

## A Novel Photoproduct of 1, 3-Dimethyluracil in Phosphate Buffered-saline

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**Abstract:** 1, 3-Dimethyluracil (DMU) in phosphate buffered-saline (PBS, pH=8) was irradiated by a medium pressure mercury lamp (MPML) and produced a novel compound  $C_6H_9N_2O_6P$ . The composition and structure of the compound has been identified by elemental analysis, EIMS, UV, IR,  $^1H$  and  $^{31}P$ -NMR.

**Keywords:** UV Photolysis, 1, 3-dimethyluracil, phosphate buffered-saline(PBS).

A standard solution of DMU,  $1 \times 10^{-4}$  mol/L in twice distilled water, has been used by many researchers<sup>1-3</sup> as a secondary actinometre in the study of the aqueous photochemistry of nucleobases (uracil, thymine and cytosine) and their derivatives. Under UV irradiation the photolysis of DMU leads to the production of photohydrate and photodimer, but the content of the latter is very low, and the quantum yield of DMU was mainly determined by photohydration. However, it was reported<sup>4</sup> that the quantum yield for the photohydration of DMU in PBS was a sigmoidal function of the DMU concentrations over the concentration range  $(0.1-1) \times 10^{-3}$  mol/L. The quantum yield of photohydration of DMU varied from  $3.8 \times 10^{-3}$  at concentration  $\leq 1 \times 10^{-4}$  mol/L to  $11 \times 10^{-3}$  at concentration  $\geq 1 \times 10^{-3}$  mol/L, by an unknown mechanism.

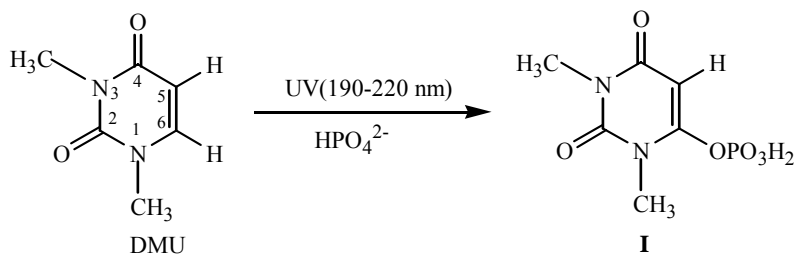
In our previous papers<sup>5-7</sup> we found that under MPML irradiation (continuous spectrum) the quantum yield of nucleobases and their derivatives was apparently enhanced by phosphates and a new photochemical reaction—photo-replacement reaction occurred, which led to a novel photoproduct with phosphate group. Herein we deal with that the photolysis of  $1 \times 10^{-4}$  mol/L DMU in 0.05 mol/L phosphate solution by irradiation of MPML to form a novel compound **I** (Scheme 1).

Analytic data of the compound **I** are as follows: Elemental analysis: Calcd. for  $C_6H_9N_2O_6P$ : C 30.51; H 3.81, N 11.86; P 13.12. Found: C 30.30; H 3.86; N 12.01; P 13.37. EIMS:  $m/z$ :  $[M+H]^+$  237(18), 207(42), 179(35), 155(100), 138(23), 82(21), 57(13). The ultraviolet spectrum of the aqueous solution of compound **I** at pH 7.0 exhibited two maxima at 278 nm and 208 nm, with the molar extinction coefficient  $9.06 \times 10^3$  and  $6.12 \times 10^4$   $L \cdot mol^{-1} \cdot cm^{-1}$  respectively.  $^1H$ -NMR (500 MHz, NaOD in  $D_2O$ ,  $\delta$

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Scheme 1



ppm): 3.32 (s, 3H, N3-CH<sub>3</sub>), 3.42(s, 3H, N1-CH<sub>3</sub>), 7.67(d, 1H, J=4 Hz, C5-H); <sup>31</sup>P-NMR (85% H<sub>3</sub>PO<sub>4</sub> as external standard δ= 0.80 ppm): 0.76(d, J = 4 Hz). IR(KBr, ν cm<sup>-1</sup>): 2856, 1695, 1669, 1470, 1370, 1220, 1162, 995, 960, 810.

The analysis results indicated that the possible structure of photoproduct is identical to that of compound **I** (1,3-dimethyl-6-phosphate uracil). Filter experiments demonstrated that the wavelengths (190-220 nm) in the spectrum of MPML are responsible for the phosphate-induced enhancement<sup>6</sup>. Since the phosphate dianions could absorb the lights (190-220 nm) and produce phosphate anion radicals (HPO<sub>4</sub><sup>•-</sup>)<sup>8</sup>. The mechanism of formation of 1,3-dimethyl-6-phosphate uracil in PBS has not been elucidated, although the result showed the addition of HPO<sub>4</sub><sup>2-</sup> at the C6 position of DMU. But if in acid solution (pH lower than 6), the photoreactive system of DMU-PBS will not produce, the photoproduct **I** was found only at pH 8.0. It suggested that the reacting species were the unionized form of DMU and the phosphate anion radicals (HPO<sub>4</sub><sup>•-</sup>).

Furthermore, it is noted that the photochemical behaviors of DMU in PBS are dependent on the DMU concentration, at concentration  $\geq 1 \times 10^{-3}$  mol/L, compound **I** could not be formed. The possible reason is that both DMU and phosphates can competitively absorb the UV light of wavelengths (190-220 nm), but the molar extinction coefficient of DMU is about 100 times larger than that of phosphates at this wavelength<sup>8</sup>. So the UV light (190-220 nm), at higher concentration ( $\geq 1 \times 10^{-3}$  mol/L) of DMU, was mostly absorbed by DMU, which acts as photohydration, while at lower concentration ( $\leq 1 \times 10^{-4}$  mol/L), both DMU and phosphates absorbed the UV light at the same time, and led to two main reactions: photohydration and photo-replacement reaction.

Our experimental results showed that it is explainable why the quantum yield for the photohydration of DMU in PBS changes with the concentration of DMU, because at lower concentration of DMU photolysis solutions lead to photohydration and photo-replacement reaction, which is an irreversible reaction (not like photohydration) and decrease the quantum yield of DMU, at higher concentration of DMU, only photohydration reaction occurred.

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**References**

1. J. G. Burr, F. H. Park, A. Chan, *J. Am. Chem. Soc.*, **1972**, *94*, 5866.
2. W. A. Summers, J.G.Burr, *J. Phys. Chem.*, **1972**, *76*, 3137.
3. R. O. Rahn, H. G. Sellin, *Photochem. Photobiol.*, **1979**, *30*, 317.
4. J. G. Burr, C. Gilligan, W.A.Summers, *Photochem. Photobiol.*, **1976**, *24*, 483.
5. F. Lin, Q. L. Ma, *Chin. Chem. Lett.*, **2003**, *14*, 1233.
6. F. Lin, Z. M. Wang, Y. F. Wang, *Chem. J. Chin. Univ.*, **2004**, *25*, 929.
7. F. Lin, J. L. Wu, J. G. Liu, *Photochem. Photobiol.*, **2000**, *131*, 49.
8. M. Halmann, I. Platzner, *J. Phys. Chem.*, **1967**, *71*, 1053.

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