in apolar solvents and in reversed micelles which contained no free water molecules.[20,29]

The behavior of pyranine in polymerized vesicles is entirely consistent with the proposed cleft formation which results from the pulling together of the head groups upon surface polymerization. The clefts are conceived of as water-filled pockets of exposed hydrocarbon chains on the vesicle surface. Electrostatic and hydrophobic interactions are responsible for pulling POH into and subsequently retaining it in the clefts of polymerized **1** vesicles. Polymerization prevents the deeper penetration of POH into the vesicle bilayer. Indeed, the whole nature of the bilayer has been altered by the photopolymerization induced surface inhomogeneity. POH can remain solubilized indefinetely in the clefts and maintain its stable, noncovalent association with the vesicles. An artists's conception of POH interaction with nonpolymerized and polymerized vesicles prepared from **1** is shown in Figure 10.

Results of anisotropy measurements also support the proposed morphological changes upon vesicle photopolymerization. Rotation of POH is more hindered and less complete in unpolymerized than in polymerized vesicles (Table III). The residual polarization of POH in nonpolymerized vesicles (ca. 0.1) indicates that POH is only able to reorient about a certain axis rather than tumble freely. In contrast, in the polymerized vesicles the POH is able to reorient almost entirely, which is consistent with the idea that the POH is water solubilized in a relatively large surface cleft on the vesicle. The fact that τ_R (ca. 4 ns) is much larger than in pure water (<100 ps, and unresolvable by our experiment) indicate that the solubilized POH is experiencing rotational hindrance in the clefts due to interactions with the exposed hydrocarbon chains.

Results of PO^- reprotonation are also consistent with the time-dependent penetration of the probe into the bilayer of nonpolymerized **1** vesicles and with its location in the aqueous clefts in polymerized **1** vesicle. After 1 day of incubation, the proton ejection ability of POH is lost in nonpolymerized but unaltered in polymerized vesicles (Table V).

The conceptualization and detailed kinetics for surfactant vesicle photopolymerization reported previously[16] make possible a computer simulation of the process, the aim of which is to provide a graphical visualization and semiquantitative characterization of the resulting surface inhomogeneity and cleft formation. Such a simulation has been carried out[26] and some of the main conclusions are mentioned here.

The main simulation parameters are the monomer–monomer equilibrium spacing in the unpolymerized vesicle, the polymer bond length, the free radical lifetime, the average chain length, and the total number of free radicals produced (i.e., the extent of the polymerization). Carrying the simulation to completion for vesicles with 10 Å of monomer equilibrium spacing, 7 Å of separation between head groups upon polymerization, and an average chain length of 15 monomers/chain shows that over 45% of the interchain separations in fully polymerized vesicles are greater than the equilibrium separation. Furthermore, 50% of these latter interchain separations are greater than 13 Å. Although the openings, or clefts, formed in the vesicle surface can in no way be considered as circular, the value of 13 Å nevertheless provides a rough idea of the linear dimension of the median cleft. The simulation also shows that this median cleft size changes very little with increasing polymerization of the vesicle, and indicates that clefts of this median dimension begin to form as soon as polymerization begins.

Additional kinetic analysis afforded by the simulation shows that, because of free radical trapping and the increasing scarcity of bondable neighbor monomers, the polymer chain lengths decrease in the latter stages of polymerization. The result is that there are many short chains in the final number of chains vs. chain length distribution, although the final weight average distribution of chain lengths is peaked near the kinetically determined average chain length. The overall effect of the chain shortening vs. degree of polymerization is to perturb the weight average chain length distribution from a normal distribution to an asymmetric one in which there is a greater weighting and buildup on the short chain side.

Demonstration of cleft formation upon vesicle surface photopolymerization opens the door to important applications. Suitable compounds may be entrapped and released upon command (depolymerization). Additionally, uniformly sized clefts with restricted polarities may well provide unique sites for reactivity control and molecular recognition.

Acknowledgment. Support of this work by the National Science Foundation and the U.S. Army Research Office is gratefully acknowledged. We thank CNPq Brazil for awards (to F. Nome and M. Politi) and NATO for a travel grant (to P. Tundo).

Registry No. 1, 93253-93-1; POH, 57206-23-2.

Interactions between Phenol and Carbon Monoxide under Cryogenic Conditions. Evidence for a Phenol–CO Complex

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Abstract: Phenol has been matrix-isolated in argon, nitrogen, and carbon monoxide. The magnitude of the shifts of key OH bands from gas-phase values indicates that phenol–matrix interactions increase in the series Ar < N_2 < CO. Phenol forms a 1:1 complex with CO in argon-doped matrices. On the basis of the downward shift of ν_{OH} (the OH stretch) and the shift of $\nu_{C\equiv O}$ to higher frequency, it is concluded that phenol is hydrogen bonded to the carbon terminal of carbon monoxide. Phenol in solid carbon monoxide behaves as if there is an equilibrium between "free" and complexed forms. The observation of a 1:1 complex between phenol and CO in argon offers the novel prospect of assessing substituent effects under cryogenic conditions.

Introduction

Complexes formed between proton donors and acceptors have been of essential interest because of their importance to an understanding of intermolecular interactions in biological and chemical systems, and to a general theory of hydrogen bonding.[1-5] The study of one extreme, involving weakly interacting donor and acceptor components of a dimer, is a contemporary activity of

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Table I. Characteristic OH Frequencies (cm^{-1}) of Phenol Isolated in Various Matrices[a]

matrix	ν_{OH}	δ_{OH}	γ_{OH}
Ar	3633.5	1175.0	
	3638.5	1177.0	310.0
N_2	3623.0	1189.0	364.0
	3628.0	1196.0	372.0
CO	3575.0		
	3590.5	1194.0	362.0
	3623.5	1206.0	415.0

[a] T_d = 20 K; spectra were recorded at 12 K.

considerable possibilities, since advances in technology and theory have made such phenomena increasingly accessible to experiment and calculation.[6–17] Despite the potential of modern techniques, there are still only very limited data bearing on the properties of weak complexes involving proton donors and acceptors.

Davies and Hallam's report[18a] of the complex between hydrogen chloride and carbon monoxide in gas matrices is an important prototype that has stimulated research leading to the characterization of gas-phase hydrogen halide–carbon monoxide complexes by pulsed Fourier-transform microwave spectroscopy.[10] Recently these studies have been further supplemented by FT-IR spectra of the dimers in gas matrices.[18b] There is now direct structural evidence indicating that OC···HX complexes possess a linear geometry with hydrogen bonding to carbon, and that the heavier hydrogen halide forms the weaker hydrogen bond.[12–16] These microwave studies have also received support from theory in the form of ab initio SCF-MO calculations.[17]

During the course of studies of the photolysis of salicylaldehyde (**1**) in solid CO, we observed a profound perturbation on the frequency of the phenolic OH stretch of a photoconformer (ν_{OH}^{CO} 3562 cm^{-1} as compared with ν_{OH}^{Ar} 3638 cm^{-1}) which we attributed to a hydrogen-bonded complex between CO and the anti form of salicylaldehyde (one in which the formyl group has rotated 180°).[19] This observation has led us to study the effect on phenols of gas matrices doped with CO, and to gather evidence in support of the formation of phenol–CO dimers. Phenol (**2**) has previously been used as a model proton donor in order to gauge the effects of substituents on the strength of hydrogen bonds in various complexes.[20] The possibility of studying such effects under cryogenic conditions has never been exploited and provides an additional dimension to this research.

Experimental Section

A description of the apparatus as well as the purification of argon (Matheson, prepurified 99.998% min) and the procedure for sample preparation has been reported previously.[21] Carbon monoxide and nitrogen of research grade purity were supplied by Matheson and were used without further purification. Phenol (Mallinckrodt Chemicals) of analytical grade purity was purified by bulb-to-bulb transfer. Phenol-*O-d* was prepared by isotope exchange with deuterated water. Exchange was monitored by infrared spectroscopy until the OD stretch had completely replaced the OH stretch of phenol.

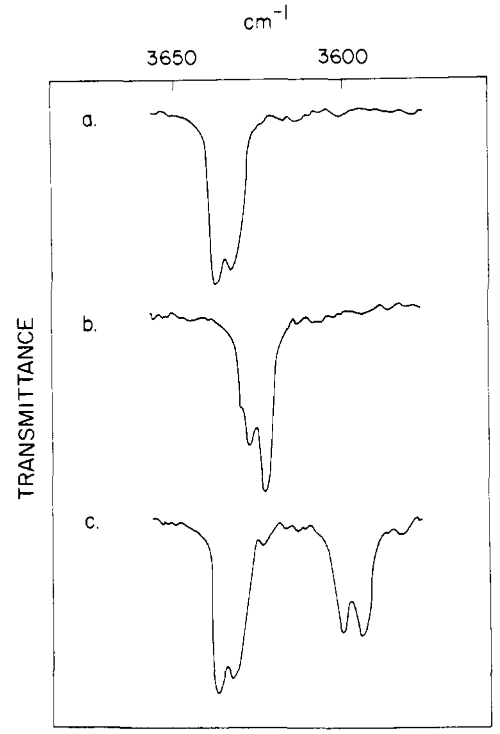

Figure 1. O–H stretch region of phenol in matrices at 12 K (abscissa expansion ×10): (a) phenol + Ar (1:1500), (b) phenol + N_2 (1:1500), (c) phenol + CO + Ar (1:5:1000).

Results and Discussion

Argon-Matrix-Isolated Phenol. A complete vibrational assignment for phenol (**2**) and phenol-*O-d* has been known for more than 20 years.[22,23] The key modes associated with the OH group are the stretch, ν_{OH}, the in-plane bend, δ_{OH}, and the OH torsion, γ_{OH}. These bands are strongly shifted upon the formation of a hydrogen bond; e.g., ν_{OH} is shifted to lower frequency, and δ_{OH} and γ_{OH} are moved to higher frequency.[24] The extent of this shift, especially for ν_{OH} and the very sensitive γ_{OH}, is often regarded as an indirect measure of the hydrogen-bond strength.[4,5] The position of these bands in gas matrices is recorded in Table I.

The IR spectrum of argon-matrix-isolated phenol exhibits absorption attributable to ν_{OH} (3633.5, 3638.5 cm^{-1}), δ_{OH} (1175.0, 1177.0 cm^{-1}), and γ_{OH} (310 cm^{-1}). A similar pattern is observed in N_2 matrices (Table I), but ν_{OH} is shifted to lower frequencies whereas γ_{OH} and δ_{OH} are shifted to higher energy in a direction indicative of hydrogen-bond formation. Murto et al.[25] have previously noted a reciprocal relationship between ν_{OH} and γ_{OH} for alcohols isolated in gas matrices; they observed that the larger the upward shift of the γ_{OH} band, the larger the downward shift of ν_{OH}. The trend for Ar and N_2 above is in keeping with a stronger, more specific interaction between N_2 molecules and alcoholic OH groups, and is even more pronounced for CO (Table I, Figures 1 and 4); vide infra.

Phenol shows weak splitting of key bands (Table I) in both Ar and N_2. Splittings may arise from diverse phenomena including Fermi resonance and combination with external modes, environmental effects, multiple complexes, contribution from aggregates, conformers, and quantum-mechanical tunneling effects.[26–28]

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Table II. Relevant Stretching Frequencies of CO Doped Argon Matrices Containing Phenol or Anisole[a,b]

compound	$\nu_{OH}{}^b$	$\nu_{CO}{}^b$
phenol	3596.0	2151.0
	3601.0	2153.0
		2157.0
anisole		2132.5

[a] Experimental conditions were as described in the caption for Figure 2. [b] $\nu_{CO}{}^f$ = 2138.5 cm^{-1}.

That the split bands are not caused by Fermi resonance is supported by the observation that the phenol-*O-d* stretch shows a similar pattern (2685 and 2688 cm^{-1}) to that observed for phenol, but one which is isotopically shifted. Phenol dimers are not contributing to our spectra as no significant absorption characteristic of the dimer (i.e., ν_{max}^{Ar} 3481, $\nu_{max}^{N_2}$ 3480 cm^{-1}) is detected in Ar or N_2.[24] The most likely causes of the small splitting are environmental effects (multiple trapping sites) or perhaps quantum-mechanical tunneling.

Recycling of the system (argon-matrix-isolated phenol) from 12 to 26.5 K results in slight changes in the relative intensities of the split bands, but these changes are reversible and thus cannot be related to metastable trapping sites that are susceptible to annealing.

It is conceivable that the splitting is a consequence of (a) inhomogeneous sites (a single site in which phenol can fit two different ways) or (b) two sites of slightly different structure and symmetry that the cage assumes in order to accommodate phenol. Alternatively there may be two "different" phenols, one which has "normal" bond lengths and angles in the vicinity of the hydroxyl group and another which is slightly distorted by its interactions with a particular matrix site. Subtle effects of this type are difficult to establish without precise structural information derived from very sensitive probes of structure.

Splitting of the bands due to quantum-mechanical tunneling has to be considered seriously because of the indistinguishability of the two states separating phenol rotamers.[29] Microwave and far-infrared studies have shown that phenol is planar with a twofold barrier to internal rotation of the hydroxyl group of about 3.5 kcal/mol.[30] This situation lends itself to tunneling, and the observed splitting in the microwave spectra has been attributed to this phenomenon.

Phenol in Argon Matrices Containing Carbon Monoxide. Carbon monoxide doping of argon matrices containing phenol results in perturbations of the phenolic OH and carbon monoxide stretching modes. A most profound effect of doping is on the O–H stretch of phenol which is shifted −37.5 cm^{-1} to the region of 3600 cm^{-1} (split band 3596 and 3601 cm^{-1}), as illustrated in Figure 1c for PhOH:C≡O:Ar (1:5:1000). Concomitantly, the 2138.5-cm^{-1} band of monomeric CO is shifted to higher frequencies and split into three bands (2151, 2153.0, and 2157.0 cm^{-1}; Table II, Figure 2b). At fixed conditions of deposition, the ratio of the integrated intensity of the OH stretch of the complex, $I(\nu_{OH}{}^b)$, to that of isolated monomer, $I(\nu_{OH}{}^f)$, is linearly related to the ratio of CO to phenol molecules (Figure 3).[31] This relation provides a satisfactory indication that we are dealing with a 1:1 complex consisting of single molecules of phenol and carbon monoxide. The stoichiometry of the complex and the spectral shifts from monomeric frequencies are clearly in favor of a specific interaction between CO and the phenolic OH group.

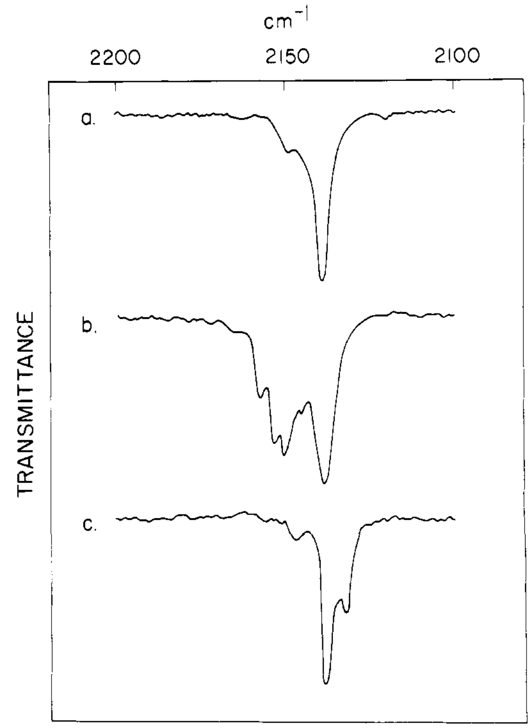

Figure 2. C≡O stretch region in doped matrices at 12 K (abscissa expansion ×10): (a) CO + Ar (1:100), (b) phenol + CO + Ar (1:5:1000), (c) anisole + CO + Ar (1:5:500).

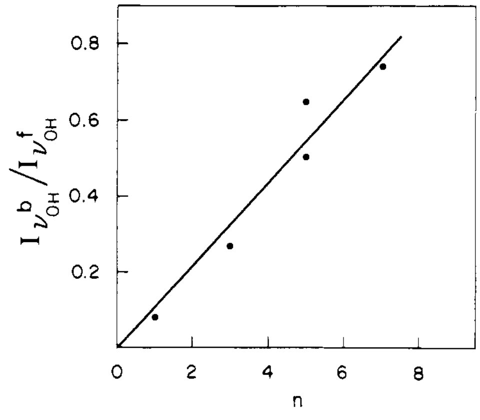

Figure 3. The ratio of integrated intensities of ν_{OH}^b/ν_{OH}^f as a function of *n* in doped matrices containing phenol + CO + Ar (1:*n*:1000) at 12 K. The temperature of deposition was kept constant, T_d = 20 K.

A priori, a number of 1:1 complexes between phenol and CO can be envisaged and need to be considered as possible structures for the dimer. These complexes fall into distinct categories involving hydrogen bonding (**3**), π complexation (**4**), σ interactions (**5**), chelates (**6** and **7**), and phenolic oxygen as donor (**8**). Analogous complexes with carbon monoxide rotated 180° can be drawn in which the position of the oxygen and carbon terminals are reversed.

From the magnitude and direction of the shifts induced by CO on the OH stretch, it seems clear that the interaction involves hydrogen bonding between phenol and carbon monoxide. The shift of the carbon monoxide stretch to higher frequency (Figure 2b) in the complex is most consistent with the notion of hydrogen bonding to the carbon terminal of CO.[12-17] Anisole, which cannot form important hydrogen bonds to CO, induces a new band at ν 2132.5 cm^{-1} (Figure 2c). This shift to lower frequency is in sharp

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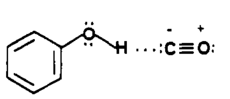
(31) (a) The magnitude of the displacement of the OH stretch induced by carbon monoxide is represented as $\Delta\nu_{OH} = \nu_{OH}{}^f - \nu_{OH}{}^b$ (where $\nu_{OH}{}^f$ and $\nu_{OH}{}^b$ are respectively ν_{max} of free and carbon monoxide bound hydroxyl of a specific phenol in argon). The corresponding shift of the CO stretch which occurs on complexation is designated $\Delta\nu_{CO} = \nu_{CO}{}^f - \nu_{CO}{}^b$ (where $\nu_{CO}{}^f$ and $\nu_{CO}{}^b$ represent respectively, ν_{max} of the free and phenol-bound carbon monoxide in argon). (b) The *extent* of complex formation is very much dependent upon deposition conditions. At constant Ar:CO:PhOH the $I(\nu_{OH}{}^b)/I(\nu_{OH}{}^f)$ increases with increasing temperature. This correlation suggests that the complex at least in part is formed by surface diffusion during the deposition. All our spectra refer to samples that were condensed at T_d = 20 K.



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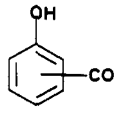

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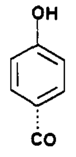

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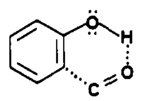

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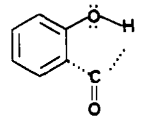

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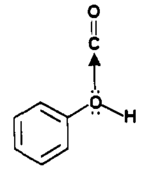

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contrast to the high-frequency shifts of the CO stretch that are induced by phenol.

The direction of the phenol-induced shift on the CO stretch is understandable in simple terms from the contribution of doubly and triply bonded resonance forms of CO to the hybrid of the complex. Hydrogen bonding to carbon, i.e., PhOH···$^-$C≡O$^+$, should increase the contribution of the triply bonded form of CO (compared with monomeric CO), because the electrophilic character of the proton draws electrons from oxygen to carbon. Electron donation by phenol as in complexes **4–8** would reduce the CO bond order from its value in the simple monomer and shift the stretch to lower frequency. Ab intio calculations on alcohol–nitrogen complexes using STO-3G and 4-31G basis sets, in fact, predict complexes of the type ROH···CO to be the most stable.[32]

The splitting and shifting of the carbon monoxide stretch to higher frequencies by proton donors was first observed by Davies and Hallam[18a] for CO-doped matrices containing hydrogen chloride. The hydrogen chloride–carbon monoxide dimer has hydrogen bound to the carbon terminal.[13] The effect of phenol on CO very closely resembles Davies and Hallam's results and the recent, more thorough work of Andrews[18b] with FT-IR on hydrogen halide complexes. The magnitude, direction, and patterns of the hydrogen halide induced shifts point toward a similar interaction between phenol and CO.

As in the case of the argon-matrix-isolated phenol there is a small splitting (5 cm^{-1}) of ν_{OH} of the dimer. It is possible that the splitting may be due to environmental effects or a deviation of the hydrogen bond from linearity giving rist to two slightly different complexes.

Finally, our viewpoint that the primary interaction between phenol and CO involves hydrogen bonding is buttressed by the effect of meta and para substituents of phenols on the position of the O–H stretch. The magnitude of the shifts are, in general, greatest for the more acidic phenols and are consistent with the notion that the more acidic the phenol, the stronger the hydrogen bond, and therefore the greater the effect on the OH stretch.[33]

Phenol in Carbon Monoxide Matrices. Phenol isolated in solid carbon monoxide exhibits a complicated spectrum that is temperature dependent. Three bands are observed reproducibly in the O–H stretch region (3623.5, 3590.5, 3575.0 cm^{-1}) at 12 K. Warming of the matrix above 20 K (Figure 4) results in loss of intensity at ν 3623.5, 1194, and 362.0 cm^{-1} and a simultaneous increase in absorptions at ν 3590, 1206, and 415 cm^{-1}. Cooling to 12 K reverses intensities to the initial condition. O-Deuterated phenol in solid CO exhibits the same pattern with three bands in the O–D stretch region ν 2636 (s), 2649 (s), and 2679 (w) cm^{-1}. Warming of the matrix causes disappearance of the band at 2679 cm^{-1}, and concomitantly, absorption at ν 2649 cm^{-1} is increased. Bands at ν 3575 (ν_{OH}) and 2636 cm^{-1} (ν_{OD}) show only very slight changes on warming, and the integrated intensity appears to be constant.

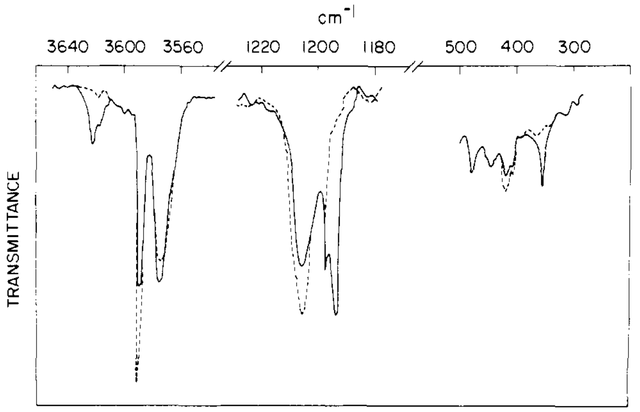

Figure 4. The infrared spectrum of phenol in a carbon monoxide matrix: solid curve, 12 K; dashed curve, 22 K. The OH stretch and in-plane bending regions are expanded ×5.

Besides the possibility of specific interactions between isolated phenol and individual carbon monoxide molecules, phenol comes under the influence of the entire force field of carbon monoxide, especially those molecules which comprise the cage or nearest neighbors. Thus there are numerous possibilities to consider, and without a direct probe of structure it is difficult to establish precisely which interactions will prevail.

It is noteworthy that the bands at ν 3623, 1194, and 362 cm^{-1} are the least perturbed frequencies corresponding to OH modes and are very similar in position to those observed in nitrogen matrices. In contrast to argon, both nitrogen and carbon monoxide are expected to strongly interact electrostatically with trapped species.[18a] The bands at ν 3623 and 362 cm^{-1} have values that can be regarded as indicative of a "free" OH mode (species I). It is tempting to consider their positions as being characteristic of a free "OH" mode that is modified by the carbon monoxide force field but is not specifically bound to individual carbon monoxide molecules.

The other OH stretches that are observed can then be attributed to more specific interactions between phenol and carbon monoxide, and present a dilemma. One possible interpretation is that the band at ν 3590.5 cm^{-1} involves an interaction between phenol and individual carbon monoxide molecules of the cage. This species II may be engaged in a more specific, stabilizing interaction with CO than the species absorbing at ν 3623 cm^{-1}. The lowest OH stretching frequency at 3575.0 cm^{-1} can be attributed to a species III resulting from an even stronger interaction, perhaps a phenol:CO complex which is surrounded by a cage of carbon monoxide molecules.

Thus, the dynamics between species I and II may involve the interconversion of a "free phenol" and a phenol interacting with individual (perhaps one or two) molecules of the cage. The most stable species III may not be interconvertible with I or II, because of the barrier to incorporation into the lattice cage of the (phenol-complexed) carbon monoxide molecule. Thus, we speculate that the three species could represent degrees of complexation of phenol. Phenomena of this type will be heavily dependent upon the relative energies of the lattice[34] vs. the hydrogen-bond strength of the complex.

Presently, we cannot rule out contributions from complexes **4–8** to the spectrum of phenol in solid CO. It is noteworthy that Murto et al.[34] have observed that alcohol molecules in CO matrices behave as if there is an equilibrium that involves one CO molecule, but these authors have not specified the molecular interaction. In particular, the temperature dependence of the IR spectrum of 1,1,1,3,3,3-hexachloropropan-2-ol (**9**) in carbon monoxide is similar to that of phenol in CO.[35]

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Summary

Phenol has been matrix-isolated in argon, nitrogen, and carbon monoxide and its spectrum recorded. A 1:1 complex involving phenol hydrogen bound to the carbon terminal of carbon monoxide has been observed in argon matrices containing phenol doped with carbon monoxide. This discovery permits the study of substituent effects in gas matrices, since ν_{OH} of phenolic complexes of carbon monoxide can, in principle, be viewed as an indicator of the strength of hydrogen bonding.

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Registry No. Ar, 7440-37-1; N_2, 7727-37-9; CO, 630-08-0; phenol, 108-95-2.

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Substituent Effects on Weakly Bound Complexes of Phenols and Carbon Monoxide in Argon Matrices. Hydrogen Bonding at Cryogenic Temperatures

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Abstract: Quenching at 20 K of gaseous mixtures consisting of argon, a monosubstituted phenol, and carbon monoxide (M:R:CO = 500:1:5) leads to complexes which have ν_{OH} and ν_{CO} stretching frequencies shifted 28–60 and 10–16.5 cm^{-1}, respectively, from monomeric values. The magnitude and direction of shifts involving meta- and para-substituted phenols are consistent with a hydrogen-bound dimer (ArOH···CO) as proposed for the parent phenol. In argon matrices containing ortho-substituted phenols doped with CO, 1:1 complexes are also formed which most likely possess bifurcated hydrogen bonds. For para- and meta-substituted phenols the evidence indicates that the acidity of the phenol is a major factor in inducing shifts of ν_{OH} and ν_{CO}. The shifts induced by ortho-substituted phenols do not correlate well with known aqueous acidities. Speculation thus centers about the role of intrinsic acidities in determining the properties of proton donors in rare-gas matrices. This work represents the first study devoted to substituent effects in gas matrices.

Introduction

Experimental evidence for the formation of weakly hydrogen-bonded complexes of hydrogen halides with carbon monoxide (**1**) in gas matrices has been presented by Hallam and Davies for hydrogen chloride,[3] and in a recent more comprehensive study by Andrews.[4] From microwave data,[5-7] a linear equilibrium structure in which the atoms are in the order OC···HX (X = F, Cl, Br) has recently been assigned to such complexes and theoretical calculations support this structure.[8,9] In the preceding paper, we have presented infrared spectral data bearing on a weakly bound complex of carbon monoxide (**1**) with phenol (**2**) in gas matrices.[10] This complex exhibits a band (split 5 cm^{-1}) in the OH stretch region of the IR, at 37.5 cm^{-1} lower frequency than the OH stretch (also split 5 cm^{-1}) of monomeric phenol (**2**) in argon. The C≡O stretch of carbon monoxide is concomitantly shifted 12.5 cm^{-1} to higher frequency. We regard the direction and magnitude of these shifts, and stoichiometry of the complex (1:1), as evidence for a hydrogen-bonded complex between phenol and CO (eq 1).

$$\underset{\mathbf{1}}{CO} + \underset{\mathbf{2}}{PhOH} \rightarrow PhOH\cdots CO \qquad (1)$$

This phenomenon, if it is general, offers a unique opportunity to investigate substituent effects at cryogenic temperatures. The structural simplicity of the complex, in which the acidity of the phenol can be extensively varied with (meta and para) ring substituents remote from the hydrogen bond, also makes this system an appealing target for theoretical considerations. Of special interest is the manner in which the acidity of phenols is expressed in gas matrices at cryogenic temperatures.

In this study we determine the perturbation induced by substituents on ν_{CO} and ν_{OH} stretching modes and analyze the data with respect to the known acidity of the relevant phenols. All the phenols that we have investigated in argon matrices doped with carbon monoxide show ν_{OH} shifted to lower frequencies by 30–60 cm^{-1}, and produce new bands in the C≡O stretch region which are at higher frequency (>10 cm^{-1}) than $\nu_{CO}{}^{f}$. A common index for the strength of hydrogen bonding, which we refer to herein, is $\Delta\nu_{OH}$, the shift of the OH stretch of a substituted phenol upon complexation with carbon monoxide.[11]

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(11) The magnitude of the displacement of the OH stretch induced by carbon monoxide is represented as $\Delta\nu_{OH} = \nu_{OH}{}^{f} - \nu_{OH}{}^{b}$ (where $\nu_{OH}{}^{f}$ and $\nu_{OH}{}^{b}$ are respectively, ν_{max} of the free and carbon monoxide bound hydroxyl of a specific phenol in argon). The corresponding shift of the CO stretch which occurs on complexation is designated $\Delta\nu_{CO} = \nu_{CO}{}^{f} - \nu_{CO}{}^{b}$ (where $\nu_{CO}{}^{f}$ and $\nu_{CO}{}^{b}$ represent respectively ν_{max} of the free and phenol-bound carbon monoxide in argon).

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