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Solution Phase Photodimerization of Tetramethyluracil. Further Studies on the Photochemistry of Ground-State Aggregates[1]

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Abstract: The photolysis of tetramethyluracil (TMU), in water and organic media, affords the cis-anti and trans-anti dimers as the major photoproducts, with the product distribution essentially independent of solvent. Quantum yields (ϕ_{DF}) are 0.015 in water and 0.004–0.007 in organic solvents. Quenching and sensitization studies indicate that the products are singlet derived, though the TMU triplet is detectable by energy transfer and can be cycloadded to vinyl acetate. The progressively increasing (stacking) association constants (thermal osmometry) for dimethyluracil (DMU), dimethylthymine (DMT), and TMU in water parallel the increasing degree of excited singlet state involvement in the photodimerization of these substrates in organic solvents. The role of trace aggregates in organic media is discussed.

The self-association of organic solutes in water, via "stacking" in a sandwichlike array, is a well-substantiated, experimentally observable phenomenon.[4] Because of the proximity caused by such preassociation, one expects that these aggregates could play a significant role in photodimerization; such is the case for dimethylthymine (DMT),[5,6] thymine,[7] and dimethyluracil (DMU)[8] in water, and other unrecognized examples undoubtedly exist.[9]

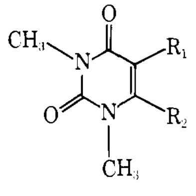
The possible involvement of such aggregates in photodimerization in nonaqueous media has generally been ignored, because "stacking" is commonly attributed to "hydrophobic" interactions unique to an aqueous environment,[4] and is not thought of as being of import in organic media.[10] However, the mechanism of "stacking" does, at least in part, involve attractive van der Waals forces between the monomers,[4] which may lead to small, but physically undetectable, amounts of aggregates in organic solvents. Thus inefficient photodimerization could result from an efficient reaction of trace aggregates, and we have suggested[5c] that several features of the photodimerization of DMT in nonaqueous solvents can be so rationalized.[11-33] In fact, a little-noted report[14a] has demonstrated that the extent of intramolecular cycloaddition for thymidylyl-(3′ → 5′)-thymidine (T_pT) in a number of nonaqueous solvents varies as a linear function of the (negative) changes in free energy which occur when T_pT assumes the "stacked" conformation having parallel, adjacent bases.[14b]

In order to study the effects of structural changes on aggregation vis-á-vis photodimerization, and to explore further the potential role of trace aggregates in nonaqueous solvents, we undertook a study of the photochemistry of 1,3,5,6-tetramethyluracil (TMU). This molecule was chosen because (1) it was known that increased methylation of purines enhances their stacking ability in water (presumably a consequence of the increased polarizability of CH_3 vs. H)[15] and (2) the increased extent of singlet involvement in the photodimerization of DMT, by comparison with DMU, in *organic media* (see below), seemed to correlate with the ability of these substrates to associate in *water*.

Results

A. Preparation of Tetramethyluracil. The title compound was synthesized by methylation of 5,6-dimethyluracil; purification by chromatography provided a sample which was pure by TLC and melted some 8 °C higher than the literature value.[16]

B. Vapor Pressure Osmometry. The apparent molecular weights for the series DMU, DMT, and TMU were measured in aqueous solution, as a function of concentration, using osmometry.



DMU, $R_1 = R_2 = H$
DMT, $R_1 = CH_3$; $R_2 = H$
TMU, $R_1 = R_2 = CH_3$

The data are best fit to

$$\frac{1 - \phi}{(2\phi - 1)^2} = K_a M \qquad (1)$$

which is valid for association to dimers.[17a] Plots of the data, according to this equation, are shown in Figure 1, and associ-

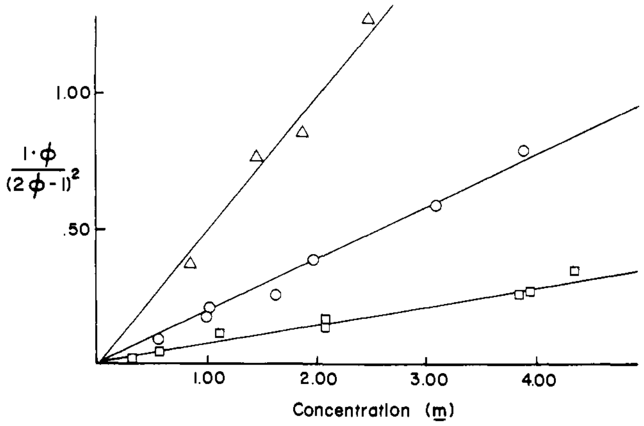


Figure 1. Thermal osmometric determination of association constants, plotted according to a dimer model: △, TMU; ○, DMT; □, DMU.

Table I. Association Constants for DMU, DMT, and TMU in Water[a]

Compd	K_a, L mol^{-1}
DMU	0.73 ± 0.08
DMT	1.94 ± 0.14
TMU	4.94 ± 0.52

[a] Obtained via vapor pressure osmometry at 37 °C; cf. Figure 1.

ation constants derived from the least-squares analysis are presented in Table I.[17b] The association constant of 4.94 corresponds to 38% ground-state dimers at 0.1 M (the concentration used for most of the photochemical studies). Osmometric measurements on TMU in organic media (benzene, ethyl acetate) give no evidence of association. As was observed for DMT,[5c] Beer's law studies give no indication of association in water or organic solvents. However, evidence for association has been obtained from a heat of dilution study for TMU in dichloromethane (see Discussion below).

C. **Preparative Photolysis of TMU in Aqueous Solution. Isolation and Identification of Three TMU Photodimers.** Photolysis of TMU (0.12 M) in aqueous solution with Corex-filtered light from a medium-pressure mercury lamp ($\lambda > 270$ nm) results in the formation of three dimers observable by GLC. One of these (A) precipitates from solution as a GLC pure solid, mp 291.5–292.1 °C; column chromatography provides B (mp 262.0–262.2 °C) and C (mp 270–278 °C dec). Elemental analyses and molecular weight determinations confirm the dimeric character of these products; spectral analysis confirms that they are vinyl-vinyl [2 + 2] cycloadducts. Thus, the NMR data (cf. Experimental Section) show the methyl protons at chemical shifts analogous to the dimers of DMT[5] and the IR spectra likewise give carbonyl doublets (5.92 and 6.09 μ) similar to those observed for the DMU[18] and DMT[5c] dimers. No oxetane absorption (8.39 μ)[19] is observed in any of the spectra.

Dimer A has been assigned the trans-anti configuration on the basis of x-ray diffraction studies. Intensity data were collected on a Picker card driven diffractometer. A 2θ scan with a counter scan rate of 1.0 deg/min was used to measure the integrated intensities, and the scan width was 2.4°. Background counts were determined for 20 s on both sides of the scan range. One quarter of a hemisphere of data was measured out to $2\theta = 130°$. The intensities of three standard reflections were measured every 60 reflections, and the data were corrected for intensity falloff. The data were also corrected for Lorentz and polarization factors. The structure was solved using direct methods[20] and refined to an R factor of 0.15. The following crystal data were determined for photodimer A: $C_{16}H_{24}N_4O_4$; mol wt 336.4; orthorhombic; systematic absences, $0kl$ $k = 2n$, $h0l$ $l = 2n$, $0k0$ $k = 2n$, $001 = 2n$, space group either $Pca2_1$ or $Pbcm$. The dimensions, volumes, and densities of the cell are as follows: $a = 8.335$ (1); $b = 15.587$ (2); $c = 12.615$ (1) Å; $Z = 4$; ρ (exptl) 1.365 g/cm^3; ρ (calcd) 1.363 g/cm^3. The structure of A is shown below.

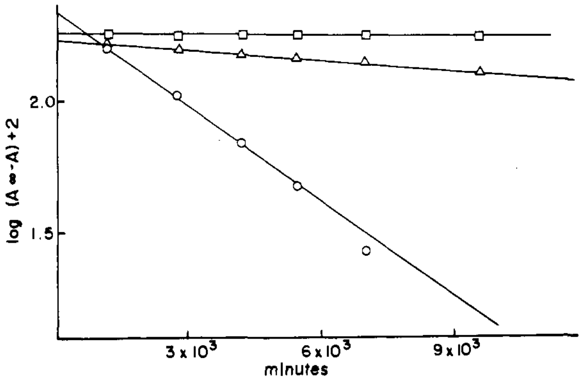
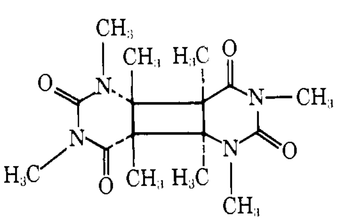
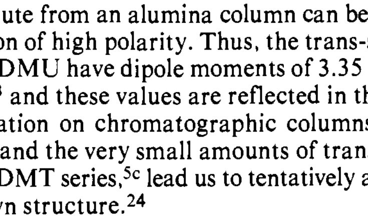


Figure 2. Monomerization of TMU dimers with 6 N HCl at 40 °C: dimer A, △; dimer B, ○; dimer C, □.



dimer A

Dimer B is assigned the cis-anti structure on the basis of acid-catalyzed monomerization experiments. It has been demonstrated by a number of workers[18,21,22] that the syn pyrimidinedione dimers are stable under mild acid conditions (6 N), but that the anti dimers are easily cleaved to monomers. Treatment of the three TMU dimers with 6 N HCl at 40 °C resulted in the monomerization of dimers A and **B**, and the first-order rate plots are shown in Figure 2. It is clear that the most reactive of the three dimers is dimer B, even more so than the already identified anti dimer, dimer A. We therefore assign B to the alternate anti structure shown below.



dimer B

Dimer C must then be one of the two syn dimers. Its assignment cannot be made unequivocally, but the fact that it is the last to elute from an alumina column can be interpreted as an indication of high polarity. Thus, the trans-syn and cis-syn dimers of DMU have dipole moments of 3.35 and 6.33 D, respectively,[23] and these values are reflected in their relative rates of migration on chromatographic columns. The high polarity of C, and the very small amounts of trans-syn dimer formed in the DMT series,[5c] lead us to tentatively assign dimer C as the cis-syn structure.[24]

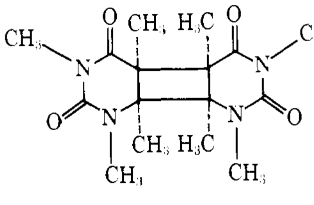
D. Dimer Distribution as a Function of Solvent. The effect of solvent on product distribution was determined at low conversions; the data are given in Table II.

E. Quantum Efficiencies of Dimer Formation (ϕ_{DF}). Quantum efficiencies were measured for 0.1 M TMU solutions, using 313-nm light. The data are given in Table III.

Table II. Distribution of Dimers as a Function of Solvent Polarity[a]

Solvent	Trans-anti, %	Cis-anti, %	Cis-syn, %
Water	27.8	63.1	9.1
Acetonitrile	24.9	68.2	6.7
Methanol	31.4	68.6	0.0
Glyme	32.3	67.7	0.0
Ethyl acetate	34.2	65.8	0.0
Toluene	38.0	62.0	0.0

[a] All data for solutions 0.1 M in TMU, at room temperature.



dimer C

F. Effect of Piperylene on the Photodimerization. There is no quenching of TMU (0.1 M) photodimerization in methanol, acetonitrile, ethyl acetate, or glyme by 0.1 M piperylene. (In some cases, a slight enhancement is actually observed.)[25] Likewise, 0.1 M 2,4-hexadienol has no effect on TMU photolysis in water. At 0.6 M piperylene, ϕ_0/ϕ values ranging from 1.03 (acetonitrile) to 1.17 (methanol) are observed.

G. Quantum Efficiencies for TMU Intersystem Crossing (ϕ_{isc}). Quantum efficiencies for intersystem crossing were determined with 0.1 M cis-piperylene as a triplet counter.[26] Data were corrected for direct irradiation of the diene and represent minimum values. The ϕ_{isc} values are in methanol, 0.009 ± 0.002; in acetonitrile, 0.020 ± 0.004; in glyme, 0.014 ± 0.003. Separate experiments using up to 0.3 M piperylene in acetonitrile and glyme demonstrated that the interception of TMU triplets was complete at 0.1 M diene.

H. Sensitization Experiments. Under conditions whereby acetone effects 69-100% sensitized conversion of DMT to dimers, no dimerization of TMU in methanol, acetonitrile, or ethyl acetate can be detected. Using known[5c] values for the quantum efficiencies of DMT dimerization by direct irradiation, and the fraction of this dimerization which originates from the triplet, one can calculate $^3\phi_{DF}$ values for DMT in various solvents, as from 1×10^{-3} to 1×10^{-4}. The sensitivity of our analyses allows us to estimate that triplet dimerization for TMU is, at best, 1-2% as efficient as DMT, thus placing the $^3\phi_{DF}$ value for TMU at $<1 \times 10^{-5}$ (we assume that triplet energy transfer from acetone to TMU is of comparable efficiency to that for DMT; the assumption is reasonable in the light of the respective triplet energies, and confirmed by the sensitized cycloaddition of TMU to vinyl acetate (see below)).

I. Sensitized Cycloaddition of TMU to Vinyl Acetate (VA). When an acetonitrile solution of TMU (0.1 M), vinyl acetate (0.7 M), and acetone (0.49 M) is irradiated for 24 h with Pyrex-filtered light, the TMU is completely consumed and four photoproducts are detected by GLC. The adducts can be isolated as two mixtures (D and E), each containing two components; the mixtures could not be further resolved and were analyzed as such. For D, mass spectral data give no molecular ion but TMU and VA fragment ions; the IR shows three carbonyl stretching vibrations at 5.7 (acetate), 5.85, and 6.01 μ (5,6-saturated TMU) and the NMR shows δ 4.8 (m, 1 H, X portion of an ABX pattern), 3.22, 2.90, 1.48, and 1.40 (singlets, 3 H each, characteristic of methyl groups in a 5,6 saturated TMU system), 2.00 (singlet, 3 H, CH_3CO), and 2.0-2.9 (m, 2, AB portion of an ABX pattern).

Likewise, E gives a molecular ion at *m/e* 254, IR bands at 5.75, 5.9 (shoulder), and 6.05 μ, and NMR signals, at δ 5.2 (m, 1 H, X part of ABX), 3.19, 2.92, 1.42, and 1.30 (singlets, 3 H each, saturated TMU), 2.05 (singlet, 3 H, CH_3CO), and 1.8-3.0 (m, 2 H, AB part of ABX).

Table III. Quantum Yields for TMU Dimerization (ϕ_{DF})[a]

Solvent	ϕ_{DF}[b]
Water	0.015 ± 0.001
Acetonitrole	0.0047 ± 0.0000
Methanol	0.0040 ± 0.0000
Ethyl acetate	0.0068 ± 0.0001$_5$
Glyme	0.0055 ± 0.0004$_5$

[a] All data for solutions 0.1 M in TMU at 32 °C. [b] Data are the averages of duplicate determinations and include average deviations.

These data confirm that [2 + 2] cycloaddition of TMU to VA has occurred; no detailed characterization of the individual cycloadducts was attempted.

J. Photocycloaddition of TMU with VA by Direct Irradiation. When TMU (0.1 M) and VA (0.1 M) are irradiated in acetonitrile, both the cycloadduct mixture and the dimer mixture was observable by GLC. By contrast with the photodimerization reaction, TMU + VA cycloaddition can be completely quenched by the addition of 0.1 M piperylene.

Discussion

As outlined in the introduction, our study of TMU was originated in anticipation of its increased aggregation in water, relative to DMU and DMT. The osmometry data plotted in Figure 1, and the resultant association constants tabulated in Table I, confirm that TMU is indeed appreciably more associated in water than its homologues. Our experiments were then designed to elucidate the photochemical consequences of such increased association, especially the potential consequences for photochemistry in organic media. At the outset, a number of expectations seemed qualitatively justified: (1) Photodimerization of TMU as a 0.1 M solution in water should be readily observed. (2) Such photodimerization would be singlet derived, as has been demonstrated for DMT[5,6] and DMU.[8] (3) Because of the very short singlet lifetimes in the uracil series,[27] singlet dimerization would be due to (and limited to) the excitation of ground-state aggregates (again by analogy with DMT[5,6] and DMU[8]). Steric effects aside, the increased aggregation of TMU should result in an increased quantum efficiency for the dimerization. (4) The additional methyl group on the uracil ring (by comparison with DMT) should create a greater steric barrier to dimerization which would partially counteract the effect of aggregation. This has been dramatically demonstrated[33] for the 1,1′-trimethylenebisuracil series, where a 5-methyl group (T-C$_3$-T) gave ϕ_{dim} = 0.04, and the 6-methyl analogue (6-MeU-C$_3$-6-MeU) had $\phi_{dim} = 6 \times 10^{-4}$.[34] (5) As with DMT and DMU, photodimerization of TMU should also be observed in organic media. (6) If such photodimerization involves trace aggregates, and if the increased association of TMU in water is reflected in a corresponding increase in organic media, then (a) singlet-derived dimerization should be favored by such association, (b) triplet-derived dimerization, which is normally extensive in organic media, and does not appear to be aggregate derived,[5c] should particularly suffer from the steric effects mentioned above.[35]

Our experimental observations are strikingly consistent with this scenario. TMU does photodimerize in water and with a quantum efficiency of total dimer formation (ϕ_{DF}) of 1.5×10^{-2} (0.1 M), equal to that observed for DMT. The dimerization is unquenchable and thus completely singlet derived at this concentration.[36] It has previously been shown[5,6] that quantum yields of singlet dimerization of this magnitude are

Table IV. Photodimerization of DMU, DMT, and TMU in Organic Solvents

Substrate	Solvent	% singlet (ϕ)	% triplet (ϕ)
DMU[a]	Benzene	0–25	75–100 (1.4×10^{-3})
	Dioxane	0–25	75–100 (4×10^{-3})
	Acetonitrile	0–25	75–100 (2.6×10^{-3})
DMT[b]	Ethyl acetate	61 (1.6×10^{-3})	38 (9×10^{-4})
	Acetronitrile	89 (1.3×10^{-3})	11 (1.5×10^{-4})
	Methanol	96 (1.9×10^{-3})	4 (1.0×10^{-4})
TMU[c]	Ethyl acetate	100 (6.8×10^{-3})	0 ($<1 \times 10^{-5}$)
	Acetonitrile	100 (4.7×10^{-3})	0 ($<1 \times 10^{-5}$)
	Methanol	100 (4.0×10^{-3})	0 ($<1 \times 10^{-5}$)

[a] Reference 40; 0.2 M DMU; the dimerization is reported as 100% triplet, but ambiguities arise from the nature of the quenching experiments. [b] Reference 5c; 0.1 M DMT. [c] 0.1 M TMU.

incompatible with a mechanism involving diffusion of picosecond-lived monomer singlets[27] and require the excitation of preassociated species. This being the case, the fact that the singlet dimerization is equally efficient for TMU and DMT indicates that for TMU in water, increased association and increased steric inhibition are counterbalanced.[34]

Divergence from the DMT system becomes obvious when the photochemistry of TMU is studied in nonaqueous solvents. Whereas the dimer distribution for DMT varies appreciably as a function of solvent, the TMU dimer ratio is relatively insensitive to the medium (Table II). The constancy of this ratio suggests that a common precursor is involved in all media, and the lack of quenching by piperylene confirms the singlet origin for the photodimers in all solvents.[37] The absence of triplet dimerization is not for lack of triplet formation; ϕ_{isc} values for TMU are comparable to those observed for DMT (e.g., ϕ_{isc}, TMU:DMT (solvent) 0.009:0.005 (methanol); 0.020:0.006 (acetonitrile); 0.014:0.019 (glyme)). Furthermore, TMU triplets created by sensitization likewise resist dimerization. These triplets are clearly not especially short lived (since they can be completely intercepted by 0.1 M piperylene) nor unreactive to all substrates (since they add to vinyl acetate).[38] Rather, the steric inhibition to dimerization introduced by the 5-methyl[35] and accentuated by the 6-methyl[33] has now become dominant for the TMU triplet. Thus, the ϕ_{DF} values for TMU in organic media are singlet quantum efficiencies, and significantly, *these exceed the singlet quantum efficiencies for DMT, despite the opposing steric effect.* A more complete compilation of the data is presented in Table IV, where it can be noted that within the uracil series and for organic media, *singlet dimerization increases with additional methylation whereas triplet dimerization diminishes.* The net consequence is a dramatic reversal from almost total triplet (DMU) to total singlet (TMU) dimerization.[39]

The mechanism which we suggest for TMU dimerization in *all solvents* is summarized in Scheme I.

Scheme I

$$\mathrm{TMU} \xrightarrow{h\nu} {}^1\mathrm{TMU} \tag{1}$$

$$(\mathrm{TMU})_2 \xrightarrow{h\nu} {}^1(\mathrm{TMU})_2 \tag{2}$$

$$ {}^1\mathrm{TMU} \xrightarrow{k_{\mathrm{ic}}} \mathrm{TMU} \tag{3}$$

$$ {}^1\mathrm{TMU} \xrightarrow{k_{\mathrm{isc}}} {}^3\mathrm{TMU} \tag{4}$$

$$ {}^1(\mathrm{TMU})_2 \xrightarrow{k_{\mathrm{DF}}} \mathrm{dimers} \tag{5}$$

$$ {}^1(\mathrm{TMU})_2 \xrightarrow{k'_{\mathrm{ic}}} 2\,\mathrm{TMU} \tag{6}$$

TMU represents ground-state monomer, $(\mathrm{TMU})_2$ represents the dimeric ground state associate(s), ${}^1(\mathrm{TMU})_2$ represents the excited associate(s) (presumably rapidly converted to, but not identical with, an excimer). The usual steady-state treatment provides

$$\phi_{\mathrm{DF}} = \frac{F_{\mathrm{ex}} 2K_{\mathrm{a}}[\mathrm{TMU}]}{1 + 2K_{\mathrm{a}}[\mathrm{TMU}]} \tag{7}$$

where F_{ex} is that fraction of excited associates which go on to dimer. For water (where K_{a} is measurable by osmometry), $\phi_{\mathrm{DF}} = 0.015$ and $K_{\mathrm{a}} = 4.94$, giving $F_{\mathrm{ex}} = 0.030$. This value agrees well with F_{ex} for DMU (0.028)[33] and DMT (0.065).[5c]

There is now little question regarding the validity of this scheme for water,[5,6,7,33] but its application to organic solvents warrants some discussion. There are two alternative mechanisms which have been discussed in some detail for DMT singlet dimerization in organic media.[5c] These are (1) a diffusional process and (2) a rapid reaction of nearest-neighbor (but unassociated) molecules. The first of these is improbable since even diffusion controlled rate constants in competition with a k_{ic} of $\sim 10^{12}\ \mathrm{s}^{-1}$ give potential ϕ_{DF}s two- to sixfold lower than the experimental results (and this assuming an $F_{\mathrm{ex}} = 1.0$ for any intermediate excimer).[41] The possibility of nearest-neighbor reactions is not so readily dismissed and is quantitatively capable of accommodating the observed ϕ_{DF}s. Thus,

$$F_n = 1 - (1 - X_{\mathrm{s}})^n \tag{8}$$

gives the fraction of molecules having TMU as a nearest neighbor (F_n), with X_{s} as the mole fraction of solute molecules, and n as the number of total possible nearest neighbors.[42] The F_n fractions calculated exceed ϕ_{DF} even when $n = 1$.

However, our initial objections[5c] to such a statistical approach are reinforced by the TMU data. Such a random reaction in no way explains the trends represented in Table IV, where structural features clearly are important to singlet dimerization. For example, neither the increased efficiency of singlet dimerization with increased methylation nor the ability of the TMU singlet to successfully resist the powerful steric factors is explained by this approach.[4]

The ultimate proof of our hypothesis of trace aggregation requires the direct observation of TMU associates in organic media. The fact that the association is below the limits of detection by osmometry requires that K_{a} be of the order of 0.2 L mol^{-1} or less.[43] Attempts to observe deviations from Beer's law have proven ineffective, even for aqueous solutions where association is unequivocal.[5c] However, a heat of dilution study on dichloromethane solutions of TMU *has now provided direct and unambiguous evidence for TMU association.*[44] A nonlinear heat of dilution is observed for 0.2 M TMU diluted in five steps to 0.01 M, with approximately 0.1–0.3 cal absorbed in each dilution. The fit to an "association to dimer" model is quite good; at 25 °C $K_{\mathrm{a}} = 0.226$, $\Delta H = -4.83$ kcal/mol, and $\Delta S = -20.6$ eu.

Conclusions

Our studies with TMU now complete the uracil series. Experimentally, there is a remarkable change for photodimerization in organic solvents, from predominantly triplet (DMU) to entirely singlet (TMU). There is a concomitant increase in the ground-state association constants in water. Our observations for TMU fit well with those predicted by the proposal that (inefficient) singlet photodimerization for these uracils in organic solvents derives from efficient reaction of trace aggregates. Evidence for such aggregates in organic media has been obtained from a heat of dilution study. We believe it likely that other types of substrates also depend on the presence of ground-state associates for their photoreactivity.[9]

Experimental Section

Chemicals. Spectral quality solvents were used in all photochemical experiments. Acetonitrile (Aldrich Spectrophotometric Grade Gold Label), benzene (Mallinckrodt SpectrAR), ethyl acetate (Mallinckrodt AR or Aldrich Spectrophotometric Grade Gold Label), and methanol (Mallinckrodt SpectrAR or Baker Spectrophotometric) were used as received. Glyme (1,2-dimethoxyethane, Ansul Co.) was purified by refluxing 1 pint for 40 h with 5 g of $SnCl_2 \cdot 2H_2O$, distilling and then redistilling from calcium hydride. Water was purified by distillation from basic potassium permanganate. Piperylene (Chemical Samples Co.) was a mixture of cis and trans or 100% cis (GLC pure), and was molecular distilled prior to use. Vinyl acetate and 2,4-hexadien-1-ol were from MCB and were distilled prior to use. Uracil (Sigma), thymine (Sigma), and 5,6-dimethyluracil (Aldrich) were used as received.

Instrumentation. Infrared spectra were taken on a Perkin-Elmer 137 spectrophotometer; ultraviolet spectra were obtained on a Cary 15 or Beckman DUR with Gilford 222-A photometer; NMR spectra were taken on a Varian A-60A, Varian XL-100, or Perkin-Elmer R-32 spectrometer with tetramethylsilane or sodium 3-(trimethylsilyl) propanesulfonate as standards. Mass spectra were obtained on an Hitachi RMU-6A by the Purdue Chemistry Department Mass Spectroscopy Center. Melting points were taken on a Thomas-Hoover Uni-Melt apparatus or a Mel-Temp instrument and are uncorrected. Osmometry data were obtained on a Mechrolab Inc. vapor pressure osmometer, Model 301-A.

Analyses. TMU dimers were analyzed on a 4.75 ft × 1/8 in. stainless steel column packed with 3% SE-30 on 100-120 mesh Gas-Pack, acid washed, DMCS treated, operated at 205 °C. Triptycene was used as an internal standard and retention times (nitrogen flow 20 mL/min) were (min) TMU, 1.6; triptycene, 3.7; A, 7.9; B, 10.1; C, 13.7. *trans*-Piperylene was analyzed on a 20 ft × 1/8 in., 20% β,β'-oxydipropionitrile on Chromosorb P column, operated at 0 °C. Cyclohexane was used as the internal standard. All analytical work was done with Varian 1200 or 1400 chromatographs.

Photochemical Apparatus. Comparative runs were done on a rotating turntable in a water bath at 26 °C, using a 450-W Hanovia mercury lamp. Tubes were either 25 mm o.d. Corex 9700 or 14 mm o.d. Pyrex. The Corex tubes had 0% transmittance below 240 nm and 50% transmittance at 276 nm. The Pyrex tubes had 0% transmittance below 265 nm and 50% transmittance at 320 nm. The tubes were matched using uranyl oxalate and matched to ±2-3%. Cylindrical filters were Corex 9700 (2 mm, $A_{270nm} = 2.00$; $A_{283nm} = 1.00$), Pyrex (2 mm, $A_{287nm} = 2.00$, $A_{299nm} = 1.00$), uranium yellow (1.5 mm, $A_{333nm} = 2.00$, $A_{343nm} = 1.00$); absorbances are for two thicknesses of the filter. Light intensities were determined by uranyl oxalate actinometry with the quantum yield for decomposition of oxalic acid at 313 nm as 0.56.[45]

Tetramethyluracil. TMU was prepared by the method of Davidson and Baudisch,[46] using the base-catalyzed methylation of 5,6-dimethyluracil by dimethyl sulfate. The TMU was purified by chromatography on silica gel using 7% methanol in dichloromethane as eluent. Under these conditions, TMU elutes first and the major impurity, trimethyluracil, elutes second. After sublimation (120 °C, 1 mm), TMU melts at 139.0-139.9 °C (lit.[47] 131-132 °C); NMR ($CDCl_3$) δ 3.45, 3.38, 2.27, 2.02 (all singlets of identical area); λ_{max} (KBr) 5.93, 6.11 μ; UV λ_{max} (H_2O) 274 nm (ϵ 9970).

Dimethylthymine. This was prepared by the same method used for TMU; sublimation (90 °C, 0.1 mm) gave a sample which was GLC and TLC pure, mp 151.6-152.9 °C (lit.[5c] 154 °C).

Table V. Aqueous Thermal Osmometry Data

Compd (mol wt)	Molal concn	Obsd mol wt
DMU (140)	0.030	141.7
	0.058	145.7
	0.112	151.8
	0.206	155.0
	0.207	157.8
	0.384	162.1
	0.393	162.8
	0.435	166.6
DMT (154)	0.053	165.4
	0.099	172.4
	0.101	175.1
	0.162	178.4
	0.195	185.4
	0.307	193.9
	0.388	200.3
TMU (168)	0.144	216.8
	0.185	220.3
	0.246	230.2
	0.322	242.3

1,3-Dimethyluracil. This was prepared by the same method used for TMU; sublimation (71 °C, 0.5 mm) gave a sample which was GLC and TLC pure, mp 115.8-118.5 °C (lit.[46] 120-121 °C).

Osmometry. Molal concentrations and observed molecular weights, for DMU, DMT, and TMU, are presented in Table V.

Preparation of the TMU Dimers. A 100-mL aqueous solution of 0.12 M TMU was deoxygenated for 30 min with argon and photolyzed for 160 h with a Corex-filtered, 450-W lamp. After photolysis, 442 mg (22%) of pure dimer A was filtered off. The filtrate was evaporated to dryness and chromatographed on a 7 cm i.d. column containing 80 g of 60-200 mesh aluminum oxide. Elution was with ether and ethanol/ether (1-4%). A 1.46-g sample of residue (put on the column with 7 mL of chloroform) provided B (18%) and C (4%).

Dimer A: mp 291.5-292.1 °C; λ_{max} (KBr) 5.83, 5.97 μ; NMR ($CDCl_3$) δ 3.24 (s, 3), 3.02 (s, 3), 1.39 (s, 6).

Anal. Calcd for $C_{16}H_{24}N_4O_4$: mol wt, 336; C, 57.13; H, 7.19; N, 16.66. Found: mol wt, 339 (osmometry); C, 57.00; H, 7.22; N, 16.82.

Dimer B: mp 262.0-262.2 °C; λ_{max} (KBr) 5.83, 6.00 μ; NMR ($CDCl_3$) δ 3.12 (s, 3), 3.01 (s, 3), 1.54 (s, 3), 1.43 (s, 3).

Anal. Calcd for $C_{16}H_{24}N_4O_4$ (see above). Found: mol wt, 341 (osmometry); C, 57.24; H, 7.40; N, 16.51.

Dimer C: mp 270 °C dec; λ_{max} (KBr) 5.85, 6.00 μ; NMR ($CDCl_3$) δ 3.15 (s, 3), 2.98 (s, 3), 1.49 (s, 6).

Anal. Calcd. for $C_{16}H_{24}N_4O_4$ (see above). Found: mol wt, 337 (osmometry); C, 57.11, H, 7.19; N, 16.53.

Density of A. A tared 25-mL specific-gravity bottle was filled with doubly distilled water and weighed. The exact volume of the bottle was determined from the temperature of the water and density at that temperature. In a separate vessel, hexane (20 mL) was saturated with the dimer and carbon tetrachloride added until A fell slowly. A crystal of A was added and additional carbon tetrachloride added until A was suspended in solution. At this point $\rho_A = \rho$ solution. The solution was transferred to the specific gravity bottle and weighed. From the weight of the known volume, ρ solution could be calculated. Measured values of ρ_A were 1.364 and 1.354 g/cm^3.

Monomerization of the TMU Dimers. These data were obtained by measuring the change in absorbance at 275 nm, for ~0.1 mM solutions of the dimers in 6 N HCl at 40 °C in a constant-temperature bath. A representative run is presented in Table VI.

Quantum Yields of Dimer Formation (ϕ_{DF}). These data were obtained at 32 °C using a 7-cm jacketed quartz cell or a 5-cm Suprasil cell, and irradiation by the 450-W Hanovia lamp filtered with potassium chromate/potassium hydroxide solution to give 313-nm incident light.[48] Uranyl oxalate actinometry was employed, conversions were generally ≤4%, and corrections were made where incomplete absorption of the light was calculated to be occurring. Quantum yields in each solvent were as follows: water (0.0139; 0.0165); methanol (0.00401; 0.00400); acetonitrile (0.00475; 0.00471); ethyl acetate (0.00662; 0.00692); glyme (0.00601; 0.00505).

Table VI. Monomerization of TMU Dimers with 6 N HCl[a]

Time, h	Absorbance (A)	Absorbance (B)	Absorbance (C)
0	0.018	0.058	0.203
19	0.078	0.543	0.218
46	0.157	1.096	0.243
70	0.228	1.454	0.262
90	0.283	1.684	0.272
116	0.349	1.894	0.264
160	0.465	2.159	0.294

[a] 0.10 mM solutions at 40 °C.

Table VII. Photolysis of TMU in the Presence of 0.1 M Piperylene[a]

Solvent	[Piperylene], M	% conversion to dimers
CH_3OH	0.0	2.33
	0.0	2.11
	0.1	2.41
CH_3CN	0.0	9.7
	0.0	10.7
	0.1	10.9
	0.1	10.2
EtOAc	0.0	17.9
	0.0	17.6
	0.0	18.3
	0.1	18.4
	0.1	17.6
	0.1	17.6
Glyme	0.0	4.6
	0.0	4.5
	0.0	4.7
	0.1	4.6
	0.1	5.0
	0.1	4.9

[a] 0.1 M TMU.

Quenching Studies. These studies were carried out on degassed, 0.1 M TMU solutions using a turntable. The data with 0.1 M 99% piperylene are given in Table VII.

Continuous Stern–Volmer data were obtained for methanol and ethyl acetate, using 0.1–0.8 M piperylene. Values of ϕ_0/ϕ were as follows: methanol ([Q], (ϕ_0/ϕ)): 0.1 (0.92), 0.2 (1.02), 0.3 (1.04), 0.4 (1.13), 0.5 (1.12), 0.6 (1.14). Ethyl acetate: 0.4 (1.13), 0.5 (1.04), 0.6 (1.06), 0.8 (1.08).

Quantum Efficiencies of Intersystem Crossing (ϕ_{isc}). These were obtained at 0.1–0.3 M *cis*-piperylene, using the Pyrex-filtered mercury lamp and a turntable. Since photodimerization of TMU is unquenched at 0.1 M diene, the photodimerization was used as the actinometer. All data were corrected for back reaction, and the maximum amount of diene isomerization caused by direct irradiation (determined by a simultaneous photolysis of tubes containing only the piperylene solution). The data are as follows: methanol, 0.0054, 0.0090, 0.0126; acetonitrile, 0.0216, 0.0216; glyme, 0.0189, 0.0124, 0.0118. Several measurements were also made at 0.3 M piperylene: acetonitrile, 0.0178, 0.0216; glyme, 0.0213, 0.0170, 0.0097.

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Isomerization of Linear Octene Cations in the Gas Phase[1]

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Abstract: Using high-resolution electron impact data, metastable ion characteristics, collisional activation spectra, and field ionization kinetic measurements in conjunction with ^2H and ^{13}C labeling it is demonstrated that the decomposing molecular ions of 1-, 2-, 3-, and 4-octene isomerize to a mixture of interconverting structures within 10^{-9} s after ionization, while isomerization of the nondecomposing ions is incomplete. The energy barrier for this isomerization seems to be higher for 1-octene than for the other octenes. At the shortest resolvable ion lifetime ($\sim 2 \times 10^{-11}$ s) 1-octene molecular ions fragment predominantly by specific mechanisms while the decomposition becomes unspecific at $t > 10^{-10}$ s. As a result $CH_3\cdot$, $C_2H_5\cdot$, and C_3H_6 are eliminated in similar ratios from both ends of the molecular ion after $\sim 10^{-9}$ s suggesting that the equilibration of double bond isomers is mainly due to radical site migration accompanied by hydrogen rearrangements, which, however, do not involve the terminal hydrogens to a larger extent. At long ion lifetimes skeletal rearrangements are only pronounced prior to ethylene loss, but of lesser importance for other fragments originating directly from the molecular ion. In contrast, heptenyl ions, generated by methyl loss from 1-octene, decompose after complete randomization of all carbons.

The molecular ions of small alkenes (propenes and butenes) as well as the isomeric cycloalkanes with sufficient internal energy to undergo decomposition ("reactive" ions) isomerize to a common structure or a mixture of interconverting structures *prior* to decomposition as shown by ^2H and ^{13}C labeling,[3] metastable ion characteristics,[4] heats of formation data,[5] and field ionization kinetic measurements,[6] while the nondecomposing ions retain partially their original structure.[7,8] Such isomerization processes are, however, incomplete or negligible in larger alkene ions independent of the internal energies and ion lifetimes.[9-11] Apparent exceptions are the molecular ions of those alkenes differing only in the position of the double bond where it has been assumed that facile migration of the radical site (accompanied by hydrogen rearrangement) leads to an equilibration between the various double bond isomers making a location of the double bond by means of mass spectrometry difficult.[12] To shed further light on the details of this isomerization process we studied 1-, 2-, 3-, and 4-octene (in the trans configuration) with various techniques (electron impact (EI), metastable ion (MI) characteristics,[13] collisional activation (CA),[14] and field ionization kinetics (FIK)[15] in conjunction with ^2H and ^{13}C labeling).

Experimental Section

Instrumental Details. High-resolution EI data were obtained with a Varian MAT 711 double focusing instrument at the resolution of $M/\Delta M = 25\,000$ (electron energy 70 eV, electron beam 800 μA, source temperature 200 °C). They are the means of five individual measurements. MI and CA spectra were run on a double focusing mass spectrometer of reversed geometry constructed by us (magnetic sector field preceding electrostatic sector field) equipped with a collision cell in front of the energy resolving slit (acceleration voltage 8 kV, electron energy 70 eV, electron beam 30 μA, source temperature ca. 150 °C). The technique for taking and evaluating CA spectra has been described previously.[9,14,16] All data are the means of at least two measurements.

An instrument of identical geometry, but equipped with a nonfocusing FI source, was used for ion lifetime measurements and for FI-CA measurements.[35] (With all three instruments samples were introduced via the indirect inlet system). Complete mass spectra as function of the ion lifetime were obtained by increasing the voltage

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