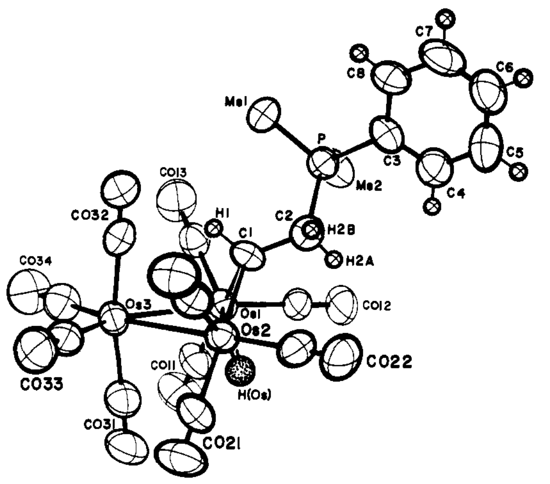

Figure 1. Structure of $HOs_3(CO)_{10}(^{-}CHCH_2P^{+}Me_2Ph)$ determined by x-ray crystallography.

Os(1)-H-Os(2) system makes an angle of 110.25° with the Os_3 plane.

The dipolar $>^{-}CHCH_2P^{+}Me_2Ph$ ligand is in a symmetrical bridging mode with ∠Os(1)-C(1)-Os(2) = 80.8(3)°, Os(1)-C(1) = 2.148 (9) Å, and Os(2)-C(1) = 2.173 (8) Å and takes up an all-staggered conformation. Bond lengths within this moiety are as follows: C(1)-C(2) = 1.514 (12), C(2)-P = 1.823 (9), P-Me(1) = 1.813 (9), P-Me(2) = 1.816 (10), and P-Ph = 1.784 (9) Å. The Os(1)-C(1)-Os(2) bridge makes an angle of 108.97° with the Os_3 plane and an angle of 140.78° with Os(1)-H-Os(2) system.

Preliminary results indicate that among group 5 ligands the reaction exemplified by the formation of **2** is specific to phosphorus donors. Thus, compounds analogous to **2** were formed under similar conditions from treatment of **1** with $P(n\text{-}Bu)_3$ and $P(OMe)_3$, but no reaction was observed with $AsMe_2Ph$, NC_5H_5, NEt_3, or $NHEt_2$. Steric as well as electronic effects at the reacting center must be important, since PPh_3 also did not react with vinylic complex **1**. However, kinetic factors may determine whether a reaction is observed in a particular case. After 8 h in chloroform solution $HOs_3(CO)_{10}(CH\text{-}CH_2P(OMe)_3)$ is almost completely dissociated to **1** and $P(OMe)_3$. In contrast, **2** is only a few percent dissociated after 48 h.

Carty and co-workers[10] recently reported attack by phosphite ligands on the σ,π-bridged alkynyl ligand in a dimeric iron complex, $Fe_2(CO)_6(\mu\text{-}C_2Ph)(\mu\text{-}PPh_2)$. Although the bridging moiety formed differs in detail from that found for **2**, these two examples suggest unusual reactivity for polynuclear compounds.[11] We are currently investigating the interaction of **1** and related compounds with a wider variety of nucleophiles in order to assess the potential for elaboration of cluster-bound hydrocarbon groups.

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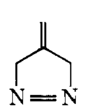
Kinetic Confirmation and Synthetic Circumvention of the Cascade Mechanism for Population of the Triplet Ground State of a Trimethylenemethane[1]

Sir:

The transformation of singlet reactant molecules by thermal (nonphotochemical) excitation into triplet intermediates or products continues to attract interest because the details of the change of multiplicity are not well understood. We recognize two broad mechanistic categories: type I, a "direct" mechanism, in which passage from the singlet to the triplet energy surface occurs without intervention of a discrete intermediate,[2] and type II, a "cascade" mechanism, reactant → singlet intermediate → ground state triplet.[3,4]

The thermal decomposition of azo compound **1** has a low entropy of activation, which is attributed to a requirement for a spin-forbidden process in the type I direct generation of N_2 and the triplet ground state of trimethylenemethane (**2**).[5] On the other hand, in the case of the thermal decomposition of the related azo compound **3** to N_2 and the diyl **4**, we interpret the chemical evidence[6,7] as strongly suggestive of a type II mechanism. The apparent paradox makes the application of the kinetic criterion to that case imperative. The present paper reports the confirmation of the type II mechanism for **3** by such experiments and also describes two methods for the generation and reaction of triplet **4** free of the singlet species that necessarily precedes it in the cascade.



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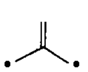

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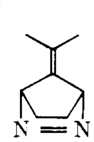

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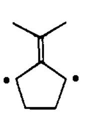
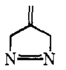
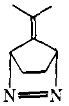


4

The decomposition of **3** at several temperatures between 40 and 80 °C can be monitored by analysis for unreacted **3**, which

Table I. Activation Parameters[d] for Thermal Decomposition of Azo Compounds

Compound	E_a, kcal/mol	log A[a]	$\Delta S^\ddagger$, eu	Ref
5 	37.3	14.9	8.7	8, 9
6 	42.4	15.9	11.2	8
1 	32.6	13.3	−1.1	5
3 	28.8[b] 27.6[c]	15.1 14.7	8.3 6.5	This work This work

[a] A in s^{-1}. [b] In benzene solvent, initial [3] ~ 0.15 M. [c] In CH_3CN solvent, initial [3] ~ 0.15 M. [d] Estimated errors are 0.25 kcal/mol in E_a 0.7 eu in $\Delta S^\ddagger$.

Table II. Ratios[j] of Products (F/B) from 3[h] and Olefins

Olefin	Conc, M	F/B Pyr.[a]	Dir.[b]	Xan[c]	Matrix[d]	"Pure triplet"[i]
Acrylonitrile	1.7[e]	7.8	12	3.5	–	
	1.3[e]	4.8	12	3.5	–	3.0[e]
	6.93[f]	17	38	3.9	3.7	
	13.9[g]	26	34	3.6	4.6	
Methyl acrylate	3.4[f]	–	7.8	4.3	4.0	
	5.1[f]	–	14	4.2	3.4	2.7[e]
	10.2[g]	–	26	3.4	4.3	
Dimethyl-fumarate	0.12[e]	4.5	–	0.8	–	0.7[e]

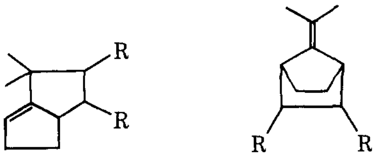
[a] From pyrolysis at 60°. [b] From direct photolysis at 350 nm near 0°. [c] Xanthone photosensitizer present in sufficient concentration to absorb 94–100% of incident light. Ratios for the runs using xanthone concentrations insufficient for 100% absorption are corrected for the small amount of F/B ratio contributed by direct photolysis. [d] Reaction mixture prepared by irradiation of a frozen mixture of 3 and olefin, followed by warming. [e] In CH_3CN. [f] In MTHF. [g] Neat. [h] Initial concentrations 0.004–0.5 M. [i] Reference 7. [j] Estimated experimental error ~15%.

can be quickly (10^{-3} s) and quantitatively decomposed in the injection port (230°) of a gas chromatograph (GC). The evolved nitrogen (retention time about 4 min) is estimated by GC peak area using a 40/60 mesh molecular sieve column (0.25 in. × 6 ft) operated at 50°. The data are given in Table I, which also lists Arrhenius parameters for **1** and two other model compounds, **5** and **6**.

The activation energy terms, E_a, show quite regular behavior. Incorporation of the pyrazoline unit in a bicyclic system lowers E_a by about 5 kcal/mol in both the parent series (**5**, **6**) and the olefinic series (**1**, **3**), presumably because of approximately equal increments of strain energy released in the transition states of the bicyclic reactants. Similarly, the stabilization of the olefinic transition states by incipient trimethylenemethane (TMM) resonance (ΔE_a for **6**–**1** and **5**–**3** each about 10 kcal/mol) is constant.

However, the $\Delta S^\ddagger$ term for the bicyclic TMM precursor **3** is strongly positive, like those for the parent compounds **5** and **6**, which are not TMM precursors, and unlike that for **1**, which is. The absence of any kinetic indication of a spin-forbidden pathway in the thermal decomposition of **3** is compatible with the previous assignment[6,7] of a type II mechanism. Reciprocally, the proposed type I mechanism for **1**[5] in principle could be tested by trapping experiments similar to those used[6,7] for **3**.

We previously have shown[6,7] that the singlet form of diyl **4** can be selected for reaction free of any contamination from the triplet by scavenging the latter with oxygen. We now find that xanthone-photosensitized decomposition of **3** leads directly to the triplet ground state[10,11] of **4**. When the decomposition is effected in solutions containing an olefinic trapping agent, the value (Xan.) of the ratio of fused (F) to bridged (B) cycloadducts from entrapment of the diyl (Table II) is the same as the previously determined[7] F/B ratio extrapolated to infinite dilution of the trapping olefin in the thermal decomposition of **3**. This value is the capture ratio characteristic of the triplet.[7]



F B

Direct photolysis of **3** in the presence of olefinic trapping agents (RCH=CHR) in fluid media gives much higher F/B ratios (Dir., Table II), but direct photolysis of **3**/olefin mixtures in a frozen 2-methyltetrahydrofuran (MTHF) or neat olefin matrix at −196° constitutes a second method for generation of the pure triplet: Electron spin resonance (ESR) spectra of these mixtures show no loss of triplet TMM signal intensity 30 min after irradiation is stopped. Certainly on this time scale the immobilized diyl is in its equilibrium mixture of states. Warming the matrix (MTHF to −160°, neat olefin to −80°) releases the diyl and olefin, which now diffuse together and combine in the typical triplet ratio (Matrix, Table II).

Ratios F/B ~30-75 are observed[7] when azo compound **3** decomposes thermally in the presence of high olefin concentrations or molecular oxygen. These high ratios are characteristic of the singlet diyl **4**[12] and provide a sensitive indicator of even a small amount of singlet contribution to the product mixture, since the triplet F/B ratios (0.7–3) are much smaller. A conservative estimate places the singlet contribution to the F/B ratios Xan. and Matrix of Table II at <5%, which indicates that both photosensitization in fluid medium and the Boltzmann distribution of states in frozen matrices produce the triplet as effectively the only species reactive to the olefinic trapping agents. The facts are consistent with an irreversible cascade, as would be required if the actual singlet–triplet energy spacing were even approximately as large (18–21 kcal/mol) as predicted[13] by theory.

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Temperature Dependence of Positron Lifetimes in Carbonic Anhydrase

Sir:

There are numerous reviews dealing with positron annihilation in matter,[1] yet biochemical applications are still in their early stages. The technique was applied to optical isomers[2] and amino acids[3] but positron annihilation in proteins was reported only recently.[4] Here we present preliminary results for the temperature dependence of the lifetime and intensity parameters in carbonic anhydrase and attempt to correlate the variation of free volume and the changes in conformation of this enzyme.

The sample was prepared by mixing 2.0 g of chromatographically pure bovine carbonic anhydrase (carbonate dehydratase, EC 4.2.1.1)[5] with 4.0 g of deionized distilled water and placing the homogeneous mixture into a glass sphere (22 mm i.d.; 1-mm wall thickness). The source was prepared by enclosing 15 μCi of carrier-free ^{22}Na (as aqueous NaCl) in a sealed thin-walled glass bead (1 mm o.d.; <0.1 mm wall thickness).[6] The bead was positioned at the center of the glass sphere containing the sample. The system was degassed and sealed under vacuum (10^{-5} Torr) and it was immersed in a jacketed cell connected to a circulating thermostat. Positron lifetimes were measured with a standard fast-slow coincidence system[7] utilizing constant fraction timing and Naton 136 scintillators (3.8 cm diameter; 1.3 cm thickness) mounted to RCA 8575 photomultipliers with a time resolution of 0.2 ns. The geometry of the system and the sample thickness (200 mg/cm^2) were chosen to optimize the solid angle between the source and detectors. The time spectra were analyzed on an IBM 360/50 computer using a computational method developed by Cumming.[8]

Positron annihilation intensities and lifetimes were measured over a temperature range −20 to 50°. The lifetime spectra could be resolved into two components. In all cases the lifetime (τ_1) of the short-lived component remained constant within experimental uncertainties. The temperature dependence of the lifetime (τ_2) and the intensity (I_2) of the long-lived component is shown in Figures 1 and 2. The lifetime τ_2 increases moderately between −20 and 40° and then rises steeply to 50°. The intensity I_2 decreases slightly from 27 ± 1 to 23 ± 1% in the temperature range −20 to 50°. Within experimental uncertainties the product $I_2\tau_2$ (Figure 3) is constant over the temperature range −20 to 30°. Above this temperature rapid increase of $I_2\tau_2$ is observed. Over the temperature range 0–50° the activity of carbonic anhydrase increases steadily[9] (Figure 4).

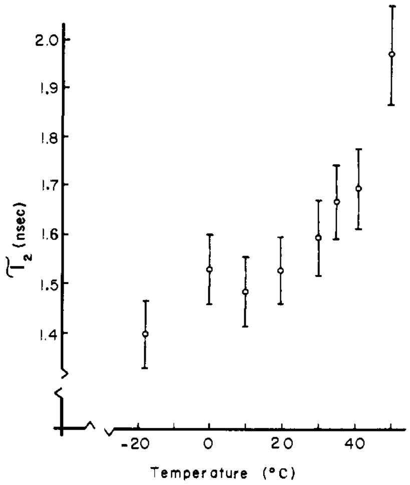

Figure 1. Temperature dependence of the lifetime of the long-lived component of positron annihilation in carbonic anhydrase.

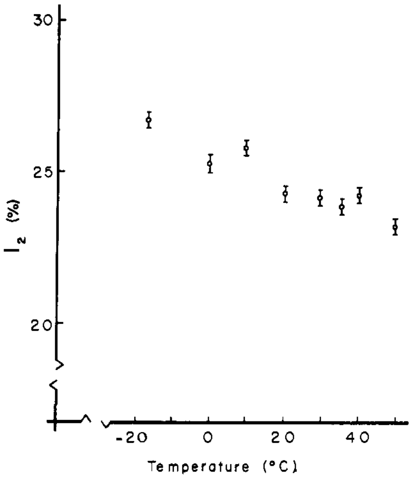

Figure 2. Temperature dependence of the intensity of the long-lived component of positron annihilation in carbonic anhydrase.

Changes in activity are associated with conformational changes of the molecule. At the present time, the nature of these changes is not well understood.[10] Qualitative evaluation of our data in terms of the free volume model[11] allows for the following speculative interpretation of I_2 and τ_2. Since pick-off annihilations are associated only with the long-lived component, the I_2 values represent the number of free volume sites where pick-off annihilations occur.[12] The decrease in the number of free volume sites at higher temperatures is interpreted as the redistribution and collection of free volumes into a system compatible with the new conformation at the elevated temperature. Increasing τ_2 values may correspond to an increase of the average size of the free volume sites which is a further indication of the collection of free volumes. In carbonic anhydrase the total free volume, $I_2\tau_2$ (Figure 3) increases with increasing temperature in the range of 30–50°. These findings, when correlated with enzyme activity measurements, indicate that the increase in activity involves conformational changes