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Mercury Photosensitized Production

Of Trapped Radicals In Organic Glasses At ≤ 77 K¹

by N. Bremer, B. J. Brown, G. H. Morine, and J. E. Willard

Department of Chemistry, University of Wisconsin

Madison, Wisconsin 53706

Solutions of mercury in liquid hydrocarbons ($\sim 5 \times 10^{-6}$ M at 25°C)² may be stabilized in the glassy state by quench cooling in liquid nitrogen at 77 K (Fig. 1)³. When a glassy solution in 3-methylpentane (3MP) is exposed to 254 nm radiation absorbed by the Hg, the intensity of the Hg absorption band diminishes while a broad absorption from 200 nm to 300 nm (Fig. 2) attributable, in part, to 3-methylpentyl radicals appears in parallel with growth in the known ESR signal of the radicals. The rate of growth of the radical concentration approaches zero with continued monochromatic 254 nm illumination (Fig. 3), but increases upon exposure to broad band 200 nm-300 nm light. Exposure of a fresh 3MP-Hg glass sample to the broad band light at 77 K causes continuous growth in the radical concentration with no plateau, many radicals being produced for each Hg atom present (Fig. 4). These observations indicate that a species formed in a primary or secondary act following photoactivation of the Hg by 254 nm light (e.g. HgH, HgR or HHgR) absorbs in the broad band region and is decomposed, liberating Hg which again absorbs 254 nm photons and produces more radicals. No ESR signal from the intermediate has been found, indicating that it is not paramagnetic or that the spectrum is too broad to detect.

The initial rate of radical production by illumination of a fresh 3MP-Hg sample is directly proportional to the light intensity. At

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plateaus of the type of Fig. 3, the ratio of radicals to Hg atoms which have disappeared may be greater than unity and it increases with the light intensity, but to a power less than first order. This seems to imply that the initially formed intermediate absorbs 254 nm to regenerate Hg (e.g. $\text{HgH} \xrightarrow[254]{h\nu} \text{Hg} + \text{H}$) in competition with a reaction which forms a species with relatively low extinction coefficient for 254 nm (e.g. $\text{HgH} + \text{R}\cdot \rightarrow \text{HHgR}$), which is decomposed at other wavelengths of the broad band light (e.g. $\text{HHgR} \xrightarrow{h\nu} \text{Hg} + \text{RH}$).

Illuminations with the broad band light at 5 K do not produce continuing radical growth as at 77 K, but rather lead to a steady state concentration at ~ 0.2 radicals per Hg atom (Fig. 4). This may be attributed to concerted formation within the low temperature parent cage of a compound with the properties attributed above to HHgR, coupled with an ability of the low temperature matrix to deactivate the HHgR without decomposition when it is activated by a photon from the broad band source. At 23 K the plateau is higher than at 5 K, while at 58 K continued growth occurs, though at a lower rate than at 77 K. Thermal decay of the radicals produced by the photosensitization is only a few percent per hour at 77 K and is undetectable over hours at the lower temperatures studied.

These studies indicate: 1) energy transfer from $\text{Hg}(6^3\text{P}_1)$ atoms to molecules in a hard organic glass inducing bond rupture as in the gas⁵ and liquid phases⁵; 2) a new method of producing trapped radicals for study in glassy matrices; 3) a means of trapping intermediates from Hg photosensitization reactions which may in further investigations assist in identifying them and their reactions; 4) a potential source

of information on the kinetics of radical-radical reactions in radical clusters in solids; 5) the possibility of false interpretation of photochemical results in condensed systems containing unsuspected Hg as a contaminant.

All experiments were made with purified degassed reagents; optical measurements used a 5 cm light path; radical concentrations were determined from the double integral of the first derivative ESR spectrum.

References

1. This work has been supported in part by the U. S. Energy Research and Development Administration under Contract No. AT(11-1)-1715 and by the W. F. Vilas Trust of the University of Wisconsin.
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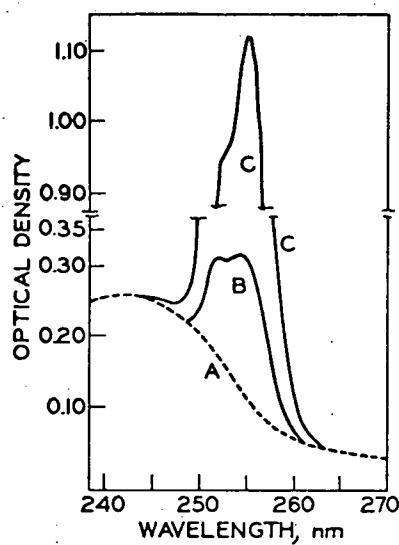


Fig. 1. Spectra of Hg in 3MP glass at 77 K (5-cm pathlength in two 2.5-cm² quartz cells): (A) spectrum of cell walls, 3MP is transparent in this region; (B) 3MP saturated with Hg at 25°C and quenched to 77 K; (C) 3MP saturated with Hg at ~55°C and quenched to 77 K.

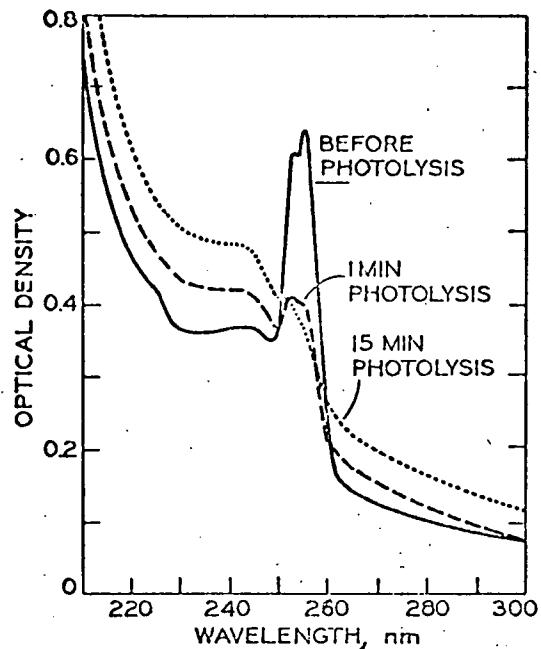


Fig. 2. Spectra of 3MP-Hg glass at 77 K at different times of illumination with 200 nm-300 nm medium pressure Hg lamp.

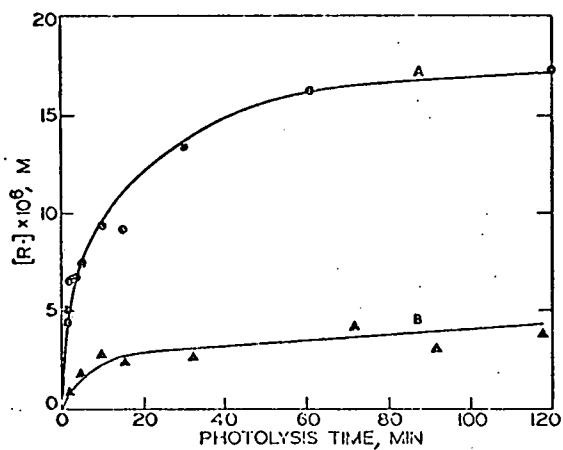


Fig. 3. Concentration of trapped radicals, measured by ESR, as a function of time of illumination of 3MP-Hg glass at 77 K with 254 nm light from Vycor low pressure Hg lamp. Curve A, 4.1×10^5 ergs cm⁻² sec⁻¹; Curve B, 3.7×10^4 ergs cm⁻² sec⁻¹.

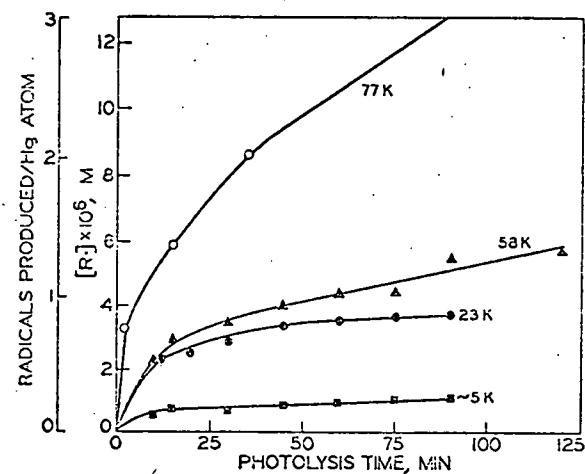


Fig. 4. Concentration of trapped radicals, as a function of time of illumination of 3MP-Hg glass at 77 K, 58 K, 23 K and 5 K with 200 nm-300 nm light from medium pressure Hg lamp.