Kinetic Evidence for a Large Separation between Singlet and Triplet Methylene

By H. M. Frey
(*Department of Chemistry, The University, Whiteknights Park, Reading* RG6 2AD)

Summary Reinterpretation of the results obtained in some photochemical systems leads to a value of around 8 k cal mol^{-1} for the separation between singlet and triplet methylene.

The energy separation between the $^3B_1$ and the $^1A_1$ states of methylene (hereafter called $^3CH_2$ or triplet and $^1CH_2$ or singlet methylene) has been a subject of considerable interest and much controversy for the past decade. Theoretical calculations[1] of increasing sophistication and accuracy appear to be converging on a value of about 11 kcal mol^{-1} with an estimated accuracy of ± 2 kcal mol^{-1}. On the other hand, kinetic and thermodynamic consideration of experimental data[2,3] has been interpreted to yield a very small separation between the states of 1—2 kcal mol^{-1} and 2·5 kcal mol^{-1}.

It does not seem to have been generally realised that given the very low chemical reactivity of $^3CH_2$ compared with $^1CH_2$, no appreciable product yields due to the triplet species would be observed in a conventional (steady state) photochemical system, if the energy separation between the states were very small. This may easily be demonstrated by considering the following example. Let us assume that in a particular system consisting of keten with a paraffin the photolysis of keten initially yields methylene entirely in the triplet state. The reaction of $^3CH_2$ with keten is believed to have a collision efficiency of less than 10^{-7} and lower still with paraffins.[4] It must therefore make numerous collisions before it reacts chemically with either species. Since, however, the reaction $^1CH_2 + M \rightarrow {}^3CH_2 + M$, where M is a paraffin (or indeed some other molecule) has a relatively high collision efficiency ($>10^{-2}$) then the reverse reaction will also be efficient but slower by the Boltzmann factor of exp ($-E/RT$). For a 1·4 kcal mol^{-1} energy separation this means that approximately 1 collision in 1000 or less of $^3CH_2$ yields $^1CH_2$, and most of the $^1CH_2$ will react with the paraffin before it undergoes spin inversion to the ground state. Even those singlets that do revert to the ground state have a much higher probability of being re-excited and teacting as singlets than reacting as triplets. Since triplet methylene reactions do occur in systems of the type just considered we conclude that the energy separation between the states must be much greater than 1·4 kcal mol^{-1}.

We now attempt to estimate the likely value of the energy separation by first considering the photolysis of keten at 2700 Å.

$$CH_2CO + h\nu \longrightarrow {}^1CH_2 + CO$$

$${}^1CH_2 + CH_2CO \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} {}^3CH_2 + CH_2CO \tag{1, -1}$$

$${}^1CH_2 + CH_2CO \xrightarrow{k_2} C_2H_4 + CO \tag{S}$$

$${}^3CH_2 + CH_2CO \xrightarrow{k_3} C_2H_4 + CO \tag{T}$$

It is possible to separate reactions (S) and (T) by studying the system in the presence and absence of oxygen.[5] A stationary state treatment of the above mechanism yields equation (I).

$$S/T = k_2(k_{-1} + k_3)/k_1k_3 \qquad \text{(I)}$$

Experimentally S/T was found to be approximately 2·3. For convenience we use collision efficiencies rather than rate constants. As mentioned k_3 has a collision efficiency of less than 10^{-7}, and taking the ratio $k_2/k_1 = \alpha$, we obtain $2{\cdot}3 \simeq \alpha\ (k_{-1} + 10^{-7})/10^{-7}$. Since reactions (1) and (−1) are very fast[6] it is unlikely that either has a collision efficiency appreciably different from 10^{-2}. Taking α equal to unity we obtain $k_1/k_{-1} \simeq 1{\cdot}3 \times 10^{-5}$ which leads to a value for the energy separation between the singlet and triplet states of methylene of 6 kcal mol^{-1} (this takes into account the spin degeneracy of the triplet species).

This is a lower limit for the energy separation since 10^{-7} is a maximum for the collision efficiency for k_3 and it is very unlikely that α can be appreciably less than unity though it may well be somewhat larger. Big changes are required to reduce the value for the energy separation below 6 kcal mol^{-1} whereas relatively small changes result in an appreciably larger value for the separation.

The results obtained by Ring and Rabinovitch[7] using diazomethane and propane in the presence of a large excess of inert gas have been reinterpreted[6] in terms of reactions of residual singlet methylene, but this does not consider the process ${}^3CH_2 + N_2 \longrightarrow {}^1CH_2 + N_2$. If we take Rabinovitch's results and assume that all insertion products noted at high dilution are due to singlet methylene rather than triplet methylene we obtain a value for ΔE of 8 kcal mol^{-1}. Similarly, in the reactions of methylene (from keten) with ethers in the presence of a large excess of inert gas characteristic singlet products were observed even at very high dilutions.[8] If it is assumed that the attack of triplet methylene on a primary C–H bond in an ether has a collision efficiency of 10^{-8} (which is still at least an order of magnitude faster than with methane) then we obtain a value for ΔE of 8·5 kcal mol^{-1}.

Further quantitative information is required about the magnitude of some rate constants before the singlet, triplet energy difference can be determined precisely, but a value of around 8 kcal mol^{-1} appears a reasonable one and hence there no longer appears to be a serious discrepancy between the kinetic estimates and the latest theoretical calculations.

(*Received*, 28*th June* 1972; *Com.* 1126.)

---

[1] J. F. Harrison and L. C. Allen, *J. Amer. Chem. Soc.*, 1959, **91**, 807; C. F. Bender and H. F. Schaefer, *ibid.*, 1970, **92**, 4987; S. V. O'Neil, H. F. Schaefer, and C. F. Bender, *J. Chem. Phys.*, 1971, **55**, 162; P. J. Jay, W. J. Hunt, and W. A. Goddard have obtained a value of 11·5 kcal mol^{-1} for the separation and C. F. Bender, H. F. Schaefer III, D. R. Franceschetti and L. C. Allen a value of 11·0 kcal mol^{-1} (in the press *J. Amer. Chem. Soc.*, and personal communication).

[2] R. W. Carr, T. W. Eder, and M. G. Topor, *J. Chem. Phys.*, 1970, **53**, 4716.

[3] M. L. Halberstadt and J. R. McNesby, *J. Amer. Chem. Soc.*, 1967, **89**, 3417.

[4] P. S. T. Lee, R. L. Russell, and F. S. Rowland, *Chem. Comm.*, 1971, 18.

[5] A. N. Strachan and W. A. Noyes, jun., *J. Amer. Chem. Soc.*, 1954, **76**, 3258.

[6] J. A. Bell, *J. Phys. Chem.*, 1971, **75**, 1537 and references therein.

[7] D. F. Ring and B. S. Rabinovitch, *Canad. J. Chem.*, 1968, **46**, 2435.

[8] H. M. Frey and M. A. Voisey, unpublished experiments.