

D_2O SOLVENT EFFECT ON PHOTOPRODUCT COMPOSITIONS OF PYRIMIDINES

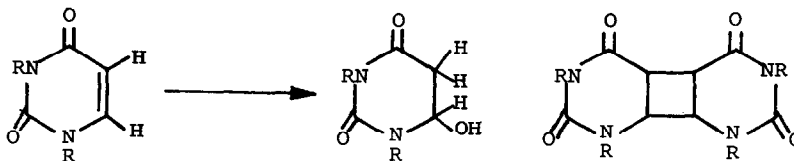
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Quantum yields (1,2) and rates (3) of photohydration of pyrimidines in D_2O solvent are about one half the value obtained in H_2O or pH 7 buffered aqueous solutions. Though these results suggest participation of H_2O molecules in rate-controlling steps of the photohydration reaction, they give no clue to the nature of the effect of these media on the formation of photoproducts other than photohydrates. Therefore, comparative studies of photoproducts formed in H_2O and D_2O solutions of pyrimidines irradiated with UV light (254 nm) were carried out. In this communication we wish to report the novel observation that 3 to 10 times more photoreversible dimeric products are formed in D_2O than in H_2O solvent.

FIGURE



In our studies of rates of photohydration in different media, slight increases of absorbancy in the 300-360 nm region were observed during irradiation of many pyrimidines in D_2O . On the other hand, such increases were clearly absent in H_2O . These results suggested that photoproducts other than hydrates may be formed in D_2O . For further investigation, various concentrations of 1,3-dimethyluracil and uridine solutions were irradiated in H_2O and D_2O , respectively (Table). The irradiation was allowed to proceed to 10, 50 and 80% decreases of the characteristic UV spectra (4). Quantitative determination

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of percentage of hydration was assayed from acid or base catalyzed spectral reconstitution (2,4) and further confirmed by isolation (4,5). The remaining percentage would essentially be equal to the cyclobutyldimers except in the case of uridine dimer. A fluorescent material with R_f 0.22 was separated from uridine dimer (R_f 0.08 from 2-butanol saturated with water) and was formed in less than 4% of the total amounts. The structure of this minor product is being characterized. Chromatographic and spectroscopic data of isolated compounds indicated that the cyclobutyl dimers formed in D_2O are identical to those from H_2O and frozen solutions (6,7).

TABLE

Percentage of Photoproducts in H_2O and in D_2O Solutions

Uracils	Conc. (mM)	(%) Hydration Product		(%) Dimerization	
		H_2O	D_2O	H_2O	D_2O
1,3-Me ₂	0.1	97	89	3	11
	0.5	95	72	5	28
	1.0	96	57	4	43
	5.0	84	38	16	62
	10.0	65	25	35	75
Uridine	0.1	95	86	5	14
	0.5	92	77	8	23
	1.0	93	68	7	32
	5.0	85	44	15	56
	10.0	64	33	36	67

As seen in the Table, irradiation of 1,3-dimethyluracil (4) or uridine (5) at various concentrations yielded primarily photohydrates in H_2O , but in D_2O dimerization predominated as the concentration of pyrimidine increased. It is also seen that there were 2 to 3 times more dimeric products formed in D_2O than in H_2O at the lowest and the highest concentrations. However, the amount increased to 4 to 10 times more at the intermediate concentrations.

The results shown in the Table were determined for reaction mixtures resulting from 50% spectral decreases and agreed well with those obtained for 10% and 80%.

To our knowledge, this represents the first documentation of such a dramatic D₂O solvent effect in the photochemistry of pyrimidines. This result suggests that some re-evaluations and re-interpretations of earlier studies (2) of polynucleotides in D₂O and H₂O may be needed. Currently, the mechanism by which these D₂O solvent effects operate is under investigation.

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