spin-orbit coupling.[2] The theory can predict the lowest 5d ← 4f excited Kramers doublet of $[Ce(OH_2)_8]^{3+}$ present in an energy region much lower than the lowest component of $[Ce(OH_2)_9]^{3+}$ as shown in Figure 7 in which the distance Ce-O is assumed to be conserved in $[Ce(OH_2)_8]^{3+}$ and $[Ce(OH_2)_9]^{3+}$. A ligand-field stabilization is obtained at the expense of the bond dissociation. Since the calculations do not take proper account of variations in the repulsion energies, the model cannot determine exactly which configuration is the most stable. For their small energy differences, however, the structure of the excited octacoordinate species in solution must be fluxional between dodecahedron, square antiprism, and/or cube.

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Registry No. $[Ce(OH_2)_9]^{3+}$, 59922-22-4; $[Ce(OH_2)_8]^{3+}$, 70273-04-0.

Detection of H_2, HD, and D_2 by Raman Spectroscopy: A Powerful Aid for the Elucidation of Reaction Mechanisms

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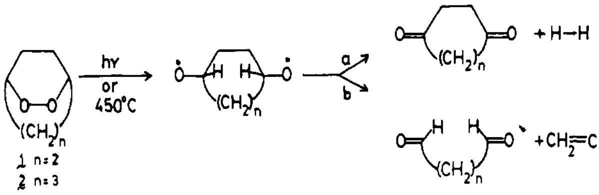
Abstract: The detection of H_2, HD, and D_2 by gas-phase Raman spectroscopy has shown that the photochemical and thermal dehydrogenation of dioxabicyclo[*n*.2.2]alkanes occurs by an intramolecular process. The general applicability of the Raman technique for the identification of dihydrogen produced in the course of a reaction is based upon the high-scattering cross section of dihydrogen, which allows the ready detection of submicromolar quantities of the gas.

There are many chemical reactions in which dihydrogen is evolved. For some of these, a determination of the isotopic composition of the gas that is produced from reactants labeled at specific sites with deuterium could provide valuable mechanistic information. However, at present there appears to be no generally recognized method for effecting such an analysis, especially where the reactions are carried out on a small scale. One of us (R.J.H.C.) has previously shown that Raman spectroscopy can be used for this purpose in a study of the photolysis of pentamethylcyclopentadiene.[1] In the present work, we have extended the use of the technique to investigate the mechanism by which certain saturated bicyclic peroxides (dioxabicyclo[*n*.2.2]alkanes) undergo dehydrogenation when pyrolyzed in the gas phase[2] or photolyzed in solution.[3] In addition to reporting these results, we wish to draw attention to the sensitivity and convenience of Raman spectroscopy as a method for detecting and distinguishing between H_2, HD, and D_2. The mechanistic value of this capability has been demonstrated, and the potential now exists for the application of this technique to a wide range of systems.

Results and Discussion

Bicyclic peroxides were photolyzed or thermolyzed in sealed vessels, and the gaseous phase above each sample was then examined by Raman spectroscopy. The photolyses were carried out in benzene solution with benzophenone as sensitizer, whereas the thermolysis was effected in the gas phase by a flash pyrolytic technique. The following samples were examined: (i) photolyzed 2,3-dioxabicyclo[2.2.2]octane (**1**), (ii) thermolyzed 6,7-dioxabicyclo[3.2.2]nonane (**2**), (iii) photolyzed **2** (in C_6D_6), (iv) photolyzed 1:1 mixture of **1** and 1,4-dideuterio-2,3-dioxabicyclo-[2.2.2]octane (**1**-d_2), and (v) photolyzed **1**-d_2.

Previous work has established that photolysis[3] or flash vacuum pyrolysis[2] (FVP) of the [*n*.2.2] peroxides **1** and **2** affords good yields of cycloalkane-1,4-diones, and it was suggested that these arise by extrusion of molecular hydrogen from intermediate cycloalkanedioxyls (eq 1a). Competitive formation of α,ω-dialdehydes was detected under FVP conditions and was attributed to an alternative mode of double β-scission in which ethylene is extruded (eq 1b).



(1)

The presence of ethylene among the thermolysis products was confirmed, but the detection of dihydrogen was precluded by the nature of the analytical techniques used.

The Raman spectrum of the gas above a photolyzed sample of the [2.2.2] peroxide [experiment i] is shown in Figure 1a. The presence of dihydrogen is unambiguously established by the observation of lines assigned to the $J = 0 \rightarrow 2$, $J = 1 \rightarrow 3$, $J = 2 \rightarrow 4$, and $J = 3 \rightarrow 5$ transitions, i.e., to the pure rotational $S_0(J)$ lines of dihydrogen.[4,5] The relative intensities of these lines are governed by the nuclear spin and by the populations of the relevant states[6] and provide additional confirmation of the assignment of these transitions. Evidence for the presence of ethylene is also available, through the observation of its pure rotational spectrum,[7] particularly in the highly structured region between 60 and 100 cm^{-1}, along with bands attributed to the ν_1 (a_g, 3019 cm^{-1}), ν_2 (a_g, 1625 cm^{-1}), and ν_3 (a_g, 1344 cm^{-1}) fundamentals.[8] Under the conditions of the experiment, the rotational structure associated with these bands was not resolved. The remaining bands are assigned to the ν_1 (a_g, 3073 cm^{-1}), ν_2 (a_g, 992 cm^{-1}), and ν_2

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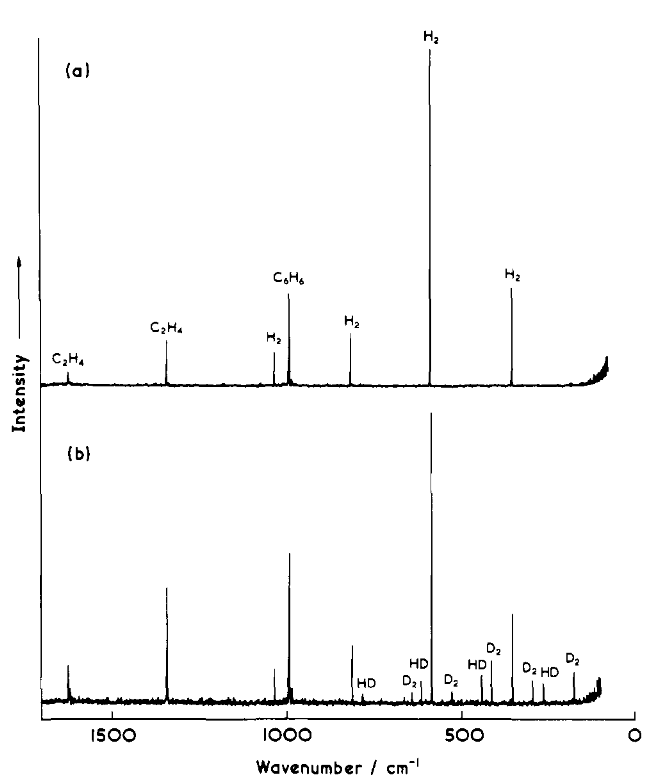
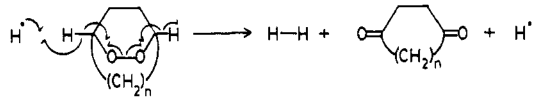


Figure 1. Raman spectra of the gaseous products from the photolysis of **1** (a) and from the photolysis of a mixture of **1** (51%), **1**-d_1 (12%), and **1**-d_2 (37%) (b). Benzene was used as the solvent for both reactions. The samples were excited with a single pass of ca. 700 mW of 514.5-nm radiation. Spectra were collected by using a spectral band pass of 0.75 cm^{-1} (at 0 cm^{-1}) with a scan speed of 0.2 cm^{-1} s^{-1} and an integration time of 0.5 s. The sensitivities were 2000 counts s^{-1} (a) and 1000 counts s^{-1} (b).

($^{12}C_5{}^{13}CH_6$) (a_1, 985 cm^{-1}) fundamentals of the solvent, benzene.[9] Thus, this experiment not only confirms that molecular hydrogen is a product of decomposition (eq 1a) but also indicates that the competing fragmentation (eq 1b) identified under FVP conditions is also operative in photolysis.

The formation of dihydrogen and ethylene from thermolysis of the [3.2.2] peroxide was similarly established [experiment ii]. The main significance of this result is that it demonstrates the high sensitivity of the technique. Thus, although only 6.1 mg (48 μmol) of **2** was pyrolyzed in a vessel of volume 20 cm^3, the pure rotational Raman spectrum of dihydrogen could be easily picked out (Figure 2) and bands resulting from the ν_3 and ν_5 vibrations of ethylene could just be distinguished from the noise. This suggests that with the type of setup used in the photolysis experiments where there is ca. 1 cm^3 of gas space, there should be no difficulty in detecting the formation of submicromolar quantities of dihydrogen.

Deuterium labeling was used to test further the mechanism proposed in eq 1. The Raman spectrum of the gas above a photolyzed sample of the [3.2.2] peroxide in C_6D_6 [experiment iii] indicated the presence of H_2 and the absence of HD. This rules out the possibility that the molecular hydrogen arises by reaction of the solvent with hydrogen atoms formed by single, independent β- scissions in the cycloalkanedioxyl. However, given that benzene is not a very good hydrogen donor, the intervention of hydrogen atoms remains a possibility, with a chain process involving induced decomposition of the peroxide (eq 2) being well worthy of consideration, viz.



(2)

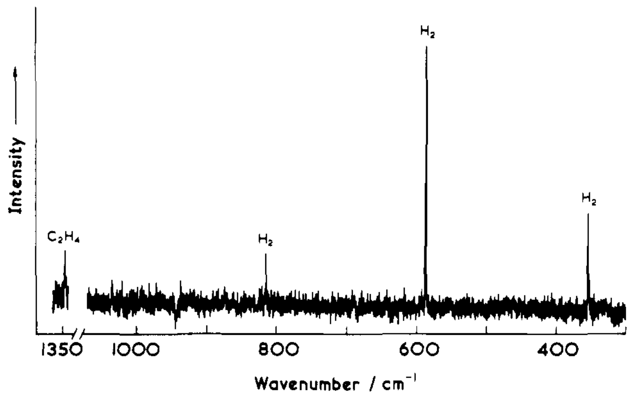


Figure 2. Raman spectra of the gaseous products of the thermolysis of 48 μmol of **2**. The sample was excited with ca. 1 W of 514.5-nm radiation. Spectra were collected by using a spectral band pass of 1.5 cm^{-1} (at 0 cm^{-1}) with a scan speed of 0.2 cm^{-1} s^{-1} and an integration time of 0.5 s. The sensitivity was 500 counts s^{-1}.

The bimolecular pathway outlined in eq 2 was, however, ruled out by the isotopic composition of the dihydrogen produced from photolysis of a 1:1 mixture of the 1,4-dideuterio[2.2.2] peroxide and the fully protio compound [experiment iv]. The ratio of the concentrations of D_2 and HD was found to remain unchanged in this experiment compared to that found for photolysis of the 1,4-dideuterio[2.2.2] peroxide alone [experiment v]. (HD arises because the sample contains ca. 24% of mondeuteriated peroxide (**1**-d_1) as shown by mass spectroscopy.) The relative concentrations were established by considering the relative intensities of each of the rotational Raman lines and confirmed by duplicate spectra (Figure 1b). Clearly, if an intermolecular mechanism for dihydrogen formation were important, a markedly increased relative concentration of HD would be expected in experiment iv. Hence the intramolecular extrusion mechanism (eq 1)[2] is supported by these findings.

Conclusion

These experiments demonstrate the sensitivity and convenience of Raman spectroscopy as applied to the identification of dihydrogen and its isotopes, and hence to the elucidation of certain organic reaction mechanisms.

Experimental Section

Materials. 2,3-Dioxabicyclo[2.2.2]octane (**1**) and 6,7-dioxabicyclo-[3.2.2]nonane (**2**) were prepared as previously described.[10] 1,4-Dideuterio-2,3-dioxabicyclo[2.2.2]octane (**1**-d_2) was prepared from cyclohexane-1,4-dione as follows. The dione was converted into a mixture of 1,4-dideuteriated 1,3- and 1,4-cyclohexadienes by Franzus's method.[11] The crude mixture containing 2-propanol was photo-oxygenated,[12] and column chromatography (SiO_2, CH_2Cl_2) of the product afforded 1,4-dideuterio-2,3-dioxabicyclo[2.2.2]oct-5-ene: ^1H NMR (CCl_4) δ 6.70 (2 H, s), 2.45–2.05 (2 H, m), 1.75–1.2 (2 H, m); ^2H NMR (CCl_4) δ 4.47; ^{13}C NMR ($CDCl_3$) δ 132.26, 70.60 [t, $^1J(^2H-^{13}C)$ = 23.3 Hz], 21.54. Reduction of this endoperoxide with diimide in the usual way[10] and purification by column chromatography (SiO_2, CH_2Cl_2) gave **1**-d_2: ^1H NMR (CCl_4) δ 2.45–2.0 (4 H, m), 2.0–1.45 (4 H, m); ^2H NMR (CCl_4) δ 3.95; ^{13}C NMR ($CDCl_3$) δ 71.24 [t, $^1J(^2H-^{13}C)$ = 23.0 Hz], 24.16; mass spectrum, *m/e* 116 (M^+); a peak at *m/e* 115 indicated the presence of *ca.* 24% of monodeuteriated peroxide, **1**-d_1.

Photolysis. For each experiment, a solution of the bicyclic peroxide (40 mg; 30 mg each for the mixture of **1** and **1**-d_2) and benzophenone (5 mg) in benzene (1.5 cm^3; benzene-d_6 for **2**) was placed in a Pyrex NMR tube (5 mm o.d.) fitted with a ground glass joint for attachment to a vacuum line. After 3 freeze–pump–thaw cycles, the tubes were sealed under vacuum. The free space above the solution was ca. 1 cm^3 in each case. The samples were irradiated for 40 h with a Hanovia medium-pressure mercury arc fitted with a Pyrex sleeve.

Thermolysis. An h-shaped cell, open at the top left-hand side, was contructed from 8.2 mm (i.d.) Pyrex tubing. The horizontal section was

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ca. 10 cm long, and there was a constriction just above it to facilitate sealing; the total volume up to the constriction was 20 cm^3. Crystals of **2** (30 mg) were placed in the left-hand leg, and after 3 freeze-pump-thaw cycles the cell was sealed under vacuum. An electrical heating tape was wound around the horizontal section, the right-hand leg was immersed in liquid N_2, and the horizontal section was then heated to 450 °C. With the aid of a hot-air gun, some of the peroxide (6.1 mg) was passed through the hot zone.

Raman Spectra. Raman spectra were recorded by using Spex 1401 (1200 lines mm^{-1}) and 14018 (1800 lines mm^{-1}) spectrometers in conjunctions with a Coherent Radiation model CR12 argon ion laser. Detection of the scattered radiation was by photon counting, with RCA C31034 photomultiplier tubes.

Raman spectra of the gaseous photolysis products were obtained by focusing the laser in the center of the reaction tube, ca. 3 cm from the meniscus of the solution. The samples were aligned so that the laser beam did not pass through any of the solution. For a 90° scattering geometry with vertical slits and a single pass of ca. 700 mW of 514.5-nm radiation, it was found to be sufficient to clamp the reaction tube inclined ca. 15° from horizontal. The thermolysis sample was studied by focusing the laser in the center of the horizontal section of the reaction cell.

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Registry No. 1, 280-53-5; **1**-d_1, 95589-82-5; **1**-d_2, 95589-83-6; **2**, 283-35-2; H_2, 1333-74-0; HD, 13983-20-5; D_2, 7782-39-0; O_2, 7782-44-7; 1,4-dideuteriated-1,3-cyclohexadiene, 89829-68-5; 1,4-dideuteriated-1,4-cyclohexadiene, 17647-19-7; 1,4-dideuterio-2,3-dioxabicyclo[2.2.2]-oct-5-ene, 95589-84-7; cyclohexane-1,4-dione, 637-88-7.

Fusogenic Behavior of Didodecyldimethylammonium Bromide Bilayer Vesicles

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Abstract: The ability of surfactant vesicles, prepared from didodecyldimethylammonium bromide (DDAB), to undergo fusion in the presence of a variety of organic and inorganic anions has been investigated. The occurrence of fusion was examined by electron microscopy. The kinetics of fusion was monitored continuously by following the decrease of energy transfer between two fluorescent phospholipid analogues occurring when DDAB vesicles, containing these fluorophores, fuse with nonlabeled vesicles. Vesicle fusion was induced upon addition of the divalent anion of dipicolinic acid (DPA), resulting in the formation of "giant" vesicles with a diameter of 2-3 μm. The DPA dianion (DPA^{2-}) displayed a threshold concentration of ca. 30 μM, below which fusion could not be detected. Since vesicle aggregation, as monitored by absorbance measurements, revealed a threshold DPA^{2-} concentration of ca. 15 μM, it is likely that fusion represents the rate-limiting step in the overall process. Hence, after vesicle aggregation, structural membrane alterations must occur which subsequently render the membranes susceptible to fusion. Remarkably, only vesicles with a diameter of at least 3000 Å are prone to fusion, whereas smaller vesicles, despite the fact that they readily aggregate, do not fuse, even at high DPA^{2-} concentrations. Preliminary results revealed that anions other than DPA^{2-} were also capable of inducing fusion of DDAB vesicles, provided that they display dual functional properties by containing either a divalent charge or a monovalent charge in addition to a group which presumably prefers hydrophobic membrane interactions.

An interesting area of membrane mimetic chemistry has emerged from the development of simple membrane-forming amphiphiles.[1] Surfactant vesicles, formed upon sonic dispersal of a variety of single- and double-chained synthetic amphiphiles, have been shown to resemble in many respects membrane bilayers formed from synthetic and natural phospholipids. For example, amphiphilic bilayers undergo thermotropic phase transitions[2] while, depending on their size, they also display osmotic sensitivity.[2a,3] Moreover, it has been demonstrated that closed vesicle bilayers can be formed from a double-chained amphiphile carrying an *N*-methylpyridinium head group and that bilayers from this surfactant could be reconstituted containing the biologically active protein rhodopsin. These results indicate that these surfactant vesicles may be employed to mimic cell-membrane functions.[4]

Studies with synthetic membrane mimics may provide relevant information concerning the properties of lipid/water interfaces and structural effects on membrane stability. With respect to the latter, it is relevant to note that surfactant vesicles are generally much more stable than phospholipid vesicles. Biological membranes can display an inherent but transient destabilization, occurring during membrane fusion which takes place during physiologically important processes such as endocytosis, exocytosis, and virus infection.[5] Although phospholipid vesicles have been used extensively as models in studies of membrane fusion mechanisms,[6] some recent investigations have suggested that bilayers prepared from synthetic amphiphiles may also become transiently instable and, subsequently, fuse.[7]

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