Exothermic Cyclic Peroxide Reactions. Decomposition of a 1,2,4-Trioxane

Gary B. Schuster* and Lynn A. Bryant

Department of Chemistry, Roger Adams Laboratory, University of Illinois, Urbana, Illinois 61801

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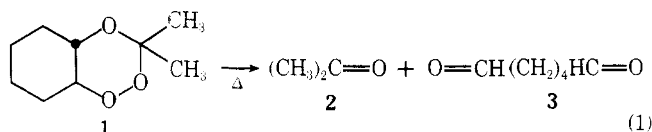
Recent reports on the thermolysis of cyclic peroxides[1,2] and the suggestion that the 1,2,4-trioxane ring may be a key chemiluminescent intermediate[3] prompt us to communicate our results on the thermolysis of *trans*-4,4-dimethyl-2,3,5-trioxabicyclo[4.4.0]decane (1). Peroxides containing the



1,2,4-trioxane ring system have been prepared previously.[4] However, the products and the kinetic behavior of this molecular class were not reported. In this note we relate our findings on the thermal behavior of 1,2,4-trioxane 1.

Degassed solutions of peroxide 1 in octane or diphenyl ether were thermolyzed at temperatures ranging from 160 to 189 °C. Analysis of the resulting product mixture by mass and NMR spectroscopy and gas chromatography revealed acetone (2) and adipaldehyde (3) (see eq 1). The yield of acetone was essentially quantitative; however, the amount of aldehyde 3 formed was dependent upon the extent of the reaction. Extrapolation to very low conversion indicated that the adipaldehyde was formed in ~95% yield. Independent control experiments confirmed that aldehyde 3 was unstable under the reaction conditions.

Investigation of the kinetics for the decomposition of peroxide 1 indicated that the rate of reaction was cleanly first order in peroxide concentration for at least four half-lives. Moreover, it was observed that the addition of *n*-butyl mercaptan did not inhibit the thermal decomposition of 1 (see Table I). The activation parameters for the thermal cleavage of peroxide 1 were determined by investigating the effect of temperature on the observed rate of this reaction. Least-squares analysis of the thermal rate data indicated that $\Delta G^{\ddagger}$ for the rate-determining step of this reaction is 39.9 ± 1.4 kcal/mol at 175 °C.

The results of the investigation of the rate and products of the thermal decomposition of peroxide 1 are consistent with the unimolecular thermal cleavage of the oxygen–oxygen bond as the initial bond-breaking step. The activation energy and the small rate enhancement in more polarizable solvents,[5] as well as the products observed, are in agreement with this

Scheme I

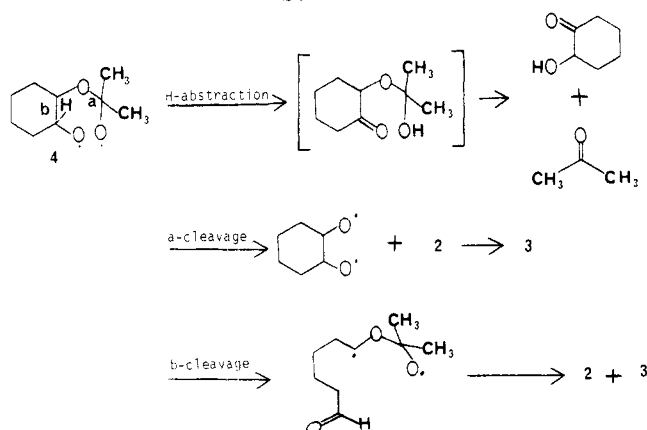


Table I. Thermal Reaction Rate of Peroxide 1

Solvent[a]	Temp,[b] °C	Added substrate	$k \times 10^5$, s^{-1}
Octane	188.9		48.4
Octane	181.9		22.4
Octane	180.0	*n*-Butyl mercaptan[c]	16.4
Diphenyl ether	172.0		61.6
Octane	169.4		7.54
Octane	161.0		2.73

[a] Peroxide concentration was typically 2.5×10^{-2} M. [b] Temperature was regulated to within 0.2 °C. [c] The mercaptan concentration was 5×10^{-2} M.

conclusion. The 1,6 diradical formed from this bond cleavage (4) has several reaction paths open to it.

Hydrogen atom abstraction through a six-membered ring transition state is a common reaction of alkoxy radicals. If this were to occur from diradical 4, we anticipate that adipoin (5) would result (see Scheme I). No 5 was found in the reaction mixture. Moreover, it was determined that the adipoin was stable under the reaction conditions. The lack of adipoin formation can be understood if the lifetime of diradical 4 is extremely short. This would be the case if a fast irreversible reaction of 4 were occurring.

A second common reaction of alkoxy radicals is α cleavage to form carbonyl compounds. Biradical 4 must break two α bonds to form the observed products. Three choices for the sequence of bond-breaking steps from this intermediate seem apparent. First, if the bond labeled a (see Scheme I) cleaves first, acetone and a 1,4 biradical will be formed. It should be noted that this 1,4 biradical is the anticipated intermediate in the chemiluminescence of the corresponding 1,2-dioxetane.[6] Alternatively, initial cleavage of the bond labeled b would generate the 1,4 biradical, resulting from the as yet unknown 1,3-dioxetane ring system. Finally, bonds a and b could cleave simultaneously, generating the observed products in one step from the 1,6 biradical. Our results cannot distinguish between these possible reaction pathways.

Peroxide 1 is potentially a chemiluminescent intermediate.[3] Group equivalent calculations[7] indicate that the reaction of 1 to 2 and 3 is exothermic by ~37 kcal/mol. Inclusion of the observed activation energy suggests that ~77 kcal/mol is available for the formation of electronically excited states. This quantity is probably sufficient to populate the triplet state of simple carbonyl compounds with reasonable efficiency. Moreover, if the suspected biradical intermediate (4) goes on to product by cleaving bond a, a mechanistic pathway consistent with previous light-forming reactions is available. Unfortunately, the high temperatures required to decompose peroxide 1 mitigate against the detection of a low yield of electronically excited states. The lifetime of carbonyl excited states is shortened at high temperatures so that radiative and energy-transfer processes are at a competitive disadvantage. We did not observe any chemiluminescence that we could assign to the unimolecular decomposition of 1.

In summary, we have observed that upon thermolysis the relatively stable cyclic peroxide 1 undergoes unimolecular cleavage to form carbonyl compounds 2 and 3 with high efficiency. In addition, the suspected intermediate biradical formed from homolysis of the oxygen–oxygen bond must rearrange rapidly (most probably) by an α-cleavage reaction. Finally, no chemiluminescence was observed during this reaction, although sufficient energy is available to form the lowest triplet state of the observed products.

Experimental Section

NMR spectra were determined with Varian T-60 and EM-390 spectrometers using tetramethylsilane as an internal standard. IR

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spectra were recorded on a Perkin-Elmer 137 instrument. Analytical gas chromatography was carried out on a Varian 2700 all-glass chromatograph equipped with flame ionization detectors, using a 6 ft × 0.25 in. o.d. glass column with 3% SE-30 on Chromosorb Q at 175 °C. All solvents were Aldrich spectrophotometric grade and were used without further purification.

***trans*-4,4-Dimethyl-2,3,5-trioxabicyclo[4.4.0]decane (1).** Peroxide 1 was prepared by the procedure of Payne and Smith.[8] Purification was accomplished by distillation [bp 45–50 °C (0.5 mm)], followed by repeated recrystallization from pentane to yield 15% of the analytically pure peroxide: mp 24–25 °C; IR (CCl_4) 3.3, 7.3–7.4 (*gem*-dimethyls), 8.2, 9.3, 10.6 μm; NMR (CCl_4) δ 1.3 (s, 3 H), 1.6 (s, 3 H), 3.68 (m, J = 11, 8, 3.5 Hz).

Procedure for Determination of Reaction Rate. Solutions of peroxide 1, typically 2.5×10^{-2} M, and an internal standard, usually decane, were prepared in Pyrex test tubes. The samples were degassed at 5×10^{-4} mm through three freeze–pump–thaw cycles and sealed under vacuum. The tubes were then thermolyzed and analyzed at intervals by gas chromatography as described. The rate of reaction of the peroxide and appearance of acetone were both first order. The rate constants were extracted from these data by least-squares analysis and are reported in the Table I.

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β Radioloysis of Crystalline ^{14}C-Labeled Amino Acids

William A. Bonner,* Richard M. Lemmon, and H. Pierre Noyes

Department of Chemistry, Stanford University, Stanford, California 94305, Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720, and Stanford Linear Accelerator Center, Stanford University, Stanford, California 94305

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In an investigation of the possible validity of the Vester–Ulbricht β-decay parity violation mechanism[1–3] for the abiotic origin of molecular chirality, one of us has recently shown[4,5] that 10–20% net longitudinally polarized 120-keV electrons produced in a linear accelerator caused the asymmetric degradation of DL-leucine. "Natural" antiparallel spin-polarized electrons preferentially degraded the D-leucine component of the racemate, and parallel spin electrons selectively destroyed the L enantiomer. This was the first positive demonstration of asymmetric degradation by β particles since Garay's 1968 report[6] that 0.36 mCi of $^{90}SrCl_2$ in aqueous solution caused more rapid decomposition of dissolved D-tyrosine than of L-tyrosine. Earlier studies[1–3,7] and our subsequent attempts[8,9] to modify and extend Garay's experiments to other amino acids, both solid and dissolved, using a 61 700-Ci ^{90}Sr–^{90}Y source at Oak Ridge National Laboratory led to no observable asymmetric radiolyses. More recently, Darge and co-workers[10] made the remarkable report that DL-tryptophan in frozen aqueous solution suffered 33% total degradation and (based on its optical rotation of 0.0007 ± 0.0004°) a 19% optical enrichment of the D enantiomer during its 12-week exposure to 0.63 mCi of dissolved [^{32}P]phosphate. In view of the several positive reports of asymmetric β radiolysis reviewed above, we have been encouraged to examine for β-induced optical activity a number of ^{14}C-labeled DL amino acids of high specific radioactivity (~300–600mCi/mol) prepared 17–25 years ago at the Lawrence Berkeley Laboratory, University of California.

The racemic amino acids studied and the radiochemical and analytical data pertaining to them are recorded in Table I. Three of the amino acids listed in Table I (DL-Ala, DL-Asp, and DL-Nva) have been examined previously[11] for optical activity (using ORD measurements) and percent decomposition (using the amino acid analyzer), with the observation of no selective radiolysis. In the present study we have used quantitative gas chromatography (GC) as our analytical criterion for both the enantiomeric composition of the undercomposed amino acid residues as well as for percent degradation (using the "enantiomeric marker" technique[12]). GC not only provides the important advantage (over optical rotation) of looking at *only* the residual enantiomers of interest (uncontaminated by accompanying degradation products which may or may not be optically active) but is capable, particularly with microquantities, of superior accuracy and precision (~0.2%)[13] in the quantitative analysis of enantiomers. The DL amino acids in Table I were converted to their *N*-trifluoroacetyl isopropyl esters as previously described[13] and analyzed in replicate with the aid of a digital electronic integrator,[13] using 150 ft × 0.02 in stainless steel capillary GC columns[13] coated with the optically active GC phases *N*-lauroyl-[14] or *N*-docosanoyl-L-valine *tert*-butylamide.[15] All GC analyses were interspersed "back-to-back" with an equal number of replicate GC analyses of the corresponding nonradioactive, authentic DL amino acid as a control. For comparison purposes, Table I also summarizes radiochemical, percent decomposition, and enantiomeric composition data, similarly obtained, for a number of labeled D and L amino acids, which had been prepared by optical resolution of several of the racemic amino acids in Table I.

The enantiomeric compositions in Table I indicate that the D/L ratios of the radioactive DL amino acids examined are 50:50, within experimental error, and that they suffered no asymmetric degradation, despite self-radiolyses as high as 67%. The enantiomeric compositions of the resolved amino acids show further that racemization does not necessarily accompany self-radiolysis in the dry state, although comparison of the enantiomeric compositions noted for D-norvaline-*3*-^{14}C and D-leucine-*3*-^{14}C with those estimated from the original optical rotations of the samples suggests that some racemization may be possible. From the specific radioactivity of the samples and their ages, one can calculate the number of β particles emitted during the lifetimes of the samples. From these numbers (not shown) and the percent decompositions, one can calculate the number of molecules decomposed per β particle, which proves to vary between about 6000 and 36 000 among our samples. These numbers are higher than the ~3000 molecules decomposed per electron observed during our previously reported[4] asymmetric degradations of DL-leucine with longitudinally polarized linear accelerator electrons. The variability in the percent decomposition and hence the number of molecules decomposed per electron, as well as the G values observed for comparable samples (e.g., D-, L-, and DL-valine-*4,4'*-^{14}C, D- vs. DL-leucine-*3*-^{14}C, etc.), is noteworthy and may be due, we suspect, to the variability of trace impurities, including moisture, in the 17–25-year-old samples. Finally, the racemic nature of the radiolyzed DL amino acids in Table I further indicates that microbial degradation could not have been operative during the lifetimes

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