extinction coefficient of the complex were calculated. The value of the molecular extinction coefficient was found to be 9830 at both temperatures. The value of the equilibrium constant, K_3, was calculated to be 0.381 mole^{-1} 1. at 25° and 0.398 at 20°.

DAVIS, CALIFORNIA

Intramolecular Carbon Isotope Effect in the Decarboxylation of Normal Malonic Acid in Quinoline Solution

BY PETER E. YANKWICH AND R. LINN BELFORD

The intramolecular carbon isotope effects for the decarboxylation of malonic acid in quinoline solution have been measured between 86 and 138°. Combination of the results with those obtained previously under similar conditions for the intermolecular carbon isotope effect permits a new test of simplified models which have been proposed for the decomposition. A modification of Bigeleisen's model results in improved agreement between the experimental results and the theoretical calculations. A suggestion is made as to the manner of carrying out a stringent test of the modified model.

Introduction

In a recent paper[1] we presented the results of experiments on the decarboxylation of malonic acid in quinoline solution which were designed to yield the temperature coefficient of the intermolecular carbon isotope effect under conditions of homogeneous decomposition. The differences between the magnitudes of the isotope effects observed and those predicted by calculation based on the corrected[2] simple model suggested by Bigeleisen[3,4] were explained by postulation of the existence of one or more rapid solvation equilibria antecedent to the rate determining step, which is a bimolecular process involving a solvent molecule.

In the investigation to be reported here, the experiments with quinoline medium were extended to the determination of the intramolecular isotope effect in the temperature range 86–138°.

Experimental

Materials.—The malonic acid used was Eastman Kodak Company white label grade. Preliminary tests indicated that it was of high purity and the material was used as received. The quinoline employed was Eastman Kodak Company white label grade (synthetic). It was found to have been dried thoroughly and was used as received.

Apparatus and Procedure.—The apparatus and general procedure have been described in previous publications.[1,5] About 100 mg. of dried malonic acid and 25 ml. of quinoline were combined after being brought to the decarboxylation temperature; an exception to this procedure was required in the runs at 138°, in which the acid was heated to just below its melting point. The sweep rate of pre-heated, carbon dioxide-free helium was approximately 100 cc. per min. The time allowed for decarboxylation to reach essential completion varied from 40 minutes at 138° to 10 hours at 86°.
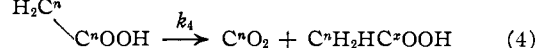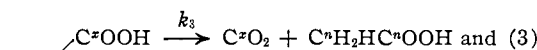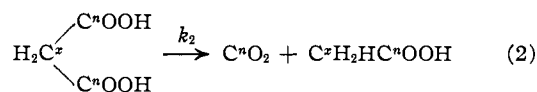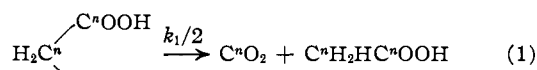
Degradations.—If accurate isotope effect calculations are to be made, one must have information as to the isotopic constitution of the carboxyl and methylene carbon atoms of the malonic acid starting material. Lindsay, Bourns and Thode[6] compared the carbon isotope ratios of carbon dioxide obtained from the combustion of a sample of Eastman Kodak Co. malonic acid and that obtained by the combustion of methane produced from the methylene carbon atom via soda lime–sodium acetate pyrolysis. They found these ratios to be insignificantly different.

In the course of another investigation,[7] it was found that the isotopic constitution of the carbon atoms of acetic acid depends upon the source of that material; accordingly, one would expect that different samples of malonic acid (which is produced by the sequence acetic acid–chloroacetic acid–cyanoacetic acid–malonic acid) might have carboxyl and methylene carbon atoms of differing isotope make-up. Samples of the malonic acid used in this investigation were decomposed in the absence of solvent and the resultant acetic acid degraded by a modification[7] of Phares' application[8] of the Schmidt reaction.[9]

Isotope Analyses.—The carbon isotope ratios of the various samples were obtained from measurements with a Consolidated-Nier Isotope-Ratio Mass Spectrometer. The ratio was determined once on each of at least three introductions of sample carbon dioxide into the manifold of the spectrometer. Frequent checks were made among the samples and two working standards. The mass spectrum of each gas sample was determined in the range m/q 27 to 48; the sample was rejected if this spectrum deviated appreciably from that of tank carbon dioxide which had been subjected to the same high vacuum manipulations. The observed carbon isotope ratios were corrected for the contribution to the ion current at m/q 45 of the species $C^{12}O^{16}O^{17}$ and for incomplete resolution.

Calculations.—Bigeleisen and Friedman's[4] notation for the description of the carbon isotope effects in malonic acid decarboxylation is

$$\begin{array}{c} \diagup C^nOOH \\ H_2C^n \qquad \xrightarrow{k_1/2} \quad C^nO_2 + C^nH_2HC^nOOH \qquad (1) \\ \diagdown C^nOOH \end{array}$$

$$\begin{array}{c} \diagup C^nOOH \\ H_2C^x \qquad \xrightarrow{k_2} \quad C^nO_2 + C^xH_2HC^nOOH \qquad (2) \\ \diagdown C^nOOH \end{array}$$

$$\begin{array}{c} \diagup C^xOOH \xrightarrow{k_3} C^xO_2 + C^nH_2HC^nOOH \text{ and } (3) \\ H_2C^n \\ \diagdown C^nOOH \xrightarrow{k_4} C^nO_2 + C^nH_2HC^xOOH \qquad (4) \end{array}$$

(where n and x denote different isotopes or concentrations of isotopes of carbon); the deviation from unity of the ratio k_4/k_3 is a measure of the intramolecular isotope effect, while that of $k_1/2k_3$ is one measure of an intermolecular effect. The former can be determined from analysis of the carbon dioxide obtained by complete decarboxylation to acetic acid, while the latter is gotten from analysis of the first carbon dioxide evolved. Other intermolecular isotope effects are related to the ratios $k_1/2k_4$ and k_1/k_2.

(1) P. E. Yankwich and R. L. Belford, THIS JOURNAL, **75**, 4178 (1953).

(2) J. Bigeleisen, J. Phys. Chem., **56**, 923 (1952).

(3) J. Bigeleisen, J. Chem. Phys., **17**, 425 (1949).

(4) J. Bigeleisen and L. Friedman, ibid., **17**, 998 (1949).

(5) P. E. Yankwich, R. L. Belford and G. Fraenkel, THIS JOURNAL, **75**, 832 (1953).

(6) J. G. Lindsay, A. N. Bourns and H. G. Thode, Can. J. Chem., **29**, 192 (1951).

(7) P. E. Yankwich and A. L. Promislow, THIS JOURNAL, **75**, 4881 (1953).

(8) E. F. Phares, Arch. Biochem. Biophys., **33**, 173 (1951).

(9) K. F. Schmidt, Ber., **57B**, 704 (1924).

Let the corrected isotope ratio of the effluent carbon dioxide be R_C, that of carbon dioxide obtained from complete combustion of malonic acid be R_D, and that of the carbon in the methylene position of the diacid be R_M. If $R_D = R_M$, methylene and carboxyl carbons isotopically homogeneous, $(k_4/k_3)_{obsd} = 2(R_D/R_C) - 1$; if not, $(k_4/k_3)_{obsd} = (3R_D - R_M - R_C)/R_C$.

Results

The corrected carbon isotope ratio for each sample is given in Table I, along with the value of k_4/k_3 to which it corresponds; the appended errors are average deviations. The values of $\ln(k_4/k_3)_{obsd}$ calculated from the last column of Table I are plotted vs. $1/T$ in Fig. 1. The vertical rectangles encompass the calculated average deviations, while the short horizontal bars represent the maximum and minimum result obtained at each temperature. The other solid line is a similar plot of the results obtained for $(k_1/2k_3)_{obsd}$, quinoline medium,[1] corrected for carbon isotope inhomogeneity; the dashed line is plotted from a calculation of $k_1/2k_3$ based on Bigeleisen's revised model.[2]
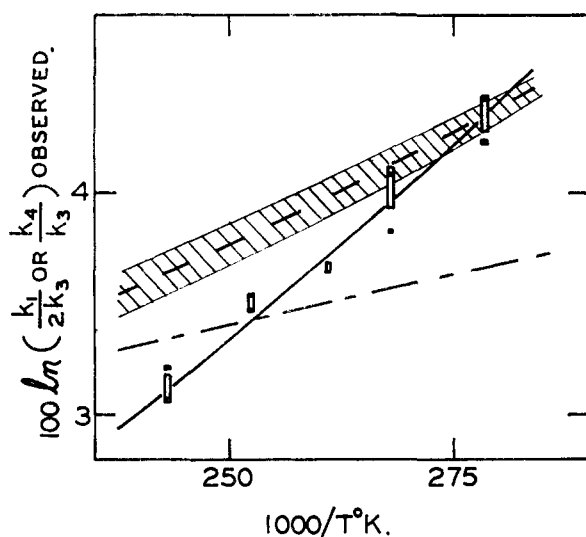

Fig. 1.—Influence of temperature on carbon isotope effects: ———, intramolecular effect, $(k_4/k_3)_{obsd}$, this research; — - —, intermolecular effect, $k_1/2k_3$, calculated for Bigeleisen's simplified model; — — —, intermolecular effect, $(k_1/2k_3)_{obsd}$ results of Yankwich and Belford (the shading represents the smoothed average deviations of the experimental points).

Discussion

Fry and Calvin[10] have investigated the intramolecular isotope effect for the decarboxylation in dioxane–aqueous hydrochloric acid solution of α-naphthyl and phenylmalonic acids. The isotope effects for decomposition under these conditions are about a third larger than those observed when the liquid acids are decarboxylated at their melting points. In the case of α-naphthylmalonic acid, runs in solution were carried out at two different temperatures but the experimental errors were so large as to mask any appreciable temperature dependence.

Bigeleisen[3] predicts for k_4/k_3 the value 1.0198 at any temperature. In light of this prediction and
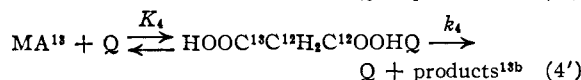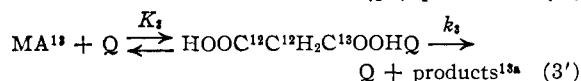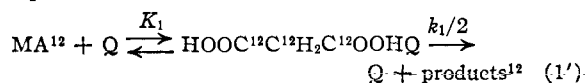
(10) A. Fry and M. Calvin, *J. Phys. Chem.*, **56**, 901 (1952).

TABLE I

CORRECTED ISOTOPE RATIOS OF EXPERIMENTAL SAMPLES; CALCULATED INTRAMOLECULAR ISOTOPE EFFECTS

Run temp., °C.	Run no.	$R_C \times 10^4$	(k_4/k_3) obsd	Av. $(k_4/k_3)_{obsd}$
A. Samples from decarboxylations				
86	68	10666 ± 2	1.0433	
	70	10656 ± 0	1.0452	
	80	10657 ± 1	1.0450	1.0445 ± 0.0008
100	61	10675 ± 1	1.0416	
	66	10675 ± 2	1.0416	
	69	10689 ± 1	1.0390	
	73	10675 ± 1	1.0416	1.0410 ± .0009
110	81	10698 ± 2	1.0374	
	82	10699 ± 1	1.0372	1.0373 ± .0001
123	83	10706 ± 1	1.0358	
	84	10708 ± 2	1.0354	1.0356 ± .0002
138	74	10728 ± 1	1.0316	
	75	10723 ± 1	1.0326	
	76	10731 ± 1	1.0310	1.0317 ± .0006

B. Samples from combustion of malonic acid

$$R_D \times 10^4$$

11–13   10881 ± 1

C. Samples from degradation of malonic acid

$$R_M \times 10^4$$

PM2-4   10848 ± 2

the three plots shown in Fig. 1, it is apparent that in quinoline solution there are impressed upon the *intra*molecular isotope effect additional isotope effects originating, probably, in the one or more rapid reversible equilibria antecedent to the rate determining step as proposed[1] for the case of the *inter*molecular isotope effect. There is little evidence for the detailed nature of these equilibria, but they must affect very appreciably the state of binding about the carboxyl carbon atoms.

We shall not attempt to specify a particular solvation state, but indicate as follows the influence of a solvent molecule on the processes described by equations 1, 3 and 4

$$MA^{12} + Q \underset{}{\overset{K_1}{\rightleftharpoons}} HOOC^{12}C^{12}H_2C^{12}OOHQ \xrightarrow{k_1/2}$$
$$Q + \text{products}^{12} \quad (1')$$

$$MA^{13} + Q \underset{}{\overset{K_3}{\rightleftharpoons}} HOOC^{12}C^{12}H_2C^{13}OOHQ \xrightarrow{k_3}$$
$$Q + \text{products}^{13a} \quad (3')$$

$$MA^{13} + Q \underset{}{\overset{K_4}{\rightleftharpoons}} HOOC^{13}C^{12}H_2C^{12}OOHQ \xrightarrow{k_4}$$
$$Q + \text{products}^{13b} \quad (4')$$

the K's are equilibrium constants or products of such constants, while the superscripts a and b are appended to indicate that the C^{13} appears in carbon dioxide in reaction 3' and in acetic acid in reaction 4'. The result of the equilibrium step(s) is to multiply the *thermal* rate constant ratio by that of the related K's, whence $(k_1/2k_3)_{obsd} = (K_1/K_3)(k_1/2k_3)$ and $(k_4/k_3)_{obsd} = (K_4/K_3)(k_4/k_3)$.

One would expect that K_3 be rather different from K_1 and K_4 since the former involves solvation about a C^{13} carboxyl group and the latter the same about a C^{12} carboxyl group.[11] Further, one would expect

(11) G. Fraenkel, R. L. Belford and P. E. Yankwich, THIS JOURNAL, **76**, 15 (1954).

the influence upon K_1 of isotopic substitution at least two atoms away from the site of solvent interaction to be negligible compared with the effect of similar substitution at the carbon of the carboxyl group so solvated; thus $K_1 = K_4$, and $(K_1/K_3) = (K_4/K_3)$. This conclusion permits two interesting calculations to be made.

First, since $(k_1/2k_3)_{obsd} = (K_1/K_3)(k_1/2k_3)$ and $(k_4/k_3)_{obsd} = (K_4/K_3)(k_4/k_3)$,

$$\frac{(k_1/2k_3)_{obsd}}{(k_4/k_3)_{obsd}} = (k_1/2k_4)_{calcd} \qquad (5)$$

The quotient $k_1/2k_4$ is the ratio of rates of rupture of C^{12}–C^{12} linkages in unlabeled and labeled molecules. It should be noted that the division performed in 5 removes the antecedent equilibrium effects of medium from the results obtained. The simplified model[3] leads to the prediction that $k_1/2k_4$ will be slightly greater than unity at all temperatures and that its deviation from unity will be more strongly dependent upon temperature than that of $k_1/2k_3$. (This is the result of the requirement[2] that k_4/k_3, $(k_1/2k_3)/(k_1/2k_4)$, be a constant greater than unity.) Figure 2 is a plot of 100 $\ln(k_1/2k_4)_{calcd}$ vs. $1000/T$; the effect of the experimental errors in the two sets of data required for computation by equation 5 is shown. It will be noted that at the higher
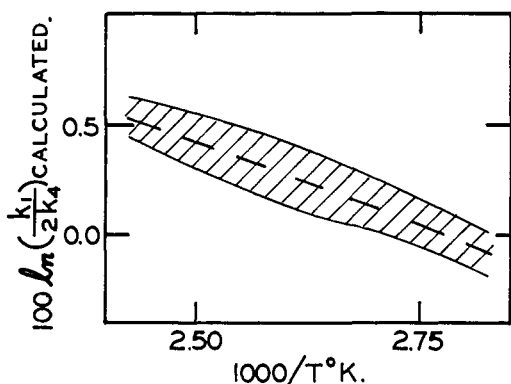

Fig. 2.—Intermolecular isotope effect $k_1/2k_4$ calculated from the experimental results exhibited in Fig. 1. The dashed line is calculated from the best fitting curves for the data employed; the shaded band represents the effect upon this calculation of the experimental errors.

temperatures $(k_1/2k_4)_{calcd}$ is greater than 1.000, as predicted, but that as the temperature falls $(k_1/2k_4)_{calcd}$ falls also, instead of increasing in magnitude, and that somewhere near 90° this rate constant ratio becomes smaller than unity. Values smaller than 1.000 of analogous rate constant ratios have been observed previously in the dissociation of propane by electron impact,[12] thermal deammonation of phthalamide,[13] and in the reaction of acetone with alkaline hypoidite.[14]

Second, one can calculate $(K_1/K_3) = (K_4/K_3)$ from the relation $(K_1/K_3) = (k_1/2k_3)_{obsd}/(k_1/2k_3)_{model}$, then compute k_4/k_3 from the observed values

(12) O. Beeck, J. W. Otvos, D. P. Stevenson and C. D. Wagner, J. Chem. Phys., 16, 255 (1948).

(13) F. W. Stacey, J. G. Lindsay and A. N. Bourns, Can. J. Chem., 30, 135 (1952).

(14) A. Roe and E. L. Albenesius, THIS JOURNAL, 74, 2402 (1952).

$$\frac{(k_4/k_3)_{obsd}}{(k_1/2k_3)_{obsd}/(k_1/2k_3)_{model}} = (k_4/k_3)_{calcd} \qquad (6)$$

Here, too, the division performed removes the antecedent equilibrium effects of the medium from the results obtained. With values of $(k_1/2k_3)_{model}$ based upon the suggestions of Bigeleisen,[2] k_4/k_3 ratios were calculated by equation 6. Figure 3 is a plot of 100 $\ln(k_4/k_3)_{calcd}$ vs. $1000/T$; the experimental errors are indicated as in Fig. 2. While the placement and slope of the resultant curve are dependent upon the details of any satisfactory model adopted for calculation of $(k_1/2k_3)_{model}$, the sign of the slope is not.
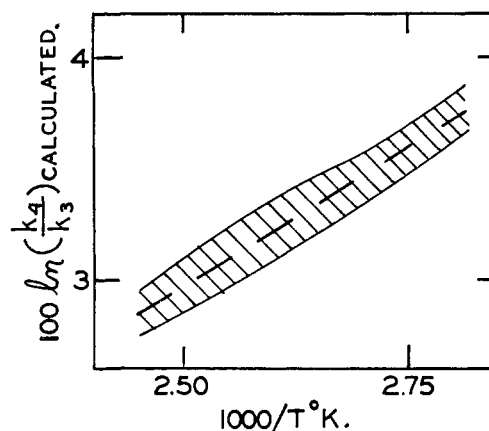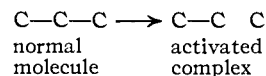

Fig. 3.—Intramolecular isotope effect k_4/k_3 calculated from the experimental results exhibited in Fig. 1 and Bigeleisen's model for $k_1/2k_3$. The dashed line is calculated from the best fitting curves for the data employed; the shaded band represents the effect upon this calculation of the experimental errors.

One explanation which might be offered for these apparent discrepancies between theory and experiment is that the mathematical manipulations just described do not correct for general solvent effects, the models, after all, having been contrived in terms of "gaseous" molecules. This would be a valid criticism of the conclusions reached above; it could be tested by obtaining data for $(k_1/2k_3)_{obsd}$ and $(k_4/k_3)_{obsd}$ under solvent conditions very different from those employed in this investigation and carrying out similar computations with the results.

Another possibility for resolution of the difficulty lies in complicating the model for the decomposition which has been proposed by Bigeleisen and which has been used[2] with some success to explain the intermolecular isotope effects in this and several other decarboxylation reactions. The principal feature of that model is that activation consists of C–C bond rupture

$$\text{C—C—C} \longrightarrow \text{C—C} \quad \text{C}$$
$$\text{normal} \qquad\qquad \text{activated}$$
$$\text{molecule} \qquad\qquad \text{complex}$$

Since the disjunct carbon is C^{12} in one case, equation 1, and C^{13} in the other, equation 3, a vibration frequency is lost upon activation which is affected by this isotopic substitution. The free energy factor in the calculation of the rate constant ratio by the methods of Bigeleisen[15] and Bigeleisen and

(15) J. Bigeleisen, J. Chem. Phys., 17, 675 (1949).

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

$$ \text{C—C—C} \longrightarrow \text{C}\!\doteq\!\text{C}\cdots\text{C} $$

<div align="center">normal molecule   activated complex</div>

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

(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

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.

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

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

Received December 8, 1953

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 deter-

(1) S. Nagakura and H. Baba, This Journal, 74, 5693 (1952).

mine 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–