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.

Acknowledgment. We gratefully acknowledge generous financial support from the National Science Foundation, Grant No. CHE 7811563, and the expert assistance of Dr. Helmut Nickels. We also thank Mrs. Lynda Jacob for her skillful assistance in the preparation of this manuscript.

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

---

(35) Murto, J.; Kivinen, A.; Rasanen, M.; Perttila, *Spectrochim. Acta* **1977**, *33*, 291.

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

J. Gebicki[1] and A. Krantz*[2]

Contribution from the Departments of Chemistry and Pharmacological Sciences of the State University of New York, Stony Brook, New York 11794. *Received June 4, 1984*

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).

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

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]

---

(1) On leave from the Institute of Applied Radiation Chemistry, Technical University, Lodz, Poland, 1979–81.

(2) Present address: Syntex, Inc., 2100 Syntex Ct., Mississauga, Ontario, Canada L5N 3X4.

(3) Davies, J. B.; Hallam, H. E. *Trans. Faraday Soc.* **1971**, *67*, 3176.

(4) Andrews, L.; Arlinghaus, R. T.; Johnson, G. L. *J. Chem. Phys.* **1983**, *78*, 6347.

(5) Legon, A. C.; Soper, P. D.; Keenan, M. R.; Minton, T. K.; Balle, T. J.; Flygare, W. H. *J. Chem. Phys.* **1980**, *73*, 583.

(6) Soper, P. D.; Legon, A. C.; Flygare, W. H. *J. Chem. Phys.* **1981**, *74*, 2138. Legon, A. C.; Soper, P. D.; Flygare, W. H. *Ibid.* **1981**, *74*, 4944.

(7) Keenan, M. R.; Minton, T. K.; Legon, A. C.; Balle, T. J.; Flygare, W. H. *Proc. Natl. Acad. Sci. U.S.A.*, **1980**, *77*, 5583.

(8) (a) Politzer, P.; Kammeyer, C.; Bauer, S. J.; Hedges, W. L. *J. Chem. Phys.* **1981**, *75*, 4057. (b) Benzel, M. A.; Dykstra, C. E. *Ibid.* **1982**, *77*, 1602.

(9) Hinchliffe, A. *Adv. Mol. Relaxation Int. Processes* **1981**, *21*, 151.

(10) Gebicki, J.; Krantz, A., *J. Am. Chem. Soc.*, preceding paper in this issue.

(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).

0002-7863/84/1506-8097$01.50/0 © 1984 American Chemical Society

Table I. Shifts of ν_{OH} and ν_{CO} Stretching Frequencies in CO-Doped Argon Matrices Containing Meta- and Para-Substituted Phenols at 12 K[a]

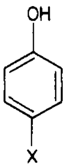
sample	ν_{OH}^{f}, cm^{-1}	ν_{OH}^{b}, cm^{-1}	$\Delta\nu_{OH}$, cm^{-1}	ν_{CO}^{b}, cm^{-1}	$\Delta\nu_{CO}$, cm$^{-1\,b}$
phenol (**2**)	3633.5	3596.0	37.5	2151.0	−12.5
	3638.5	3601.0		2153.0	
				2157.0	
p-fluorophenol (**3**)	3639.5	3600.5	39.0	2150.0 ms	−11.5
				2155.0 w	
p-chlorophenol (**4**)	3635.0	3606.5	28.5	2150.0 ms	−11.5
				2155.5 w	
p-bromophenol (**5**)	3635.5	3605.5	30.0	2151.0 ms	−12.5
				2156.0 w	
p-cresol	3646.0	3614.0	32.0	2148.5 s	−10.0
				2153.0 w	
p-methoxyphenol (**6**)	3638.5	3606.0	32.5	2151.0	−12.5
	3650.5				
m-chlorophenol (**7**)	3632.0	3587.5	44.5	2153.5	−15.0
	3639.0	3597.0	42.0		
m-bromophenol (**8**)	3636.0	3587.0	49.0	2153.5	−15.0
	3638.0	3596.0	42.0		
m-fluorophenol (**9**)	3633.5	3588.0	45.5	2155.0	−16.5
	3639.5	3595.0	44.5		

[a] The tabulated frequencies were calibrated against polystyrene. The error in the readings was ±0.5 cm^{-1}. [b] Calculated with reference to ν_{CO}^{f} 2138.5 cm^{-1}. The most intense band attributable to the complex in the CO stretch region was employed as ν_{CO}^{b}.

Results

Weakly hydrogen-bonded dimers between ring-substituted phenols and carbon monoxide are formed under cryogenic conditions when a mixture containing the host gas, the phenol of interest, and carbon monoxide are condensed at 20 K. A discussion of the spectral properties of substituted phenols and their CO complexes is divided below into ortho-, meta-, and para-substituted systems. The symmetry properties of the meta- and para-substituted systems, and proximity effects in ortho-substituted phenols, are unique and introduce factors that call for the separate treatment of these positional isomers.

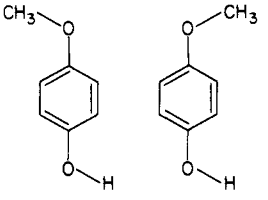
Para-Substituted Phenols. The *p*-halophenols, fluoro-, chloro-, and bromophenols (**3–5**, respectively), all possess C_s symmetry.



3, X=F
4, X=Cl
5, X=Br

For these phenols ν_{OH}^{f} is represented by an intense singlet band between 3635 and 3640 cm^{-1} (Table I, Figure 1), which even under high resolution (0.5 cm^{-1}) does not exhibit splitting. A sharp, intense band attributable to the OH torsion, γ_{OH}, is observed for **3–5** at 280, 300, and 302 cm^{-1}, respectively. The presence of carbon monoxide as an additional impurity (500:1:5; M:R:CO) results in shifts of the OH stretch to lower frequency ($\Delta\nu_{OH}$ = 28.5–39 cm^{-1}). Note that ν_{OH}^{b} is also unsplit. In the carbon monoxide stretching region, the complexes exhibit a band of medium intensity near 2150 cm^{-1} (shifted ~12 cm^{-1} from ν_{CO}^{f}) and a very weak band close to 2155 cm^{-1} (vide infra).

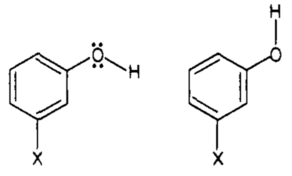
p-Methoxyphenol (**6**), on the other hand, can exist as two distinct conformers with the methoxy function syn or anti to the hydroxyl group. Additional rotamers are possible depending upon the relation of the methyl C–H's to the aromatic ring. Both ν_{OH} (Figure 1c) and γ_{OH} of argon-matrix-isolated *p*-methoxyphenol are split into two bands at 3638.5 and 3650 cm^{-1} and 257 and 267 cm^{-1}, respectively. The ratio of the intensities of these bands is invariant upon annealing between 12 and 30 K. Only a single band at ν_{OH} 3606 cm^{-1} is apparent in the OH stretch region for the CO complex of **6**.



anti syn

6

Meta-Substituted Phenols. *m*-Halophenols possess two bands in the OH stretch region which are separated by only a few cm^{-1} (Table I, Figure 2). For *m*-chloro- (**7**) and *m*-bromophenol (**8**), split bands at ν_{max} 310 s, 316 m, 324 w cm^{-1} are also observed in the γ_{OH}^{Ar} region. The γ_{OH} band of the nitrogen-matrix-isolated species exhibits a still more complicated pattern but is less intense than γ_{OH}^{Ar}. Splittings of ν_{OH}, similar to those of the species in argon, are observed for the three halophenols in solid nitrogen; this result indicates that, rather than being matrix-induced, such splittings are an intrinsic property of the halophenol. Annealing the sample does not eliminate the splittings and often sharpens the bands. A plausible explanation is that the split bands belong to individual conformers, since meta-substituted phenols can exist as distinct syn and anti rotamers that are not expected to differ significantly in energy. Indeed, either raising or lowering of the temperature of the matrix causes reversible changes in the IR spectrum of *m*-halophenols. Broadening of the bands above 20 K severely compromises the resolution so that we have only been able to monitor changes in the relative intensities of stretches with reasonable precision for *m*-fluorophenol (**9**) in solid nitrogen. Over the range of 13.1 to 22.9 K, the estimated value for ΔG is 0.015 kcal mol^{-1}.[12]



syn anti

7, X=Cl
8, X=Br
9, X=F

---

(12) (a) The far-infrared gas-phase spectrum of **9** has been interpreted to yield a potential energy difference of 1053 J mol^{-1} favoring the syn form: Manocha, A. S.; Carlson, G. L.; Fateley, W. G. *J. Phys. Chem.* **1973**, *77*, 2094. (b) Schaefer et al. [Schaefer, T., Salman, S. R., Sebastian R. [*Ibid.* **1981**, *85*, 499] from NMR studies have concluded that the anti is the more stable form (ΔG = 2 kJ mol^{-1}) in CCl_4, CS_2, C_6D_6, and $CDCl_3$, but its relative stability decreases as the dielectric constant of the solution increases.

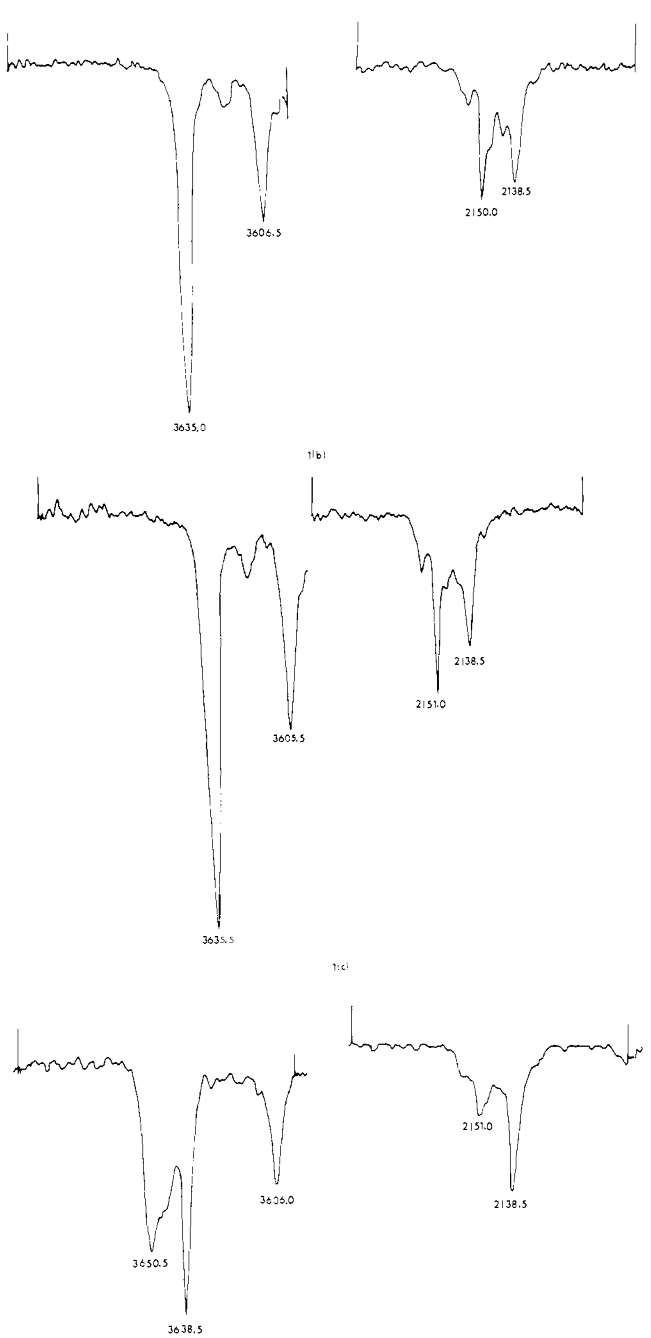


Figure 1. The OH stretching and CO stretching regions of the IR spectrum of CO-doped argon matrices containing para-substituted phenols at 12 K (M/CO/R ~ 1:5:500). The abscissa has been expanded 10X. Both free and uncomplexed phenols are present in the mixture. The amount of the sample deposited is indicated below in mm: (a) *p*-chlorophenol/CO/Ar, 30 mm; (b) *p*-bromophenol/CO/Ar, 24 mm; (c) *p*-methoxyphenol/CO/Ar, 35 mm.

Although it is tempting to attribute this value to the energy difference between the individual conformers of **9**, the miniscule energy difference could be due to a variety of factors including environmental effects on the intensities. The fact that the barrier between the conformers of **9** is seemingly overcome at temperatures below 25 K is curious since the twofold barrier for phenol[13] is ca. 3.5 kcal mol.$^{-1}$ Note that a tunneling effect is operative in **2**.

Argon matrices containing meta-substituted phenols and carbon monoxide show a split pattern for $\nu_{OH}{}^{b}$ of the complex (Figure 2). For **7**, **8**, and **9**, the shifts of ν_{OH} and ν_{CO} are in the range of 45 and 15 cm^{-1}, respectively, and are consistently greater than the shifts induced by the corresponding para phenols.

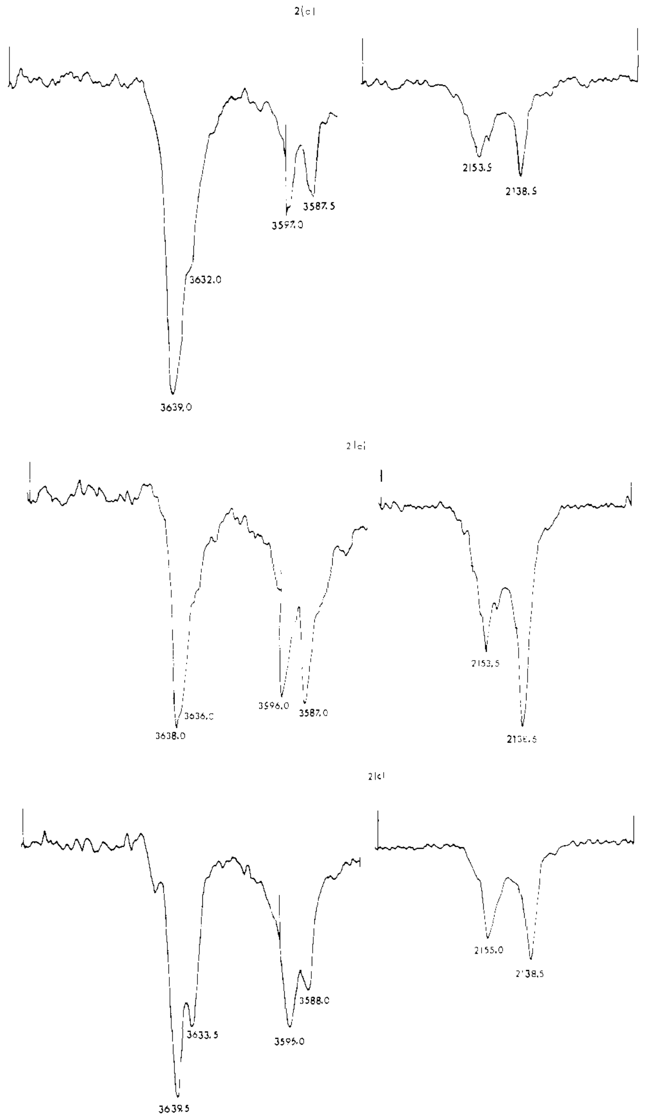
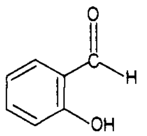


Figure 2. As in Figure 1, except meta-substituted phenols are employed as the proton donors: (a) *m*-chlorophenol/CO/Ar, 30 mm; (b) *m*-bromophenol/CO/Ar, 28 mm; (c) *m*-fluorophenol/CO/Ar, 30 mm.

Ortho-Substituted Phenols. Ortho-substituted phenols can exist either in syn or anti forms. If the substituent X is an electron-pair donor, an intramolecular hydrogen bond may be formed. When the hydrogen bond strength is modest (1–3 kcal/mol), two conformers have been observed at room or elevated temperatures. For X = CHO or NO_2 very strong hydrogen bonds are established (6–9 kcal/mol). The anti form (**10**) of salicylaldehyde has recently been trapped by irradiating salicylaldehyde (λ 250 nm, *t* = 20–30 min, M/R 500) in gas matrices at 12 K.[14] Presumably the significant barrier to rotation of the formyl group[15] inhibits quantitative formation of the chelate from vibrationally hot



10

---

(13) Mathier, E.; Welti, D.; Bauder, A.; Günthard, Hs.H. *J. Mol Spectrosc.* **1971**, *37*, 63.

(14) Gebicki, J.; Krantz, A. *J. Chem. Soc., Perkin Trans. 2* **1984**, 1617.

(15) (a) Antypas, W. G., Jr.; Siukola, L. V. M.; Kleier, D. A.*J. Org. Chem.* **1981**, *46*, 1172. (b) Tabei, M.; Tezaka, T.; Hirota, M. *Tetrahedron* **1971**, *27*, 301.

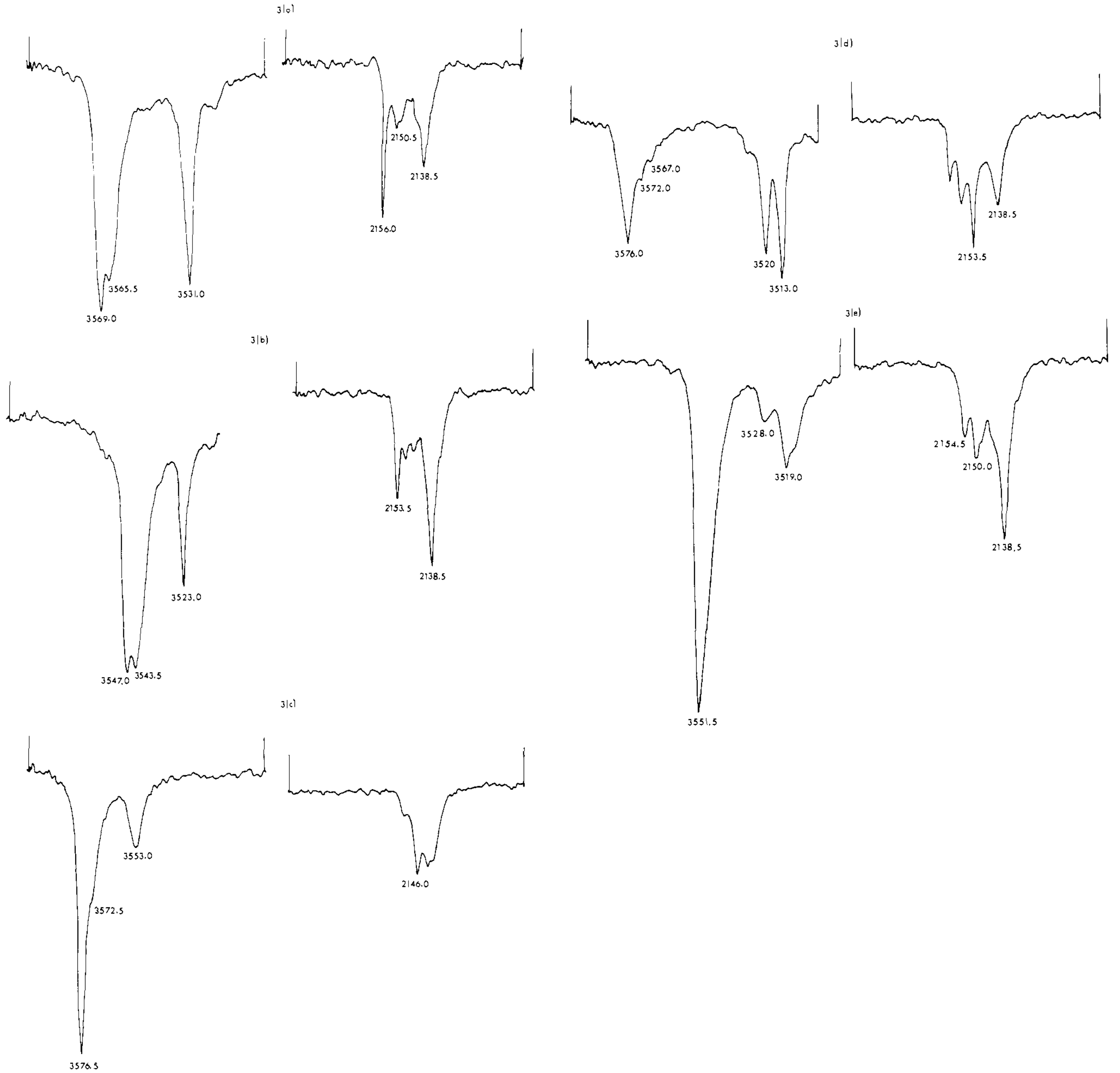
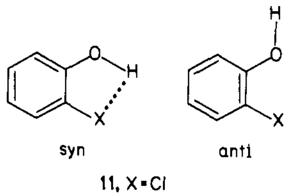


Figure 3. As in Figure 1, except ortho-substituted phenols are employed as the proton donors: (a) *o*-chlorophenol/CO/Ar, 20 mm; (b) *o*-bromophenol/CO/Ar, 28.5 mm; (c) *o*-methoxyphenol/CO/Ar, 17 mm; (d) *o*-cyanophenol/CO/Ar, 35 mm; (e) 2,6-dichlorophenol/CO/Ar, 40 mm.

salicylaldehyde. However, under cryogenic conditions, on photoirradiation of argon matrix-isolated systems **11**, **12**, and **14**



11, X=Cl
12, X=Br
13, X=OCH_3
14, X=CN

(which do not have rotameric possibilities around X), we have been unable to trap anti forms.

It is difficult to believe that irradiation at λ 250 nm for 20–30 min of systems **11–14** does not produce the (ground state) anti conformer upon internal conversion of excited-state forms. The syn form would completely dominate the equilibrium if a mechanism of interconversion was available. Evidently, equilbrium is estabished either by tunneling (of the OH) of the trapped species, or during the cascade from the excited state to the thermally quenched product.

Intense absorption is observed for argon-matrix-isolated *ortho*-substituted phenols **11-13** between ν 3545 and 3576 cm^{-1}, in the form of a single band showing slight splitting (4 cm^{-1}) or a shoulder at high resolution (Figure 3). [The pattern for **14** (X = CN) is more complex; vide infra.] Warming the matrix to 30 K broadens ν_{OH}, but this change is reversed upon lowering the temperature to 12 K. No significant absorption is observed in the range of ν 3620 to 3650 cm^{-1}, where $\nu_{OH}{}^{f}$ of the anti form of **11–14** would be expected to absorb. In accordance with this observation, the OH torsion region exhibits one major band for 2-bromo- (397 cm^{-1}) and 2-chlorophenol (398 cm^{-1}), but no absorption attributable to the anti form can be detected. (The anti form is known to absorb at 30–35 cm^{-1} lower frequency than the syn conformer).[16]

For the *o*-halophenols, the stoichiometry of the complexes are clearly 1:1 as judged by plotting ratios of [CO] to [*o*-halophenol]

---

(16) (a) Carlson, G. L.; Fateley, W. G.; Manocha, A. S.; Bentley, F. F. *J. Phys. Chem.* **1972**, *76*, 1553. (b) Carlson, G. L.; Fateley, W. G. *Ibid.* **1973**, *77*, 1157.

Table II. Shifts of ν_{OH} and ν_{CO} Stretching Frequencies in CO-Doped Argon Matrices Containing Ortho-Substituted Phenols at 12 K

sample	$\nu_{OH}{}^{f}$,[a] cm^{-1}	$\nu_{OH}{}^{b}$,[b] cm^{-1}	$\Delta\nu_{OH}$,[c] cm^{-1}	$\nu_{CO}{}^{b}$, cm^{-1}	$\Delta\nu_{CO}$,[d] cm^{-1}
o-methoxyphenol (**13**)	3572.0	3553.0	23.5	2141.5	−7.5
	3576.5			2146.0	
o-chlorophenol (**11**)	3565.5	3531.0	38.0	2150.5	−17.5
	3569.0			2156.0	
o-bromophenol (**12**)	3543.5	3523.0	24.0	2153.5	−15.0
	3547.0				
o-cyanophenol (**14**)	3576.0	3513.0	63.0	2153.5	−15.0
	3572.0	3520.0		2158.0	
	3567.0				
2,6-dichlorophenol (**17**)	3551.5	3519.0	32.5	2150.0	−11.5
		3528.0		2154.5	

[a] $\nu_{OH}{}^{f}$ of monomer. [b] $\nu_{OH}{}^{b}$ of bifurcated hydrogen-bonded complex. [c] $\Delta\nu_{OH} = \nu_{OH}{}^{f} - \nu_{OH}{}^{b}$. The most intense band attributable to the complex in this region was taken as $\nu_{OH}{}^{b}$. [d] Calculated with reference to $\nu_{CO}{}^{f}$ 2138.5 cm^{-1}. The most intense band attributable to the complex in the CO stretch region was employed as $\nu_{CO}{}^{b}$.

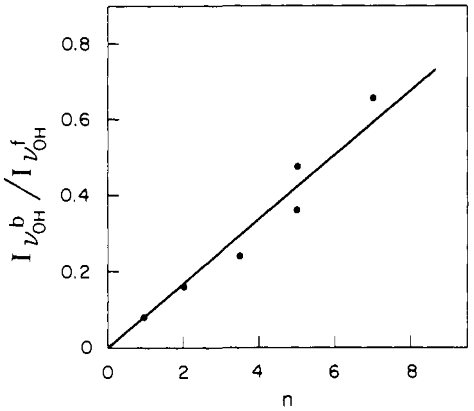


Figure 4. Plot of the ratio of integrated intensities $I(\nu^{b}_{OH})/I(\nu^{f}_{OH})$ vs. n in CO-doped matrices for *o*-bromophenol: CO:Ar = (1:*n*:500). The temperature of deposition (T_d) = 20 K.

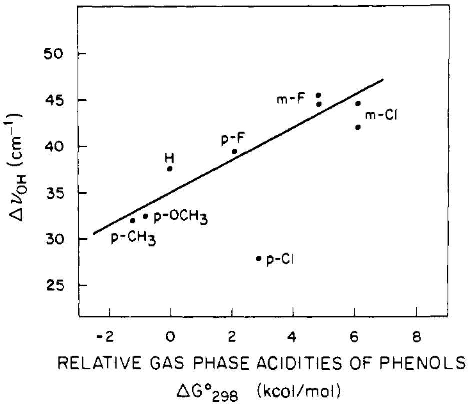


Figure 5. Plot of $\Delta\nu_{OH}$ for meta- and para-substituted phenols vs. reported gas-phase acidities (relative to phenol).[23] For meta-substituted phenols two ν_{OH} bands are observed and thus two values of $\Delta\nu_{OH}$ are plotted.

vs. the ratio of the intensities of $\nu_{OH}{}^{b}$ and $\nu_{OH}{}^{f}$ (Figure 4). Each complex appears to involve a hydrogen-bound CO molecule as implied by the direction of $\Delta\nu_{OH}$ and $\Delta\nu_{CO}$ (Table II).

Interestingly, the ability to form a complex with CO may depend to some extent on the hydrogen-bond strength of the ortho-substituted phenol, as neither *o*-nitrophenol nor salicylaldehyde (which form strong internal hydrogen bonds) shows any evidence of complex formation (no effect on ν_{CO}) in argon matrices doped with CO.

Discussion

Para- and Meta-Substituted Phenols. In argon matrices containing a substituted phenol and carbon monoxide, the position of $\nu_{OH}{}^{b}$ in the resulting complex is shifted 28.5–49 cm^{-1} from $\nu_{OH}{}^{f}$ of the matrix-isolated phenol (Table I). A concomitant shift ranging from 10 to 16.5 cm^{-1} is observed for ν_{CO}. Despite the narrow range, the trend is in the proper direction to support the view that hydrogen bonding between CO and the substituted phenol is responsible for the altered OH stretch.

The magnitude of the shifts ($\Delta\nu_{OH}$ Table I) are of a proper scale for a hydrogen-bonding interaction between the carbon of CO and the variously substituted phenols, if one considers the corresponding shifts induced by CO, for the weaker acid methanol ($\Delta\nu_{OH}$ 22 cm^{-1}),[17,18] and on ν_{HX} of the hydrogen halides (HF, 165; HCl, 51; and HBr, 39 cm^{-1}).[4] The fact that methanol as well as the hydrogen halides are known to form 1;1 complexes with CO, in which the proton donor is bound to carbon,[4] strengthens our proposal for a similar interaction between CO and the phenols listed in Table I.

The range of the shifts $\Delta\nu_{CO}$ are also quite reasonable as compared with those induced by HF, HCl, and HBr (ν_{CO} 24, 16, and 14 cm^{-1}, respectively). Only the more acidic phenols give rise to shifts ($\Delta\nu_{CO}$ and $\Delta\nu_{OH}$) comparable to those observed for the HCl and HBr complexes.

Splitting patterns of the OH stretching mode for meta- and para-substituted phenols (Figures 1 and 2) are in accord with the anticipated number of conformers populating local energy minima. Thus *p*-halophenols each show a single sharp band with no apparent splitting (resolution, 0.5 cm^{-1}), *p*-methoxyphenol exhibits a complicated pattern, and the *m*-halophenols exhibit two bands of comparable intensity. A single band near 300 cm^{-1} dominates the OH torsion region of **3**–**5**. By contrast, splitting of γ_{OH} for meta-substituted phenols is generally more complex. Annealing causes changes in the appearance of γ_{OH} (mostly broadening at the high end of the cycle), but these changes are reversible. No significant changes in the spectrum of the matrix-isolated species are observed after irradiating with λ 250 nm (20 min). It is thus tempting to assume that, at a resolution of 0.5 cm^{-1}, the phenols show splitting patterns that reflect their conformational composition.

Correlations of the strength of hydrogen bonding with $\Delta\nu_{OH}$ have previously been reported for phenols with a wide range of electron-pair donors.[21,22] Studies by previous investigators have indicated that the magnitude and strength of hydrogen bonding

---

(17) Murto, J.; Ovaska, M. *Spectrochim. Acta, Part A* **1983**, *39*, 149.

(18) The difference $\Delta\Delta\nu_{OH}$ for methanol and phenol is only 15.5 cm^{-1} but covers a range of 5.5 pK_a units in aqueous acidities[19] and 27 kcal/mol in gas-phase acidities.[20]

(19) Albert, A.; Serjeant, E. P. "Ionization Constants of Acids and Bases"; Wiley: New York, 1962.

(20) Bartmess, J. E.; Scott, J. A.; McIver, R. T., Jr. *J. Am. Chem. Soc.* **1979**, *101*, 6046.

(21) Singh, S.; Murthy, A. S. N.; Rao, C. N. R. *Trans. Faraday Soc.* **1966**, *62*, 1056, and references therein.

(22) (a) Epley, T. D.; Drago, R. S. *J. Am. Chem. Soc.* **1967**, *89*, 5570. (b) Drago, R. S.; Epley, T. D. *Ibid.* **1969**, *91*, 2283. (c) Vogel, G. C.; Drago, R. S. *Ibid.* **1970**, *92*, 5347.

in donor-acceptor systems are dependent on the acidity of the proton donors.[21,22]

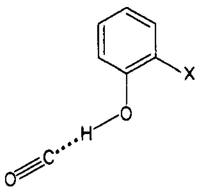
To the extent that the complex is of the same type for each phenol:CO dimer, a monotonic relationship would be expected between $\Delta\nu_{OH}$ and the hydrogen-bond strength.[22] Linearity between $\Delta\nu_{OH}$ and ΔH has previously been observed for systems of comparable hydrogen-bond energies or hydrogen-bond lengths.[21] Substituents which affect the acidity of the phenol also affect the thermodynamics of hydrogen bonding. For phenolic complexes involving benzophenone and triethylamine in CCl_4 at 25 °C, the effect of substituents on spectral parameters, including $\Delta\nu_{OH}$, has been correlated with substituent constants.[21]

Figure 5 compares the shift $\Delta\nu_{OH}$ induced by CO bound to meta- or para-substituted phenols, with gas-phase acidity data for the monosubstituted phenols.[23] McIver observed that there is a good correlation for meta and para substituents between gas-phase acidity data for monosubstituted phenols and the corresponding ionization constants in water at 298 K.

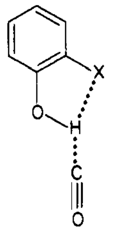
Considering that environmental effects in matrices are poorly understood and could be severely perturbing and specific, the correlation in Figure 5 is surprisingly good. The major outlier is *p*-chlorophenol (**4**) with $\Delta\nu_{OH} = 28$ cm^{-1}. Although the gas-phase acidity for *p*-bromophenol (**5**) has not been reported, the aqueous acidity ($pK_a = 9.36$) of *p*-bromophenol is greater than that of phenol and almost identical with that of *p*-chlorophenol.[19] Thus $\Delta\nu_{OH}$ of **5** is also lower than expected.

It is worthwhile pointing out that the gas-phase acidity measured for **4** at 600 K is 6.6 kcal/mol,[24] whereas the value reported by McIver[23] at 298 K is 2.9 kcal/mol. In this context the observed $\Delta\nu_{OH}$ for **4** is provocative and could point toward temperature effects on the acidity of *p*-chlorophenol that are not emcompassed by entropy considerations.

Ortho-Substituted Phenols. To account for the spectral shifts observed following complexation of CO with ortho-substituted phenols, we considered two structures:[25] the anti structure **15** in which the initial chelate is disrupted and a bifurcated structure **16**. A decision between these alternatives is predicated upon an evaluation of the magnitude of the shifts, $\Delta\nu_{OH}$ and $\Delta\nu_{CO}$. This analysis (vide infra) establishes that the observed values of $\nu_{OH}{}^{b}$ are much lower than would have been predicted for anti complexes of structure **15**.



15



16

To illustrate the point, we assume a standard value for $\nu_{OH}{}^{f}$ of matrix-isolated anti conformers. This assumption is necessary since, in this study, only syn forms of ortho-substituted phenols have been detectable under conditions of matrix isolation; we have been unable to induce formation of the anti conformers of **11**–**14** by photoirradiation.

A reference value for matrix-isolated anti forms can be approximated from known values of free phenolic OH stretches since these are fairly constant in a single phase.[14,16] Values for the stretch of matrix-isolated meta- and para-substituted phenols are between ν_{max} 3630 and 3650 cm^{-1}, and generally lie close to 3635 cm^{-1}. Even the anti form of salicylaldehyde with a powerfully electron-withdrawing formyl function absorbs at 3638 cm^{-1}.

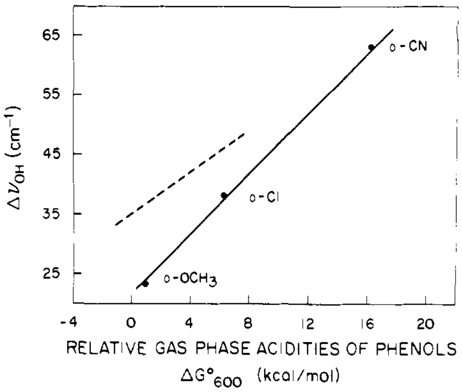


Figure 6. Plot of $\Delta\nu_{OH}$ for ortho-substituted phenols vs. reported gas-phase acidities (relative to phenol).[24] Dashed line indicates correlation obtained for meta- and para-substituted phenols as plotted in Figure 5.

If we assign $\nu_{OH}{}^{f}$ 3640 cm^{-1} as "standard value" for matrix-isolated anti conformers, then shifts of ν_{OH}, upon complexation of ortho-substituted phenols with CO, would range from 87 to 121 cm^{-1}, relative to the free anti form. These values are clearly out of line with those observed for the meta- and para-substituted systems (Table I, $\Delta\nu_{OH}$ 28.5–49 cm^{-1}) in which the magnitude of $\Delta\nu_{OH}$ appears to be related to the acidity of the phenolic component. If the acidity of the phenol is the principal determinant of the magnitude of the shift, then $\Delta\nu_{OH}$ for anti ortho-substituted phenols should not be very different from the values recorded in Table I. For example, the acid strengths of the anti forms of *o*-halophenols do not differ significantly from the acid strengths of the corresponding *m*- and *p*-halophenols.[26] The complexes of anti *o*-halophenols would be expected to absorb at $\nu_{OH}{}^{b}$ 3595 ± 10 cm^{-1}.

It is also noteworthy that the actual shifts, $\Delta\nu_{CO}$ and $\Delta\nu_{OH}$, for ortho-substituted phenols (Table II) are of a similar magnitude to those observed for meta- and para-substituted phenolic CO complexes (Table I). In light of these similarities it is unlikely that the *o*-phenol:CO complexes that we have discovered involve anti forms. On the other hand, bifurcated hydrogen bonding has precedents in carbohydrates and other systems.[27,28] Calculations by Newton[29] confirm that an asymmetrical bifurcated geometry can provide substantial stabilization relative to the separate, secondary electron-pair donor and the primary hydrogen-bonded complex.

On thermochemical grounds, it also seems unreasonable to expect the weakly basic carbon monoxide molecule to outcompete Br and Cl for exclusive control of the hydrogen bond, in either the gas phase or under cryogenic conditions, given the option of a bifurcated structure.

Accordingly, we have studied 2,6-dichlorophenol (**17**) which by symmetry cannot form an anti complex and may, therefore, be biased in its interactions as a proton donor toward a bifurcated complex. Quenching of gaseous mixtures of **17** and CO in argon leads to a species that has qualitatively the earmarkings of a complex with shifts of ν_{OH} and ν_{CO} in the expected directions. However, there is a considerably lower yield of complex observed with **17** than with **11** (Figure 2a and 2e) perhaps owing to a proximity effect of the unchelated chlorine atom. The spectral features are of greater than the usual complexity observed for monohalophenols, suggesting that there may be more than one

---

[23] (a) McIver, R. T., Jr.; Silvers, J. H. *J. Am. Chem. Soc.* **1970**, *92*, 8462. (b) Bartmess, J. E.; McIver, R. T., Jr. In "Gas Phase Ion Chemistry"; Academic Press: New York, 1979; Vol. 2.

[24] McMahon T. B.; Kebarle, P. *J. Am. Chem. Soc.* **1977**, *99*, 2222.

[25] Twisting of the hydroxyl group out of plane is destabilizing owing to a reduction in p–π overlap. Such twisted forms are unlikely candidates for the phenolic component of the complex.

[26] For example, *o*-halophenols, which exist predominantly in the syn form, are less acidic than their corresponding para- and meta-substituted analogues in the gas phase[20] and differ from the corresponding *m*-halophenols by only 0.5 pK_a unit in aqueous media.[19] The anti forms of *o*-halophenols are less stable than the corresponding syn compounds by ~1.6 kcal/mol.[16] Thus, the anti form of *o*-chlorophenol is about as acidic as *m*-chlorophenol in the gas phase; the difference in aqueous pK_a's between anti *o*-halophenols and *m*-halophenols is ca. 1 pK_a unit.

[27] Alonso, J. L.; Wilson, E. B. *J. Am. Chem. Soc.* **1980**, *102*, 1248.

[28] Jeffery, G. A.; Takagi, S. *Acc. Chem. Res.* **1978** *11*, 264.

[29] Newton, M. D.; Jeffery, G. A.; Takagi, S. *J. Am. Chem. Soc.* **1979**, *101*, 1997.

complex present. Nevertheless, this experiment demonstrates that a phenol incapable of assuming an anti conformation can interact with CO to give a new species with the magnitude and direction of $\Delta\nu_{OH}$ and $\Delta\nu_{CO}$, suggestive of a hydrogen-bound complex.

All of the phenols studied in argon matrices doped with CO have the imprint of a hydrogen-bonded complex. Each phenol exhibits a decrease in ν_{OH} when bound to CO and shows a concomitant shift of ν_{CO} to higher frequency. When our data are plotted against gas-phase data for ortho-substituted phenols relevant to this study,[24] a reasonable correlation is observed (Figure 6). However, gas-phase data for ortho-substituted phenols are not well correlated with the corresponding pK_a's in aqueous solutions.[23] For the halophenols the ortho compounds are the most acidic of the positional isomers in aqueous solution[19] and are about 0.5 pK_a more acidic than their meta analogues. In the gas phase, the ortho fluoro- and chlorophenols are less acidic than the meta analogues by 1.5 to 2.0 kcal/mol.[23] The limited data correlated in Figure 6 imply that it is the intrinsic acidity of the proton donor that is expressed in rare-gas matrices.

Although the strongest acid, *o*-cyanophenol (**14**), shows the largest shift of ν_{OH} (63.0 cm^{-1}), and the weakest acid, *o*-methoxyphenol (*13*), shows the smallest shifts ($\Delta\nu_{OH}$ and $\Delta\nu_{CO}$ = 23.5 and 7.5 cm^{-1}, respectively), in line with a hydrogen-bound complex, there are several puzzling features recorded in Table II. Bromophenol, which shows shifts comparable to chloro in the meta and para series, in the ortho case exhibits a considerably lower $\Delta\nu_{OH}$ than the chloro analogue **11**, but possesses a similar $\Delta\nu_{CO}$. For *o*-cyanophenol, $\Delta\nu_{OH}$ is nearly 2.5 times that of the value for *o*-bromophenol, but they possess the same $\Delta\nu_{CO}$.

The *o*-cyanophenol system is the most complicated that we have investigated. It exhibits $\Delta\nu_{OH}{}^{f}$ = 3576 cm^{-1} with shoulders at 3572 and 3567 cm^{-1}. In contrast to the complexes with **11** or **12**, *o*-cyanophenol bound to CO shows two bands for $\nu_{OH}{}^{b}$ (3513 and 3520 cm^{-1}), two bands for $\gamma_{OH}{}^{f}$ (379 and 392 cm^{-1}), and a complicated C≡O stretch region. The complexity of the data suggests that more than one species is present.

It is not surprising to find that IR spectra of ortho-substituted phenols and their complexes under cryogenic conditions are not straightforward. If the ortho complexes are indeed bifurcated, there are likely to be proximity effects stemming from the interaction of CO and the electron-pair donor at the ortho position. The steric constraints on such complexes in the matrix environment (cage effects between host and guest) could play an important role in determining the structure of the bifurcated complex and lead to interactions that are complex-specific.

Matrix Effects Involving CO. For argon matrices containing both CO and a phenol (M:R:CO = 500:1:5), annealing results in a number of observable effects. Carbon monoxide can diffuse[30] to occupied sites in the matrix and form more dimer or form multimers with available phenols, or aggregate, cause broadening, and otherwise complicate the spectrum. The temperature is thus a critical factor in determining the composition of the medium. Numerous investigators have pointed out that the infrared spectral features of CO are highly sensitive to experimental conditions,[31-35] particularly concentration and deposition rate. Thus the CO stretch region is more complicated than the OH stretch region of the phenol and is more difficult to interpret. Among the factors that contribute to the complexity of the CO stretch region are traces of H_2O (OC···H_2O complex at ν_{max} 2148 cm^{-1}),[30] aggregates, and the fact that CO complexes absorb in a narrow range. Almost all of our spectra show a weak absorption near ν_{max} 2155 cm^{-1}, which has not been assigned, although it may be due to a higher order complex between CO and phenol molecules. We regard the most intense CO band in the region between 2138 and 2160 cm^{-1} as being characteristic of a phenol–CO dimer.

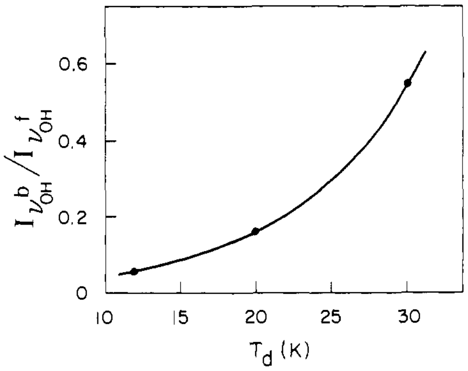


Figure 7. Plot of the ratio of the integrated intensities $I(\nu^{b}_{OH})/I(\nu^{f}_{OH})$ for *o*-bromophenol in argon containing CO (M:R:CO = 500:1:2) vs. the temperature of quenching (T_d) of the gaseous sample.

An interesting point is that surface diffusion upon deposition of the sample is made manifest in carefully controlled experiments in which the gaseous sample is quenched as a function of temperature within a narrow range (Figure 7). This experiment indicates that at least a portion of the complex is formed upon deposition of the sample at 20 K. At this temperature, diffusion can be controlled to give predominantly the dimer ArOH···CO by adjustment of the concentration of CO (as illustrated for *o*-bromophenol in Figure 4).

Experimental Section

A description of the apparatus and the preparation of volatile samples has been reported previously.[36] Phenols with very low vapor pressures were placed in a glass U-tube (located between the cryostat and the needle valve that was used to control the matrix gas flow rate), equilibrated at 77 K, and then maintained between -15 and 25 °C, depending upon the sample, during deposition. Flow rates of matrix gases (0.2–1.2 mm/min) were experimentally adjusted in order to obtain sufficient isolation (no detectable dimers) and spectral intensity. Flow rates of matrix gases containing volatile phenols pumped from a 3-L bulb were 0.3–0.4 mm/min. Generally between 20 and 30 mm of the gaseous mixture was deposited. For dilute mixtures (high M/R ratios) up to 45 mm of gas was transferred. M/R (M = matrix host; R = phenolic guest) ranged from 200 to 2000. The relative ratio of the intensities of $\nu_{OH}{}^{b}$ and $\nu_{OH}{}^{f}$ and appearance of the infrared spectrum were dependent upon the temperature at which the gaseous sample was quenched (T_d). All the data presented herein were obtained from experiments carried out at T_d = 20 K, except where otherwise noted.

Argon (Matheson, prepurified, 99.98% min) was purified according to procedures previously described.[36] Carbon monoxide and nitrogen of research grade purity were supplied by Matheson and used without further purification. The phenols utilized in these studies were supplied by Aldrich Chemical Co. The purity of samples was established by infrared spectroscopy and gas chromatography.

Photochemical reactions were carried out with a 1000-W mercury-xenon lamp (Hanovia No. B977B0010) as the light source. Interference filters (Oriel, No. G-572 and Zeiss Jena) were used as indicated. Using infrared spectroscopy to follow the reaction, total irradiation times were generally in the range of 15 to 60 min for 20 to 30 mm of sample (M/R ~ 500–600).

Summary

This work describes the first systematic study of substituent effects (on the spectral properties of a complex) in rare-gas matrices. Dimers consisting of CO and a phenolic component are formed when a gaseous mixture made up of argon, carbon monoxide, and a phenol (M:R:CO = 500:1:5) are quenched at 20 K. Despite the considerable uncertainties in interpreting spectral features of the species formed from CO and a phenol in argon, the trend in spectral shifts, $\Delta\nu_{OH}$ and $\Delta\nu_{CO}$, indicates that the acidity of the phenolic component is a major determinant of the magnitude of these shifts. The structure of the complexes involving meta- and para-substituted phenols are probably similar

---

(30) Dubost, H. *Chem. Phys.* **1976**, *12*, 139.

(31) Vu, H.; Atwood, M. R.; Vodar, B. *J. Chem. Phys.* **1963**, *38*, 2671.

(32) Abramowitz, S.; Broida, H. P. *J. Res. Natl. Bur. Std., Sect. A 68*, 331.

(33) Maki, A. G. *J. Chem. Phys.* **1961**, *35*, 931.

(34) Leroi, G. E.; Ewing, G. E.; Pimentel, G. C. *J. Chem. Phys.* **1964**, *40*, 2298.

(35) Hallam, H. E.; Davies, J. B. *J. Chem. Soc., Faraday Trans. 2* **1972**, *68*, 509.

(36) Krantz, A.; Laureni, J. *J. Am. Chem. Soc.* **1981**, *103*, 486. Gebicki, J.; Krantz, A. *Ibid.* **1981**, *103*, 4521.

to that of the parent phenol–carbon monoxide dimer. The spectral shifts for complexes between ortho-substituted phenols and CO are consistent with a bifurcated hydrogen-bonded structure. The limited data correlate with the intrinsic acidity of phenols. This is not unreasonable considering the nonpolar properties of solid argon. A significant portion of the complex is formed upon deposition as a result of surface diffusion. The importance of this work is that it provides information as to how substituent effects and acidity are expressed at cryogenic temperatures in a rare-gas matrix. It would be interesting to determine whether such complexes can be detected in the gas phase.

Acknowledgment. We gratefully acknowledge generous financial support from the National Science Foundation, Grant No. CHE 7811563, and the expert assistance of Dr. Helmut Nickels. We also thank Mrs. Lynda Jacob for her skillful assistance in the preparation of this manuscript.

Registry No. 1, 630-08-0; **2**, 108-95-2; **3**, 371-41-5; **4**, 106-48-9; **5**, 106-41-2; **6**, 150-76-5; **7**, 108-43-0; **8**, 591-20-8; **9**, 372-20-3; **11**, 95-57-8; **12**, 95-56-7; **13**, 90-05-1; **14**, 611-20-1; **17**, 87-65-0; *p*-cresol, 106-44-5.

Kinetics and Mechanism of Molecular A-Frame Formation in Reactions of $[Pt_2(PPh_3)_2(\mu\text{-dppm})_2](PF_6)_2$ with Diazomethane, Carbon Monoxide, Sulfur Dioxide, Sulfur, and Hydrogen Chloride

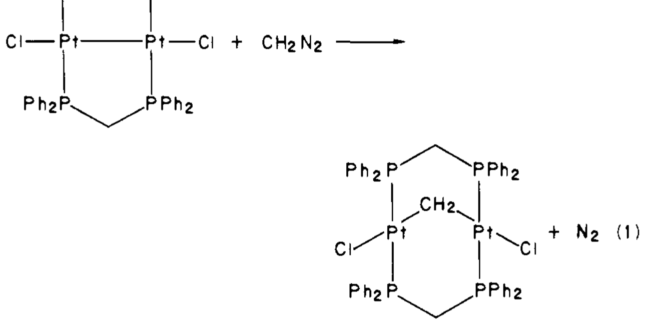
S. Muralidharan and James H. Espenson*

Contribution from the Ames Laboratory and the Department of Chemistry, Iowa State University, Ames, Iowa 50011. *Received May 14, 1984*

Abstract: The mechanism of the formation of "A" frames of the type $[Pt_2(PPh_3)_2(\mu\text{-}Y)(\mu\text{-dppm})_2](PF_6)_2$ (Y = CH_2, CO, S, SO_2) from $[Pt_2(PPh_3)_2(\mu\text{-dppm})_2](PF_6)_2$ by reaction with CH_2N_2, CO, S, and SO_2 (R) in CH_2Cl_2 and other organic solvents has been investigated by using kinetic studies and product analysis. Pseudo-first-order kinetic data (excess $[R]_0$) are consistent with either preequilibrium association of R with the complex prior to rate-limiting product formation or unimolecular formation of a common intermediate which is then attacked by R to form the "A"-frame product. Kinetic studies with $[R]_0 \le [\text{complex}]_0$ substantiate the latter. The most likely intermediate leading to the products is one with a dangling dppm ligand formed by Pt–P bond heterolysis. When $[R]_0$ is very large, formation of this intermediate becomes rate limiting and is independent of the nature of R, with $k = 2.73 \pm 0.05 \times 10^{-2}\ s^{-1}$ (at 25 °C; $\Delta H^‡ = 25.0$ kcal mol^{-1} and $\Delta S^‡ = 18.5$ cal $mol^{-1}\ K^{-1}$). The same process and mechanism is observed for R = HCl, although with minor numerical differences; similar salt and solvent polarity effects occur in all of the reactions.

The dimeric platinum(I) and palladium(I) complexes with bridging bis(diphenylphosphino)methane (dppm) ligands, such as $Pt_2Cl_2(\mu\text{-dppm})_2$, are among the rapidly growing number of binuclear compounds which form A-frames.[1-3] Among other reasons, interest in these novel compounds is aroused by their resemblance to intermediates in Fischer–Tropsch reactions and other catalytic processes.[3-6] The process by which small groups are "inserted into" the metal–metal bond of the parent dinuclear complex has been well characterized in a preparative and structural sense.[7-14]

Relatively little is known about the mechanism(s) such reactions follow, however, although the kinetics of insertion of CH_2 upon reaction with diazomethane into the platinum–platinum bond of $Pt_2Cl_2(\mu\text{-dppm})_2$ (eq 1) and such analogues as $[Pt_2Cl(CO)(\mu\text{-dppm})_2]^+$ and $[Pt_2(CO)_2(\mu\text{-dppm})_2]^{2+}$, has recently been examined.[15]



---

[1] (1) Puddephatt, R. J. *Chem. Soc. Rev.* **1983**, *12*, 99.

[2] (2) Balch, A. L. *Adv. Chem. Ser.* **1982**, *196*, 243.

[3] (3) (a) Brown, M. P.; Fisher, J. R.; Franklin, S. J.; Puddephatt, R. J.; Thomson, M. A. *Adv. Chem. Ser.* **1982**, *196*, 231; (b) Balch, A. L. *ACS Symp. Ser.* **1981**, *155*, 167.

[4] (4) Sanger, A. R. *Can. J. Chem.* **1982**, *60*, 1363.

[5] (5) Kubiak, C. P.; Woodstock, C.; Eisenberg, R. *Inorg. Chem.* **1982**, *21*, 2119.

[6] (6) (a) Brady, R. C., III; Pettit, R. *J. Am. Chem. Soc.* **1980**, *102*, 6181. (b) Brady, R. C., III; Pettit, R. *J. Am. Chem. Soc.* **1980**, *103*, 1287.

[7] (7) Brown, M. P.; Puddephatt, R. J.; Rashidi, M.; Manojlovic-Muir, L.; Muir, K. W.; Solomun, T.; Seddon, K. R. *Inorg. Chim. Acta* **1977**, *23*, L33.

[8] (8) Olmstead, M. M.; Hope, H.; Benner, L. S.; Balch, A. L. *J. Am. Chem. Soc.* **1977**, *99*, 5502.

[9] (9) Brown, M. P.; Puddephatt, R. J.; Rashidi, M.; Seddon, K. R. *J. Chem. Soc., Dalton Trans.* **1978**, 1540.

[10] (10) Brown, M. P.; Fisher, J. R.; Franklin, S. J.; Puddephatt, R. J.; Seddon, K. R. *J. Chem. Soc., Chem. Commun.* **1978**, 749.

[11] (11) Benner, L. S.; Balch, A. L. *J. Am. Chem. Soc.* **1978**, *100*, 6099.

[12] (12) Benner, L. S.; Olmstead, M. M.; Hope, H.; Balch, A. L. *J. Organomet. Chem.* **1978**, *153*, C31.

[13] (13) Rattray, A. D.; Sutton, D. *Inorg. Chim. Acta* **1978**, *27*, L85.

[14] (14) Brown, M. P.; Fisher, J. R.; Puddephatt, R. J.; Seddon, K. R. *Inorg. Chem.* **1979**, *18*, 2808.

[15] (15) Muralidharan, S.; Espenson, J. H. *Inorg. Chem.* **1983**, *22*, 2786.

0002-7863/84/1506-8104$01.50/0