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TRIMETHYLENEMETHANE

ACTIVATION ENERGY FOR RING-CLOSURE OF THE DIRADICAL[1]

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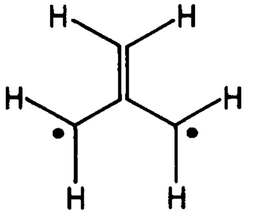
Abstract—The energy of activation for ring-closure of ground state triplet trimethylenemethane (I) to methylenecyclopropane has been measured by following the rate of disappearance of the electron spin resonance spectrum over the temperature range −155° to −140°, in a series of frozen solid matrices. The experiments described make use of 3-methylenecyclobutanone and methylenecyclopropane as precursors to trimethylenemethane.

Kinetic results obtained starting from methylenecyclopropane were most satisfactory and lead to an energy of activation for ring-closure of 7 kcal/mole. This value is significantly smaller than the approx. 20 kcal/mole barrier estimated on the basis of theoretical models. Truncation of the barrier by a tunnelling mechanism is made unlikely by the finding that trimethylenemethane-d_6(I-d_6) undergoes ring-closure with the same 7 kcal/mole energy of activation as the parent I.

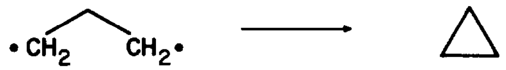
Trimethylenemethane (I), the parent, conjugated ground state triplet was the first 1,3-diradical to be detected spectroscopically. This substance has now become a reactive intermediate of broad mechanistic and theoretical significance.[2]



I

TRIMETHYLENEMETHANE

The carbon-centered 1,3-diradicals lie at the center of a major current theoretical controversy, typified by that surrounding the trimethylene diradical II.[3] Thermodynamic and kinetic considerations assign a theoretical activation energy of approx. 9 kcal/mole, the Benson barrier, to the ring-closure of trimethylene (II) to cyclopropane.[4] This value is to be contrasted with the nil barrier derived by the application of quantum mechanical methods.[5] The parent trimethylene diradical II being unknown as an observable intermediate, there has, until recently,[6] existed no means of resolving this conflict.



II

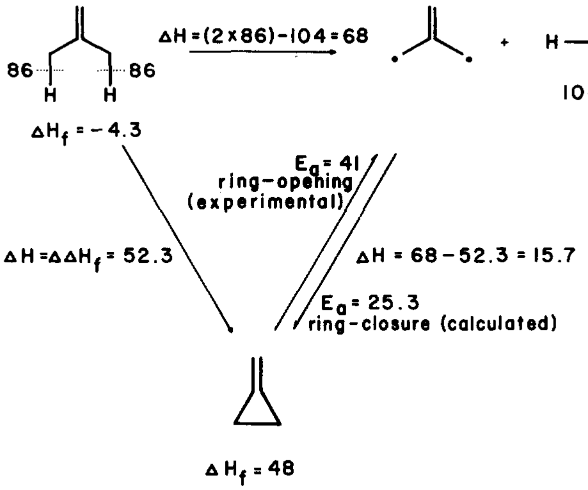
By contrast, triplet trimethylenemethane I has been observed using low temperature electron spin resonance spectroscopy, making this triplet 1,3-diradical (I) directly available for study. Moreover, the predictions of theory with respect to the ring-closure of trimethylenemethane (I) to methylenecyclopropane and with respect to the magnitude of the splitting between the singlet and triplet states of I are as interesting and provocative as those of trimethylene II.

A major advantage in considering the *parent* trimethylenemethane (I) is that the heats of formation of methylenecyclopropane (48 kcal/mole)[7] and isobutylene (−4.3 kcal/mole) are known and can be used to construct a thermodynamic-kinetic cycle modeled after that of Benson's trimethylene-cyclopropane cycle.[4]

The cycle, shown in Scheme 1, begins by considering the energy required for homolytic cleavage of the allylic C–H bonds of isobutylene. The bond dissociation energy of the first C–H bond is taken to be 86 kcal/mole.[8] Analysis of the second allylic C–H bond cleavage is not straightforward, since the effect of the presence of the first radical on the bond dissociation energy of the second C–H bond is unknown. At this point; any number chosen for the bond dissociation energy of the second C–H bond would be an arbitrary one. This problem is one of the major points to be addressed in this paper. Strictly for the purpose of the immediate argument, the explicit assumption is made that there exists no interaction between the first and second radical centers, that the bond dissociation energy for the second C–H bond is the same as that of the first. This first arm of the cycle then requires energy equal to 172 − 104 = 68 kcal/mole ($2D_{C-H} - D_{H-H}$).

A second arm of the cycle, with enthalpy equal to 52.3 kcal/mole, is constructed by taking the difference between the heats of formation of isobutylene (ΔH_f° = −4.3 kcal/mole) and methylenecyclopropane (ΔH_f° = 48 kcal/mole).[7] The third arm completes the cycle and is the enthalpy required to open the allylic C–C ring bond of methlyenecyclopropane to the trimethylenemethane diradical I; it is 15.7 kcal/mole, the difference between the enthalpies of the first two arms.

The energy of activation for ring-opening of methylenecyclopropane to the diradical I is taken to be 41 kcal/mole. This is the value established by Chesick for isomerization of ethylidenecyclopropane to methylmethylenecyclopropane.[9] The barrier to ring-closure of the diradical I will be the difference between the activation energy for ring-opening and the enthalpy for the third arm of the cycle: 41-15.7 = 25.3 kcal/mole. This



Scheme I

hypothetical transformation is summarized by the energy profile shown in Fig. 1.

In reality, trimethylenemethane (I) is stable indefinitely at the bp of liquid nitrogen, but at −140° the electron spin resonance spectrum decays in minutes. Such marked lack of stability is not in accord with the existence of a 25 kcal/mole potential well. For this reason it appeared to be worthwhile to investigate the thermal stability of the triplet I in quantitative fashion.

Triplet state trimethylenemethane will be used in the quantitative experiments to be described. Accordingly, it should be asked whether there exists any conflict between the experiments to be conducted using the triplet I and the argument embodied in Scheme I which almost certainly best refers to the singlet state of I, a requirement imposed by the Chesick thermal isomerization experiment.

The purpose of the present experiments is to establish the energy of activation for ring-closure and to determine to what degree it approaches that of empirical and theoretical models, such as the thermo-kinetic cycle of Scheme I. Since the triplet state is expected to be more stable than the singlet state, the energy of activation for ring-closure of the triplet will be be greater than that of the singlet and the measured value well be a maximum experimental value for the trimethylenemethane system.[10]

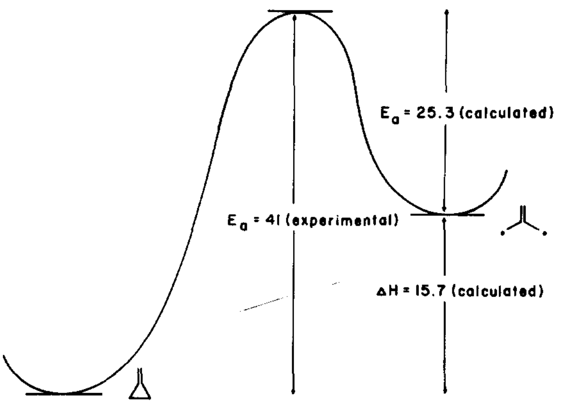


Fig. 1. Hypothetical energy profile for the ring-closure of trimethylenemethane to methylenecyclopropane according to the thermodynamic cycle of Scheme I.

The magnitude of the resonance stabilization afforded the allyl radical is important to the argument. If the stabilization is taken to be smaller than the generally accepted value of 12 kcal/mole, the barrier to ring closure in Scheme I and in Fig. 1 will be lower.

The weight of present experimental evidence[8] strongly supports the use of the 12 kcal/mole value. So much so that it would be considered eccentric not to use it. Indeed, an electron spin resonance experiment by Krusic[11] has led him to conclude that the barrier to rotation about the C–C bond of the allyl radical exceeds 17 kcal/mole. If this barrier is identified with the resonance energy of the allyl radical, then the 12 kcal/mole value would seem to be a conservative one.

On the other hand, a recent ion cyclotron resonance experiment has led to a value of 7.1 kcal/mole as the resonance energy to be associated with the allyl radical.[12] For the reasons stated above, we will use the 12 kcal/mole value, bearing in mind that the day may come when this value must be revised downward or upward.

If the arguments concerning the magnitude of the allylic resonance stabilization energy and the irrelevance of the multiplicity, singlet or triplet, of the diradical be accepted, then the crux of the Benson cycle emerges and it is one of great interest.

There are in the cycle two unknowns; the barrier to ring-closure and the dissociation energy of the second C–H bond leading to the diradical. These values are unknown for any molecule and are, thereby, of substantial importance from a theoretical standpoint. The beauty of the thermodynamic cycle is that once the energy of activation for ring-closure is established, then, the energy required to cleave the second C–H bond must inevitably become known. This is one of the most important points to be put forward in this paper.

Further illumination of the ring-closure is provided by an empirical analysis based on Hückel molecular orbital theory. This is not an independent approach because the barriers derived from it are based on the experimental value for the resonance energy of the allyl radical. Nonetheless, it is instructive to examine the geometric changes which must occur in the ring-closure reaction and the estimated cost in terms of the energy required for the steps involved. Again, no distinction is made between singlet and triplet states and strictly for the purpose of the present argument the ring-closure reaction is broken down into the two discrete steps discussed below.

For the Hückel analysis it is important to choose an appropriate value of the resonance integral β. This is done by taking the resonance energy of the allyl radical to be 12 kcal/mole and setting this value equal to the expression, $(2\sqrt{2}-2)\beta$, for the resonance energy of the allyl radical. The β value equal to 14.5 kcal/mole thus obtained may then be used as shown in Scheme II to evaluate the course of the ring-closure.

If one starts with planar (0,0,0) trimethylenemethane and turns one of the methylene groups 90° to the molecular plane giving the 0,0,90 trimethylenemethane, part of the resonance energy of the trimethylenemethane system is consumed. The energetic requirement for this step can be evaluated by subtracting the total π-electron energy of the allyl radical, $4\alpha+2\sqrt{2}\beta$, from that of trimethylenemethane, $4\alpha+2\sqrt{3}\beta$, yielding an energy of $0.64\,\beta = 9.2$ kcal/mole. The second step requires rotation of the second methylene group for which the resonance energy of the allyl radical, 12 kcal/mole, is required. The total energy required to convert the 0,0,0 to the 0,90,90 trimethylenemethane is approx. 21 kcal/mole. It is assumed that ring-closure of the 0,90,90 form to methylenecyclopropane occurs with little or no activation barrier. Thus, the very qualitative Hückel method yields an estimate for the ring-closure activation energy of the same order of magnitude as the Benson thermochemical cycle described in Scheme 1.

Attempts to understand the properties of trimethylenemethane (I) using more highly sophisticated quantum mechanical methods have focussed on the magnitudes of the splittings among the electronic energy levels of the diradical and on the geometries of the lower energy states.[13] One of the most striking and interesting results to emerge from this line of research is the finding of Yarkony and Schaefer[13a] that in the singlet manifold the energy of the planar (0,0,0) form is within a few kcal/mole of that of the (0,0,90) conformer, in which one of the methylene groups is rotated perpendicular to the plane of the molecule. Estimates of the difference in energy between the planar ground triplet state and the lowest singlet state(s) have ranged from a low of 11 kcal/mole[13d] to a high of 45 kcal/mole.[13c] At the time that the experiments to be described in this paper were carried out, the value favored for the singlet-triplet splitting was predicted to be in the range 17–20 kcal/mole.[13a,g,h,i] In the time since this work was published in preliminary form,[1] the best value for the singlet-triplet splitting has been revised downward to 14.1 kcal/mole.[13f]

RESULTS

Trimethylenemethane (I) was generated by photolysis of dilute solutions of 3-methylenecyclobutanone[14] frozen at the bp of liquid nitrogen in solid matrix solutions of methycyclohexane glass, polycrystalline hexafluorobenzene, methylenecyclopropane or tetrahydrofuran.[15] A typical spectrum in methylcyclohexane glass is shown in Fig. 2. For the kinetic runs, the field of the electron spin resonance spectrometer was locked at 3110 G the position of maximum absorption of the low-field xy line. The temperature was then raised abruptly to a predetermined point in the temperature range −155 to −140°, a short time was allowed to elapse for the temperature to become stable, then the recorder was swept using the abscissa as a time axis and the ordinate to measure the decay in the intensity of the xy line. A typical decay curve is shown in Fig. 3(a) and a first-order plot is shown in Fig. 3(b). The rate constants obtained from runs made over the temperature range −155° to −140° lead to the Arrhenius plot shown in Fig. 4. Results for the series using 3-methylenecyclobutanone as precursor in the several different matrices are shown in Table 1.

The results shown in Table 1 confirmed what was suspected: that the activation energy for ring-closure would be found to be substantially below that predicted by the thermo-kinetic cycle of Scheme 1. However, there are two disturbing features associated with this opening series of experiments. First, there is too much scatter among the energies of activation obtained from experiments carried out in different matrices. It might be argued that the scatter is not great, since these are kinetic experiments carried out under most unorthodox and unfavorable conditions, the solid state not being the medium of choice for rate measurements. Nonetheless, the scatter and apparent dependence on matrix do exist and make the results shown in Table 1 less than completely satisfactory. The second disturbing feature,

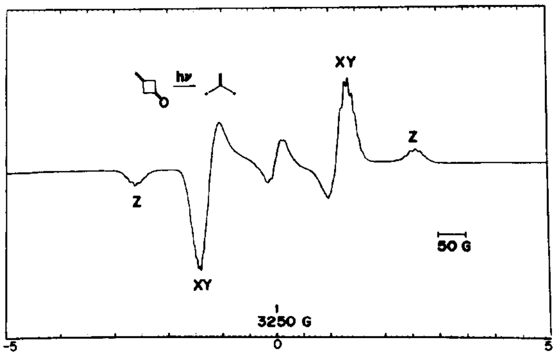
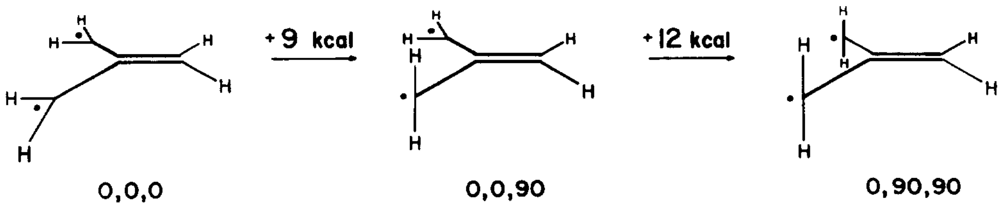


Fig. 2. Electron spin resonance spectrum of trimethylenemethane (I) from photolysis of 3-methylenecyclobutanone in methylcyclohexane at −186°C.



Scheme 2.

Table 1. Activation energies for the ring-closure of trimethylenemethane prepared from 3-methylenecyclobutanone

Starting Material	E_a, kcal/mole[e]	log A[e]	Temperature Range, °K
3-Methylenecyclobutanone[a]	2.0 ± 0.4	6.7 ± 0.8	109.0 - 128.0
3-Methylenecyclobutanone[b]	5.0 ± 0.8	5.8 ± 1.4	113.9 - 138.2
3-Methylenecyclobutanone[c]	2.8 ± 0.7	2.1 ± 1.4	104.6 - 121.1
3-Methylenecyclobutanone[c]	3.5 ± 0.7	3.0 ± 1.4	110.6 - 118.1
3-Methylenecyclobutanone[d]	4.8 ± 0.6	6.1 ± 1.1	108.1 - 124.2

[a]In methylenecyclopropane solvent. [b]In decalin solvent. [c]In methylcyclohexane solvent. [d]In perfluoromethylcyclohexane solvent. [e]With standard deviation.

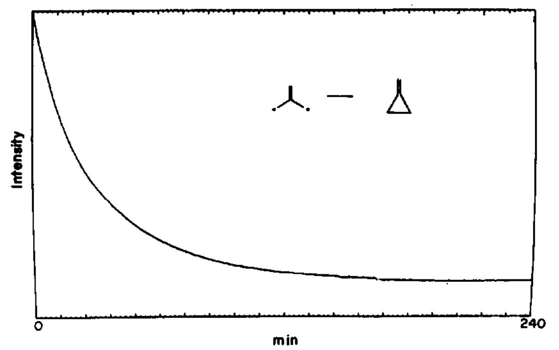


Fig. 3. Trimethylenemethane decay at −145°C.

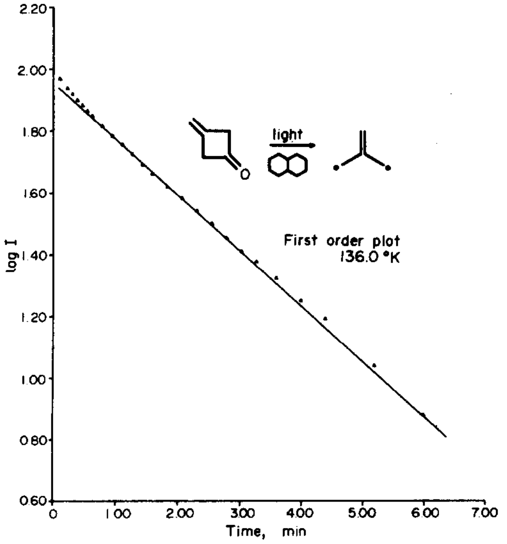


Fig. 3(b). First-order plot of the ring-closure at −137°C of trimethylenemethane produced from photolysis of a 0.5 M solution of 3-methylenecyclobutanone in decalin.

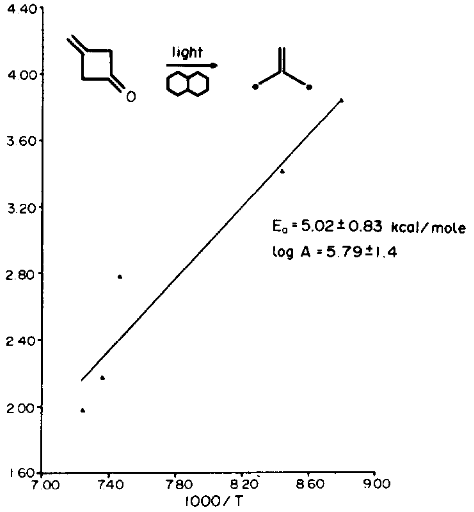


Fig. 4. Arrhenius plot of −log k vs 1/T for ring-closure of trimethylene-methane produced by photolysis of a 0.5 M solution of 3-methylenecyclobutanone in decalin.

which may impinge on the first, is the low and variable values of the pre-exponential factor.

In order to confirm the low activation barrier observed for trimethylenemethane ring-closure and because the results from these first experiments were not as sharply defined as had been hoped, use of another precursor to trimethylenemethane was explored. Irradiation of methylenecyclopropane with γ-rays from a ^{60}Co source yields the spectrum of the trimethylenemethane diradical (I) shown in Fig. 5. Kinetic results obtained from examination of the decay of trimethylenemethane (I) generated by radiolysis of methylenecyclopropane are presented in Table 2.

Examination of Table 2 reveals a more self consistent picture than that obtained starting from 3-methylenecyclobutanone. The energy of activation derived from the results shown in Table 2 is 7 ± 1 kcal/mole, a value preferred to the lower ones obtained from 3-methylenecyclobutanone. The lack of internal consistency in the latter experiments may be a consequence of a perturbing influence of the carbon monoxide fragment, as indicated by the fluctuation of the log A values, but this is purely speculation and should be taken as such.

There exists the possibility that the ring-closure reaction occurs by a tunneling mechanism, in which the 7 kcal/mole activation energy represents a truncated barrier. This suggestion has the virtue that it would account for the discrepancy between the 7 kcal/mole found and the approx. 20 kcal/mole barrier expected on the basis of theoretical models. In order to explore this question, fully deuterated methylenecyclopropane-d_6 was prepared. Examination of the ring-closure of tri-

Table 2. Activation energies for the ring-closure of trimethylenemethane prepared from methylenecyclopropane

Starting Material	E_a, kcal/mole[a]	log A[a]	Temperature Range, °K
Methylenecyclopropane[b]	7.8 ± 0.7	9.9 ± 1.2	120.1 - 135.0
Methylenecyclopropane[c]	7.1 ± 0.6	8.9 ± 0.9	120.7 - 135.0
Methylenecyclopropane[d]	6.2 ± 0.9	7.7 ± 1.6	124.2 - 137.1

[a]With standard deviation. [b]Neat sample. [c]5.4 M in hexafluorobenzene. [d]4.3 M in hexafluorobenzene.

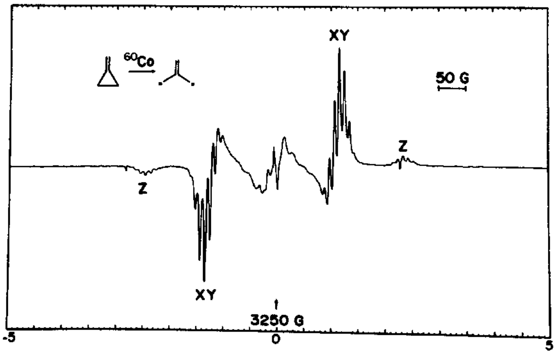


Fig. 5. Electron spin resonance spectrum at −160°C of trimethylenemethane produced by radiolysis of methylenecyclopropane.

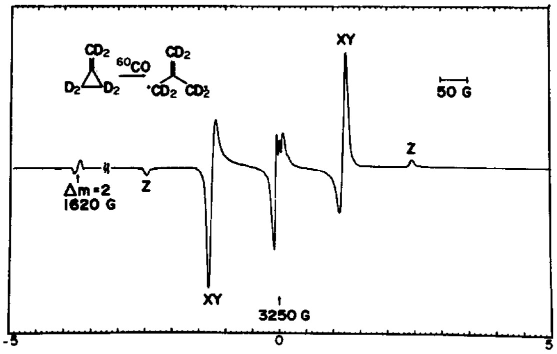


Fig. 6. Electron spin resonance spectrum of trimethylenemethane-d_6 produced by radiolysis of methylenecyclopropane-d_6.

methylenemethane-d_6 (Fig. 6) obtained by γ-radiolysis of the methylenecyclopropane-d_6 yielded the data shown in Fig. 7 and in Table 3. These experimental results provide no support for a tunneling mechanism. On this basis the value of 7 kcal/mole will be taken as the barrier to ring-closure of the triplet diradical I.

Since the values for the energy of activation obtained from the methylenecyclobutanone experiments (Table 1) are uniformly lower than the 7 kcal/mole value above, they do not conflict with the conclusion drawn here that 7 kcal/mole is the maximum experimental value for the energy of activation of the ring-closure reaction of the triplet diradical I.

DISCUSSION

The measured ring-closure activation energy of 7 kcal/mole is in conflict with the higher values (*ca* 20 kcal/mole) anticipated on the basis of the qualitative theoretical models: simple Hückel MO theory and the thermodynamic-kinetic theory developed as the cycle shown in Scheme I.

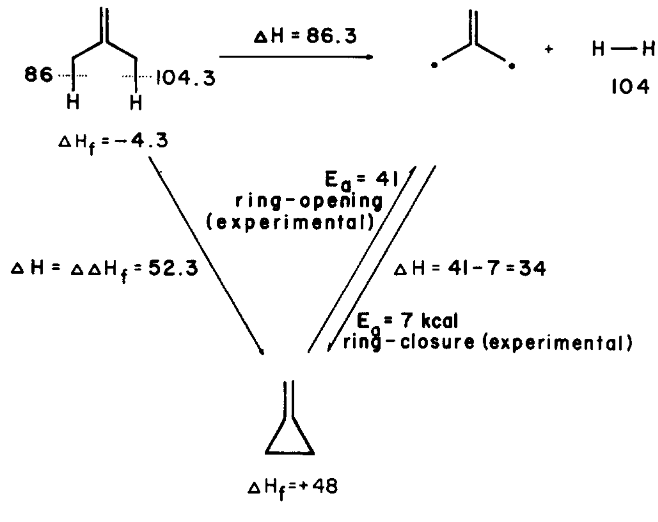
The latter conflict is more apparent than real. At the outset of the thermodynamic-kinetic argument the explicit assumption was made that cleavage of the second allylic C–H bond in isobutylene requires an amount of energy equal to that which characterizes the first C–H bond cleavage. With an experimental value for the activation energy for ring-closure of the diradical available for the first time, it is now possible to establish an experimental value for the energy required to cleave the second C–H bond in isobutylene by recasting the thermo-kinetic cycle as that shown in Scheme III and Fig. 8.

With the activation energy for ring-closure taken to be

Table 3. Activation energies for the ring-closure of trimethylenemethane-d_6 prepared from methylenecyclopropane-d_6

Starting Material	E_a, kcal/mole[a]	log A[a]	Temperature Range, °K
Methylenecyclopropane-d_6[b]	7.3 ± 0.3	9.1 ± 0.5	119.5 - 135.6
Methylenecyclopropane-d_6[c]	7.4 ± 0.8	9.8 ± 1.3	117.7 - 131.9
Methylenecyclopropane-d_6[d]	6.6 ± 2.1	9.1 ± 3.9	112.6 - 122.5

[a]With standard deviation. [b]Neat sample. [c]4.8 M in hexafluorobenzene. [d]2.8 M in hexafluorobenzene.



Scheme 3.

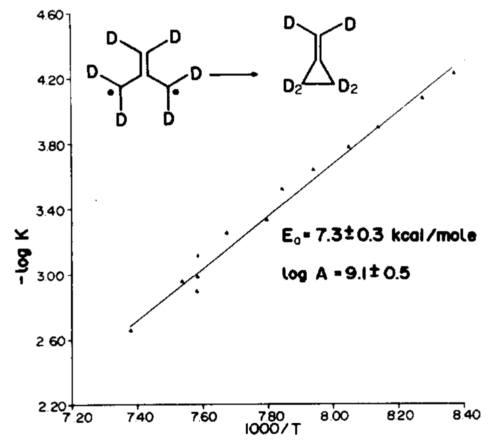


Fig. 7. Arrhenius plot of −log k vs 1/T for ring-closure of trimethylene-methane-d_6 produced by radiolysis of methylene-cyclopropane-d_6.

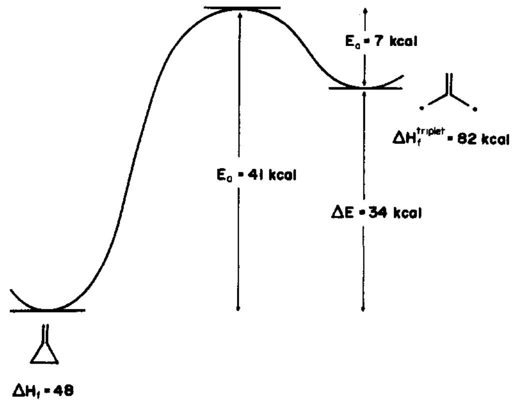


Fig. 8. Energy profile based on the thermodynamic cycle of Scheme III.

7 kcal/mole the enthalpy for the ring-closure step becomes 41 − 7 = 34 kcal/mole. When this value is combined with the 52.3 kcal/mole difference between the heats of formation of methylenecyclopropane and isobutylene, a new value, 86.3 kcal/mole, for the enthalpy of the C–H bond cleavage step is obtained. Addition of 104 kcal/mole, the standard dissociation energy of the H–H bond, yields 190.3 kcal/mole, the sum of the energies required to cleave both C–H bonds of isobutylene. The energy required to cleave the first C–H bond of isobutylene requires 86 kcal/mole. Cleavage of the second C–H bond therefore requires 104.3 kcal/mole, a bond strength slightly greater than that of a normal saturated C–H bond.[12]

The 7 kcal/mole energy of activation for ring closure, is of special interest as a measure of the extent of resonance stabilization afforded to the ground state triplet of I. Simple Hückel MO theory predicts an incremental resonance stabilization of 9 kcal/mole over that of the allyl radical for I. This value suggests a dissociation energy of 89 kcal/mole for the second allylic C–H bond of isobutylene. More sophisticated theoretical methods have also assigned comparably substantial stabilization energies to the ground triplet state of I and, consequently, make a similar prediction for the dissociation energy of the second allylic C–H bond. By contrast, the value of 104 kcal/mole, derived from the experiments described here, for homolytic cleavage of the second C–H bond of isobutylene, leading to I, is approximately that of a normal, saturated primary C–H bond. This discrepancy between theory and experiment may be taken as a measure of the energetic destabilization of conjugated open-shell, four-π-electron molecules.

If the path to ring-closure leads from the ground triplet state through the lowest singlet state enroute to (singlet) methylenecyclopropane, then the 7 kcal/mole activation energy provides a measure of the singlet–triplet splitting for the trimethylenemethane system, one which is substantially below that provided by theory.[13] That the singlet–triplet splitting is probably substantially lower than theory would indicate is supported by a further experimental determination using a substituted trimethylenemethane.[2b] It has also been pointed out that if triplet trimethylenemethane could pass directly to methylenecyclopropane at the intersection of the singlet and triplet energy surfaces, [2b] the 7 kcal/mole would be a minimum value for the singlet-triplet splitting. The latter would constitute a concerted closure of triplet-trimethylenemethane to methylenecyclopropane—a forbidden reaction.[17]

EXPERIMENTAL

General. NMR spectra were recorded on either Varian A-60 or Varian T-60 spectrometers. Chemical shifts are expressed in units of δ (ppm downfield from TMS) and coupling constants (J values) are given in Hertz (Hz). IR spectra were taken on a Perkin–Elmer 247 grating infrared spectrophotometer, using NaCl cells or KBr pellets. MPs were taken on either a Fisher-Johns or a Mel-Temp m.p. apparatus; and are uncorrected. MS were obtained on an LKB 9000 gas chromatograph-mass spectrometer at ionizing voltages of 70 and 15 eV using either a direct insert probe or analytical GLC columns. Exact mass measurements were obtained on a MAT CH5 mass spectrometer.

ESR spectra were run on a Varian E-4 ESR spectrometer (X-band, frequency 9.102 GHz) equipped with an E-257 variable temp. sample probe.

Photolysis of 3-methylenecyclobutanone to trimethylenemethane (I). A dilute soln (10 μl in 0.2 ml, *ca* 0.5 M) of 3-methylenecyclobutanone in methylcyclohexane was placed in a quartz ESR tube (4 mm outside diam and 3 mm inside diam). Photolysis at −196° for about 40 min using a PEK 100 W medium pressure mercury lamp yielded the ESR spectrum of trimethylenemethane. Similar experiments were also carried out using dilute solns of other solvents as follows: 0.4–0.6 M of 3-methylenecyclobutanone in perfluoromethylcyclohexane, *cis*-1,3-pentadiene, decalin, and methylenecyclopropane. The ESR spectrum in methylcyclohexane is shown in Fig. 2. Absorptions at 2987, 3104, 3387 and 3514 G are assigned to the $\Delta m_s = 1$ transitions of the spectrum. The half-field absorption corresponding to the $\Delta m_s = 2$ transition was observed at 1620 G. In addition, absorption due to a monoradical impurity was always present at 3250 G.

Radiolysis of methylenecyclopropane to trimethylenemethane (I). Neat methylenecyclopropane (0.15 ml) was distilled into a quartz ESR tube connected to a vacuum line. The sample was degassed four or five times by a series of freeze-thaw cycles then sealed at 10^{-4} mm Hg. Dilute solns of 5.4 M, 4.3 M, and 2.3 M methylenecyclopropane in hexafluorobenzene were degassed and sealed in ESR tubes in a similar fashion. The sealed samples were placed in a standard, silvered, one-pint Dewar flask, cooled in liquid N_2 and γ-irradiated in a ^{60}Co source (11.915 curies) at −196° for periods of 3–6 hr. The irradiated samples were stored in liquid N_2 prior to the ESR measurements. At each run, the sample was quickly introduced into the precooled ESR spectrometer cavity. The spectrum shown in Fig. 5 reveals the well-resolved hyperfine structure of the trimethylenemethane diradical (I).

Preparation of cupric oxalate. Cupric oxalate was prepared by slow addition of a soln of 6 g oxalic acid in 100 ml water to a vigorously stirred, boiling soln of 8 g of $CuSO_4 \cdot 5H_2O$ in 300 ml water contained in a 1 l. Erlenmeyer flask. When the addition was complete, the mixture was stirred for 40 min at 100°. The mixture was then cooled to room temp and filtered with suction. Cupric oxalate was collected as a fine pale blue powder.

Pentaerythritol-d_8. In a 500 ml, three-necked, round-bottomed flask, equipped with a stirrer and a thermometer was placed 30 g (0.94 mole) of paraformaldehyde-d_{2n} and 150 ml of D_2O. To the stirred suspension was added a soln of 10 g (0.21 mole) of acetaldehyde-d_4 in 30 ml of D_2O and 0.045 g of solid cupric oxalate. A mixture of 7 g (0.125 mole) of CaO in 30 ml D_2O was then added in portions with stirring. When about half of the CaO had been added, cuprous oxide (0.176 g) was added. The CaO remaining was then added over a period of 40 min, the reaction temperature being maintained at 20–24°. The mixture was stirred for 19 hr after the addition was complete. The reaction was then treated with oxalic acid (*ca* 13.5 g) until calcium oxalate precipitation was complete, and the white calcium oxalate ppt was removed by suction filtration through supercel. The filtrate was evaporated to dryness on the rotary evaporator. The residue from the evaporation was dissolved in 35 ml of hot EtOH, then cooled yielding 19.8 g of crude pentaerythritol-d_8. The mother liquor was evaporated to dryness on the rotary evaporator, the residue was taken up in 20 ml hot EtOH then cooled yielding an additional 1.7 g of white solid. The total product was dried in a vacuum desiccator at 0.04 mm Hg for one day affording 21.1 g (71%) crude pentaerythritol-d_8, mp 190–206° (lit.[18] mp 260°). The NMR spectrum (DMSO-d_6) showed only an OH singlet at δ4.2. The methylene proton peak ordinarily found at δ3.6 was completely absent. The IR spectrum (KBr) showed bands at 3000–3600 (O–H); 2100, 2167, and 2212 (C–D) cm^{-1}. The mass spectrum (15 eV) showed peaks at *m/e* (relative intensity): 76(86), 62 (54), and 47 (100).

Pentaerythrityl trichlorohydrin-d_8. A three-necked flask was equipped with a dropping funnel, a magnetic stirrer, a drying tube, and a condenser. In the flask were placed 19.5 g (0.135 mole) crude pentaerythritol-d_8 and 32.1 g (0.406 mole) pyridine. The mixture was stirred vigorously and cooled in an ice bath. To the cooled slurry 48.3 g (0.406 mole) thionyl chloride was added dropwise over a 35 min period. The ice bath was removed and the mixture was refluxed for 6 hr. The resulting dark brown mixture was cooled to about 30°, water (80 ml) was added, and the reaction was stirred for a few min. The soln was then extracted with 100 ml benzene. The benzene layer was removed and the aqueous layer was extracted with four 16 ml portions benzene. The combined benzene extracts were dried overnight over Na_2SO_4, then for 15 min over $MgSO_4$, and filtered. The benzene was distilled through a short column at 25°/130–140 mm Hg. The residue was transferred to a 100 ml distilling flask and distilled through a short column at 5 mm Hg. The pentaerythrityl trichlorohydrin-d_8, bp 95–105°/5 mm was obtained as white crystals, mp 60–62°, weighing 17.01 g (63%). The NMR spectrum (CCl_4) showed only OH protons at δ2.1. The multiplet ordinarily present at δ3.6–3.7 was completely absent. The IR spectrum (CCl_4) showed bands at 3644 (O–H); 2184 and 2108 (C–D) cm^{-1}. The mass spectrum (70 eV) showed peaks at *m/e* (relative intensity): 183, 181, 179, (0.9:3.4:3.4, M^+-DHO); 169, 167, 165(0.6:3.1:3.7, M^+-CD_2OH); 146, 144, 142(5.1:24.4:33.4, M^+-DCl-DHO); 134, 132, 130(9:55:100, M^+-HCl-$CD_2 = 0$).

Oxidation of pentaerythrityl trichlorohydrin-d_8 to tris(chloromethyl) acetic acid-d_6. The HNO_3 oxidation was carried out in an efficient hood. In a 250 ml one-necked round-bottomed flask equipped with a stirrer, boiling stones, and a condenser was placed 15.53 g (0.078 mole) pentaerythrityl trichlorohydrin-d_8. An excess (32 ml) conc HNO_3 was added to the reaction flask. The mixture was heated with a heating mantle, cautiously at the outset, until reaction became apparent. At first the chlorohydrin dissolved, then two layers appeared, and then brown fumes of nitrogen oxides were vigorously evolved. At this point heating was suspended for 10 min. The reaction was then refluxed for 12 hr. The resulting clear, nearly colorless soln was cooled and diluted with 70 ml water. The crude acid separated as a white ppt. The mixture was filtered yielding 10.62 g tris-(chloromethyl)-acetic acid-d_6, m.p. 97–100°. The filtrate was evaporated to dryness on a rotary evaporator. The resulting solid was washed with a small amount of water yielding an additional crop of 0.93 g crude acid, m.p. 106–108°. The total crude acid (11.55 g, 70%) was dried in a vacuum desiccator for several hr.

The NMR spectrum ($CDCl_3$) showed a singlet carboxylic acid proton at δ10.4. The singlet methylene protons ordinarily found at δ3.83 were completely absent from the NMR spectrum. The IR spectrum (KBr) showed strong carboxyl group absorption at 1720 and 3500–2300 cm^{-1}. The mass spectrum (15 eV) showed peaks at *m/e* (relative intensity): 179, 177, 175(2.6:6.0:9.0, M^+–Cl); 163, 161, 159(5:26:39, M^+–CD_2Cl); 97, 95, 93(10:62:100).

3-*Chloro*-2-(*chloromethyl*)-1-*propene*-d_6. In a 50 ml one-necked, round-bottomed flask attached to a short fractionating column was placed 11.63 g (0.055 mole) crude tris-(chloromethyl)-acetic acid-d_6 and 7.1 g (0.055 mole) quinoline (distilled from calcium hydride and stored over molecular sieves). The mixture was heated with an oil bath and gas evolution was observed at a bath temp of 100°. The product was isolated by distillation as it was formed at 235–70 mm (the vacuum improved as gas evolution slowed) and an oil bath temp of approx. 100°. The distillation yielded 3.6 g (50%) of a colorless liquid. The proton NMR spectrum showed no absorption at ordinary amplitudes. The IR spectrum showed C–D bands at 2150, 2180 and 2250 cm^{-1}. The mass spectrum (70 eV, adsorbed on charcoal) shows peaks at *m/e* (relative intensity); 134, 132, 130(1.0:7.4:12.5, Parent); 97(16); 95(74); 93(72); 24(100).

Methylyenecyclopropane-d$_6$. A 100 ml, three-necked, round-bottomed flask was equipped with a reflux condenser, a magnetic stirrer and a dropping funnel. The reflux condenser was connected to three traps set in series to form a vacuum line equipped with a connection to a N_2 source. The product being volatile, care was taken to ensure that there were no leaks in the system. In the flask was placed 0.9 g (37 mmole) Mg metal. The system was twice evacuated and flushed with N_2. The Mg was then covered with dry THF (freshly distilled from a purple benzophenone-sodium soln). The three traps were cooled to −78° with dry ice-acetone. A few crystals of I_2 and about 0.6 g (4.6 mmole) 3-chloro-2-(chloromethyl)-1-propene-d$_6$ were added to the reaction flask. When the reaction commenced, a soln of 2.8 g (21.4 mmole) 3-chloro-2-(chloromethyl)-1-propene-d$_6$, together with a small amount of THF, was collected in the first trap. No material was collected in the second or third trap. The material in the first trap was then distilled bulb-to-bulb at 105 mm Hg to the second trap, cooled with dry ice-acetone. A second bulb-to-bulb distillation to the third trap was carried out in the same way. The resulting pure methylenecyclopropane-d$_6$ was then distilled into the ESR tubes at 0.05 mm Hg. The ESR samples were degassed three times at 0.03 mm Hg, and sealed off while frozen in liquid N_2. Sufficient methylenecyclopropane-d$_6$ was obtained (about 0.3 g) to make four samples for ESR experiments. No absorption was observed in the NMR spectrum of the methylenecyclopropane-d$_6$. The IR spectrum (CCl_4) showed C–D absorption at 2300, 2224 and 2183 cm^{-1} and C=C absorption at 1746 and 1712 cm^{-1}. The mass spectrum (70 eV) showed peaks at *m/e* (relative intensity): 60(96, parent), 59(4), 40(100). Examination of the parent peak cluster reveals that the product is comprised of 96% C_4D_6 and 4% C_4HD_5.

Radiolysis of methylenecyclopropane-d$_6$ to trimethylenemethane-d$_6$. Sealed samples of neat methylenecyclopropane-d$_6$ and dilute solns of 4.8 M, 2.8 M and 1.2 M methylenecyclopropane-d$_6$ in hexafluorobenzene were placed in a standard silvered pint Dewar flask filled with liquid N_2 and were irradiated with γ-rays (^{60}Co source) at −196° for period of 4–6 hr. Since trimethylenemethane (I) is stable in liquid N_2, the samples were readily transported and stored until needed for kinetic analysis. The irradiated samples were introduced into the precooled ESR spectrometer cavity at a temp of −175°. The strong spectrum of trimethylenemethane-d$_6$, shown in Fig. 6, was obtained. There are in the spectrum four $\Delta m_s = 1$ absorptions located at 3000, 3120, 3365 and 3493 G. The half-field absorption corresponding to the $\Delta m_s = 2$ transition is also observed at 1620 G. In addition, a monoradical impurity absorption at 3250 G and a pair of sharp lines, corresponding to the H atom, at 2970 and 3482 G are observed. The samples can be reused. When a kinetic run is complete, the sample tube is warmed to room temp and shaken to mix the contents. The tube is then cooled in liquid N_2 and irradiated as before. For all practical purposes, this process can be continued indefinitely.

Kinetic measurements. Kinetic experiments were carried out on a Varian E-4 spectrometer equipped with an E-257 variable temp accessory. Temp was measured by a platinum resistance sensor (Rosemount Engineering Company) placed in the ESR tube, completely immersed in the frozen matrix of the sample and connected to a potentiometer. The Pt resistance sensor was calibrated by Rosemount at the freezing point of water, the bp of liquid N_2 and the bp of liquid He. Temp control was accurate to ±0.3°. The decay of the trimethylenemethane was monitored by the time-dependent decrease in the intensity of the ESR signal at 3110 G. The measurement was terminated when the change in intensity was too small to be significant (six to eight half-lives). Smooth exponential decay curves were observed (Fig. 3a). The rate constants and the activation parameters are collected in Tables 1–3.

The monoradical impurity at 3250 G from photolysis or radiolysis was quite stable up to temps of −100°. The H atom from radiolysis disappeared at −158°. The intensity of the monoradical peak did not change to any significant degree during the kinetic runs.

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Alternatively, the triplet could proceed directly to methylenecyclopropane (a forbidden reaction[17]) through a transition state which is: higher than, the same as, or lower in energy than that which might obtain for the singlet diradical. For the first two possibilities there is no conflict with the proposed experiments. The last possibility, which would be in conflict with the experimental plan, is the least likely of the three. Theoretical calculations[13] quite emphatically point to a substantial energy gap between twisted (0,0,90 and 0,90,90) singlet and triplet diradicals, favoring the singlet by approx. 20 kcal/mole.

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Alternatively, if the 7 kcal/mole experimental barrier to ring

closure is used in conjunction with the 90.9 kcal/mole bond dissociation energy, then the dissociation energy of the second C–H bond of isobutylene will be 99.1 kcal/mole.

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