

### Short Communication

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#### An estimate of direct N—H bond cleavage in the photolysis of indole derivatives

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(Received May 12, 1977)

A recent investigation of indole photolysis in cyclohexane [1] reported a quantum yield of 0.05 for direct photolytic cleavage of the N—H bond to form radicals and H atoms. In aqueous solution radical production may result from either photoionization, with a quantum yield of about 0.10 [2], or direct N—H bond cleavage. Feitelson [3] found no evidence for the latter process in the photolysis of indole and 3- $\beta$ -hydroxyethylindole. In view of a recent suggestion [4] that radical production may substantially exceed electron production in the photolysis of N-acetyl-L-tryptophanamide (NATA), it became important to re-evaluate the contribution of direct N—H bond cleavage to radical production. The experiments reported here provide an estimate of the relative importance of photoionization and N—H bond cleavage in aqueous solutions.

The experimental details are identical to those described earlier [5]. Aqueous solutions containing  $2 \times 10^{-5}$  M NATA or 5-methoxyindole and 0.1 M isopropanol (ROH) were photolyzed at pH 3 and pH 9. These compounds contain no ionizable groups in this range and therefore pH changes should not affect the primary process. Excitation wavelengths of 254 nm and  $\lambda > 290$  nm were chosen to examine the role of  $^1L_a$  and  $^1L_b$  states in these processes. At 254 nm NATA absorbs primarily into the  $^1L_a$  band, while both the  $^1L_a$  and  $^1L_b$  bands are produced at  $\lambda > 290$  nm. In 5-methoxyindole these bands are sufficiently resolved [6] to permit excitation exclusively into the  $^1L_b$  band at  $\lambda > 290$  nm. Furthermore, since 5-methoxyindole has been shown not to form solvent exciplexes [7], the participation of solvent in the photoionization process should differ markedly from that for other indoles.

At pH 3 electrons from photoionization are quantitatively scavenged by H<sup>+</sup> and converted to H<sub>2</sub> which was analyzed chromatographically.



TABLE 1

Compound	$\lambda_{\text{excitation}}$	$\text{H}_2$ ( $\mu\text{mol min}^{-1}$ )		$\text{H}_2(\text{pH } 9)/\text{H}_2(\text{pH } 3)$
		pH 3 <sup>a</sup>	pH 9 <sup>b</sup>	
NATA	254 nm	0.030 $\pm$ 0.001	0.0003	0.010
NATA	>290 nm	0.0035 $\pm$ 0.0001	0.00005	0.014
5-methoxyindole	>290 nm	0.025 $\pm$ 0.001	0.0004	0.016

<sup>a</sup>Error limits are the deviation from the mean for duplicate runs.

<sup>b</sup>Single determinations; the estimated uncertainty, based on standards of similar quantities of  $\text{H}_2$ , is  $\pm 20\%$ .

Hydrogen atoms from direct NH bond cleavage also participate in reaction (2), so the  $\text{H}_2$  yield measures both photoionization and NH bond cleavage in acid solution. At pH 9  $e_{\text{aq}}^-$  disappears by reaction with ground state indole rather than with  $\text{H}^+$ . Consequently, the  $\text{H}_2$  yield in basic solutions is a measure of NH bond cleavage only.

The rate of  $\text{H}_2$  production was found to be independent of time up to about 20% indole decomposition. The rates reported in Table 1 were obtained at indole decompositions less than or equal to 5%.

Uranyl oxalate actinometry [8] of the 254 nm source by the method of equivalent optical density permitted calculation of a quantum yield of 0.13 for  $\text{H}_2$  production at pH 3 in good agreement with  $\phi(e_{\text{aq}}^-) = 0.10$  estimated for tryptophan photolysis at 265 nm [2]. Direct N—H bond scission, therefore, has a quantum yield of only 0.001 - 0.002 under these conditions. These yields are too small to determine differences between the  $^1L_a$  and  $^1L_b$  states except to note the qualitative similarity in their photoprocesses. The different exciplex forming abilities of the two indoles, however, do not, within experimental error, alter the ratio of photoionization to direct dissociation, suggesting that a specific solvent interaction is not required for either process. These results extend the observations of Feitelson [3] to additional indoles and experimental conditions. Direct N—H bond cleavage is a negligible source of radicals in the photolysis of aqueous solutions of indole derivatives at wavelengths greater than or equal to 254 nm.

### Acknowledgment

This work was supported by NSF Grant CHE-73-04592.

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