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Electrical conductivity of biological and organic compounds. — Part III. Induced conductivity by gamma irradiation in long chain saturated hydrocarbons, fatty acids and their keto-derivatives

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SEZIONE II

(Fisica, chimica, geologia, paleontologia e mineralogia)

Chimica. — *Electrical conductivity of biological and organic compounds.* – Part III. *Induced conductivity by gamma irradiation in long chain saturated hydrocarbons, fatty acids and their keto-derivatives*(*). Nota di ALBERTO BRECCIA, GIUSEPPINA NUCIFORA e SERGIO DELLONTE, presentata (**) dal Socio G. SEMERANO.

RIASSUNTO. — Misure di conducibilità elettrica e di energia di attivazione, sono state eseguite su alcuni idrocarburi, acidi grassi e chetoderivati ad alto numero di atomi di C allo stato solido.

Ne sono state, inoltre, studiate le variazioni per irradiamento gamma con dose di 0,5 Mrad. Misure sono state eseguite su alcuni campioni allo stato liquido.

INTRODUCTION.

The electrical conductivity of long chain and saturated hydrocarbons and their keto and carboxyl derivatives has not yet been investigated. The literature reports data on activation energy and specific conductivity only for liquid hydrocarbons; i.e. *n*–hexane and *n*–heptane [1, 2, 3].

In the present work solid long chain and saturated hydrocarbons, ketones and fatty acids have been investigated as a function of the molecular weight.

Preliminary results are given on a possible correlation of activation energy and specific conductivity with the chain length of these compounds. Other information was found by comparing the data concerning hydrocarbons, acids and ketones with the same number of C–atoms in terms of structure parameters.

Conductivity after gamma irradiation and conductivity in the liquid state have been investigated to get data on the trapping effects and the trapping distribution [4].

EXPERIMENTAL PROCEDURE.

Hydrocarbons and fatty acids were supplied by the Lachat Co., Chicago. The purity controlled by chromatographic and spectrophotometric techniques was higher than 99.5 %.

Ketones were sintetized by Kipping methods [5], purified by elution into alumina columns and controlled by U.V. and I.R. spectra.

(*) Work carried out with C.N.R. aid in the Laboratorio di Fotochimica e Radiazioni d'Alta Energia – Bologna (Istituto Chimico « G. Ciamician » dell'Università).

(**) Nella seduta del 19 aprile 1969.

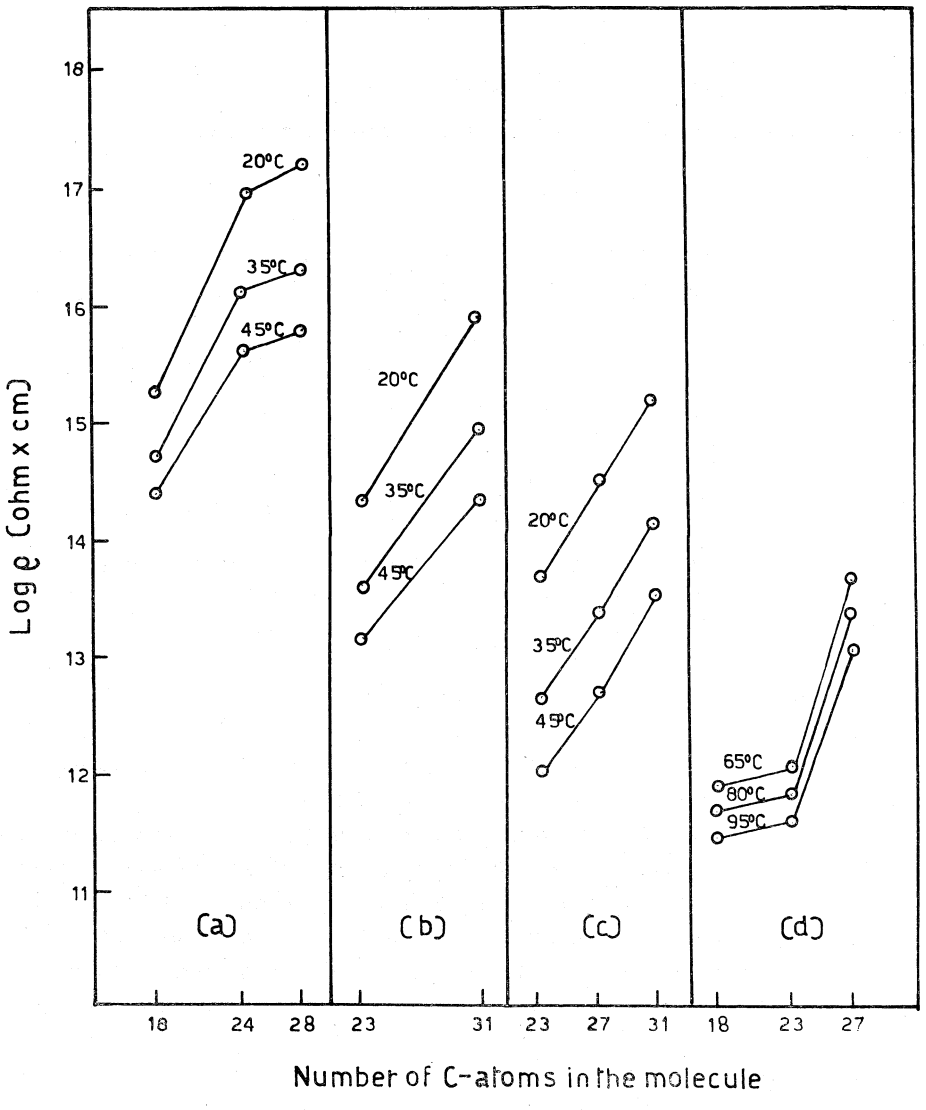

Fig. 1. – Resistivity versus the number of C-atoms in the molecule.
(*a*) Fatty acids; (*b*) Hydrocarbons; (*c*) Ketoderivatives; (*d*) Melted hydrocarbons.

Samples were investigated in the state of compressed powdered form; the dimensions of each specimen were: 0,15 cm in height and 0,785 cm^2 in cross section. Measurements were carried out into a quartz cell with Pt electrodes.

For the liquid state, a teflon cell with Pt electrodes (cross-section = 0,7225 cm^2) was used. Before measuring the conductivity in N_2 atmosphere and at normal pressure, samples were left for 24 h under vacuum (10^{-4} mm Hg) at 45° C to eliminate adsorbed moisture.

The direct voltage source was a Keithley Voltage Supply mod. 246 with regulation between 0 to $\pm$ 3100 V; the current was measured with a Keithley electrometer mod. 610 B and the temperature was controlled with

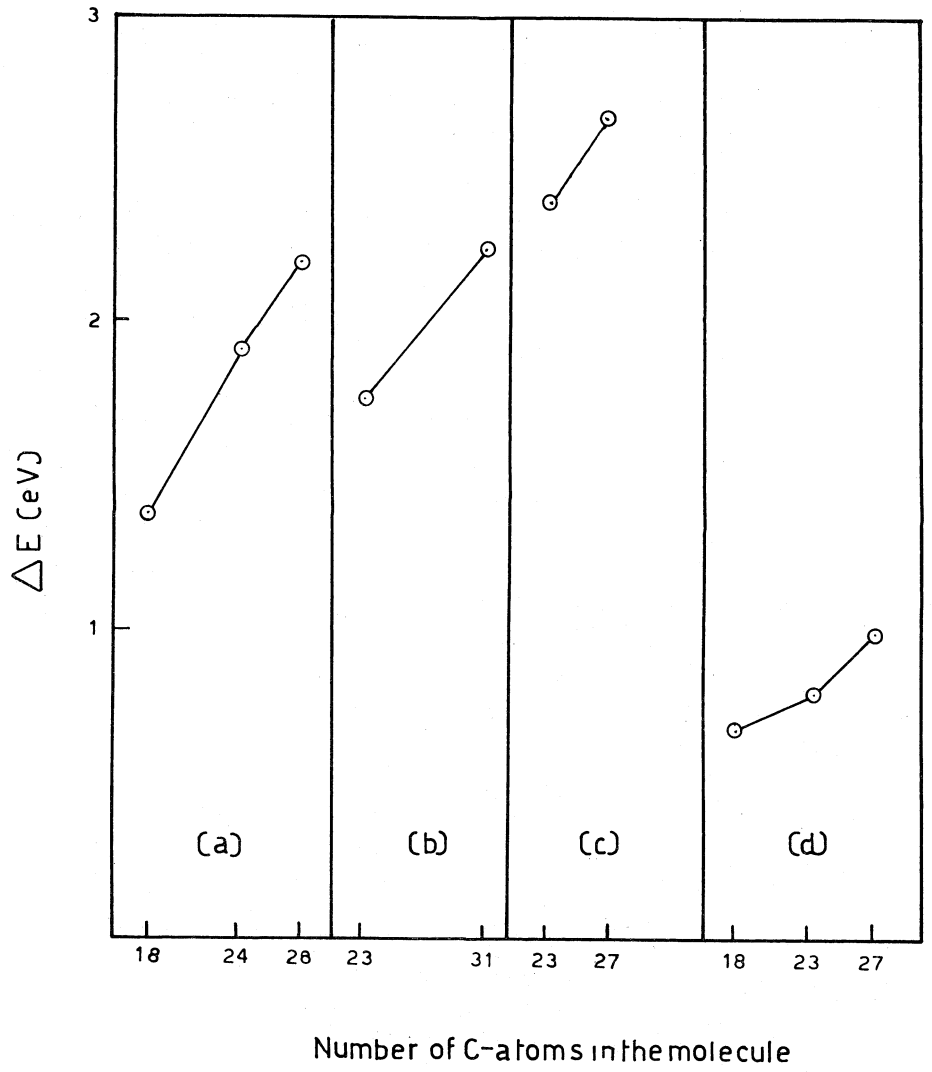

Fig. 2. – ΔE versus the number of C–atoms in the molecule.
(*a*) Fatty acids; (*b*) Hydrocarbons; (*c*) Ketoderivatives; (*d*) Melted hydrocarbons.

a type 4 thermocouple potentiometer of the Croydon Precision Instruments Co. The measurements were made with the equipment previously described [6, 7].

For each compound current-voltage measurements were carried out to determine the voltage to which the samples obeyed Ohm's law. For the acids and the ketones there was linearity up to 700 V; for the hydrocarbons, on the contrary, the ohmic law was respected up 400 V. The applied voltage was consequently 500 and 250 V.

The curves of resistivity at different temperatures versus the number of C–atoms in the molecule are shown in fig. 1.

The values of activation energies versus the number of C–atoms in the molecule are presented in fig. 2.

Results and discussion.

a) Variation of activation energy and resistivity as a function of the chain length.

As showed in fig. 1 it is possible to notice a rather regular increase of resistivity with the chain length both in solid and melted hydrocarbons. Moreover, fatty acids and ketones, whose molecules have a similar structure to that of hydrocarbons, show the same property.

Increasing the number of C–atoms, also activation energies increase, as showed in fig. 2.

b) Comparison of resistivity values of hydrocarbons, ketones and acids with the same number of C–atoms.

Electrical conductivity is proportional to the charge carriers density and to their mobility. Unfortunately, it has not been possible to measure experimentally charge carriers mobility. However, if we admit that charge carriers are electrons or holes, mobility values can be approximately determined by the equation [8]

$$\sigma = e\,\mu N_0 \exp\cdot(-E/2\,kT)$$

where

σ = specific conductivity
e = electron charge in coulombs
μ = mobility in cm^2/V sec.
N_0 = effective density of states in the conductive levels
E = activation energy

Mobility values so calculated are given in Table I.

Tabella I.

Compounds	Mobility ($cm^2V^{-1}\cdot sec^{-1}$)
n–Tricosane	$0{,}21\cdot 10^{-1}$
n–Hentriacontane	0,75
Octadecanoic Acid	$0{,}14\cdot 10^{-5}$
Tetracosanoic Acid	$0{,}11\cdot 10^{-2}$
Octacosanoic Acid	$0{,}16\cdot 10^{-1}$
12–Tricosanone	$0{,}26\cdot 10^{5}$
14–Heptacosanone	$0{,}67\cdot 10^{6}$
16–Hentriacontanone	$0{,}81\cdot 10^{5}$

With the exception of octadecanoic acid, whose mobility value is very low, in all other compounds, charge carriers mobility do not considerably change with the chain length.

While for ketones the mobility is very high, for hydrocarbons and acid it is almost of the same order to that experimentally measured in *n*–hexane by Le Blanc [3].

Considering compounds with the same number of C–atoms, mobility values enable us to understand why ketones show lower resistivity although

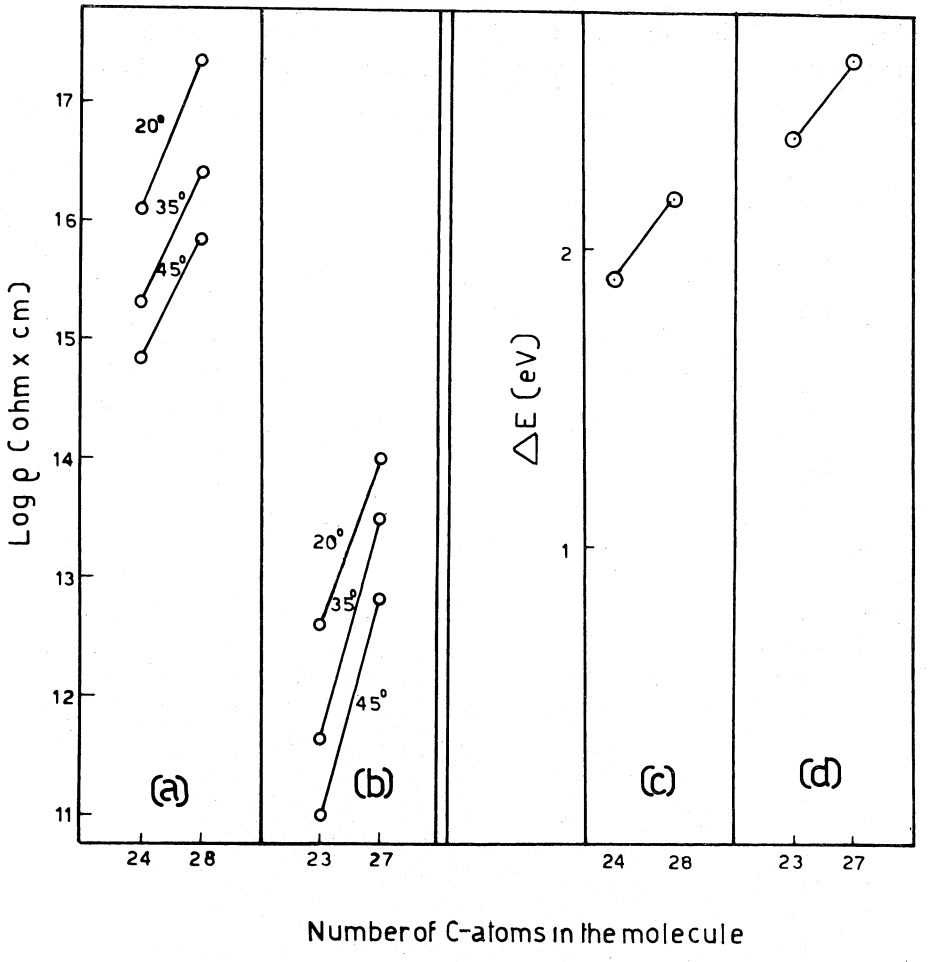

Fig. 3. -- Resistivity and ΔE versus the number of C–atoms in the molecule. (*a*) Irradiated acids; (*b*) Irradiated ketones; (*c*) ΔE of irradiated acids; (*d*) ΔE of irradiated ketones.

the activation energies are higher; but it is difficult to explain why the acids show a resistivity higher than hydrocarbons. Actually the only explanation is in the structure of the fatty acids.

According to Muller [9] the length of *c* axis in the unitarian cell of aliphatic acids is equivalent to two appositely arranged molecules, linked by hydrogen bonds through two carboxyl groups. Therefore, two acid molecules form a dimer and this double chain could explain why the acids show the highest values.

c) Melted compounds.

Very low values of resistivity and of activation energies have been found for three melted hydrocarbons.

The correlation between activation energies and resistivity with the chain length is however the same as in the solid compounds.

A decrease of the order of 10^2 in resistivity for the melted sample $C_{23}H_{48}$ is probably due to the increase of charge carriers due to the disappearance of reticular defects that act as traps in the solid state.

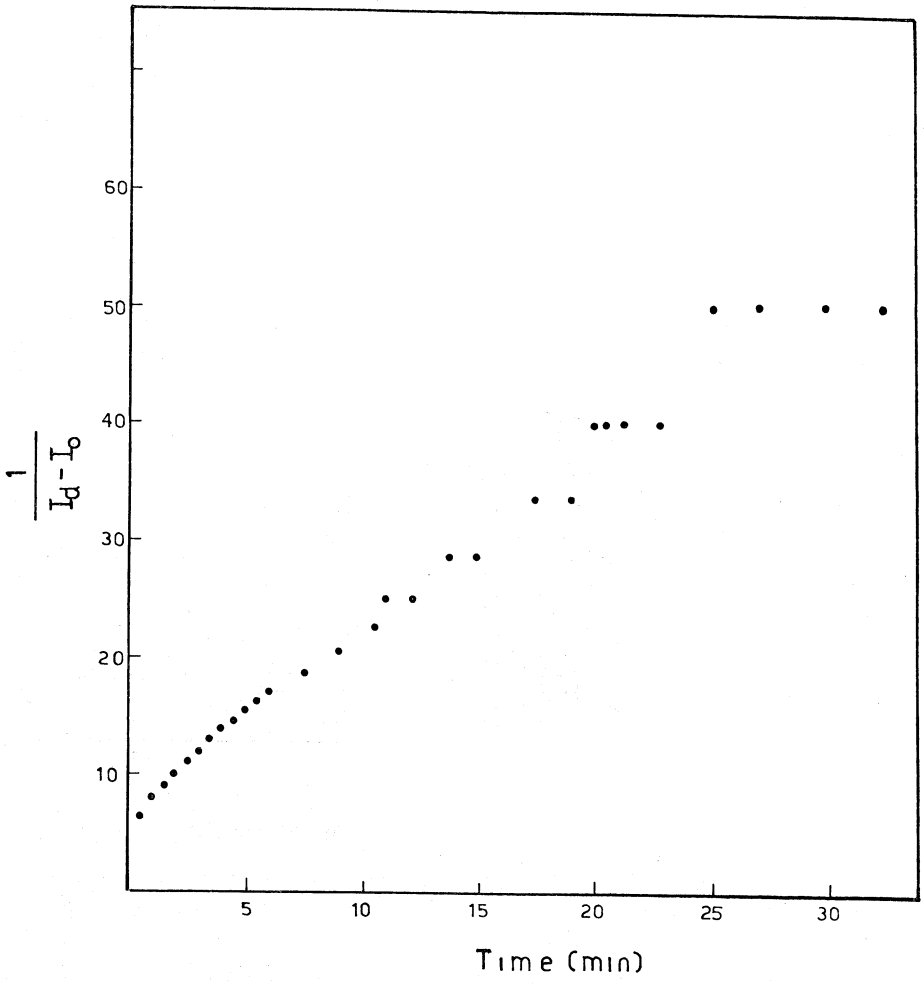

Fig. 4. – Variation of induced current in the compound 14–heptacosanone.

d) Irradiated compounds.

Four samples shown in fig. 3, have been irradiated with 0.5 Mrad. Traps distribution has been studied by the decay of the induced current which was generally higher than the dark one of a factor 10. After 25 minutes induced current reached the normal value of the dark as shown in fig. 4.

Also the radical population disappeared after the same time as shown in fig. 5, while the radicals remain for long time without applying voltage.

This fact suggests a correlation between radicals and induced current. Linearity between $i/I_d - I_0$ [4] versus the time, let suppose a linear distribution of traps in these kind of compounds.

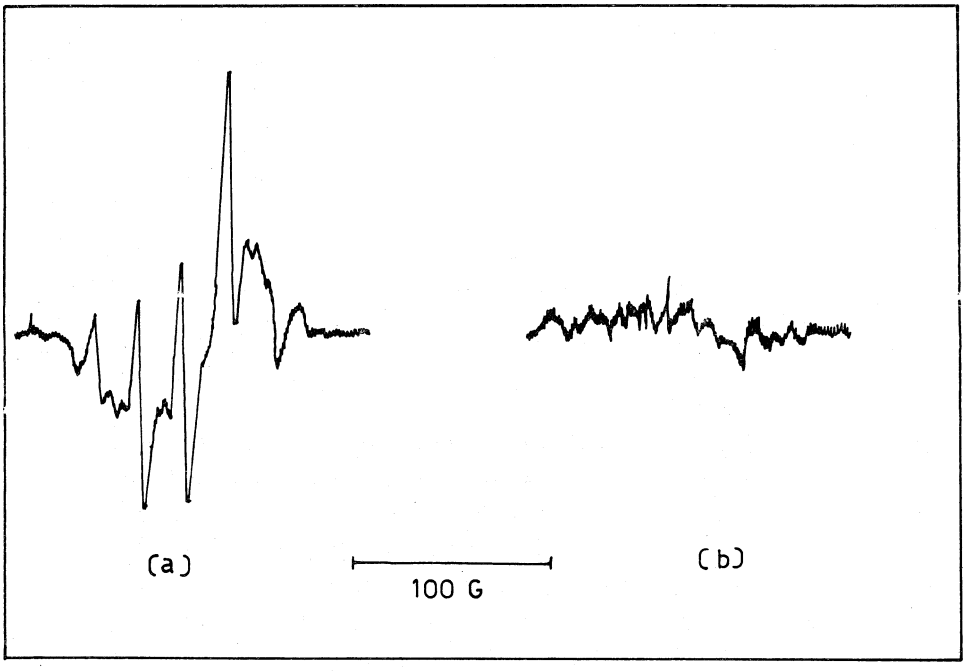

Fig. 5. – EPR spectra of Tricosane.
(a) Immediately after irradiation; (b) After decay.

The resistivity and the activation energy values of the irradiated compounds are presented in fig. 3. The behaviour does not show remarkable difference from the same non irradiated compounds and suggests the formation of the same kind of carriers, probably free electrons by ionization.

REFERENCES.

[1] E. O. FORSTER, « J. Chem. Phys. », *40*, 91 (1964).
[2] C. W. SMITH *et alt.*, *Advances in electronic and electron Physics*, *22*, 1003 (1966).
[3] O. H. LE BLANC, « J. Chem. Phys. », *30*, 1443 (1959).
[4] J. F. FOWLER, « Proc. Roy. Soc. », *A236*, 464 (1956).
[5] F. S. KIPPING, « J. Chem. Soc. », *63*, 453 (1893).
[6] A. BRECCIA, A. M. CRESPI, « Memorie Accad. Patavina », *79*, 351 (1966–67).
[7] A. BRECCIA, R. BUDINI, « Memorie Accad. Patavina », *79*, 359 (1966–67).
[8] A. MANY, E. HARNIK and D. GERLICH, « J. Chem. Phys. », *23*, 1733 (1955).
[9] A. MULLER, « Proc. Roy. Soc. », A *120*, 437 (1928).