alyses performed by Mr. R. H. Roberts have made parts of this study possible.

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DAYTON, OHIO

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Aromatic Compounds as Donor Molecules in Hydrogen Bonding[1]

BY MILTON TAMRES

RECEIVED JULY 20, 1951

The ability of several substituted benzenes and naphthalenes to behave as donor molecules in hydrogen bonding was investigated by a calorimetric and a spectroscopic method. The study shows that aromatic compounds are capable of forming hydrogen bonds with such molecules as chloroform and methanol-*d*. The association between an aromatic compound and chloroform occurs in a one to one ratio. Halogen substitution in the benzene ring decreases the electron donor ability of aromatic compounds toward hydrogen bonding, whereas methyl substitution increases the electron donor ability. There is some indication, however, that excessive methyl substitution may produce steric interference in the formation of hydrogen bonds with chloroform and with bromoform.

Introduction

The postulation that the aromatic nucleus is an electron donor[2] and, therefore, a Lewis base has received considerable support in recent years. A number of techniques have been developed to measure the relative basicities of aromatic compounds by determining the extent to which they associate with acids. Among the acids reported in the literature may be listed iodine,[3] silver ion,[4] aluminum bromide,[5] hydrogen chloride[6a] and fluoboric acid.[6b] Of these only the last two are proton acids, and they are strong acids.

Numerous studies have shown that weak proton acids can form hydrogen bonds with electron donor molecules. However, the donor molecules most frequently cited are those which contain a fluorine, oxygen or nitrogen atom. Recently, Jones and Badger[7] have reported that aromatic hydrocarbons behave as donor molecules toward methanol. Also, observations in this Laboratory of similar interactions between aromatic compounds and methanol-*d* were pointed out in a previous publication.[8] The present paper reports a more extensive study based upon these initial observations.

Two methods were employed in this investigation. One was a calorimetric method to determine the heats of mixing of aromatic compounds with chloroform, with bromoform and with carbon tetrachloride. The second was a spectroscopic method to determine the effect of aromatic compounds on the frequency shift of the OD band in the infrared spectrum of methanol-*d* solutions. The choice of these techniques, and in particular the use of methanol-*d* rather than methanol was prompted by the fact that there exist in the literature[8-10] data for similar hydrogen bonding studies with other electron donors. By employing the same techniques, then, there is an opportunity for direct comparison of the electron donor ability of aromatic compounds with some of the more well known donor substances.

Experimental

Materials.—The refractive index of each liquid at 20° is given in parentheses for the sodium D line. Measurements were made with a Bausch and Lomb Abbe-56 refractometer.

Chloroform and carbon tetrachloride were purified as specified by Fieser[11]: chloroform (1.4660); carbon tetrachloride (1.4602).

With the exception of benzene, toluene, *o*-xylene and *o*-chlorotoluene which were from the Allied Chemical and Dye Company, all the aromatic compounds were Eastman Kodak Company chemicals. These were dried for several days over calcium chloride and distilled over sodium using a six-inch column with a heated jacket and packed with glass helices. The fraction distilling over a narrow temperature range was taken, the first and last fractions being discarded: 1,2-dichlorobenzene (1.5510); chlorobenzene (1.5246); bromobenzene (1.5588); α-chloronaphthalene (1.6326); *o*-chlorotoluene (1.5255); benzene (1.5009); toluene (1.4968); α-methylnaphthalene (1.6108) (no noticeable change in refractive index after several redistillations); *m*-xylene (1.4964); *p*-xylene (1.4956); *o*-xylene (1.5049); mesitylene (1.4962).

Methanol-*d*, b.p. 64.5–65°, and bromoform (1.5969 at 20.9°) were kindly supplied by Dr. Scott Searles of Northwestern University.

Apparatus and Method.—The apparatus and method employed for the heat of mixing determinations[8] were essentially those described by Zellhoefer and Copley.[12] For the aromatic compounds which gave the highest heats of mixing with chloroform, namely, mesitylene and the xylenes, duplicate determinations were made at 50 mole % chloroform. The results indicate that the values reported are reproducible to within ±4 cal. per mole of solution.

Infrared spectra were determined[8] with a Perkin–Elmer Model 12B spectrometer equipped with a lithium fluoride prism, and calibration of the instrument was made on the rotational fine structure of hydrogen bromide using the grating data of Plyler and Barker.[13]

The spectroscopic method has been described by Gordy and consists of comparing the position of the monomeric OD band in a 0.1 molar solution of methanol-*d* in a reference solvent with the OD band in 1.0 molar solutions of methanol-*d* in various electron donor solvents. Gordy used benzene as his reference solvent, whereas carbon tetrachloride was the reference solvent chosen for this investigation. An example of the infrared spectra obtained is shown in Fig. 1.

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[1] Presented before the Division of Physical and Inorganic Chemistry at the 119th Meeting of the American Chemical Society, Cleveland, Ohio, April, 1951.

[2] S. Winstein and H. J. Lucas, THIS JOURNAL, **60**, 836 (1939).

[3] (a) H. A. Benesi and J. H. Hildebrand, *ibid.*, **71**, 2703 (1949); (b) *ibid.*, **70**, 2832 (1948).

[4] (a) I. J. Andrews and R. M. Keefer, *ibid.*, **72**, 5034 (1950); (b) *ibid.*, **72**, 3113 (1950); (c) *ibid.*, **71**, 3644 (1949).

[5] R. E. Van Dyke, *ibid.*, **72**, 3619 (1950).

[6] (a) H. C. Brown and J. Brady, *ibid.*, **71**, 3573 (1949); (b) D. A. McCaulay and A. P. Lien, *ibid.*, **73**, 2013 (1951).

[7] L. H. Jones and R. M. Badger, *ibid.*, **73**, 3132 (1951).

[8] S. Searles and M. Tamres, *ibid.*, **73**, 3704 (1951).

[9] W. Gordy, *J. Chem. Phys.*, **7**, 93 (1939).

[10] W. Gordy and S. C. Stanford, *ibid.*, **8**, 170 (1940).

[11] L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., Boston, Mass., 1935, pp. 308, 309.

[12] G. F. Zellhoefer and M. J. Copley, THIS JOURNAL, **60**, 1343 (1938).

[13] E. K. Plyler and E. F. Barker, *Phys. Rev.*, **44**, 984 (1933).

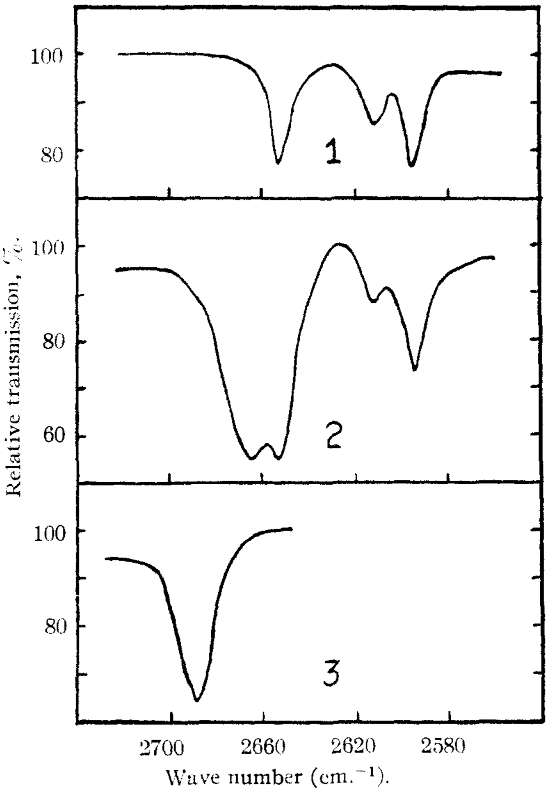

Fig. 1.—Infrared spectra at 25° of (1) benzene (cell thickness = 0.16 mm.); (2) 1.0 molar solution of methanol-*d* in benzene (cell thickness = 0.16 mm.); (3) 1.0 molar solution of methanol-*d* in carbon tetrachloride (cell thickness = 0.32 mm.). [The slit width was not constant for all spectroscopic observations; thus the results are expressed in terms of relative transmission. Each curve in this graph was obtained by comparing the observed spectrum with the smoothest curve that could be drawn for each spectrum to represent 100% transmission. This seems sufficient to indicate the position and sharpness of the OD bands.]

It may be seen that the OD band is fairly narrow and the center of the band is quite pronounced. As a check on the method, several of the spectroscopic observations were duplicated at different times and the results of the OD shifts were found to be reproducible to approximately ±1 cm.$^{-1}$. However, since solvent interaction may shift the apparent band maximum in some cases, the uncertainty of locating the true band center is undoubtedly greater than the experimental reproducibility.

Results and Discussion

Inductive Effects.—The calorimetric and spectroscopic data are given in Table I. A comparison of the heats of mixing of the aromatic compounds with chloroform and with carbon tetrachloride indicates that the aromatic ring does behave as an electron donor in forming hydrogen bonds with relatively weak proton acids. Although the heats of mixing and OD shifts obtained are comparatively small, they are nevertheless sufficiently pronounced to distinguish among the basicities of the aromatic compounds, the magnitude of the heat of mixing or of the OD shift serving as a measure of the electron donor ability. As may be seen from the data, neither method is sufficiently sensitive to distinguish among the basicities of the three xylene isomers.

TABLE I

HEATS OF MIXING PER MOLE OF SOLUTION AT 25° OF EQUIMOLECULAR AMOUNTS OF AROMATIC COMPOUNDS WITH CHLOROFORM AND WITH CARBON TETRACHLORIDE, AND THE POSITIONS OF THE OD BAND OF METHANOL-*d* IN AROMATIC COMPOUND SOLUTIONS 1.0 MOLAR IN METHANOL-*d*

	Compound	Heat of mixing with chloroform, cal./mole	Heat of mixing with carbon tetrachloride, cal./mole	Position of OD band, cm.$^{-1}$	Shift of OD band, cm.$^{-1}$
	Carbon tetrachloride			2689	Ref.
1	1,2-Dichlorobenzene	0	−69	2676	13
2	Chlorobenzene	29	−34	2668	21
3	Bromobenzene	34	−38	2669	20
4	α-Chloronaphthalene	37	−69	2670	19
5	*o*-Chlorotoluene	37	−27	2670	19
6	Benzene	90	−38	2665	24
7	Toluene	157	− 3	2663	26
8	α-Methylnaphthalene	(160)[a]	..	2661	28
9	*m*-Xylene	202	− 3	2660	29
10	*o*-Xylene	203	−21	2659	30
11	*o*-Xylene	207	− 8	2660	29
12	Mesitylene	216	−35	2655	34

[a] A reaction seemed to occur which resulted in the formation of a precipitate. The value reported was not reproducible and is to be taken as a probable upper limit.

As pointed out in a previous paper,[8] the experimental data cannot be attributed solely to the formation of hydrogen bonds. Other factors[7] are of importance, but it is not unreasonable to assume that a considerable part of the observed interactions may be attributed to hydrogen bonding. Consequently, some correlation between the calorimetric and the spectroscopic data is to be expected. This is borne out in Fig. 2 by the straight line drawn using the method of least squares. In general, an aromatic compound which gives a high heat of mixing with chloroform will also produce a large shift of the OD band of methanol-*d*. (It is possible that, for certain aromatic compounds, steric factors may offset this generalization. See discussion of Steric Effects.)

Substitution of a methyl group for a hydrogen atom in the benzene ring increases the electron donor ability of aromatic compounds toward hydrogen bonding, whereas substitution of a chlorine or bromine atom decreases the electron donor ability. This is in agreement with the effects on basicity reported by other investigators.[3,4,6,7] Thus the strengths as bases are in the order xylene > toluene > benzene > chlorobenzene >1,2-dichlorobenzene. However, from a comparison in Table I of the spectroscopic and calorimetric data for *o*-chlorotoluene with the data for toluene and chlorobenzene, it does not appear to follow that substituting both a more electronegative and a less electronegative atom or group in the benzene ring results in a cancellation of effects. The basicity of *o*-chlorotoluene does not seem to be intermediate between the basicity of toluene and chlorobenzene, but seems to be more nearly the same as that of chlorobenzene. The spectroscopic data for interaction of methanol-*d* with α-methylnaphthalene and with toluene compare favorably, and a similar favorable comparison for methanol and these compounds was reported by Jones and Badger.[7] Also, the electron donor ability of α-chloronaphthalene seems to be about the same as that of chlorobenzene. This

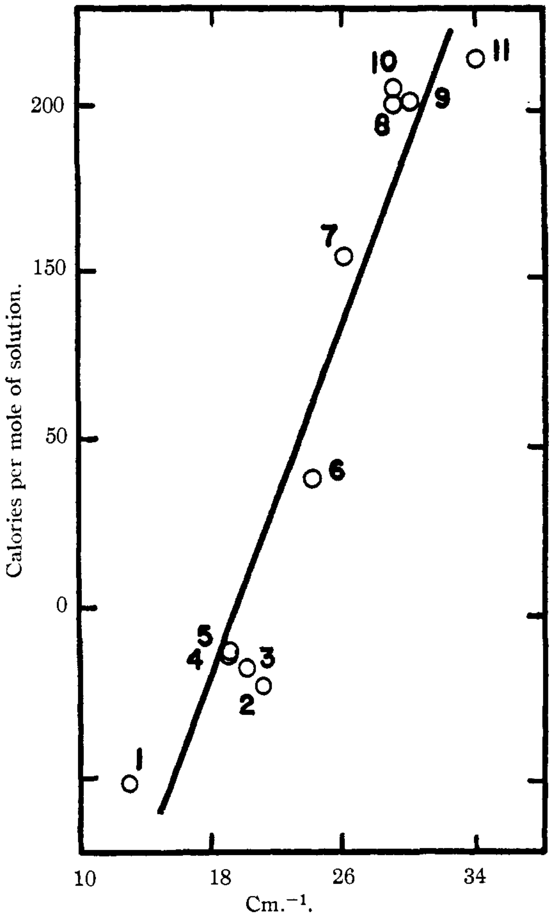

Fig. 2.—Heat of mixing at 25° of chloroform with aromatic compounds (50 mole %) *vs.* shift in vibrational frequency of OD band of methanol-*d* in aromatic compounds: (1) 1,2-dichlorobenzene; (2) chlorobenzene; (3) bromobenzene; (4) α-chloronaphthalene; (5) *o*-chlorotoluene; (6) benzene: (7) toluene; (8) *m*-xylene; (9) *p*-xylene; (10) *o*-xylene; (11) mesitylene.

would indicate that naphthalene and benzene should be of approximately the same basicity. Toward silver ion, however, Andrews and Keefer[4c] have shown that naphthalene is a stronger base than benzene or toluene.

Steric Effects.—Jones and Badger[7] showed that methyl substitution in the benzene ring produces a pronounced doublet of the third harmonic of the OH band of methanol in aromatic hydrocarbon solvents. This was interpreted as showing that the methyl groups in the aromatic hydrocarbon increase the strength of hydrogen bond formation with methanol, but simultaneously decrease the probability of bond formation.

Solutions of methanol-*d* in aromatic compounds should show a similar OD doublet. However, the experimental method used for this investigation is not sufficiently sensitive to resolve the doublet. The OD shifts should be considered as "average" values, but it is interesting to note that for the series benzene, toluene, *m*-xylene and mesitylene there appears the expected increase in OD shift with increasing methyl substitution.

Examination of the calorimetric data in Table I for the series benzene, toluene, *m*-xylene and mesitylene shows that substitution in the benzene ring of the first, second and third methyl group increases the heat of mixing with chloroform by 67, 45 and 14 cal./mole, respectively. Thus toward chloroform, it is possible that steric factors offset part of the increase in basicity expected from the inductive effect of methyl substitution in the benzene ring.

This factor should become more pronounced with bulkier proton acids. In Table II there are given the heats of mixing of equimolar quantities of bromoform with the same aromatic hydrocarbon series. Here, the increase in the heat of mixing with increasing methyl substitution is 60, 12 and 2 cal./mole, respectively. The last value is within the limits of experimental error; thus *m*-xylene and mesitylene may be considered to be of equal base strength toward bromoform. It is to be noted also that the heats of mixing of aromatic compounds with bromoform are less than the heats of mixing with chloroform. This is to be expected because chloroform is a stronger acid than bromoform.

TABLE II

HEATS OF MIXING PER MOLE OF SOLUTION AT 25° OF EQUIMOLECULAR AMOUNTS OF AROMATIC COMPOUNDS WITH BROMOFORM

	Compound	Heat of mixing with bromoform cal./mole
1	Benzene	34
2	Toluene	94
3	*m*-Xylene	106
4	Mesitylene	108

These data support the interpretation of Andrews and Keefer[4a] that there is steric hindrance between silver ion and substituted benzenes. Their results showed that mesitylene is much less effective than benzene in forming a complex with silver ion. With such acids as iodine[3] or hydrogen chloride[6a] no steric effects have been noted, and toward fluo-

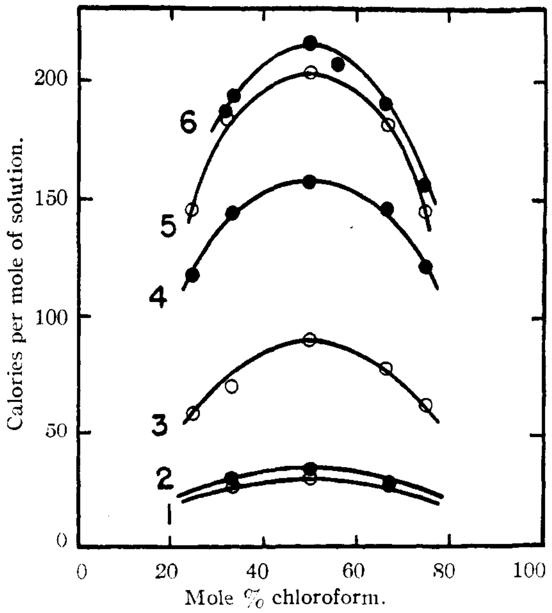

Fig. 3.—Heat of mixing at 25° of chloroform with aromatic compounds; (1) chlorobenzene; (2) bromobenzene; (3) benzene; (4) toluene; (5) *p*-xylene; (6) mesitylene.

boric acid McCauley and Lien[6b] have shown that hexamethylbenzene is a stronger base than any of the other methylbenzenes.

Association Ratio.—A study was made to determine the nature of the association of chloroform with several aromatic compounds, namely, mesitylene, *p*-xylene, toluene, benzene, bromobenzene and chlorobenzene. This was done calorimetrically by determining the concentration at which maximum heat evolution per mole of solution is obtained when the liquids are mixed. Plots of the heats of mixing per mole of solution *versus* the mole % of chloroform are shown in Fig. 3. The symmetrical shape of the curves indicates that association between chloroform and an aromatic compound occurs in a one-to-one ratio.

Andrews and Keefer[4] have shown that a silver ion adds to an aromatic molecule in a one to one ratio and, to a smaller extent, in a two to one ratio. The present investigation shows no evidence for hydrogen bond formation of two chloroform molecules with a single aromatic molecule. This lack of evidence may be due in part to a lack of sensitivity of the method, rather than to the complete absence of such association. This would be true particularly for the weak electron donors which give broad heat of mixing–composition curves, making the location of the peaks more difficult. It may be concluded, however, that if there is association of chloroform to aromatic compound in two to one ratio, it must exist to an extent appreciably smaller than that of one to one ratio.

Acknowledgment.—The author wishes to thank Miss Elizabeth Petersen for making the spectroscopic observations.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Elastoviscous Properties of Amorphous Polymers in the Transition Region. I

BY J. BISCHOFF, E. CATSIFF AND A. V. TOBOLSKY

RECEIVED DECEMBER 27, 1951

Experimental data on the stress–relaxation modulus $E_{r,T}(t)$ of a GR-S gum vulcanizate at a series of temperatures in the transition region are presented, and a "master curve" of log $Q(t/K)$ *versus* log (t/K) is thereby constructed. The characteristic relaxation time, K, for each temperature is defined and tabulated. A distinctive temperature, T_d, is observed at which the activation energy for K is a maximum. Analytical expressions are given which describe the GR-S master-curve with great accuracy. The same analytical procedure can be successfully applied to data previously obtained for polymethyl methacrylate. A reduced equation is proposed which describes the time and temperature dependence of $Q(t/K)$ in the transition region for both polymers.

Introduction

It has been shown previously that for a given amorphous polymer, the stress relaxation curves determined at different temperatures may be made to coincide by a translation along the logarithmic time axis.[1] This makes possible the construction of a composite stress relaxation curve or "master curve" valid over an extended time scale at any given temperature. The master curve can be conveniently plotted in the form of log $E_{r,T_0}(t)$ *versus* log (t), where $E_{r,T}(t)$, the relaxation modulus at a temperature T, is the stress per unit strain in a sample maintained at a constant small strain for a time, t. When plotted in this form a master curve for a given polymer is also valid at any other temperature by simply shifting the origin of the log time axis.

From the master curve $E_{r,T}(t)$ and from the amount of shift of the log time scale at each temperature a new function $Q(t/K)$ may be defined as

$$E_{r,T}(t) = Q(t/K) \qquad (1)$$

In equation (1) K is a function of temperature alone which will be more explicitly defined subsequently, and t has the same numerical value on both sides of the equation. The function $Q(t/K)$ is a universal function of t/K which is valid at all temperatures, and may therefore be called the universal master relaxation curve for a given polymer.

An analytical or graphical representation of $Q(t/K)$ together with an analytical expression or tabulation of K as a function of T are a complete representation of the viscoelastic properties of an amorphous polymer at all times and temperatures in the range of strains where the Boltzmann superposition principle applies. They can be used in principle to calculate any other property such as dynamic modulus.

In a previous paper, it was shown that the viscoelastic behavior of amorphous polymers can be classified into three distinct regions: a glassy region ($E_{r,T}(t)$ $\sim 10^{10.5}$ dynes/cm.^{2}) where the mechanical properties depend on previous thermal history, a transition region where the relaxation modulus lies approximately between 10^7 dynes/cm.^{2} and $10^{10.5}$ dynes/cm.^{2} and is independent of thermal history and of the molecular weight of the polymer, and a rubbery region where the relaxation modulus is less than 10^7 to $10^{7.5}$ dynes/cm.^{2} and depends on the molecular weight of the polymer and on the presence or absence of cross links.[2]

In this paper new experimental data for $E_{r,T}(t)$ of a GR-S gum vulcanizate at a series of temperatures in the transition region are presented. The GR-S vulcanizate used is identical with that used and previously described.[1] A master curve is constructed, an analytical formulation of $Q(t/K)$ is given, and the K values at different temperatures are tabulated. The results are compared with those previ-

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[1] A. V. Tobolsky and R. D. Andrews, *J. Chem. Phys.*, **13**, 3 (1945). See also J. D. Ferry, This Journal, **72**, 3746 (1950).

[2] A. V. Tobolsky and J. R. McLoughlin, *J. Polymer Sci.*, in press.