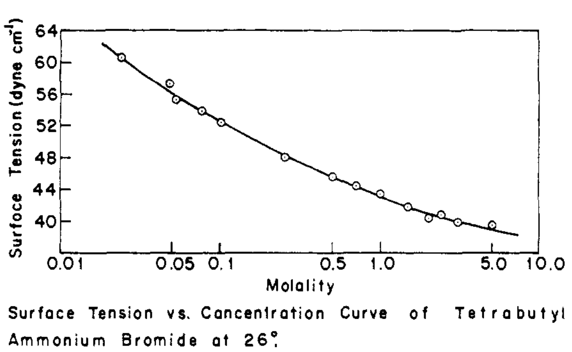

Figure 3. Test for a "critical micelle concentration" of tetrabutylammonium bromide in water at 25°.

range of our experiment. The results are displayed in Figure 3, from which no sharp break such as would suggest a critical micelle concentration can be found. That none is observed at lower concentrations was shown by a similar study of Tamaki's.[26]

The behavior of the thermodynamic properties for solution of benzene in the less concentrated solutions of tetrabutylammonium bromide provides a clear example of "hydrophobic bonding" [27,28] in a very simple system. The results over that part of the curve can be accommodated readily if one considers that the thermodynamics are dominated by the release of water molecules due to aggregation of the benzene with the hydrophobic alkyl chains of the salt. The release of bound water is an endothermic process accompanied by a favorable gain in entropy. This would be true regardless of the nature of the interaction between the water and the hydrophobic chains, and we will make no further attempt to specify the mechanism through which it takes place.

One of the most interesting features of Figure 2 is the sharp reversal in enthalpy and entropy taking place at 1.2 *m* salt. Reversals of this type have been documented for many processes (see above), and for cases where data are available, it has been found close to the composition of hydrate–clathrates of the cosolvent. The clathrate–hydrate composition of tetrabutylammonium bromide (32.6 to 1[7]) corresponds to a 1.70 *m* tetrabutylammonium bromide solution, the melting point of the clathrate being 12.5°. The composition and stability of the crystalline clathrate–hydrate must depend upon geometrical lattice forces which are absent in solution. Although we maintain a skeptical attitude toward the existence of clathrates in solution,[6,29] we note that the phenomena portrayed in Figure 2 could be explained completely if there were a competition between benzene and the tetrabutylammonium bromide for structuring of water. Exothermic structure making by benzene should be most successful in the absence of any competitor, that is in pure water. From pure water to a composition in the neighborhood of the clathrate, structure making by benzene would become increasingly difficult (endothermic). After the clathrate stoichiometry of the tetraalkylammonium salt had been satisfied, structure making of water around the benzene molecule could then proceed in the direction of decreasing entropy and exothermic enthalpy. We are uncomfortable with this facile interpretation, but feel compelled to draw attention to it since it fits the facts.

In conclusion, we wish to emphasize the sharp difference between tetrabutylammonium bromide and mineral uniunivalent salts in aqueous solution and the close similarity of it to nonpolar cosolvents. In the present instance, the phenomena have a closer resemblance to "hydrophobic bonding" than to classical salting-in or salting-out phenomena.

Acknowledgment. We are grateful to Mr. Dimitrous Giannakidis for performing a number of the surface tension measurements.

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Singlet Oxygen in the Environmental Sciences. IX.[1] Product Distribution from Reactions of Singlet Molecular Oxygen in the Gas Phase

W. S. Gleason, I. Rosenthal, and J. N. Pitts, Jr.[2]

Contribution from the Department of Chemistry, University of California, Riverside, California 92502. *Received December 31, 1969*

Abstract: The product distribution for the reactions of $O_2(^1\Delta_g)$ with various olefins in the gas phase was determined and compared with those for the liquid-phase dye-sensitized process. The absence of a free-radical autoxidation mechanism in reactions in the gas phase was also noted.

Dye-sensitized photooxygenations of olefins and polynuclear aromatic hydrocarbons have been studied extensively.[3-6] Additional research into the generation of singlet oxygen by the reaction of hydrogen peroxide and sodium hypochlorite has shown that this

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method produces the same products as photooxygenation.[7-10] Furthermore, the stereoselectivity of the material reacting with the singlet oxygen appears to be independent of the method by which the singlet oxygen is produced.[10] However, in both of these methods, the reaction is carried out in solution. Little work has been done on singlet oxygen reactions in the gas phase and nothing has been reported for those gas-phase reactions where more than one product is produced.[11-16] In this paper, the product distributions resulting from the gas-phase reaction of singlet oxygen with several butenes, pentenes, and cyclohexenes are reported and compared with the results obtained from radical autoxidation reactions and from reactions of singlet oxygen generated in solution by photosensitization.

Experimental Section

Materials. All of the olefins used were obtained from Chemical Products, Inc., except for the 1,2-dimethylcyclohexene, which was obtained from K and K Laboratories. Although these materials were better than 99% pure, they were further purified by distillation and then passed several times through activated alumina.

Those reaction products which could not be obtained commercially were either synthesized or generated by photooxygenation and then separated and purified by preparative gas chromatography.

Gas-Phase Reactions. The apparatus for the generation of singlet oxygen in the gas phase using a microwave discharge has been described previously,[15,16] except that cobalt oxide wire was removed during these experiments. Each olefin was injected into the flow system at a rate of 1×10^{-6} mol/sec, where the total oxygen flow rate and pressure were 7×10^{-5} mol/sec and 6.0 Torr, respectively. The reactant and products were recovered quantitatively in liquid nitrogen traps and dissolved in ether. Volatile compounds were removed under vacuum at room temperature and the crude hydroperoxides were reduced to their corresponding alcohols with triphenylphosphine in ether.[17] This solution was analyzed on a Varian Aerograph Model 1200 flame-ionization gas chromatograph (He carrier gas) using either a 6 ft × $^1/_8$ in. Teflon column of 3% XE-60 and 3% Carbowax 20 M on Chromosorb P or a 10 ft × $^1/_8$ in. Teflon column of 5% Carbowax 20 M on Chromosorb P. The product ratios were determined from the peak areas using a Disc Integrator. The alcohols produced were identified by comparison of glc retention times with those of authentic samples. The sensitivity of the flame-ionization detector to the various alcohols was also checked and calibrated against authentic samples. The crude hydroperoxides produced in gas-phase reactions were also tested with KI. Their infrared and mass spectra were essentially identical with spectra of hydroperoxide mixtures prepared by the dye-photosensitized oxidation of the same olefin. There was no indication that carbonyl compounds were also formed in the gas-phase reactions, confirming the absence of reactions with $O(^3P)$ and O_3.

The alcohols produced in the 2-methyl-2-butene reaction were isolated by preparative gas chromatography and were identified by comparison of their ir, nmr, and mass spectra with those of authentic samples.

Photosensitization Reaction. The photooxygenation reactions were carried out using the procedure developed by Foote,[9] except that purified methylene blue was used as the photosensitizer instead of Rose Bengal. The separation, purification, and analytical procedures were the same as those used for the products obtained from the gas-phase reaction.

Results and Discussion

The passage of a stream of oxygen through a microwave discharge is known to produce atomic oxygen and electronically excited molecular oxygen in the $^1\Delta_g$ and $^1\Sigma_g{}^+$ states. Mercuric oxide deposited immediately downstream from the microwave discharge, and the mercury vapor carried over in the oxygen stream has been shown to efficiently scavenge atomic oxygen and ozone. In this work the efficient removal of oxygen atoms was confirmed periodically by the absence of the NO_2 air glow.[14] Thus the gas stream contained only molecular oxygen in its ground and excited states and a trace of Hg.

Since no products were detected when the discharge was off, the reactions most likely involve singlet oxygen in the $^1\Delta_g$ state, the only reactive species in the stream (*vide infra*).

The distributions of products obtained from the gas-phase reaction of $O_2(^1\Delta_g)$ with the nine hydrocarbons used are given in Table I. The results are the mean of four analyses after the hydroperoxides had been reduced to the alcohols. For comparison, the products formed in solution from the dye-photosensitized oxygenation reactions of the same olefins are also presented.

The differences in the product ratios between gas-phase singlet oxygen oxidations and photosensitized oxidations in solution, although small, seem to be real since the work-up for both reactions was practically identical.

The widely suggested "ene mechanism" for singlet oxygen reactions[6] has found support in the observations that for compounds where steric hindrance was not a problem, no Markovnikov-type directing force was observed. Tertiary and secondary hydroperoxides were produced in equal proportions and different substituents had no effect on the product distribution. Furthermore, a lack of solvent effect appeared to rule out a two-step reaction involving an ionic intermediate.[10] Nevertheless, even for reactions which are not markedly solvent sensitive, it is not necessarily assumed that the solvent molecules have no effect. It is possible that the solvent may alter the precise conformation of the olefins and thus affect the relative rates of competitive pathways. This may explain the difference in product distributions obtained in solution and in the gas phase. Moreover, if the intermediate in the hydroperoxide formation is a "hot" molecule, as has been observed,[16] then the energy distribution could favor the formation of the tertiary hydroperoxide. This effect may not be as apparent in a solvent which acts as an energy sink.

Another mechanism for singlet oxygen reactions which involves formation of an intermediate "perepoxide," proposed by Sharp[18] and Kopecky,[19] has recently found additional support from experimental evidence.[20]

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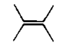
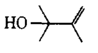
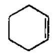
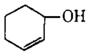
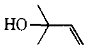
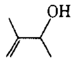
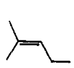
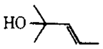
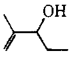
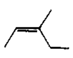
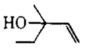
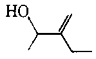
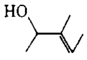
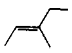
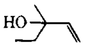
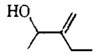
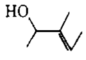
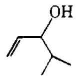
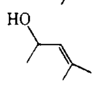
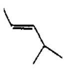
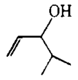
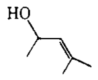
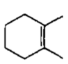
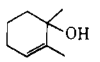
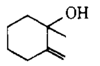
Table I. Product Distribution for Reaction of Olefins with $O_2(^1\Delta_g)$

Olefin	Alcohols[a]	Gas-phase reaction, %	Photosensitized reaction, % This work	Lit.
		100	100	100[b]
		100	100	100[b]
		70.9	56.9	54[b]
		29.1	43.1	46
		57.4	50.2	51[c]
		42.6	49.8	49
		63.3	52.6	
		36.7	45.0	
		0	2.4	
		80	70.03	
		20	20.35	
		0	9.62	
		98.1	97.3	96[c]
		1.9	2.7	4
		96.5	93.4	
		3.5	6.6	
		5	10	11[c]
		95	90	89

[a] Alcohols obtained by reduction of hydroperoxides with triphenyl phosphite. [b] Reference 6. [c] Reference 10.

However, it is difficult to correlate the preferential formation of a tertiary hydroperoxide with this kind of intermediate.[21]

Ogryzlo[22] has reported that $O_2(^1\Sigma_g^+)$ is able to survive no more than 10–100 collisions in H_2O or CH_3OH solutions. However, although $O_2(^1\Sigma_g^+)$ is readily deactivated in solutions it could well be important in the gas phase. In order to check this, several experiments were rerun, injecting water vapor into the flow system upstream from the points of olefin injection. If $O_2(^1\Sigma_g^+)$ was reaching the reaction zone the water vapor should have deactivated it and produced changes in the singlet oxygen concentration, the rate of reaction, and eventually in the product distribution. When 2,3-dimethyl-2-butene was oxidized in the presence of water vapor, no change in the reaction rate or in the concentration of singlet oxygen could be observed.[16] Moreover, when 2-methyl-2-butene was treated with singlet oxygen in the presence of water vapor, no change in the product distribution occurred. This indicates that $O_2(^1\Sigma_g^+)$ does not contribute significantly to the reaction of singlet oxygen with olefins and that the primary oxygen reactant is $O_2(^1\Delta_g)$.

A final consideration involves the question of whether or not the gas-phase reactions of $O_2(^1\Delta_g)$ may also proceed by a radical autoxidation mechanism. Foote[10] has reported that when singlet oxygen reacts with 1,2-dimethylcyclohexene, the normal autoxidation product, 1,2-dimethyl-3-hydroxycyclohexene, is not formed. Since 1,2-dimethyl-3-hydroxycyclohexene was not detected in our reaction of $O_2(^1\Delta_g)$ with 1,2-dimethylcyclohexene, it appears that the gas-phase reaction also does not proceed through a radical autoxidation pathway.

These results indicate that studies of singlet oxygen reactions in solution, although qualitatively similar, may not always be extrapolated quantitatively to the gas phase, for example in problems dealing with photochemical air pollution.[23] This is especially true when dealing with complex reactions which involve "hot" molecules, reactive intermediates, and multiple product formation.

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