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Absorption of Various Substituted Phenols by Nylon 6

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We have previously reported the absorption by Nylon 6 of a range of hydroxylic solvents.[1] In the course of this work, it was noted that phenol was absorbed to an unusual degree and a separate investigation of phenol absorption seemed warranted. We have therefore examined the equilibrium absorption by Nylon 6 of a range of para-substituted phenols from solutions in carbon tetrachloride and in benzene at 30 °C and have analyzed the results in terms of the Hammett linear free energy relationship.

In order to stabilize the initial crystalline structure of the polymer (1-mil extruded Capran 77C film, a Nylon 6 supplied to us by Allied Chemical Corp.), the film was first heated in an oven to 160 °C for 2 h and then cooled to room temperature in a vacuum desiccator, before carrying out swelling measurements. The solvents used were Baker Analyzed grade and were dried over anhydrous magnesium sulfate before use. The phenols were all reagent grade or better, except 4-*tert*-butylphenol which was purified by recrystallizing from cyclohexane to mp 99–100 °C. All liquid phenols displayed a single gas chromatographic peak using a polar column. Solutions of the various phenols were prepared, each 0.1 M phenol in solvent. Solutions in both carbon tetrachloride and benzene were used, except in cases where insolubility prevented this. Film samples weighing initially about 0.25 g were immersed in the solutions at a constant temperature of 30 °C until equilibrium was reached. The samples were periodically removed from the solution, dried with filter paper, and weighed on an analytical balance, to measure the gain in weight. As in the previous study, at least three duplicate samples were averaged and observations were made over a sufficient period of time to ensure that equilibrium had been attained. Control samples immersed in the pure solvents under identical conditions but without dissolved phenol showed weight changes varying from −1.0 to +2.0% which may be considered negligible within experimental error.

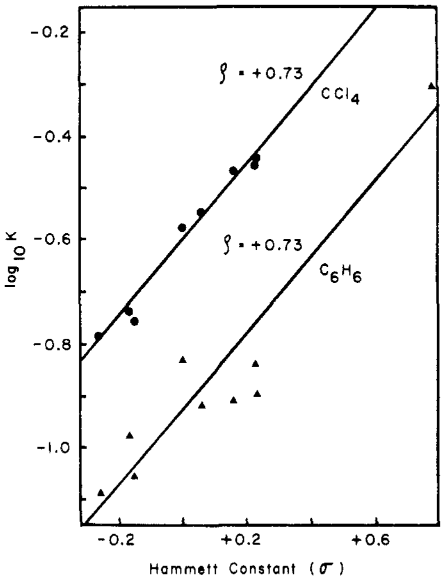

Figure 1. Hammett linear free energy plot for absorption of para-substituted phenols by Nylon 6 from carbon tetrachloride and benzene solutions.

The swelling data obtained for the phenol solutions are shown in Tables I and II. Table I gives data for solutions in CCl_4 while Table II gives data for solutions in benzene. The equilibrium swelling values are given both as weight percent increase based on weight of the dry film and as moles of phenol per mole of monomer units or amide groups. It will be noted that degrees of swelling both greater and less than that of unsubstituted phenol are obtained for the substituted phenols, and two of these (4-*tert*-butyl and 4-phenoxy) gave zero absorption. An effective equilibrium constant for the absorption, K, is defined, as in our previous publication, as:

$$K = [\text{concn absorbed (mol/mol)}] = e^{-\Delta G°/RT} = e^{-\Delta H°/RT} e^{\Delta S°/R} \quad (1)$$

The values of both K and $\log K$ are given in Tables I and II.

Values of the Hammett constant σ are also listed in the two tables for the various substituents (using literature values of McDaniel and Brown[2]). The corresponding Hammett equation can be written in the simplified form:

$$\log K = \log K_0 + \rho\sigma \quad (2)$$

where σ represents the ability of the substituent to donate electrons to the reactive site, ρ is a constant characteristic of the particular process involved, and K_0 is the equilibrium constant for the unsubstituted aromatic ring. This simplified form neglects steric considerations, but should be appropriate because the benzene ring should give an approximately constant steric effect except in the case of the very largest substituents. A plot of $\log K$ vs. σ is given in Figure 1 for both sets of solutions. This plot has several interesting features. First, a linear relation is obtained for both sets of solutions, as predicted by eq 2. The two sets of solutions do not fall on the same straight line, but the slopes of the two straight lines seem to be the same (corresponding to $\rho = +0.73$, as drawn). This suggests that the same process is taking place in the polymer, independent of the solvent used to make the phenol solution.

The positive slope (value of ρ) indicates an increase of absorption, or value of K, with electron-withdrawing groups (which have positive values of σ) and a corresponding decrease of absorption with electron-releasing groups (with negative σ values). Nitrophenol (with a highly positive σ value) could represent a unique case (electron withdrawal assisted by a conjugated position in the ring); however, this compound nevertheless seems to fall on the same straight line as the other phenols.

The value of $\rho = +0.73$ can be compared with the standard reference value of $\rho = +1.00$ for the substituent effect on the ionization of benzoic acids. The substituent effect observed here is therefore less strong than in the

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Table I
Equilibrium Swelling of Nylon 6 in 0.1 M Solutions of Various Phenols in Carbon Tetrachloride

phenol	mol wt	substituent	σ	% absorption (w/w)	K[a]	log K
4-bromophenol	173.0	Br	+0.232	54.9 ± 1.5	0.359	−0.445
4-chlorophenol	128.6	Cl	+0.227	40.5 ± 1.2	0.356	−0.449
4-iodophenol	220.0	I	+0.180	65.1 ± 2.0	0.334	−0.475
4-fluorophenol	112.1	F	+0.062	28.2 ± 1.9	0.284	−0.547
phenol	94.1	H	0.000	22.1 ± 0.6	0.266	−0.575
4-ethylphenol	122.2	C_2H_5	−0.151	19.0 ± 1.0	0.176	−0.755
4-cresol	108.1	CH_3	−0.170	17.6 ± 1.0	0.184	−0.735
4-methoxyphenol	124.1	CH_3O	−0.268	18.1 ± 2.0	0.165	−0.783
4-*tert*-butylphenol	150.2	$C(CH_3)_3$	−0.197	0.0 ± 1.0	0.000	
4-phenoxyphenol	186.2	C_6H_5O	−0.320	0.0 ± 1.0	0.000	

[a] mol of phenol/113 g (mol unit) of Nylon or per amide group.

Table II
Equilibrium Swelling of Nylon 6 in 0.1 M Solutions of Various Phenols in Benzene

phenol	mol wt	substituent	σ	% absorption (w/w)	K[a]	log K
4-bromophenol	173.0	Br	+0.232	19.5 ± 1.0	0.127	−0.907
4-chlorophenol	128.6	Cl	+0.227	16.5 ± 1.0	0.145	−0.839
4-iodophenol	220.0	I	+0.180	24.2 ± 1.0	0.124	−0.907
4-fluorophenol	112.1	F	+0.062	12.0 ± 1.0	0.121	−0.917
phenol	94.1	H	0.000	12.3 ± 1.0	0.148	−0.830
4-ethylphenol	122.2	C_2H_5	−0.151	9.5 ± 1.0	0.088	−1.056
4-cresol	108.1	CH_3	−0.170	10.0 ± 1.0	0.105	−0.979
4-methoxyphenol	124.1	CH_3O	−0.268	10.8 ± 1.0	0.098	−1.009
4-nitrophenol	139.1	NO_2	+0.778	61.3 ± 1.0	0.498	−0.303

[a] mol of phenol/113 g (mol unit) of Nylon or per amide group.

benzoic acid ionization, but in the same direction.

This type of dependence on the inductive effect has been found for systems in which a charge transfer complex is formed: for example, the complexes formed between iodine and phenyl-substituted amides,[3] and complexes between aromatic amines and electron-accepting benzene derivatives[4]. However, the inductive effect should also affect the formation of hydrogen bonds by the hydroxyl groups of the phenols in our own case. An electron-releasing effect to the oxygen of the hydroxyl group should facilitate the formation of hydrogen bonds to the oxygen atom as would take place in phenol–phenol association. We have seen that electron-releasing groups in fact decrease the degree of absorption. This is the opposite of the effect which would be expected if hydrogen bonds were being formed between the oxygen of the phenol and the hydrogen of the Nylon amide group. However, if the hydrogen bonds were formed between the hydrogen of the phenol hydroxyl and the carbonyl oxygen of the amide group of the Nylon, the effect would be in the direction observed, and this is undoubtedly the true situation. This is in accord with the general picture of phenol as an "acidic" proton donor in hydrogen bond formation.

A steric limitation appears to be the likely explanation for the zero absorption obtained for the 4-*tert*-butyl- and 4-phenoxyphenols (not shown in Figure 1 since $K = 0$); this is strongly suggested by the fact that the σ value for the 4-methoxyphenol falls in between the σ values for the above two compounds and yet it shows 18% absorption.

The difference of behavior observed for the two solvents (absorption greater from CCl_4 than from benzene) can be understood from their different tendency to form hydrogen bonds with phenol. CCl_4 is widely regarded as an "inert" solvent with no tendency to form hydrogen bonds, whereas benzene acts as a weak "basic" electron donor (from the π-electron system) and forms hydrogen bonds with phenol having a strength of about 1.2 kcal/mol.[5] This difference is reflected by a difference in heat of solution of phenol in the two solvents: +6.27 kcal/mol in CCl_4, and +4.72 kcal/mol in benzene, as determined by Arnett et al.[5] (Somewhat lower values of +4.10 and +3.07 kcal, respectively, are given for the "initial" heat of solution, near zero concentration, for phenol in these two solvents in the most recent Landolt–Börnstein tables.[6]) Both values are endothermic, indicating that the intermolecular bonding is stronger in the solid phenol than in either solution, and that the thermal effect of solution comes primarily from the breaking of this bonding in the solid. Measurements of the hydrogen bonding of phenol with low molecular weight amides indicate[5] that the hydrogen bond formed in this case has a strength of about 7 kcal/mol. In a comparison[7] of different basic electron donors which form hydrogen bonds with phenol, the amides fall in line with the carbonyl compounds, strongly suggesting that the hydrogen bond between phenol and the amide group is between the hydrogen of the phenol and the oxygen of the carbonyl, in agreement with our earlier discussion. All current evidence indicates that the phenol–carbonyl hydrogen-bonded complex is of a simple 1:1 type.

The relative values of K for absorption from the two solvents, shown by the displacement of the straight lines in Figure 1, corresponds to a difference in log K of 0.325; this corresponds to a difference in $\Delta G°$ of 0.45 kcal/mol for absorption from the two solvents. Comparison of this value with the difference in $\Delta H°$ calculated as 1.55 kcal/mol from the Arnett data allows the difference in $\Delta S°$ for absorption from the two solvents to be calculated. The value obtained is 3.64 eu, or a difference in $T\Delta S°$ of 1.10 kcal/mol at 30 °C. This must represent the entropy change involved in forming the hydrogen-bonded complex between phenol and benzene. This assumes that the swollen state of the Nylon is the same (thermodynamically) in the two cases, which seems a reasonable assumption. Although the second decimal place should not be taken too seriously, it does appear that the primary reason that absorption of phenol by Nylon is less out of benzene than out of carbon tetrachloride is one of energy rather than entropy. Use of the Landolt–Börnstein heat of solution values gives a difference in $\Delta H°$ of 1.03 kcal/mol, and a difference of $\Delta S°$ of 1.98 eu or of $T\Delta S°$ of 0.59 kcal/mol.

A decomposition of the swelling process itself (phenol entering the Nylon) into its enthalpy and entropy components is not yet possible due to a lack of adequate enthalpy data. It is of interest to note that the Hammett equation has been applied to the enthalpy term alone in a study[8] of the hydrogen bonding of phenol with small-molecule donors.

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Solid State Photochemistry of Polycarbonates

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PhotoFries rearrangement observed on photolysis of aryl esters and carbonates has been the subject of numerous mechanistic investigations[1-10] as have α-C–C or -C–O bond homolysis and 1,3-acyl shifts occurring in a broad class of β,γ-unsaturated ketonic chromophores.[15-17] Meyer and Hammond[10] reported that gas-phase photolysis of phenyl acetate yields not only the photoFries product but products anticipated on the basis of formation of methyl radicals on α-C–O bond homolysis during the rearrangement. On the other hand Bellus,[3] and more recently Humphrey[2] et al., have concluded that although α-C–O bond homolysis is an ubiquitous side reaction obtained on photolysis of aryl esters, carbonates, or polymers thereof, photoFries rearrangement in these systems is a concerted 1,3-acyl shift originating from the first $\pi^* \leftarrow n$ singlet. Here we report quantum yield of photoFries rearrangement in a polycarbonate film as functions of temperature and humidity. We conclude that the mechanism and quantum yield of photoFries rearrangement in the solid state is markedly different from that in other media. In the homogeneous amorphous phase it is a concerted process proceeding either from the $\pi^* \leftarrow n$ singlet, in which case it must be subject to considerable self quenching, or from a triplet. The latter is presumably the first triplet since the lifetime of higher triplets is expected to be very short in condensed (solid) phase. We have also monitored the rate of chain scission as a function of irradiation period using FTIR (Fourier transform infrared spectroscopy) and gel permeation chromatography (GPC). It will be further demonstrated that the measurement of lifetime of the parent excited state is essential if a model of photodegradation of the film is to be developed, particularly when conversion is appreciable. Reports on transient detection and kinetics as well as development of such a model will be the subject of a future communication. The data used in these calculations were reported by Kolyer and Mann.[1]

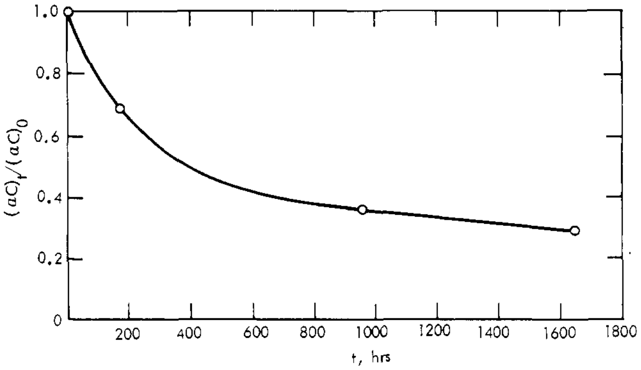

Figure 1. Rate of Lexan photodegradation (measured by following increase in A_{360} for a 24-h exposure) vs. age of lamp in hours.

Experimental Section

Experimental techniques and data handling are detailed in ref 1. The following test environments were used:

a. Indoor Testing Chamber. This chamber consists of a box fitted with a 2500 W ozone-free, high pressure Xenon lamp, blowers, and safety devices such as air-flow and temperature sensors. Spectral characterization of the lamp was carried out as a function of the age of lamp. It was found that there was a drop in the ultraviolet output in the region 300–310 nm, but no decrease at wavelengths higher than 310 nm. This drop in ultraviolet output reduces the initial rate of Lexan photodegradation. We may plot increase in absorbance at 360 nm for a 24-h exposure of fresh Lexan films vs. age of the lamp. This plot may be integrated to obtain the integrated UV intensity absorbed by Lexan when tests are carried out for long periods ($\lesssim$50 h) as a function of total duration of the test. This plot is shown in Figure 1 and has been used to correct all observed rates of Lexan photodegradation.

Short-wavelength ultraviolet was filtered with a Pyrex filter, so that the spectral distribution resembled air mass 1 solar irradiance. Infrared was filtered with a water filter in order to obtain a better control of the temperature. Humidity could be controlled by enclosing the sample in quartz vessels containing the requisite partial pressure of water vapor. Control runs were carried out in inert gas atmospheres.

b. EMMA and EMMAQUA. These are solar concentrators set up at DSET, Inc., of Phoenix, Ariz. and consist of aluminum mirrors mounted on a steel frame tracking the sun. The nominal acceleration factor is 800%, although deviation could be caused by loss of reflectivity of the mirrors, particularly in certain spectral regions. Samples are placed in a holder cooled by a blower and they may receive periodic (15 minutes) spray of deionized water (EMMAQUA).

c. Outdoor Exposure Tests. Samples were placed outdoors in Miami, Fla. and Phoenix, Ariz. at 45° south and in horizontal positions.

Absorbance at 360 nm was measured in a Cary 16. Weathered samples obtained through the courtesy of Dr. Kolyer were examined by using FTIR (ATR) spectroscopy and gel permeation chromatography (solvent CH_2Cl_2).

Initial rate studies were carried out with these data assuming that ϵ_{360} of phenyl salicylate is 1.1 L mol^{-1} cm^{-1}. Light input was estimated by multiplying the integrated input of the lamp (as a function of wavelength) to the absorbance of the film as a function of wavelength and integrating the resulting function in the range 290–340 nm.

Results and Discussion

UV-vis spectra of the film and its solution in dichloromethane are presented in Figure 2. The solution follows Beer's law up to the highest concentration used (12.3 mg/mL). Weak shoulders are observed at 322 nm and 308 nm. A Gaussian analysis of the spectrum reveals that the main Lexan absorption extends to 340 nm. The long-wavelength absorption may be attributed to a low-flying $\pi^* \leftarrow n$ singlet, or to the first triplet or a combination

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