

Figure 1. Beer's law plot for **1** at 313 nm.

dilution is accompanied by a dramatic decrease in initial quantum yield for dimer formation ($\phi_{10.4M} = 0.14$; $\phi_{1.0M} = 0.03$). The quantum yields and dimer distributions are independent of the amount of light absorbed up to 10^{-5} einstein cm^{-2} , which indicates that the dimers must be primary photoproducts. On prolonged irradiation *cis*-1,3,5-hexatriene, the major primary product at 313 nm ($\phi_{10.4M} = 0.45$; $\phi_{1.0M} = 0.82$), competes with **1** on an increasingly successful basis for the light.¹¹

Irradiations were also performed at 254 nm, near the maximum of the first absorption band of **1**. At this wavelength the quantum yield for dimer formation in neat diene is very low (6×10^{-3}) and the only dimers detected are traces of **2**, **4**, and **5**. As at 313 nm, the major primary product is the *cis*-triene ($\phi_{10.4M} = 0.46$; $\phi_{1.0M} = 0.56$).¹²

The completely different photochemistry observed at 254 and 313 nm demonstrates that the diene excited singlet state is not involved in the dimerizations at the longer wavelength, and the presence of comparatively major amounts of new dimers at 313 nm indicates that precursors other than the lowest triplet excited state of **1**¹⁴ must be responsible for the formation of these products.

A plausible explanation of these results is that absorption by ground-state aggregates of **1** occurs at 313 nm. That such complex formation does occur is indicated by the observation that the Beer's law plot for rigorously degassed solutions of **1** in cyclohexane shows substantial curvature at 313 nm; the apparent ϵ 's range from 0.05 at 1.0 M to 0.08 at 10.4 M (*cf.* Figure 1).

We suggest that excited dimeric or polymeric species are formed by direct excitation and that their decay to new chemical products does not duplicate paths open to excimers which are formed by diffusive encounter of excited monomers with ground-state monomers.

(11) For this reason, the chemical yield of dimers from preparative irradiations of neat **1** at 313 nm is extremely low (0.6%).

(12) The original designation¹³ of the *trans*-triene as the primary photoproduct was in error: unpublished results from this laboratory and private communication from Professor E. Havinga.

(13) R. J. DeKock, N. G. Minnaard, and E. Havinga, *Recl. Trav. Chim. Pays-Bas*, **79**, 922 (1960).

(14) $E_{T1} = 54 \text{ kcal mol}^{-1}$; D. T. Evans, *J. Chem. Soc.*, 1735 (1960).

The phenomenon, absorption of light by weakly interacting pairs of neighboring molecules followed by unusual photoreaction, may be fairly common when systems containing very high concentrations of chromophoric species are exposed to light of wavelengths longer than that absorbed by monomeric species. The mechanism may be involved in degradation of some materials on exposure to sunlight.

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Yves L. Bahurel,¹⁵ Donald J. MacGregor
Thomas L. Penner, George S. Hammond*

Contribution No. 4344

The Gates and Crellin Laboratories of Chemistry
California Institute of Technology, Pasadena, California 91109

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Theoretical Investigations of the Trimethylene Biradical¹

Sir:

There is currently much interest in establishing the mechanisms and potential surfaces involved in the geometric and structural isomerizations of small cyclic compounds such as cyclopropane.^{2–8} We report here the results of *ab initio* calculations on several configurations of trimethylene (open cyclopropane) using the generalized valence bond (GVB) method.⁹

We will use the following notation in describing the trimethylene configurations: θ is the central CCC angle; (90,90) indicates that the plane of each terminal CH_2 group is perpendicular to the CCC plane; (0,0) indicates that both terminal CH_2 groups are in the CCC plane; (0,90) is the obvious combination; a subscript *c* [*e.g.*, (0,90)_c] indicates that the terminal group is canted from planar to the nearest staggered configuration^{7,8} (with respect to the bonds of the central carbon).

The geometric isomerizations of cyclopropane involve breaking of one C–C bond [in the (90_c,90_c) configuration] followed by rotation of one (path I) or both (path II) terminal CH_2 groups. If the shape of each CH_2 group is kept fixed as one CH_2 group is rotated, there would occur three relative maxima in each of which both bonds of this group would eclipse the bonds of the central carbon; in between would be two points [both (0_c,90_c)] at which the bonds would be staggered,

(1) Partially supported by a grant (PF-013) from the President's Fund of the California Institute of Technology and by a grant (GP-15423) from the National Science Foundation.

(2) D. W. Setser and B. S. Rabinovitch, *J. Amer. Chem. Soc.*, **86**, 564 (1964); B. S. Rabinovitch, E. W. Schlag, and K. B. Wiberg, *J. Chem. Phys.*, **28**, 504 (1958).

(3) W. L. Carter and R. G. Bergman, *J. Amer. Chem. Soc.*, **91**, 7411 (1969).

(4) H. E. O'Neal and S. W. Benson, *J. Phys. Chem.*, **72**, 1866 (1968).

(5) R. Hoffmann, *J. Amer. Chem. Soc.*, **90**, 1475 (1968).

(6) A. K. Q. Siu, W. M. St. John III, and E. F. Hayes, *ibid.*, **92**, 7249 (1970). This work used CC bond lengths of 1.30 Å, somewhat shorter than the 1.54 Å we used. They carried out a 2×2 CI calculation, starting with the Hartree-Fock triplet orbitals. This procedure corresponds to the first iteration in the GVB method and should be adequate for $\theta > 100^\circ$.

(7) L. Salem, *Bull. Soc. Chim. Fr.*, 3161 (1970).

(8) Y. Jean and L. Salem, *Chem. Commun.*, 382 (1971).

(9) P. J. Hay, W. J. Hunt, and W. A. Goddard III, *Chem. Phys. Lett.*, in press; see also W. A. Goddard III and R. C. Ladner, *J. Amer. Chem. Soc.*, **93**, 6750 (1971).

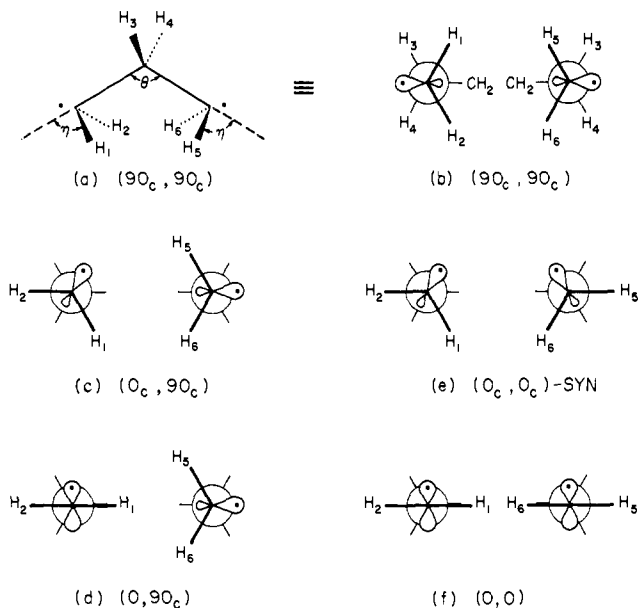


Figure 1. Schematic representation of some of the trimethylene configurations. In (b-f) the molecule is shown twice, each part emphasizing one of the terminal groups.

leading to relative minima. However, the minimum energy path for rotating the CH_2 by 360° need not keep the shape of the CH_2 group fixed. By allowing the CH_2 group to wobble as it rotates, one can avoid eclipsing more than one bond, leading to a slightly lower (~ 0.5 kcal) barrier height. The saddle point for this path (I) is expected to be $(0,90_c)$. For path II the two groups can be rotated either in a conrotatory or a disrotatory sense and the saddle point is expected to be $(0,0)$. Some of these configurations are shown schematically in Figure 1.

The calculated energy curves for the $(90_c,90_c)$, $(0,90_c)$, and $(0,0)$ configurations (Figure 2a) indicate that for $\theta \leq 130^\circ$ the unrotated $(90_c,90_c)$ configuration remains below both possible saddle points and that the saddle points for paths I and II have comparable energies (60.9 and 60.5 kcal) and angles (112 – 114°).

Keeping the terminal groups planar and conrotating from $(0,0)$ to $(90,90)$ leads to no hump in the potential curve, as shown in Figure 2b, and the similar rotation from $(0,90_c)$ to $(90,90_c)$ also should lead to no significant hump (at most a very slight one, ~ 0.5 kcal). We found that starting with trimethylene in the $(90_c,90_c)$ configuration and closing the ring involved no energy barrier; hence there should be no significant energy barrier to ring closure from either saddle point.

If the terminal groups of trimethylene are taken as planar, we obtain the potential curves in Figure 2c. The $(0,0)$ energy curve shows a minimum for $\theta = 114^\circ$, which is essentially at the angle (115°) where the $(90,90)$ curve crosses the $(0,0)$ curve. On the other hand, the $(0,90)$ curve remains about 1 kcal above the $(0,0)$ curve in the $\theta = 110$ – 120° region. These results are in qualitative agreement with the extended Hückel calculations of Hoffmann⁵ who found the $(90,90)$ and $(0,0)$ curves to cross at $\theta \sim 117^\circ$ with the $(0,90)$ curve somewhat higher. [He found the $(0,0)$ minimum to occur at $\theta = 125^\circ$ with an energy 44 kcal above that of cyclopropane; considering an extensive set of geometries, he found a cycle-closing barrier of about 1 kcal.] Our

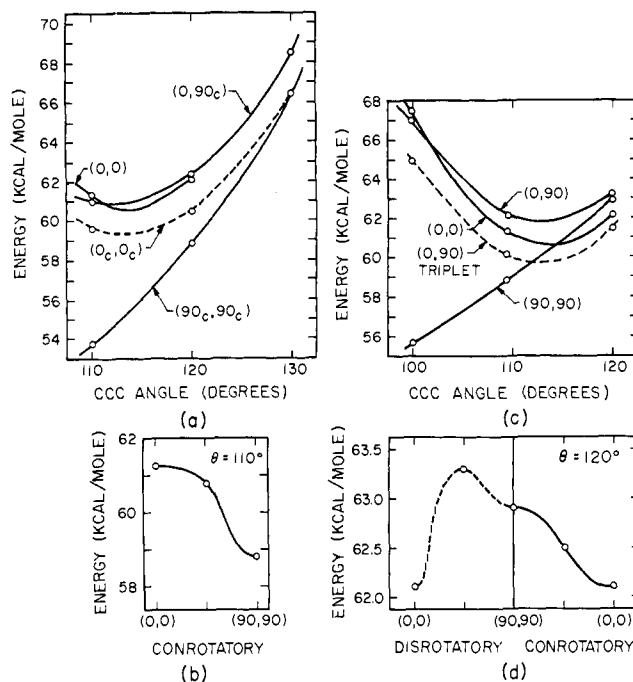


Figure 2. (a) Energy curves for the $(0,0)$ and $(0,90_c)$ saddle points of trimethylene compared with $(0_c,0_c)$ and $(90_c,90_c)$ curves; (b and d) potential curve for rotation of planar terminal CH_2 groups at $\theta = 110$ and 120° , respectively; (c) energy curves for the case of planar terminal groups.

results are also in fair agreement with *ab initio* calculations on the $(0,0)$ and $(90,90)$ states by Siu, St. John, and Hays⁶ [they find the crossing to occur at $\theta = 109.5^\circ$ and the minimum in the $(0,0)$ curve at 114.3° with an energy of 32 kcal above that of cyclopropane (leading to a cycle-closing barrier of about 1 kcal if the surface between $(0,0)$ and $(90,90)$ is assumed to be smooth)].

We also examined the energy changes for disrotatory and conrotatory motions of the planar terminal groups (see Figure 2d). As suggested earlier by Hoffman,⁵ the conrotatory motion is favored, but only slightly.

Although for planar terminal groups the $(0,0)$ form is more stable than the $(90,90)$ for $\theta > 115^\circ$, staggering of the terminal bonds relative to the central bonds lowers the energy (1.6 and 4.0 kcal, respectively, at 120°), with $(90_c,90_c)$ remaining more stable than $(0_c,0_c)$ for $\theta < 130^\circ$ (Figure 2a). There are both syn and anti forms of $(0_c,0_c)$, but at $\theta = 120^\circ$ these differ only by 0.1 kcal. The extra stability due to canting was first pointed out by Salem⁷ who found energy lowerings of 1 kcal for $(0_c,0_c)$ relative to $(0,0)$ and 6.2 kcal for $(90_c,90_c)$ relative to $(90,90)$ (at $\theta = 113^\circ$).

We have ignored the triplet states in most of this discussion since the singlet states are most relevant for these reactions. For triplet states the $(0,90_c)$ configuration was an energy about 1 kcal lower than $(0,0)$ and $(90_c,90_c)$. The $(0,90)$ triplet is compared with some singlet curves in Figure 2c.

Summarizing we find that the barrier height for cis-trans isomerization of cyclopropane is essentially the same (calculated value, 60.5 kcal) whether one or both of the terminal CH_2 groups are rotated after opening of the CC bond. The calculated barrier height compares well with the estimate of 61.1 kcal by Lin and Laidler¹⁰ based on RRKM calculations using the ex-

(10) M. C. Lin and K. J. Laidler, *Trans. Faraday Soc.*, **64**, 927 (1968).

perimental results¹¹ ($E_a = 64.2$ kcal). However, we find no justification for the common assumption⁴ of a large ring-closing barrier (usually assumed to be about 9 kcal⁴) for trimethylene biradical.¹² This result of no significant ring-closing barrier does not contradict experimental results³ and is in agreement with extended Hückel calculations on trimethylene⁵ and tetramethylene.¹³

(11) B. S. Rabinovitch, E. W. Schlag, and K. B. Wiberg, *J. Chem. Phys.*, **28**, 504 (1958).

(12) In the usual calculation⁴ of the ring-closing barrier of trimethylene, one starts with propane and breaks a terminal CH bond on each end. This procedure leads to a mixed spin state (neither singlet nor triplet). The singlet state is strongly bound for configurations near (90, 90) and leads to energies below the saddle point, which may explain the low values usually obtained.⁴

(13) R. Hoffmann, S. Swaminathan, B. G. O'Dell, and R. Gleiter, *J. Amer. Chem. Soc.*, **92**, 7091 (1970).

(14) (a) National Science Foundation Predoctoral Fellow; (b) NDEA Fellow; (c) Alfred P. Sloan Foundation Fellow.

P. J. Hay,^{14a} W. J. Hunt,^{14b} W. A. Goddard III*^{14c}

Contribution No. 4269

Arthur Amos Noyes Laboratory of Chemical Physics
California Institute of Technology, Pasadena, California 91109

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Stabilities of the Anion Radicals of Nitrobenzyl Derivatives

Sir:

Several reports have appeared recently concerning the stabilities of the anion radicals of the nitrobenzyl halides¹⁻⁴ and thiocyanates.⁵ Although all reports are in agreement that the stabilities of the halogenated anion radicals increase with increasing strength of the carbon-halogen bond, the rate constants measured or estimated recently by Mohammad, *et al.*,^{2,3} are considerably smaller than the values which we reported earlier.^{1,6} Because the difference in the reported stabilities of each of the anion radicals of the nitrobenzyl derivatives is so large, we undertook additional electrochemical studies to check our earlier results. During the course of these studies we also investigated the redox behavior of 4-nitrobenzyl cyanide, one of the compounds included in the report by Mohammad and coworkers.² In further contrast to their work, we find that the redox behavior of 4-nitrobenzyl cyanide differs significantly from that of the other nitrobenzyl derivatives.

The electrochemical reduction of 4-nitrobenzyl bromide, chloride, and thiocyanate in acetonitrile was shown in our earlier work^{1,5} to be a one-electron process which initially yields the corresponding anion radical. The anion radical decomposes with loss of anion to form 4-nitrobenzyl radical which subsequently dimerizes or

(1) J. G. Lawless, D. E. Bartak, and M. D. Hawley, *J. Amer. Chem. Soc.*, **91**, 7121 (1969).

(2) M. Mohammad, J. Hajdu, and E. M. Kosower, *ibid.*, **93**, 1792 (1971).

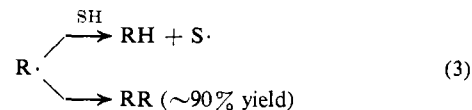
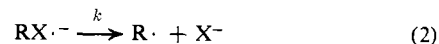
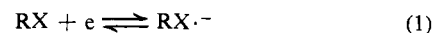
(3) M. Mohammad and E. M. Kosower, *ibid.*, **93**, 2713 (1971).

(4) P. Peterson, A. K. Carpenter, and R. F. Nelson, *J. Electroanal. Chem. Interfacial Electrochem.*, **27**, 1 (1970).

(5) D. E. Bartak, T. M. Shields, and M. D. Hawley, *ibid.*, **30**, 289 (1971).

(6) Our measured values of 6×10^8 and 2×10^4 sec⁻¹ for the decomposition rate constants of 4-nitrobenzyl bromide and chloride anion radicals, respectively, may be compared with their estimated value (footnote 14 of ref 2) of 10^3 sec⁻¹ for 4-nitrobenzyl bromide anion radical and their reported value of 10-20 sec⁻¹ for 4-nitrobenzyl chloride anion radical.

abstracts a hydrogen atom from the solvent system (eq 2 and 3). Both 4,4'-dinitrobenzyl and 4-nitro-



toluene are electroactive and are reduced to the dianion and anion radical, respectively, at a cyclic voltammetric peak potential of -1.23 V vs. sce (eq 4 and 5). The



reduction of 4,4'-dinitrobenzyl has been shown by chronoamperometric and thin-layer coulometric methods to consist of two closely spaced one-electron processes with the anion radical, $\text{RR}^{\cdot -}$, as an intermediate.^{1,7}

Chronoamperometry was used here to set a lower limit on the rate constant for decomposition of the 4-nitrobenzyl chloride anion radical. In this technique the potential of the working electrode is changed abruptly from a value which is insufficiently negative (-0.6 V) to cause reduction of the 4-nitrobenzyl derivative to a value sufficiently cathodic (-1.5 V) so as to cause concurrent reduction of the 4-nitrobenzyl halide ($E_{1/2} = -1.09$ V) and the products of the radical decomposition, 4,4'-dinitrobenzyl and 4-nitrotoluene (both $E_{1/2} = -1.20$ V). Theory predicts^{8,9} for this sequence of electrochemical and chemical reactions that the apparent value of n (n_{app}) should vary from a lower limit of 1.0 when kt is small (*i.e.*, the only reaction which occurs is the one-electron reduction of the nitrobenzyl halide to its anion radical) to a limit of 2.0 when kt is large (*i.e.*, reactions 1-5 proceed to completion). We find experimentally that the electrochemical reduction of 4-nitrobenzyl chloride at -1.5 V is diffusion controlled for all values of t greater than 200 μsec and that all chemical reactions (eq 2 and 3) must occur rapidly since n_{app} equals 2 (Figure 1). If it is arbitrarily assumed that a value of 1.8 or smaller is required for n_{app} before kinetic control can be detected, then a lower limit of 10^4 sec⁻¹ can be set for the decomposition rate constant of the anion radical of 4-nitrobenzyl chloride.⁹ The value of 2×10^4 sec⁻¹ measured earlier by us by another procedure^{1,10} must

(7) J. E. Harriman and A. H. Maki, *J. Chem. Phys.*, **34**, 778 (1963).

(8) G. S. Alberts and I. Shain, *Anal. Chem.*, **35**, 1859 (1963).

(9) M. D. Hawley and S. W. Feldberg, *J. Phys. Chem.*, **70**, 3459 (1966).

(10) The decomposition rate constants reported earlier by us^{1,5} were calculated from the anodic shifts which occur in the cyclic voltammetric peak reduction potentials when the anion radicals decompose. This procedure¹¹ requires an estimate of the half-wave reduction potential of the nitrobenzyl halide in the absence of a follow-up chemical reaction and is obtained from a plot of $E_{1/2}$ vs. σ for a series of substituted nitrobenzenes which form stable anion radicals. Since ρ is a function of the supporting electrolyte and the solvent, the value was determined under our experimental conditions. Our value of $\rho = 0.33$ V is consistent with previously reported values ($\rho = 0.22$ to 0.42 V) for the reduction of substituted nitrobenzenes in dipolar aprotic solvents.^{12,13}

(11) R. S. Nicholson and I. Shain, *Anal. Chem.*, **36**, 706 (1964).

(12) W. C. Danen, T. T. Kensler, J. G. Lawless, M. F. Marcus, and M. D. Hawley, *J. Phys. Chem.*, **73**, 4389 (1969).

(13) P. Zuman, "Substituent Effects in Organic Polarography," Plenum Press, New York, N. Y., 1967, p 102.