Tetrahedron Letters No. 19, pp 1661 - 1664, 1977. Pergamon Press. Printed in Great Britain.

PH DEPENDENT QUANTUM YIELD IN THE PHOTOCYCLIZATIONS OF N-CHLOROACETYLDIMETHYLAMINOPHENETHYLAMINES. USE OF 1,3-DIMETHYLURACIL AND CYCLOHEPTA-1,3-DIENE AS SIMPLE AND CONVENIENT ACTINOMETERS FOR 2537 Å RADIATION

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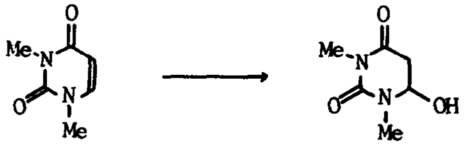
(Received in Japan 14 March 1977; received in UK for publication 28 March 1977)

Among many chemical actinometers,[1] potassium ferrioxalate is most widely used because of its high sensitivity in a wide range of wavelength, viz., the blue region of the visible spectrum as well as the uv region.[2] This feature, however, sometimes causes serious disadvantages. Thus the actinometer must always be shielded from laboratory lights even in the photoreactions proceeding by uv lights below 300 nm, and is so sensitive as to be useful only for short time irradiations. In the course of a study on the intra- and inter-molecular photoreactions between electron-rich aromatics and chloroacetamides,[3] which proceeded smoothly but sometimes not so efficiently by irradiation with a low pressure mercury lamp (practically monochromatic at 2537 Å), it became desirable to have a more convenient actinometer. We wish to report here a potential utility of 1,3-dimethyluracil (DMU) and cyclohepta-1,3-diene (CHD)[4] as secondary chemical actinometers for the 2537 Å light and their application for the quantum yield measurements in the photocyclizations of N-chloroacetyldimethylaminophenethylamines (I, II).[5]

It is well known that the uv absorption of uracils disappears by irradiation with 2537 Å light in water mainly because of their conversion to the corresponding monohydrates.[6] Many, but somewhat discrepant data for the quantum yield of the photohydration of DMU has been reported,[7] and we have now reexamined.

Taking into account practical use, 0.55 mM aqueous solution of DMU [λ_{max} 266 nm (ε 8900)] were irradiated with a 60 W low pressure lamp on a merry-go-round apparatus and the quantum yield for the disappearance of DMU was determined relative to 6-12 mM potassium ferrioxalate solutions as 0.0130 ± 0.0007.[9] Because the quantum yield is quite low, this DMU actinometer will be useful for photoreactions with low efficiency.

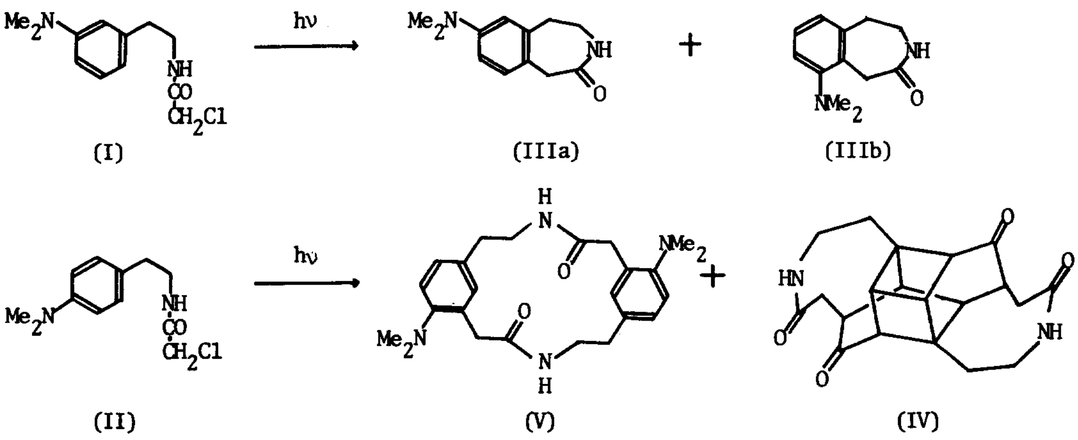


As another actinometer for more efficient photoreactions, CHD was next examined. When CHD was irradiated with 2537 Å light, its diene chromophore disappeared mainly by the formation of bicyclo[3.2.0]hept-6-ene through a disrotatory electrocyclic reaction.[11] Ethanol solution (20 mM) of CHD [λ_{max}^{EtOH} 246 nm (ε 7750)][12] were irradiated under similar conditions and the quantum yield for the disappearance of CHD was determined to be 0.48 ± 0.01.[14] These two actinometers can be used properly according to the efficiency of photoreactions.

Recently we reported that N-chloroacetyldimethylaminophenethylamines (I, II) cyclized to benzazepinones (IIIa, IIIb), the cage compound (IV) and the diaza[5.5]metacyclophane (V) on irradiation with 2537 Å light. Intramolecular photoreactions affording III and IV[15] proceeded smoothly even in strong acidic solution as well as in alkaline solution, while the yield of V obtained intermolecularly was strongly depressed by acid.[5] In order to interpret these photoreactions, their quantum yields at various pH have been measured relative to the above actinometers.

Equal aliquots of each solution of I (10 mM) in 50% aqueous acetonitrile, the 0.55 mM DMU and/or the 20 mM (or 10 mM) CHD actinometers were irradiated on the merry-go-round with the 60 W low pressure lamp. Quantum yields for disappearance of I and formation of III were plotted against pH as shown in Fig. 1. Similarly quantum yields in the photolysis of II were also plotted in the same figure.[17] The formation of III and IV is little affected by the change in pH, whereas the formation of V and the disappearance of II show sigmoidal character with the inflection point roughly at the ground state pKa (5.21)[18] of dimethylaniline.

This type of photocyclizations is known to occur only in electron-rich aromatic compounds involving an exciplex in a broad sense.[3] In acidic solutions, therefore, the exciplex formation must occur after deprotonation from the singlet excited anilinium cation moiety.[19] Because of no effect of pH, both the deprotonation and the intramolecular exciplex formation must be quite rapid processes. On the other hand, the intermolecular exciplex formation, which cannot exceed the diffusion controlled limit, competes and is overcome with the quenching of the deprotonated singlet excited state by proton.[21]



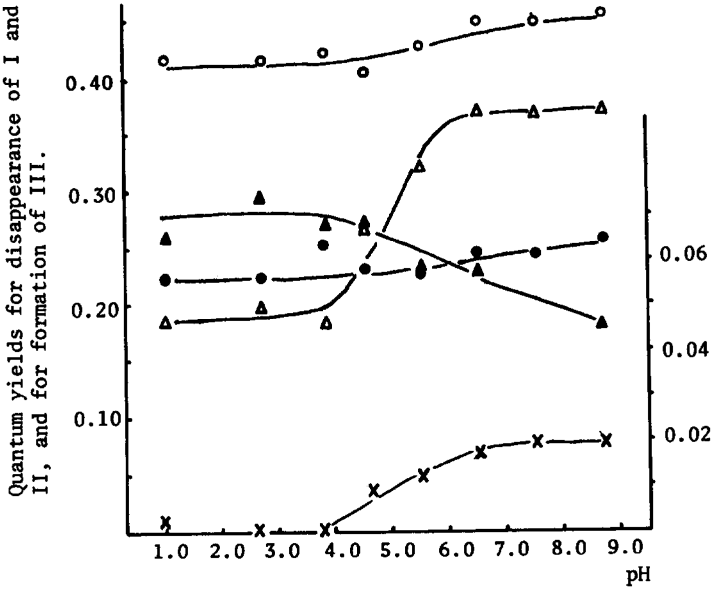
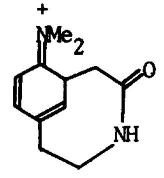
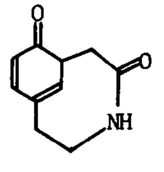


Fig. 1. Quantum yields in the photolysis of I and II:
Disappearance of I (—o—) and II (—△—);
Formation of III (—●—), IV (—▲—) and V (—x—).



(VI)



(VII)

Detailed kinetics of the photoreaction of dimethylaniline and methyl monochloroacetate as a model experiment based on fluorescence quenching and reaction quantum yields will be reported soon.

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1) J. G. Carvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966, p 780; S. L. Murov, "Handbook of Photochemistry," Marcel Dekker, New York, N. Y., 1973, p 119.

2) C. G. Hatchard and C. A. Parker, Proc. Roy. Soc. (London), A 235, 518 (1956).

3) S. Naruto and O. Yonemitsu, Tetrahedron Lett., 3399 (1975); Y. Okuno and O. Yonemitsu, Heterocycles, 4, 1371 (1976), and references cited therein.

4) Both compounds were chosen for the following reasons. (1) They are commercially available. (2) Under appropriate conditions, the sole photoreaction occurs nearly quantitatively. (3) Preparation and measurement of actinometer solutions are easy to perform. (4) They have λ_{max} near to 2537 A. (5) Because they have no absorption above 300 nm, all experiments can be run without shading.

5) N. Numao and O. Yonemitsu, Heterocycles, 4, 1095 (1976).

6) A. D. McLaren and D. Shugar, "Photochemistry of Proteins and Nucleic Acids," Pergamon, Oxford, 1964, p 174.

7) Very recently, Burr et. al. reported that the quantum yield was a sigmoidal function of the DMU concentration in the range 0.1-1.0 mM and the value at 0.5 mM was 0.0068.[8]

8) J. G. Burr, C. Gilligan, and W. A. Summers, *Photochem. Photobiol.*, **24**, 483 (1976), and references cited therein.

9) To ensure that the DMU and actinometer solutions absorbed equal amounts of the 2537 Å radiation, and to avoid too high concentration because of the quite low quantum yield of the DMU disappearance, the concentration of DMU was made up to 0.55 mM (the optical density at 2537 Å; ca. 3.5). Equal aliquots (5 ml) of each of the DMU solution and the 6 mM (or 12 mM) ferrioxalate solution in 14 x 150 mm quartz test tubes were irradiated with the 60 W low pressure lamp (Eikosha PIL-60) on the merry-go-round apparatus (Rayonet MGR-500) [$(2.88 \pm 0.10) \times 10^{-6}$ einstein/min]. The disappearance of DMU measured by the decrease in absorbance at 266 nm at time intervals followed pseudo zeroth-order kinetics in the range that transmission of the incident light was negligible (at least up to 50% conversion). The quantum yield of 0.3 mM DMU solution was measured similarly to be 0.0126 ± 0.0003 (less than 10% conversion). The quantum yield of the 0.55 mM DMU was also measured in 10 mm quartz uv cells by irradiation with a monochromatic light from a spectroirradiator (JASCO-FA) relative to the ferrioxalate actinometer and a calibrated thermocouple: Wavelength, average light intensity, quantum yield; 254 nm, 1.55×10^{-7} einstein/min,cm^2, 0.013 ± 0.001; 266nm, 2.69×10^{-7} einstein/min, cm^2, 0.0124 ± 0.0002. These values are close to Wang's data,[10] not to Burr's data.[8]

10) S. Y. Wang, *Photochem. Photobiol.*, **1**, 135 (1962).

11) W. G. Dauben and R. L. Cargill, *Tetrahedron*, **12**, 186 (1961); O. L. Chapman, D. J. Pasto, G. W. Borden, and A. A. Griswold, *J. Am. Chem. Soc.*, **84**, 1220 (1962).

12) CHD was synthesized from cycloheptatriene by K-reduction in liq NH$_3$ according to the published procedure[13] and purified through twice distillations on an auto annular spinning band distillation system (Perkin-Elmer, Nester-Faust NFA-200). CHD (97%) is also available commercially.

13) K. Hafner and W. Rellensmann, *Chem. Ber.*, **95**, 2567 (1962).

14) The decrease of the chromophore of CHD at 246 nm also follows pseudo zeroth-order kinetics at least up to 50% conversion, though the quantum yield for the disappearance of CHD depends slightly on its concentration: Concentration of CHD, quantum yield; 10 mM, 0.46 ± 0.01; 20 mM, 0.48 ± 0.01; 40 mM, 0.51 ± 0.02.

15) The initial step in the formation of IV must be an intramolecular cyclization to VI, which (or after hydrolysis to dienone VII) dimerizes thermally in Diels-Alder fashion, followed by the intramolecular (2 + 2) cycloaddition.[16] Therefore, the formation of IV requires three photons.

16) T. Iwakuma, H. Nakai, O. Yonemitsu, and B. Witkop, *J. Am. Chem. Soc.*, **96**, 2564 (1974).

17) Quantitative analyses were performed on a thinchrograph (Iatron TFG-10) with N,N-dimethyl-m-dimethylaminobenzamide as an internal standard.

18) J. A. Dean, ed., "Lange's Handbook of Chemistry," McGraw-Hill, New York, N. Y., 1973, p 5-24.

19) Though the pKa values of the S$_1$ and T$_1$ states of dimethylaniline are still unknown, they can be estimated to be ca. -2 and ca. 3, respectively, from the values of 2-naphthylamine.[20] Therefore, the quantum yield of the deprotonation above pH 0 must be almost unity.

20) G. Jackson and G. Porter, *Proc. Roy. Soc.* (London), **A 260**, 13 (1961).

21) The proton quenching of the loosely bound intermolecular exciplex also cannot be neglected.