where $\partial \mu / \partial \mathbf{Q}$ is the transition dipole, ϵ is the permittivity of free space, m is the reduced mass of the harmonic oscillator, ν_0 is the vibrational frequency of the free molecule, and σ is the hard-sphere diameter. The liquid structure parameter $\xi(\rho,T)$ approaches zero for random molecular orientations and increases as the liquid structure becomes more orientationally ordered. Vibrational frequencies are predominantly determined by static molecular structure rather than by the dynamical processes occurring through intermolecular and intramolecular interactions. Since the liquid molecules confined to spaces as small as several molecular diameters are less freely randomized compared to molecules in a bulk liquid, the local orientational order of the restricted molecules should be enhanced which, in turn, will result in a larger Δv_{RIVC} according to eq 3.

Obviously, Logan's model does not consider any surface interactions, and hence it is not too surprising to find that $\Delta \nu_{RIVC}(R)$ of the nonmodified glasses does not follow the theoretically predicted trend. However, for modified glasses, where the surface interactions have been reduced significantly, $\Delta \nu_{RIVC}(R)$ does increase as pore size decreases (Figure 3). The possible confined geometry-induced changes in $\Delta \nu_{RIVC}$ for the nonmodified glasses, although not observable within the experimental error, are by no means as large as the effects for the modified glasses as shown in Figure 3. This is indicative of the local molecular structure for confined liquids in nonmodified glasses being significantly affected by the surface interactions and, therefore, may counteract the confined geometry-induced changes, with the net result of a smaller change in $\Delta v_{RIVC}(R)$ compared to that observed in the modified glasses.

The theoretical work of Klafter et al.¹⁶ concerning energy relaxation under the effect of geometrical confinement was a strong motivating force in initiating this investigation. One of their major conclusions in studying the direct resonant energy transfer of restricted molecules is that the geometry (such as the cylindrical pores) slows down the relaxation rate of the direct energy transfer. A slower relaxation rate implies a narrower line width for a particular relaxation mechanism, and so in our experimental work it is expected that $\Delta\Gamma_{RIVC}$ will also decrease as the pore size is decreased. These theoretical predictions were qualitatively confirmed by our experimental results (Figures 4 and 5). While peak shifts are determined by the static molecular structure, the line widths are much more dependent on the dynamic processes involving intermolecular and intramolecular interactions. Resonant intermolecular vibrational coupling occurs through energy transfer between molecules of the same species. Therefore, any surface perturbation, regardless of magnitude, will change the energy of the vibration for molecules associated with the surface resulting in nonresonance with the original energy levels. The degree to which the surface perturbation affects the energy level is unimportant as any difference will result in a reduced ability to relax through interaction with surface associated molecules. One would expect that any surface perturbation will affect the RIVC relaxation rate in a similar manner. In agreement with our expectations, it appears that the surface interactions of the nonmodified glasses do not affect significantly the RIVC relaxation rate as shown in Figure 5.

Conclusion

The influence of geometric confinement on the molecular dynamics of liquid methyl iodide was studied by Raman scattering. The RIVC of the v_2 vibrational mode in methyl iodide turns out to be an excellent probe to explore the effects of geometric confinement as the results for the resonant intermolecular vibrational coupling mechanism of this mode provide qualitative experimental evidence of changes due to geometric confinement. The experimental results, which show that the smaller the pore size the smaller the line widths and the larger the line shifts induced by RIVC, are qualitatively explained by using the theoretical models of Logan¹⁵ and Klafter et al.¹⁶ This finding suggests that the liquid methyl iodide confined to very small pores has a higher reorientational order and slower resonant energy transfer relaxation rates.

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Gas-Phase Reactions Involving Hot ¹⁸O(³P) Atoms and Formaldehyde

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We report an investigation of the low-pressure gas-phase reactions involving hot ${}^{18}O({}^{3}P)$ atoms with translational energies in excess of 1 eV and formaldehyde. Using mass spectrometry, ${}^{18}O$ incorporation in C¹⁶O¹⁸O and HC¹⁸O products was observed. These results strongly suggested that carbonyl bond addition was an important reaction at these energies.

Introduction

Past investigations concerned with the mechanistic and kinetic aspects of $O(^{3}P)$ reactions with aldehydes have led to the conclusion that the predominant reaction at room temperature is abstraction of the weak aldehydic hydrogen.¹⁻⁸ The spectroscopic

studies on the nascent internal state distributions of the hydroxyl radical product also support this finding.9 However, there is no reason to exclude the possibility that atom attachment to the carbonyl bond is also an important pathway. In fact, Chang and Barker¹⁰ have observed a substantial yield of primary product at m/e 44 in their flow-tube experiments involving O(³P) + H₂CO. They presumed that this mass signal was due to CO₂ formed somehow as a result of such an addition reaction. While this may be true, their study did not provide any direct evidence for hydrogen atom migration in the methylenebis(oxy)H₂CO₂ adduct. It was later suggested by Dupuis and Lester,¹¹ in an ab initio study of the same system, that the isomerization of this adduct to triplet formic acid would require at least 30 kcal/mol. It is therefore highly unlikely that such migrations are possible for the triplet adduct in a room-temperature experiment.

Chang and Barker's results were best explained either by collision-induced intersystem crossing to singlet methylenebis(oxy), where hydrogen atom migration here would require a substantially lower activation energy, or by stepwise hydrogen atom elimination from the triplet adduct. The former explanation should at least play a significant role in view of the fact that their studies were carried out at the rather high pressure of 1.6 Torr.

The present paper reports low-pressure results on the rapid mass spectrometric detection of certain products which support the hypothesis that the $O(^{3}P) + H_2CO$ addition reaction is an important process. These studies were made possible using ion beam sputtering from an isotopically enriched atomic oxygen-18 source for generating these hot atoms.¹²⁻¹⁴

Experimental Section

A detailed description of the source characteristics¹⁴ and the low-pressure reaction cell have been published elsewhere.¹⁵ The system utilized a 150-cm Isotope Separator (High Voltage Corp.) for generating and mass resolving a 40-keV argon ion beam. This beam was focused with an electrostatic lens through a 4.8-mm entrance aperture onto a Ta_2O_5 target. Generally, about 15 mA of beam was used to bombard the target. This target was mounted at an angle of 30°, measured between the surface normal and the beam axis, in order to optimize the oxygen atom flux. It was also rotated on axis for better uniformity in that flux, when the oxide became depleted.

The enriched oxide target was prepared by anodizing a 0.05mm-thick tantalum foil (Atomergic Chemetals Corp.) with a 0.01 N KI solution with ¹⁸O-enriched H₂O (Monsanto Research Corp., Mound Laboratory: isotopic distribution 97.1% ¹⁸O; 2.0% ¹⁷O; 0.9% ¹⁶O).¹⁶ Although oxide thicknesses were not measured, the process yielded what appeared to be a uniform gray coating that surpassed thicknesses that could be matched to specific interference colors.

Oxygen atoms sputtered from Ta_2O_5 with 40-keV argon ions were found to be dominantly neutral and resided exclusively in their ${}^{3}P_{J}$ ground electronic state.¹⁴ Energy distributions for these atoms were previously measured and reported by us¹⁴ for selected scatter angles. These measurements were found to coincide with the distributions expected from a modified collision cascade sputtering model reported by Garrison.¹⁷ The distribution extends well over the 1-20-eV range but peaks at about 6 eV.

Formaldehyde was prepared on-line by decomposing paraformaldehyde (Aldrich Chem.) at 440 K. The paraformaldehyde was dried under vacuum at 370 K for several days before use. The formaldehyde was introduced into the sputtering chamber through a heated 0.25-in. stainless steel tube. The absolute substrate pressure was measured with a Barocel gauge (MKS) and controlled to 1×10^{-5} Torr using a sapphire seated variable leak value (Varian) maintained at 370 K.

The primary chamber was differentially pumped by a turbomolecular pump (Balzer Inc.) and a 4-in. oil diffusion pump, isolated by a liquid nitrogen cooled baffle, to achieve a base pressure of 8×10^{-7} Torr. The forechamber was pumped by a 6-in. oil diffusion pump and also isolated by a liquid nitrogen cooled baffle to achieve a base pressure of 2×10^{-7} Torr.

Primary products were analyzed with an on-line quadrupole mass filter that had a resolution of about 50 in the low mass range (Dycor 200 mass range head). Electron impact was used for ionization along with a Channeltron type electron multiplier detector. The detector assembly was mounted perpendicular to the axis of the primary argon ion beam (60° from the target



Figure 1. Energy correlation diagram depicting possible triplet pathways.

surface normal) where the ionizer was spaced 2.5 cm from the impact point on the surface and sampled products through a 2.5-cm aperture. The large solid angle afforded excellent product detection sensitivity. Selected m/e values were monitored with 4-ms time resolution and plotted as ion signal (ampere) versus scan time. During a typical scan, the oxygen atom concentration was modulated several times by manually chopping the primary argon ion beam.

Results and Discussion

1

Figure 1 represents an energy correlation diagram for the triplet pathways of the reaction intermediates generated from $O(^{3}P) + H_{2}CO.^{18}$ Although not shown in this figure, the addition reaction as well as some of the other steps that are exothermic may in fact exhibit slight activation energies.

As pointed out earlier, it has long been presumed that hydrogen atom abstraction is the predominant reaction at room temperature for the ground-state oxygen atom. In fact, it is slightly more exothermic than addition to the carbonyl bond. The fact that this addition reaction is also exothermic and possesses an activation energy barrier of perhaps only a few kcal/mol,¹⁰ suggests that it too should be important. Unfortunately, room-temperature studies carried out under single or near single collision conditions will generate an unstable triplet adduct that will either dissociate back to reactants or eliminate hydrogen atoms to yield CO_2 . This is because the energy of activation for isomerization to excited formic acid lies somewhere in excess of 30 kcal/mol.¹¹ This is well above the 15.3 kcal/mol of energy released through the exothermic addition reaction. Of course, high collision frequencies would expedite the intersystem crossing between the ${}^{3}B_{2}$ and ${}^{1}A_{1}$ states of the methylenebis(oxy) adduct. Once formed, the singlet adduct could easily isomerize to the ground ${}^{1}A_{1}$ state of formic acid (a process that is nearly 110 kcal/mol exothermic) with only a few kcal/mol of energy needed to surmount the energy barrier. Unfortunately, high-pressure studies tend to cloud the primary processes of interest.

When using ¹⁸O as the reacting atom, one can expect a number of labeled and unlabeled primary products. Reactions 1 and 2

$${}^{18}O({}^{3}P) + H_2CO \longrightarrow {}^{18}OH + CH^{16}O$$
 (1)

$${}^{8}O({}^{3}P) + H_{2}CO \longrightarrow H_{2}C^{16}O^{18}O$$
 $({}^{3}B_{2})$
 $\stackrel{a}{\longrightarrow} HC^{16}O^{18}OH$
 $({}^{3}A_{1})$
 (2)
 $a' HC^{18}O^{16}OH$
 $({}^{3}A_{1})$

depict the primary abstraction and addition pathways. Aside from



Scan Time (sec.)

Figure 2. Collected spectrum of ion signals measured at m/e 31 and 46 over two modulation cycles of the ¹⁸O-atom source.

direct hydrogen atom elimination yielding C¹⁶O¹⁸O, reaction 2 depicts two additional isomerization pathways of the methylenebis(oxy)H₂C¹⁶O¹⁸O adduct formed in these hot atom studies that would yield triplet formic acid. Decomposition is expected of this acid through either reaction 3 or 4. Studies on the de-

$$HC^{16}O^{18}OH \xrightarrow{c} HC^{16}O + {}^{18}OH$$
$$\xrightarrow{c} H_2{}^{18}O + C^{16}O$$
$$\xrightarrow{d} C^{16}O^{18}O + H_2 \text{ (or 2H)}$$
(3)

$$HC^{18}O^{16}OH \xrightarrow{b'} HC^{18}O + {}^{16}OH$$
$$\xrightarrow{c'} H_2{}^{16}O + C{}^{18}O$$
$$\xrightarrow{d'} C{}^{18}O{}^{16}O + H_2 \text{ (or 2H)}$$
(4)

composition of triplet formic acid have shown that only pathways c and d occur,^{19,20} largely due to the endothermicity of pathway b (8.6 kcal/mol). As seen from the correlation diagram, the sequence for hydrogen atom elimination from the triplet acid can have very different energetics depending on whether it follows a stepwise or concerted process.

It should be noted that CO_2 may also arise from the direct stepwise elimination of hydrogen atoms in the triplet methylenebis(oxy) adduct. In fact, such a reaction would be isoelectronic with the displacement reaction observed for $O(^{3}P) + C_{2}H_{4}$.²¹

From the chemical pathways listed above one might expect to see reactive contributions to the ion signals measured at m/e 17, 18, 19, 20, 28, 29, 30, 31, 46, and 47. Unfortunately, the mass spectrum of H₂CO created too high a background at m/e 28, 29 and 30, which prevented us from detecting the reactive contributions to these masses. Likewise, the high H_2O background in our system which we attributed to the state of hydration of our paraformaldehyde, caused high reactive signals at m/e 17, 18, 19 and 20 from hot ¹⁸O-atom reaction with H_2O .

A sampling of the kind of spectra one obtains from two modulation cycles is shown in Figure 2. Each point is plotted on a per second time basis and is representative of only one of the many 4-ms periodic samplings. Reactive signals could be seen for m/e31 and 46 and were attributed to HC¹⁸O and C¹⁶O¹⁸O products, respectively, although the C¹⁶O¹⁸O signal-to-noise was significantly lower than that of the HC¹⁸O product. In addition, no reactive contributions to m/e 47 were observed above the background signal, indicating a lack of HC¹⁶O¹⁸O product.

Certain features of reaction were evident from even the few observations that we were able to make in this study. On the one hand, our observation of products such as HC18O and C16O18O leads us to conclude that hydrogen atom abstraction is not the only reaction mechanism operative in this system. In light of the energy considerations, it seems likely that carbonyl bond addition is an important reaction. Unfortunately, the qualitative nature of this study and the inherent detection limitations prevented us from drawing any conclusions regarding what the branching ratio was for the two pathways. Even so, carbonyl bond addition may not be unique to the hot atom reaction. This reaction may be just as important at thermal energy as suggested by Chang and Barker.¹⁰ Interestingly, what appears unique to our studies is the observation of an addition-fragmentation channel yielding HC¹⁸O, which occurs at high collision energies. However, given the paucity of the data at hand, the full mechanistic implications of this channel are not known at this time.

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