namic cycle (see below from the bond energy data).

Using the Miyazaki values of $E_{\rm H}$ and $E_{\rm C}$ (Table VII) with the thermodynamic cycle (Table VI) leads to the enthalpy change (Δ_E) for reaction 4.1 on various metals listed in Table VII. The value for Ni in Table VII agrees well with our computed value (sum of ΔH° s in Table II) for the ending transition metals (18 kcal) as determined by an independent procedure. For the middle transition-metal elements, our computed value of 36 kcal compares well with the values 44 kcal for Fe or 34 kcal for Os but poorly with 15 kcal for Ru. This illustrates the difficulty of the broad generalizations we have used in an attempt to fit all elements. The analysis also points out the fact that hydrogenation of surface C to hydrocarbons is an uphill process energetically. This statement is true for most hydrocarbon-forming reactions. Generally, the energy barriers to be overcome are larger for the early and middle transition metals than for the ending transition metals.

Appendix 5

Let us offer some comments concerning the mechanism treated in this work. We have considered a reversible sequence of hydrogenation steps of CH_x (x = 0-2) based upon the mechanism of Bell.¹ Bell noted that reversible steps were considered, since reversible reactions are observed in organometallic complexes involving these species. Further support for reversible reactions comes from methane decomposition reactions on Ni/SiO₂ catalysts²⁹ and on metal films.³⁰ In these cases decomposition of methane to adsorbed C and H is observed, particularly when H concentration is low. Yet in some mechanisms, irreversible reaction steps are proposed, involving no CH_x (x = 1-3) decomposition. There may be some systems in which the back-reaction is negligible and the model treated here is not applicable.

$$CO + S \rightarrow C + O \tag{5.1}$$

can be incorporated into the corrected pseudo-first-order preexponential factor (k_0^{corr}) by

$$k_0^{\rm corr} = k_0 (1 - \Sigma \theta_x) \tag{5.2}$$

where the partition function for the surface site is taken as C_0 and the sum is over all adspecies except CO. Computations utilizing this approximation produce results similar to those discussed in this paper with a slightly smaller value for the CO decomposition activation energy (≈ 2 kcal/mol smaller). For reactions of the type

$$CH_x + S \to C_{x-1} + H$$
 $x = 1-3$ (5.3)

we have already noted the need for a preexponential factor reduced from the typical value $1 \times 10^{13} \text{ s}^{-1}$. The need for the bare site S may also be a factor responsible for this reduction. Clearly, this is an area for future work on this model.

One final comment concerns our calculated result that surface CH is present in greater concentration than undissociated CO at 1-atm pressure as displayed in Table IV. Good spectroscopic evidence has been compiled^{23b} to indicate that under reaction conditions undissociated CO is the dominant surface species. Although our computations agree with this result at pressures greater than 20 atm, perhaps our model or parameters could be improved to better describe the situation. One area for consideration concerns the possibility that CO dissociation may occur at a special site different from and in lower concentration than the sites for storage of undissociated CO. Clearly, this is a matter for further investigation.

Registry No. CO, 630-08-0.

Cyclopentylperoxyl and Cyclohexylperoxyl Radicals in Aqueous Solution: A Study by Product Analysis and Pulse Radiolysis

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Radiolysis of N_2O/O_2 (4:1 v/v) saturated aqueous solutions of cyclopentane generates cyclopentylperoxyl radicals which decay by a second-order rate process ($2k = 1.5 \times 10^7 M^{-1} s^{-1}$) and give rise to the following products (*G* values in parentheses): cyclopentanone (1.7), cyclopentanol (0.8), glutaraldehyde (1.2), 5-hydroxypentanal (0.8), organic peroxidic material (0.5), and H_2O_2 (1.7); oxygen is consumed with G = 5.0. The corresponding data for cyclohexane solutions are as follows ($2k = 1.2 \times 10^7 M^{-1} s^{-1}$): cyclohexanoe (2.5), cyclohexanol (0.9), total aldehydes (0.8), organic peroxidic material (0.9), H_2O_2 (1.6), and oxygen uptake (4.0). During the bimolecular decay of the cycloalkylperoxyl radicals small amounts ($G \approx 0.5$) of HO_2 · ($H^+ + O_2^{-}$) are formed. It is proposed that in the rate-determining step a short-lived tetroxide is formed which breaks up by four main routes: (i) O_2 , cycloalkanol, and cycloalkanone, (ii) H_2O_2 and two molecules of cycloalkanone, (iii) O_2 and two cycloalkanone, (iii) O_2 and two cycloalkanone and the acyclic aldehydes are formed), and (iv) O_2 and two cycloalkanone, (iii) The cycloalkoxyl radicals undergo a 1,2-H shift, a reaction which eventually leads to the formation of the intermediate O_2^{-} . In the cyclopentane system the fragmentation (mainly the concerted process iii) is the most important single process (40%) whereas in the cyclohexane system this route does not exceed 15%. A fragmentation of the acyclic radicals is not observed.

Introduction

In the presence of oxygen most carbon-centered radicals are converted into the corresponding peroxyl radicals with near diffusion-controlled rates. Under natural conditions oxygen is widely present and peroxyl radical reactions are important environmentally. The fate of peroxyl radicals has mainly been studied in nonpolar media or in the gas phase, and comparatively little was known until recently about their reactions in aqueous solutions. The results from systems that have been studied in our laboratory, e.g., the peroxyl radicals generated by the reaction of OH radicals and molecular oxygen with methane,² ethylene,³ methanol,⁴ eth-

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We have treated unimolecular reactions leading to two product species without the need for an additional vacant site (S). Clearly, this is an approximation. The need for an additional site in

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anol,⁵ 2-propanol,⁶ 2-methyl-2-propanol,⁷ glucose,⁸⁻¹⁰ diethyl ether,¹¹ dihydrouracil,¹² uracil,¹³ and trimethyl phosphate¹⁴ indicate that in aqueous solution mechanisms different from those observed in nonpolar systems might prevail. We now extend our studies to cyclopentyl- and cyclohexylperoxyl radicals in aqueous solutions for which some data on products and kinetics in hydrocarbon solutions are already available.¹⁵⁻¹⁷

In aqueous solution peroxyl radicals are most conveniently generated by using radiation techniques. In the radiolysis of water OH radicals, solvated electrons (e_{aq}^{-}), and H atoms are formed as free-radical intermediates (reaction 1). In a solution saturated

$$H_2O \xrightarrow[radiation]{radiation} OH, e_{aq}, H, H_2O_2, H_2$$
 (1)

$$e_{aq}^{-} + N_2 O \rightarrow OH + N_2 + OH^{-}$$
(2)

$$H \cdot + O_2 \to HO_2 \cdot \tag{3}$$

$$\cdot OH + RH \rightarrow H_2O + R \cdot \tag{4}$$

$$\mathbf{R} \cdot + \mathbf{O}_2 \to \mathbf{R}\mathbf{O}_2 \cdot \tag{5}$$

$$2RO_2 \rightarrow \text{products}$$
 (6)

with a 4:1 (v/v) mixture of N_2O and O_2 , the solvated electrons are converted into OH radicals (reaction 2) and the H atoms into HO2. radicals (reaction 3). The HO2. radical is a fairly strong acid $(pk_a = 4.7^{18})$ and around neutrality this species is fully dissociated into H^+ and O_2^- . The OH radicals generated in reactions 1 and 2 readily react with solutes such as cyclopentane or cyclohexane by hydrogen abstraction (reaction 4). The resulting alkyl radicals are rapidly converted into the corresponding peroxyl radicals (reaction 5). These interact with each other, thereby forming the products (reaction 6). Cyclopentane and cyclohexane are only slightly soluble in water $(2.5 \times 10^{-3} \text{ and } 6.8 \times 10^{-4} \text{ M})$, respectively).¹⁹ This makes a complete product analysis at low conversions (<10%) conveniently possible for the more soluble cyclopentane but more difficult for cyclohexane such that the ring-opened aldehydic products could not be separately determined. Kinetic measurements can be done with pulse radiolytic techniques. Such studies have already been reported earlier for the cyclopentane system,²⁰ and our pulse-radiolytic results largely corroborate but in some details also supplement the previous observations.

Experimental Section

Cyclopentane (Merck) was purified by fractional distillation to a purity of 99.9% (GC). Cyclohexane (Merck) contained <0.5% impurities (GC) and was used without further purification. Solutions were prepared by adding the cycloalkanes to triply distilled water which had been presaturated with N_2O/O_2 (4:1

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TABLE I: Products and Their G Values from the γ -Radiolysis of Cyclopentane (2.5 \times 10⁻³ M) in N₂O/O₂ (4:1 v/v) Saturated Aqueous Solutions at pH 6.5

product	G value	
cyclopentanone	1.7	
cyclopentanol	0.8	
glutaraldehyde	1.2	
5-hydroxypentanal	0.8	
acidic products	<0.1	
formaldehyde	absent	
organic peroxidic material	0.5	
H ₂ O ₂	1.7	
oxygen uptake	5.0	

v/v). ⁶⁰Co γ -irradiations were carried out at room temperature (19 ± 1 °C) at a dose rate of 0.26 Gy s⁻¹. For cyclopentane solutions the absorbed doses were between 80–310 Gy, i.e., conversions were kept below 7%. For the cyclohexane solutions the highest dose was lower (250 Gy) and conversions reached 19%.

The cyclic alcohols and ketones in the irradiated aqueous solutions were determined by GC using cyclohexanone as the internal standard for the cyclopentane system and cyclopentanone for the cyclohexane system. For the spearation a 52-m OV-1 glass capillary column coupled with a 10-m Carbowax 20 M precolumn was used. The column was operated at 85-200 °C, at 4 °C min⁻¹. The carrier gas was N_2 at 1 mL min⁻¹. Attempts to determine glutaraldehyde and 5-hydroxypentanal quantitatively by GC by direct injection of the irradiated aqueous solutions were unsuccessful. In water, glutaraldehyde undergoes very rapid hydration and the cyclic monohydrate exists in equilibrium with the openchain mono- and dihydrates.²¹ 5-Hydroxypentanal in aqueous solution exists as an equilibrium mixture composed of 2hydroxytetrahydropyran and the open-chain form.²² For this reason these carbonyl compounds were converted into the 2,4dinitrophenylhydrazones and separated by HPLC (column: 4.6 \times 150 mm Nucleosil 5C18, eluent acetonitrile/water (3/2) at 0.8 mL min⁻¹). In the case of cyclohexane acyclic aldehydes were determined photometrically in total, using 3-methylbenzothiazol-2-one hydrazone hydrochloride as reagent.²³ The acetylacetone method was used to test for formaldehyde.²³ Total (hydro)peroxide was determined iodometrically according to Allen et al.²⁴ Organic (hydro)peroxides were determined separately in this way after H_2O_2 had been decomposed by catalase. The organic (hydro)peroxides were further characterized by glutathione peroxidase catalyzed reduction of hydroperoxides to the corresponding alcohols (cf. ref 25): To a 1-mL sample of irradiated solution were added 0.2 ml solution of glutathione peroxidase (EC 1.11.1.9, Boehringer, 0.5 unit/mL), 0.2 mL of 0.038 M reduced glutathione (Boehringer), 0.5 mL of phosphate buffer (0.1 M, pH 7.75), and 0.1 mL of 0.01 M EDTA. After 30 min the solution was analyzed by GC (see above). Total acid was determined by potentiometric titration against 0.01 M NaOH. Oxygen uptake was measured with an oxygen-sensitive electrode (Wiss. Techn. Werkstätten, Weilheim).

A 2.8-MeV van-de-Graaff electron accelerator was used to generate electron pulses of $1-4-\mu s$ duration with doses in the range of 10–90 Gy. The optical and ac-conductivity detection techniques in pulse radiolysis have been described previously.^{26–28} Dosimetry for the optical detection method was carried out with a N₂O-

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TABLE II: Products and Their G Values from the γ -Radiolysis of Cyclohexane (0.68 × 10⁻³ M) in N₂O/O₂ (4:1 v/v) Saturated Aqueous Solutions at pH 6.5

product	G values
cyclohexanone	2.5
cyclohexanol	0.9
total acyclic aldehydes	0.8
acidic products	<0.1
formaldehyde	absent
organic peroxidic material	0.9
H_2O_2	1.6
oxygen uptake	4.0

saturated 0.01 M KSCN solution taking ϵ (480 nm) = 7600 M⁻¹ cm⁻¹ and G = 6.0 for (SCN)₂^{-.29} For the conductivity detection method a CH₃Cl-saturated solution containing 0.1 M 2-methyl-2-propanol was used taking G(HCl) = 3.1.³⁰

Superoxide dismutase (EC 1.15.1.1., Sigma, 24 units/mL) was used to catalyze the bimolecular decay of O_2^{-} in the pulse radiolysis of basic solutions.

Results

Radiolysis of Oxygenated Cyclopentane Solutions. In the radiolysis of cyclopentane in N_2O/O_2 (4:1) saturated aqueous solutions the ring-closed products cyclopentanol and cyclopentanone are not the only products. Considerable amounts of the open-chain products glutaraldehyde and 5-hydroxypentanal are formed. The major peroxidic compound is hydrogen peroxide. There are also small amounts of organic peroxidic material which is likely to be largely cyclopentyl hydroperoxide. Hydroperoxides are known to decompose in the hot injection block of the gas chromatograph by elimination of water thus yielding the corresponding ketone. Reduction of the organic peroxidic material with glutathione catalyzed by glutathione peroxidase reduced the yield of cyclopentanone by the same amount as the yield of cyclopentanol was increased (G = 0.5), values that agree well with the total yield of organic peroxidic material. This result very much favors our assignment of the peroxidic material as being mainly cyclopentyl hydroperoxide. Special care has been taken to check whether formaldehyde is formed and it has been found to be absent. The yields of all products increased linearly with dose. From the linear dose-yield plots G values were calculated. They are compiled in Table I. Since the gas chromatographic analysis was distorted by the decomposition of cyclopentyl hydroperoxide the cyclopentanone value given in Table I is taken from the glutathione-reduced samples whereas the cyclopentanol value is taken from the untreated samples. The material balance between $G(\cdot OH) = 5.4$ and the sum of the G values of the products containing the pentyl unit (G = 5.1) agrees within experimental error. This also holds for G(oxygen uptake).

Radiolysis of Oxygenated Cyclohexane Solutions. The analysis of the products from cyclohexylperoxyl radicals is not as detailed as that of the cyclopentylperoxyl radicals. The cyclic compounds cyclohexanone and cyclohexanol are more prominent than the corresponding productss in the cyclopentane system. The ringopened products have not been characterized as well as in the cyclopentane system and were determined in total ("acyclic aldehydes", Table II) by assuming the same extinction coefficient as the glutaraldehyde derivative in the color test used. For this reason the G value obtained for this fraction is necessarily fraught with a considerable potential error. Upon glutathione/glutathione peroxidase treatment the increase in the yield of cyclohexanol with the concomitant decrease in cyclohexanone yield should give the yield of cyclohexyl hydroperoxide. This corresponds to two thirds of the yield found for organic peroxidic material. It is possible that the unidentified fraction of the organic peroxidic material is an acyclic hydroperoxide. Under this assumption the relationship G(hexyl units in the products) = 5.2 vs. G(OH) = 5.3 is obtained. As can be calculated from the G values given in Table II, material balance has been achieved (G(products) = 5.1; G(OH) = 5.3) within the limits of the errors involved in these measurements which are considered to be $\pm 10\%$ or better. The value for oxygen consumption (Table II) also agrees well with the oxygen content of the products and their G values.

Pulse Radiolysis. The results of our pulse radiolytic investigation of N₂O/O₂-saturated cyclopentane solutions agree well with those of the earlier study²⁰ in many aspects. The shape of the absorption spectrum of the cyclopentylperoxyl radical (C₅H₉O₂·) as well as its extinction coefficient at the maximum (ϵ (270 nm) = 1100 ± 100 M⁻¹ cm⁻¹) are similar to the previous results. The decay of the optical absorption of the C₅H₉O₂· radical at 270 nm followed second-order kinetics. This was further confirmed by variation of the doses from 20 to 90 Gy delivered by 4- μ s electron pulses (1 Gy produces 5.4 × 10⁻⁷ M C₅H₉O₂· and 6 × 10⁻⁸ M HO₂·/O₂⁻· radicals). An average value for the rate constant 2*k*(C₅H₉O₂· + C₅H₉O₂·) = (1.5 ± 0.3) × 10⁷ M⁻¹ s⁻¹ was obtained, which is in reasonable agreement with the reported²⁰ value of 2*k* = 2.4 × 10⁷ M⁻¹ s⁻¹.

However, in contrast to this earlier report²⁰ we have found evidence for the formation of albeit small amounts of H^+/O_2^- . from the bimolecular decay of cyclopentylperoxyl radicals. Conductivity measurements in N_2O/O_2 -saturated solutions of cyclopentane irradiated by an electron pulse at pH 6.5 showed that, in addition to the initial conductivity increase due to H⁺ and O_2^- from reaction 3 (G(H⁺) = 0.5), there was a conductivity buildup (net $G(H^+) = 0.4$) with a second-order rate constant 2k= $(3 \pm 1) \times 10^7$ M⁻¹ s⁻¹. This conductivity buildup consisted of a transient component (assumed to be H^+/O_2^-), which decayed over 50–100 ms, and a permanent component (G(permanent acid) = 0.15). In basic solutions of cyclopentane (pH 9.5-10.6) the same yield and rate constant were obtained for the corresponding decrease in conductivity (the formation of an acid in basic solution gives rise to the removal of OH⁻ by the proton and thus a net loss of conductivity). Since O_2^- disappears very slowly in basic solution¹⁸ any contribution of a permanent acid besides HO₂ to the observed conductivity drop cannot be recognized within the time scale of our pulse radiolysis experiments. This difficulty was overcome by the addition of a catalytic amount of superoxide dismutase to the cyclopentane solution at pH 9.5. Under this condition the conductivity drop was found to have only a transient component, which disappeared completely within 20 ms. The conductivity drop in the pulse radiolysis experiment described above is therefore assigned exclusively to the formation of O_2^{-} .

Pulse radiolysis study of the cyclohexane/N₂O/O₂ system yielded results quite similar to that of the cyclopentane/N₂O/O₂ system. The cyclohexylperoxyl radical has an absorption maximum at 260 nm with $\epsilon = 750 \pm 80 \text{ M}^{-1} \text{ cm}^{-1}$ and this absorption decays with a second-order rate constant of $2k = (1.2 \pm 0.2) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$.

The conductivity of a N₂O/O₂-saturated cyclohexane solution irradiated at pH 6.5 by electron pulses of 10-40 Gy showed in addition to the prompt increase due to H^+/O_2^- from reaction 3 a buildup with net $G(H^+) = 0.4$ with a second-order rate constant of $2k = (2.0 \pm 0.4) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$. After reaching its maximum level the conductivity of the solution decreases to a lower and constant level corresponding to $G(H^+) = 0.2$. In basic solutions (pH 9.6-10.6) a conductivity drop corresponding to net G("acid")= 0.6 was observed. The second-order rate constant again is identical with that observed at pH 6.5. As in the case of cyclopentane, O_2^- exclusively was found to be responsible for the conductivity drop in pulse-irradiated basic solutions of cyclohexane.

Discussion

The reactions of the cyclopentylperoxyl radicals leading to the various products observed are presented in Scheme I according to our present knowledge about the fate of secondary alkyl peroxyl radicals in aqueous solution (cf. ref 31). It appears to be now

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Scheme I



generally accepted that two peroxyl radicals form a short-lived tetroxide (reaction 7) which either reverts to the peroxyl radicals (reaction 8) or yields the products. Two concerted reactions have been recognized. Beside the Russell mechanism (cf. ref 32) which leads to one molecule each of cyclopentanol, cyclopentanone, and oxygen (reaction 9), there is another concerted reaction (cf. ref. 4, 7, and 16) that leads to two molecules of cyclopentanone and one molecule of hydrogen peroxide (reaction 10). In competition with these two concerted reactions the tetroxide can break down into two oxyl radicals and oxygen (reaction 12). Combination of the two resulting oxyl radicals (reaction 15) usually plays a minor role at least in aqueous solutions (cf. ref 2). The disproportionation reaction (reaction 14) is the free radical analogue of the Russell mechanism from which we cannot distinguish it. In competition, the cyclopentoxyl radical can undergo β -scission (reaction 13), a process that has been observed with alkoxyl radicals both in organic solvents^{33,34} and in aqueous solutions.¹¹ In aqueous solutions the oxyl radicals can also undergo a 1,2-H shift (reaction 16, cf. ref 35–38), whereupon the resulting α -hydroxycyclopentyl radicals again rapidly add oxygen (cf. ref 39). The α -hydroxycyclopentylperoxyl radicals thus formed eliminate $HO_2 \cdot (H^+ + O_2^-)$ (reaction 18, for a review see ref 40). The formation of H^+ and O_2^- from reaction 18 probably (see also below) gives rise to the transient conductivity observed in the pulse radiolysis experimentss. As an alternative to the fragmentation of the ring with free oxyl radicals as intermediates (reaction 12 followed by reaction 13) one might consider a concerted process, expulsion of oxygen with a concomitant formation of the carbon-oxygen double bond and cleavage of the neighboring C-C bond (reaction 11).

As seen in Table I there is more than twice as much cyclopentanone than cyclopentanol, which shows that the Russell

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mechanism (reaction 9) is not the exclusive route for the bimolecular self-reaction of cyclopentylperoxyl radicals. Together with its free radical analogue (reaction 14) it amounts to only about 30% in the present system (as suggested by the cyclopentanol yield). The other concerted reaction yielding the larger part of cyclopentanone contributes about 20% (reaction 10). There is little transient conductivity ($G(O_2^{-}) = 0.4$) which means that reaction 16 followed by reaction 18 is of relatively small importance here compared to other systems (cf. ref 11). In any case, 0.4 constitutes an upper limit for G(reaction 16) (see below). Reaction 15 is probably insignificant and G(organic peroxidic material) = 0.5 has been attributed (see above) mainly to the formation of the hydroperoxide (reaction 19). Thus about 8%

$$\begin{array}{cccc} & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & & \\ & & & \\ & & & \\ & & & & \\ & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & &$$

of the cyclopentylperoxyl radical reacts via reaction 19.

As a single process by far the most important reaction is fragmentation (reactions 11 and 13). The ring-opened radical will add oxygen generating the ω -formylperoxyl radical (reaction 17). The products derived from this peroxyl radical are glutaraldehyde and 5-hydroxypentanal; the sum of their G values equals 2. This means that nearly 40% of the cyclopentylperoxyl radicals take the fragmentation route (reactions 11, 12, and 13). The decay processes of the ring-opened peroxyl radicals appear to be very similar to those of the cyclic ones, with the exception of the fragmentation reaction (see below). The carbonyl compound, glutaraldehyde, is again in excess over the alcohol, 5-hydroxypentanal. Thus again, other mechanisms beside the Russell mechanism (cf. reaction 9) must be considered, such as, in particular, ω -formylalkoxyl radical formation but, important to note, a further fragmentation analogous to reaction 13 which would result in the formation of formaldehyde (reaction 20) can be rejected on account of the absence of formaldehyde.

$$CHO(CH_2)_3CH_2O \rightarrow CHO(CH_2)_2CH_2 + CH_2O \quad (20)$$

The ω -formylalkoxyl radical is expected to undergo a 1,2-H shift (analogous to reaction 16). The resulting α -hydroxyalkyl radical then adds oxygen and the corresponding peroxyl radical can eliminate HO₂ (cf. reaction 18). Under the high does rate conditions of pulse radiolysis such peroxyl radicals are known^{4,5} to form carboxylic acids in the course of their bimolecular decay. This reaction is taken here to account for the small yield of permanent acid observed in the pulse-irradiated neutral solutions. In basic solutions, however, OH⁻ induces rapid O₂⁻ elimination

and no permanent acid is formed.

The precise contribution of each reaction route to the entire radiolysis cannot be calculated readily because the cyclic and the acyclic peroxyl radicals do not react independently. The percentages given above are therefore meant to give the essential featuress. As already mentioned the ring-opened peroxyl radicals are generated in smaller quantities than the primary cyclopentyl peroxyl radicals and statistically they stand a better chance to decay by cross-termination rather than by self-termination. But using the simplified approach of self-termination one arrives at the rough estimate that the fragment radicals mainly decay by the Russell mechanism or its free radical analogue (G = 1.6, i.e., 80% based on G(5-hydroxypentanal) = 0.8). The excess of glutaraldehyde (G = 0.4, i.e., 20%) can be explained by a reaction similar to reactions 10 and 18.

In principle, the same scheme as the one given for the cyclopentylperoxyl radicals can be written for the cyclohexylperoxyl radicals, although there are some quantitative differences. Most strikingly, there is less fragmentation (ca. 15% vs. 40%), as suggested by the low yield of the open-chain compounds. This leads to the question whether in the present systems fragmentation occurs mainly via free oxyl radicals as intermediates (e.g., reaction 12 followed by reaction 13) or in the concerted process (reaction 11). In the latter case the ring strain of about 3 kcal mol^{-1} of the cyclopentyl system could speed up this reaction in competition with the other decomposition processes (reactions 14-16). The predominance of fragmentation in the cyclopentyl system compared to the cyclohexyl system is not as easily understood if oxyl radicals are the intermediates. It has been shown³⁷ that in aqueous

solutions cyclopentoxyl radicals undergo the 1,2-H shift (reaction 16) rather than the fragmentation (reaction 13). Processess involving 1,2-H shift reactions (cyclic and open-chain radicals) are unimportant in this system (G = 0.4) as concluded from the conductivity experiments. This leads us to the conclusion that the major pathway to the fragment radicals is the concerted process 11. Although there are peroxyl radical systems where it appears to have been convincingly shown that oxyl radicals are important intermediates (e.g., ref 11) it is not unlikely that such fragmentation reactions in other systems might also be due to the concerted pathway.3

Although considerable progress has by now been made in unravelling the products and some mechanistic details of the bimolecular decay of peroxyl radicals in aqueous solutions, there remains the puzzling question why the rate constants for the biomolecular decay of primary and secondary peroxyl radicals vary so much, spanning a range from 1.2×10^7 to 1.7×10^9 M⁻¹ s^{-1} , i.e., two orders of magnitude (e.g., present work and ref 3, 5, 7, 11, 12, 14, and 20). The question of the bimolecular termination of peroxyl radicals is by no means an unimportant one. In environmental studies it appears to be generally accepted that peroxyl radicals play a dominant role in the degradation of organic material, especially if it is inaccessible to biological degradation. Since autoxidation is a chain reaction, the rate of termination, among other factors, controls the efficiency of this important natural cleansing process.

Registry No. Cyclopentane, 287-92-3; cyclohexane, 110-82-7; cyclohexylperoxy radical, 2143-59-1; cyclopentylperoxy radical, 20682-76-2.

Statistical-Limit Line Broadening in the S₂ State of Phenanthrene in Supersonic Jets

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In this paper we report on the absorption and fluorescence excitation spectra for the $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ transitions of phenanthrene in pulsed planar supersonic expansions. The line profile of the electronic origin of $S_0 \rightarrow S_2$ transition is Lorentzian with a homogeneous width of 11 cm⁻¹ for electronic relaxation in the isolated molecule. The $S_0 \rightarrow S_2$ origin of the isolated molecule, which corresponds to the statistical limit, drastically differs from the same transition of phenanthrene in durene which reveals the features of the intermediate-level structure. The dramatic medium effect on the interstate S_2-S_1 coupling is attributed to the modification of the electronic energy gap.

Introduction

The spectroscopic manifestations of interstate coupling and intramolecular electronic relaxation in a bound-level structure of large isolated molecules have been considered for a long time.¹⁻⁴ Ross¹⁻³ proposed that intravalence, spin-allowed $S_0 \rightarrow S_n$ (n >1) transitions to high electronically excited states of large molecules are expected to be homogeneously broadened due to effective internal conversion. The experimental verification of the occurrence of homogeneous relaxation broadening in excited states of large isolated molecules was fraught with considerable difficulties in view of large contributions from thermal inhomogeneous broadening, i.e., rotational broadening and vibrational sequence congestion, which obsure the homogeneous contribution to the line broadening. Spectroscopy of guest molecules in low-temperature solids, i.e., mixed molecular crystals^{5,6} and Shpolskii

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matrices,⁷ provided information on homogeneous line broadening due to electronic relaxation in S_n (n > 1) states of large aromatic and heterocyclic molecules $^{4\text{--}6}$ and in the S_1 state of azulene. $^7\,$ With the advent of spectroscopy in seeded supersonic expansions, high-resolution absorption line shapes of large isolated molecules became amenable to experimental interrogation.^{8,9} One recent implication emerging from fluorescence excitation¹⁰⁻¹³ and absorption studies¹⁴ of large molecules pertains to the manifestation of the effects of interstate coupling and of electronic relaxation on the optical line shapes for the $S_0 \rightarrow S_2$ transition, which fall into two categories.

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