Resonance Raman bands have also been observed in the TR^3 spectra of hemoglobin ligation reactions which cannot be directly identified with either ligated forms of Hb or Hb itself. The bands may signal the presence of conformationally distinct forms of Hb present only as reaction intermediates.

FLUORESCENCE SPECTROSCOPY OF SUBPICOSECOND STATES IN LIQUIDS

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Experiments with synchronized laser pulses have allowed the observation of fluorescence from weakly emitting states, populated by a consecutive two-photon process. By utilizing different experimental degrees of freedom we are able to obtain fundamental new information about the relaxation properties of electronically excited states of aromatic species. A scan of the emission spectra from upper states and their dependence on excitation wavelengths has furnished evidence of spectral hole-burning. Measurements of the absolute intensities of these spectra give rise to decay time estimates which agree very well with those based on the linewidths of fine structure observed in these low-quantum-yield spectra.
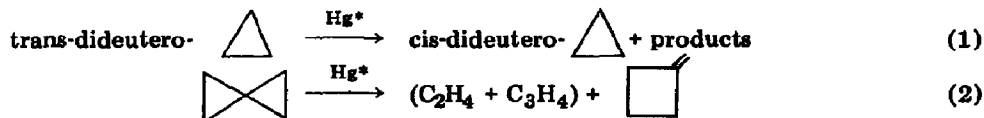
Monitoring the upper state fluorescence intensity as a function of relative excitation pulse arrival time allows an extension of these principles to the direct study of singlet lifetimes longer than about 10^{12} s. We report the first direct measurements of several important photochemically active aromatic species, including acridine, quinoxaline and 9-fluorenone.

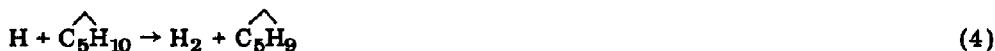# THE MERCURY PHOTOSENSITIZED REACTIONS OF CYCLOALKANES

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The interactions of Hg $6(^3P_1)$ (Hg*) with the cycloalkanes have been the subject of many investigations [1]. A controversy over the major primary mode of reaction of Hg* with cyclopropane concerned the occurrence of C—C (excited molecule) or C—H bond cleavage. This controversy has been settled only recently [2 - 4]. Thus, for the three-membered ring compounds, the major primary interaction leads to the cleavage of a C—C bond, followed by molecular rearrangement or ring closure to the original form:

$$\text{trans-dideutero-} \quad \triangle \quad \xrightarrow{\text{Hg*}} \quad \text{cis-dideutero-} \quad \triangle + \text{products} \qquad (1)$$

$$\bowtie \quad \xrightarrow{\text{Hg*}} \quad (C_2H_4 + C_3H_4) + \quad \square \qquad (2)$$

The sum of the quantum yields of ethylene (or allene) and methylenecyclobutane was 0.5, independent of substrate pressure.

For the larger ring cycloalkanes, the interaction with Hg* leads primarily to C—H cleavage [1]. Gunning and his coworkers [5] have studied the mercury photosensitized reactions of cyclopentane in detail. They proposed the following mechanism

$$\widehat{C_5H_{10}} + Hg^* \rightarrow H + \widehat{C_5H_9} + Hg\ 6(^1S_0) \tag{3}$$

$$H + \widehat{C_5H_{10}} \rightarrow H_2 + \widehat{C_5H_9} \tag{4}$$

$$2\widehat{C_5H_9} \rightarrow \widehat{C_5H_{10}} + \widehat{C_5H_8} \tag{5}$$

$$2\widehat{C_5H_9} \rightarrow (\widehat{C_5H_9})_2 \tag{6}$$

$$H + \widehat{C_5H_8} \rightarrow \widehat{C_5H_9} \tag{7}$$

to account for the major products and their yields as a function of reaction time. Extrapolation to zero reaction time, with very pure substrate, gave $\Phi(H_2) = 0.8$, $\Phi(C_5H_8) = 0.4$ and $\Phi((C_5H_9)_2) = 0.4$, indicating a loss of 20% of the Hg* formed. Part of this apparent "loss" is due to the value of $\Phi(H_2)_{propane}$ used in the actinometric determinations [6]. This value, which is now considered to be 0.58 instead of 0.50, can be used to revise $\Phi(H_2)_{cyclopentane}$ to 0.92.

The Hg* photosensitization of cyclopentane was studied as a function of reaction time at 28 ± 2 °C and 106 ± 1 Torr substrate pressure. The intensity of the 2537 Å resonance line was 7.2×10^{15} photons s^{-1}. From the cell geometry, one calculates that this intensity would lead to disappearance of 0.15% of the cyclopentane per minute if $\Phi(H_2)$ is unity. Plots of $\Phi(H_2)$ and $1/\Phi(H_2)$ are given in Fig. 1 as a function of reaction time. Part of the discrepancy (8%) remaining between the present work and the earlier work by Stock and Gunning [5] could be due to the lower light intensity used in the present study.
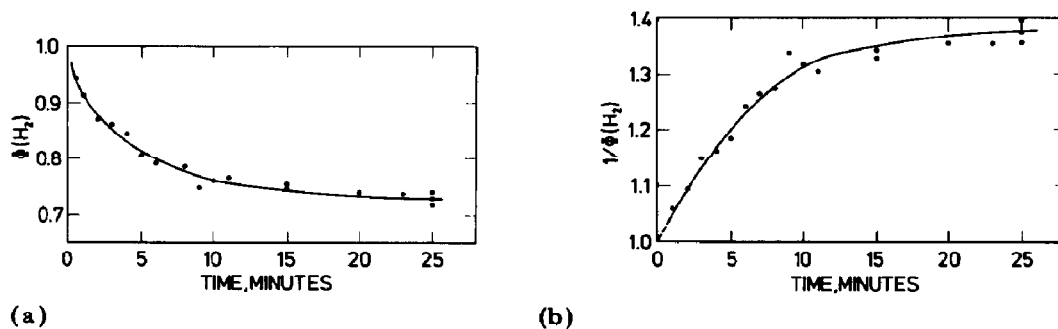

(a)   (b)

Fig. 1. Plots of (a) $\Phi(H_2)$ and (b) $1/\Phi(H_2)$ as a function of reaction time.

In conclusion, it is now apparent that, within experimental error, all of the Hg* atoms react with cyclopentane to give C—H bond cleavage. "Olefinic-type" quenching, observed for the cyclopropanes, does not occur.

1 See the excellent review by R. J. Cvetanovic, Prog. React. Kinet., 2 (1964) 39.
2 D. W. Setser, B. S. Rabinovitch and E. G. Spittler, J. Chem. Phys., 35 (1961) 1840.
3 G. R. De Maré, L. G. Walker, O. P. Strausz and H. E. Gunning, Can. J. Chem., 44 (1966) 457.
4 O. P. Strausz, P. J. Kozak, G. N. C. Woodall, A. G. Sherwood and H. E. Gunning, Can. J. Chem., 46 (1968) 1317.
5 R. J. Stock and H. E. Gunning, Can. J. Chem., 38 (1960) 2295; 42 (1964) 375; and references cited therein.
6 Y. Rousseau, Ph. D. Thesis, Univ. of Alberta, 1963;
   T. L. Pollock, Ph. D. Thesis, Univ. of Alberta, 1971.