intermediates was observed, as double-labeling experiments revealed.

Phenylacetylene. With more than 96% of the total activity in the acetylene part, there is strong support for a C_2H_x ($x = 0, 1,$ or 2) precursor which reacts with a benzene molecule in a second step, rather than the decomposition, as part of a random fragmentation, of one particular, possibly $C_{13}H_{12}$, intermediate. Additional support comes from the high concentration of label in both the α and β carbon. The pickup of another carbon atom by a fast ^{14}C atom can, as classical mechanical calculations for inelastic two-body collisions show, occur at rather high energies, *via* a stripping mechanism, rendering the product C_2 fast and reactive. Some of these precursors may, however, originate from a "low-energy" mechanism as proposed by Rose, *et al.*, for acetylene.[32] On the other hand, acetylene may also be formed *via* the stripping mechanism. The double-labeling experiments on the acetylene formation[36,37] in various systems are not necessarily incompatible with such a stripping mechanism since the "stripped" carbon may very well carry along its hydrogen(s), because of their small mass.

Temporary incorporation of carbon into the ring with incomplete fragmentation could be the source, besides for phenylacetylene at lower energies, for various *n-alkylbenzenes*, of which we have identified all up to $n = 7$ in the hydrogenated sample. Their degradation is pending.

Benzene and Biphenyl. These compounds may be due to the same initial process, however, the decay mode being the exact reverse (benzene), or quasi-reverse, leading to a phenyl radical which reacts with another benzene molecule. The 80% activity in the 1 carbon is quite surprising because, if we are dealing with a phenyl radical in a "hot spot," we would expect little restriction to isomerization. This is another indication for the virtual absence of "thermalization" in such a hypothetical "hot spot."

U-2. The two hydrogenation products, toluene and methylcyclohexane, exhibit equal (within the error limits) methyl/ring activity ratios. Label incorporation into the phenyl ring is highest here of all phenyl-labeled products. However, the significance of this fact depends very much on the origin and identity of U-2.

Throughout the preceding discussions we attempted to explain the formation of each product with one type of mechanism only. This may, occasionally, permit different products (such as cycloheptatriene and toluene) depending on certain dynamic parameters, such as internal energy, of the transition state pertaining to the particular mechanism. We do not wish to imply by the foregoing discussion that there could not be two, or even more, completely different routes in some cases, particularly with respect to the two extremes of the energy scale. Alternatives are readily conceived. Support or exclusion of the suggested mechanisms may come from experiments now in progress, namely, determination of the energy dependence of the integral reaction probability, coupled with degradations of products from low-energy irradiations.

Acknowledgment. This research was sponsored, in part, by the U. S. Atomic Energy Commission.

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Photolysis of Matrix-Isolated 1,3,5-Cyclooctatriene and Bicyclo[4.2.0]octa-2,4-diene. Spectra of Their Transient Photolysis Products[1]

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Abstract: Ultraviolet and infrared spectroscopy have been used to study the photochemistry of 1,3,5-cyclooctatriene (I) and bicyclo[4.2.0]octa-2,4-diene (IV) suspended in inert vapor matrices at 20°K. *cis,cis*-1,3,5,7-Octatetraene, benzene, and ethylene were found to be common primary photoproducts of the two parent valence isomers. Photolysis of I also yields another primary product. This product reverts to the starting material at room temperature and has a vibrational spectrum which supports its assignment as a strained cyclic stereoisomer of I. These results are discussed in conjunction with the results of previous flash photolysis and solution photochemical mechanisms involved.

The photochemistry of cyclic polyenes has attracted a great deal of recent interest. Numerous rearrangements and attempts at mechanistic interpretation have been reported and are summarized in a recent review.[3]

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[1] This research was supported by the Air Force Office of Scientific Research (SRC), Office of Aerospace Research, U. S. Air Force, Grant No. 837-67.

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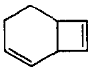
Photodecomposition of 1,3,5-cyclooctatriene (I) in a variety of solvents with light in the 2400–3000-Å region yields a bicyclic isomer (II) and a tricyclic isomer (III) as stable products.[4,5] Under similar conditions the valency tautomeric bicyclo[4.2.0]octa-2,4-diene (IV) yields benzene and ethylene as well as I, II, and III.[6]


I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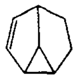
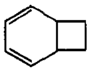

III


IV

Flash photolysis studies[7] of I in cyclohexane and *n*-hexane led to the detection of two transient species with respective lifetimes (at 25°) of 91 msec and 23 sec, and the more stable of these has been identified as *cis,cis*-1,3,5,7-octatetraene (V).

In an effort to confirm the results of the flash photolysis experiments[7] and to shed more light on the identity of the shorter lived transient, we have studied the photolyses of I and IV in argon matrices at 20°K. The infrared and ultraviolet spectra of the photolyses products have been obtained.

The photolysis of I under these conditions yields two species which are unstable at room temperature, as well as benzene and ethylene. No evidence for the presence of the solution photolysis products II and III could be obtained. Spectroscopic evidence will be presented to show that one of the unstable species is V, and the other is probably a strained, cyclic, stereoisomer of I.

Under the same conditions the photolytic decomposition of IV yields V, benzene, and ethylene as the only detectable products.

These results differ markedly from those reported by previous workers[4,6] who failed to isolate 1,3,5,7-octatetraene as a major photoproduct of either I or IV.

Experimental Section

The miniature cryotip refrigerator used in this study was built by Air Products and Chemicals, Inc., Allentown, Pa., and is similar to one described by White and Mann[8] for optical studies at low temperature.

A CsI plate in contact with a copper block with indium O-rings supported the matrix deposit for infrared spectral studies. The infrared-transmitting outer windows were also CsI. Suprasil quartz cells, containing continuously circulating cold $NiSO_4$ filter solution, served as windows for photolysis. The window temperatures were monitored with a Teflon-coated copper–constantan thermocouple. For ultraviolet spectral observation, the inner cold CsI window was replaced with LiF, and the two outside CsI windows were replaced with Suprasil quartz.

Infrared spectra were recorded between 4000 and 250 cm^{-1} using a Perkin-Elmer IR 521 grating spectrophotometer equipped with CsI optics. The spectra were calibrated to 1.0 cm^{-1} using H_2O, HCl, CH_4, and NH_4 as standards.[9]

A Perkin-Elmer Model 220 uv prism-grating spectrophotometer was used to record the visible and ultraviolet spectra.

A general Electric H 100A38-4/T medium-pressure mercury arc lamp with a portion of the Pyrex envelope removed to expose the inner quartz discharge tube was used as a photolysis source. The $NiSO_4$ solution used as a filter was circulated through an ice bath to isolate radiation between 2400 and 2700 Å.

Purified gases were used for matrix material. Linde argon (estimated purity 99.9%) was further purified inside the vacuum line by distillation from bulb to bulb at liquid O_2 (−185°) temperature.

I and IV were synthesized, separated, and purified according to the procedure described by Cope and coworkers.[10,11]

The refractive index of each isomer agrees well with the literature. The observed nmr and infrared spectral measurements indicate no appreciable impurity present in either of the isomers.

All measurements were carried out at 20°K. Gaseous samples, ranged in M/R (moles of the matrix gas per moles of reagent gas) from 100 to 1000.

Results

Photolysis of I in an argon matrix (M/R = 1000) with $NiSO_4$-filtered mercury lamp light was first studied by uv spectroscopy. The spectra of I at 20°K before and after photolysis are shown in Figure 1. Photolysis was carried out at 2-min intervals until the absorption due to decomposition products grew to a steady state. The prominent peaks that appear during photolysis were readily identified from the published solution spectra[12,13] as due to the formation of 1,3,5,7-octatetraene. After photolysis the cryotip cold window was warmed to room temperature. As the sample evaporated, it was pumped through a trap maintained at liquid nitrogen temperature. The spectrum of the window after evaporation of the sample showed no residual absorption. The material in the trap was then mixed with the same amount of argon as was in the original sample and again deposited on the window at 20°K. The features at 2650, 2710, 2840, and 2990 Å had completely disappeared and the resulting spectrum was identical with that of 1,3,5-cyclooctatriene except that some additional absorption near 2100 Å persisted.

Photolysis of IV in an argon matrix (M/R = 1000) at 20°K was carried out in a similar manner. Representative uv spectra are shown in Figure 2. The prominent features which appear during photolysis are again clearly due to the formation of 1,3,5,7-octatetraene.

A comparison of the rate of formation of 1,3,5,7-octatetraene during the photolyses of I and IV is given in Figure 3. The intensity *vs.* time plots for the 2990- and 2840-Å bands are very similar, all reaching a maximum after 30 min.

Experiments on I and IV in argon at M/R ratios ranging from 100 to 500 were followed by infrared spectroscopy. A technique of successive small depositions and photolyses for 30-min intervals enabled us to build up the concentration of the photolysis products to a much greater extent than when the same sample was deposited all at once and then photolyzed.

Figure 4 shows the spectrum of I before and after photolysis in the 300–450-, 600–1050-, 1300–1850- and 2800–3100-cm^{-1} regions for a sample with M/R = 200. The omitted regions show only a few absorptions due to I and none attributable to photoproducts. The infrared spectrum taken after the sample had been warmed to room temperature and redeposited included absorption peaks due to I and also some of the photolysis product peaks. A large number of the peaks which had been produced by photolysis had disappeared, but no new absorption features were present. Table I lists all of the

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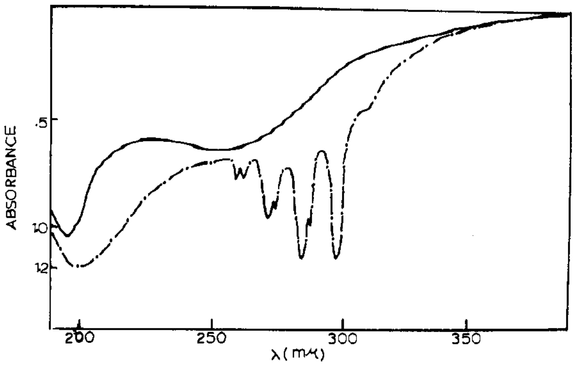

Figure 1. Ultraviolet spectra of matrix-isolated 1,3,5-cyclooctatriene before (———) and after (· · · · · ·) photolysis.

bands attributed to photoproducts of I with an asterisk designating the ones which survived the warm-up procedure.

Table I. Infrared Absorption Bands of the Photolysis Products of 1,3,5-Cyclooctatriene (cm^{-1})[a]

3095*	1595	965	755
3060*	1555	956	740
3040	1540	949*	720
2980*	1480*	935*	705
2950	1435*	902	675*
2860	1350	890	645
1805	1035*	875	620
1795	1005	800	415
1635	992	780	370

[a] An asterisk designates bands which reappeared following warm-up to room temperature (see text).

It appeared that the absorption due to I had increased relative to the stable photoproducts following the warm-up. This fact and the absence of any new absorption suggested that the products which disappeared reverted to I. A relative increase in I could also be due to sample which had originally been deposited on portiont of the cold window which were not exposed to the photolysis beam. To resolve this question the experiment was repeated with CCl_4 added. The intensity of bands due to the stable products decreased slightly relative to the 770-cm^{-1} band of CCl_4 whereas the intensity of absorption due to I increased by almost a factor of 2 following the warm-up.

Studies of the rate of formation of the photoproducts showed that all of the observed bands—those due to products which are stable at room temperature, as well as those due to products which disappear—display the same growth patterns. In particular, there was no evidence of any product with a latent period of formation as would be expected if a secondary photolysis mechanism was operative.

Table II. Infrared Absorption Maxima of the Photolysis Products of Bicyclo[4.2.0]octa-2,4-diene (cm^{-1})[a]

3095*	1477*	992	890
3060*	1435*	949*	800
2980*	1037*	935*	675*
1635	1005	900	620

[a] An asterisk designates bands which reappeared following warm-up to room temperature (see text).

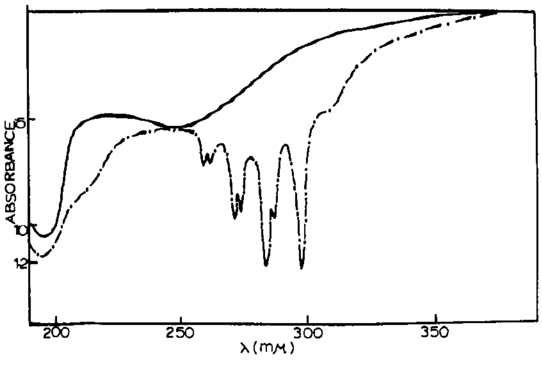

Figure 2. Ultraviolet spectra of matrix-isolated bicyclo[4.2.0]octa-2,4-diene before (———) and after (-· · · -) photolysis.

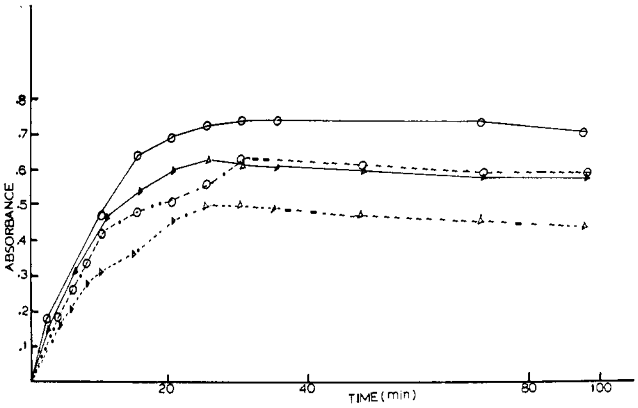

Figure 3. Rate of formation of 1,3,5,7-octatetraene. Photolysis of 1,3,5-cyclooctatriene: 2990-Å band (-○-○-○-), 2840-Å band (-△-△-△-). Photolysis of bicyclo[4.2.0]octa-2-4-diene: 2990-Å band (--○--○--○), 2840-Å band (--△--△--△--).

Identical experiments were performed on samples of IV. Figure 5 shows typical spectra before and after photolysis. The infrared maxima of the photoproducts are given in Table II with an asterisk again indicating reappearance following warm-up to room temperature. Several additional features appeared following warm-up, all of which were clearly identifiable as due to the formation of I.

Discussion

The results of the ultraviolet spectral studies on I confirm the formation of V as an important photoproduct as was found in the previous flash photolysis investigation.[7] The second short-lived intermediate was not detected in the uv since its absorption spectrum is very similar to that of I and is much less intense than is that of V.[7] The uv results on the photolysis of IV again demonstrate that V is a major photoproduct. Previous solution studies[6] show that I and its photoproducts, as well as benzene and ethylene, were produced when IV was subjected to long-term solution photolysis. The rate of formation of V during the photolysis of both I and IV (see Figure 3) shows no induction period and indicates that a secondary photolytic mechanism is not responsible in either case. Since benzene, ethylene, II, and III are all weak absorbers in the region studied, the uv experiments alone shed no light on the role of any of these compounds in the photochemistry of I or IV.

A comparison of the infrared results given in Tables I and II indicates that within experimental error all of

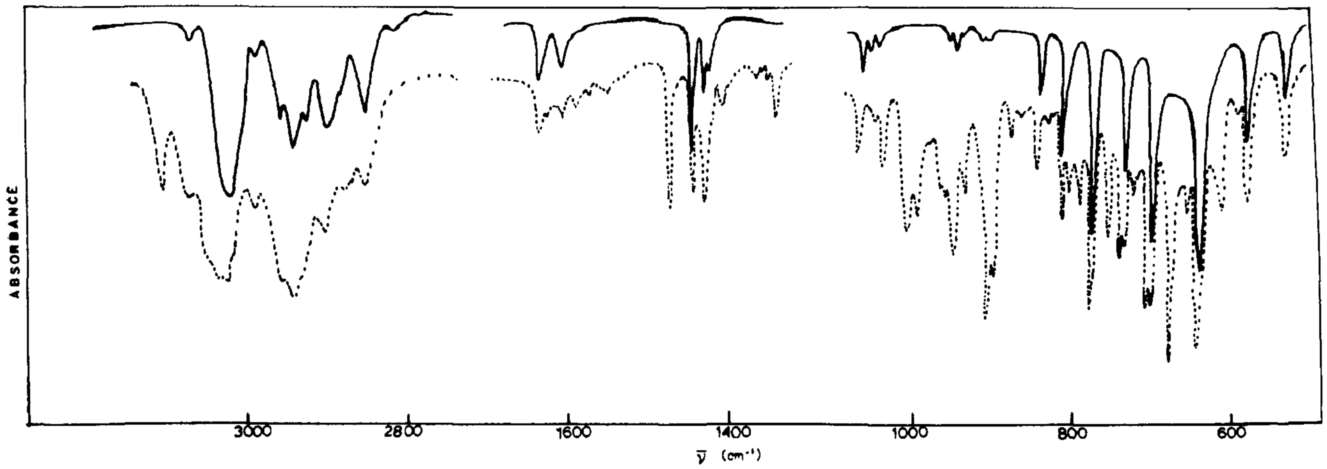

Figure 4. Infrared spectra of matrix-isolated 1,3,5-cyclooctatriene before (———) and after (- - - - - - - -) photolysis.

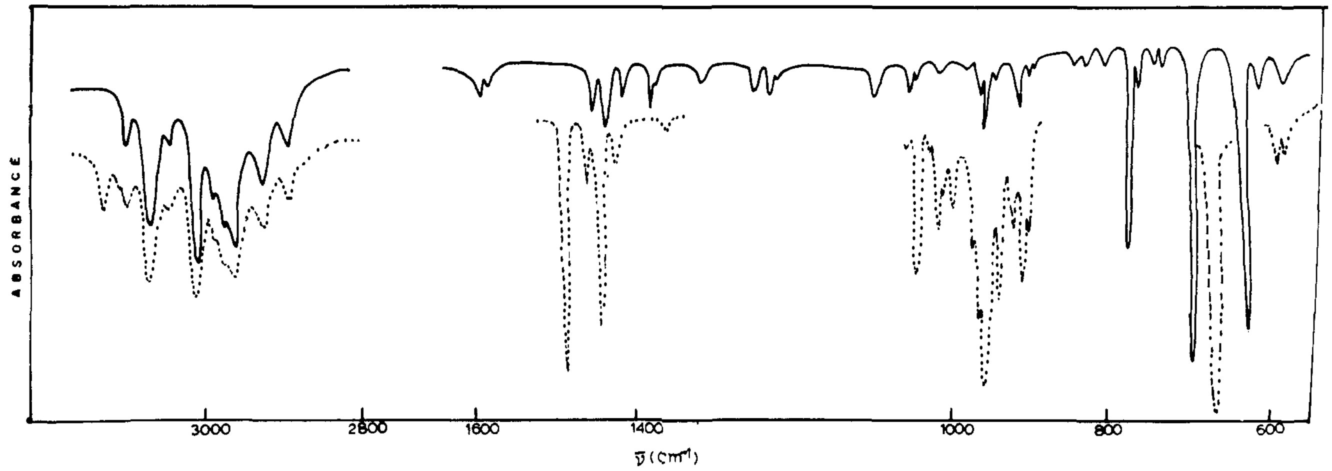

Figure 5. Infrared spectra of matrix-isolated bicyclo[4.2.0]octa-2,4-diene before (———) and after (- - - - - - - -) photolysis.

the features produced during the photolysis of IV were also produced during the photolysis of I.

Examining first the infrared absorption due to species which survived warming to room temperature, we find that the bands at 3095, 1435, 949, and 935 cm^{-1} correspond to the most intense ones of ethylene,[14] and the remaining bands at 3060, 2980, 1480 (or 1477), 1035 (or 1037), and 675 cm^{-1} correspond to the strongest ones of benzene.[15] This result was confirmed by obtaining a spectrum of benzene and ethylene in argon (1:1:200) deposited on the cryotip window at 20°K. The frequency and relative intensities of this spectrum agreed, within experimental error, with the stable product spectrum produced by photolyzing either I or IV.

The photoproduct peaks at 1635, 1005, 992, 902 (or 900), 890, 800, and 620 cm^{-1} are common to the experiments on both I and IV. The results of the uv studies suggest that V is a likely candidate for the molecule responsible for these absorptions. A comparison with the published spectra of *trans,trans*-1,3,5,7-octatetraene[16] and *cis,trans*-1,3,5,7-octatetraene[13] provides considerable support for this identification. The 620- and 800-cm^{-1} bands have strong counterparts in the spectrum of the *cis,trans* isomer, and the other bands correspond closely to the strongest ones appearing in the spectra of both the *cis,trans* and *trans,trans* isomers. The 800-cm^{-1} band is characteristic of an out-of-plane CH deformation vibration of *cis* hydrogens in a conjugated polyene such as V.[17]

Some of the remaining photoproduct bands, listed only in Table I, may also be due to V but are not listed in Table II either because they were weak and the small yield of V during the photolysis of IV precluded their detection, or because of uncertainty due to interfering absorption by IV. Included in this group are the bands at 875, 956, 965, 1350, 1595, 1795, 1805, 2860, 2950, and 3040 cm^{-1}. The other bands resulting from the photolysis of I clearly indicate the formation of at least one other product which reverts to I upon warming to room temperature. This confirms the results of the flash photolysis work[7] which led the authors to speculate that this short-lived intermediate might be a strained cyclic stereoisomer of I. The two strong broad absorption features at 370 and 415 cm^{-1} are readily explicable in terms of out-of-plane motions of such a ring system. In a molecule of this kind the double bonds would be less conjugated and would be likely to give rise to the features observed at 1540, 1555, and 1595 cm^{-1}. All of the

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(14) See, for example, G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Co., Inc., Princeton, N. J., 1945, p 326.

(15) Reference 14, p 365.

(16) E. R. Lippincott, W. F. Feairhellers, Jr., and E. W. White, *J. Am. Chem. Soc.*, 81, 1316 (1959).

(17) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen & Co., Ltd., London, 1954, p 48.

other bands could also be assigned to the skelatal or hydrogen motions of a stereoisomer of I.

The failure to observe the formation of I during the photolysis of IV and its appearance only after warm-up indicates that the reported formation of I during the solution photolysis of IV[6] involves the primary photochemical formation of V followed by thermal ring closure to produce I.

Failure to observe any evidence of II or III during the matrix photolysis of I, taken together with the flash photolysis results,[7] strongly suggests that the efficiency of the formation of these products is at least an order of magnitude lower than that of the photopathways which lead to V and to benzene and ethylene. Although the volatility of ethylene could easily explain how it escaped detection, it is more difficult to understand why benzene, which appears to be a major photoproduct, was not reported by any of the previous workers.[4-6] The possibility that I is converted first to IV and then to benzene is ruled out by failure to observe any evidence for the formation of IV despite the fact that IV does not photolyze appreciably faster than I. It is possible, although rather unlikely, that the low-temperature matrix environment might greatly favor benzene and ethylene production as compared to the room-temperature solution conditions.

The flash photolysis work on solutions of I in hydrocarbon solvents[6] showed that four or five times as much ring opening to V results from decomposition of the short-lived cyclic intermediate than from direct opening of I. However, the relative absorption peak heights indicate that in the matrix experiments the concentration of V is at least twice that of the other unstable product. Preliminary flash photolysis experiments on I in the gas phase result in the formation of V only, with no evidence of the other transient.[18] A mechanism suggested by these results involves photoexcitation of I to an excited singlet state followed by a transition to an excited vibrational level of the ground electronic state of the cyclic stereoisomer. If this excited vibrational state is only metastable with respect to ring opening, the rapid formation of V would compete successfully with vibrational deactivation in the gas phase, whereas in the condensed phase, collisional deactivation would result in the stabilization of the stereoisomer. In an argon matrix vibrational deactivation would be intermediate between gas and liquid resulting in the observed intermediate ratio of V to the strained stereoisomer.

Little can be inferred from the experiments about the mechanism of benzene and ethylene formation from I other than that it does not involve the secondary photolysis of either of the other products. On the basis of energy requirements (breaking of two bonds), it almost certainly must occur from an electronically excited state. The increased efficiency of benzene and ethylene formation relative to the yield of V is not surprising since a Franck-Condon transition from IV would result in an electronic state that had a more appropriate geometry for this process than in the case of I.

[18] Unpublished results recently obtained in our laboratories.

Mechanism of Chemiluminescence from Peroxy Radicals

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Abstract: Chemiluminescence accompanying disproportionation of peroxy radicals is studied. This reaction produces triplet states specifically ($T/S > 10^4$) and with high efficiency. The low emission yield, $\Phi_C \cong 10^{-8}$–10^{-10}, is ascribed to quenching in the cage by the eliminated O_2.

Chemiluminescence accompanying air oxidation of saturated hydrocarbons has been studied extensively.[1] The chain-step oxidation is usually summarized by initiation

$$I\cdot + R_2CH_2 \longrightarrow IH + R_2CH\cdot \qquad (1)$$

$$R_2CH\cdot + O_2 \longrightarrow R_2CHOO\cdot \qquad (2)$$

propagation

$$R_2CHOO\cdot + R_2CH_2 \longrightarrow R_2CHOOH + R_2CH\cdot \qquad (3)$$

termination

$$2R_2CHOO\cdot \longrightarrow R_2CHOH + R_2C{=}O + O_2 \qquad (4)$$

and branching

$$R_2CHOOH \longrightarrow R_2CHO\cdot + \cdot OH \qquad (5)$$

By identifying the weak chemiluminescence with the termination step, it has been possible to devise experiments to measure the rate constants for each of the above reactions.[2-6]

There is much evidence that the disproportionation is concerted: (1) since the reaction exothermicity is ~115–150 kcal[7] and the luminescence state of the carbonyl is commonly 75–80 kcal, a concerted reaction is virtually required to concentrate the energy in the ketone fragment, at least for those events leading to luminescence; (2) the termination rate constant for secon-

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