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Photophysical Separation and Identification of Reactive Free Radicals

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Summary

An analytical method is proposed for volatilizable free radicals: In a film of liquid helium II, they are floated by heat-flush, heated selectively by nondestructive radiation, and separated by heat-exchange force, with which their spectra are then scanned. Alternative photophysical processes are briefly described. An adaptation of the heat-exchange method is suggested as an aid in the analysis of free radicals formed in irradiated solids. The heat-exchange method is shown to be important in the ultrapurification of materials.

INTRODUCTION

The main difficulty in studying chemical reactions that involve free radicals as intermediates has been the lack of a satisfactory method for analyzing the mixtures of highly reactive, unstable free radicals that fleetingly appear.

The direct application of a spectrometric method to such a mixture normally causes a troublesome superposition of many different spectra and hence is desirable only for the study of short-lived excited states of free radicals.

When reactive free radicals form exceptionally simple samples, they can often be separated sufficiently for their individual spectra to be distinguished, as the following three examples show.

Singly charged molecular ions in the gas phase are free radicals that can be separated and identified by mass spectrometry.

A simple gaseous mixture of reactive free radicals that are polar and not too large can be resolved by focusing individual rotational states of the radicals in a molecular-beam method that also yields their infrared (IR) spectra (*1*).

A popular separation method consists of immobilizing the free radicals in an inert, rigid matrix that later is slowly warmed up to permit ever larger free radicals to diffuse. The electron spin resonance (ESR) spectrum of the mixture then gradually becomes simpler as some species of free radicals disappear due to termination reactions. Only very simple samples give unambiguous results.

In this paper an analytical method is proposed for complicated mixtures of reactive and often unstable free radicals (in their ground energy levels) that are available in the gas phase. The free radicals are stabilized, separated photophysically, and then identified by a microspectrometric technique. An adaptation of this method is suggested as an aid in the analysis of complicated mixtures of free radicals produced in solids by destructive radiation.

The mainly proposed photophysical separation method utilizes the selective absorption of nondestructive radiation by free radicals dispersed in liquid helium. The differences in efficiency with which free radicals absorb radiant energy and degrade it into heat are converted into differences in their rates of displacement by heat-exchange force generated in liquid helium II.

HELIUM II

Natural helium, which consists of almost pure ^{4}He, condenses at 4.22°K into a classical liquid referred to as helium I. Liquid helium undergoes an abrupt change of state, the so-called lambda transition, at T_λ, 2.17°K. Below T_λ it becomes a quantum liquid, termed helium II, that at moderate pressures remains liquid even at zero temperature.

Helium II has extraordinary properties (*2*, *3*), but only those essential to the present task will be described in this paper. In the range from 2.1 to 1.1°K it shows a pattern of behavior which is defined as the linear region of helium II because, in experiments involving sufficiently small fluxes of mass or heat, the relations between its main properties can be described by linear equations.

The properties of helium II are best understood in the linear region, to which this paper is restricted. They can be inferred from an analogy known as the two-fluid model, according to which helium II behaves as if it were a mixture of two interpenetrating fluids which can flow independently, without mutual friction. These two imaginary fluids are called the superfluid and the normal fluid. The superfluid, which corresponds to the ground state of the quantum liquid, has no viscosity and no entropy. The normal fluid, which represents the thermal excitations in the quantum liquid, is identical to helium I and so has both viscosity and entropy. These component fluids are interconvertible and their equilibrium concentrations vary with temperature from T_λ, at which only the normal fluid can exist, to absolute zero, at which helium II consists entirely of superfluid. For practical purposes, however, the two-fluid model begins to fail when very little of either fluid is present. For example, just below 1.1°K, with less than 1% normal fluid left, experiments within the linear region are almost impossible because the allowed fluxes of mass or heat become extremely small.

Helium II partly possesses superfluidity (and therefore is the most sensitive leak detector known). The superfluid, which has no viscosity, penetrates easily through a "superleak," i.e., any porous wall with orifices small enough to immobilize the normal fluid. Superfluid is postulated to consist of helium atoms and, as these possess mass and velocity, its flow has momentum. Nevertheless, a current of superfluid, being frictionless, cannot drag along an object immersed in it. Nor can superflow carry heat, as the superfluid has no entropy. Care must be taken that the superflow never exceeds a critical velocity with reference to the channel walls, so that the experiments remain within the linear region. The critical velocity is inversely proportional to the thickness of the layer of flowing superfluid; e.g., a film as thin as 200 Å can flow at ca. 300 mm/sec, but a layer 4 mm thick must not exceed ca. 0.3 mm/sec (*3*). The critical velocity also varies with the temperature, but conflicting reports on this dependence (*3*, *4*) indicate that it is strongly influenced by the experimental conditions. In the supracritical region of helium II in which the critical velocity is exceeded, thermal excitations are created mechanically in the former superfluid which becomes viscous and its kinetic energy partly converted into heat. The existence of a critical velocity can be considered a macroscopic quantum phenomenon—the superfluid is unable to accept less than a certain minimum energy.

The effective heat conductivity of helium II is so high that it prevents the establishment of an appreciable temperature gradient in the liquid. For example, helium II boils without forming bubbles by merely vaporizing at its free surface. This is because no classical heat conductance exists in the linear region of this quantum liquid; instead, heat is transported in it by a mechanism that amounts to internal convection due to the two component fluids. In the heated zone, their equilibrium is displaced toward a higher concentration of normal fluid. The resulting concentration gradient within the helium II is rapidly equalized by normal fluid streaming out of the heated zone and superfluid flowing into it. No bulk motion of the helium II takes place, because in this case the flow rates of the two component fluids are equal and opposite. At the colder walls of the container, the same process occurs in reverse. As superflow is involved in this mechanism, it follows that there is a critical heat flux through helium II beyond which the two-fluid model is no longer valid.

Particles that are nonuniformly heated by diffuse radiation while tumbling through helium II experience a radiometer force, i.e., each recoils from the normal fluid that streams away from its hottest side. Helium II is transparent over a very wide spectral range and its viscosity at, e.g., 1.1°K is only 12% of that of helium gas at room temperature. The situation is analogous to the photophoresis of aerosols (*5*), and the particles are similarly set in random motion.

HEAT-FLUSH

Molecules and particles are not dissolved in helium II and sink in it because its density is scarcely 0.15 g/cm^3. They are displaced by the motion of normal fluid which is a feature of heat transport in this liquid. In a sufficiently large heat flux through helium II, they are swept from the heat source to the heat sink; this effect was discovered in 1948 by Lane et al. who named it heat-flush (*6*).

When helium II is cooled by pumping off its vapor, the heat-flush carries molecules or particles up to the free surface because the latter then acts as a heat sink (*7*). In this case, the heat-flush can be visualized as an upward flow of liquid that prevents sinking particles from reaching the bottom. Upward flow would cause the surface of a classical liquid to rise, but helium II can flow without bulk motion. The saturated vapor pressure of helium II at, e.g., 1.1°K is 0.29 Torr, and what evaporates is neither of the two fictitious component fluids but helium II that consists of indistinguishable atoms.

HEAT-EXCHANGE FORCES

Particles that are heated (uniformly or not) in helium II can be transported in a predetermined direction by generating heat-exchange force in the liquid. In the simplest case, the particles are irradiated within helium II in which superfluid is caused to flow through stationary normal fluid. The superfluid then exerts a drag force only on those particles that absorb radiant heat. Superflow momentum is transferred to the heated particles because at their surfaces flowing superfluid is converted into flowing normal fluid.

A very small, spherical particle that is heated uniformly is dragged (*8*) by the heat-exchange force $F_{\text{H.E.}} = \dot{Q}v_s/S_nT$ in the experiment just described. $\dot{Q}$ is the rate at which heat flows from the particle to the helium II; no minimum irradiation intensity is required. v_s is the flow velocity of the superfluid; the equation is valid only if v_s remains below the critical velocity that depends on the temperature and on the thickness of the layer. S_n is the specific entropy of the normal fluid; it rises sharply with temperature. T is the temperature of the helium II; lowering it enhances $F_{\text{H.E.}}$ even when v_s is affected adversely. Due to the thermal boundary resistance between the different materials, the irradiated particles remain somewhat hotter than the liquid (*2, 3*).

The existence of heat-exchange forces is implied in the two-fluid model that was developed in 1938 and 1941. For decades little notice was taken of these forces (*9*), though recently it turned out that they had been unwittingly observed in several instances (*8, 10*). In 1967 their effects were calculated for proposed torque experiments intended to check on the validity of the two-fluid model (*11*) and to study the quantization of the circulation of superfluid (*12*). In 1968 Penney and Hunt calculated the resulting particle motions (*8*). Heat-exchange forces were first measured by Hunt (*13*), who in 1968 performed the experiment on the quantization of circulation that had been proposed (*12*) and experimentally checked the earlier calculations. The latter were also confirmed by a modified version of this torque experiment, which was carried out in 1970 (*14, 15*).

PHOTOTHERMAL CONVEYOR

Figures 1 to 3 illustrate (very schematically) an apparatus in which molecules or particles are transported in directions that depend on the

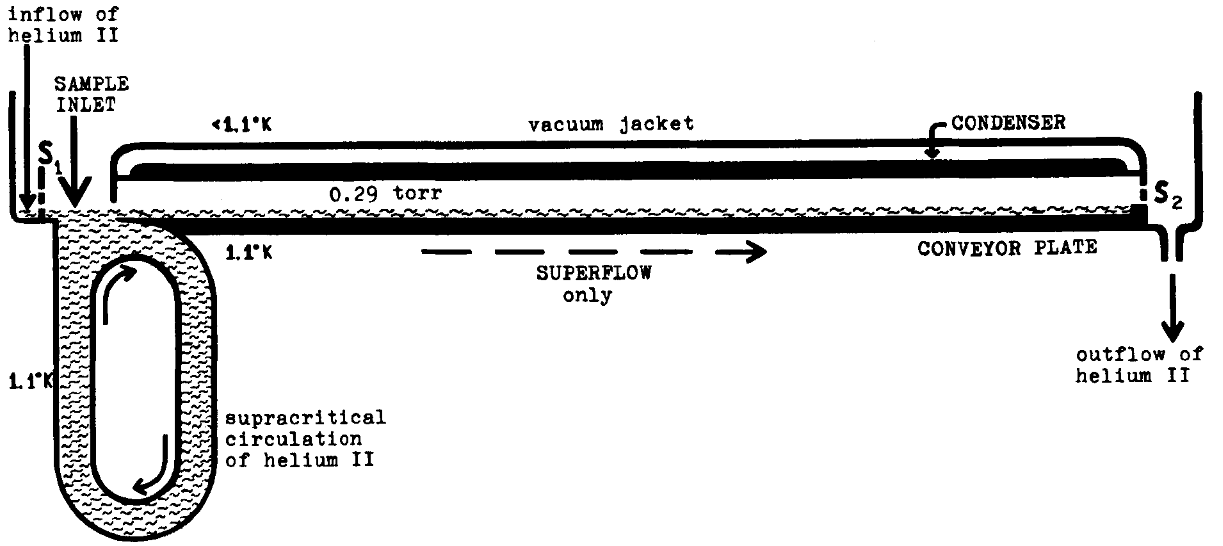

Fig. 1. Photothermal conveyor, viewed from side.

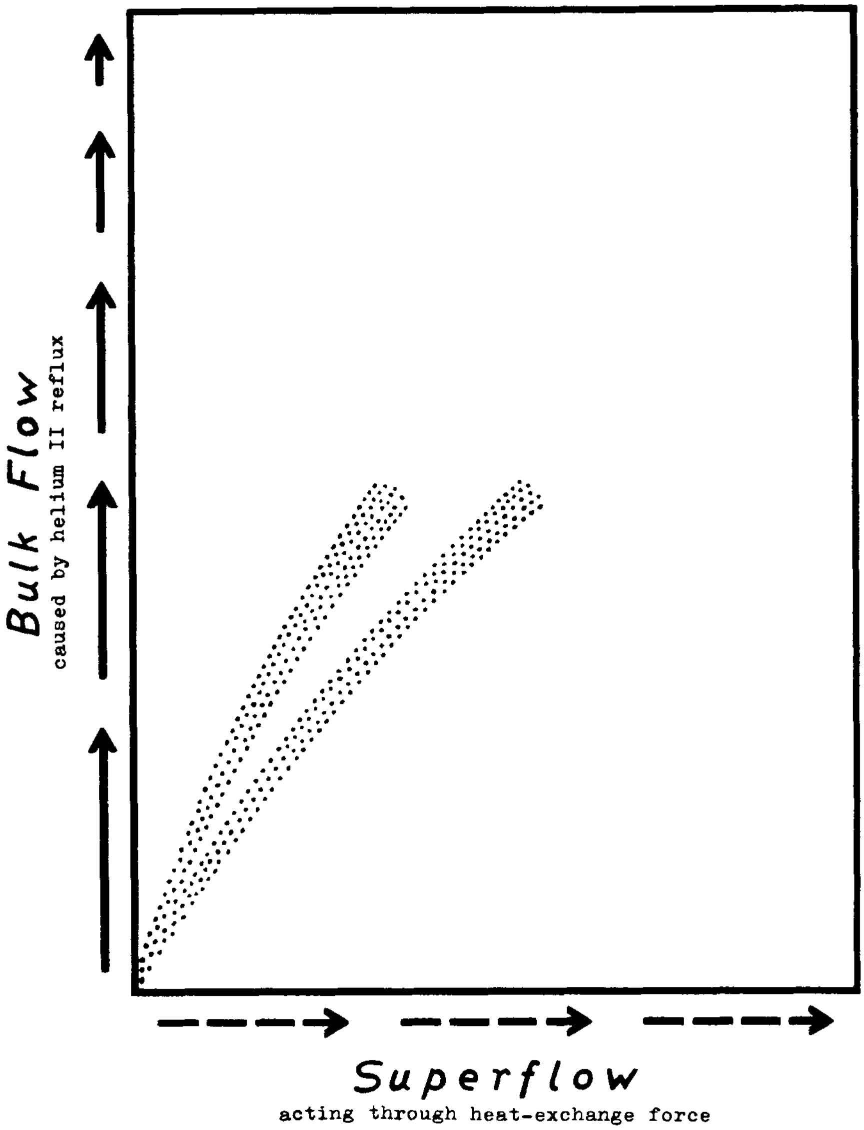

FIG. 2. Conveyor plate, viewed from top.

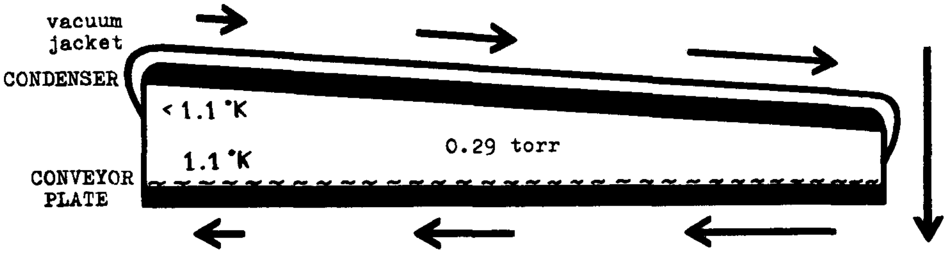

FIG. 3. Helium II reflux, viewed from S_1 to S_2.

rates at which they convert radiation into heat. The sample is introduced continuously into this photothermal conveyor, and is separated into pure species whose spectra are analogously scanned. The apparatus utilizes properties of helium II, and the materials of which it is built must be pure and transparent at the wavelengths used for irradiation.

At the sample inlet, indicated in Fig. 1, the free radicals continuously arrive either as a molecular beam or within falling, solid particles that are precooled. To stabilize them for subsequent separation, they are dispersed in a swift bulk current of helium II that is kept at 1.1°K by a surrounding cryostat (not shown). (The latter eliminates the heat removed from the sample, the heat generated by the supracritical flow of helium II, etc. The mechanism causing the circulation of the liquid has also been omitted). The flowing liquid carries up the sample, which by then has reached 1.1°K, and sweeps some of it onto the conveyor plate. (The sample inlet can be made simpler but less effective in cooling. For example, radicals from a molecular beam can reach the plate by diffusing through the residual helium gas; falling particles can be blown onto the plate by this gas).

The conveyor plate, shown in Fig. 2, must be accurately horizontal. For the observation of radioactive free radicals, its upper side is coated with a thin layer of inorganic scintillator for β-particles. As shown in Fig. 1, helium II covers the plate with a layer whose thickness of, e.g., 0.2 mm is determined by the threshold below S_2. The plate is fixed on top of a cryostat (not shown) that normally keeps it at 1.1°K. [Persistent currents (*2*, *3*) that may accidentally arise when the plate is first covered with the liquid should be destroyed by holding the temperature just above T_λ for several hours].

Superfluid flows over the conveyor plate by gravity, as can be seen in

Fig. 1, in the direction from superleak S_1 to superleak S_2; the latter immobilize the normal fluid. [Film flow (*3*) causes drainage that should be minimized by constructing S_2 as a narrow horizontal strip]. The superflow across the plate is kept at its maximum safe velocity of, e.g., 4 mm/sec by adjusting the inflow of helium II. [The thermomechanical effect (*2*, *3*) makes it possible to control the inflow rate with an electric current used for heating (*16*). As for the flow on the plate, the onset of its critical velocity can be detected by the fact that heat is suddenly generated].

To prevent the sample swept onto the conveyor plate from descending within the layer of helium II, heat-flush is generated in the latter by means of the condenser. The thermostated plate then acts as a heat source, and the free surface of the helium II becomes a heat sink because the residual helium gas conducts heat toward the condenser and because the liquid slowly evaporates. The heat-flush should be barely intense enough to float the sample; this is regulated by the temperature of the condenser.

A slow bulk stream of helium II flows across the conveyor plate, as shown in Fig. 2, with gradually diminishing velocity, at right angles to the superflow. This stream, which allows the sample introduction to be continuous, is caused by draining the reflux from the condenser down one wall onto the side of the plate, as shown in Fig. 3. [Due to film flow (*3*), a very small part of the reflux will flow down the other walls that support the condenser].

The sample on the conveyor plate is exposed to intense, usually monochromatic, radiation that its components absorb selectively and convert into heat without experiencing chemical change. The plate should be irradiated with homogeneous intensity from many directions. [A beam of radiation can, while being switched on, create third sound (*17*), which accelerates the random spreading of the sample; also, it superimposes an often unpredictable direction on the photophoretic motions of particles (*5*), which affects their separation]. In any particular spot on the plate, the species comprising the sample are dragged equally by the bulk flow, while the heat-exchange force drags them in proportion to the rates at which they generate heat. Each species then moves according to the resultant of these two forces, along trajectories as illustrated in Fig. 2. (Molecules or particles that have coalesced in the helium II—a rare event that depends on the rate at which the sample is introduced—migrate along changed trajectories because the aggregate has different properties).

When the separation has progressed to the stage shown in Fig. 2, the separated free radicals are ready for spectrometric identification, and for this the separating irradiation is switched off. To determine their spectra, the rates at which the separated species are displaced by the heat-exchange force are recorded as a function of the frequency of the radiation to which they are exposed.

ANALYSIS OF FREE RADICALS AVAILABLE IN THE GAS PHASE

The conveyor plate accommodates so few free radicals that, for their detection there, they have to be labeled with a short-lived radioisotope. If the free radicals are to be derived from an organic compound, the latter must first be synthesized so that each molecule contains one atom of ^{11}C, a positron emitter of 20.5 min half-life.

The radioactive compound is carried by a preparative gas chromatograph from the synthesis apparatus to the chemical reactor in which free radicals are continuously produced.

Gas-phase reactions involving free radicals can be studied with some simple reactor; the free radicals join a molecular beam that effuses from it. For example, propagation reactions can take place within a coaxial mixing chamber (*18*).

Volatile free radicals produced in a liquid solution can be collected in a molecular beam from a thin film of an involatile solvent exposed to low vacuum. Figure 4 shows a chemical reactor with which radical-forming redox reactions can thus be studied. The larger conical rotor resembles those used in centrifugal molecular stills as evaporators that can form a liquid film of 1–5 microns thickness and 1–5 milliseconds lifetime (*19*). The smaller conical rotor is similar to those used in centrifugal aerosol generators (*20*) and can produce a spray of droplets of nearly uniform diameter of 6 μ accompanied by much smaller satellite droplets (*21*). The temperature of the solutions is adjusted by IR heating of the rotors. The rate of most redox reactions can further be controlled by varying the concentration of the nonradioactive solution. Photochemical and thermal dissociations can be investigated analogously on a single rotor.

The sample now effuses in a molecular beam that consists only partly of free radicals. To prevent overcrowding on the spot where the radicals are swept on the conveyor plate, it is desirable to eliminate molecules without unpaired electrons from the beam. This is done in a Stern-

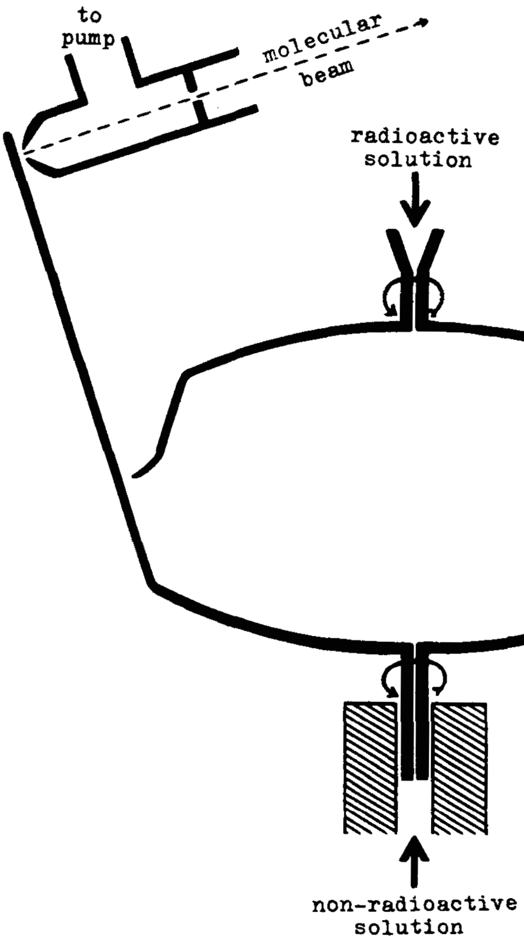

FIG. 4. Chemical reactor for radical-forming redox reactions.

Gerlach apparatus (*22*) by splitting the molecular beam in an inhomogeneous magnetic field and utilizing only the component beam deflected into the field.

Next, the molecular beam enters the photothermal conveyor through a tube (like the one in Fig. 4) that is evacuated between orifices through which the beam passes. The tube is vertical and the orifice at its lower end almost reaches the surface of the helium II in the sample inlet (Fig. 1). The free radicals entering as a beam are much larger and faster than the helium atoms with which they collide in the gas phase and hence are not much deflected before they plunge into the liquid.

The free radicals are separated on the conveyor plate by selective radiant heating, preferably with IR radiation. Suitable IR wavelengths can be chosen in advance from the spectrum of an identical mixture of nonradioactive free radicals trapped in a matrix of frozen noble gas, if reactants and stable products are not also trapped. One irradiation rarely isolates every species of free radicals; this normally requires several separations at different single wavelengths. The migration of the ^{11}C on the conveyor plate is continually recorded on a chart with a point-plotter by synchronously scanning the plate with a photomultiplier that does not count the dimmer scintillations due to annihilation radiation.

Finally, the spectra of the separated species of free radicals are determined on the conveyor plate. IR spectra are obtained by irradiating the plate with IR radiation from, e.g., a scanning monochromator. Similarly, optical, ultraviolet, and circular-dichroism spectra are scanned for free radicals that withstand such radiation. Rotational spectra of moderate resolution are obtained of free radicals having permanent dipole moments by irradiating with microwaves. ESR spectra are scanned after placing the conveyor plate between the poles of a magnet.

ALTERNATIVE PHOTOPHYSICAL PROCESSES

Probably only electromagnetic radiation can be both delicate and selective enough to separate reactive free radicals. It could also be utilized in cheaper photophysical processes, as the following two proposals illustrate.

By IR heating during alternating molecular distillations, different species of volatile free radicals that are not thermolabile can be transported in different directions (*23*). A monochromator irradiates them by repeatedly scanning a narrow spectral range during distillation from a transparent, stationary disk to a very close, parallel disk. The latter moves, within its plane, along directions that depend on the wavelengths; these directions are reversed during each such distillation from the moving disk to the stationary one. The free radicals enter this still in a molecular beam through a pinhole at the center of the stationary disk and leave the still at the edges of this disk. Outside, they are trapped in frozen noble gas that is gradually deposited around the still, and after considerable time they can be detected and identified by conventional spectrometry.

By IR irradiation of an aerosol at atmospheric pressure, thermolabile free radicals can be separated more quickly and with higher resolution because their random motion is retarded by attaching a particle to each and by lowering the temperature. Free radicals in a molecular beam enter a vacuum chamber cooled by liquid hydrogen and are trapped on a "cold finger" within a layer of matrix consisting of a mixture of argon and mostly neon. The chamber is then filled with helium and a sudden flow of liquid nitrogen inside the "cold finger" causes explosive dispersion of the matrix into many more argon particles than the free radicals that it contained, thus forming a polydisperse aerosol. To stabilize the aerosol by dilution, it is made to flow through a tube cooled by liquid argon; at this momentarily higher temperature, homogeneous droplets of argon evaporate but every droplet seeded by a free radical merely shrinks. The tube leads into the top of a vertical, cylindrical cloud chamber in which a slow upflow of helium reduces the settling speed of particles. The cloud chamber is gradually cooled by liquid neon and each aerosol droplet grows, as argon condenses on it, and freezes into a particle with a free radical near its surface. A coil consisting of one superconducting loop, wound around the center of the cloud chamber, produces an inhomogeneous magnetic field that tends to align the tumbling particles. This region is exposed to intense monochromatic IR radiation that is strongly absorbed by the sample. Due to the magnetophotophoresis (*5*) that ensues, particles with free radicals that absorb the radiation are isolated because they cannot settle to the bottom: those containing unpaired electrons aligned parallel to the magnetic field hover just above the coil, and those with antiparallel electrons are suspended just below the coil. The IR spectrum is scanned by gradually changing the wavelength of the irradiation—the weaker the absorption, the more particles are released by the coil. The lower part of the cloud chamber contains a particle counter. While scanning electronic spectra, the magneto-photophoresis must be maintained by unvaried IR irradiation. ESR can be scanned only intermittently by substituting a homogeneous magnetic field for the inhomogeneous one during momentary exposures to monochromatic microwaves, so that a spectrum with dotted lines is obtained.

Heat-exchange force separates volatilizable free radicals with by far the highest ratio of directed motion to random motion. Moreover, it is applicable to free radicals that cannot be volatilized.

ANALYSIS OF FREE RADICALS FORMED IN IRRADIATED SOLIDS

Of the common solids, those having an organic structure are the most easily damaged by electromagnetic or corpuscular radiation. Free radicals result in them in pairs, whose partners can diffuse apart instead of promptly recombining. After they are spaced apart from each other by a few atoms, their diffusion can be hindered by keeping the solid at a sufficiently low temperature; thus a pair of free radicals is "stabilized."

Research interest is centered on the case just described. The irradiation of monomolecular layers or of polymeric molecules dispersed in frozen noble gas is of little practical interest, though free radicals formed in these artificial solids could be made available in the gas phase to separate the partners of the pairs.

The following analytical method is for an organic solid in which many different species of reactive free radicals arise. The sample is converted into a stream of solid particles; these fall through an irradiation zone and next into the photothermal conveyor. The radiation intensity is adjusted so that during their passage most particles suffer no damage, in many particles one pair of free radicals is formed, and in a negligible number of them two pairs of radicals are produced. The irradiated particles are set in motion on the conveyor plate, first to assort stabilized free radicals in identical pairs, and then to obtain for each of the latter superposed spectra for the identification of every pair of species that are formed together.

This analysis is a limited spectrometric improvement over the conventional direct application of spectrometry to an irradiated bulk solid, and both methods should be used. They are subject to the same chemical and crystallographic ambiguities, such as the following. A radical commonly formed in irradiated organic solids is the hydrogen atom, which can abstract another one elsewhere and thus produce a new free radical. Paramagnetic crystal defects caused by irradiation mimic free radicals by giving rise to ESR lines and optical absorption bands.

To obtain the stream of particles, a monodisperse aerosol of the sample is continuously generated (*24*) within helium gas at 0.29 Torr pressure and at the required temperature.

Only if the aerosol particles are similar in size and shape can the photothermal conveyor sort them according to the enclosed free radicals. Moreover, the particles have to be microscopic for the following reasons. The tiny sample must consist of very many particles, so that after the weak irradiation there will be many that contain a pair of free radicals.

Particles of normal density sink in helium II at a speed proportional to their size, and particles large enough to exceed their critical velocity generate heat—as if absorbing radiation. Each particle should be warmed up within a reasonable time by radiant heat that is absorbed in it by only one or two free radicals. When particles floated by the heat-flush are heated, they experience a drag force also from the downflowing superfluid; only for minute particles does the drag of the normal fluid predominate (*8*). A pair of free radicals should not be surrounded in its particle by too much material for a high enough signal-to-noise ratio in IR spectrometry.

From the aerosol generator the particles descend to the photothermal conveyor through a vertical tube that is filled with helium gas at 0.29 Torr. There is a temperature gradient in the helium within this long tube from the top that is at, e.g., room temperature to the bottom that is at 1.1°K. The particles are irradiated in the tube at the height which is at the desired temperature.

This aerosol must be dilute to delay agglomeration, as the Brownian motion of its particles is vigorous—for them, gas at low pressure is not a continuous medium. The particles descend in the tube at a macroscopic terminal velocity resulting from their gravitational fall among the helium atoms and from their thermophoresis, which is caused by their differential bombardment by helium atoms due to the temperature gradient.

(Irradiated particles need no concentrating device—analogous to the Stern-Gerlach apparatus—because they can be detected with more sensitivity than radioactive molecules).

The particles enter the photothermal conveyor through the lowest section of the vertical tube, which leads into the sample inlet (Fig. 1). On the conveyor plate the particles are rendered visible by dark-background illumination: they are irradiated horizontally by radiation with a wavelength of, e.g., 0.9 μ that they scatter without absorption, and are viewed vertically through an image converter that transforms only radiation in the near-IR range into visible light.

(The particles can instead be made radioactive, e.g., by tagging them with a radioisotope in the vertical tube, where they serve as condensation nuclei for traces of gases such as ^{127}Xe or ^{37}Ar. But this observation method introduces the new source of errors that even x-ray emitters deposited on a particle will sometimes produce more free radicals in it).

The particles are sorted on the conveyor plate by using the IR wavelengths corresponding to the new absorption bands that arose in the bulk solid after it has been similarly exposed to destructive radiation. The separation process takes place in a single IR irradiation that consists of consecutive monochromatic periods, one for each available wavelength. The particles enclosing free radicals change direction whenever a different wavelength is switched on and thus move along a zigzag trajectory that becomes divided into branching paths whenever a separation occurs. When enough wavelengths are used, the ends of these paths consist of particles having identical pairs of radicals.

(This separation process can be avoided by observing single particles. The conveyor plate is exposed to spectrally unresolved radiation consisting of the usable wavelengths, and particles with minimal photophoretic motions are selected from those farthest displaced by the heat-exchange force. But is is difficult to fit an ultramicroscope into this apparatus, and laborious to successively observe numerous single particles).

The IR spectrum of every pair of free-radical species is scanned on the conveyor plate. So are the optical, ultraviolet, and circular-dichroism spectra of these free radicals, if such radiation does not initiate chemical reactions. In this case, these wavelengths can also be used to sort the particles.

The ESR spectra of the free radicals can be obtained with the photothermal conveyor only if the molecules among which they are trapped in the particles have a permanent dipole moment that is negligibly small. If it is not, the previously irradiated bulk solid must be used, preferably at 1.1°K, for ESR spectrometry in which magnetic field modulation is replaced by temperature modulation due to chopped IR radiation (*25*). The individual ESR spectra can be distinguished by thus scanning the composite ESR spectrum repeatedly, each time with another wavelength chosen from the previously determined IR spectra of the free radicals for being absorbed mostly by a single species.

(The photothermal conveyor cannot be used directly for ESR of radicals trapped in polar materials because such particles are heated, due to dielectric loss, by microwave frequencies—not by lower frequencies, but these do not resolve the splitting of the signal by atomic nuclei. Nor can it be used to sort, by the method described above, groups of particles as samples for conventional ESR because at 1.1°K each must comprise at least 10^{10} particles).

These techniques can also be applied to research on radiation damage to biological cells to study the propagation reactions of the resulting free radicals. The cells are exposed to a radiolysis flash, quenched after different time intervals, and treated as particles for the spectrometric identification of their free radicals.

ULTRAPURIFICATION OF MATERIALS

The photothermal conveyor can be used for the analytical separation of other types of samples, e.g., isotopically-labeled compounds or conformational isomers, but less expensive separative devices exist for these.

In the ultrapurification of experimental quantities of materials (*26*), the photothermal conveyor is often irreplaceable. This ultrapurification consists of dividing highly pure material into many more particles than the impurities that it contains, and eliminating the contaminated particles. A material that was purified as much as practicable by a method for bulk matter, such as zone refining, is dispersed into an aerosol in helium at 0.29 Torr. The aerosol particles descend in this gas through a vertical tube into the photothermal conveyor. There they are exposed to spectrally unresolved radiation, consisting of wavelengths that the pure material does not absorb, and the particles which the heat-exchange force removes from the majority are rejected.

Minute samples of ultrapure materials are needed for research, e.g., on the transmission of thermal waves ("second sound") through monoisotopic single crystals.

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