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Effect of Ultraviolet Irradiation on Phase Transformations in HMX Polymorphs

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1,3,5,7-Tetranitro-1,3,5,7-Tetrazacyclooctane, commonly known as HMX in the explosives field, exists in four polymorphic forms.[1] During a study of solid phase transitions in these polymorphs of HMX, utilizing Differential Thermal Analysis, we have found that prior irradiation with 2537 Å light causes the β to δ transformation to occur approximately 15°C below the transition point of unirradiated material. Also, a similar but smaller effect, i.e. a decrease of 5°, is observed after irradiation of β-HMX with 3100–3400 Å light which is in the region of the apparent absorption edge. Previous reports of similar effects were not found in the literature.

Presumably, the four polymorphic forms of HMX are conformational isomers as suggested by Bedard *et al.*,[2] from studies of the IR spectra and electrical polarizations. The literature[3] on the temperature ranges in which the different polymorphs are stable is contradictory. However, the polymorphs prepared by us,[4] starting from purified HMX, have reproducible endotherms obtained by differential thermal analysis. Their transition temperatures are shown in column 2 of Table 1.

For irradiation, about 1 g of the polycrystalline sample was placed in a quartz tubular container that was rotated horizontally by a stirrer to ensure that the sample was uniformly exposed to light. The source of 2537 Å radiation was a low pressure Hg lamp. With this arrangement it was not possible to measure the light intensities precisely. For each run the relative light intensities were

measured with a thermopile placed in the location normally occupied by the sample container. Prior to irradiation the sample container was flushed with nitrogen and stoppered. The transition temperatures, as a function of UV dose, were determined with a Perkin-Elmer Differential Scanning Calorimeter[5] operated at a heating rate of 20° per min and with the sample in an N_2 atmosphere. The transition temperatures were determined from the peak of the endotherm since this procedure appears to be the most accurate. However, the peaks were always symmetrical and when the peak was displaced the onset of the endotherm was displaced by the same amount.

TABLE 1 Effect of UV Irradiation on the Transition Temperatures (°C) of HMX Polymorphs

	Unirradiated	Irradiated with 2537 Å	ΔT
β to δ	201°	186.2°	−14.8°
α to δ	203°	203°	—
γ to δ	184°	182°	−2°

The effect of the UV light on the transition temperature was largest for the β to δ transition. The details are shown in Fig. 1. The maximum decrease in transition temperature, namely 13 to 15°, was produced by prolonged irradiation. X-ray powder patterns were obtained before and after irradiation and after heating above the transition. Comparison with the known patterns[3] shows that the UV irradiations did not produce an observable transition. Upon heating, the δ polymorph was always obtained, i.e. the other forms were never detected. A similar effect was observed for the γ to δ transition but not for the α to δ transition.

Figure 1 shows that the effect of UV irradiation on the transition temperature of β-HMX tends to be reversed for prolonged exposure. This is most clearly demonstrated for the highest light intensities.

An explanation for this may come from a detailed study of the photochemical process.

The irradiation induced change in transition temperature decreases when the irradiated samples are allowed to stand at room temperature. The decrease continues for several days. Separate experiments were done to determine the kinetics of this process.

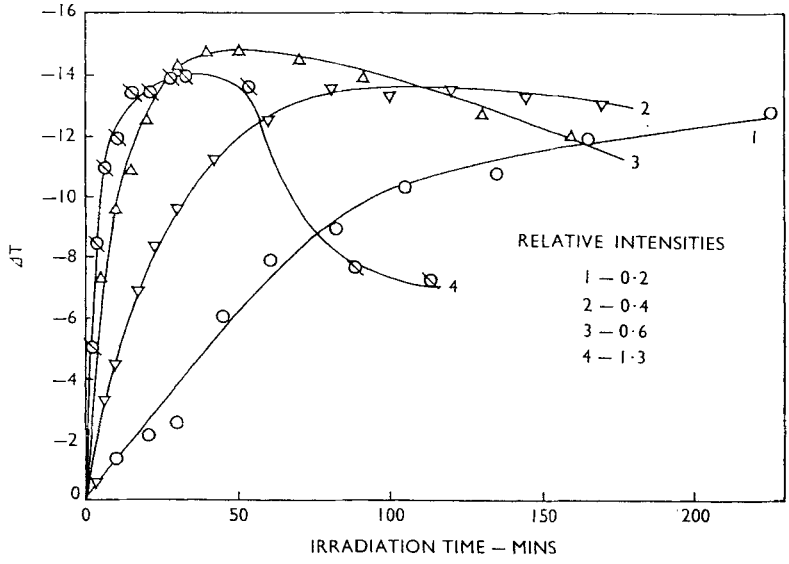

Figure 1. Decrease in $\beta \rightarrow \delta$–HMX transition temperature at a heating rate of 20°/min. as a function of time of irradiation of β-HMX with 2537Å.

The irradiated HMX sample was stored at 130° and its transition point measured as a function of the "annealing" time. The initial ΔT of 14.7° reduced to 6.7° after 16 hr. The kinetic data indicates that the order of the reaction is close to 2, however because of experimental scatter an unequivocal fit cannot be obtained. One possible explanation for the irradiation induced decrease in transition temperature is suggested by earlier work[4] on the photolysis of HMX. When this material is exposed to 2537 Å radiation, N_2, NO, N_2O, CO and CO_2 are the major gaseous products. During one of the measurements described above (curve

3, Fig. 1), the total gas formed during the irradiation that produced the maximum ΔT was found to be 0.36 ml (STP) per gram of HMX. This is equivalent to approximately 0.06% decomposition. The photolysis produces numerous decomposition sites and these may favor nucleation of the new phase produced by heating. However, it is not clear why the presence of additional nuclei should affect the transition temperature. Also, this explanation does not account for the fact that ΔT reaches a maximum and then decreases after prolonged irradiation.

Exposure to UV light is expected to produce free radicals and/or trapped electrons and/or holes. At least one of these species was found using electron spin resonance (e.s.r.) techniques. Before irradiation a very small e.s.r. signal is detectable in HMX samples. After 2537 Å irradiation, sufficient to produce a maximum ΔT, a large e.s.r. signal is observed. It is a single broad line approximately 35 gauss wide with a g-value of 2.003. Annealing at 130° for 4 hr reduces the signal twenty-fold, but the remaining signal is still much larger than the one present before irradiation. These results clearly show that the irradiation produces a paramagnetic species. The species is relatively stable at room temperature and unstable at 130°. During the 4-hr 130° anneal 1.1 ml of gas was released. This is in addition to the 0.36 ml released during irradiation.

Thus the irradiation produces a decrease in transition temperature, a paramagnetic species, and causes photolysis. Both the change in transition temperature ΔT, and the concentration of paramagnetic species are reduced by heating. Both of these processes are accompanied by gas evolution. The gas evolution and e.s.r. data indicate that the photolysis and gas evolution mechanisms are related and probably involve a free radical or trapped charge. Also, the observed change in transition temperature could be related to the same species. However, at the moment, the precise connection is not clear. Furthermore, it is not clear why the α to δ transformation is not affected by radiation or why the γ to δ transformation is only slightly affected. Further studies in progress on the photochemical process should afford an explanation for these effects.

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REFERENCES

1. Cady, H. H., Larson, A. C., and Cromer, D. T., *Acta Cryst.* **16**, 617 (1963).
2. Bedard, M., Huber, H., Myers, J. L., and Wright, G. F., *Can. J. Chem.* **40**, 2278 (1962).
3. Cady, H. H. and Smith, L. C., *Studies on the Polymorphs of HMX*, LAMS-2652, Los Alamos Scientific Laboratory, University of California, Los Alamos (1962).
4. Suryanarayana, B., Graybush, R. J., and Autera, J. R., unpublished work.
5. Watson, E. S., O'Neil, M. J., Justin, J., and Brenner, N., *Anal. Chem.* **36**, 1233 (1964).