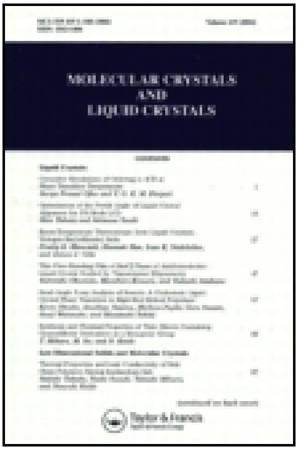

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Laser Induced Degradation and Cluster Ion Formation Studied by Ablative Photodecomposition of Organic Solid Material

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LASER INDUCED DEGRADATION AND CLUSTER ION FORMATION STUDIED BY ABLATIVE PHOTODECOMPOSITION OF ORGANIC SOLID MATERIAL

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Abstract

Photoablative studies of organic solid materials have been carried out with the aim to shed some light on the mechanism of interaction between laser radiation and crystalline structures. The results illustrate two reaction pathways: fragmentation and cluster formation. Fragmentation occurs through a retro Diels-Alder ring-opening process. Clusterization is reminiscent of the crystal structure of the solid, which is dominated by hydrogen bonding.

Keywords: Laser, Degradation, Cluster, Ablation, Triazines

INTRODUCTION

Pulsed laser irradiation of organic solid materials may give rise to a photochemical or thermal transformation within a restricted zone of the target material. A photochemical process occurs only if absorption of the radiation excites the molecules to an upper electronic level that may directly dissociate or may be crossed by a dissociative state. Internal conversion of the absorbed energy to vibrational excitation of the ground state provokes the equivalent of a thermal process within the small area hit by

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** ENEA, Dipartimento TIB C.P. 00044 Frascati, ITALY the laser. The thermal excitation caused by the laser may in turn give rise in the solid to the loss of crystallinity through melting due to the relaxation of bonding forces in the lattice or direct evaporation of the solid constituents to the gas phase without melting.

These two features are of relevant importance for any mechanistic deduction of the reaction. The two alternative explanations are: (a) a chemical process occurring within the solid at various depths or (b) a reaction at the boundary surface between the solid and the gas phase products. The processes may be described as "thermal" or "nonthermal" in nature and in both cases the laser radiation falling on the surface of the organic material produces spontaneous ablation. The time of removal of the solid particles from the surface is of the order of the laser pulse duration as it was estimated from spectroscopic studies of the light emission from the plume. Any reaction occurs in a shorter time[1].

Previous studies on ablation of inorganic solid materials have shown that chemical reactions between the components of the target can take place[2]. Organic solid compounds behave similarly on irradiation by a pulsed laser. The chemical analysis of the material ablated from chlorodiaminotriazines has shown several reaction pathways[3]. The present study will deal with the laser ablation of very simple s-triazines in order to identify the principal products with exclusion of side reactions. The results are compared with those obtained from more complex s-triazines. These compounds are characterized by a crystalline structure with the triazine ring packed through hydrogen bonding.

RESULTS AND DISCUSSION

The photoablative decomposition of solid s-triazines has been performed by a frequency quadrupled Nd-YAG laser (λ=266 nm). The apparatus and procedure have been previously described[2]. Samples of s-triazines were commercial high purity products. The positive and negative ions resulting from the ablation process were analyzed by a time of flight mass spectrometer, and their relative abundances are averaged over several spectra. The solid target used in laser ablation experiments are: 2,4,6 – triazinetriol (cyanuric acid); 2,4,6 – triamino-s-triazine (melamine); 2-chloro-4,6 diamino-s-triazine. Data on more complex triazines containing chloro or methylthio such as 2-chloro-4,6-bis-ethylamino-s-triazine (symazine) and 2-methylthio-4,6-bis–isopropylamino-s-triazine (prometryne) previously studied[3] will be discussed and compared with present results.

A typical mass spectrum of a triazine is shown in figure 1. This figure reports: a) ions at m/z lower than the parent; b) ions at m/z above the parent ion. The ions in figure 1a) are produced from fragmentation of the molecular solid. In the higher mass range reported in figure 1b) two aggregation processes are identified. Clusters of dehalogenated parent molecules of formula $(M-Cl)_n$ and clusters of chlorine atoms with dehalogenated molecules of formula: $Cl(M-Cl)_n$ are observed. It can be noted from the fragments in figure 1a) that a ring opening process takes place i.e. a 4 + 2 bond rupture.

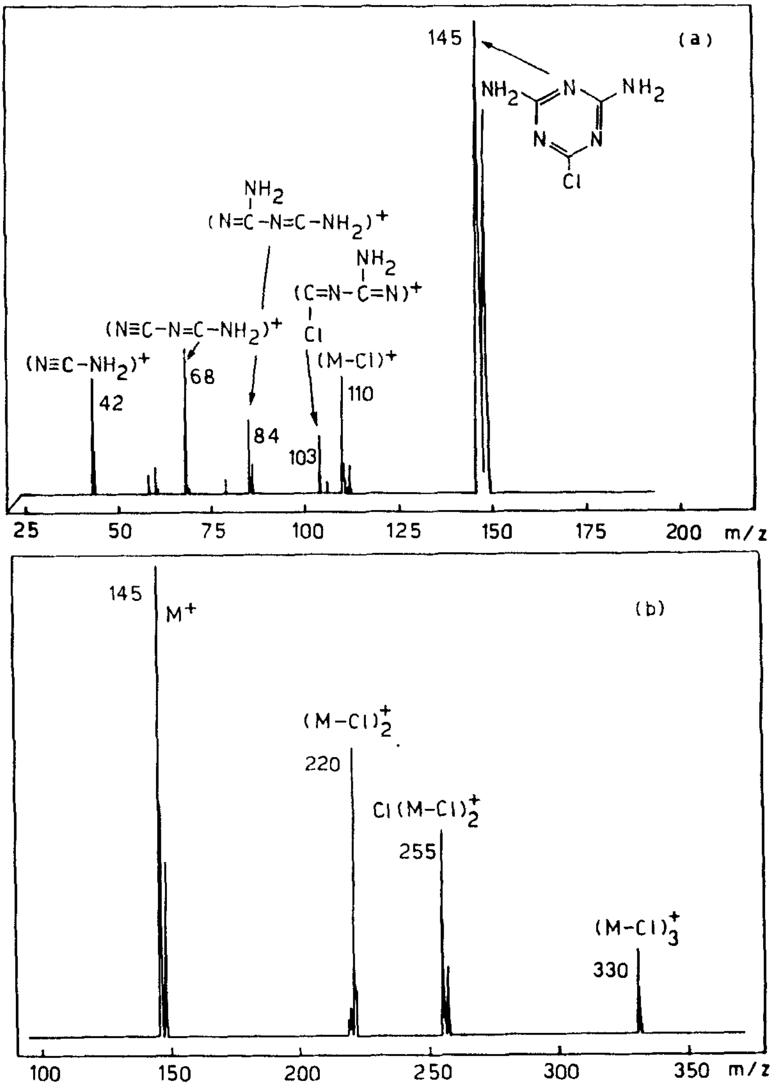
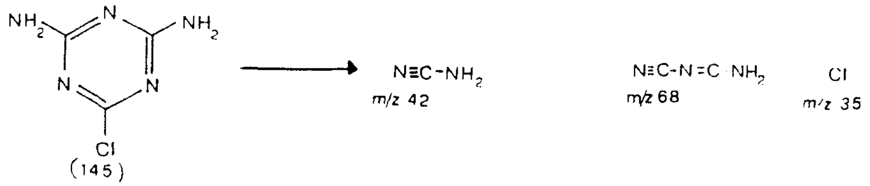


Figure 1: Positive ion mass spectrum of 2-chloro-4,6 diamino-s-triazine: a) fragmentation mass spectrum; b) cluster ion formation.

One of the possible ring opening process is typically the following:



2-chloro-4,6-diamino-s-triazine

This behaviour is common for all compounds examined in this and previous work[3]. Triazine molecules strongly absorb in the UV region at 272 nm and 222 nm with assignment to n->π^* and π->π^* transitions.The wavelength of the frequency quadrupled Nd-YAG laser falls in this range and therefore a photochemical process is feasible. It is difficult to answer why the main process is ring opening rather than side chain loss. Bonding within atoms of the ring or of the substituents to the ring are both strong (100-150 Kcal/mol) and do not justify a preferential rupture. The preferential ring rupture observed may be due to absorption of photons of UV wavelength which excite specific bonds in the ring.

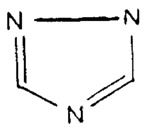
The other pathway of the laser induced process in the solid is formation of aggregates with structures based on the parent molecule. It has been observed that 2-chloro-4,6-diamino, 2-chloro-diethyl-4,6-diamino and 2-methylthio-4,6-diamino-1,3,5 s-triazine form clusters containing ring units of a few parent molecules. Typical clusters observed have m/z corresponding to [M-Cl] and [M-SCH_3] units[3]. Aggregation may occur with molecules that have lost either chlorine or the methylthio group from the ring. The stability of these clusters may be due to hydrogen bonding where nitrogen atoms are the specific sites. It is not clear what role the chlorine or methylthio substituents play in the cluster stabilization. A structural effect due to a steric hindrance may be important. In the very dense plasma produced by the laser, Cl or SCH_3 abstraction may be an important step. It is surprising that structurally simpler compounds such as melamine or cyanuric acid do not produce clusters. The X-ray crystal structure of melamine is built on hydrogen bonding and it could be expected that clusterization would be possible. It may be inferred that our experimental conditions may not favour ablation and condensation of these molecules.

The spectra of the negative ions of all triazines have almost identical trends. Fragments from the triazine ring are the main constituents. Negative ions et m/z 26 and m/z 40 found in the spectra may be assigned to $[C\equiv N]^-$ and $[N=C=N]^-$ respectively. Only the spectra of cyanuric acid and chlorodiamino-s-triazine contain negative ions of the parent molecule. The retro Diels Alder ring openings of cyanuric acid and prometryne yield respectively NCO^- and NCS^- negative ions. The same rupture from the other triazines examined leads simply to carbon-nitrogen fragments.

A strong signal at m/z 66 found in all spectra may be assigned to a linear or a ring structure as follows:

$$[N = C = N = C = N]$$

or



CONCLUSIONS

The results of the present investigation may provide some indications on the phenomema occurring during laser ablation. Volatilization, ionization, and chemical reactions are related to the nature of the organic material interacting with the laser. In a very simplified model laser ablation is characterized by two regions where different processes occur: i) a region of very high temperature (5.000 - 7.000 K) where direct interaction of the laser with the surface takes place; such a zone is characterized by fragmentation and ionization of the parent molecule; ii) a region of relatively low temperature where bulk and molecular evaporation with ionization are the main processes; in this region cluster formation is favoured.

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REFERENCES

1) R. Srinivasan and B. Braren, Chem. Rev. 89, 1303 (1989).

2) A. Mele, D. Consalvo, D. Stranges, A. Giardini-Guidoni, R Teghil, Int. J. Mass Spectrom Ion Proc. 95, 359 (1990)

3) A. Giardini-Guidoni, A. Mele, G. Pizzella, R.Teghil, Org. Mass Spectrom. 26, 779, (1991).