds as they emerged from the G.C. column. The chemical names of these carriers have been added to the corresponding peaks. When a radioactive (red) peak emerges from the column at precisely the same time as a known added compound, the identity of the radioactivity-containing product is established. As can be seen, we added cyclo-octatetraene, thinking it might be a product. However, it appears that little or none of this compound is formed in our irradiations. We have many minor radioactive products that are not yet identified; the most prominent of these is labeled "X".

Most of our $^{14}C$ beam research has concerned the organic chemist's favorite molecule, benzene. This relatively simple hydrocarbon, $C_6H_6$, is the parent molecule from which a huge number of both natural and synthetic compounds are formed. It has great theoretical and practical interest to organic chemists [see "The Nature of Aromatic Molecules," by Ronald Breslow; SCIENTIFIC AMERICAN, August 1972]. What would an energetic carbon do when it struck this very important molecule?

The first thing we discovered was that an accelerated $^{14}C$-ion reacted with the benzene to give us $^{14}C$-labeled benzene. The result was unexpected because, somehow, the $^{14}C$ had to remove one carbon atom from the benzene, while it itself had to remain behind and be incorporated into a new, $^{14}C$-containing benzene product. One might imagine the process as taking place somewhat as shown in the illustration . 9 . . . The benzene molecule is known to consist of a ring of six carbon atoms, to each of which is attached a hydrogen atom (omitted in the illustration). The carbons are attached to each other by what might be called "1-1/2 bonds"--a situation responsible for benzene's great theoretical interest, and one well described

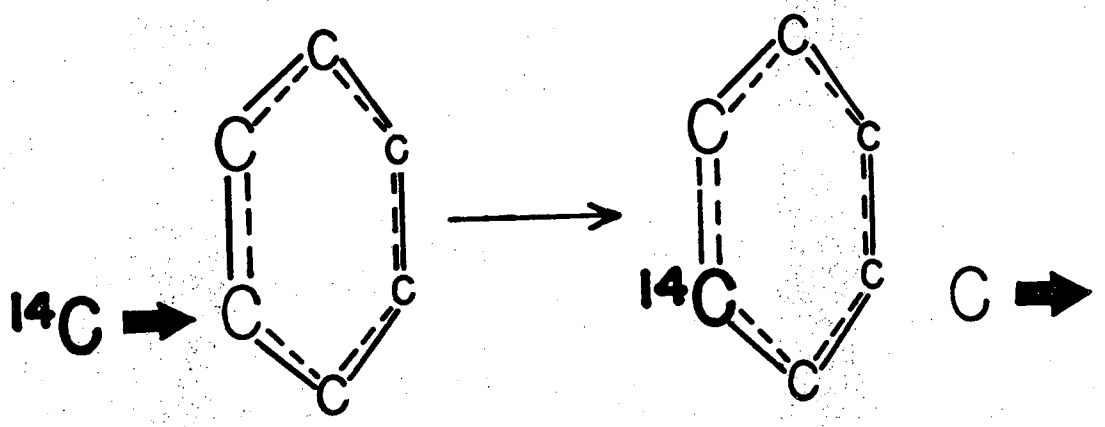



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Illustration 9.

ONE POSSIBLE MECHANISM for the replacement of a carbon atom of the benzene molecule by an energetic $^{14}C$ atom. The benzene molecule is a regular hexagon of six-carbon atoms (to each of which is attached one hydrogen atom--not shown here). If the incoming $^{14}C$ struck one of the benzene's carbons "squarely" it might replace it in a kind of "billiard ball" collision. Experimental and theoretical evidence argues against this simple mechanism.

in the Breslow article. The replacement of an ordinary atom of carbon ($^{12}C$) in the benzene ring by the incoming $^{14}C$ is the kind of situation that might exist if the carbon atoms were hard, impenetrable spheres, something like very tiny billard balls. If they were, the incoming $^{14}C$ might hit a $^{12}C$ "squarely", giving up all its forward momentum and energy to the struck $^{12}C$. The latter would thus be knocked away, leaving the $^{14}C$ behind to become part of a new ring of six carbon atoms--that is, a new, $^{14}C$-containing, benzene molecule. But, in our experiments, about one in thirty of the incoming $^{14}C$ atoms got incorporated into a new benzene molecule. The probability of such perfect (center-to-center), complete-momentum-transfer hits was far below one in thirty. Furthermore, from what we know about the collisions of atoms, they do not, in general, behave like little billiard balls. The complex forces of both repulsion and attraction that take effect as atoms approach each other make them behave in a much more "mushy" or "sticky" way, more like putty balls of varying degrees of hardness. If one throws a piece of putty at a ring of six putty balls stuck to each other, it's extremely unlikely that the thrown putty ball will replace one of the six and form a new six-membered ring.

Both statistics and atomic theory told us that our incoming carbons couldn't simply replace one of a benzene molecule's carbons by a billiard ball collision. So did our own data, which showed that the yield of $^{14}C$-containing benzene was independent of the energy with which the carbon struck the benzene. We found that about 3% of the incoming ions were incorporated into new benzene molecules, regardless of whether the carbons struck at a high (5,000 eV) or low (2 eV) energy, or any value in between. The carbon-carbon bond in benzene has an energy value ("strength") of 3.2 eV, and two carbon-carbon bonds must be broken to accomplish the replacement of

one of the benzene's carbon atoms by the incoming $^{14}C$. Therefore, the 2 eV irradiations could not give us labeled benzene by the billiard-ball mechanism. In addition, the other major products we found, and the distribution of $^{14}C$ atoms in these products (see illustration . . . 10 .) suggested that the labeled benzene came from an intermediate that contained 7 carbon atoms (the 6 of the benzene target, plus the incoming energetic carbon). Such an intermediate could be a "bridged" compound, for example, the one shown at the left of the illustration . . . 11 . The excess energy contained in the electrons of the accelerated carbon atom could be used to break the bonds between the carbon numbered 6 and those numbered 1 and 5. If carbon-6 was thus "broken out", we'd be left with a 6-carbon ring ($C_6H_5$) that could become a new, $^{14}C$-containing benzene product molecule. On the other hand, if only the bond between C-1 and the $^{14}C$, or that between C-5 and the $^{14}C$, was broken, we'd achieve the carbon configuration of a new, labeled toluene molecule. (The additional, needed, hydrogen atoms could be "grabbed" from nearby benzene molecules.)

Another of our products, the eight-carbon phenylacetylene (see illustration . . . 10 .) suggests that our labeled benzene might have been formed from the 8-carbon intermediate shown on the right of the illustration . . . 11 . In order for such an intermediate to be formed, the incoming, high-energy $^{14}C$ would have to break off one carbon atom from a benzene molecule, thus forming a two-carbon fragment that could go on and form a two-carbon bridge across another benzene molecule. We were able to rule out the 8-carbon intermediate idea in the following way: Instead of irradiating benzene with our $^{14}C$ beam, we irradiated toluene. This molecule, with a $CH_3$ group attached, for example, at carbon-6, could break out a $C\text{-}CH_3$ from either the one- and two-carbon bridged intermediate

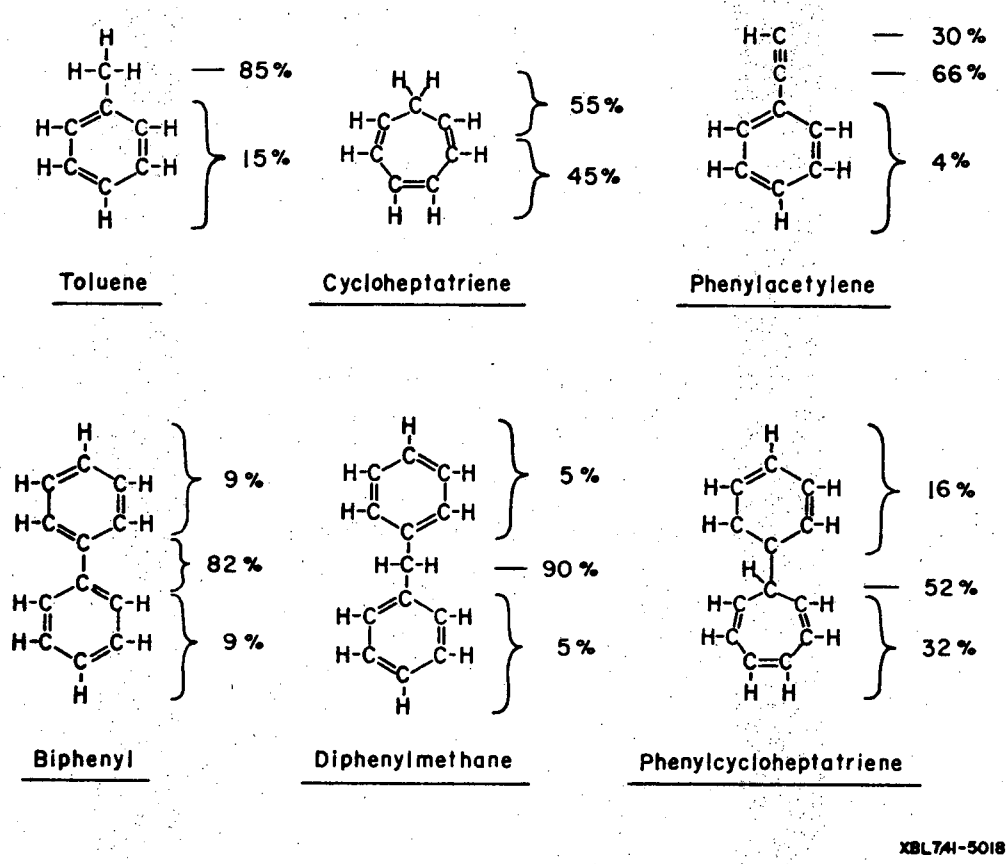
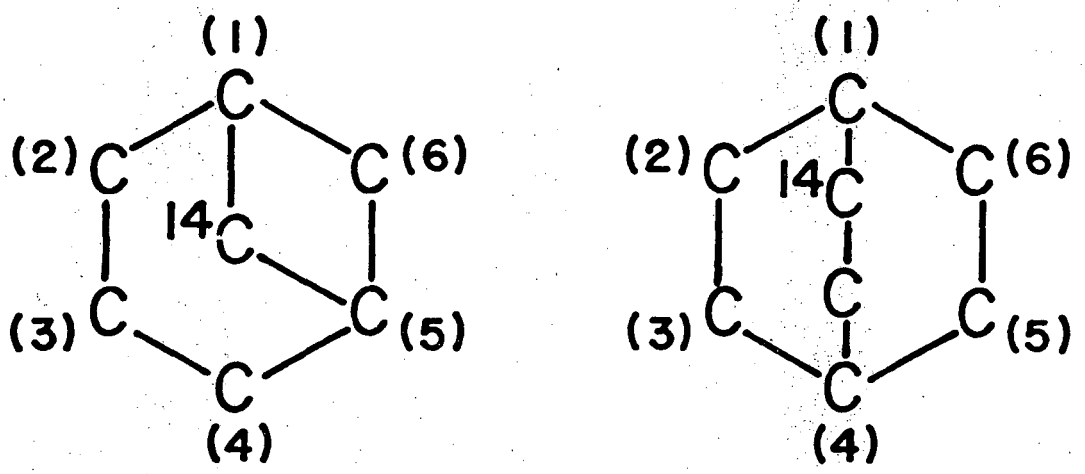



Illustration 10.

MAJOR PRODUCTS OF THE IRRADIATIONS OF BENZENE with energetic (5,000 eV) $^{14}C^{+}$ ions. The percentage figures show the frequency with which the $^{14}C$ appeared in certain positions of the product molecules. For example, for every 100 molecules of toluene formed, 85 had $^{14}C$ in the carbon of the $H\overset{H}{C}H$ (methyl) group. The other 15 had the $^{14}C$ in one of the positions of the six-carbon ring. For cycloheptatriene, 55 had a $^{14}C$ in one of the upper three carbons, 45 had the $^{14}C$ in one of the lower four carbons.




XBL 741-5020

Illustration 11.

POSSIBLE INTERMEDIATES on the route to $^{14}C$-containing benzene, and to other $^{14}C$-labeled products (hydrogen atoms attached to the carbons have been omitted, and individual carbon atoms have been designated by a number). The experimental evidence indicates that a 7-carbon intermediate, such as the one on the left, is involved on the route to the $^{14}C$-containing benzene, and that an 8-carbon intermediate (right) is not.

to give the labeled benzene product. Indeed, we found labeled benzene, in addition to labeled toluene, as a product of the irradiation of toluene. Next, we irradiated a dimethyl benzene, a compound with $CH_3$ groups attached to carbons 5 and 6 of the illustration. A two-carbon bridged intermediate should be able to "span" carbons 5 and 6 and give us labeled benzene product; a one-carbon bridged intermediate would not be able to do this. The result was that no labeled benzene product was formed, although we did find labeled toluene. These results point to the one-carbon bridged, 7-carbon intermediate shown at the left of the illustration. This intermediate is probably formed whenever a solar-wind or cosmic-ray carbon atom encounters, at an appropriate energy, <u>any</u> aromatic molecule. It is an intermediate unsuspected before studies were undertaken with energetic carbon.

Other major products that high-energy carbon gives on reaction with benzene are shown in the illustration . (10) . The first one, toluene (at the upper left), may come from the same 7-carbon, bridged intermediate which, we believe, also leads to labeled benzene. The next, the 7-carbon ring cycloheptatriene, appears to come from an insertion of the energetic carbon between two carbons of the benzene ring. The phenylacetylene, as we mentioned above, appears to result from a process of the incoming carbon's stripping off one carbon atom and continuing on as a two-carbon fragment to react with yet another benzene molecule. This is shown by the fact that when we reduce the energy of our $^{14}C$ down towards 2 eV the yield of phenylacetylene decreases sharply. At the lower energies the $^{14}C$ does not have enough velocity to strip a carbon atom from a benzene molecule. Therefore, fewer two-carbon fragments are formed. The biphenyl

product (lower left in the illustration) doubtless results from a reaction between the newly labeled, energy-rich $C_6H_5$ ring and a nearby benzene to form the resultant twelve-carbon compound, biphenyl. Similarly, a newly formed seven-carbon species could react with a nearby benzene to form one of the thirteen-carbon products, diphenylmethane or phenylcycloheptatriene.

The figures in the illustration . . . . also include radioactivity-distribution values--that is, the relative numbers of a given product molecule that have their $^{14}C$ in a given position. (These values were obtained by chemical degradation procedures, in which parts of a molecule are broken out by systematic chemical procedures; the amount of radioactivity in each of these parts may then be measured.) The greater the energy the $^{14}C$ brings to an intermediate 7-carbon species, the greater the chances of shifting hydrogen atoms about in that species and the greater the chance of breaking different carbon-carbon bonds; the result is more rearrangement of $^{14}C$ into different positions of the final product molecules. The radioactivity-distribution percentages shown were obtained as a result of irradiating benzene at 5,000 eV energy, and we were engaged for some time in determining how these values changed as we continued to lower the energy with which the accelerated $^{14}C$ struck the benzene. What we found was that radioactivity distributions in product molecules did not change as we varied the incoming $^{14}C$'s energy from 5000 eV all the way down to 6 eV. The reason appears to be that, regardless of the energy with which the $^{14}C$ strikes the benzene, the ultimate bond-forming reaction takes place at a kinetic energy of about 5 eV or lower. A higher velocity $^{14}C$ loses energy by fragmenting benzene

molecules. From measurements on the yields of various products we could also see that below 100 eV the incoming carbons had a diminished opportunity to combine with hydrogen atoms before combining with benzene.

At 5 eV there is a sudden increase in the amount of radioactivity appearing in the benzene (6-carbon) rings of some of our products. In the case of toluene, this amount jumped from 15% (see illustration . . . .) to about 40%. The explanation for this effect appears to be that at 5 eV and lower energies we are observing only "first collision" reactions, that is, our $^{14}C$ has had no previous collisions with benzene molecules before forming an intermediate of the type shown . . . The 5 eV kinetic energy brought by the $^{14}C$ seems to be the maximum energy that the 7-carbon intermediate can tolerate without breaking into fragments. However, that energy does cause much rearranging of the radioactivity in the product molecules. At lower energies, such as 2 eV, we also have "first collision" reactions, but the rearranging is sharply reduced (toluene, formed at 2 eV, has only 6% of its radioactivity in its ring). In fact, all the products that we have checked have shown maximum rearrangement at 5 eV, and minimum rearrangements at 2 eV. These observations reveal mechanisms that could have been uncovered only by high-energy studies. They give us a glimpse of the quite unusual chemical processes that may take place when the available energies are high enough.

Although the major products of our benzene irradiations are established, the red tracing of the illustration . . . . shows us many minor products whose identities we do not know. We can be nearly certain that some of these minor products are of structures not known to contemporary carbon chemistry--and it is conceivable that the mechanisms leading to

some of these structures may have been important for the emergence of life. For example, a high energy process may have been necessary for the first appearance of a particular, indispensible-for-life molecule on the prebiological Earth. Once made, that molecule may have been able to replicate itself by autocatalysis, the process by which the presence of a particular molecule greatly speeds up the production of like molecules. Our continued efforts will be toward establishing the identitities of our high energy products and mechanisms, both for benzene and for other key organic targets. We are confident that such research will tell us much about the carbon chemistry that goes on around us in our energy-rich universe.

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*TECHNICAL INFORMATION DIVISION*
*LAWRENCE BERKELEY LABORATORY*
*UNIVERSITY OF CALIFORNIA*
*BERKELEY, CALIFORNIA 94720*