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RATES OF SPIN-FORBIDDEN ORGANIC REACTIONS. II. IMPLICATIONS FOR THE METHYLENE SPLITTING QUESTION

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Early investigations of the *thermal* decomposition of diazomethane (DM) sought, in analogy with the thermolysis of N_2O, to find if the ground state product (triplet methylene) is formed by a spin-forbidden event or by subsequent deactivation of an excited product. Setzer and Rabinovitch[1] showed that the loss of stereochemistry when methylene from DM adds to *cis*-2-butene derives from subsequent reaction of vibrationally excited cyclopropane. Thus, invoking Skell's hypothesis[2] that singlet carbenes add to olefins so as to retain stereochemical integrity while triplets do not,[2b] it was shown that the major product trapped under these conditions of DM thermolysis is, in fact, the singlet carbene.[3]

In the intervening years a considerable body of experimental and theoretical work on methylene has accumulated, which, coupled with our own theoretical investigations, lead us to reinterpret these early experiments.

In 1973, Halevi and coworkers calculated a CNDO surface for the thermal dissociation of DM and calculated the spin-orbit coupling of the singlet-triplet crossing point.[5]

We have used their results in both RRKM[6] and classical trajectory analyses to compare the relative rates of direct formation of singlet and triplet methylenes[7] from diazomethane and to analyze the existing kinetic data on its decomposition.

Our model involves following the singlet path to the crossing point, allowing the Landau-Zener[8,9] formalism to describe passage through this region where spin is no longer a "good" quantum number and then continued passage along either the singlet or triplet surface until dissociation is achieved. This process is shown schematically in Fig. 1.

The RRKM-calculated rates are perhaps more directly comparable with experiment. Table 1 indicates the frequencies used for the ground state diazomethane, and the critical configurations (assumed equal for singlet and triplet). The triplet reaction was retarded with the addition of Landau-Zener transmission coefficient of *ca* 1/500, corresponding to a spin-orbit coupling of 12 cm^{-1}.[5]

The resulting ratio is

$$\frac{k_T}{k_S}\ (\mathrm{RRKM}) = \frac{10^{12.2}}{10^{15.0}}\ \exp(\Delta E^{\ddagger}/RT)$$

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Figure 1. Schematic representation of a slice through the dizomethans energy hypersurface.

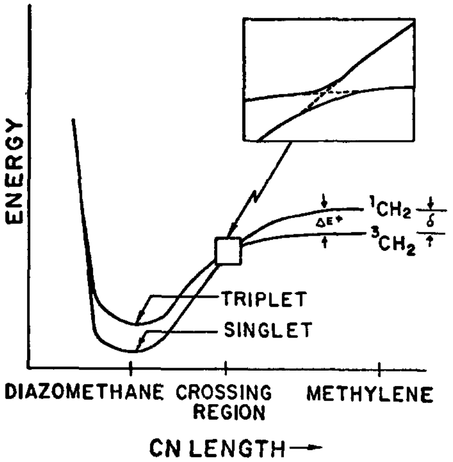


Table 1. Vibrational frequencies used in RRKM calculations of diazomethane decomposition.

Vibration	Ground state[a]	Critical config.[b]
CH asym str	3184	3184
CH sym str	3077	3077
N=N str	2101	2101
HCH scissor	1414	1000
CN str	1170	reactive
HCH wag	1109	600
HCH rock	564	300
CNN in plane	421	100
CNN out plane	406	100

[a] Reference 10.

[b] Our estimate.

where $\Delta E^{\ddagger}$ is stabilization of the triplet relative to the singlet when each is at its critical configuration. The values 15.0 and 12.2 are the RRKM estimates of the logarithms of the singlet and triplet reaction preexponentials, respectively.

If, as Halevi's calculations show,[5] the singlet-triplet crossing occurs before the critical configurations are reached, then the methylene splitting, δ, will be reflected in the $\Delta E^{\ddagger}$ term. Equation (1) predicts increased direct formation of triplet methylene as δ is increased. Even if $\Delta E^{\ddagger}$ is as low as 6kcal/mol (vide infra), some 20% of the methylenes should be born as triplets. Nonetheless, they apparently escaped detection.

If we choose δ as 9-10kcal/mol using Staemmler's[11] impressive calculation, and follow an argument similar to that of Frey,[12] the experimental absence of substantial amounts of triplet trapping is perhaps explicable, even if $\Delta E^{\ddagger}$ is in the 6-10kcal/mol range.

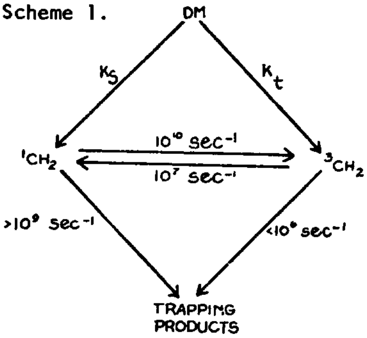
At the temperatures used by Setser and Rabinovitch (500-700°K), a 10kcal/mol splitting, δ, is not enough to prevent the activation of triplet methylene to singlet. Since the geometric reorganization required for this interconversion is simply an H-C-H angle deformation (from 135° to 105°), the frequency factor for this "uphill" (and normally ignored process[13] can reasonably be estimated at 10^{13}. This leads to a rate of activation of

$$k_{T\to S} = \rho 10^{13} \exp(-10000/RT) \tag{2}$$

where ρ is the transmission coefficient for the spin-inversion, which can be estimated from knowledge of the spin-orbit coupling[9] as 5×10^{-3} by using the Landau-Zener relationship.[8]

At 600°K, equation (2) yields a rate of 10^7 sec^{-1} for triplet methylene going to singlet. While singlet methylene adds to cis-2-butene only about ten-fold slower than the collisional rate,[14] Gaspar and Hammond, using data from Rowland and coworkers,[15] argue that triplet methylene may react on less than 10^{-4} of its collisions.[14c] At the pressures and temperatures used in the experimental study,[1] the rate of triplet trapping would then be less than 10^6 sec^{-1}[16] — slower than the equilibration of the methylenes. Scheme 1 summarizes these rate estimates which predict that even if triplet methylene is formed directly from diazomethane, only a fraction of it should be trapped.[3]

Scheme 1.



Consider however the prediction of this scenario, using Lineberger's recent experimental value for δ (ca 20 kcal/mol).[17] Surely, $\Delta E^{\ddagger}$ must then be estimated as much larger than 6 kcal/mol, say at least 12 kcal/mol. Then direct production of triplets should exceed singlets by at least 10^2, and such a large δ would prevent rapid conversion of triplets to singlets even at 700°K. Therefore, contrary to experiment, this model predicts substantial triplet methylene trapping by cis-2-butene in DM thermolysis. Only if $\Delta E^{\ddagger}$ is essentially zero or if the RRMK-calculated singlet and triplet A factors are badly in error does the Lineberger value accomodate the trapping data.

It is therefore of interest to apply the kinetic criterion for spin-forbidden reactions to this system.[18]

The kinetics of thermal decomposition of diazomethan have been variously reported as

	REF.
$k_\infty = 10^{10.9}\ \exp(-31{,}400/RT)$	19
$\sim 10^{13}\ \exp(-35{,}000/RT)$	1
$= 10^{13.8}\ \exp(-36{,}000/RT)$	20

The last cited includes a RRKM analysis which, however, allows no loosening of the activated complex other than motion along the reaction coordinate, an assumption we feel is unreasonable. When other (e.g., H_2C-N-N bending) vibrations are loosened as in Table 1, the experimental A factor is too low for a purely singlet reaction.[21] We feel that the observed Arrhenius parameters are the resultant average of two competing reactions, one formally spin-allowed (higher A factor, higher Ea) and one spin-forbidden. The rate retardation caused by the lower A factor of the latter is compensated for at these temperatures in its more favorable exponential term. Moreover, the difference in Ea and $10^{2.8}$ factor[22] in the pre-exponential are too small to cause the resultant curved Arrhenius plot to be distinguishable from linearity within the experimental error over any reasonable temperature range.

In summary we have shown that a large singlet-triplet splitting in methylene requires unjustified assumptions ($\Delta E^{\ddagger} = 0$ or negligible spin-orbit coupling) to account for the lack of triplet-derived cyclopropanes when DM is thermolyzed in cis-2-butene. The theoretically predicted separation of 9-10 kcal/mol would indicate a substantial direct generation of triplet methylene which by activation to the perhaps much more reactive singlet could be drained away before adding to an olefin. Unimolecular reaction rate theory predicts that the observed pre-exponential factor for DM decomposition fits a combination of predicted singlet and triplet reaction parameters but neither by itself. Clearly, further experimental work seems warranted.

References and Notes

(1) D.W. Setser and B.S. Rabinovitch, Can. J. Chem., 40, 1425 (1962).

(2) P.S. Skell and R.C. Woodworth, J. Amer. Chem. Soc., 78, 4496 (1956). The possibility that a stereospecific addition of triplet methylene can occur at low pressures where inert gas collisions do not force the methylene/olefin pair out of a least motion approach (Cs symmetry) and into the entropy-favored trimethylene region is being explored by C.T.

(3) It is of note in this context that even at total pressures over 1000mm, some 10% of the cyclopropanes have trans stereochemistry. No more than 1% can be ascribed to hot molecule reactions.[4]

(4) F.S. Rowland, P.S.-T. Lee, D.C. Montegue, and R.L. Russel, Disc. Farad. Soc., 53, 111 (1972).

(5) E.A. Halévi, R. Pauncz, I. Schek, and H. Weinstein, Jerusalem Symposium on Quant. Chem. and Biochem., Vol. VI, p. 167 (1974). Note that these spin orbit coupling formulae are valid only for systems with all heavy atoms colinear.

(6) See inter alia, P.J. Robinson and K.A. Holbrook, "Unimolecular Reactions", John Wiley, London (1972) for a description of this method.

(7) S.N. Datta, C.D. Duncan, N.O. Pamuk, and C. Trindle, J. Phys. Chem., in press.

(8) L.D. Landau and E.M. Lifhitz, "Quantum Mechanics", Vol. 3, Addison Wesley, Massachusetts (1958).

(9) R.F.W. Bader and J.I. Generosa, Can. J. Chem., 43, 1631 (1965).

(10) C.B. Moore and G.C. Pimentel, J. Chem. Phys., 40, 329, 342 (1964).

(11) (a) V. Staemmler, Theoret. Chim. Acta, 31, 49 (1973). This calculation involved a very large basis set using the independent electron pair approximation. It should account for 80-90% of the electron correlation and therefore be immune to a recent criticism[11b] of calculations at the Hartree-Fock limit. (b) J.H. Meadows and H.F. Schaefer, J. Amer. Chem. Soc., 98, 4383 (1976).

(12) H.M. Frey, Chem. Comm., 1972, 1024.

(13) See, however, H.D. Roth and M.L. Manion, J. Amer. Chem. Soc., 98, 3392 (1976) for an investigation where triplet to singlet interconversion is demonstrated for a substituted carbene.

(14) (a) Addition of ${}^1CH_2$ to cis-2-butene is 6x faster than insertion into a C-H bond[1] which itself must be only 10^{-2} slower than collision.[14b] (b) W. Braun, A.M. Bass and M. Piling, J. Chem. Phys., 52, 5131 (1970), found ${}^1CH_2$ inserts into a paraffinic C-H bond with a collisional efficiency of 10^{-2}. (c) See P. Gaspar and G. Hammond in "Carbenes", R. Moss and M. Jones, eds., Vol. II, CH 6, pp. 339-346, for a fuller explanation.

(15) F.S. Rowland, C. McKnight, and E.K.C. Lee, Ber. Bunsengess., 72, 236 (1968), and discussion thereafter.

(16) (a) Collisional rate constants are on the order of 10^{11} l/mol/sec and the concentration of the reactants was roughly 0.03 mol/l. (b) K. Laidler, Chemical Kinetics, McGraw-Hill, New York, 2nd ed., p. 65 (1965).

(17) P. Zittel, G. Ellison, S. O'Neil, E. Herbst, W. Lineberger, and W. Reinhardt, J. Amer. Chem. Soc., 98, 3731 (1976).

(18) See J.A. Berson, C.D. Duncan, G.C. O'Connell, and M.S. Platz, J. Amer. Chem. Soc., 98, 2358, (1976) for a recent description and application of this method.

(19) P.S. Shantarovich, Doklady. Akad. Nauk. SSR., 116, 225 (1957).

(20) M.B. Gabunia and A.A. Shteinman, Russ. J. Phys. Chem., 44, 944 (1970).

(21) A factors for reactions of a single precursor yielding two products are typically ca. 10^{15}. See, for example, R.J. Crawford and A. Mishra, J. Amer. Chem. Soc., 88, 3963 (1966).

(22) (a) This factor is to be contrasted with the oft-quoted[22b] but poorly justified 10^{6} prohibition of spin-forbidden processes. (b) See inter alia, P. Lechtken, R. Breslow, A.H. Schmidt, and N. Turro, J. Amer. Chem. Soc., 95, 3125 (1973).