different for both systems (only 1.7 kcal/mol for the former and 9.3 kcal/mol for the latter). These values reveal a particular characteristic of the HOMO of imidazoles. This is a π-type orbital (see Figure 6), and an inspection of its wave function indicates that the atomic orbitals centered on N1 do not participate in it, whereas the contribution from those atomic orbitals centered on C5 is noticeable. Consequently, in 5-methylimidazole there is a certain contribution to the HOMO wave function coming from the atomic orbitals centered on the methyl group (a typical hyperconjugative effect), a contribution which is forbidden if the methyl group is bound to N1. Accordingly, the energy of the HOMO of the 1-methyl derivative does not change appreciably upon methyl substitution.

This absence of hyperconjugation for *N*-methyl-substituted imidazole has another important consequence. Heteroaromatic compounds can be taken, in general, as aromatic derivatives where the heteroatom plays the role of a perturbation. Thus, azines, like pyridine, would be a benzene with a basic center (aza and lone-pair effects). However, this is no longer true for N-substituted azoles; i.e., there is nothing in aromatic chemistry comparable to the N–R bond of an azole. This fact has been recognized by experimentalists[37] but was never satisfactorily explained. Figure 6 and the preceding discussion on the characteristics of the HOMO provide a simple explanation.

Conclusions

From the results discussed throughout this paper we can conclude that the ionic hydrogen bonds between azoles (pyrazoles and imidazoles) and NH_4^+ are not linear. Although deviations from linearity are small, they are neither constant nor regular, revealing in some significant cases strong repulsive interactions between the NH_4^+ cation and the substituent groups of the azolic system. Deviations from linearity are very small for pyrazoles due to the repulsive interaction between the second ring nitrogen and the nitrogen belonging to the NH_4^+ system.

In the equilibrium conformation the proton of the NH_4^+ cation has almost been transferred to the azolic system. In all cases the distance from the proton to the basic center of the azolic compound decreases as its proton affinity increases.

The gap between the gas-phase basicities of imidazole and pyrazole when the reference acid is NH_4^+ is about 6 kcal/mol smaller than if the reference acid is a proton, due mainly to differences in charge–dipole interactions. This result agrees with previous findings reported in the literature[6,10] for other kinds of bases and acids.

The hydrogen-bond energies for $B-NH_4^+$ complexes where B is an azolic system, increase with the increasing proton affinity of the azole, but these dissociation energies are smaller than the corresponding relative proton affinities, showing that the gas-phase basicity of azoles when the reference acid is softer than the proton undergoes a certain attenuation. This attenuation effect is slightly greater for pyrazoles than for imidazoles.

Moreover, these hydrogen-bond dissociation energies are linearly correlated to the 1s orbital energy of the basic center of the azole, though these linear relationships are different for α- and β-substituted compounds.

Both pyrazoles and imidazoles behave as reasonably hard bases. Their absolute hardness decreases upon methyl substitution and varies like the ionization potential. Consequently, we have found that, in general, the multivariate linear correlations gas-phase basicities vs. E_{1s} and E_{HOMO} may yield some useful information on the changes undergone by the hardness of the base upon substitution.

Acknowledgment. This research has been partially supported by the CAICYT Project Number 913/82. All calculations have been performed at the UAM/IBM and CC/UAM Centers, Madrid.

Supplementary Material Available: Comparison between ammonium affinities obtained from STO-3G//INDO and STO-3G//STO-3G calculations for small bases, scaled INDO optimized geometries of azole–NH_4^+ complexes, including imidazole, pyrazole, and their monomethylated derivatives, and a graph of ammonium affinities (ΔAA) vs. the energy of the HOMO for methylpyrazoles referred to the parent compound (4 pages). Ordering information is given on any current masthead page.

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Thiol–Olefin Cooxidation (TOCO) Reaction. 7. A ^1H NMR Study of Thiol Solvation

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The examination of ^1H NMR spectra of *p*-chlorothiophenol in various solvents, including some olefins, indicates the presence of two types of interactions, namely, the formation of hydrogen-bonded and charge-transfer complexes. The association constants for some of these interactions are estimated. The chemical shifts of the sulfhydryl proton of various substituted thiophenols in the presence of indene supports the existence of charge-transfer complexes.

Introduction

In view of our work with thiols in the thiol–olefin cooxidation reaction,[1-6] and with solvent effects in the noncatalyzed oxidation of thiols by molecular oxygen,[7] it was also of interest to study the nature of thiol solvation by means of ^1H NMR. The elucidation of solute–solvent

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Table I. Sulfhydryl Chemical Shifts in Organic Solvents[a] for *p*-Chlorothiophenol

no.	solvent	dielectric[b] constant	Hz	ΔHz[c]	no.	solvent	dielectric[b] constant	Hz	ΔHz[c]
1	Freon 113		191.0	3.2	27	cyclohexene	2.22	195.0	−0.8
2	hexane	1.89	194.2	0.0	28	styrene	2.43	177.0	17.2
3	cyclohexane	2.02	190.0	4.2	29	indene		172.0	22.2
4	cyclopentane	1.96	190.0	4.2	30	indene-*1,3,3*-d_3		180.0	14.2
5	cyclooctane	1.94[d]	189.0	5.2	31	norbornene		170–76	20.2
6	CCl_4	2.24	195.8	−1.6	32	*β*-pinene	2.64[d]	195.0	−0.8
7	$CHCl_3$	4.81	204.3	−10.1	33	camphene	2.33[d]	193.0	1.2
8	CH_2Cl_2	8.90	210.5	−16.3	34	Δ^3-carene		194.0	0.2
9	cyclohexanone	18.20	252.0	−57.8	35	cyclooctene		192.0	2.2
10	acetone	20.70	258.0	−63.8	36	1-octene		198.0	−4.2
11	Me_2SO	46.68	324.0	−129.8	37	amylene		193.0	1.2
12	DMF	36.71	330.0	−135.8	38	*p*-*tert*-butylstyrene		173.0	20.8
13	CH_3CN	37.50	234.0	−39.8	39	*p*-methylstyrene		175.0	18.8
14	toluene	2.38	170.2	24.0	40	*p*-fluorostyrene		183.0	12.2
15	benzene	2.38	176.1	18.1	41	*p*-chlorostyrene		188.0	6.8
16	fluorobenzene		186.0	8.2	42	*p*-bromostyrene		190	4.2
17	chlorobenzene	5.62	188.6	5.6	43	mesitylene	2.27[d]	168.0	26.2
18	bromobenzene	5.40	192.3	1.9	44	*tert*-butylbenzene	2.36	174.0	20.2
19	iodobenzene	4.60	195.8	−1.6	45	benzotrifluoride		185.0	8.8
20	benzonitrile	25.20	192.3	−24.0	46	CH_3OH	32.70	249.0	−54.8
21	nitrobenzene	34.82	222.5	−28.3	47	acetic acid	6.15	226.0	−31.8
22	anisole	4.33	195.0	−0.8	48	trifluoroacetic acid		205.0	−10.8
23	benzaldehyde	17.80	231.6	−37.4	49	*α*-pinene	2.50	199.0	−4.8
24	*p*-methylbenzaldehyde		230.0	−35.8	50	pyridine	12.4	312.0	−117.8
25	acetophenone	17.39	234.2	−40.0	51	4-vinylpyridine		128.0	66.2
26	cyclopentene		195.0	−0.8					

[a] Concn: 4.6×10^{-1} M. Temp: 40 ± 2 °C. Me_4Si was used as internal standard. [b] Unless stated otherwise, values are taken from the Eastman Organic Chemical Bulletin, Vol. 47, 1 (1975). [c] Relative to the chemical shift in hexane. [d] Values are taken from *Handbook of Chemistry and Physics*, 55th ed.; 1975, CRC Press: Cleveland, p E62.

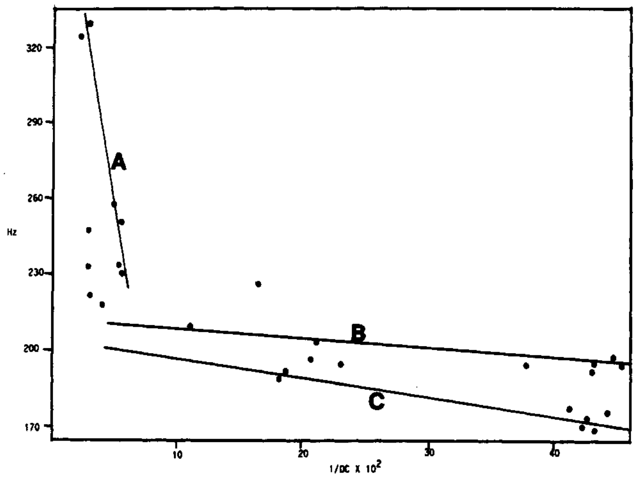

Figure 1. Chemical shift of the sulfhydryl proton of *p*-chlorothiophenol in different solvents.

interactions by means of ^1H NMR has been described previously.[8,9]

Results

The chemical shift of the sulfhydryl proton of *p*-chlorothiophenol was observed in a variety of solvents (Table I). Three distinct linear relationships were obtained when the chemical shifts were plotted against the reciprocal dielectric constants of the solvents (Figure 1).

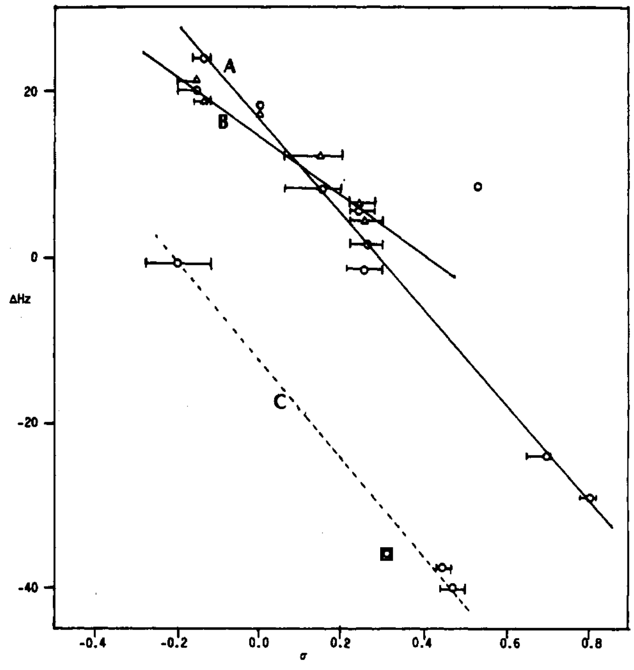

Figure 2. Chemical shift of the sulfhydryl proton of *p*-chlorothiophenol in the presence of substituted benzenes (○) and substituted styrenes (△).

While solvents with polar sites follow slope A, slope B is followed by nonaromatic solvents without polar substituents, and the benzenoid solvents fall, more or less, on slope C.

The chemical shifts induced by the presence of different solvents are best discussed with reference to the chemical shift observed in hexane (Table I, ΔHz) in which specific solute–solvent interactions can be assumed to be minimal.

In an attempt to elucidate the nature of the solute–solvent associations, a Hammett plot of the benzenoid solvents was examined (Figure 2). It can be seen that the solvents fall into three groups: simple non-oxygen-con-

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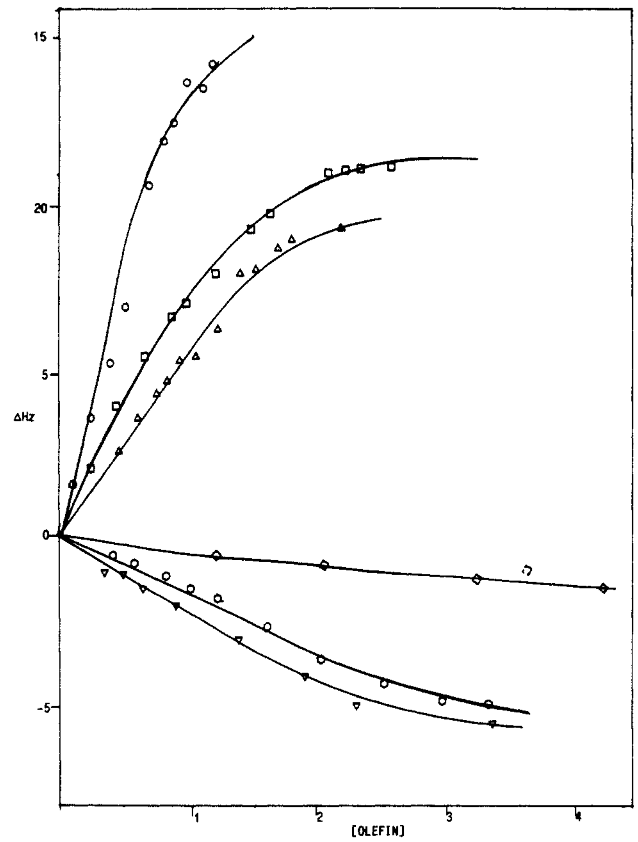

Figure 4. Change in the chemical shift of the sulfhydryl proton of *p*-chlorothiophenol as a function of olefin concentration: (○) indene, (△) benzocyclohexene, (□) benzocycloheptene, (◇) cyclopentene, (▽) cyclohexene, (○) cycloheptene.

taining benzene derivatives (A), substituted styrenes (B), and oxygen-containing benzene derivatives (C). The oxygen-containing benzenoid solvents (no. 22–25 in Table I) show downfield chemical shifts expected of typical hydrogen bonding between the sulfhydryl and the oxygen substituents. However, while the chemical shifts in nonoxygen-containing substituted benzenes and substituted styrenes give a linear Hammett relationship, the chemical shifts are *upfield*, except for the nitro and cyano substituents.

A similar analysis (Figure 3)[10] of the published[11] chemical shifts exhibited by the sulfhydryl protons of thiophenol and *n*-butyl mercaptan in different benzenoid solvents (with reference to cyclohexane) shows a lower ρ value for the aliphatic thiol (27.6 Hz/σ) than for the aromatic thiols (52.9 and 54.3 Hz/σ for thiophenol and *p*-chlorothiophenol, respectively). We note that most of the chemical shifts shown in Figure 3 are downfield and the lowest downfield shift is given by the aliphatic thiol in nitrobenzene. The values of the chemical shifts in benzene are *p*-chlorothiophenol > thiophenol > *n*-butyl mercaptan, i.e., in order of the relative acidities of the thiols.

The ^{1}H NMR spectra of *p*-chlorothiophenol were also determined in the presence of increasing amounts of several olefins (Figure 4) in order to determine the association constants (K^{AD}) as described in the literature.[9] Interestingly enough, while the family of styrene analogues again produced *upfield* shifts, the cyclic monoolefins gave downfield shifts. Also, the magnitude of the equilibrium constants were found to vary in the two series as follows: indene > benzo-1,2-cycloheptene > benzo-1,2-cyclohexene, and cyclohexene > cycloheptene > cyclopentene (Table II, Figures 5 and 6).

Table II. Determination of Association Constants for the Complexes between *p*-Chlorothiophenol and Several Olefins in Freon 113 at 25 °C[a]

no.	olefin	ΔHz/m^0_D	$K^{AD}_{complex}$	corr for 1/ΔHz vs. 1/m^0_D
1	cyclopentene	−0.4	0.0355	0.9950
2	cyclohexene	−2.5	0.1335	0.9921
3	cycloheptene	−1.6	0.0838	0.9907
4	indene	14.2	1.1167	0.9966
5	benzocyclohexene	6.9	0.2524	0.9935
6	benzocycloheptene	8.7	0.5516	0.9956

[a] Initial concentration of *p*-chlorothiophenol in Freon 113 is 0.3 M.

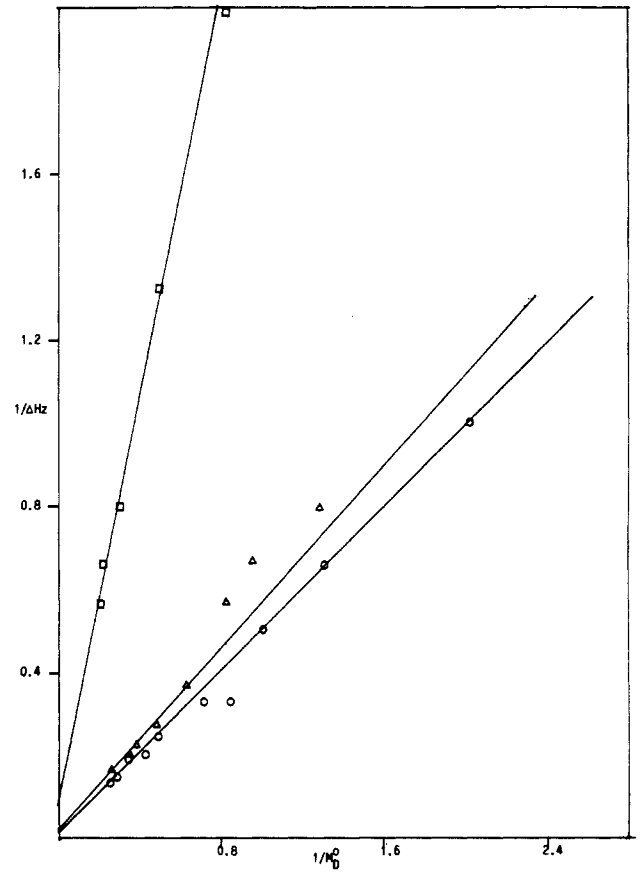

Figure 5. Plots of 1/ΔHz vs. 1/m^0_D for the formation of complexes between *p*-chlorothiophenol and (□) cyclopentene, (○) cyclohexene, and (△) cycloheptene.

Another approach to the study of thiol solvation is the examination of the effect of solvents in a series of substituted thiophenols (Table III). In deuteriochloroform the downfield shifts follow the acidity of the thiols and these shifts increase as the temperature is lowered and, apparently, as the solvation through hydrogen bonding $DCCl_3 \cdots H-S-Ar$ is promoted. However, in the presence of indene the downfield chemical shifts are smaller than those in deuteriochloroform and the changes no longer follow the relative acidities of the thiols (Figure 7).[10] Also, it is noteworthy that the magnitudes of the chemical shift decrease as the temperature is lowered. A Hammett plot of the difference between the chemical shifts of the sulhydryl proton of thiophenols in deuteriochloroform alone, and the latter in the copresence of indene, shows (Figure 8)[10] a linear relationship at the highest temperature employed, but at the two lower temperatures the curvatures suggest competitive solvations that are affected by the

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[10] See paragraph at the end of paper about supplementary material.
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Table III. ArSH Chemical Shift Displacements[a]

	T (°C)								
	−41.8			+2.8			+30.9		
substit on thiophenol	Hz_{SH} ($CDCl_3$)	Hz_{SH} ($CDCl_3$ + indene, 1:1 v/v)	ΔHz_{SH}	Hz_{SH} ($CDCl_3$)	Hz_{SH} ($CDCl_3$ + indene, 1:1 v/v)	ΔHz_{SH}	Hz_{SH} ($CDCl_3$)	Hz_{SH} ($CDCl_3$ + indene, 1:1 v/v)	ΔHz_{SH}
p-NO_2	238	173.5	64.5	231.3	186.4	44.9	229	192	37
p-Cl	212	174	38	207.9	179.4	28.5	205.6	181.4	24.2
m-CH_3	209	183	26	204.2	183.2	21.0	202	192	10
p-OCH_3							200	205.4	−5.4

[a] Measured by means of side-band techniques.

Table IV. Effect of Indan and Indene on the Chemical Shifts of the Sulfhydryl Proton in Substituted Thiophenols at 30.9 °C

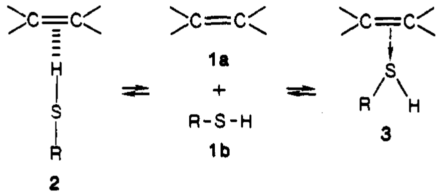
X	Hz_1 ($CDCl_3$)	Hz_2 ($CDCl_3$ + indan, 1:1 v/v)	Hz_3 ($CDCl_3$ + indene, 1:1 v/v)	ΔHz ($Hz_1 - Hz_2$)	ΔHz ($Hz_1 - Hz_3$)
p-NO_2	229	199	192	30	37
p-Cl	205.6	185	181.4	20.6	24.2
m-CH_3	202	188	192.3	14	10.3
p-OCH_3	200	186	205.4	14	−5.4

substituents in an opposite way.

In order to distinguish the effect of the benzene π system and that of the conjugated π system of indene, the chemical shifts of the substituted thiols were examined in the presence of either indene or indan (Table IV). It is clear that the conjugated π system responds in a different manner to the presence of the thiol substituents when the latter are electron-withdrawing or electron-donating in character, and indene actually induces a downfield shift in the case of p-methoxythiophenol.

Discussion

The pronounced downfield shifts of the sulfhydryl proton induced by the solvents that follow slope A of Figure 1 can be attributed to strong hydrogen bonding involving their hard, basic sites. The lack of such sites in the so-called inert solvents that follow slope B accounts for the much smaller value of this slope. Here, the solute–solvent interactions can be thought to involve primarily dispersion forces and, where applicable, weak dipole–dipole forces. The nature of the interactions between thiol and the benzenoid solvents that follow slope C is not easily elucidated because both the anisotropic effect and the electron-donating ability of the π system can contribute to the interaction. However, the simple olefinic systems can be expected to be engaged in the following competitive equilibria. The existence of such equilibria is consistent



with the opposite effects of the two different classes of olefins on the chemical shift of the sulfhydryl proton. In a charge-transfer interaction 3 in which the olefin is the donor, one would expect an upfield shift of the sulfhydryl proton, while a chemical shift in the opposite direction may be expected in a hydrogen-bonded complex 2. The experimentally observed chemical shifts of the sulfhydryl proton apparently correspond to the appropriate mix of the downfield shift due to hydrogen bonding and the upfield shift due to the magnetic anisotropy of the π bond.

The position and nature of the equilibria between the "free" and associated reactants seems to depend on the nature of the thiol and olefin. The negative slope in Figure 2 indicates that the aromatic π system of the benzenoid solvent is involved in the interaction with the thiol, and all the solvents that obey this relationship are apparently engaged in a similar interaction. The downfield deviation induced by the oxygen-containing solvents is probably due to the dominant contribution of the hydrogen-bonded complex.

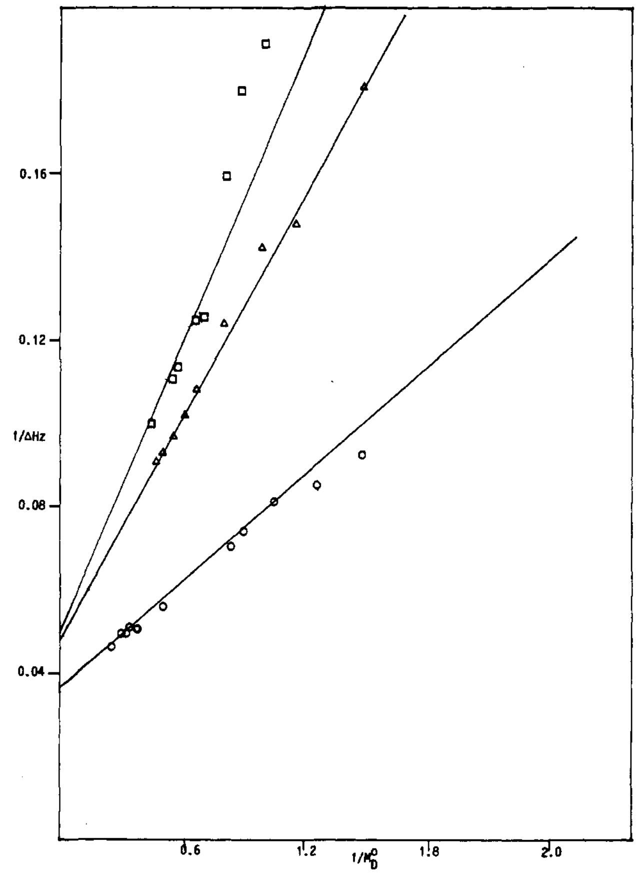
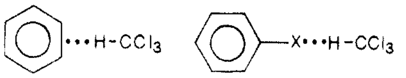


Figure 6. Plots of $1/\Delta Hz$ vs $1/m^0_D$ for the formation of complexes between p-chlorothiophenol and (○) indene, (□) benzocyclohexene, and (△) benzocycloheptene.

The observed chemical shift of thiols in the presence of benzenoid solvents can be best explained by the formation of a charge-transfer complex (3) between the thiol and the π system. Although a prominent hydrogen-bonding interaction with the π system cannot be ruled out, it is unlikely that a mix of different contributions to the chemical shift would yield a good Hammett relationship. The mix of π and n electron interactions proposed by Reeves and Schneider[12] for the chemical shift of the chloroform proton in various aromatic solvents fails to give a linear Hammett plot (Figure 9).[10]



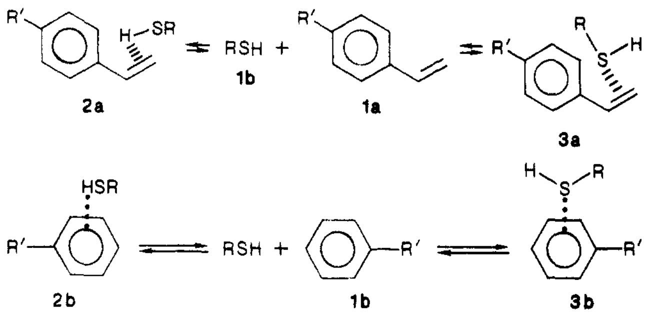
X = Cl, Br, or NO_2

The possibility of a charge-transfer interaction between thiols and aromatic systems has been suggested by Fava[13] and invoked to explain the thiol–olefin cooxidation behavior in the case of conjugated olefins and thiols.[3] Also, the charge-transfer complex formation between indene and a series of substituted methyl aryl sulfides was studied by means of UV–vis spectroscopy[14] and the appearance of charge-transfer bands was observed in the case of negatively substituted thiols in line with the donor character of the olefin.

Benzenoid solvents with electron-donating substituents have favorable HOMO energy levels to interact with LUMO level of *p*-chlorothiophenol, and this results in an increased electron density of sulfur and produces a more highly shielded sulfhydryl proton and an upfield chemical shift. On the other hand, the lower energy levels of solvents with electron-withdrawing substituents may result in an interaction of the LUMO levels of the solvent with the HOMO levels of *p*-chlorothiophenol. This reversal in the charge-transfer would be expected to decrease the electron density of sulfur and to produce a relatively deshielded sulfhydryl proton and a downfield chemical shift. Thus, the nature of the donor–acceptor interactions is likely to depend on the energy levels of the thiols involved, and the reversal from the electron-accepting to the electron-donating role of the thiol would depend on the relative energy levels of the solvents. In the case of *p*-chlorothiophenol this reversal is observed only in the case of solvents with substituents that have electron-withdrawing ability greater than $\sigma = 0.28$, whereas in the case of thiophenol this effect is observed in the case of solvents with electron-withdrawing substituents of σ greater than 0.10. Finally, in the case of *n*-butyl mercaptan this effect is observed even in the case of benzene (compare Figure 2 and 3).[10]

The linear Hammett plot with a negative ρ value obtained for the upfield chemical shift of sulfhydryl proton of *p*-chlorothiophenol in the presence of substituted styrenes (Figure 2) reflects the lowering of the HOMO levels of the donors (styrenes) with reference to the fixed LUMO level of the acceptor (*p*-chlorothiophenol). A slightly smaller slope in the case of substituted styrenes, as compared to that of the substituted benzenes, can be attributed to the dampening of the upfield shift because of the coexistence of the competitive hydrogen-bonding interaction as shown in Scheme I.

Scheme I



The results (Table II and Figure 4) obtained in the interaction between *p*-chlorothiophenol and the family of cyclic styrene analogues indicate that the electron-donating ability of these olefins is inversely proportional to the degree of conjugation of the double bond with the benzene ring. The planar five-membered ring in indene optimizes conjugation, whereas the six-membered ring induces a greater twist of the π bond out of the plane of the benzene ring than the seven-membered ring. In Mulliken's description of a charge-transfer complex[15]

$$\Psi_n\text{AD} = a\Psi_0(\text{A,D}) + b\Psi_1(\text{A}^- - \text{D}^+)$$

the contribution to the ground-state energy Ψ_n(AD) by the dative function $\Psi_1(\text{A}^- - \text{D}^+)$ will decrease as the conjugation of the system decreases. The Ψ_1 function corresponds here to a structure of the olefin–thiol complex in which one electron has been completely transferred from the donor to the acceptor.

One the other hand, the interaction of *p*-chlorothiophenol with isolated olefins can be best explained by hydrogen bonding. The results obtained with the series of isolated cyclic olefins (Figures 4 and 5) reflect the relative hydrogen-bonding ability of these olefins. This sequence parallels their oxidizability and also the stability of their I_2 complexes.[16,17] This behavior can be explained on the basis of the I strain.[18]

The linear relationship with a positive slope obtained in the interaction between a series of substituted thiols with indene (Figure 8)[10] can be seen to result from the increase of the LUMO energy levels of the acceptor (thiophenols) as the electron-withdrawing character of the substituents increases with reference to a fixed HOMO level of the donor (indene). The observed temperature effect in these interactions is compatible with the shift of the equilibrium toward greater complex formation at the lower temperatures.

The existence of the equilibria similar to the ones shown in Scheme I and the dependence of the equilibria on the nature of the substituents in the thiophenol explain why the effect of indene is greater than that of indane (Table IV) in the case of more acidic thiols, while the opposite is true in the case of less acidic thiols. These observations are consistent with the expectation that charge-transfer complex formation is more sensitive to the relative HOMO–LUMO energy levels of the interacting donors and acceptors than is the sensitivity of hydrogen bonding toward the π electron density and polarity of the hydrogen acceptor and hydrogen donor, respectively.

The competitive equilibria between olefinic and thiol systems represented by the formation of **2** and **3** are believed to play an important role in the thiol–olefin cooxidation (TOCO) reaction as well as in the noncatalyzed oxidation of thiols. These subjects are discussed elsewhere.[19] They also have a bearing on the stereochemistry in the addition of thiols to indene as indicated by the

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increase in the yields of cis adducts as the complex-forming ability of the substituted thiols[6] increases.

Experimental Section

Materials. *p*-Chlorothiophenol (Aldrich Chemical Co.) was recrystallized from aqueous ethanol, mp 51–52 °C. Styrene (Eastman Organic Chemicals) was freshly vacuum distilled, bp 38–39 °C (10 Torr). Substituted styrenes (obtained from Dow Chemical Co. by courtesy of Dr. R. Dolinski) were freshly vacuum-distilled before use. Indene (Eastman Organic Chemicals) was freshly vacuum-distilled before use, bp 60–61 °C (12 Torr). All the other solvents reported in Table I were reagent grade and were used without further purification. The thiophenols reported in Tables III and IV were freshly vacuum-distilled before use. Benzo-1,2-cyclohexene and benzo-1,2-cycloheptene (obtained from the University of Puerto Rico by courtesy of Professor Oswaldo Cox) were found to be sufficiently pure to be used without further purification.

^{1}H NMR. The chemical shifts reported in Tables I, III, and IV were determined by means of a Varian A 60 spectrometer calibrated by side band techniques using a Hewlett Packard Model 4204 A oscillator and a Model 5216 A electronic counter. Samples were contained in a 5-mm o.d. NMR tube.

Determination of Thiol–Olefin Complex Formation. A Freon 113 solution of *p*-chlorothiophenol of known concentration was placed in a 5-mm o.d. NMR tube. The tube was fitted with a rubber septum and flushed with nitrogen, and 0.01 mL of tetramethylsilane was injected. The ^{1}H NMR spectra were recorded by means of a Varian EM 360 A spectrometer. Known volumes of the olefin of interest were injected into the NMR tubes and the spectra were recorded after each injection. The addition of olefin were continued until no change in the chemical shift of the S*H* signal was observed. The error in chemical shift measurements was ±0.1 Hz. The association constants ($K^{AD}{}_{complex}$) were calculated from the slope and the intercept of the plot of reciprocal change in chemical shift ($1/\Delta$Hz vs. reciprocal molality ($1/m^0{}_D$) as described in ref 9, 142.

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Supplementary Material Available: Figures 3 and 7–9 (4 pages). Ordering information is given on any current masthead page.

Thiol-Olefin Cooxidation (TOCO) Reaction. 8. Solvent Effects in the Oxidation of Some Thiols with Molecular Oxygen

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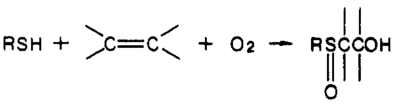
The rates of the noncatalytic oxidation of various thiols by molecular oxygen are a function of the chemical environment of the thiol. A relationship between the chemical shifts of the sulfhydryl proton and the rate of oxidation of the given thiol is demonstrated and discussed.

Introduction

In our search for a self-consistent mechanism of thiol–olefin cooxidation (TOCO) reaction[1–6] under conditions



$$RSH + \rangle C{=}C\langle + O_2 \rightarrow RS(=O)CCOH$$

that avoid the intentional formation of free radicals, we were led to question the suggested[7] initiation of the reaction through thiyl radicals generated by the interaction of thiols with molecular oxygen:

$$RSH + O_2 \rightarrow RS^\bullet + HOO^\bullet$$

This initiation of a free-radical chain reaction may indeed be valid when the TOCO reaction is catalyzed photochemically or by means of chemical radical initiators. Also, it may be valid during the later stages of a TOCO reaction in which the accumulation of hydroperoxides eventually can lead to a self-catalyzed, rapid, homolytic reaction.[8] However, at the early stage of the TOCO reaction carried out under conditions that avoid the intentional formation of thiyl radicals, the latter would have to arise from the reaction of thiols and molecular oxygen. Hence, it was of interest to investigate this reaction per se.

Results

The oxygen consumption in the noncatalyzed oxidation of *p*-chlorothiophenol to the disulfide by means of molecular oxygen in various solvents was observed to follow a pseudo-first-order rate law. The first-order rate constants obtained and corrected for solubility of oxygen in the given solvent are reported in Table I. Two distinct linear relationships could be obtained when these corrected rate constants were plotted against the reciprocal dielectric constants of the solvents (Figure 1). The pronounced effect of the dielectric constants on the rate of oxidation seen in slope A is produced by dipolar aprotic solvents and amines. The oxidation rates were relatively insensitive to the changes of the dielectric constants of the less polar solvents.

This relationship bears a remarkable similarity with the relationship of the chemical shift of a sulfhydryl proton with the reciprocal dielectric constant of the solvent.[9] The

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