Relative Basicities of Cyclic Polyenones from Hydrogen-Bonding Studies

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Abstract: The 1:1 equilibrium constants have been determined in CCl_4 by an infrared technique for the association of phenol with di-*tert*-butylcyclopropenone, cyclohexanone, tropone, 9-fluorenone, tetraphenylcyclopentadienone, diphenylcyclopropenone, di-*n*-butylcyclopropenone, and cycloundecenocyclopropenone. The relative Lewis basicities established from the equilibria studies on the cyclic polyenones are:disubstituted cyclopropenones > tropone ≫ tetraphenylcyclopentadienone. These results were found to qualitatively correlate with CNDO/2 calculations. Spectral studies in the 2000–1500 cm^{-1} region have been employed to establish the basic site of each compound. These studies have also provided a basis for the assignment of the carbonyl stretching frequency of cyclopropenone to the band near 1640 cm^{-1}.

Numerous experimental studies have shown that carbonyl compounds can act as Lewis bases in a variety of situations. These include the formation of hydrogen-bonded complexes,[1] charge-transfer complexes,[2] protonation in superacids[3] at low temperatures, and the formation of protonated species in the gas phase.[4] Several carbonyl compounds in which the carbonyl group is directly connected to a cyclic polyene system have demonstrated what appears to be unusually strong basic character for a carbonyl group.[5] Tropone and the cyclopropenones have been reported to be converted to the corresponding hydroxy salts by the action of strong acids.[5a] The relative basicity of several cyclopropenones has been estimated by Breslow and coworkers in concentrated sulfuric acid by an nmr technique which monitors the chemical shift as a function of the Hammett H_0 values. Their results, summarized in a recent review article,[5c] indicate that the substituent attached to cyclopropenone has a profound effect on the apparent basicity. This study was undertaken to provide definitive experimental data on the hydrogen-bonding capabilities of cyclic polyenones which would establish the relative Lewis basicities of these compounds with respect to cyclohexanone in a noncoordinating solvent such as CCl_4. The compounds studied include tropone, cyclohexanone, 9-fluorenone, tetraphenylcyclopentadienone (TPCP), diphenylcyclopropenone (DPCP), di-*n*-butylcyclopropenone (DBCP), di-*tert*-butylcyclopropenone (DTCP), and cycloundecenocyclopropenone (CUCP). An infrared technique[6] was employed to determine the 1:1 equilibrium constant for the hydrogen bonding of phenol with the base. Since π electrons[7] are known to act as Lewis base sites in hydrogen-bonding systems, spectral studies were performed in the carbonyl stretching region to ascertain if the carbonyl oxygen was the basic site for the 1:1 association. Furthermore, the infrared spectral studies on the cyclopropenone–phenol solutions in the carbonyl region have been used as a basis on which to assign the carbonyl and the carbon–carbon double bond stretching frequencies of the cyclopropenone system. Molecular-orbital calculations of the CNDO/2 type were also performed for several of the ketones and their complexes in an attempt to better understand the variations in basicities observed.

Experimental Section

All spectra were recorded with a Beckman IR-12 spectrometer using a variable path-length cell set at path lengths suitable for each experiment. The temperature of the cell was regulated at 25 ± 1° by circulating water through a jacket attached to the cell. The temperature of the cell was monitored by means of copper–constantan thermocouple in contact with a window of the cell. Spectroscopic grade CCl_4 was dried over Linde molecular sieve (4A) and stored in a dry box where all solutions were prepared and the cell filled. Only when the solutions were prepared in the dry box could reproducible data be obtained.

The equilibrium measurements of the phenol concentrations were obtained by monitoring the absorbance of the band centered at 3611.5 ± 0.5 cm^{-1} assigned to the OH stretching frequency of monomeric phenol.[6] The extinction coefficient for monomeric phenol was determined from measurements at the band maxima for solutions containing phenol concentrations below 5×10^{-3} M where only monomeric phenol is present. The equilibrium constants, K_{eq}, were calculated for a 1:1 model using the observed equilibrium concentration of free phenol calculated from the peak absorbance at 3611.5 cm^{-1}. Figure 1 shows typical spectra obtained in the 3600 cm^{-1} region for the phenol solution and the solution containing phenol and the base. The broad band due to the hydrogen bonded OH group did not overlap the monomeric band in any of the compounds studied. However, some of the carbonyl compounds showed weak absorptions near 3600 cm^{-1}. Consequently, a correction to the absorbance at 3611.5 cm^{-1} was made for these compounds. In each experimental determination, the absorbances of three solutions were used to obtain the concentration of the monomeric phenol at equilibrium. These included A_1 for phenol at concentration C^0_{ph}, A_2 for phenol (C^0_{ph}) plus base (C^0_B), and A_3 for the base alone (C^0_B). The concentration of the monomeric phenol was taken to be $C_{ph} = (A_2 - A_3)(C^0_{ph}/A_1)$. In all equilibrium studies, the cell path length was held constant at 5 mm.

The band maxima for the hydrogen bonded OH stretching frequencies were determined by a triangulation procedure. The intersection of the lines that best fit the sides of the band was taken to be the center of the peak.

9-Fluorenone and tetraphenylcyclopentadienone were obtained from the Aldrich Chemical Co. and used without further purification. Tropone was prepared by a modification of the procedure described in the work of Harmen, *et al.*,[8] and purified by vacuum distillation. Cyclohexanone was reagent grade material which had been distilled at atmospheric pressure. Diphenylcyclopropenone, di-*n*-butylcyclopropenone, and di-*tert*-butylcyclopropenone were prepared according to the literature procedures.[9-11] The literature preparation of cycloundecenocyclopropenone was modified as follows; instead of using a sealed tube, the reaction was run at reflux in 1,1,2-trichloroethane. The reaction was monitored in the infrared and was assumed to be completed when the intensity of the 1840- and 1620-cm^{-1} bands stopped increasing, which was at $t \simeq$ 2 hr. Nmr and ir spectra of all the cyclopropenones were identical with those reported.

Results

In Table I, the concentrations and the absorbance data employed to calculate the hydrogen-bonding equilibrium constants for each compound are listed. Each entry is the average of at least two separate determinations. The average value of the K_{eq} values are taken to be the true thermodynamic equilibrium constants since the solutions are ex-

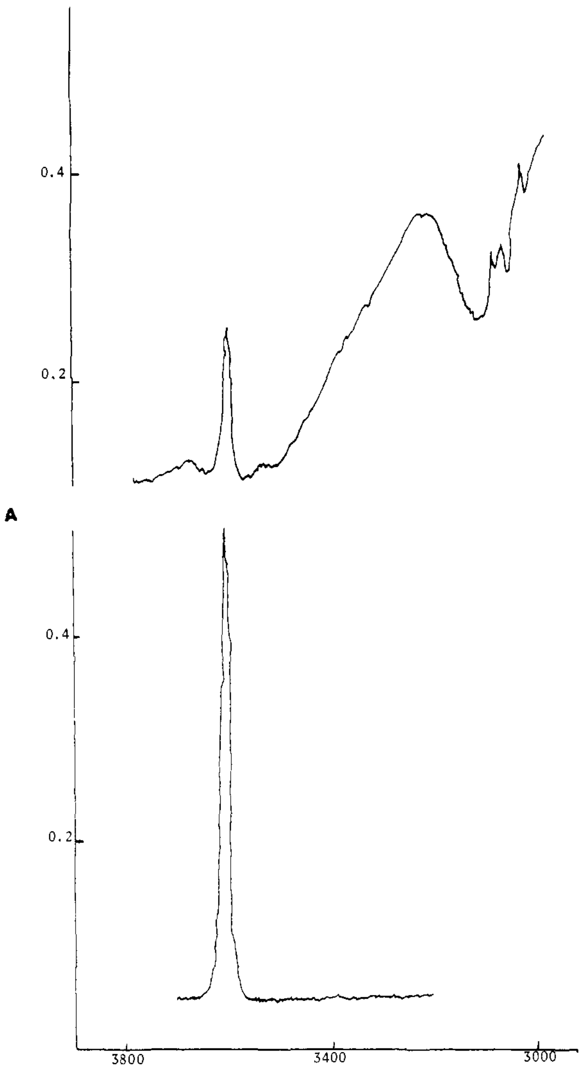


Figure 1. The 0.00268 *M* phenol spectrum in CCl_4 (bottom) and spectra of 0.00268 *M* phenol in CCl_4 containing 0.0235 *M* DBCP (top).

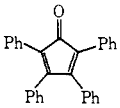
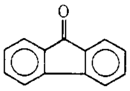
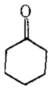
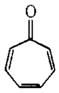
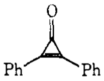
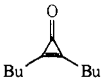
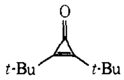
tremely dilute. The reported K_{eq} values are uncertain by at least ±5%. This large uncertainty is primarily due to the difficulty in measuring the absorbance values and the influence of the presence of small concentrations of water in the CCl_4.

In a separate set of experiments, the position of the maximum absorption for the hydrogen-bonded OH stretching frequency was determined for each compound. The positions of the maxima were not very sensitive to the concentrations of the bases but are uncertain by at least ±2 cm^{-1} because of the broadness of the band (Figure 1). The frequency shifts established as $\bar{\gamma}$(phenol) − $\bar{\gamma}$(H-bonded) = $\Delta\bar{\gamma}$ are tabulated along with the average K_{eq} values in Table II.

Two intense bands appear in the 1600–1900 cm^{-1} region of the infrared spectra for each of the cyclopropenones studied. These bands are undoubtedly related to the carbonyl and double-bond stretching vibrations, but the exact assignment of these bands has proved to be difficult.[12] Consequently, the variation of these bands was studied at several concentrations of phenol in CCl_4 in an attempt to clarify the assignment and establish the basic sites of these molecules.

For each of the cyclopropenones studied here, the intense band near 1640 cm^{-1} moved to lower wave numbers in the presence of phenol. The exact location of the maximum of the shifted band was difficult to assess because of overlap with a strong phenol band near 1600 cm^{-1}. However, when the spectra were obtained *vs.* a reference containing the same concentration of phenol, the shifted peak could be observed along with a well-defined isosbestic point. The spectra obtained in this way for di-*n*-butylcyclopropenone are shown in Figure 2. Similar spectra were obtained for all the cyclopropenones studied with a maximum observed $\Delta\bar{\gamma}$ of ≃20 cm^{-1} in each case. The same experiment performed with 9-fluorenone and tetraphenylcyclopentadienone produced maximum $\Delta\bar{\gamma}$ values of 10 cm^{-1} and 0 cm^{-1}, respectively, for the carbonyl bands at 1723 and 1719 cm^{-1}.

Table I. Equilibrium Constant Data for the 1:1 Complexes

	C^o_{ph}, M	C^o_B, M	A_{ph}	A_{mix}	K_{eq}	$\Delta\bar{\gamma}_H$
	0.00227	0.00867	0.314	0.296	7.1	98
	0.00134	0.00962	0.116	0.158	5.3	
	0.00268	0.0197	0.338	0.301	6.3	
	0.00106	0.0166	0.139	0.116	12.4	186
	0.00106	0.0332	0.139	0.100	12.0	
	0.00111	0.0172	0.148	0.120	13.4	
	0.00111	0.0218	0.148	0.105	18.9	245
	0.00111	0.0327	0.148	0.096	16.6	
	0.00111	0.0206	0.129	0.078	32.4	336
	0.00111	0.0309	0.137	0.072	30.2	
	0.00134	0.00775	0.222	0.139	83.2	376
	0.00134	0.00775	0.227	0.135	83.3	
	0.00134	0.0193	0.256	0.081	119	378
	0.00134	0.00965	0.250	0.122	117	
	0.00268	0.0193	0.488	0.157	121	
	0.00268	0.00784	0.462	0.275	101	381
	0.00268	0.0131	0.462	0.208	105	
	0.00268	0.0183	0.462	0.171	102	
	0.00134	0.00832	0.217	0.094	175	398
	0.00251	0.0166	0.401	0.111	178	

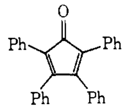
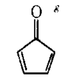
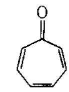
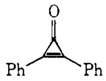
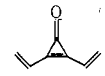
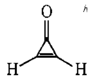
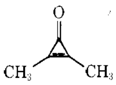
When the intense band near 1850 cm^{-1} was observed in the presence of excess phenol, this band was found to be virtually unchanged for DBCP and CUCP. The same band for DPCP was observed to change in shape in a fashion similar to that observed for this compound in the presence of methanol.[11] For di-*tert*-butylcyclopropenone, the 1850 cm^{-1} band consists of a complicated multiplet. As phenol is added, this multiplet changes shape and position as is shown in Figure 3. Several isosbestic points are observed, and a general shift to higher wave numbers is evident.

The spectrum of tropone in the carbonyl region consists of two intense bands, a broad peak at 1595 cm^{-1} and a band with a main peak at 1647 cm^{-1}, and a shoulder at 1635 cm^{-1}. When tropone (0.062 *M*) is mixed with phenol (0.013 *M*), the 1647- and 1635-cm^{-1} peaks are virtually unchanged, whereas the intensity at 1595 cm^{-1} is diminished and a shoulder appears at 1575 cm^{-1}. At a much higher phenol concentration (0.134 *M*), the 1595-cm^{-1} peak is completely shifted to 1575 cm^{-1}, but the bands above 1600 cm^{-1} have reversed in relative intensity; *i.e.*, the 1635-cm^{-1} band is the main peak with a shoulder at 1647 cm^{-1}.

Discussion

Previous workers[13] have shown that the carbonyl stretching frequency of ketones moves to lower wave numbers by

Table II. Comparision of Hydrogen Bonding Results with CNDO/2 Calculations[k]

Base	K_{eq}	$\Delta\bar{\gamma}_H$	$\Delta\bar{\gamma}_{C=O}$	HOMO[a]	ρ_0[b]	$-\Delta E_+$[c]
	6.2	98	~0			
 [g]				$-12.999(\pi_z)$[d]	−0.207	8.597
 [g]	31.3	336	~20	$-11.50009(\pi_z)$[e]	−0.307	10.054
	83.2	376	~20			
 [i]				$-10.850(\Gamma_{\sigma_y})$[f]	−0.371	10.208
 [h]				$-11.473(\Gamma_{\sigma_y})$[f]	−0.368	9.456
	117	398	~20			
 [j]				$-10.7422(\Gamma_{\sigma_y})$[f]	−0.365	10.136

[a] Energy of the highest occupied molecular orbital of the cyclic polyenone in electron volts, with the MO type indicated in parentheses. [b] Total charge density of the carbonyl oxygen atom. [c] The calculated energy of protonation (eV) with the proton located 1.5 Å from the carbonyl oxygen and at an angle of 120° to carbonyl bond. [d] This MO antisymmetric on reflection through plane containing CO group and perpendicular to ring, thus localized on ring carbons. [e] Delocalized over whole π system but largest coefficient (0.577) at oxygen. [f] This MO is significantly oxygen lone pair in character (~50%) although delocalized over the whole three-membered ring. [g] Atom positions were calculated on the basis of localized single- and double-bond lengths as found for cycloheptatrienone by microwave spectroscopy [C. L. Norris, R. C. Benson, P. Beak, and W. H. Flygare, *J. Amer. Chem. Soc.*, 95, 2766 (1973)]. [h] Atom positions based on molecular geometry found by R. C. Benson, W. H. Flygare, M. Oda, and R. Breslow, *J. Amer. Chem. Soc.*, 95, 2772 (1973). [i] The vinyl groups were positioned as shown with bond lengths (γ_{CH} = 1.08, $\gamma_{C=C}$ = 1.35, γ_{C-C} = 1.47 Å) and 120° bond angles. [j] The tetrahedral methyl groups used γ_{CH} = 1.09, γ_{C-C} = 1.50 Å. [k] P. A. Dobosh, CNINDO: CNDO and INDO Molecular Orbital Program (Fortran IV), QCPE No. 141.

8-20 cm^{-1} when the ketones form a hydrogen-bonded complex with phenol. Since the carbonyl stretching frequencies of TPCP and 9-fluorenone can conventionally be assigned to the intense bands found for each compound above 1700 cm^{-1}, the shifts found for these bands indicate that the carbonyl oxygen is the basic site in 9-fluorenone but not necessarily for TPCP. The absence of any shift for TPCP is surprising since the K_{eq} of 6.2 is very similar to that found for benzophenone[13c] where $\Delta\bar{\gamma}_{C=O}$ = 8 cm^{-1} and K_{eq} = 7.8. Furthermore the spectra were run at phenol and base concentrations where ~50% of the ketone is complexed. This would be consistent with the π-electron system of TPCP providing the basic site in the molecule.

In the tropone spectrum, the 1595 cm^{-1} band has been assigned to the carbonyl stretching motion from the oxygen isotope spectral variations.[14] The shift of this band to 1575 cm^{-1} in the presence of phenol supports this assignment and establishes the carbonyl oxygen as the most basic site in the tropone molecule. At higher phenol concentrations, the band contour of the peak above 1600 cm^{-1} changes to a shape similar to that found in CH_2Cl_2.[15] Since the changes observed in the shape of the 1640 cm^{-1} band occur only at high phenol to base concentrations and are similar to the changes observed upon going to more polar solvent, this phenomenon is probably due to a solvent-dependent Fermi resonance.[16]

The spectral shifts observed for the cyclopropenones are all quite similar, *i.e.*, the band maxima near 1640 cm^{-1} are shifted to lower wave numbers by 20 cm^{-1} upon complexation with phenol. Since the band near 1850 cm^{-1} is not shifted in any way by the presence of phenol for DBCP and CUCP, the 1640 cm^{-1} band can be clearly assigned in these compounds to a molecular vibration that primarily involves the stretching of the carbonyl bond. The variations in the intensities of the peaks found in the band near 1850 cm^{-1} for DPCP are similar to the changes found for the band above 1600 cm^{-1} in the tropone spectrum. Furthermore, the complex variations found for the 1850-cm^{-1} band of DTCP all involve a shift to higher wave numbers. This shift is inconsistent with the assignment of the absorption band to a carbonyl stretching motion. Again, it is possible that this variation is due to a Fermi resonance phenomenon. In view of these observations it is unlikely that the two intense bands found in all cyclopropenones near 1850 and 1640 cm^{-1} result from a heavy coupling of the carbonyl and double-bond stretching vibration which has previously been suggested.[17] Our observations on the variation of these bands upon hydrogen-bond formation parallels the results found when substituents are placed on the phenyl ring in DPCP; *i.e.*, the 1850-cm^{-1} band is insensitive to substituents effects.

The large intensity of the 1850-cm^{-1} band in all the cyclopropenones is inconsistent with the assignment of this band to a vibration consisting mainly of the stretching of the carbon–carbon double bond. However, it is possible that this band is due to a molecular vibration of the three-membered ring as suggested by Agranat and Bergmann.[18] A complete assignment for the cyclopropenone system and a

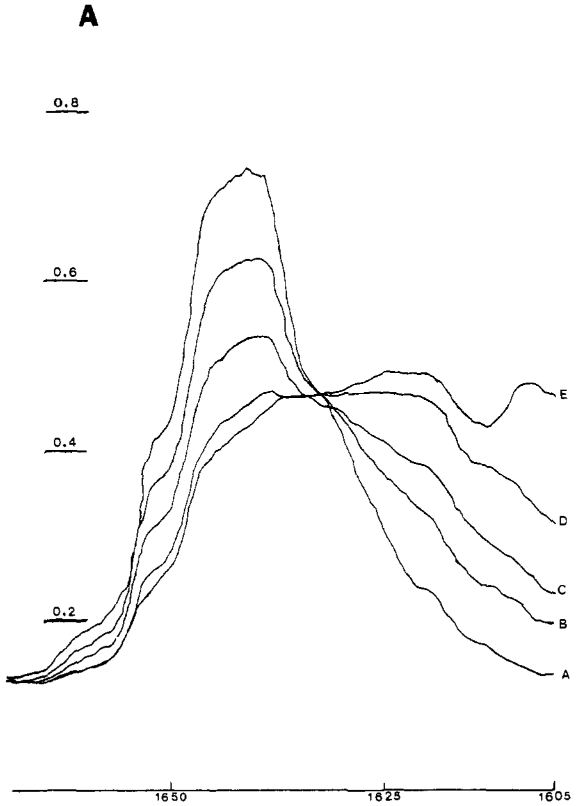


Figure 2. The 1642-cm^{-1} band of di-*n*-butylcyclopropenone (0.012 *M*) is shown at several molar concentrations of phenol: (A) 0.00; (B) 0.0045; (C) 0.0091; (D) 0.0181; (E) 0.0227.

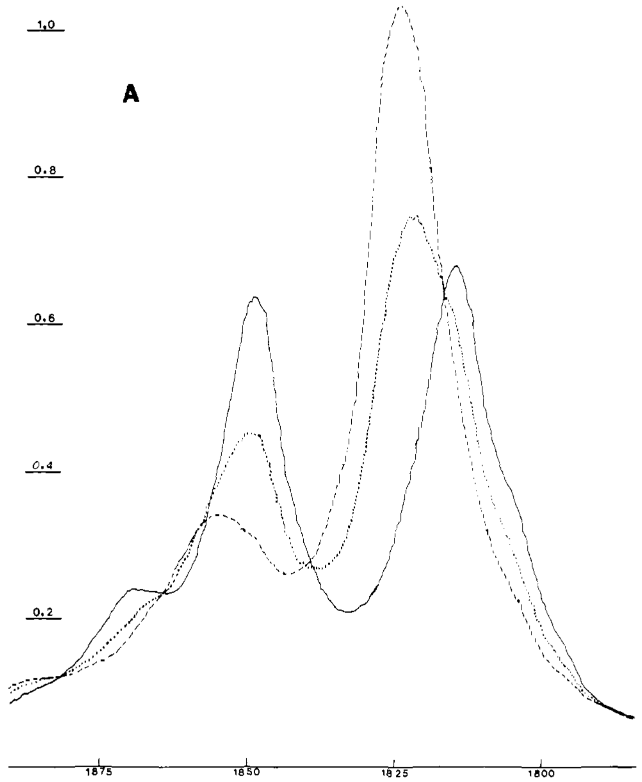


Figure 3. The 1800–1875-cm^{-1} region of the spectrum of di-*tert*-butylcyclopropenone (C = 0.006 *M*) is shown at molar concentrations of phenol of 0.000 (———), 0.0103 (. . . . .), and 0.041 (- - -).

normal coordinate analysis will be required before a definitive assignment of the 1850-cm^{-1} band can be made.

An inspection of the equilibrium constants obtained in this study provides a dramatic indication of the remarkable variation of the Lewis basicity of carbonyl compounds conjugated with cyclic polyene systems. The order of basicity established here, *i.e.*, cyclopropenone > tropone ≫ cyclopentadienone, is exactly in the order which is predicted from simple resonance theory and the Hückel ($4n + 2$) rule.

The K_{eq} determined for TPCP is the lowest value found for any carbonyl compound complexing with phenol. Furthermore, the frequency of the carbonyl stretching vibration of TPCP is virtually unaffected when excess phenol is present where at least 50% of the base is complexed. Consequently, it is possible that the hydrogen bond is not formed at the carbonyl oxygen. 9-Fluorenone also has a small K_{eq}, but a value which is comparable to the K_{eq} values previously observed for carbonyl compounds. Tropone has a K_{eq} larger than any carbonyl compound previously studied[1c] but considerably smaller than the values observed for the cyclopropenones.

The large spread in the K_{eq} values found for the substituted cyclopropenones is quite striking. On the basis of known Hammett σ constants for phenyl, methyl, and *tert*-butyl,[19] the K_{eq} observed are in the expected order. However, in the alkyl-substituted cyclopropenones, the K_{eq} values increase with the increasing size of the alkyl group. This can be interpreted to indicate that the larger alkyl groups can more effectively stabilize the positive charge that develops at the carbonyl carbon upon complexation. The recently found variations in the gas-phase basicities of oxygen-containing compounds have been attributed to the ability of the more polarizable groups to stabilize the charge.[20] Since the *tert*-butyl group would be the most polarizable alkyl substituent studied, the increased K_{eq} of DTCP is in agreement with this interpretation. However the lower K_{eq} value found for diphenylcyclopropenone is not easily explained on a polarizability basis.

It is also of interest to compare the hydrogen-bonding K_{eq} values with the results obtained in concentrated acid solutions. Taking the half-protonation point as the pK_B, diphenyl- and dipropylcyclopropenone are observed to have pK_B values of -2.5[5b] and -1.9,[5b] respectively. Since dipropylcyclopropenone is expected to have a pK_B very close to that of di-*n*-butylcyclopropenone, the pK_B values found for cyclopropenones[5c] appear to follow the same order observed for the K_{eq} values in the hydrogen-bonding equilibria.

An enthalpy of complexation was not determined for any of the carbonyl compounds. However, the change in the phenol OH stretching frequency, $\Delta\bar{\gamma}_H$, was determined, which has been shown[21] to be directly proportional to $\Delta H°$ for hydrogen-bond formation. The $\Delta\bar{\gamma}_H$ values tabulated along with the K_{eq} values in Table I increase in the same order as the K_{eq} values. A plot of log K_{eq} *vs.* $\Delta\bar{\gamma}_H$ was fitted by means of a least-squares analysis to give a linear fit with a correlation coefficient of 0.92. However, the $\Delta\bar{\gamma}_H$ values found for the cyclopropenones are all quite close, indicating that the entropy contribution to $\Delta G°$ may also be a function of the alkyl group present.

Comparison with CNDO/2 Calculations. An analysis of the results tabulated in Table II indicates that a good qualitative correlation exists between the CNDO/2 calculation and the thermodynamic hydrogen-bonding studies. Since the electron-pair donor strength of the bases might be expected to be related to the total electron density at the basic site, it is encouraging that the ρ_O values reflect the observed basicities. The relative basicities predicted from the ρ_O values are in remarkable agreement with the observed equilibrium constants for the three ring sizes studied, *i.e.*, cyclopropenone > tropone ≫ cyclopentadienone.

However, the availability of the electrons at the basic site for a weak interaction should also depend on the energy and type of highest occupied molecular orbital (HOMO). The HOMO of cyclopentadienone is considerably lower in energy than the other systems studied, predicting, on the basis of this criterion, that TPCP would be the least basic compound. It should also be noted that this HOMO is entirely localized in the five-membered ring with zero electron density at the carbonyl oxygen. The highest energy orbital of σ nature with a reasonable concentration of charge at the carbonyl oxygen lies 0.33 eV below the HOMO. This would suggest that the carbonyl oxygen might not be the most basic site in the molecule. The failure to observe any shift in the carbonyl stretching frequency found for the hydrogen-bonded complex of TPCP is consistent with this aspect of the CNDO/2 calculations.

The tropone HOMO is ~1.5 eV higher in energy than that found for cyclopentadienone and places appreciable electron density at the carbonyl oxygen, which is again in agreement with the experimental results. For the parent cyclopropenone, the energy of the HOMO is virtually identical with that for tropone, but the divinyl and dimethyl compounds have HOMO's ~0.6 eV higher than tropone. Consequently, the relative energies of these HOMO's nicely support the correlation of the ρ_0 values with the thermodynamic data, if the vinyl and methyl groups may be considered analogs for the phenyl and alkyl substituents.

Although the hydrogen-bonding complexes do not involve a complete proton transfer, the relative basicities measured by the hydrogen-bonding process usually parallel those found for the proton-transfer process, at least for aqueous systems.[6] The calculated energy change, ΔE_+, for the proton attachment at the carbonyl oxygen predicts that tropone and the cyclopropenones should be considerably more basic than the cyclopentadienone system. However, the ΔE_+ found for cyclopropenone is smaller by 0.5 eV than that for tropone. Yet, when ΔE_+ is determined for the divinyl or dimethyl cyclopropenones, these compounds are predicted to be slightly more basic than tropone which is in the same direction as the experimental results. The parent cyclopropenone has recently been observed to have a pK_B in concentrated acid solution of -5.2 which would indicate that it is the least basic of all the cyclopropenones[22] as is indicated by CNDO/2 results. These results suggest that it would be interesting to experimentally determine the hydrogen-bonding ability of the parent cyclopropenone.

While the CNDO/2 results do correlate qualitatively with a substantial portion of the experimental data, the variation in basicity found for the substituted cyclopropenones is not reflected in the calculations except that the parent cyclopropenone is predicted to be a weaker base than the substituted compounds by the HOMO and ΔE_+ comparison.

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References and Notes

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