Properties of the Triplet States of Thymine and Uracil in Aqueous Solution

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Abstract: Properties of the triplet states of thymine and uracil in aqueous solution have been examined by the technique of flash photolysis. The transient species observed in thymine decays by spontaneous deactivation at rate 0.8×10^4 sec^{-1} or can be quenched by O_2 with rate constant 3.5×10^9 M^{-1} sec^{-1}. Self-quenching, leading in part to the formation of permanent photodimers, occurs with rate constant 2.3×10^9 M^{-1} sec^{-1}. Identical self-quenching is observed when the species is obtained through acetone sensitization rather than direct excitation. Previous studies of the uracil triplet have been extended to provide a comparison with thymine. From this comparison we conclude that in thymine about one-fifth of the triplets which are quenched by the parent lead to dimers, whereas in uracil this fraction is one-half. In addition intersystem crossing in thymine is about fourfold lower than in uracil.

The excited states of pyrimidine molecules have received extensive study. Apart from an intrinsic theoretical interest in photoreactions of unsaturated nitrogen heterocyclics, the nucleic acids form permanent photoproducts in DNA which result in biological inactivation.[1,2] The main photoproducts are the hydrate, in which water is added across the 5,6 double bond (detected in uracil and cytosine but not in orotic acid and thymine) and the dimer (produced in all four pyrimidines). The dimer consists of two molecules covalently linked by a cyclobutane ring between the 5 and 6 positions. Evidence derived from the separation of the products from ultraviolet-irradiated dilute solutions of orotic acid, uracil, and thymine has suggested that the formation of the photodimer results from the reaction of one molecule in an excited triplet state with a second in its ground state. Figure 1 shows a model, based on one first proposed by Sztumpf-Kulikowska, Shugar, and Boag,[3] for this reaction. The reaction kinetics predicted by this model have been confirmed for steady-state irradiation of dilute aqueous solutions of uracil,[4] thymine,[5] and orotic acid.[3,6] Moreover, in the cases of orotic acid and uracil a transient state has been observed in the flash photolysis of such solutions, and the reaction rates of these species agree with observations made in the steady-state systems.[7,8] The transient species is almost certainly the triplet state.

Similar reactions can be produced in nonaqueous solutions of pyrimidines. In such solutions the intersystem crossing efficiencies of the pyrimidine may be quite large. For example, Lamola[9] reports values of 0.40 for uracil and 0.20 for thymine which are at least an order of magnitude larger than those observed in aqueous solutions of the bases.[4,5] Recently, Szabo *et al.*,[10] have reported the observation by flash photolysis of a triplet state of thymine in acetonitrile, and Hayon[11] has described a triplet state of uracil in acetonitrile obtained by flash photolysis and also by triplet–triplet transfer from the solvent excited by pulse radiolysis. Hayon reports a similar species observed in water but gives no details. Wagner and Bucheck[12] have studied the photodimerization of thymine and uracil in acetonitrile. The lifetimes described by these authors are about one-half of those reported by both Szabo, *et al.*,[10] and Hayon,[11] and agree more closely with the lifetime of the uracil triplet in water reported by Whillans, *et al.*[8] However, the photochemistry and the triplet states seen in acetonitrile may be quite different from those observed in aqueous solution. For example, $k_3/(k_1 + k_1')$ given by Wagner and Bucheck for thymine is 3×10^{-4} in acetonitrile, whereas Fisher[5] observes a ratio of 5×10^{-6} in water. Thus comparisons between transients seen in acetonitrile and water must be made cautiously.

We now report the direct observation of a triplet state of thymine in flash photolysis of aqueous solutions and we give further information on the triplet state of uracil. In particular, we describe the rate constants for the reactions of these triplets, formed by direct excitation and by acetone sensitization, their absorption spectra, and a relative measure of intersystem crossing. These results are compared with former observations obtained in steady-state irradiations.

Experimental Section

The flash photolysis system used in these experiments is an improvement upon that already reported,[8] and a more detailed description will be found elsewhere.[13] The discharge dissipates 300 J of electrical energy in a flash whose width at half-height is 1.3 μsec, resulting in about 10^{18} photons incident on the cell in the range 200–320 nm as measured by MGL.[14] The light level from the flash at 5.0 μsec after initiation of the flash is less than 0.2% of its peak value. A typical flash profile is shown in Figure 2a. By the use of a pulsed analyzing source with 20-fold gain in light

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[1] J. Eisinger and R. G. Shulman, *Science*, **161**, 1311 (1968).

[2] A. D. McLaren and D. Shugar, "Photochemistry of Proteins and Nucleic Acids," Pergamon Press, New York, N. Y., 1964.

[3] E. Sztumpf-Kulikowska, D. Shugar, and J. W. Boag, *Photochem. Photobiol.*, **6**, 41 (1967).

[4] I. H. Brown and H. E. Johns, *ibid.*, **8**, 273 (1968).

[5] G. J. Fisher and H. E. Johns, *ibid.*, **11**, 429 (1970).

[6] D. W. Whillans and H. E. Johns, *ibid.*, **9**, 323 (1969).

[7] M. A. Herbert, J. W. Hunt, and H. E. Johns, *Biochem. Biophys. Res. Commun.*, **33**, 643 (1968).

[8] D. W. Whillans, M. A. Herbert, J. W. Hunt, and H. E. Johns, *ibid.*, **36**, 912 (1969).

[9] A. A. Lamola and J. P. Mittal, *Science*, **154**, 1560 (1966).

[10] A. G. Szabo, W. D. Riddell, and R. W. Yip, *Can. J. Chem.*, **48**, 694 (1970).

[11] E. Hayon, *J. Amer. Chem. Soc.*, **91**, 5397 (1969).

[12] P. J. Wagner and D. J. Bucheck, *ibid.*, **92**, 181 (1970).

[13] J. C. LeBlanc, M. Herbert, D. Whillans, W. B. Taylor, and H. E. Johns, manuscript in preparation.

[14] G. J. Fisher, J. C. LeBlanc, and H. E. Johns, *Photochem. Photobiol.*, **7**, 757 (1967).

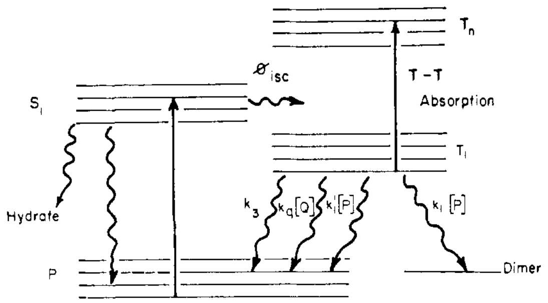

Figure 1. Model for excited-state reactions of pyrimidines. ϕ_{isc} represents the intersystem crossing efficiency. The rate constants for triplet reactions are as follows: k_3, spontaneous deactivation to the solvent; k_q, bimolecular quenching by Q; k_1', self-quenching by pyrimidine not leading to product formation; and k_1, self-quenching by pyrimidine in the formation of photodimers.

level and a three-pass path of this light through a 15-cm cell the sensitivity of the system has been increased to a very high level. The noise level is equivalent to an absorbance signal of less than 0.0003 for signals of 20-μsec duration and with somewhat less precision (0.001) for longer lived species because of long-term fluctuations in the intensity of the analyzing light beam. Typical absorption signals are shown in Figures 2b and 2c. There is negligible contribution to the signal from scattered light 5 μsec after the initiation of the flash and the decay curves are strictly exponential.

Uracil (Pabst Laboratories) and thymine (Calbiochem A grade) solutions were prepared in triply quartz-distilled water and concentrations were determined using extinction coefficients of $8.2 \times 10^3\ M^{-1}\ \text{cm}^{-1}$ at 259 nm for uracil and $7.9 \times 10^3\ M^{-1}\ \text{cm}^{-1}$ at 264 nm for thymine.[15] The pH was about 5.9 for both solutions. Most samples were degassed using prepurified N_2 (Canadian Anaesthetic Gases Ltd., >99.997% N_2); otherwise oxygen concentration in solution was controlled by bubbling O_2–N_2 mixtures of the same quality prior to photolysis and calculated from a solubility of oxygen of $1.3 \times 10^{-3}\ M$ at 25° and the per cent of oxygen in the mixture.

Acetone used for sensitization was Analar reagent grade. A study of excited species of this material alone, as well as those formed in spectroscopic grade acetone, demonstrated that at the level of our sensitivity no evidence of contamination existed in either solution.

Results

Self-Quenching. The triplet state of thymine or uracil may be deactivated by four processes as indicated in Figure 1. Self-quenching by pathway k_1 leads to permanent photodimers with rate $k_1[\text{P}]$, while pathway k_1' quenches the triplet at rate $k_1'[\text{P}]$ without the formation of a permanent product. Pathways k_1 and k_1' can be replaced equally well by a single pathway leading to an excimer. A fraction of these excimers leads to stable dimers and the rest fall apart to give back parent molecules. Separation of these two processes cannot be done by any experiment which varies [P], since both paths have the same dependence on concentration.

In the absence of additional quenching by Q the triplet state disappears at rate k_{obsd} with lifetime τ_{obsd} given by

$$1/\tau_{\text{obsd}} = k_{\text{obsd}} = k_3 + (k_1 + k_1')[\text{P}] \qquad (1)$$

The decay of the transients (Figures 2b and 2c) was strictly exponential enabling us to determine k_{obsd} and τ_{obsd}. By plotting k_{obsd} *vs.* concentration we obtained a straight line yielding the rate constants k_3 and $(k_1 + k_1')$.

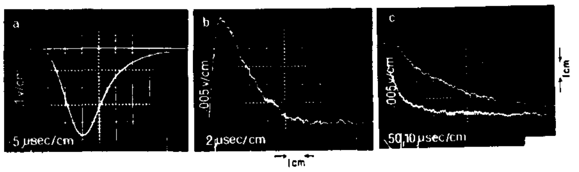

Figure 2. (a) Typical profile of light flash at 0.5 μsec/cm; λ 260 nm. (b) Typical absorbing species observed in $6 \times 10^{-5}\ M$ uracil with 15-cm path at 2 μsec/cm and 0.005 V/cm. Initiation of the discharge occurs 1 μsec to the left of the photograph; λ 330 nm. (c) Typical absorbing species observed in $1 \times 10^{-5}\ M$ thymine with 45-cm path at 10 and 50 μsec/cm and 0.005 V/cm. Flash energy somewhat larger than that used in observing (b); λ 330 nm. In these photographs light intensity is downward and absorption upward.

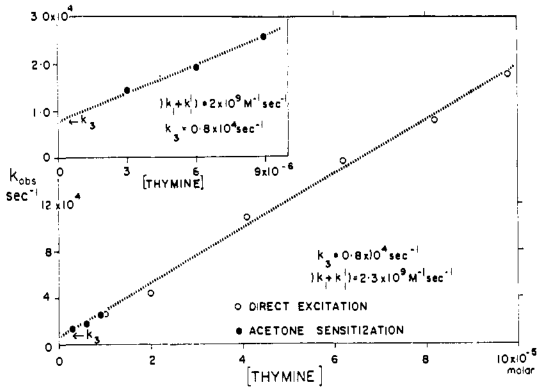

Figure 3. Main graph shows observed decay rate, k_{obsd}, of thymine transient *vs.* thymine concentration produced by direct excitation of aqueous solution. Insert shows a similar result obtained at lower concentrations by sensitization with 0.05 *M* acetone. These points also appear on the main graph. For both graphs $[O_2] = 0$.

Figure 3 shows the results of such a study of thymine. The value k_{obsd} varies linearly with concentration over the range 10^{-5}–$10^{-4}\ M$. Higher concentrations could not be used because of the difficulty in getting analyzing light through 45 cm of solution. Lower concentrations (down to 10^{-7}) were observed using acetone sensitization. Results are shown on the insert and on the main graph, indicating that the rates are the same in water as when the species is sensitized with 0.05 *M* acetone. The rate constant, k_3, for spontaneous deactivation is $0.8 \times 10^4\ \text{sec}^{-1}$, yielding a lifetime of 125 μsec. Since k_3 is small the error in the natural lifetime τ_0 is large (100–175 μsec).

Other Quenchers. The transient is quenched by the triplet quencher, molecular O_2, according to

$$k_{\text{obsd}} = (k_3 + (k_1 + k_1')[\text{P}]) + k_2[O_2] \qquad (2)$$

and the results are given in Figure 4. The linear relation allows us to determine $k_2 = 3.5 \times 10^9\ M^{-1}\ \text{sec}^{-1}$ and a value for $k_3 + (k_1 + k_1')[\text{P}]$ which agrees with the results of Figure 3.

Table I compares the rate constants for thymine obtained in this study with those previously obtained with uracil and orotic acid.

Sensitization. The absorbing species observed in the flash photolysis of uracil or thymine decays according to the kinetic model of Figure 1 and is quenched by O_2. This, of course, does not prove that it is a triplet state, since other species such as free radicals might be responsible. Langmuir and Hayon,[16] *e.g.*,

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(15) D. Shugar and J. J. Fox, *Biophys. Biochem. Acta*, **9**, 199 (1952).

(16) M. E. Langmuir and E. Hayon, *J. Chem. Phys.*, **51**, 4893 (1969).

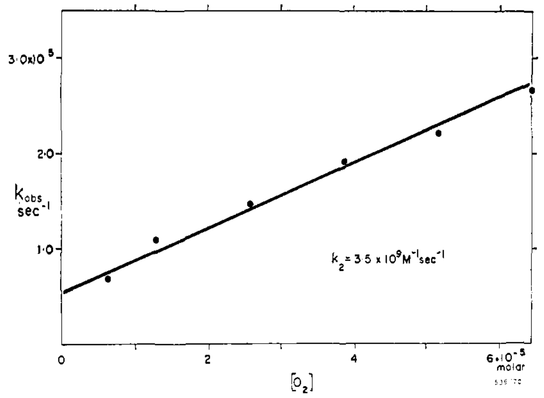

Figure 4. Oxygen quenching of the thymine transient at [T] = 1.4×10^{-5} *M*.

have shown that in bromouracil free-radical formation produces a species whose properties are similar to ours. Convincing evidence for the triplet state is provided by photochemical sensitization experiments. A suitable sensitizing agent for aqueous solutions of thymine and uracil is acetone because its triplet energy is just above theirs and its intersystem crossing efficiency is 1.0.[17] Greenstock, *et al.*,[18] have observed that dimer products of uracil and thymine can be formed by long-wavelength irradiation through acetone sensitization. Photolysis of a 0.05 *M* solution of acetone alone produced a large transient which decayed exponentially, with a lifetime of 16 μsec and a spectrum extending to about 370 nm. The high concentration relative to the pyrimidine ensured that, although the ground-state spectrum overlapped that of the pyrimidines, virtually all exciting light was absorbed by the acetone. However, because the acetone lifetime was longer than that of uracil (always less than 6 μsec), the uracil transient could not be observed after the decay of the acetone triplet. The longer lived triplet at low concentrations of thymine is easily observed at 385 nm. Figure 3 shows that the transient produced by direct excitation of thymine is quenched by thymine in the same way as that produced by acetone sensitization. We conclude that the transient formed by direct photolysis of thymine can also be obtained by triplet–triplet transfer from acetone and is thus a thymine triplet state.

Table I

	Thymine	Uracil	Orotic acid[a]
$(k_1 + k_1')$, M^{-1} sec^{-1}	$2.3 \pm 0.2 \times 10^9$	2.9×10^9	1.9×10^9
k_2, M^{-1} sec^{-1}	$3.5 \pm 0.2 \times 10^9$	3.9×10^9	3.0×10^9
k_3, sec^{-1}	$0.8 \pm 0.2 \times 10^4$	1.66×10^5	0.9×10^4
τ_0, μsec	100–175	6.1	110

[a] Neutral form, pH 1.

Triplet–Triplet Absorption Spectrum. Figure 5 shows the absorption spectrum of the triplet species of both uracil and thymine as seen in flash photolysis. For both pyrimidines a fixed concentration was flashed and the transient absorption as well as the analyzing light level were measured as a function of wavelength. In addition, we demonstrated that the output of the flash lamp itself did not vary by more than ≃5% throughout the experiment. However, because we do not know the absolute extinction of these species at any one wavelength, these spectra may *not* be compared in terms of absolute values, but one does observe similar spectra for uracil and thymine with peaks at 370 and 340 nm, respectively. In Figure 5 the curves have been arbitrarily normalized to the same value at these peaks. The ground-state spectra have peaks, respectively, at 259 and 264 nm and nearly the same extinction.[15]

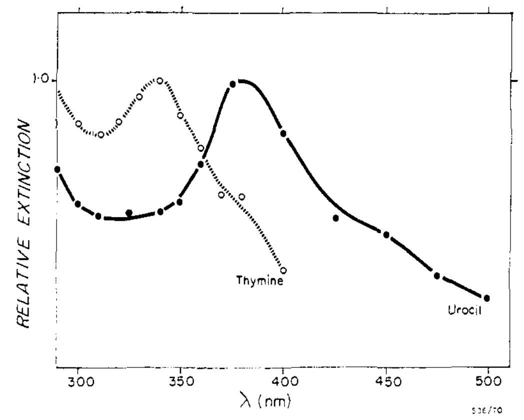

Figure 5. Triplet–triplet absorption spectra of uracil and thymine. Spectra have been normalized at their peak values but no absolute comparison is intended.

It is difficult to make a valid comparison of the uracil spectrum with that reported by Hayon in acetonitrile. He observes no peak at 370 nm but a major one at 285 nm. We cannot observe in the region below 290 nm because of ground-state absorption, but by inference from other studies in our laboratory[19] on orotic acid we expect a major peak below 300 nm. No detailed triplet absorption spectra for thymine have been reported.

Relative Triplet Yields. Intersystem crossing, ϕ_{isc}, cannot be determined from dimer yields because of the pathway k_1'. All that can be determined from such studies is ϕ_{isc}/R, where $R = (k_1 + k_1')/k_1$. For orotic acid, uracil, and thymine steady-state studies from our laboratory at 254 nm indicate that ϕ_{isc}/R is 0.13, 0.008, and 0.0008, respectively.[5] ϕ_{isc} cannot be determined without a knowledge of k_1 and k_1'. Unfortunately, ϕ_{isc} cannot be obtained from luminescence studies since luminescence is not, in general, observed at room temperature in pyrimidines.[1] Recently, Jellinek and Johns[20] studied the reaction between the uracil triplet and the amino acid cysteine. Their results[20] suggest that for uracil *R* is about 2. In addition, Eisinger and Lamola[21] have studied the related compounds uridylic acid (UMP) and thymidylic acid (TMP) and have determined triplet yields using a Eu^{3+} triplet counter. If we assume that UMP and TMP are similar to uracil and thymine, their findings indicate that *R* is about 1 for uracil and about 16 for thymine. In order to study this problem

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(17) R. F. Borkman and D. R. Kearns, *J. Chem. Phys.*, **44**, 945 (1966).

(18) C. L. Greenstock and H. E. Johns, *Biochem. Biophys. Res. Commun.*, **30**, 21 (1968).

(19) M. A. Herbert, personal communication.

(20) T. Jellinek, and R. B. Johns, *Photochem. Photobiol.*, **11**, 349 (1970).

(21) J. Eisinger and A. A. Lamola, *J. Chem. Phys.*, in press.

Table II

	Uracil	Thymine	
$\phi_{isc}[k_1/(k_1 + k_1')]$	0.008	0.0008	Steady state,[5] λ 254
ϕ_{isc}	0.016[a]	0.004[b]	Using data from Jellinek, *et al.*,[20] λ 254 nm and this study, λ 200–290 nm
$(k_1 + k_1')$, M^{-1} sec^{-1}	2.9×10^9	2.3×10^9	This paper, calcd
k_1, M^{-1} sec^{-1}	1.4×10^9	4.4×10^8	With the reservations described in footnotes *a* and *b*
k_1', M^{-1} sec^{-1}	1.4×10^9	1.9×10^9	
$k_1/(k_1 + k_1')$	0.5	0.2	

[a] This assumes that Jellinek and Johns observed all pathways for triplet deexcitation. [b] Assumes uracil and thymine have the same T–T extinction at their respective peaks, which yields $(\phi_{isc})_U/(\phi_{isc})_T = 3.8$ and that ϕ_{isc} for uracil is 0.016.

directly, we have compared the relative yields of the uracil and thymine triplets by flash photolysis.

Since our irradiation facility is not easily amenable to accurate dosimetry, we have avoided the difficulty by choosing equal concentrations of uracil and thymine (10^{-5} *M*). Thus for an equal flux of photons through the sample cell nearly equal numbers of uracil and thymine excited singlet states are formed, because of the near identity of their ground-state absorption spectra. The relative measure of the number of triplet states is the size of the transient signal detected. This measure, however, is subject to two corrections.

(a) **Decay within Flash.** The more important correction is due to the finite width of the flash itself, particularly with respect to the short-lived uracil triplet. The transient which would be observed in the absence of scattered light from the exciting flash is, accurately, a convolution of the flash profile with the exponential decay of the species. That is

$$N(t) = C\int_0^t F(\tau)e^{-k(t-\tau)}\mathrm{d}\tau \qquad (3)$$

where $N(t)$ is the number of triplets present at time t which are decaying at rate k and are produced by a flash whose profile is given by $F(t)$. C is a constant which contains scaling parameters identical for both uracil and thymine, as well as the factor ϕ_{isc}. Figure 6 shows $N(t)$ and $F(t)$ as a function of time for the case of uracil at 10^{-5} *M* where the decay is 1.9×10^5 sec^{-1}. The number which would be present, $N_p(t)$, at time t if there were no decay is simply

$$N_p(t) = C\int_0^t F(\tau)\mathrm{d}\tau \qquad (4)$$

$N(t)$ and $N_p(t)$ can be constructed from the flash profile using the value of k determined from an analysis of the decay of the species for times after the flash profile has reached zero. This time τ_F is about 5 μsec. For uracil the observed signal must be increased by the factor 2.1 to correct for decay during the flash. For thymine, whose decay rate is 3.1×10^4 sec^{-1}, the factor is 1.08.

(b) **Relative Extinctions.** In order to maintain a valid comparison, the uracil and thymine transients were monitored at the same wavelength, 330 nm. If the triplet absorption spectra shown in Figure 5 for thymine and uracil were identical, no correction would be required. Unfortunately, they are not the same, so we somewhat arbitrarily matched the two spectra at their peaks (340 and 370 nm) and thus increased the uracil signal measured at 330 nm by a factor of 1.8. It would have been more satisfactory to match the integrated spectra, but again this could not be done since the spectra below 300 nm are not known. This normalization procedure introduces the most uncertainty in our calculation.

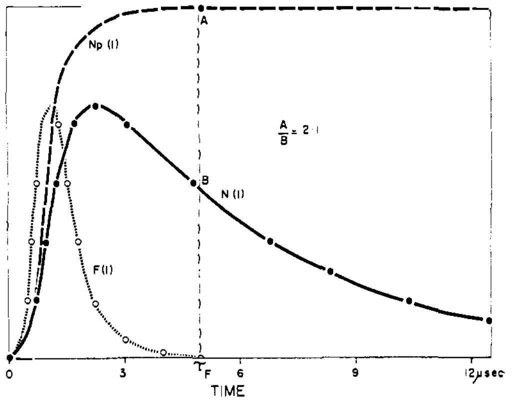

Figure 6. Profiles for correction of 10^{-5} *M* uracil transient for decay during the flash. $F(t)$ represents the flash profile, $N(t)$ the actual transient present as a function of time for a decay rate of 1.9×10^5 sec^{-1}, and $N_p(t)$ the number which would be present an any time t if there were no decay. The final value of this curve gives the number produced.

When both corrections are applied the relative yield of uracil triplets to that of thymine, that is, the ratio of intersystem crossing efficiencies $(\phi_{isc})_U/(\phi_{isc})_T$, equals 3.8. Steady-state experiments show that $(\phi_{isc}/R)_U/(\phi_{isc}/R)_T = 10$. Hence these experiments show that $(R)_T/(R)_U \simeq 2.6$.

Discussion

The results presented in this study together with data from others allow us to determine the rate constants given in Table II. By counting the dimer products formed, Brown, Fisher, and Johns[4,5] have obtained values for ϕ_{isc}/R for uracil and thymine of 0.008 and 0.0008, respectively, for irradiation at 254 nm. By cysteine quenching experiments, Jellinek and Johns obtained a higher estimate of intersystem crossing in uracil. If we assume that their value (0.016) represents a true intersystem crossing efficiency, we can determine the true intersystem crossing (0.004) for thymine using our factor of 3.8. From these data, then, values for R for both uracil and thymine combined with our data for $(k_1 + k_1')$ lead immediately to values for k_1 and k_1', shown in Table II. It should be noted that $(k_1 + k_1')$ for uracil and thymine are about the same, as might be expected, since these molecules are quite similar in structure. The rate is close to the diffusion-controlled value one might expect for reaction between a ground state and an excited triplet. If we consider this interaction as leading to an excimer, then the rate of excimer formation for some given concentration of triplets is nearly the same for thymine and uracil. However, the fraction of these excimers which lead to dimers is about one-half in uracil and one-fifth in thymine. This fact, combined with a somewhat lower ϕ_{isc} in thymine, accounts for the greatly reduced yield of photodimers of thymine in aqueous solution.

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Iron(II)- and Manganese(I)-Carborane Complexes Formed through Metal-Carbon σ Bonds

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Abstract: 1,2-Dicarba-*closo*-dodecaborane(12) and 1,10-dicarba-*closo*-decaborane(10) and their C-monosubstituted derivatives react with *n*-butyllithium in ethereal solvents to form the corresponding 1-lithiocarboranes. Reaction of these 1-lithiocarboranes with manganese pentacarbonyl bromide and cyclopentadienyliron dicarbonyl iodide gives rise to a series of stable neutral derivatives containing a metal-carbon σ bond. Reaction of 1,10-dilithio-1,10-dicarba-*closo*-decaborane(10), formed from 1,10-dicarba-*closo*-decaborane(10) and 2 mol equiv of *n*-butyllithium in ethereal solvents, with 2 mol equiv of cyclopentadienyliron dicarbonyl iodide, gives rise to an analogous derivative containing two nonchelating metal-carbon σ bonds. The preparation, characterization, reactions, and proposed structures of these complexes are discussed.

Numerous π-bonded transition metal complexes with $B_9C_2H_{11}{}^{2-}$, $B_8C_2H_{10}{}^{4-}$, $B_7C_2H_9{}^{2-}$, and $B_6C_2H_8{}^{4-}$ ligands have been prepared in this laboratory.[1-10] In addition, a series of extremely stable anionic chelated biscarborane-transition metal complexes containing unusually stable carbon-metal σ bonds has been reported.[11,12] Complexes containing platinum(II)-carborane metal-carbon single σ bonds have also been reported.[13] Preliminary evidence[14] indicated that an extensive series of stable neutral iron(II)- and manganese(I)-carborane complexes incorporating the 1,2-$B_{10}C_2H_{11}{}^-$, 1,10-$B_8C_2H_9{}^-$, and 1,10-$B_8C_2H_8{}^{2-}$ ligands through metal-carbon σ bonds could be prepared. We now wish to report a compilation of results obtained on these two series of carborane complexes containing stable iron(II)- and manganese(I)-carbon σ bonds.

σ-Bonded Iron(II)-Dicarba-*closo*-decaborane(10) Complexes. When a solution of $(\pi\text{-}C_5H_5)Fe(CO)_2I$[15] in ethyl ether was treated with a solution of 1-Li-10-CH_3-1,10-$B_8C_2H_8$[16] in ethyl ether at reflux for 0.5 hr, a deep brown color formed. Isolation of the products by rotary evaporation of the reaction mixture, elution of the yellow product from a silica gel column with hexane, and vacuum sublimation of the yellow solute afforded yellow, diamagnetic crystals of 1-[$(\pi\text{-}C_5H_5)Fe(CO)_2$]-10-$CH_3$-1,10-($\sigma$-$B_8C_2H_8$), mp 68-69°, in 75% yield. The mass spectral parent ion peak (Table I) was observed at *m/e* 310, corresponding to ${}^{10}B_2{}^{11}B_6{}^{12}C_{10}{}^{1}H_{16}{}^{16}O_2{}^{56}Fe_1{}^+$. Elemental analysis (Table I) supported this formulation. The infrared spectrum of a Nujol mull (Table II) exhibited a strong B—H stretching absorption at 2560 cm^{-1} and two sharp strong C═O stretching absorptions at 2040 and 1970 cm^{-1}, as expected for a $(\pi\text{-}C_5H_5)Fe(CO)_2$– derivative having a single symmetry plane.[17] No carborane C-H stretching absorption around 3060 cm^{-1} was observed, indicating the product to be a C-substituted cyclopentadienyl iron dicarbonyl derivative. A band indicative of the π-C_5H_5 group was observed at 845 cm^{-1}. The 60-MHz ^{1}H nmr spectrum (Table III) consisted of a very sharp singlet of intensity 5.0 at τ 4.94, which was assigned to the π-C_5H_5 protons,[17] and a sharp singlet of intensity 3.0 at τ 7.23,

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(1) M. F. Hawthorne, *Accounts Chem. Res.*, **1**, 281 (1968).

(2) M. F. Hawthorne, D. C. Young, T. D. Andrews, D. V. Howe, R. L. Pilling, A. D. Pitts, M. Reintjes, L. F. Warren, Jr., and P. A. Wegner, *J. Amer. Chem. Soc.*, 90, 879 (1968).

(3) M. F. Hawthorne and T. A. George, *ibid.*, **89**, 7114 (1967).

(4) M. F. Hawthorne and A. D. Pitts, *ibid.*, **89**, 7115 (1967).

(5) T. A. George and M. F. Hawthorne, *ibid.*, **90**, 1661 (1968).

(6) J. N. Francis and M. F. Hawthorne, *ibid.*, **90**, 1663 (1968).

(7) T. A. George and M. F. Hawthorne, *ibid.*, **91**, 5475 (1969).

(8) M. F. Hawthorne and H. R. Ruhle, *Inorg. Chem.*, **8**, 176 (1969).

(9) L. F. Warren, Jr., and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **92**, 1157 (1970).

(10) G. B. Dunks and M. F. Hawthorne, *ibid.*, **92**, 7213 (1970).

(11) D. A. Owen and M. F. Hawthorne, *ibid.*, **92**, 3194 (1970).

(12) D. A. Owen and M. F. Hawthorne, *ibid.*, **93**, 873 (1971).

(13) S. Bresadola, P. Rigo, and A. Turco, *Chem. Commun.*, 1205 (1968).

(14) J. C. Smart, P. M. Garrett, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **91**, 1031 (1969).

(15) R. B. King, Ed., "Organometallic Syntheses," Vol. I, Academic Press, New York, N. Y., 1965, p 175.

(16) P. M. Garrett, J. C. Smart, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **91**, 4707 (1969).

(17) T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **2**, 38 (1956).