Mayer[16] is thus greater than unity, the ratio of the reduced masses of the heavy and light molecules along their coördinates of decomposition is greater than unity, and the product of these two quantities (which is $k_1/2k_3$) is greater than 1.02 and temperature dependent.

If it is assumed that the activated complex differs from the normal molecule only in the state of binding between carbon atoms, and that this state is one where one C–C bond is stretched and weakened while the other is shortened and strengthened

$$\underset{\text{normal molecule}}{\mathrm{C{-}C{-}C}} \qquad \longrightarrow \qquad \underset{\text{activated complex}}{\mathrm{C}\underset{\cdots}{-}\mathrm{C}\cdots\mathrm{C}}$$

the result calculated for $k_1/2k_3$ is not sensibly different from that obtained from the Bigeleisen model. (This kind of activated complex is related to several suggested earlier by various authors for somewhat different purposes.[14,17,18]) However, a calculation for $k_1/2k_4$ (and therefore k_4/k_3) based on this new model yields very different results. The ratio of the reaction coördinate reduced masses is slightly greater than unity[19]; but the free energy factor is smaller than 1.000, approaching unity as a limit with increasing temperature. The latter conclusion is based upon the facts that in equations 1 and 4 the disjunct carbon atom is C^{12} and the vibration frequency which is reduced or lost is little affected by isotopic substitution at the antepenultimate carbon, while the frequency of the stretching vibration between the carbon atoms which remain joined is increased (an increment of 200–300 cm.$^{-1}$ yields results of the correct magnitude) and *is* markedly influenced by that isotopic substitution. The product of the reduced mass and free energy factors would be expected to be somewhat smaller than 1.000 at ordinary temperatures, and would increase with rising temperature to the value of the reduced mass factor. This is the behavior of $k_1/2k_4$ as calculated above from the experimental results.

Acknowledgments.—This research was supported by the A.E.C. We are indebted to Mrs. R. W. Hill, who performed the mass spectrometer analyses.

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[16] J. Bigeleisen and M. G. Mayer, *J. Chem. Phys.*, **15**, 261 (1947).

[17] G. A. Ropp and V. F. Raaen, THIS JOURNAL, **74**, 4992 (1952).

[18] J. Bigeleisen, *Can. J. Chem.*, **30**, 443 (1952).

[19] NOTE ADDED DURING REVIEW: In making this approximate calculation of the ratio of reaction coördinate reduced masses across the bond being weakened, we assume that the limiting effect of bond formation between the two carbon atoms which remain joined in the decomposing malonic acid molecule is such that they may be taken as a single particle. Such a computation yields the value 1.0067 for the temperature independent factor (ratio of reaction coördinate reduced masses) in $k_1/2k_4$, a value in agreement with the results shown in Fig. 2.

The paper by J. Bigeleisen and M. Wolfsberg, *J. Chem. Phys.*, **21**, 1972 (1953), which appeared after the submission of this manuscript, contains equations which permit precise evaluation of temperature independent factors. Their equation 10 relates such factors to values of a reaction coördinate parameter p; for all values of p greater than zero, the temperature independent factor in $k_1/2k_4$ is found to be greater than unity. For the data plotted in Fig. 2, p is approximately 0.2.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE INSTITUTE OF SCIENCE AND TECHNOLOGY, UNIVERSITY OF TOKYO]

Determinations of the Energy and the Entropy Change Due to Hydrogen Bonding by the Use of the Near Ultraviolet Absorption—the Effect of the Chlorine Atom on the Proton-donating and the Proton-accepting Powers

BY SABURO NAGAKURA

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Measurements of near ultraviolet absorption were made with ternary systems containing small amounts of the proton donor and the acceptor in an inert solvent such as *n*-heptane. Phenol and its chloro derivatives were used as the proton donor, and methyl, ethyl acetate and their chloro derivatives as the proton acceptor. By use of the results obtained by absorption measurements, energies and entropy changes due to hydrogen bonding were determined exactly with several sets of the proton donor and the acceptor. Consequently, the following two facts are found to be certain: first, the energy and the entropy change due to hydrogen bonding in naphtha and *n*-heptane are larger than in carbon tetrachloride. Second, the substitution of a chlorine atom for a hydrogen atom increases the proton-donating ability of phenol, whereas, it decreases the proton-accepting power of methyl or ethyl acetate. This fact can be explained on the basis of the inductive effect of the chlorine atom.

Introduction

In the previous paper,[1] the effect of hydrogen bonding on the near ultraviolet absorption spectra was investigated with phenol and aniline. Consequently it was found that the absorption band due to the hydrogen bonded molecule appears distinctly in the longer wave length side than that due to the free molecule. Furthermore, it was pointed out that the energy of hydrogen bonding between phenol and several proton acceptors can be determined by the aid of the near ultraviolet absorption spectrum.

The present investigation is undertaken to determine exactly the energy and the entropy change due to hydrogen bonding between phenol or its chloro derivatives and several proton acceptors. Moreover, using the experimental result, the influence of the solvent on the hydrogen bonding and the effect of the chlorine atom on the proton-donating and the proton-accepting powers will be discussed.

Experimental

Materials.—Phenol and *o*-, *m*-, *p*-chlorophenol are used as the proton donor. Phenol is the same as used in the previous experiment.[1] *o*-Chlorophenol was purified by fractional distillation, b.p. 68° (19 mm.); *m*- and *p*-chlorophenols were purified by repeating the fractional recrystallization. Their melting points are 32.5° and 42.5–

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[1] S. Nagakura and H. Baba, THIS JOURNAL, **74**, 5693 (1952).

43.5°, respectively. Methyl trichloroacetate and ethyl trichloroacetate used as the proton acceptor were presented by Dr. Kuratani.[2]

Ethyl acetate, methyl acetate and methyl monochloroacetate were purified by repeating the distillation. Their boiling points are 76.1–77.0°, 56.8–57.1° and 128.9–129.5°, respectively. Naphtha (b.p. 50–80°) and *n*-heptane used as the solvent were purified by the method described in the previous paper.[3] Carbon tetrachloride was purified by the method of Williams and Krchma.[4]

Method.—Absorption spectra were measured by a Beckman quartz spectrophotometer model DU, using a light path of 10 mm. The temperature of the cell compartment was controlled by the thermospacer and the cell with the cap was used to prevent the solvent from distilling during the measurement.

When the absorption band of the hydrogen bonded proton donor molecule is largely different from that of the free molecule, the equilibrium constant (K) between the proton acceptor and the proton donor in an inert solvent such as *n*-heptane, can be determined by measuring absorbance values of three solutions which are equal in the concentration of the proton donor but different in that of the proton acceptor; namely, whose proton donor concentrations are all equal to C_p, but whose proton acceptor concentrations are zero, C_A and C'_A. Of course, absorbance measurements of these solutions should be made at a constant temperature and a constant wave length. Then the equilibrium constant K can be determined by the equation[5]

$$K = \frac{C_{AP}}{(C_A - C_{AP})(C_p - C_{AP})} = \frac{C'_{AP}}{(C'_A - C'_{AP})(C_p - C'_{AP})} \doteqdot \frac{C_A(\kappa_0 - \kappa') + C'_A(\kappa - \kappa_0)}{C_A C'_A(\kappa' - \kappa)}$$

where κ_0, κ and κ' are absorbance values measured with solutions whose proton acceptor concentrations 0, C_A and C'_A, respectively, and C_{AP} and C'_{AP} represent the concentration of the hydrogen bonded proton donor molecule. The above equation should be adaptable only when the following three conditions are fulfilled: first, the concentration of the hydrogen bonded proton-donating molecule is very much smaller than that of the proton acceptor; second, the absorption spectra of both the hydrogen bonded and the free proton donor molecules obey Beer's law; and third, the absorbance of the proton acceptor is negligibly small in the wave length region used for the determination of K. The first and the second conditions are fulfilled in the present experiment where the concentration of the proton donor is about 10^{-4} mole/l., and the third condition is also satisfied, because the absorbance measurements are made in the wave length region longer than 2600 Å.

Results.—Absorption spectra of typical sets of the proton acceptor and the donor are shown in Figs. 1–2. It is seen from these figures that the absorption band due to the hydrogen bonded proton donor molecule appears distinctly in the longer wave length side than that due to the free molecule. Therefore, the equilibrium constant K can be determined by the above-mentioned method. The experimental results are given in Table I. In this table the value of K measured in the wave length λ is designated by K_λ. In the case where the equilibrium constant was measured in two or three different wave lengths, the mean value of them is represented by K_M.

TABLE I

VALUES OF EQUILIBRIUM CONSTANTS (K) BETWEEN PROTON ACCEPTORS AND PROTON DONORS

(A) Phenol–ethyl acetate in naphtha

Temp., °C.	C_A, mole/l.	C'_A, mole/l.	K_{280}	K_{278}	K_{273}	K_M	ΔF, kcal./mole[a]
2.0	0.0505	0.1010	35.9	33.0	33.2	34.0	−1.93
2.0	.0505	.2020	38.0	32.2	35.6	35.3	−1.95
6.0	.0494	.2960	32.4	27.0	31.3	30.2	−1.89
20.5	.0494	.2960	18.4	18.8	18.3	18.5	−1.70
30.0	.0505	.2020	12.0	12.1	14.2	12.8	−1.53
30.0	.1010	.4040	11.9	13.8	11.9	12.5	−1.52
40.0	.1010	.4040	10.4	10.0	10.0	10.1	−1.44
(B) Phenol–methyl monochloroacetate in naphtha							
15.0	0.2002	0.4004	6.2	6.1	6.6	6.3	−1.05
25.0	.2002	.4004	4.4	4.6	5.0	4.7	−0.92
35.0	.2002	.4004	3.3	4.7	3.4	3.8	−0.82
45.0	.2002	.4004	2.4	3.2	2.4	2.7	−0.63
(C) Phenol–methyl trichloroacetate in naphtha							
20.0	0.1998	0.3996	2.4	1.9	4.3	2.9	−0.62
(D) Phenol–ethyl trichloroacetate in naphtha							
2.0	0.0354	0.1415	2.3	2.7	5.2	3.4	−0.67

(E) Phenol–ethyl acetate in carbon tetrachloride

Temp., °C.	C_A, mole/l.	C'_A, mole/l.	K_{283}	K_{276}	K_M	ΔF, kcal./mole
20.0	0.0471	0.1885	8.8	9.6	9.2	−1.29
30.0	.0471	.1885	7.6	6.5	7.1	−1.18
45.0	.0471	.1885	5.2	4.3	4.7	−0.99

(F) Phenol–methyl acetate in *n*-heptane

Temp., °C.	C_A, mole/l.	C'_A, mole/l.	K_{260}	ΔF, kcal./mole
15.0	0.0950	0.1900	15.7	−1.58
25.0	.0950	.1900	11.5	−1.44
35.0	.0950	.1900	8.6	−1.32

(G) *o*-Chlorophenol–methyl acetate in *n*-heptane

Temp., °C.	C_A, mole/l.	C'_A, mole/l.	K_{284}	ΔF, kcal./mole
5.0	0.1927	0.3854	2.0	−0.38
15.0	.1927	.3854	1.8	− .34
25.0	.1927	.3854	1.6	− .28
35.0	.1927	.3854	1.6	− .29

(H) *p*-Chlorophenol–methyl acetate in *n*-heptane

Temp., °C.	C_A, mole/l.	C'_A, mole/l.	K_{286}	K_{292}	K_M	ΔF, kcal./mole
5.0	0.0482	0.0964	39.8	41.2	40.5	−2.04
15.0	.0482	.0964	23.4	28.2	25.8	−1.86
25.0	.0482	.0964	16.9	18.3	17.6	−1.70
35.0	.0482	.0964	11.6	13.0	12.3	−1.53

(I) *m*-Chlorophenol–methyl acetate in *n*-heptane

Temp., °C.	C_A, mole/l.	C'_A, mole/l.	K_{285}	K_{277}	K_M	ΔF, kcal./mole
15.0	0.0950	0.1900	34.6	38.4	36.5	−2.06
25.0	.0950	.1900	25.2	23.3	24.3	−1.89
35.0	.0950	.1900	17.5	17.6	17.6	−1.75

[a] ΔF represents the free energy difference due to hydrogen bonding and can be obtained by use of the equation $\Delta F = -RT \ln K$.

As is well known, the hydrogen bonding energy ΔH can be determined by measuring the temperature dependence of the equilibrium constant. When $R \ln K$ is plotted as a function of $1/T$, the points so obtained are found to lie very closely on the straight

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[2] The author wishes to express his sincere thanks to Dr. Kuratani for his kindness in giving these materials and in detecting the purity of some materials by infrared absorption measurements.

[3] S. Nagakura, *Bull. Chem. Soc. Japan*, **25**, 164 (1952).

[4] J. W. Williams and I. J. Krchma, THIS JOURNAL, **48**, 1888 (1926).

[5] According to this equation, it is possible to calculate the equilibrium constant without using the absolute value of the proton donor concentration and the molecular extinction coefficients for the free and the hydrogen bonded proton donors. Therefore it is very useful for the exact determination of the equilibrium constant.

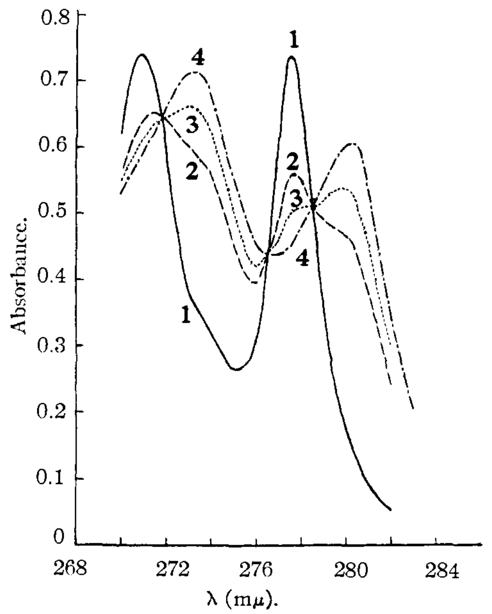

Fig. 1.—Ultraviolet absorption spectrum of phenol at 6°: curve 1, in naphtha; curves 2, 3 and 4, in mixed solvents of naphtha and ethyl acetate. The concentrations of ethyl acetate in these solvents are 0.0494, 0.0987 and 0.2960 mole/l., respectively. The concentration of phenol is 3.00 × 10^{-4} mole/l.

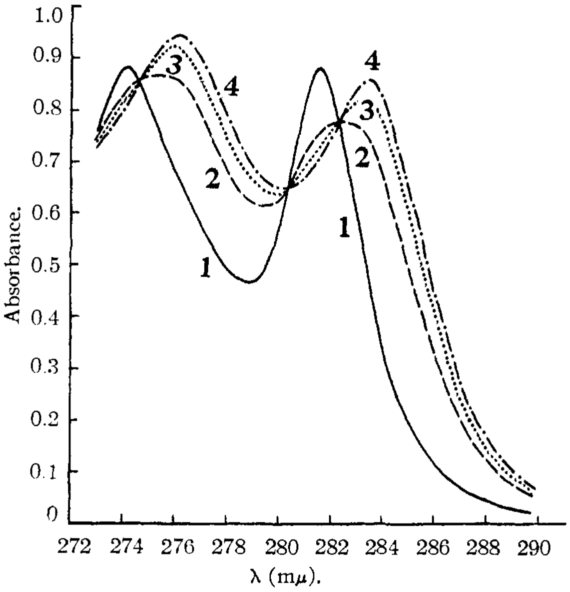

Fig. 2.—Ultraviolet absorption spectrum of *m*-chlorophenol at 15°: curve 1, in *n*-heptane; curves 2, 3 and 4, in mixed solvents of *n*-heptane and methyl acetate. The concentrations of methyl acetate in these solvents are 0.0475, 0.0950 and 0.1900 mole/l., respectively. The concentration of *m*-chlorophenol is 3.64 × 10^{-4} mole/l.

line fitted to them by the method of least squares (*cf.*, Fig. 3). From this straight line, ΔH and ΔS can be determined. The values thus obtained are given in Table II.

Discussion of Results

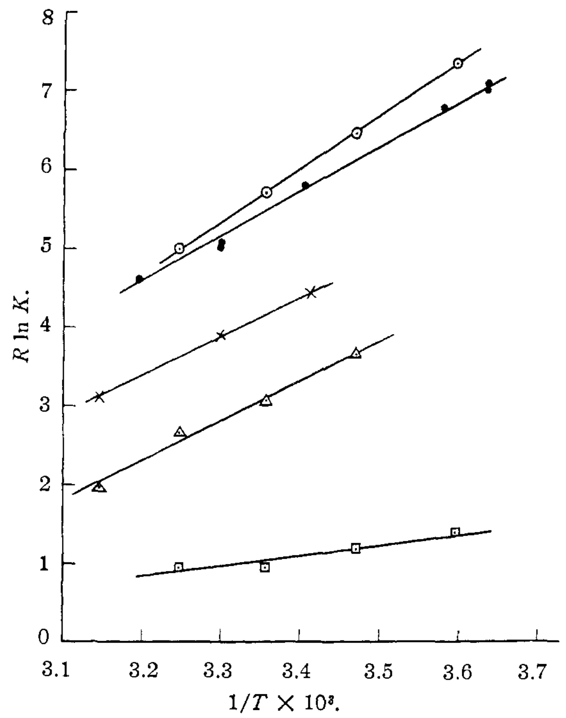

Fig. 3.—R ln K *vs.* $1/T$: ● phenol–ethyl acetate in naphtha; ×, phenol–ethyl acetate in carbon tetrachloride; △, phenol–methyl monochloroacetate in naphtha; ⊙, *p*-chlorophenol–methyl acetate in *n*-heptane; ⊡, *o*-chlorophenol–methyl acetate in *n*-heptane.

TABLE II

VALUES OF HYDROGEN BONDING ENERGIES ($|\Delta H|$) AND ENTROPY CHANGES ($|\Delta S|$)

System	ΔH, kcal./mole	ΔS, e.u.
Phenol–ethyl acetate in N.[a]	−5.7 ± (0.2)	−13.7 ± (0.6)
Phenol–methyl monochloroacetate in N.	−5.0 ± (0.4)	−13.7 ± (1.2)
Phenol–methyl trichloroacetate in N.	−4.6	−13.7 (estimated)[b]
Phenol–ethyl trichloroacetate in N.	−4.4	−13.7 (estimated)[b]
Phenol–ethyl acetate in C.T.	−4.8 ± (0.1)	−11.9 ± (0.3)
Phenol–methyl acetate in H.	−5.3 ± (0.1)	−12.8 ± (0.2)
p-Chlorophenol–methyl acetate in H.	−6.7 ± (0.1)	−16.9 ± (0.4)
m-Chlorophenol–methyl acetate in H.	−6.5 ± (0.3)	−15.2 ± (1.0)
o-Chlorophenol–methyl acetate in H.	−1.4 ± (0.3)	− 3.5 ± (1.0)

[a] In this table, naphtha, carbon tetrachloride and *n*-heptane used as the solvent are abbreviated to N., C.T. and H., respectively. [b] ΔH values of these two systems are obtained under the approximation that the entropy change of them is equal to that of the system phenol–methyl monochloroacetate.

The Effect of Solvents on the Hydrogen Bonding Energy and the Entropy Change.—It is seen from Table II that the energy of the hydrogen bonding between phenol and acetate esters is larger in naphtha or *n*-heptane than in carbon tetrachloride. The similar tendency was also observed with the hydrogen bonding between phenol and dioxane.[6] Although the reason for this is not yet conclusive, two reasons may be taken into consideration. One of them is that the electrostatic binding energy between the proton donor and the proton acceptor may probably decrease with the dielectric constant of the solvent. As the

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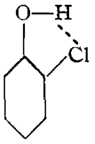
(6) S. Nagakura, *J. Chem. Soc. Japan*, **74**, 153 (1953).

dielectric constant of carbon tetrachloride is evidently larger than that of naphtha or of *n*-heptane, so the above-mentioned solvent effect can be explained from this point of view. Furthermore, this may be supported by the current belief that the hydrogen bonds are considerably electrostatic in character.[7] The other reason is that there may exist a special interaction[8] between phenol and carbon tetrachloride, so the stabilization energy due to the formation of the hydrogen bonding become smaller in carbon tetrachloride. According to the latter, it may be easy to explain the facts that the absorption band of phenol is very broad in carbon tetrachloride as compared with that in naphtha,[6] and that the entropy change is also smaller in carbon tetrachloride than in naphtha (*cf.* Table II). However, it now seems difficult to determine which is the more predominant between the above-mentioned two reasons.

The Effect of the Substitution of the Chlorine Atom on the Proton-accepting Power of the Acetate Ester and the Proton-donating Power of Phenol.—It is seen from Table II that the proton-accepting power decreases in the order of acetate > monochloroacetate > trichloroacetate. Therefore, substitution of the chlorine atom for the hydrogen atom seems to have the tendency to weaken the proton-accepting power of the acetate ester. On the other hand, its effect on the proton-donating power of phenol seems to be somewhat more complex, because $|\Delta H|$'s of *m*- and *p*-chlorophenols are evidently larger than those of phenol itself while the reverse is the case with *o*-chlorophenol. As is well known,[9] however, in the latter molecule the intramolecular hydrogen bonding such as



can be formed and consequently it will be almost impossible to form the hydrogen bond with other molecules. So this molecule may be regarded as the special example unsuitable for the determination of the effect of the chlorine atom on the proton-donating power of phenol. Therefore it seems reasonable to consider that substitution of a chlorine atom for a hydrogen atom in the benzene ring has generally a tendency to increase the proton-donating power of phenol.

From the above-mentioned facts, it becomes certain that the substitution of chlorine usually increases the proton-donating power of phenol whereas it decreases the proton-accepting power of acetate. This fact may be due to the large electron-attracting power of the chlorine atom, because it may be expected that the reduction of the effective negative charge on the oxygen atom may increase its proton-donating ability and decrease its proton-attracting one. It seems interesting in this connection that the dimer formation ability of the carboxylic acid cannot be affected by the substitution of halogen for hydrogen.[10] According to the measurement made by Lundin, *et al.*, the heat of dimerization of acetic acid and trifluoroacetic acid are 13.8 and 14.0 kcal./mole, respectively. From the present author's viewpoint, this fact may be explained as follows: in the dimerization of a carboxylic acid, the two groups of a molecule take part in hydrogen bonding; *viz.*, the C=O group acts as the proton acceptor and the O–H group as the proton donor. The substitution of halogen for hydrogen may increase the proton-donating ability of the latter group but decrease the proton-accepting ability of the former one. Therefore it may be expected that the above two effects can compensate each other.

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[7] N. D. Coggeshall, *J. Chem. Phys.*, **18**, 978 (1950).

[8] This special interaction may be very weak hydrogen bonding such as O–H....Cl.

[9] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940, p. 322.

[10] R. E. Lundin, F. E. Harris and L. K. Nash, THIS JOURNAL, **74**, 4654 (1952).