Methyl 1,3-Dioxolane-2-carboxylate. Attempts to prepare 1,3-dioxolane-2-carboxylic acid or its methyl ester from glyoxylic acid and ethylene glycol and from methyl dichloroacetate and the sodium salt of ethylene glycol were unsuccessful, but we later learned that the former method has been made to work by Newman and Chen.[36]

Our successful method began by bubbling excess ozone through a solution of 8.5 g (85 mmol) of 2-vinyl-1,3-dioxolane[12] in 100 ml of methanol at −15°. The resulting solution was added to 150 ml of 5% aqueous sodium hydroxide and 42 g (180 mmol) of silver oxide. After 1 hr of rapid stirring the solution was filtered and the filtrate extracted with 100 ml of ether. Excess carbon dioxide was bubbled into the aqueous layer which was then evaporated to dryness at 20 mm pressure. The 26.5 g of white solid was extracted with hot methanol and the filtered methanol solution evaporated to dryness, leaving 10.5 g of white crystals whose nmr spectrum in deuterium oxide indicated the presence of equimolar amounts of sodium formate (δ 7.2) and sodium 1,3-dioxolane-2-carboxylate [δ 2.78 (s, 4, CH_2) and 3.88 ppm (s, 1, CH)].[37]

Enough 18 N sulfuric acid was added to 7.5 g of an equimolar mixture of sodium formate and sodium 1,3-dioxolane-2-carboxylate in 20 ml of water at 0° to give a pH of 2. The solution was quickly extracted twice with 100-ml portions of ether to which ethereal diazomethane was added until the yellow color persisted for 1 hr. Distillation of the magnesium sulfate dried solution gave 3.1 g of methyl 1,3-dioxolane-2-carboxylate: 99.4% pure by glpc (6-ft DEGS column); bp 87–88° (24 mm); nmr (CCl_4) δ 5.22 (s, 1, CH), 4.00 (br s, 4, CH_2), 3.70 ppm (s, 3, CH_3);[38] ir (neat) in order of decreasing intensity 1740, 1130, 1222, 940, 1035, 2955, 1292, 1420, and 2900 cm^{-1}.

Kinetics. The following changes were made in the kinetic procedure used previously.[3] A Perkin-Elmer grating spectrophotometer, Model 337, was used with 0.05 mm IR Trans II cells. Under these conditions, the extinction coefficient for MeOH, which was found to follow eq 3, was somewhat smaller than that

$$\epsilon_{\text{MeOH}} = (108.8 - 5.98[\text{NaOMe}])M^{-1}\ \text{cm}^{-1} \qquad (3)$$

obtained previously. The runs at 60° were carried out by using a 2-ml sealed ampoule for each point. Ester concentrations were in the range 0.55–0.98 M and sodium methoxide concentrations in the range 0.36–0.62 M.

pK Determinations. The pK of tetrahydrofuran-2-carboxylic acid was determined by measuring the pH in a potentiometric titration against standard aqueous sodium hydroxide using a Radiometer titrator (ABU1, PHM26c, SBR2c, and type C electrode). The other two acids were used in the form of their sodium salts, which were titrated rapidly with standard acid (although reference data on other acetals show that no significant amount of hydrolysis of the acetal linkages would have occurred even under more acidic conditions). The ionic strengths at which the pH values were measured were in the range 0.005–0.020 M. The observed pH was taken to be $-\log a_{\text{H}^+}$ and ionic activity coefficients were assumed to obey the Davies equation (*i.e.*, eq 4 at 35°). In

$$\log \gamma = 0.52\left(\frac{\sqrt{\mu}}{1 + \sqrt{\mu}} - 0.2\mu\right) \qquad (4)$$

calculating the pK values proper allowance was made for the fact that the hydrogen ion concentrations were not negligible compared to the concentrations of the acid and its anion. The sodium salts used were prepared by recrystallizing from alcohol the products of the reaction of aqueous sodium hydroxide with the corresponding methyl esters. A weighed amount of each sodium salt was dissolved in deuterium oxide containing a known concentration of *tert*-butyl alcohol, the ratios of the areas of the strongest nmr peaks were found to agree with the calculated value, and no nmr peaks due to impurities could be seen.

Acknowledgment. We are indebted to Dr. Wendel Lim for carrying out preliminary studies on this investigation.

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[36] M. S. Newman and F. Chen, The Ohio State University, personal communication, 1971.

[37] Chemical shifts downfield from the carbon-bound protons of internal *tert*-butyl alcohol.

[38] Chemical shifts downfield from internal tetramethylsilane.

Effect of Solvent on the Ground States and Transition States in the Reactions of 2,4,6-Tri-*tert*-butylphenoxyl with Phenols

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Received May 13, 1971

Abstract: The absolute rate constants for the hydrogen atom transfer reaction of the 2,4,6-tri-*tert*-butylphenoxyl radical with phenols in various solvent systems have been determined at 30 and 60°. The Henry's law constants for phenol and 1,3,5-tri-*tert*-butylbenzene which had previously been shown to be a good model for the solution properties of the free radical have been determined by transpiration techniques. Utilizing infrared spectroscopy, the activity coefficients of Prigogine for the specific hydrogen bonding interactions of phenol with solvent have been determined. The results of these kinetic and solution property studies have been combined and subjected to a detailed analysis based upon activity coefficients. This type of analysis provided a detailed description of the partial molal energy changes resulting from the transfer of the activated complex, free radical, and phenol from carbon tetrachloride to other solvent systems. The findings suggest that the mechanism of the reaction involves a prior equilibrium formation of a hydrogen-bonded free radical–phenol complex, followed by hydrogen atom transfer within the complex. It is shown that this mechanism accounts for the abnormally low activation energies observed for hydrogen atom transfer between oxyl radicals and is consistent with the A factors observed for such reactions. Finally, the effect of solvent on such reactions is not consistent with the activated complex being polar in nature.

An important reaction in a number of free-radical systems is the transfer of hydrogen atoms between oxy radicals. For example, the mechanism of the phenolic inhibition of hydrocarbon oxidation involves the rapid and often reversible transfer of hydrogen atoms between phenoxy and peroxy free radicals.[1]

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[1] For a review, *cf.* L. R. Mahoney, *Angew. Chem. Int. Ed. Engl.*, 8, 547 (1969).

The synergistic behavior of mixtures of phenols as antioxidants depends upon the transfer of hydrogen atoms between hindered and nonhindered phenoxy radicals.[2] Kinetic studies in nonpolar solvents have revealed that the rates of these processes (1) possess very low temperature coefficients, *i.e.*, low apparent activation energies,[3–5] and (2) are greatly accelerated by the presence of electron-donating substitutents on the phenolic moiety; empirical correlations with σ^+ values yield ρ values comparable to those observed in reactions in which carbonium ions are formed.[6–8] With the exception of a study of the effect of solvent upon the *ratio* of rate constants for the reaction of polystyrenyl peroxy radicals with styrene and with phenols[9] the effects of polar solvents on the rates of these reactions have not been reported.

Two requirements must be satisfied in order to interpret, in terms of the transition state theory, the effect of solvent upon the rate of a bimolecular free-radical reaction. First of all, absolute rate constants for the reaction must be obtained. As Walling and Wagner emphasized[10] data obtained from the usual competitive techniques show only the effect of medium on the *difference* in free energy of the transition states involved. A second requirement is a knowledge of the effect of solvent on the ground-state properties of the reactants. If this latter requirement is not fulfilled solvent effects upon the reactants and the transition states may not be separated.

Both of these requirements are satisfied by the system chosen for the present study. The absolute rate constants for the hydrogen atom transfer reaction of 2,4,6-tri-*tert*-butylphenoxyl with phenols may be directly determined by means of stop-flow techniques[11] and the heat of formation of the radical in a variety of solvents has been determined by direct calorimetric measurements.[12] The determination of absolute rate constants in the same solvents with the additional experimental determination of the effect of solvent on the ground states of the phenolic hydrogen donor and a model compound for the radical has allowed a quantitative estimate to be made of the effect of solvent upon the free-energy contents of the activated complexes in the reactions.

Results and Discussion

Kinetic Study. A systematic study of the effect of solvent on the rates of reaction of the 2,4,6-tri-*tert*-butylphenoxy free radical, A·, with phenolic compounds was carried out. A series of substituted phenols was studied in pure carbon tetrachloride and pure benzene as solvents at 30 and 60°. The reaction with unsubstituted phenol was examined in the mixed solvent systems carbon tetrachloride–benzene, carbon tetrachloride–acetonitrile, and carbon tetrachloride–dioxane at the same temperatures.

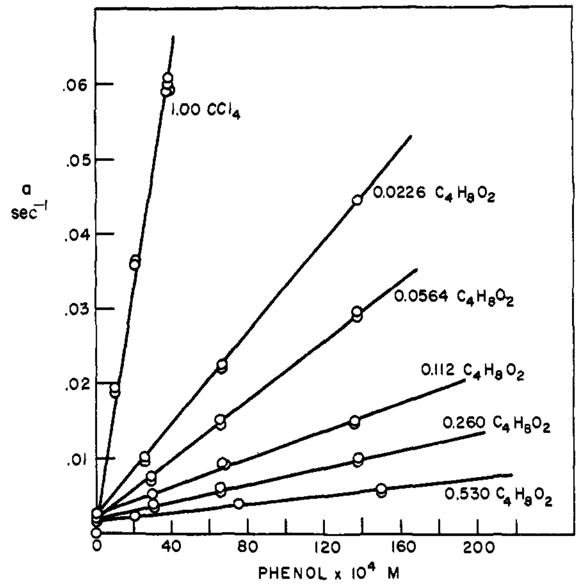


Figure 1. Plot of the value of a for the reaction of 2,4,6-tri-*tert*-butylphenoxyl with phenol in carbon tetrachloride and mixtures of carbon tetrachloride–dioxane at 30°.

With the exception of mixtures of carbon tetrachloride–dioxane, the rate of disappearance of 2,4,6-tri-*tert*-butylphenoxy free radical, A·, is accurately described by the expression

$$\frac{d[A\cdot]}{dt} = a[A\cdot][BH] \qquad (1)$$

where [BH] represents the concentration of the phenolic compound. Equation 1 is consistent with the scheme established in earlier kinetic and product studies with benzene[11] and chlorobenzene[5] as solvents, *i.e.*

$$A\cdot + BH \xrightarrow{k_2} AH + B\cdot \quad \text{(slow)} \qquad (2)$$

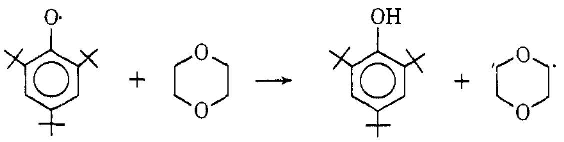
$$A\cdot + B\cdot \xrightarrow{k_3} AB \quad \text{(fast)} \qquad (3)$$

where B· is the unhindered phenoxy radical and AB is *p*-quinol ether. The constant a in eq 1 is equal to $2k_2$.

When mixtures of carbon tetrachloride–dioxane were employed as solvents there was a first-order decay of A· in the *absence* of BH and the expression for the disappearance of A· becomes

$$-\frac{d[A\cdot]}{dt} = a[A\cdot][BH] + b[A\cdot] \qquad (4)$$

The values of a and b were reproducible, *i.e.*, were not altered by repeated purification of the dioxane. The origin of the decay in the absence of BH is likely to be the abstraction reaction (eq 5). In Figure 1 are presented plots of the first-order rate constant for the reaction of A· *vs.* the concentration of phenol at various



(5)

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(2) L. R. Mahoney and M. A. DaRooge, *J. Amer. Chem. Soc.*, **89**, 5619 (1967).

(3) L. R. Mahoney and M. A. DaRooge, *ibid.*, 92, 4063 (1970).

(4) R. W. Kreilick and S. I. Weissman, *ibid.*, **88**, 2645 (1966).

(5) J. A. Howard, W. J. Schwalm, and K. U. Ingold, *Advan. Chem. Ser.*, No. 75, 6 (1968).

(6) J. A. Howard and K. U. Ingold, *Can. J. Chem.*, **41**, 1744, 2880 (1963).

(7) L. R. Mahoney, *J. Amer. Chem. Soc.*, **89**, 1895 (1967).

(8) L. R. Mahoney and M. A. DaRooge, *ibid.*, **92**, 890 (1970).

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(11) M. A. DaRooge and L. R. Mahoney, *J. Org. Chem.*, 32, 1 (1967).

(12) L. R. Mahoney, F. C. Ferris, and M. A. DaRooge, *J. Amer. Chem. Soc.*, **91**, 3883 (1969).

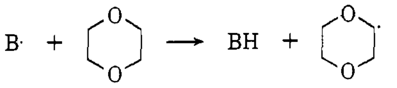
Table I. Summary of Absolute Rate Constants for the Reaction of 2,4,6-Tri-*tert*-butylphenoxyl with Phenols

Substituent	Solvent[a]	$2k_2$, M^{-1} sec^{-1} 30°	$2k_2$, M^{-1} sec^{-1} 60°
	A. Substituent Phenols in CCl_4 and C_6H_6		
4-*t*-Bu	1.0 CCl_4	190 ± 4	430 ± 30
	1.0 C_6H_6	98 ± 6	254 ± 9
3,5-Me$_2$	1.0 CCl_4	77 ± 3	147 ± 9
	1.0 C_6H_6	36 ± 3	113 ± 6
4-H	1.0 CCl_4	15.8 ± 0.8	31.5 ± 1.9
	1.0 C_6H_6	7.5 ± 0.5	17.0 ± 0.8
3-Carboethoxy	1.0 CCl_4	3.6 ± 0.3	9.1 ± 0.8
	1.0 C_6H_6	1.18 ± 0.6	2.8 ± 0.2
	B. Phenol in CCl_4-CH_3CN and CCl_4-$C_4H_4O_2$ Mixtures		
	1.0 CCl_4	15.8 ± 0.8	31.5 ± 1.9
	0.036 CH_3CN	5.34 ± 0.20	12.3 ± 0.4
	0.088 CH_3CN	2.95 ± 0.15	6.9 ± 0.2
	0.170 CH_3CN	1.63 ± 0.08	3.34 ± 0.07
	0.381 CH_3CN	0.82 ± 0.06	1.82 ± 0.10
	0.643 CH_3CN	0.54 ± 0.03	1.15 ± 0.05
	0.820 CH_3CN	0.48 ± 0.03	1.0 ± 0.05
	1.0 CCl_4	15.8 ± 0.8	31.5 ± 1.9
	0.0226 $C_4H_4O_2$	3.14 ± 0.12	10.1 ± 0.7
	0.0564 $C_4H_4O_2$	2.0 ± 0.1	8.06 ± 0.45
	0.1120 $C_4H_4O_2$	0.77 ± 0.02	2.8 ± 0.1
	0.260 $C_4H_4O_2$	0.62 ± 0.02	1.32 ± 0.07
	0.530 $C_4H_4O_2$	0.27 ± 0.01	0.87 ± 0.02

[a] The number preceding the chemical formula denotes the mole fraction of component in the solvent mixture, the remainder being CCl_4.

mole fractions of dioxane. The value of the intercept at 0.53 mol fraction dioxane, *i.e.*, 5.8 M, corresponds to a value of k_5 equal to $3 \times 10^{-4}\ M^{-1}\ \text{sec}^{-1}$.

If reaction 5 occurs it is likely that the reaction of the phenoxy radical B· with dioxane also occurs, *i.e.*



(6)

Under these conditions the value of a would be less than $2k_2$ but larger than or equal to k_2.

The values of a from eq 1 and 4 for the pure solvents and the solvent mixtures are summarized in Table I. Examination of Table I reveals that the addition of a second solvent to carbon tetrachloride leads to decreased values of k_2. In the case of benzene the decrease is only a factor of two. However, the addition of high concentrations of acetonitrile or dioxane results in values of k_2 equal to 1/30th to 1/40th as large as those observed in pure carbon tetrachloride. The relative magnitudes of these effects qualitatively parallel those which one would predict from the ability of the added solvent to form hydrogen-bonded complexes with phenols. In order to quantitatively assess the contribution of this specific effect, *i.e.*, ground solvation of the phenolic reactant, in comparison with solvent effects on A· and on the activated complexes in the reaction, it is convenient to formalize the relationships which exist between kinetic and solvent phenomena.

Relationships between Kinetics and Solvent Phenomena. The formalism we have chosen is that which Parker has so successfully utilized for the analysis of the effect of solvent upon the rates of SN2 reactions.[13] The absolute rate constant in a solvent S, k^S, and the absolute rate constant in a reference solvent, k^0, are related by eq 7 where ${}^0\gamma^S{}_{A\cdot}$, ${}^0\gamma^S{}_{BH}$, and ${}^0\gamma^S{}_{X\neq}$ are

$$\frac{k^S}{k^0} = \frac{{}^0\gamma^S{}_{A\cdot}\,{}^0\gamma^S{}_{BH}}{{}^0\gamma^S{}_{X\neq}} \tag{7}$$

the activity coefficients for the phenoxy radical, phenol, and activitated complex, respectively. Equation 7 then allows the effect of solvation of the free radical, the phenolic compound, and the activated complex to be partitioned.

Definition and Determination of ${}^0\gamma^S{}_{BH}$. The activity coefficient of a phenolic compound, ${}^0\gamma^S{}_{BH}$, is defined according to the convention which Parker[14] developed for the analysis of the effect of solvent on anions in SN2 reactions. According to these conventions ${}^0\gamma^S{}_{BH}$ reflects the change in the standard chemical potential, μ_{BH}, of the phenol, BH (hypothetical 1 M solution obeying a limiting law corresponding to Henry's law), from the standard reference solvent, carbon tetrachloride, to a second solvent, S, *i.e.*

$$\text{BH}(1\ M,\ CCl_4) \longrightarrow \text{BH}(1\ M,\ \text{S}) \tag{8}$$

Thus

$$\mu^S{}_{BH} = \mu_{BH}{}^{CCl_4} + RT \ln {}^0\gamma^S{}_{BH} \tag{9}$$

and

$$ {}^0\gamma^S{}_{BH} = (p/c)^S/(p/c)^0 \tag{10}$$

where $(p/c)^0$ and $(p/c)^S$ are the Henry's law constants in mm M^{-1} for the phenol in carbon tetrachloride and in the second solvent, respectively.

The mole fractions of phenolic compounds in the vapor phase over their dilute solutions in pure CCl_4 and in pure benzene at 60° were determined utilizing a modification of the transpiration technique of Andon, *et al.*,[15] and the Henry's law constants were determined

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[13] A. J. Parker (*Chem. Rev.*, **69**, 4 (1969)) has pointed out that this treatment rests on the assumption that transition states are in equilibrium with their surroundings. Although transition-state structures may change more drastically with solvent transfer than do the shapes and partition functions of real species, if the same basic mechanism is occurring it seems legitimate to discuss solvent effects on the activated complex by this formalism.

[14] A. J. Parker, *J. Chem. Soc.*, *A*, 220 (1966).

[15] R. J. L. Andon, J. D. Cox, and E. F. G. Herrington, *J. Chem. Soc.*, 3188 (1954).

Table II. Summary of Solution Properties of Phenols

A. Substituted Phenols in CCl_4 and C_6H_6

Substituent	Solvent	$^0\gamma^S_{BH}$ at 60°	$\Delta\bar{H}_S$, kcal/mol at 30°	$^0\gamma^S_{BH}$(calcd) at 30°
4-H	CCl_4	1.00	6.23 ± 0.06	1.00
	C_6H_6	0.35 ± 0.02	4.48 ± 0.04	0.27 ± 0.02
4-*t*-Bu	CCl_4	1.00	6.82 ± 0.08	1.00
	C_6H_6	0.32 ± 0.02	5.23 ± 0.06	0.28 ± 0.02
3,5-Me_2	CCl_4	1.00	7.58 ± 0.18	1.00
	C_6H_6	0.36 ± 0.02	6.30 ± 0.05	0.23 ± 0.02
3-Carboethoxy	CCl_4	1.00	8.34 ± 0.07	1.00
	C_6H_6	0.21 ± 0.01	8.17 ± 0.16	0.20 ± 0.01

B. Phenol in CCl_4–CH_3CN and CCl_4–$C_4H_8O_2$ Mixtures

Solvent[a]	$^0\gamma^S_{BH}$ 30°	$^0\gamma^S_{BH}$ 60°
1.00 CCl_4	1.00	1.00
0.170 CH_3CN	0.14 ± 0.01	0.18 ± 0.01
0.381 CH_3CN	0.081 ± 0.007	0.064 ± 0.005
0.648 CH_3CN	0.037 ± 0.003	0.047 ± 0.002
0.824 CH_3CN	0.035 ± 0.002	0.034 ± 0.002
1.00 CH_3CN	0.017 ± 0.001	0.028 ± 0.005
1.00 CCl_4	1.00	1.00
0.112 $C_4H_8O_2$	0.20 ± 0.02	0.19 ± 0.01
0.260 $C_4H_8O_2$	0.120 ± 0.005	0.082 ± 0.008
0.530 $C_4H_8O_2$	0.027 ± 0.001	0.044 ± 0.004
0.790 $C_4H_8O_2$	0.023 ± 0.001	0.030 ± 0.002
1.00 $C_4H_8O_2$	0.0087 ± 0.0006	0.015 ± 0.001

C. Phenol in CCl_4–CH_3CN and CCl_4–$C_4H_8O_2$ Mixtures

Solvent[a]	$[^0\gamma^S_{BH}]^H$ 30°	$[^0\gamma^S_{BH}]^H$ 60°
1.00 CCl_4	1.00	1.00
0.036 CH_3CN	0.32 ± 0.01	0.52 ± 0.02
0.088 CH_3CN	0.17 ± 0.01	0.28 ± 0.01
0.177 CH_3CN	0.097 ± 0.004	0.14 ± 0.01
1.00 CCl_4	1.00	1.00
0.0226 $C_4H_8O_2$	0.38 ± 0.02	0.67 ± 0.04
0.0564 $C_4H_8O_2$	0.193 ± 0.006	0.260 ± 0.004
0.1120 $C_4H_8O_2$	0.11 ± 0.01	0.16 ± 0.01

[a] The number preceding the chemical formula denotes the mole fraction of components in the solvent mixture, the remainder being CCl_4.

from plots of pressure of the phenols in the vapor phase *vs.* their molar concentration in solution. The values of $^0\gamma^S_{BH}$ at 60° calculated by means of eq 10 are summarized in Table II, part A. Also included in the table are values of the partial molar enthalpies of solution at high dilution of the phenols at 25° in pure carbon tetrachloride and pure benzene determined by solution calorimetry. Based on the assumption that the differences in the partial molar enthalpies of solution at infinite dilution in carbon tetrachloride and benzene are relatively constant in the temperature range of 25–50°, the values of $^0\gamma^S_{BH}$ at 30° were calculated and are summarized in Table II, part A. The values of $^0\gamma^S_{BH}$ for phenol in the mixed solvents carbon tetrachloride–acetonitrile and carbon tetrachloride–dioxane at 30 and 60° were calculated from the Henry's law constants and eq 10 and are presented in Table II, part B.

Specific Hydrogen Bonding Interactions. In addition to the relatively weak solvent interaction due to dipolar effects, a phenolic compound, BH, is capable of strong *specific* hydrogen-bonded interactions with the solvent. The change in the standard chemical potential on the transfer of BH from the reference solvent to the second solvent, S, may be divided into two parts,[16] *i.e.*

$$\mu^S_{BH} = \mu^0_{BH} + RT \ln [^0\gamma^S_{BH}]^* + RT \ln [^0\gamma^S_{BH}]^H \quad (11)$$

The activity coefficient $[^0\gamma^S_{BH}]^*$ accounts for *all* interactions which affect the standard chemical potential of BH *except* specific hydrogen bonding. The activity coefficient $[^0\gamma^S_{BH}]^H$ represents the effect on the change of the chemical potential due to specific hydrogen bonding interactions and is defined by the expression

$$[^0\gamma^S_{BH}]^H = \frac{[BH]}{[BH] + [BH \cdot S]} \quad (12)$$

where [BH] and [BH·S] are the concentrations of free and hydrogen-bonded phenol as determined by spectroscopic techniques.[17] Combining eq 12 and 16 we may write

$$\frac{1}{[^0\gamma^S_{BH}]^H}\frac{k^S}{k^0} = \frac{^0\gamma^S_A \cdot [^0\gamma^S_{BH}]^*}{^0\gamma^S_{X^\ddagger}} \quad (13)$$

This expression allows a *direct* estimate to be made of the solvation of the activated complex compared to the sum of the solvation of the free radical and the residual phenolic moiety.

Infrared studies of solutions of CCl_4–CH_3CN and CCl_4–$C_4H_4O_2$ containing phenol were utilized for the determination of the concentration of free and hy-

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(16) I. Prigogine and R. Defay, "Chemical Thermodynamics," D. H. Everett, Translator, Wiley, New York, N. Y., 1954, pp 409–436.

(17) Under conditions of sufficiently high dilution such that the activity coefficients of BH and S approximate unity, eq 12 may be replaced by

$$[^0\gamma^S_{BH}]^H = \frac{1}{1 + K[S]}$$

Table III. Summary of Activity Coefficient Ratios for the Reaction of 2,4,6-Tri-*tert*-butylphenoxyl with Phenols

A. Substituted Phenols in CCl_4 and C_6H_4

Substituent	Solvent[a]	${}^0\gamma^S_{A\cdot}{}^0\gamma^S_{BH}/{}^0\gamma^S_{X\ddagger}$ 30°	60°	${}^0\gamma^S_{A\cdot}/{}^0\gamma^S_{X\ddagger}$ 30°	60°
4-*t*-Bu	1.0 CCl_4	1.0	1.0	1.0	1.0
	1.0 C_6H_6	0.52 ± 0.06	0.56 ± 0.03	1.9 ± 0.4	1.8 ± 0.2
3,5-Me_2	1.0 CCl_4	1.0	1.0	1.0	1.0
	1.0 C_6H_6	0.46 ± 0.05	0.77 ± 0.09	2.0 ± 0.4	2.1 ± 0.4
4-H	1.0 CCl_4	1.0	1.0	1.0	1.0
	1.0 C_6H_6	0.48 ± 0.05	0.56 ± 0.09	1.8 ± 0.3	1.6 ± 0.4
3-Carboethoxy	1.0 CCl_4	1.0	1.0	1.0	1.0
	1.0 C_6H_6	0.33 ± 0.04	0.31 ± 0.04	1.7 ± 0.3	1.5 ± 0.3

B. Phenol in CCl_4–CH_3CN and CCl_4–$C_4H_8O_2$ Mixtures

Solvent[a]	${}^0\gamma^S_{A\cdot}{}^0\gamma^S_{BH}/{}^0\gamma^S_{X\ddagger}$ 30°	60°	${}^0\gamma^S_{A\cdot}[{}^0\gamma^S_{BH}]^*/{}^0\gamma^S_{X\ddagger}$[b] 30°	60°	${}^0\gamma^S_{A\cdot}/{}^0\gamma^S_{X\ddagger}$ 30°	60°
1.0 CCl_4	1.0	1.0	1.0	1.0		
0.036 CH_3CN	0.34 ± 0.03	0.39 ± 0.03	1.06 ± 0.12	0.75 ± 0.09		
0.088 CH_3CN	0.19 ± 0.02	0.22 ± 0.02	1.12 ± 0.19	0.79 ± 0.10		
0.170 CH_3CN	0.10 ± 0.01	0.11 ± 0.01	1.03 ± 0.15	0.79 ± 0.12	0.72 ± 0.11	0.61 ± 0.07
0.381 CH_3CN	0.052 ± 0.006	0.06 ± 0.006			0.64 ± 0.11	0.94 ± 0.16
0.648 CH_3CN	0.034 ± 0.003	0.025 ± 0.003			0.92 ± 0.15	0.53 ± 0.08
0.820 CH_3CN	0.030 ± 0.003	0.032 ± 0.003			0.86 ± 0.13	0.94 ± 0.13
1.0 CCl_4	1.0	1.0	1.0	1.0	1.0	1.0
0.0226 $C_4H_8O_2$	0.20 ± 0.02	0.32 ± 0.04	0.54 ± 0.08	0.59 ± 0.13		
0.0564 $C_4H_8O_2$	0.13 ± 0.01	0.26 ± 0.03	0.68 ± 0.07	1.00 ± 0.08		
0.1120 $C_4H_8O_2$	0.049 ± 0.004	0.089 ± 0.008	0.47 ± 0.10	0.56 ± 0.09	0.25 ± 0.05	0.47 ± 0.07
0.260 $C_4H_8O_2$	0.038 ± 0.003	0.042 ± 0.04			0.32 ± 0.04	0.51 ± 0.09
0.530 $C_4H_8O_2$	0.017 ± 0.001	0.028 ± 0.002			0.63 ± 0.06	0.64 ± 0.10

[a] Number preceding the chemical formula denotes the mole fraction of component in the solvent mixture, the remainder being CCl_4.
[b] Values of $[{}^0\gamma^S_{BH}]^H$ derived from eq 17.

drogen-bonded phenol at 30 and 60°. The infrared analysis did not allow the concentration of free phenol to be accurately determined at mole fractions of the donor solvents greater than 0.11 for dioxane and 0.17 for acetonitrile. The values of $[{}^0\gamma^S_{BH}]^H$ obtained from the study are summarized in Table II, part C.

Solution Properties of 1,3,5-Tri-*tert*-butylbenzene. In the earlier calorimetric study[12] it was observed that the enthalpy changes at 25° for the transfer of A· from a state of high dilution in carbon tetrachloride to states of high dilution in a series of solvents are equal (±0.5 kcal/mol) to the enthalpy changes for 1,3,5-tri-*tert*-butylbenzene (TTB). From those results it was suggested that TTB could serve as a good model compound for the solution properties of A·. Within the validity of this assumption the changes in the chemical potentials will be equal and

$$ {}^0\gamma^S_{A\cdot} = {}^0\gamma^S_{TTB} \tag{14} $$

Accordingly we have determined the mole fraction of TTB in the vapor phase at 60° above 0.1 *M* solution in carbon tetrachloride, benzene, and 0.65 mole fraction CH_3CN. The values of ${}^0\gamma^S_{TTB}$ calculated from eq 15 were equal to 1.0, 2.0 ± 0.1, and 6.0 ± 0.5, respectively. The fact that the values of ${}^0\gamma^S_{TTB}$ exceed unity is consistent with the observed endothermicity of the transfer measured at 25°.

Benzene as Solvent. In Table III, part A, are summarized the values of ${}^0\gamma^S_{A\cdot}{}^0\gamma^S_{BH}/{}^0\gamma^S_{X\ddagger}$ at 30 and 60° in benzene for phenol and a number of substituted phenols. Although the values of the individual rate constants, k^S and k^0, increase by a factor of 100 in the series 3-carboethoxyphenol to 4-*tert*-butylphenol their ratios, ${}^0\gamma^S_{A\cdot}{}^0\gamma^S_{BH}/{}^0\gamma_{X\ddagger}$, are relatively constant for all phenols. The values of ${}^0\gamma^S_{A\cdot}/{}^0\gamma^S_{X\ddagger}$ are also insensitive to temperature and are relatively constant with change of substituent. Since the value of ${}^0\gamma^S_{A\cdot}$ is constant we conclude that the solvation of the activated complexes in benzene relative to CCl_4 as measured by ${}^0\gamma^S_{X\ddagger}$ is *insensitive* to the remote substituent on the phenolic moiety.

Utilizing the value of ${}^0\gamma^S_{TTB}$ and eq 14 the values of ${}^0\gamma^S_{X\ddagger}$ were calculated for the substituted phenols from the ratios of ${}^0\gamma^S_{X\ddagger}/{}^0\gamma^S_{A\cdot}$. Within experimental uncertainties the values of ${}^0\gamma^S_{X\ddagger}$ are equal to *unity* for the substituted phenols. Thus, the free energies of the activated complexes are *unchanged* upon transfer from carbon tetrachloride to benzene and the rate difference in the two solvents is solely determined by the extent of solvation of the *reactant* molecules.

Mixtures of Carbon Tetrachoride–Acetonitrile and Carbon Tetrachloride–Dioxane as Solvents. The values of the ratios ${}^0\gamma^S_{A\cdot}{}^0\gamma^S_{BH}{}^0\gamma^S_{X\ddagger}$, ${}^0\gamma^S_{A\cdot}({}^0\gamma^S_{BH})^*/{}^0\gamma^S_{X\ddagger}$, and ${}^0\gamma^S_{A\cdot}/{}^0\gamma^S_{X\ddagger}$ for the reaction of phenol in the mixed solvents carbon tetrachloride–acetonitrile and carbon tetrachloride–dioxane at 30 and 60° are summarized in Table III, part B. In all cases the values of ${}^0\gamma^S_{A\cdot}{}^0\gamma^S_{BH}/{}^0\gamma^S_{X\ddagger}$ decrease with increasing concentrations of acetonitrile and dioxane. From the values of ${}^0\gamma^S_{A\cdot}({}^0\gamma^S_{BH})^*/{}^0\gamma^S_{X\ddagger}$ it is clear that virtually all of this decrease up to mole fractions of 0.17 acetonitrile and 0.11 dioxane[18] is due to the specific hydrogen bonding of phenol with added donor solvent. Moreover, the solvations of the activated complexes are accurately described by the sum of the solvations of the free radical and the residual solvation of the phenol, *i.e.*, ${}^0\gamma^S_{A\cdot}({}^0\gamma^S_{BH})^*$ is equal to ${}^0\gamma^S_{X\ddagger}$.

At the higher mole fractions of the added solvents where values of $[{}^0\gamma^S_{BH}]^H$ are not experimentally ob-

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(18) Due to the possible occurrence of reaction 6 the values of ${}^0\gamma^S_{A\cdot}{}^0\gamma^S_{BH}/{}^0\gamma^S_{X\ddagger}$ or all dioxane mixtures may be low by as much as a factor of two.

tainable but values of $^{0}\gamma^{S}_{BH}$ have been determined, the values of $^{0}\gamma^{S}_{A\cdot}/^{0}\gamma^{S}_{X\ddagger}$ have been calculated and are found to be somewhat less than unity in all cases. Utilizing the value of $^{0}\gamma^{S}_{TTB}$ and eq 12 the value of $^{0}\gamma^{S}_{X\ddagger}$ is found to be on the order of 10 in 0.54 M CH_3CN at 60°. Thus, the activated complex is less strongly solvated in this polar solvent mixture than in carbon tetrachloride.

Nature of the Activated Complex in Hydrogen Atom Transfer from Phenolic Compounds. As pointed out in the introductory statement the rates of reaction of oxy radicals with phenolic compounds are characterized by very low activation energies and by large rate effects due to the presence of remote substituents of phenolic moiety. In the following section the results of the present study of the effects of solvent upon the activated complex in regard to these two characteristics will be discussed.

The values of $^{0}\gamma^{S}_{A\cdot}(^{0}\gamma^{S}_{BH})^{*}/^{0}\gamma^{S}_{X\ddagger}$ in carbon tetrachloride–acetonitrile mixtures (*cf.* Table III, part B), were found to be unity. This result suggests that the specific hydrogen bonding interactions of the reactant phenol with solvent have been replaced in the activated complex by specific hydrogen bonding interactions with the free radical, *i.e.*, the activated complex resembles a hydrogen-bonded free radical–molecule complex. The addition of the reversible formation of hydrogen-bonded free-radical complexes to eq 2 leads to the scheme

$$BH + A\cdot \rightleftharpoons BHA\cdot \qquad (15)$$

$$BHA\cdot \rightleftharpoons BHA \qquad (16)$$

$$\cdot BHA \rightleftharpoons B\cdot + HA \qquad (17)$$

where $BHA\cdot$ and $\cdot BHA$ represent the hydrogen-bonded complexes of $A\cdot$ with BH and $B\cdot$ with AH. Under conditions such that the rate-controlling step in the formation of $B\cdot$[19] is the transfer reaction 16 and where $k_{16} \ll k_{-15}$

$$k_2 = k_{16}(k_{15}/k_{-15}) \qquad (18)$$

The observed activation enthalpy

$$\Delta H^{\ddagger}_{obsd} = \Delta H_{16}^{\ddagger} + \Delta H_{15} \qquad (19)$$

Since the heats of formation of hydrogen-bonded complexes, ΔH_{15}, are negative[20,21] the value of $\Delta H^{\ddagger}$ observed will be smaller than that predicted for a typical hydrogen atom metathasis reaction.[22]

From eq 18 the experimentally observed temperature-independent term of the Arrhenius equation, log A_2 = log $A_{16} + (\Delta S_{15}/2(3R))$. Utilizing the experimentally determined value of log A_2 equal to 6.0 ± 0.5 units[8] and a value of log A_{16} equal to 13.5 units, the value of ΔS_{15} is found to be −35 ± 3 eu. This value compares favorably with a value of −30 eu reported for the formation of the hydrogen-bonded complex of tetrahydrofuran with the hindered 2,6-di-*tert*-butylphenol.[23]

The question arises as to the effect on the values of k_2 due to changes in the values of k_{15}/k_{-15} with remote substitution on the phenol. The following argument suggests that this effect will be very small. Taft, *et al.*,[24] have recently demonstrated the existence of linear free-energy relationships for the formation of hydrogen-bonded complexes of various OH reference acids with a wide variety of proton acceptors. From their results at 20° in CCl_4 solution

$$\log\left[\frac{(K_f)_{\alpha\text{-naphthol}}}{(K_f)_{\text{phenol}}}\right] = -0.02(\log K)_{4\text{-fluorophenol}} + 0.16 \qquad (20)$$

where K_f refers to the value of equilibrium constant for the formation of the hydrogen-bonded complex with a given proton acceptor. Krelick and Weissman[4] reported a value of K_f equal to 10^{-6} M^{-1} at 25° in CCl_4 for the formation of the hydrogen-bonded complex of $A\cdot$ with AH. It seems likely that the value of K_f for 4-fluorophenol with $A\cdot$ will be larger than or equal to this value due to steric effects. Utilizing that value and eq 20, the value of $(K_{15})_{\alpha\text{-naphthol}}/(K_{15})_{\text{phenol}}$ is calculated to be smaller than or equal to 2. In contrast, the value of $(k_2)_{\alpha\text{-naphthol}}/(k_2)_{\text{phenol}}$ exceeds 100.[25]

Adopting a reaction scheme (eq 15–17) the large effect of substituent on the rates of the reaction is then due to the variation in the values of k_{16} or k_{16}/k_{-16} with substituent. In very recent work from our laboratory the differences in the heats of formation of phenoxy radicals and their parent phenols were found to decrease 6.0–8.0 kcal/mol in the series 4-methoxyphenoxyl to 3-carboethoxyphenoxyl.[6] The large effects of substituent on the observed rates of hydrogen atom transfer are then manifestations of the relative *thermodynamic* stability of $BHA\cdot$ and $\cdot BHA$.

Polar Nature of the Activated Complex. Based upon the success of empirical correlations of the rates of hydrogen atom transfer from phenols with σ^+ substituent parameters[3,11] it has been suggested that the activated complexes in such reactions possess polar character. Since the reaction of 2,4,6-tri-*tert*-butylphenoxyl with phenols manifests the largest ρ value reported for a free-radical reaction, namely −2.8,[6,11] such polar character should be at its maximum. Accordingly, if the activated complex is polar, one would predict that the free-energy content of the activated complex should decrease, *i.e.*, $^{0}\gamma^{S}_{X\ddagger}$ should decrease, on transfer to a solvent more polar than carbon tetrachloride. However, we have found that $^{0}\gamma^{S}_{X\ddagger}$ exceeds unity in such a transfer.

Of course it may be argued that due to the presence of the large hydrocarbon groups on the hindered radical the effect of polar solvents is eliminated. How-

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[19] W. P. Jencks (in "Catalysis in Chemistry and Enzymology," Vol. 1, McGraw-Hill, New York, N. Y., 1969, pp 266–267) has made the interesting suggestion that the transfer of the hydrogen atom in the complex of 2,4,6-tri-*tert*-butylphenoxyl with 2,4,6-tri-*tert*-butylphenol is faster than diffusion controlled, *i.e.*, the reaction is diffusion controlled. The large isotope effects observed in the present system[11] are not consistent with a diffusion-controlled reaction.

[20] R. W. Kreilick and S. I. Weissman[4] report a value of −2.3 ± 1.0 kcal/mol for the heat of formation of the complex of $A\cdot$ with AH.

[21] L. M. Andronov, G. E. Zarkov, and Z. K. Mainges (*Russ. J. Phys. Chem.*, 41, 590 (1967)) report data consistent with the view that peroxy radicals form a hydrogen-bonded complex with water whose heat of formation from reactants is equal to −4.8 kcal/mol.

[22] J. E. Crooks and B. H. Robinson (*Trans. Faraday Soc.*, **66**, 1436 (1970)) report that the reaction of Bromophenol Blue with 2,5-lutidine in chlorobenzene has an apparent $\Delta H^{\ddagger}$ equal to −1.4 kcal/mol. These workers suggest that the rate-controlling step is the reaction of the hydrogen-bonded intermediate whose concentration is decreased with increasing temperature.

[23] S. Singh and C. N. R. Rao, *J. Amer. Chem. Soc.*, **88**, 2142 (1966).

[24] R. W. Taft, D. Gurka, L.-Joris, P. R. Schleyer, and J. W. Rakehys, *ibid.*, **91**, 4801 (1969).

[25] The rate of reaction of α-naphthol with $A\cdot$ is too rapid to measure at room temperature with our stop-flow spectrophotometric apparatus. This observation places a lower limit value of k_2 equal to 10^3 M^{-1} sec^{-1}.

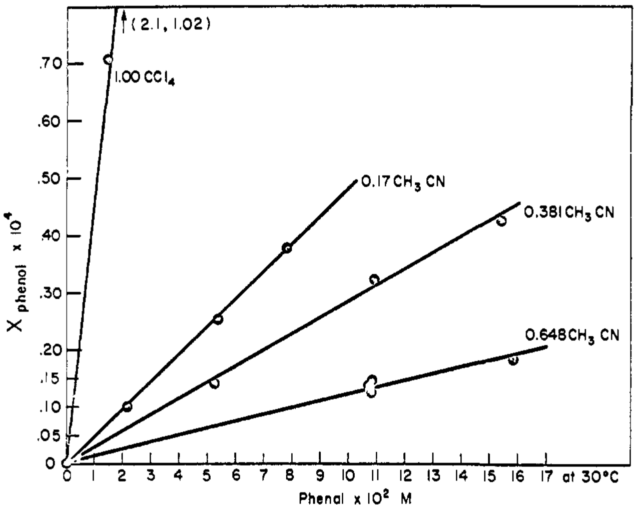
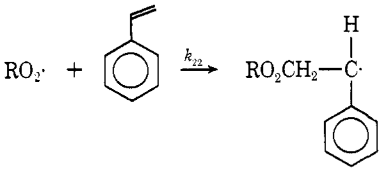


Figure 2. Plot of the mole fraction of phenol in the gas phase *vs.* phenol concentration in the liquid phase for carbon tetrachloride and mixtures of carbon tetrachloride–acetonitrile at 30°.

ever, the failure to observe a response of ${}^0\gamma^S{}_{X\ddagger}$ in the direction predicted on transfer to polar solvents is not restricted to the reaction studied in the present work. The ratios of rate constants, k_{21}/k_{22}, for the reactions

$$RO_2\cdot + BH \xrightarrow{k_{21}} RO_2H + B\cdot \qquad (21)$$


(22)

where $RO_2\cdot$ is the polystyrenyl peroxy radical and BH is 4-methylphenol have been determined by Howard and Ingold[9] as a function of solvent at 65°. Since the ρ values for reactions 21 and 22 are −1.45 and −0.3, respectively, one would predict on the basis of the polar activated complex hypothesis that the ratio $({}^0\gamma^S{}_{X\ddagger})_{22}/({}^0\gamma^S{}_{X\ddagger})_{21}$ should decrease as the solvent polarity increases. Combining eq 7 for each of these reactions and rearranging lead to the expression

$$\frac{[{}^0\gamma^S{}_{X\ddagger}]_{22}}{[{}^0\gamma^S{}_{X\ddagger}]_{21}} = \frac{(k_{21}/k_{22})_S}{(k_{21}/k_{22})_0}\frac{({}^0\gamma^S{}_{PhCHCH_2})}{({}^0\gamma^S{}_{BH})}$$

From the data of Howard and Ingold with the reference solvent carbon tetrachloride (1.7 *M* styrene) the values of $(k_{21}/k_{22})_S/(k_{21}/k_{22})_0$ are found to be equal to 0.172 in styrene and 0.035 in acetonitrile. On the basis that benzene is a good model for styrene in solution the values of ${}^0\gamma^S{}_{PhCHCH_2}$ are equal to 1.0 in styrene and 2.56 in acetonitrile.[26] Utilizing the values of ${}^0\gamma^S{}_{BH}$ determined in the present work for phenol in benzene and in acetonitrile (of Table II) the values of the ratio $({}^0\gamma^S{}_{X\ddagger})_{22}/({}^0\gamma^S{}_{X\ddagger})_{21}$ are calculated to be 1.0 in carbon tetrachloride, 0.64 in styrene, and 3.25 in acetonitrile solution. Thus, *if* the activated complexes in these hydrogen atom transfer reactions are polar in nature they clearly *fail* to respond to solvent in a manner predicted for a polar species.

Experimental Section

Materials. All phenols were obtained from commercial sources and were purified by recrystallization to yield materials whose melting points agreed with literature values.

Solvents. Spectral grade carbon tetrachloride and benzene were stored over Linde 4A molecular sieves for several days prior to use. Spectral grade acetonitrile was refluxed over and distilled from phosphorus pentoxide and then distilled from fused sodium carbonate. Spectral grade dioxane was refluxed over and distilled from sodium metal under nitrogen.

Kinetic Study. The constant temperature stop-flow apparatus reported in earlier work from our laboratory[11] was utilized for the present study.

Solution Calorimetry. The solution calorimeter and technique for the determination of the partial molal enthalpies of solutions of the phenols in carbon tetrachloride and benzene at 25° were described in reports on earlier studies from our laboratory.[12]

Henry's Law Constants. The transpiration apparatus of Andon, *et al.*,[16] was modified for the present study. The liquid traps were eliminated and the exit tube leading from the transpiration chamber and out of the batch to a vapor trap was heated 5–10° above the temperature of the bath by electric heating tape. The saturated vapor was then led through two tared traps cooled *via* acetone–carbon dioxide mixture. The first trap efficiently condensed the vapor; no gain in weight was observed in the second trap. The total amount of material transpired during the course of an experiment did not exceed 3% of the material present initially in the transpiration tower.

With benzene as solvent the condensed liquid was extracted with 0.1 *N* sodium hydroxide and the extract was analyzed for the sodium phenoxide spectrophotometrically. In the case of carbon tetrachloride, carbon tetrachloride–acetonitrile, and carbon tetrachloride–dioxane mixtures the condensed vapor was directly analyzed spectrophotometrically for phenol. The solvent blanks for the spectrophotometric analysis were obtained by means of transpiration of the solvents not containing phenol. The concentration of TBB was determined by vpc on a GC-4 Beckman chromatograph with a hydrogen flame ionization detector utilizing columns of 1.5 and 7.5% OV17 on Chromosorb Q.

The composition of the vapor for the mixtures of CCl_4–CH_3CN and CCl_4–C_4H_4O was determined by measurements of the density of the condensed transpired vapor and comparison with standard density composition curves.[27] The total vapor pressures of the solvent mixtures were determined by means of the isothermal distillation apparatus described by Tokey.[28]

In Figure 2 is presented a plot of the mole fraction of phenol in the gas phase *vs.* its mean concentration in solution for acetonitrile–carbon tetrachloride mixtures at 30°. The slopes of such plots were multiplied by the total vapor pressure of the solution to yield values of the Henry's law constants in units of mm M^{-1}. The values of these constants are summarized in Table IV.

Our values of the activity coefficient for phenol in carbon tetrachloride (solid phenol is the standard state), *f*, calculated from eq 23, where P_{phenol} and $P^0{}_{phenol}$ represent the partial pressure of

$$f = \frac{P_{phenol}}{P^0{}_{phenol}X^{liquid}{}_{phenol}} \qquad (23)$$

phenol in the vapor phase and the vapor pressure of pure phenol and $X^{liquid}{}_{phenol}$ is the mole fraction of phenol in the liquid phase, are equal to 13.8 ± 0.5 at 60° and 22.3 ± 0.6 at 30°. These values compare favorably with the values 13.6 ± 1.2 at 50° and 20.0 ± 1.6 at 24° reported by Chevalley[29] from extrapolation of her data from solutions containing high mole fractions of phenol in carbon tetrachloride.

Infrared Studies. The infrared spectra of phenol in carbon tetrachloride and in mixtures of carbon tetrachloride–acetonitrile and carbon tetrachloride–dioxane were recorded at 30 and 60° in a 0.1-cm cell by means of a Perkin-Elmer Model 521 grading spectrophotometer with a Barnes variable temperature chamber Model 104. The base-line absorptions were determined by recording the spectra of the solvent mixtures without added phenol. The concentrations

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(26) From the data of I. Brown and F. Smith, *Aust. J. Chem.*, **8**, 62 (1955), the value of ${}^{C_6H_6}\gamma^{CH_3CN}{}_{C_6H_6}$ is calculated to be 2.56 at 45°. In contrast mixtures of benzene and carbon tetrachloride manifest nearly ideal solution behavior; *i.e.*, ${}^{C_6H_6}\gamma^{CCl_4}{}_{C_6H_6} \cong 1.0$.

(27) I. Brown and F. Smith, *Aust. J. Chem.*, 7, 269 (1954).

(28) S. A. Tokey, *J. Chem. Educ.*, 25, 352 (1958).

(29) J. Chevalley, *C. R. Acad. Sci.*, 510 (1960).

Table IV. Summary of Henry's Law Constants

A. Phenols

Solvent[a]	Substituent	Solvent vapor pressure, mm		10^3[Phenol], M	P/c, mm M^{-1}	
		30°	60°		30°	60°
CCl_4	4-*t*-Bu		439	8.4–16.8		0.33 ± 0.01
C_6H_6			392	34.0–46.0		0.105 ± 0.003
CCl_4	3,5-Me_2		439	6.1–12.2		0.99 ± 0.02
C_6H_6			392	18.0–28.0		0.36 ± 0.01
CCl_4	4-H		439	8.4–12.7		5.6 ± 0.2
C_6H_6			392	5.8–11.6		1.96 ± 0.07
CCl_4	3-Carboethoxy		439	8.0–11.0		0.16 ± 0.01
C_6H_6			392	50.0–70.0		0.034 ± 0.002
CCl_4	4-H	139.6	439.0	8.4–12.7	0.70 ± 0.02	5.6 ± 0.2
0.170 CH_3CN		207.3	627.2	16–53	0.098 ± 0.004	1.004 ± 0.002
0.381 CH_3CN		206.3	639.0	26–56	0.057 ± 0.003	0.36 ± 0.02
0.648 CH_3CN		216.7	639.7	32–54	0.026 ± 0.002	0.264 ± 0.003
0.824 CH_3CN		210.5	615.0	56–108	0.0245 ± 0.005	0.199 ± 0.005
1.00 CH_3CN		110.6	368.0	32–106	0.012 ± 0.001	0.16 ± 0.02
0.112 $C_4H_8O_2$	4-H	146.9	448.3	36–55	0.14 ± 0.01	1.05 ± 0.01
0.260 $C_4H_8O_2$		146.6	428.3	34–54	0.084 ± 0.01	0.46 ± 0.03
0.530 $C_4H_8O_2$		129.2	399.5	54–153	0.0190 ± 0.0005	0.245 ± 0.013
0.790 $C_4H_8O_2$		111.4	371.3	56–107	0.0163 ± 0.0002	0.17 ± 0.01
1.00 $C_4H_8O_2$		51.0	185.0	53–102	0.0061 ± 0.0003	0.082 ± 0.005

B. 1,3,5-Tri-*tert*-butylbenzene (TTB) at 60°

Solvent[a]	P, mm	Concn, M	$p/c \times 10^3$, mm M^{-1}
CCl_4	439.0	0.1	7.3 ± 6.2
C_6H_6	392.0	0.1	14.0 ± 0.4
0.648 CH_3CN	639.7	0.1	44.0 ± 2.0

[a] The number preceding the chemical formula denotes the mole fraction of component in the solvent mixture, the remainder being CCl_4.

of phenol were sufficiently dilute, less than or equal to 2.5×10^{-2} M, so that only the absorption of the monomeric phenol O–H stretching with a maximum at 3605 ± 5 cm^{-1} was observed in carbon tetrachloride solution. Upon the addition of the donor solvents additional broad absorption bands due to complexed phenol OH stretching appeared with maxima at 3470 ± 10 cm^{-1} for dioxane and 3450 ± 10 cm^{-1} for acetonitriles. The positions of the maxima corresponding to free OH did not change upon variation of the mole fraction of donor solvent up to 0.112 for dioxane and 0.170 for acetonitrile.

The method of Ramsey[30] was utilized to obtain the integrated absorption peaks at 3605 ± 5 cm^{-1} corresponding to the concentration of uncomplexed phenol. The ratio of the integrated absorption in the presence of the added donor solvent to that in pure carbon tetrachloride was equated[31] to the ratio of free noncomplexed phenol to total phenol, *i.e.*, the value of $[{}^0\gamma^{S}_{BH}]^{H}$ from eq 12.

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[30] D. A. Ramsey, *J. Amer. Chem. Soc.*, 74, 72 (1952).

[31] It is assumed that the oscillator strength of the free OH stretching band is independent of solvent.