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Focused Coherent Radiation (Laser) Induced Degradation of Solid Methylene Blue

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Sir:

It is clear that extensive degradation of chemical structures will take place on exposure of various materials to a focused coherent radiation beam (1). The theoretically achievable temperatures, field strengths, and time intervals involved in such exposures indicate that the experimental observations should correlate with those from other experiments in which energetic carbon atoms, carbenes, and radicals are formed. We have made a study of a series of degradations in which purified, solid methylene blue has been exposed to a focused laser (6943A) beam under a variety of conditions and wish to record observations which appear to place these results in this category.

The source of the coherent radiation for most of the experiments was a pulsed ruby laser (Lear Siegler Inc., Trion Instruments Division, Model LS-1) operated with a modified liquid nitrogen cooling system at 0.4 to 4.0 joule output per flash as measured by a beam splitting, optical diode energy monitor (Lear Siegler, Inc., Trion Instruments Division Laser Energy Monitor, Model M1-2). The laser head was mounted on an optical bench and the beam focused through a lens of 12 cm. focal length. The focal point was located and set optically. Samples (2-7 mg.) of methylene blue (freshly purified by the technique of Bergmann and O'Konski (2), vacuum dried, and stored under nitrogen or helium prior to use) in a one-two mm. diam. pyrex tube were evacuated and flushed with helium three times and then sealed under vacuum. The tube containing the solid was exposed one to twenty-five times at different spots, with the solid at the focal point. The solid was apparently completely volatilized as evidenced by a void at the focal point. The tube and contents were transferred to a device attached to a gas chromatograph (Perkin-Elmer, Model 154D) with a silica gel packing (Perkin-Elmer, J column). The tube was crushed in the device and the gaseous products swept (flow rate 12 cc./min.) into the column at 25°C with helium carrier gas. Peaks were observed at retention times of two minutes, five seconds (nitrogen); two minutes, 55 seconds (methane); sixteen minutes, 15 seconds (ethane); and 86-87 minutes (propane) which correspond to those of control samples of a mixture of nitrogen, methane, and propane. Other columns (dimethyl sulfolane; molecular sieve) gave confirmatory results. The amounts of methane and ethane formed are approximately equivalent, on the basis of peak areas, and the ratio of nitrogen to methane varies but is approximately 1:4. Appropriate controls (samples treated identically in all respects save the actual laser exposure) establish that the nitrogen is a degradation product and not an artifact. The presence of ethylene is indicated by a peak at about 28 minutes. Other unidentified peaks are present in some of the experiments. Experiments made with much higher output energy per flash (up to *ca.* 237 j. per flash and at several intermediate values) show the same products to be formed but with substantially increased amounts of propane. Control "thermal" degradations in an otherwise comparable experiment in which the sample was decomposed in an oxygen torch flame gave distinctively different results with no evidence of propane formation. The laser treated solid (examined in the unopened exposure tube) shows a strongly enhanced (3) ESR signal (Varian Model V4502-13). The residual solid shows an enhanced absorption at 205-210 mμ (Cary Model 14) as compared to untreated methylene blue. The higher intensity (19;51;237 j. per flash) exposures were made using a Maser-Optics ruby laser.

The formation of these products, methane, ethane, and propane, suggests that degradation of the methylene blue structure takes place via formation of energetic atoms, carbenes, and radicals from the dimethylamino groups. The sensitivity of dimethylamino structural units to irradiative degradation has been observed before (4). Such degradations have been regarded as involving radical intermediates (4, 5) and the sensitivity of methylene blue to loss of dimethylamino groups under a variety of conditions is well-authenticated (6). The absorption of methylene blue at, or near, the wave length of the laser radiation is regarded as a non-consequential coincidence and one other (visibly transparent) dimethylamino structure has been degraded. The formation of large quantities of ethane is provisionally attributable to cage effects, also observed in other gas phase reactions (7), and the formation of propane to hydrogen abstraction reactions. Hydrogen

abstraction reactions have been observed in other high temperature or energetic carbon reactions (8-13). Thus, toluene is formed in benzene-carbon reactions (8) and 2-methylpentane is formed from 2-methylpropane (9). Methane has been noted as a product of methylamine-carbon reactions (10) and propane has been formed in methyl radical-ethylene reactions (11) and in ethane reactions (12). It thus appears that the focused laser degradation provides an additional experimental demonstration of reactions involving energetic carbon atoms, carbene, and radicals.

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(15) This research was supported in part by funds from the University Research Committee and the National Aeronautics and Space Administration (Grant NGR-18-002-005); through the loan of laser equipment from the Army Medical Research and Development Command; and through various other sources, notably the Atomic Energy Commission (Contract AT-40-1)-2055), who have provided funds for the instruments, and the City University of New York.

Received January 7, 1966 Louisville, Kentucky