Fig. 2. Envelope of quadrupole-echo signals of Cl^{35} nuclei in polycrystalline transdichlorethane ($\nu_0 = 34.36$ MHz, T = 77°K); a - in the absence of a high-voltage pulse, b - at E = 25 kV/cm, c - at E = 50 kV/cm.

The form of the signal envelope of the spin echo in polycrystalline transdichlorethane is shown in Fig. 2 for three values of the electric field (0, 25, and 50 kV/cm). The values of the phase shifts $\Delta\nu_E$ and of R_{zzz} for the series of crystals CCl_4, $CHCl_3$, C_2Cl_6, $C_2H_4Cl_2$, CH_5Cl, and Cl_2 are in good agreement with the data obtained by the stationary NQR method [2].

In conclusion, we point out the advantages of the nonstationary procedure: First, the interpretation of the experimental data is much simpler in the pulsed procedure than in the stationary measureemnts. Second, in the pulsed procedure there is no need for exact measurements of the absolute NQR frequencies. Finally, in the proposed method the frequency shifts can be measured even in weak electric fields, where these shifts lie within the limits of the line width, something quite difficult to do in the stationary case.

The authors thank Professor V. S. Grechishkin for interest in the work.

[1]   N. Bloembergen, Magn. and Electr. Res. and Relax., Amsterdam, 1963, p. 39.
[2]   R. W. Dixon, Proc. XIII Colloq. Ampere, Amsterdam, 1965, p. 213.
[3]   W. B. Mins, Phys. Rev. 133, 835 (1964); A. A. Boguslavskii and V. V. Pechenov, Abstracts, All-union Conf. on Paramagnetic Resonance, Kazan', 1969, p. 246.
[4]   N. E. Ainbinder and V. S. Greschishkin, Izv. Vuzov, Radiofizika 10, 186 (1967)]; V. S. Grechishkin, N. E. Ainbinder, S. I. Gushin, and V. A. Shishkin, Zh. Eksp. Teor. Fiz. 55, 787 (1967) [Sov. Phys.-JETP 28, 407 (1969)].
[5]   G. G. Klyueva, Diploma Thesis, Perm' State Univ., 1966.
[6]   J. Armstrong, N. Bloembergen, and D. Gill, J. Chem. Phys. 35, 1132 (1961).

CONCERNING THE ABSENCE OF EXACT MIRROR EQUALITY BETWEEN OPTICAL ANTIPODES

A. I. Rivkind
Physico-technical Institute, USSR Academy of Sciences, Kazan'

It was shown in [1] that irreversible radiation damage is produced in many solid organic substances by powerful flashes of ultraviolet light (with energy of several hundred Joules per

light pulse). This is accompanied by the production of free radicals that produce intense EPR signals, similar to those obtained when penetrating radiation acts on a medium.

The following mechanism of radical formation was established [1]: The powerful light pulses break the R-H bonds of the molecules in the surface layer of the irradiated material, and an appreciable number of "hot" hydrogen atoms H* are produced, with a kinetic energy $\sim 1 - 3$ eV. The hot H* atoms diffuse to the interior of the material and interact with the RH molecules:

$$RH + H^* \rightarrow \dot{R} + H_2,$$ (1)
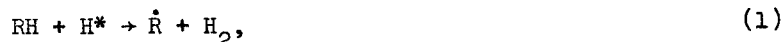
or (as demonstrated by a further study)

$$RH + H^* \rightarrow \dot{R}H_2.$$ (2)

Processes (1) and (2) cause accumulation of large amounts ($10^{16} - 10^{17}$ ml^{-1} and more) of hydrocarbon radicals inside the UV-irradiated solid organic substances.

Free-radical formation processes (1) and (2) are critical with respect to the H*-atom energy. Process (1) calls for an appreciable activation energy, and is therefore feasible only with sufficiently "hot" H* atoms. To the contrary, the probability of "capturing" atomic hydrogen via reaction (2) should increase with decreasing kinetic energy of the H* atoms.

The H* atoms produced at the instants of the UV flashes diffuse to the interior of the material along the "channels" of the crystal lattice, and pass successively through a large number (n) of potential barriers ("openings" in the interstices). If the initial kinetic energy of the H* atom is U_0 and the coefficient of energy loss on going through one barrier is α, then we have in the multiple-passage approximation

$$U \sim U_0 \alpha^n,$$ (3)

where U is the energy of the H* atom at the end of the diffusion path.

Of course, only a small fraction of the H* atoms falls into the lattice "channels" and diffuses in accordance with condition (3). However, only these H* atoms can be responsible for the formation of the free radicals deep in the material. The remaining diffusing H* atoms lose rapidly their energy in random collisions with the lattice (the character of their motion is essentially the same as in an amorphous medium.

Let us assume that for some pair of irradiated homolog substances the difference between the values of α amounts to 0.1%. Then, other conditions being equal, a diffusion path of only about 10^{-5} cm (10^3 lattice sites) suffices, according to (3), to make the energies of the H* atoms in the compared crystalline samples differ by a factor of two. The resultant large difference between the energies of the diffusing H* atoms should lead to very large differences in the radiative yields of the free radicals.

It is easy to see that the discussed molecular mechanism points to a high sensitivity of the radiative yields of the free radicals in the photolysis of crystalline objects to the least differences in the values of the coefficient α or, equivalently, to the smallest regular deviations in the crystal-lattice structure.

Starting from the foregoing, we attempted to apply the pulsed-photolysis method with

11

subsequent indication of the produced free radicals by means of the EPR spectra to determine the possible differences (deviations from mirror equality) in the structure of the optical antipodes.

The irradiation was in air at room temperature. The nominal energy of the light pulse (quartz UV region) varied in the range of about 860 to 300 J, depending on the character of the irradiated substances. The maximum summary irradiation dose was about 10^6 J. More detailed information on the irradiation process is given in [1].

Crystalline powders of optical antipodes were irradiated pairwise and then measured with an EPR spectrometer (ν_0 = 9320 MHz) under strictly identical conditions, so that the spectra for each pair of isomers (see the figure) were of comparable intensity (approximate accuracy of intensity measurement is 10 - 15%). Isomer pairs are not comparable in intensity.
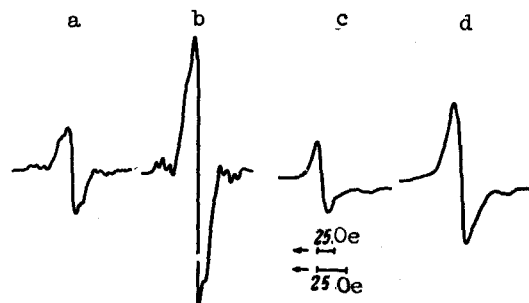
EPR spectra of free radicals of polycrystalline amino-acides irradiated by UV pulses: a - β-phenyl-α-alanine; b - ℓ-β-phenyl-α-alanine; c - d-β-phenyl-α-alanine hydrochloride. The upper magnetic-field scale pertains to the spectra of Figs. a and b, and the lower scale to Figs. c and d. The spectra of each pair of isomers are comparable in intensity.

Figures a and b show the EPR spectra of crystal powders of d- and ℓ-β-phenyl-α-alanine irradiated by UV pulses. The spectra consist of a triplet (1:2:1), each component of which is split into a quadruplet, and a single line in the center of the triplet. Perfectly analogous spectra were obtained in the radiolysis of frozen benzene and a few other solid aromatic compounds; an analysis of the spectra has shown that the free radicals conain an excess H atom connected to the phenyl ring [2]. This gives grounds for assuming that photolysis of the phenylalanine is accompanied by reaction (2) and formation of free radicals resulting from the "capture" of H* atoms by the phenyl rings of the amino-acid molecules. Under the indicated conditions, the observed many-fold difference between the intensities of the spectra in Figs. a and b indicate that the "transparency" of the d-isomer to the H* atoms is larger, namely, in some position to the right of the decimal point (more readily the third or the fourth) the value of the coefficient α [Eq. (3)] is larger for the d-isomer than for the ℓ-isomer, i.e.,

$$\alpha_d > \alpha_\ell. \tag{4}$$

By recrystallizing phenylalanine compounds in an aqueous solution of HCl, we obtained well-formed crystals of d- and ℓ-phenylalanine hydrochloride, the powders of which yielded after UV irradiation the spectra shown in Figs. c and d. The left-hand intense lines of these spectra (g_{eff} = 2.00) belong to the phenylalanine radicals, and the weak doublet lines with g_{eff} = 2.02 on the right belong to the $(H\dot{C}l)^-$ radicals. The line with $g_{eff} > 2$, which is split into a doublet, appears only following UV irradiation of substances whose lattices contain chlorine or other halogen ions. Apparently, irradiation results in "capture" of the H* atoms by

12

the halogen ions and in formation of radicals that yield a doublet line as a result of the hyperfine interaction with the associated hydrogen atom. From the intensity ratio of the spectra in Figs. c and d it follows that the condition $\alpha_d > \alpha_\ell$ holds for phenylalanine hydrochloride.

Similar results, pointing to a larger "transparency" of the crystal lattice of d-isomers to the H* atoms ($\alpha_d > \alpha_\ell$), obtained by us for the optical antipodes of α-alanine, tyrosine hydrochloride, valine hydrochloride (amino-acid), and optical antipodes of arabite (pentatomic alcohol).

Thus, compounds of left-hand (ℓ) configuration series are characterized by a closer packing of the particles in the crystal lattice and are therefore less "transparent" to the H* atoms than comounds of the right (d) configuration series. The observed structural differences (deviations from mirror equality) are extremely small and have practically no effect on the physico-chemical, crystallographic, or other properties of optical antipodes investigated by the usual methods.

All the experiments were performed on chemically pure compounds and were perfectly reproducible. Nonetheless, in view of the serious consequences of the work, we believe that our observations require further confirmation, for although it is little likely, it is nevertheless not excluded that for some unknown reason all the compounds of the left series are contaminated by a microscopic impurity that decreases the transparency of the ℓ-crystals relative to the hydrogen atoms. We are continuing our investigations in order to resolve the problem conclusively.

In conclusion, it is my duty to thank B. M. Kozyrev for support.

[1]   A. I. Rivkind and L. I. Medvedev, Dokl. Akad. Nauk SSSR 172, 137 (1967) and 181, 902 (1968).
[2]   L. A. Blyumenfel'd, V. V. Voevodskii, and A. G. Semenov, Primenenie elektronnogo paramagnitnogo rezonansa v khimii (Use of EPR in Chemistry), Novosibirsk, 1962.

MELTING OF ARGON AT HIGH TEMPERATURES

S. M. Stishov, I. N. Makarenko, V. A. Ivanov, and V. I. Fedosimov
Crystallography Institute, USSR Academy of Sciences
Submitted 18 November 1969
ZhETF Pis. Red. 11, No. 1, 22 - 25 (5 January, 1970)

The development of theoretical ideas concerning the nature of melting is hindered by the lack of experimental data. There is a particularly great shortage of information when attempts are made to reveal the general tendencies in the behavior of the thermodynamic characteristics of melting in a wide range of temperatures and volumes [1]. The situation has improved somewhat recently following the publication of [2, 3].

We present here the results of measurements of the volume of argon in the melting region at 291.6, 294.2, and 322°K. The measurements were performed with the aid of a specially constructed pressure meter, which was filled with spectrally pure argon at a pressure of 2000 kg/cm^2. The amount of investigated gas was determined by weighing, and the initial volume was calculated by using the data of [4]. After filling and weighing, the pressure meter was