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Thermoluminescence of some halogenated halifatic compounds

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Chimica. — *Thermoluminescence of some halogenated halifatic compounds* (*). Nota di Carlo Bettinali (**) presentata (***) dal Corrisp. G. Sartori.

Riassunto. — Vengono riportati i dati ottenuti dalle curve di termoluminescenza (T.L.) di composti organici alifatici irradiati. Vengono riportati i massimi delle glow curves, le energie di attivazione, la composizione spettrale della luce di T.L. emessa, la cinetica del processo, l'effetto della preirradiazione. Vengono suggeriti alcuni meccanismi di ricombinazione dei primari di radiazione.

It is well known that electron trapping occurs in many vitreous and crystalline compounds during irradiation.

Many types of traps have been suggested by different authors: electrons can polarise the medium and give rise to a potential positive well in the solid which acts as an electron trap.

Polar molecules give rise to charge distribution that can trap electrons.

The presence in irradiated substances of molecules or atoms having a high electron affinity can give rise to electron traps: halogen-containing compounds are typical, giving rise as intermediate step of radiolysis to negative atoms or molecules.

The presence in irradiated halogenated organic compounds of e.s.r. and color centers, which disappears when they are optical bleached with visible light, is also well known [1, 2, 3, 4, 5]. In a previous work [5] on the T.L. of CCl_4 I found that: (*a*) The T.L. comes from activating impurities as CS_2 and from irradiation-produced impurities as Cl_2 and $COCl_2$. (*b*) Scavengers like iodine, $CHCl_3$ which suppress the Cl_2 formation suppress also the T.L. (*c*) Optical quenching occurs. (*d*) The T.L. comes from localised process as indicated by the monomolecular shape, from different spectral composition of peaks and from different activation energies. (*e*) Mixing with solvents does not change T.L. peaks of CCl_4 indicating that it is unlikely that transition points are related to T.L. peaks.

The purpose of this research, whose results are here given, is to investigate if T.L. of some halogenated halifatic compounds is related to ionised halogen atoms or molecules formed during low temperature irradiation. That to say, if T.L. arise from a recombination of electrons coming from Cl^- or Br^- acting as electron traps, with positive centers.

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(***) Nella seduta del 12 novembre 1966.

RESULTS.

The measurements have been made with apparatus already described [6]. In Table I are shown obtained results.

In col. *a* are shown examined compounds which are reagent grade of the best purity available, in col. *b* the number and the temperature of the T.L. peaks at 0,2°/sec of heating rate. In col. *c* the relative intensities of T.L.

TABLE I.

COMPOUND THERMOLUMINESCENZE						PRE-IRRADIATION	IRRADIATION COLOR
	Tg	I	E	λ	Kinet.		
a	*b*	*c*	*d*	*d'*	*f*	*g*	*h*
CCl_4	I–160° II–135° III-105° IV–76°	3 3	0,11 0,19 0,58 : :	red (620)	monom	I and II increase	yellow
$CHCl_3$; $C_2H_2Cl_4$ C_2HCl_6	no					no effect	
C_2Cl_4	–130 (Flashes)					no effect	
C_2Cl_6	I–148° II–125° III–105° IV–95°	12 1 2 1	0,20 : : : : 0,46	red	monom	quenching	yellow
CH_2ClCH_2 CH_2O_H	–84	2	0,57	green	monom	no effect	green
CH_2ClCH_2 CH_2Cl	–100	2	0,58	green	monom	no effect	green
$CH_2BrCH_2Br^-$ CH_2Br	–134	2	0,97	red	bimolecular	increase	reddish
$CH_2ClCH_2Cl^-$ CH_2Cl	–131	weak		red	/ /	no effect	
$CH_3(CH_2)^-$ CH_2Cl	–150	2	0,98	red	monom	no effect	
$CH_3CH_{\bar{H}}$ $CHCH_2Br$	no					no effect	yellow
$CH_2BrCH_{\bar{2}}$ CH_3	–130	1	0,32	red	monom	increase	green

The spectral range in which T.L. is observed is from 300 to 680 mμ.

From the experimental data it seems very likely that: in methane and ethane series only compounds that do not contain hydrogen give T.L. (*b*) in propane and butane series all halogen containing compounds give T.L. peaks.

At irradiation dose used (few thousand roentgen) propilic alchool does not give significant T.L.

In col. *d* are given activation energies calculated both by using rising method and by glow curve shape [7, 8]. The values of activation energies change with different compounds in the range from 0,11 to 0,95 ev. The observed peak temperatures do not seem related to transition points.

In col. *d'* is indicated the spectral composition of observed peaks. The light emission consist of a wide band having large maxima from 600 to 650 mμ when indicated by "red" and 500 to 540 mμ when indicated "green".

In col. *f* is indicated the type of kinetic as calculated by glow curve shape and by isothermal decaying curves. The only compound giving an apparent second order kinetic of decay is tribromopropane.

In col. *g* is indicated the preirradiation effect on T.L. peaks. Preirradiation is effective both with u.v. and gamma rays. Differences between the two have been found. The preirradiation has been made at ambient temperature.

Preirradiation gives different results with different compounds: in CCl_4 and bromopropane derivates a strong increase appears, in other compounds no effect or quenching is observed.

In col. *h* are indicated the irradiation colors observed. The preirradiation changes irradiation colors.

To discuss T.L. mechanism the main feature that can be observed from obtained results is that activation energies are lower than 1 ev.

Taking into account that electron affinity of halogen atoms is around 4 ev the observed activation energy values are too low. On the other hand no transition points seem to be correlated to T.L. peaks.

To justify the T.L. emission process, two mechanisms can be suggested:

(*a*) The formed Cl^- can be thermally excited to a higher excited level from which electrons can be transported through exciton band until they reach positive species with which they recombined.

$$^{\bullet}R^+ + (R)_n Cl + Cl^- \rightarrow {}^{\bullet}R^+ + (R)_n + Cl^- + Cl \rightarrow {}^{\bullet}R + (R_n) Cl + Cl + \text{light}$$

(*b*) Formation of Cl_2^- molecules can be invoked. In fact in alkali halogenides irradiated at low temperature this species is present and is formed subsequently to Cl^- formation (11, 12) and disappears at —140°. A like process can occur in the organic medium

$$RCl + h\nu \rightarrow {}^{\bullet}R + Cl^- \rightarrow RCl + Cl^- \rightarrow {}^{\bullet}R + Cl_2^- \; {}^{\bullet}R^+ + Cl_2^- \rightarrow {}^{\bullet}R + Cl_2 + \text{light.}$$

I wish to thank Mr. Diego Molin for his collaboration in the experimental part of the work.

CONCLUSIONS.

In metane and ethane series the compounds having H in the molecules do not give any significant amount of T.L. In other series the presence of a halogen atom increases the T.L. Activation energies found are lower than 1 e.v. and the process is for many compounds a first order recombination.

Preirradiation effect increases the T.L. in some compounds and quenches in others. Two mechanisms can be suggested: one taking into account energy transfer through exciton band, the other one the formation of Cl_2^- molecules.

LETTERATURE.

[1] M. MAGAT, « J. Chem. Physique », *1*, 142 (1966).
[2] R. S. ALGER, T. H. ANDERSON and L. A. WEBB, « J. Chem. Phys. », *30*, 695 (1959).
[3] B. SMALLER and M. MATHESON, « J. Chem. Phys. », *28*, 1169 (1959).
[4] C. CHCHATY, III^d Rad. Res. Congress - Cortina 1966.
[5] C. BETTINALI, « J. Chem. Phys. », 1966 (in press).
[6] C. BETTINALI and G. FERRARESSO, « J. Chem. Phys. », *44*, 2262, (1966).
[7] A. HALPERIN and A. BRANNER, « Phys. Rew. », *117*, 408 (1960).
[8] L. I. GROOSWEINER, « J. Appl. Phys. », *24*, 1306 (1953).