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Intermolecular and intramolecular free valence transfer in gamma irradiated crystalline Hexadecanoic and Cis—9—octadecenoic acids

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SEZIONE II

(Fisica, chimica, geologia, paleontologia e mineralogia)

Chimica. — *Intermolecular and intramolecular free valence transfer in gamma irradiated crystalline* Hexadecanoic *and* Cis–9–octadecenoic *acids*. Nota di Antonio Faucitano, Paolo Locatelli, Fausta Faucitano Martinotti e Angelo Perotti, presentata (*) dal Socio A. Quilico.

Riassunto. — Viene descritto uno studio di risonanza di spin elettronico della migrazione non diffusiva di radicali liberi in matrici policristalline di acido esadecanoico (palmitico) e cis–9–octadecenoico (oleico) previamente irraggiati con radiazioni gamma. Esperimenti effettuati con acido palmitico contenente il 10% di acido trans–9–octadecenoico in soluzione solida e con i composti di inclusione di urea hanno permesso di dimostrare che la migrazione può aver luogo per trasferimento di atomi di idrogeno sia intermolecolare che intramolecolare. L'importanza relativa dei due meccanismi è stata valutata dal confronto delle cinetiche di trasformazione dei radicali nei composti puri e nei clatrati.

1. Introduction.

It has been shown that radicals of the type $\sim CH_2—\dot{C}H—CH_2 \sim$ (I), formed by gamma irradiation at — 196° C in polycrystalline samples of hexadecanoic (palmitic) and cis–9–octadecenoic (oleic) acids, undergo a transformation, at higher temperature, into radicals of the type:

$$\sim CH_2—\dot{C}H—COOH \quad (II)$$

and into allylic radicals

$$\sim CH_2—\overline{CH—CH—CH}—CH_2 \sim \quad (III)$$

respectively (I). These transformations take place at temperatures well below the matrix melting point, that is in conditions where translational motion of radicals is impossible, and have been therefore explained with the currently accepted mechanism of free valence migration toward carbon atoms where the weakest C—H bonds are available, according to the reaction:

$$R^{\cdot} + RH \longrightarrow RH + R^{\cdot} \quad [2, 3, 4, 5].$$

Hydrogen atom transfers may occur either intermolecularly, like for instance:

$$\begin{array}{lcl} \sim CH_2—CH_2—CH_2—COOH & & \sim CH_2—CH_2—\dot{C}H—COOH \\ & \longrightarrow & \\ \sim CH_2—\dot{C}H—CH_2—COOH & & \sim CH_2—CH_2—CH_2—COOH \end{array}$$

(*) Nella seduta del 9 maggio 1970.

or intramolecularly:

$$\sim CH_2—CH_2—\dot{C}H—CH_2—COOH \longrightarrow \sim CH_2—CH_2—CH_2—\dot{C}H—COOH\,.$$

With the purpose of obtaining experimental evidence of these two different mechanisms we have made an *esr* study of the radical transformation in a dilute solid solution of 10 % trans-9-octadecenoic (elaidic) acid in plamitic acid, and in the urea occlusion compounds of palmitic and oleic acids.

2. EXPERIMENTAL.

The formation of a solid solution by slow cooling of the molten mixture of the components was checked by thermal differential analysis (m.p. range 55-65° C). The clathrates were prepared by precipitation from cooled methanol solutions of urea [6]. The samples, enclosed in pyrex tubes, sealed under high vacuum, were irradiated in a ^{60}Co source, at — 196° C, with a gamma dose of 11 MRad. The *esr* measurements were made at room temperature for the solid solution and the clathrates, and at — 196° C for oleic acid. Calculations of *esr* spectra were made by the trial and error method, assuming a gaussian shape for the absorption lines. Radicals relative concentration measurements were made by double integration of the experimental and calculated patterns.

3. RESULTS AND DISCUSSION.

When the solid solution of elaidic acid in palmitic acid is gamma irradiated at — 196° C, most of radicals are expected to arise from homolytic rupture of C—H bonds in palmitic acid molecules, owing the relative abundance of this component in the system. After the irradiation and at higher temperatures, the free valence will start migrating within the lattice: simple intramolecular migration would only cause a transfer of three valence at the carbon atom α to the carboxylic group, but if also intermolecular migration takes place, a scavening of unpaired spins by double bonds of elaidic acid molecules, resulting, in the formation of resonance stabilized allylic radicals, would be observed. The results are shown in fig. 1. The initial spectrum (fig. 1 a), recorded after 10′ at room temperature, consists of a sextet with the central lines showing a doublet structure, and an overall splitting of 155-160 gauss. An attempt of mathematical simulation shows (fig. 1 g) that this pattern arises from the superimposition of about 60 % of a quartet, generated by radicals (II) (one α proton, $J_\alpha = 22$ gauss; 2 equivalent β protons, $I_\beta = 32$ gauss), and 40 % of a sextet, generated by radicals (I) (1 α proton, $J_\alpha = 21$ gauss; 4 equivalent β protons, $J_\beta = 31$ gauss). If the sample is stored at room temperature and successively at + 35° C and + 45° C, this hyperfine structure changes deeply (fig. 1 a–f). First the radicals (I) signal decays, as indicated by the gradual disappearance of the two outer lines (fig. 1 b), the decay being accompanied by a 30–40 % increase of radicals (II) concentration. Successively also the quartet decays, being replaced by a pattern of seven equally spaced lines, with a binomial intensity distribution, and an hyperfine splitting of 15 gauss, which is typical of type (III) allylic radicals, where two allylic and four β protons are equally interacting with the unpaired spin. These *esr* changes can be explained with the following transformations:

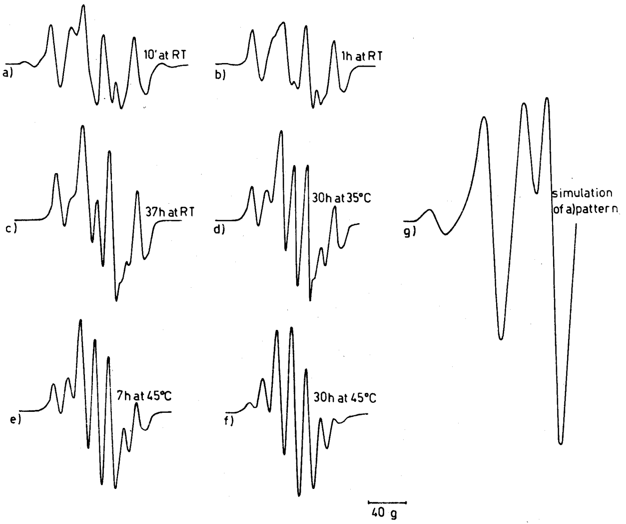

Fig. 1. – Post-irradiation *esr* changes in a solid solution of 10% elaidic acid in palmitic acid. Spectra recorded at room temperature.

$$\sim \mathrm{CH_2—\dot{C}H—CH_2} \rightarrow \sim \mathrm{CH_2—\dot{C}H—COOH} \rightarrow \sim \mathrm{CH_2—\overline{CH—CH—CH}—CH_2} \sim .$$

Although a small fraction of radicals (I) might be directly converted into allylic radicals, most of the free valences migrate first toward the carbon atom, α to the carboxylic group, the process being favoured by the higher concentration of carboxylic groups in the system, and successively toward the double bonds of the elaidic acid molecules. The latter process is much slower, presumably because of the lower concentration of double bonds, and because its first step, leading to a transfer of the free valence from an α to a β carbon atom, is endothermic. The conversion of radicals (II) takes place at measurable rate at room temperature and at 35° C, the half time being about 30 hrs at 35° C. At these temperatures, which are about 35–20° C below the initial matrix melting point, we can still safely exclude the possibility of diffusional motion of radicals and molecules. This important point is confirmed by the fact that measurements of stability of allylic radicals trapped in matrices of the solid solution did not show any appreciable decay in the time scale of 30–40 hrs. On this base the observed radical conversion can be considered as a conclusive evidence of intermolecular free valence transfers in crystalline palmitic acid.

In the clathrates, the urea molecules are arranged as in the walls of a honeycomb, leaving long hexagonal holes, about 5–6 Å in diameter, where plamitic and oleic acid molecules fit, presumably end to end [7, 8], without overlapping of hydrocarbon chains. The walls of the tubular cavities hinder intermolecular radical reactions, so that only radical transformation arising from intramolecular free valence transfers should be observed.

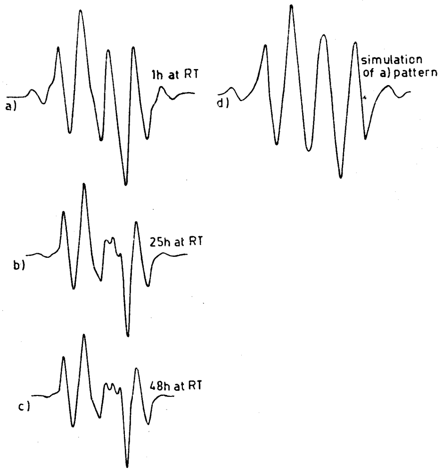

Fig. 2. – Post-irradiation *esr* changes in the palmitic acid-urea clathrate. Spectra recorded at room temperature.

The *esr* spectrum of palmitic acid-urea clathrate, recorded after about 60′ at room temperature, consists of a well resolved sextet of equally spaced lines, having an overall splitting of about 135 gauss (fig. 2 a). A comparison with the simulated pattern (fig. 2 d), shows that this spectrum arises from the superimposition of about equal percentages of a sextet (1 α proton, $J_\alpha = 22$ gauss; 4 equivalent β protons, $J_\beta = 28$ gauss) and a quartet (1 α proton, $J_\alpha = 21$ gauss; 2 equivalent β protons, $J_\beta = 33$ gauss), generated respectively by type (I), and type (II) radicals. The absence of the doublet structure, as well as the smaller overall splitting, probably reflects the higher freedom for molecular motion in the urea channels. As the sample is allowed to stand at room temperature, radicals (I) decay ($t_{1/2} \simeq 7$ hrs, fig. 3 B), leaving the pure radical (II) signal (fig. 2 b, c). The *esr* change is accompanied by an increase of radical (II) concentration in the system, proving that at least part of type (I) radicals are transformed into type (II) radicals. This is confirmed, in a less direct way, by comparison with the urea clathrate of hexadecane. In this system, where no migration toward carboxylic groups is possible, the rate of radical (I) decay is considerably slower (fig. 3 C).

These results suggest that in palmitic acid also the intramolecular type of free valence migration is possible. It might be interesting now to estimate to what extent this mechanism contributes to the overall process of migration. This can be done by simply comparing the rates of radical (I) decay (corrected for thermal decay) in the pure compound (fig. 3 A) and in the clathrate (fig. 3 B). A calculation, based on the time for 80 % decay in both systems, shows that the average rate of intramolecular migration is slower than the intermolecular migration by a factor of about 5.

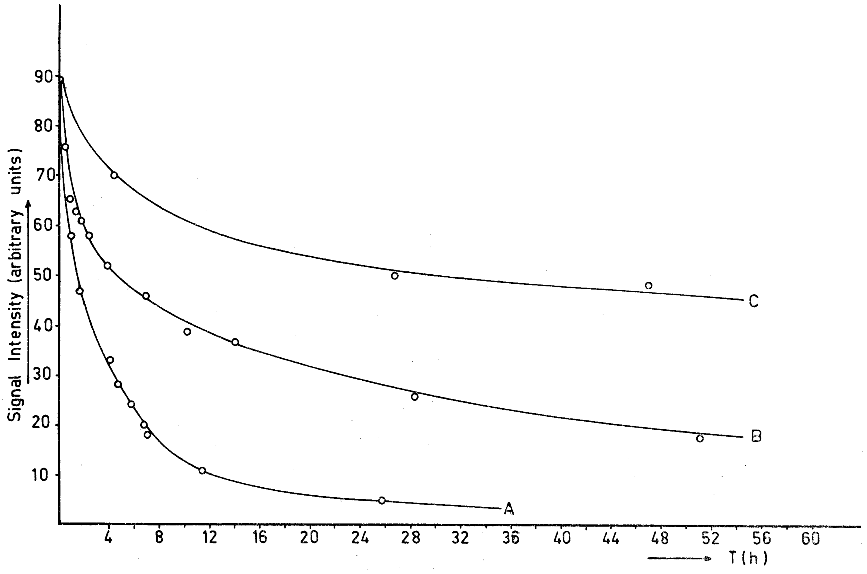

Fig. 3. – Post-irradiation decay of radicals (I) in pure plamitic acid (A), palmitic acid-urea clathrate (B), and hexadecane-urea clathrate (C). Measurements made at room temperature.

Therefore, in palmitic acid, intramolecular transfers seem to be of minor importance, although contributing significatively to the overall process.

Radical transformation in the oleic acid-urea clathrate are shown in fig. 4. The initial spectrum, recorded at — 196° C few minutes after irradiation, closely resembles that of plamitic acid clathrate (fig. 4 a), suggesting that radicals type (I) and (II) are the prominent species in the system. After 24 hrs annealing at — 78° C this hyperfine structure undergoes some minor changes, presumably related to a conformational transition (fig. 4 b), however the intensity of the two outer lines, belonging to the radical (I) signal, does not decrease appreciably, indicating that no free valence migration takes place at this temperature. At room temperature radicals (I) decay, ($t_{1/2} \simeq$ 10 hrs) the decay being accompanied by an increase in the concentration of allylic radicals, whose septet, superimposed on the radical (II) quartet, is clearly visible in the spectrum of fig. 4 c. Successively also the quartet decays, at an extremely slow rate, leaving after about 30–40 days the pure allylic radical pattern (fig. 4 d). The decay of the sextet is unequivocally caused, at least in part, by conversion of radicals (I) into allylic radicals, suggesting that in oleic acid, the free valence is capable of migrating intra molecularly from any position in the hydrocarbon chain (except the ones α to carboxyls), to carbon atoms adjacent to the double bond.

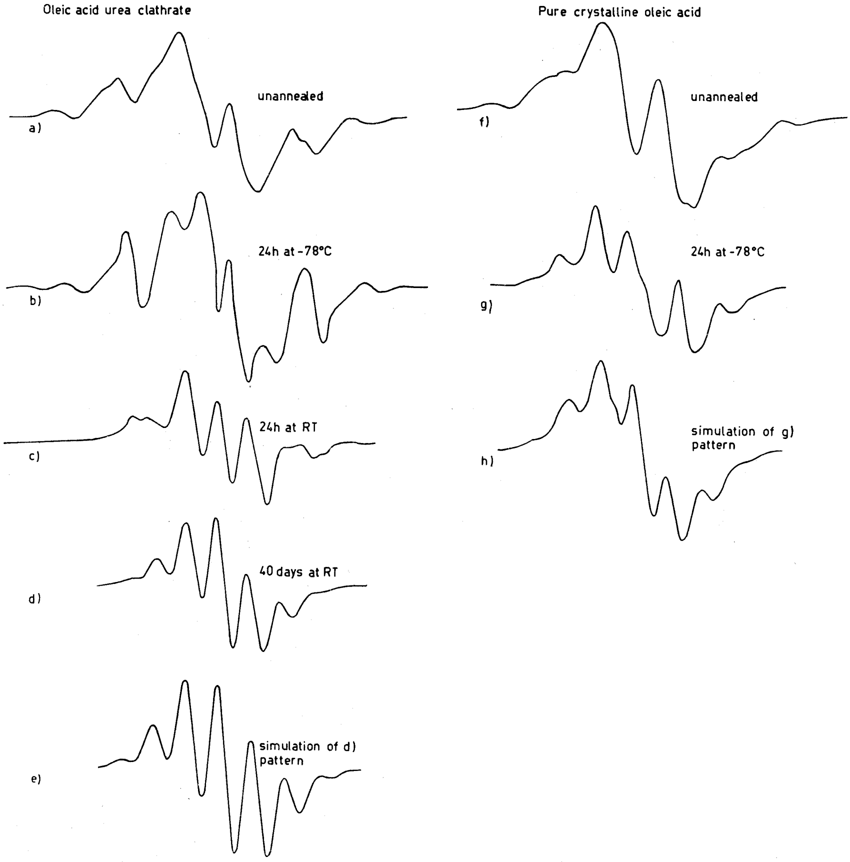

Fig. 4. – Post-irradiation changes in pure crystalline oleic acid and in the oleic acid urea clathrate.

Less clear-cut, however, is the migration toward double bonds of free valences initially located on carbon atoms α to carboxyls. In fact, owing to the large time scale involved, it proved difficult in this case to establish whether the observed *esr* change was caused by the conversion of radicals (II) into allylic radicals, or rather by a difference of thermal stability. Radical transformations into pure crystalline oleic acid are much faster and take place at lower temperature. The initial spectrum (fig. 4 f) can again be interpreted as arising from the superimposition of radical (I) and (II) signals. At — 78° C these radicals are completely transformed into allylic radicals (fig. 4 g, 4 h) in about 24 hrs, and in less than 1 hr at 0° C.

The comparison makes it fairly evident that free valence migration in crystalline oleic acid proceeds essentially through chains of intermolecular transfers, the intramolecular mechanism playing a negligible role.

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