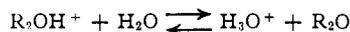


and the rate ratio for the solvent D₂O to H₂O

$$k_2^D/k_2^H = k_s^D K_{SH^+}/k_s^H K_{SD^+}$$

The ratio k_s^D/k_s^H will be close to unity as the bonding of the proton is virtually unaltered in the transition state.⁹ There will be a small secondary kinetic isotope effect. The explanation of the over-all effect must lie largely in the difference in concentration between {S·H₃O}⁺ and {S·D₃O}⁺. Qualitatively, {S·D₃O}⁺ is a weaker acid than {S·H₃O}⁺ which accounts for the faster rate in D₂O.

Approximate calculations for the solvent isotope effect for the equilibrium constant for the reaction



yield a value¹⁰

$$K_H/K_D \approx 2.2$$

(9) P. A. Long and J. Bigeleisen, *Trans. Faraday Soc.*, **55**, 2077 (1959).
(10) A. Willi, private communication.

For the hydrolysis of acetals Bunton and Shiner¹¹ calculate values for k_{D_2O}/k_{H_2O} of 1.7 and 2.5 for their covalent and electrostatic models, respectively. The change in the ratio $k_{D_2O}^{DCI}/k_{H_2O}^{HCl}$ with temperature is understandable in terms of the zero-point energy contribution, but present models appear to be too simple for accurate quantitative calculation of vibrational and rotational partition functions. It is hoped that these and additional data for other reactions over a temperature range will stimulate more exact theoretical calculations.

Acknowledgments.—The author wishes to acknowledge the help of former students, L. C. Riesch, who carried out some of the early work at the University of Pennsylvania, and A. Topol, a student aide at Argonne who performed rate studies by the spectrophotometric method. Thanks are also due to V. M. Story of the U. S. National Bureau of Standards and J. C. Sullivan of Argonne for their independent critical evaluation of the Arrhenius parameters.

(11) C. A. Bunton and V. J. Shiner, Jr., *J. Am. Chem. Soc.*, **83**, 3208 (1961).

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The Kinetics of the Isomerization of the Tetramethylbenzenes in Anhydrous Hydrofluoric Acid^{1,2}

BY MARTIN KILPATRICK, JOHN A. S. BETT AND MARY L. KILPATRICK

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This paper describes the application of the conductance method to the measurement of the rate of isomerization of prehnitene and of durene to isodurene in anhydrous hydrofluoric acid at 20° and 12°. It is shown that the reaction is fitted by a kinetic law based on the rate-determining rearrangement of the protonated species, and as the fraction of substrate protonated is changed by addition of BF₃ or NbF₅ on the one hand, and KF on the other, the rate increases or decreases, but the velocity coefficient for the postulated rate-determining step remains constant. Prehnitene and durene isomerize at practically the same rate.

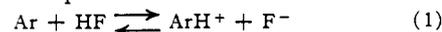
Introduction

Similar mechanisms have been proposed for the isomerization of the methylbenzenes in several Friedel-Crafts catalyst systems. Thus for the isomerization of the xylenes with AlCl₃-HCl,³ with AlBr₃-HBr,^{4,5} and with BF₃-HF⁶ the kinetic data have been explained by protonation of the aromatic nucleus followed by the rate-determining rearrangement of the protonated species.

Only in the work of McCaulay and Lien,⁶ however, was there quantitative knowledge of the extent of protonation, which in HF with BF₃ in excess over the reactant was complete. Here the system was a single liquid phase, and *o*- and *p*-xylene reacted at temperatures from 3° to 30° by the first-order law to yield *m*-xylene, the *para* isomer being the faster by a factor of ca. 5. Under the same circumstances durene (1,2,4,5-tetramethylbenzene) isomerized to isodurene (1,2,3,5-) and one measurement at 0° showed it to react more slowly than the xylenes. McCaulay and Lien suggested that in order for these isomerizations to occur there must exist, in equilibrium with the ordinary protonated hydrocarbon, a species A of higher energy having the proton attached to that ring carbon atom whose methyl group is about to shift; and that the rate-determining step is the formation

from A of the transition state (or unstable intermediate) AB in which the methyl group is shared by two ring carbon atoms. They emphasized the point that while a great difference in stability between A and AB means a high energy of activation and slow reaction, if A is very unstable its concentration will be exceedingly small, and reaction consequently slow. The stability of a cation would increase with increase in the number of methyl groups *ortho* or *para* to the added proton.

The present study of the isomerization of the tetramethylbenzenes was carried out in anhydrous hydrofluoric acid as solvent under conditions where protonation was not complete. The reaction was followed by change in conductance, and the low concentrations used ensured homogeneous solution. Both prehnitene (1,2,3,4-tetramethylbenzene) and durene gave as product the most stable protonated isomer isodurene. Kilpatrick and Luborsky⁷ used the conductance method to determine the equilibrium constant of the reaction



for each of the methylbenzenes at 20°. They found the mobilities of the various cations ArH⁺ to be within experimental error the same, and found isodurene to be roughly 50 times as basic as prehnitene or durene; consequently the concentration of protonated aromatic and the conductivity of the solution will increase as isomerization proceeds.

Experimental

Hydrofluoric Acid.—The starting material was HF from the Harshaw Chemical Co. This was at first purified as described

(7) M. Kilpatrick and F. E. Luborsky, *ibid.*, **75**, 577 (1953).

(1) Presented at the 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 14, 1962.

(2) Abstracted from the Ph.D. thesis of John A. S. Bett, Illinois Institute of Technology, June, 1962.

(3) R. H. Allen and L. D. Yats, *J. Am. Chem. Soc.*, **81**, 5289 (1959).

(4) G. Baddeley, G. Holt and D. Voss, *J. Chem. Soc.*, 100 (1952).

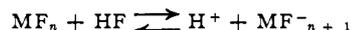
(5) H. C. Brown and H. Jungk, *J. Am. Chem. Soc.*, **77**, 5579 (1955).

(6) D. A. McCaulay and A. P. Lien, *ibid.*, **74**, 6246 (1952).

by Runner, Balog and Kilpatrick.⁸ Later, to save time and because of the inevitable contamination of the purest acid on standing or handling, the procedure was modified by omitting the treatment with sodium bifluoride and by using closely packed nickel helices in the distillation column instead of Kel-F turnings. Conductivity cell No. II, which was used principally, was attached to the line by two Kel-F valves and could be flushed out without removal from the line. With repeated flushing of the cell it was possible to obtain acid of specific conductance 9×10^{-6} ohm⁻¹ cm.⁻¹ at 20°. Most experiments, however, were performed with acid of specific conductance about 5×10^{-6} ohm⁻¹ cm.⁻¹ which could be held in the cell overnight without showing appreciable increase in conductance. From the data of Fredenhagen⁹ this figure is estimated to indicate a concentration of water of 2×10^{-4} molal at -15°, which may be taken as the upper limit for the concentration of water in our solvent at 20°.

Hydrocarbons.—The prehnitene, durene and isodurene were American Petroleum Institute samples with a quoted mole percent impurity of 0.005 ± 0.003 .

Niobium Pentafluoride.—The sample used was prepared by Dr. H. H. Hyman¹⁰ of the Argonne National Laboratory. As a check on its purity, increments of the salt were added to a 0.01 molal solution of isodurene in HF, whereupon the specific conductivity decreased slowly until the ratio (moles NbF₅)/(moles isodurene) was close to unity, and then it rose rapidly. The explanation is the same as that given⁷ for BF₃ with isodurene; in the case of NbF₅ the steepness of the rise is due to the fact that the reaction (where H⁺ represents the solvated proton)



goes further to the right with NbF₅ than it does with BF₃.

Other Reagents.—Boron trifluoride from Harshaw was purified as described by Kilpatrick and Luborsky.⁷ Anhydrous potassium fluoride was prepared from the dihydrate as described by them.

The Conductance Cells.—Nearly all the kinetic experiments were carried out in the cell shown in Fig. 1, called cell II. It was constructed of Kel-F in three sections: the two identical end blocks A holding the valves E and the electrodes F, and the central cylinder B which was clamped in place between the blocks by means of brass plates connected by the long screws C. Slightly grooved seatings in the two blocks gave a vacuum-tight seal. The volume of the cell was ca. 20 cc. The electrodes were bright platinum disks, and the cell constant was 1.83 ± 0.01 cm.⁻¹. Owing to the poor thermal conductivity of the plastic, the cell and its contents were slow to reach the temperature of the bath; conductance measurements showed the half-time for thermal equilibration to be 4.8 min.

A few experiments were carried out in cell I, also of Kel-F, with bright platinum electrodes of area ca. 4 cm.². The cell constant as measured with 0.01 N KCl solution was 0.102 cm.⁻¹; there was some polarization with the large electrodes, but the cell was used only for runs where the resistance was comparable to that of the calibrating solution.

Unless otherwise stated, kinetic experiments were carried out in cell II.

Other Apparatus.—For the kinetic runs, the conductance cell was suspended in an oil-bath at 20.1° or 12.0°, and the temperature was held constant to within $\pm 0.02^\circ$ during a run. The bath temperature was checked by means of a standard platinum resistance thermometer.

Using cell II, resistance was measured at 1000 cycles per sec. on a General Radio bridge (type 650-A); polarization was negligible in the range of resistance encountered. Using cell I, resistance was measured at 2340 cycles per sec.

The metering system for admitting BF₃ to the solution of the hydrocarbon in HF was essentially a glass manometer. The manometer was attached to a short manifold which had an outlet to a tank of purified BF₃, to an oil pump and to a flare fitting of Kel-F for attachment of the conductance cell. In operation, BF₃ was admitted to the evacuated system until the pressure reached 2 atm., then the entry valve to the conductance cell was opened briefly. The number of moles of BF₃ metered into the cell was calculated from the initial and final pressures and the known volume of the manifold plus exposed manometer by making use of the compressibility data for BF₃.¹¹

The Kinetic Experiments.—When HF of specific conductance less than 5×10^{-6} ohm⁻¹ cm.⁻¹ was obtained, the conductance cell was disconnected from the distillation column and weighed.

The hydrocarbon was put into a small Kel-F capsule which was closed with a Kel-F plug; after weighing, the capsule (minus

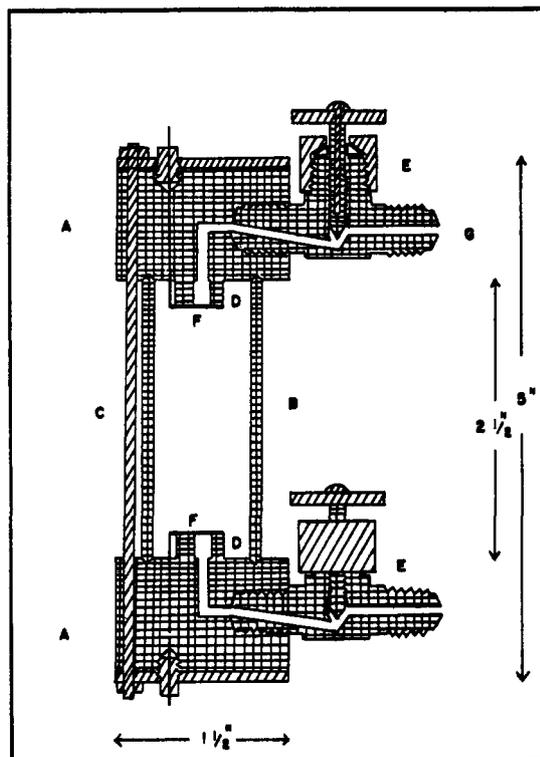


Fig. 1.—Conductance cell II.

plug) was inserted in the fore part G of the entry valve of the conductance cell, and the valve was sealed from the atmosphere by a flared Kel-F cap held in place by a 0.25 in. flare fitting of brass. On opening the valve the hydrocarbon was rinsed back and forth into the cell until the resistance showed it to be completely dissolved. The cell was then placed in the oil-bath and the change of resistance with time recorded after an initial wait of 50 minutes to allow the cell and its contents to reach bath temperature. The initial specific conductance was obtained by extrapolation.

The addition of KF or NbF₅ was made in a similar way, differing only in that the whole operation, except for weighing the capsule, was carried out in a drybox. The addition of BF₃ was made from the metering system as described above.

In the kinetic runs with BF₃, the BF₃ was added to the solution of the hydrocarbon; in those with NbF₅ or KF the order was reversed, and the resistance of the solution was measured prior to addition of the hydrocarbon.

Analysis of the Reaction Product.—Vapor-phase chromatographic analysis showed that after reaction for 3000 min. at 20° an 0.008 m solution of prehnitene yielded solely isodurene. Solutions originally ca. 0.08 m in prehnitene yielded isodurene plus ca. 10% of trimethylbenzene; pentamethylbenzene, which would also be produced in the disproportionation, was retained by the column.

The final values of the conductance in the kinetic runs with durene were indistinguishable from those of isodurene solutions of the same concentration, indicating that the isomerization is practically complete, and disproportionation negligible. The final values in the runs with prehnitene tended to be lower, but by hardly more than the error of measurement.

Results

The Isomerization in HF.—Let us consider the isomerization of prehnitene, for example, in HF alone. Representing the molecule as PH, the cation as PH₂⁺ and similarly using IH and IH₂⁺ for isodurene, the specific conductance of the reacting solution is given by the equation

$$1000L' = 1000L_s + \lambda_{PH_2^+}[PH_2^+] + \lambda_{IH_2^+}[IH_2^+] + \lambda_{F^-}[F^-] \quad (2)$$

where L_s is the specific conductance of the solvent. Since $\lambda_{PH_2^+} = \lambda_{IH_2^+}$ and

$$[PH_2^+] + [IH_2^+] = [F^-]$$

this may be written as

$$1000L' = 1000L_s + \{[PH_2^+] + [IH_2^+]\} \lambda_{A,H^+F^-} \quad (3)$$

(8) M. E. Runner, G. Balog and M. Kilpatrick, *J. Am. Chem. Soc.*, **78**, 5183 (1956).

(9) K. Fredenhagen and G. Cadenbach, *Z. physik. Chem.*, **146**, 245 (1930).

(10) H. H. Hyman, L. A. Quarterman, M. Kilpatrick and J. J. Katz, *J. Phys. Chem.*, **65**, 123 (1961).

(11) M. Kilpatrick and F. E. Luborsky, *J. Am. Chem. Soc.*, **76**, 5865 (1954).

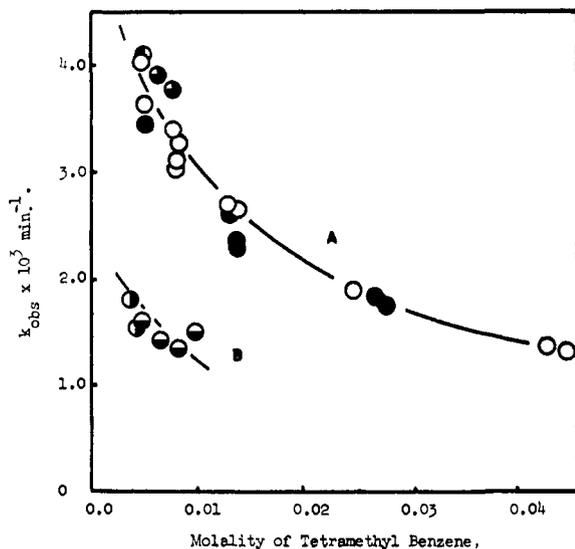


Fig. 2.— k_{obs} for the isomerization of the tetramethylbenzenes in HF at 20° and 12° in cells I and II: ○, prehnitene 20°, cell II; ●, prehnitene 12°, cell I; ●, prehnitene 20°, cell I; ●, durene 20°, cell II; ●, durene 12°, cell I; ●, durene 20°, cell I.

where $\Lambda_{ArH^+F^-}$ is the equivalent conductance of each tetramethylbenzene in the ionized form, and may be evaluated from experiments on hexamethylbenzene as described by Kilpatrick and Luborsky.⁷

Letting $[P]_0$ be the initial stoichiometric concentration of prehnitene, and $[P]_0 - x = [P]$ be that at time t , and writing $L' - L_s = L_t$, eq. 3 may be put into the form

$$1000L_t = \{\alpha_p^t[P]_0 + (\alpha_1^t - \alpha_p^t)x\}\Lambda_{ArH^+F^-} \quad (4)$$

where α_p^t and α_1^t are the fractions of prehnitene and isodurene, respectively, which are present as ions, and may be calculated from the equilibrium constants for reaction 1. Using the equilibrium constants, "theoretical" L_t 's were calculated corresponding to different stages of reaction in typical isomerization experiments, and plotted *vs.* x according to eq. 4. These plots showed L_t as increasing with x in nearly linear fashion, the curves being slightly concave upward, but from 30 to 90% conversion practically linear, and it was concluded that the equation

$$(L_\infty - L_0)/(L_\infty - L_t) = [P]_0/[P] \quad (5)$$

might be a sufficiently good approximation.

When the measured values of the specific conductance were used to test conformity to the simple first-order law in the form

$$\ln(L_\infty - L_t) = k_{obs}t + \text{constant} \quad (6)$$

the equation was found applicable only to the experiments at the lowest concentrations, *ca.* 0.005 *m*. At the higher concentrations curvature was found in the plots for 6 when the experimental L_∞ was used. For these experiments, k_{obs} was calculated by Guggenheim's method.^{11a} Figure 2 and column 2 of Table I show the results obtained.

The decrease in k_{obs} with increase in the initial concentration is as expected if the reactive species in the isomerization is a protonated form, since the fraction protonated will decrease as $[P]_0$ or $[D]_0$ increases; also the relative change in the fraction protonated during an individual experiment will be smaller, the smaller the initial concentration, which makes for better conformity to 6.

Assuming then that

$$-d[P]/dt = k_0[PH_2^+]f_{PH_2^+}/f_{\pm}$$

(11a) E. A. Guggenheim, *Phil. Mag.*, **1**, 538 (1926).

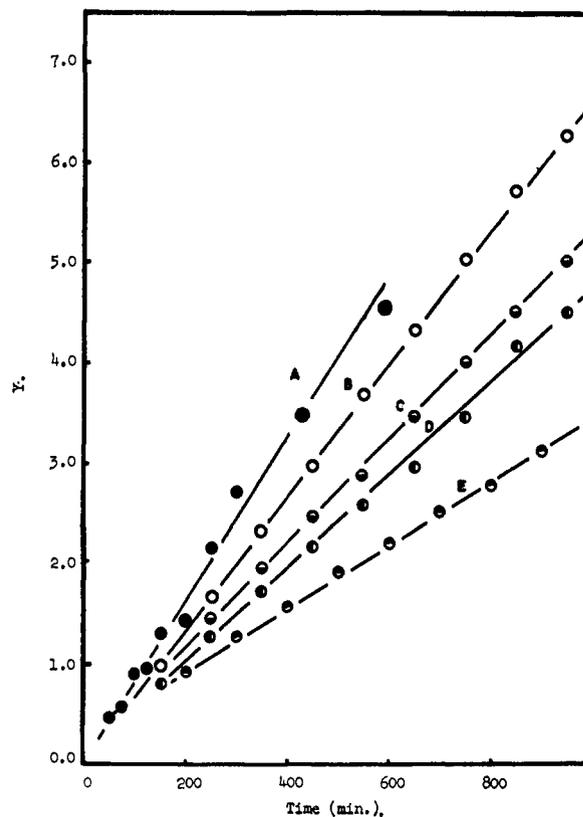


Fig. 3.—Isomerization of prehnitene in HF; evaluation of k_0 using eq. 14

$$Y = [1 + (D/K_c')L_\infty] \ln \frac{(L_\infty - L_0)}{(L_\infty - L_t)} - (D/K_c')(L_t - L_0)$$

where A = 0.0049 *m*, B = 0.0079 *m*, C = 0.0136 *m*, D = 0.024 *m*, E = 0.044 *m*.

on taking the activity coefficient ratio to be unity, and introducing α_p^t , the kinetic law becomes

$$-d[P]/dt = k_0\alpha_p^t[P] \quad (7)$$

and it follows that k_{obs} calculated by 6, or by Guggenheim's method, represents $k_0\bar{\alpha}_p$ where $\bar{\alpha}_p$ is the average value of the fraction protonated in the experiment in question. The change of α_p^t during an experiment will cause deviation from eq. 6.

A test of 7 can be made by replacing $d[P]/dt$, $[P]$ and α_p^t by their values in terms of the specific conductance and the equilibrium constant for 1. For prehnitene, the classical equilibrium constant for reaction 1 is

$$K_c = \frac{\alpha_p^t[F^-]}{(1 - \alpha_p^t)[HF]} \quad (8)$$

and upon multiplying through by $[HF] = 50$

$$K_c' = \alpha_p^t[F^-]/(1 - \alpha_p^t) \quad (9)$$

In these solutions

$$[F^-] = [PH_2^+] + [IH_2^+] = 1000 L_t/\Lambda_{ArH^+F^-} \quad (10)$$

and letting

$$D = 1000/\Lambda_{ArH^+F^-} \quad (11)$$

it follows that

$$\alpha_p^t = 1/\{1 + [F^-]/K_c'\} = 1/\{1 + (D/K_c')L_t\} \quad (12)$$

Using 5, 7 and 12 one finds

$$\{1 + (D/K_c')L_t\} \frac{dL_t}{L_\infty - L_t} = k_0 dt \quad (13)$$

$$\{1 + (D/K_c')L_\infty\} \ln \frac{L_\infty - L_0}{L_\infty - L_t} - (D/K_c')(L_t - L_0) = k_0 t \quad (14)$$

Equation 14 is based on several assumptions, *viz.*, that 5 holds, to a sufficient approximation, that K_c' and $\Lambda_{ArH^+F^-}$ are constant throughout a given experiment despite small changes in medium, and finally that the reactive species is some constant fraction of the protonated substrate. On plotting the left-hand side of 14 *vs.* time, results like those shown in Fig. 3 were obtained; straight lines were found up to 95% reacted in some cases. The results of the experiments in cell II at 20° are collected in Table I. For prehnitene, the velocity coefficient k_0 calculated by 14 appears to decrease with increase in $[P]_0$, though less rapidly than k_{obs} calculated by the simple first-order law; for durene, studied over a narrower range, k_0 is steady. Also, k_0 appears to be in substantial agreement with $k_{obs}/\bar{\alpha}_P$, or $k_{obs}/\bar{\alpha}_D$, $\bar{\alpha}$ being the fraction of substrate protonated at 50% reacted.

TABLE I
THE ISOMERIZATION OF THE TETRAMETHYLBENZENES IN ANHYDROUS HF AT 20.1°

Molality	Velocity coefficient $\times 10^3$, in min. ⁻¹			k_0 by 14	Molality	Velocity coefficient $\times 10^3$, in min. ⁻¹			k_0 by 14
	k_{obs}	$k_{obs}/\bar{\alpha}$	k_0			k_{obs}	$k_{obs}/\bar{\alpha}$	k_0	
Prehnitene					Durene				
0.00460	4.04 ^a	7.4	8.2	8.2	0.00495	3.45 ^a	7.0	7.2	7.2
.00493 ^b	3.64	6.5	7.0	7.0	.0132	2.60	5.9	6.1	6.1
.00762	3.40	6.8	6.6	6.6	.0135	2.36	6.8	7.0	7.0
.00790 ^b	3.12	7.3	7.1	7.1	.0144	2.30	6.6	6.2	6.2
.00795	3.02	6.4	7.0	7.0	.0262	1.85	6.8	6.1	6.1
.00810	3.28	6.6	6.8	6.8	.0274	1.75	7.0	6.7	6.7
.0127	2.70	6.0	5.4	5.4					
.0136 ^b	2.66	5.8	5.4	5.4					
.0242 ^b	1.89	4.5	4.7	4.7					
.0423	1.37	4.9	4.4	4.4					
.0440	1.32	3.9	3.2	3.2					

^a Calculated by 6 where L_∞ is the experimental value; in all other cases, by Guggenheim's method. ^b $L_s = 5 \times 10^{-4}$ ohm⁻¹ cm.⁻¹; in all other cases, $< 5 \times 10^{-5}$ ohm⁻¹ cm.⁻¹.

The trend in k_0 shown for prehnitene in Table I makes it desirable to examine the effect of systematic errors in the parameters occurring in the left-hand side of eq. 14.

L_∞ was known accurately to within 5% of the total change in conductance, and when it was arbitrarily altered by this amount, the plots for 14 were no longer linear.

The parameters $\Lambda_{ArH^+F^-}$, L_0 , and K_c' are interrelated. The value of $\Lambda_{ArH^+F^-}$ in a given experiment was taken as that at the start of the reaction and was calculated from L_0 and the data for hexamethylbenzene⁷ by use of the Onsager equation

$$\Lambda_{ArH^+F^-} = 478 - 451.5\{(\Lambda_0/\Lambda_{ArH^+F^-})[P]_0\}^{1/2} \quad (15)$$

where $\Lambda_0 = 1000L_0/[P]_0$ and $\Lambda_0/(\Lambda_{ArH^+F^-}) = \alpha_P^0$. The change in $\Lambda_{ArH^+F^-}$ during the course of the reaction would be less than 5%.

The equilibrium constant K_c was evaluated for each experiment from $[P]_0$ and α_P^0 . Figure 4 shows the values of K_c obtained for prehnitene, and also for durene and isodurene, by Kilpatrick and Luborsky⁷ and in the present study. The values change with ionic strength more rapidly than one predicts from the limiting law of Debye and Hückel, as shown by the dashed line on the figure, which is drawn with the theoretical slope and with an arbitrary intercept. When one takes for k_0 the arbitrary value of 7.0×10^{-3} and calculates from 14 the corresponding values of K_c for prehnitene in the experiments of Table I, one finds them to be constant to within $\pm 10\%$, in agreement with the small change predicted by theory. The linearity of the plots for 14 is not destroyed when K_c

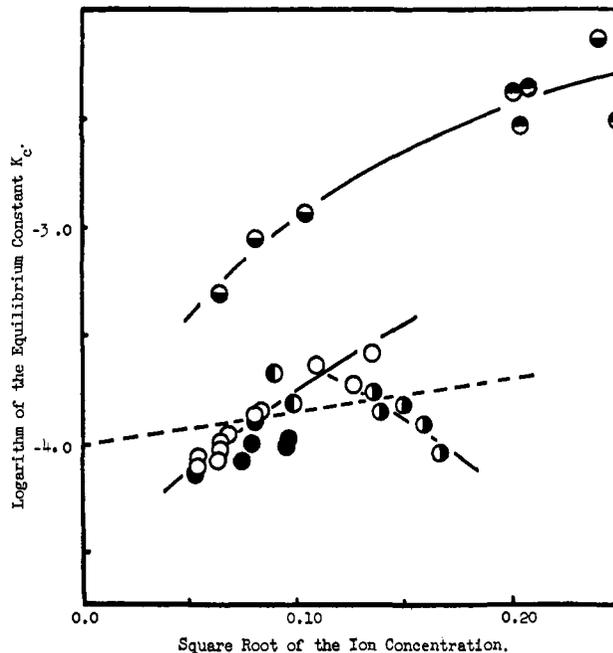


Fig. 4.—Equilibrium constants K_c for the tetramethylbenzenes in HF at 20°: ○, prehnitene; ●, durene; ●, isodurene (this work); ○, prehnitene; ●, durene; ●, isodurene (ref. 7).

is thus altered. Suspicion rests, therefore, on K_c for prehnitene, especially in the case of the more concentrated solutions of Table I where the initial drop in resistance is proportionately large. On the other hand, since k_0 for durene shows no trend, it is possible that with prehnitene disproportionation, detected at 0.08 *m*, is beginning to be significant at *ca.* 0.02 *m*.

The effect of change in temperature upon the rate of isomerization is shown by curves A and B of Fig. 2, for 20.1° and 12.0°, respectively. Although the experiments in cell I are considered less reliable than those in cell II, the results with the two are in fair agreement in those cases where comparison can be made. It is clear from the figure that durene and prehnitene isomerize in anhydrous HF at about the same rate. At a molality of 0.005 the apparent energy of activation was calculated by the Arrhenius equation using (a) the highest and (b) the lowest value of k_{obs} found at each temperature; averaging the results gave $E_A = 16.5 \pm 2.5$ kcal./mole. For prehnitene, K_c and $\bar{\alpha}_P$ at 12° were found the same, within experimental error, as at 20°; the true energy of activation should therefore be close to the apparent or over-all E_A . It took so long to dissolve durene in HF at 12° that calculation of K_c and $\bar{\alpha}_D$ was not attempted.

The Isomerization in HF with BF_3 or NbF_5 Added.—The isomerization of prehnitene in the presence of BF_3 will serve as an illustration. The measured specific conductance is

$$1000L' = 1000L_s + \lambda_{PH_2^+}[PH_2^+] + \lambda_{IH_2^+}[IH_2^+] + \lambda_{BF_4^-}[BF_4^-] + \lambda_F[F^-] \quad (16)$$

and in place of 4 one obtains

$$1000L_t = \{\alpha_P^0[P]_0 + (\alpha_1^t - \alpha_P^t)x\}\Lambda_{ArH^+F^-} - [BF_4^-]\{\lambda_F - \lambda_{BF_4^-}\} \quad (17)$$

and if $[BF_4^-]$ may be taken as practically equal to m_{BF_3} , the stoichiometric molality of BF_3 , eq. 5–7 follow as before.

The results obtained with BF_3 and with NbF_5 are given in Tables II and III. In the experiments where larger and more nearly constant fractions of substrate would be protonated, k_{obs} could be found from 6 as well as by Guggenheim's method. The mean

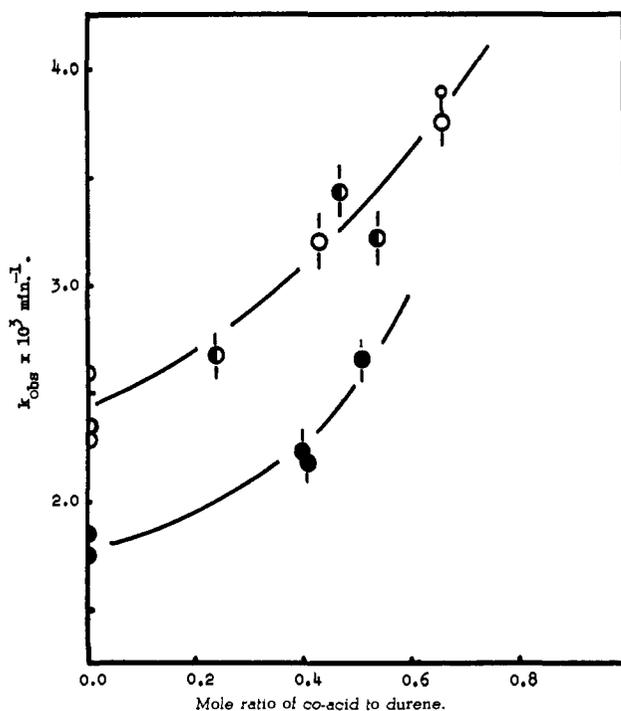


Fig. 5.— k_{obs} for the isomerization of durene in HF with added co-acids: durene *ca.* 0.013 *m*, O, with BF_3 , ●, with NbF_5 ; durene *ca.* 0.025 *m*, ●, with BF_3 .

deviation of a set of 5 runs at 0.013 *m* prehnitene and BF_3 /prehnitene mole ratio close to 0.5 was 3%; this has been taken as the reproducibility in all cases, and is shown by vertical lines through the experimental points in Fig. 5 and 6.

TABLE II
THE ISOMERIZATION OF PREHNITENE IN HF WITH BF_3 , NbF_5 OR
KF AT 20.1°

Molality of P	Additive	Mole ratio m_A/m_P	Velocity coef. $\times 10^4$, in min.^{-1}	
			k_{obs}	k_0
0.0127		0	2.70	5.4
.0136 ^a		0	2.66	5.4
.0135	BF_3	0.19	2.94	5.4
.0133	BF_3	.47	3.74	5.5
.0136	BF_3	.47	3.80	4.8
.0134	BF_3	.48	3.68	5.3
.0142	BF_3	.50	3.58	4.6
.0138	BF_3	.51	3.74	4.7
.0131	NbF_5	.40	3.70	5.4
.0126	NbF_5	.74	4.35	5.4
.0142	KF	.22	2.24	4.4
.0136	KF	.24	2.02	4.9
.0136	KF	.46	2.05	5.9
.0133	KF	.90	1.80	5.9
			Mean	5.3 ± 0.4
0.0242 ^a		0	1.89	4.7
.0201	NbF_5	0.74	3.61	4.6
.0262	BF_3	.22	2.40	3.9
.0266	BF_3	.45	3.00	3.9
.0258	BF_3	.58	3.20	4.1
.0266	BF_3	.86	3.90	3.8
			Mean	4.1 ± 0.3
.0440		0	1.32	3.2
.0423		0	1.37	4.4
.0450	BF_3	0.37	1.90	3.3
.0460	BF_3	.50	2.05	3.4
.0420	BF_3	.65	2.80	4.3
			Mean	3.7 ± 0.5

^a $L_s = 5 \times 10^{-4} \text{ ohm}^{-1} \text{ cm.}^{-1}$; in all other cases, $< 5 \times 10^{-6} \text{ ohm}^{-1} \text{ cm.}^{-1}$.

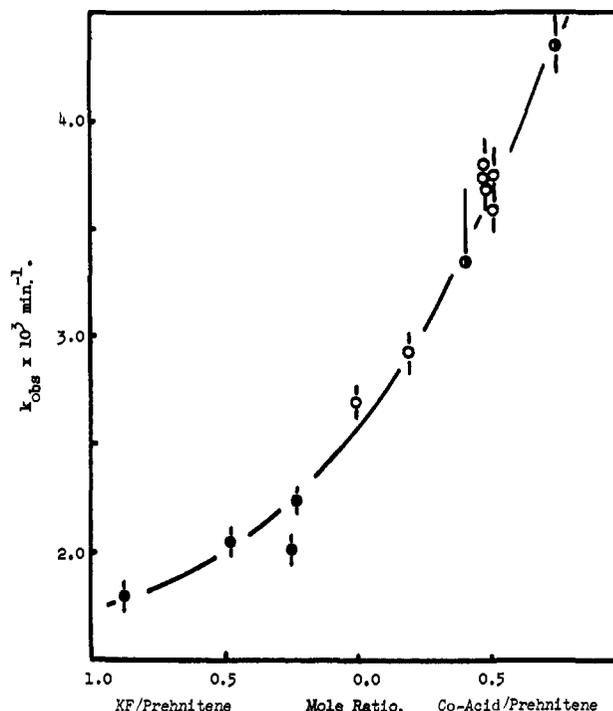


Fig. 6.—The isomerization of *ca.* 0.013 *m* prehnitene in HF with added co-acids and KF: O, BF_3 /prehnitene; ●, NbF_5 /prehnitene; ●, KF/prehnitene.

As co-acid is added in increasing amounts, the initial concentration of hydrocarbon remaining constant, the average value of the fraction protonated would become larger from experiment to experiment, and k_{obs} would increase if the reacting species is a protonated form. This increase is observed, and leads one to expect that the curves for the different initial concentrations would merge as the co-acid/hydrocarbon mole

TABLE III
THE ISOMERIZATION OF DURENE IN HF WITH BF_3 OR NbF_5 AT
20.1°

Molality of D	Additive	Mole ratio m_A/m_P	Velocity coef. $\times 10^4$ in min.^{-1}	
			k_{obs}	k_0
0.0132		0	2.60	6.1
.0135		0	2.36	7.0
.0144		0	2.30	6.7
.0139	BF_3	0.43	3.20	5.0
.0129	BF_3	.63	3.75	5.2
.0134	NbF_5	.27	2.68	6.5
.0134	NbF_5	.47	3.43	6.3
.0136	NbF_5	.54	3.22	4.9
			Mean	6.0 ± 0.6
0.0262		0	1.85	6.1
.0274		0	1.75	6.7
.0272	BF_3	0.40	2.22	5.7
.0255	BF_3	.41	2.18	5.5
.0274	BF_3	.51	2.65	5.6
			Mean	5.9 ± 0.3

ratio rises. The conductance method cannot be used to test this point as the change in resistance accompanying isomerization would vanish; it is already small enough at a mole ratio of 0.7 to make k_{obs} quite sensitive to experimental error. Nevertheless, a trend toward convergence is suggested, as shown in Fig. 5 by the results for durene.

A further test of 7 which allows for the change of α during the course of an experiment may be made in the same manner as before. From 16 it follows that

$$[\text{F}^-] = \{1000L_s - \Lambda_{\text{A}^+\text{H}^+\text{BF}_4^-}[\text{BF}_4^-]\} / \Lambda_{\text{A}^+\text{H}^+\text{F}^-} \quad (18)$$

The term

$$\Lambda_{\text{ArH}^+\text{BF}_4^-}[\text{BF}_4^-]/1000 = b \quad (19)$$

will be constant in a given experiment if $[\text{BF}_4^-]$ may be taken practically equal to m_{BF_3} , and

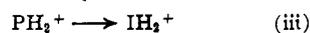
$$[\text{F}^-] = (1000/\Lambda_{\text{ArH}^+\text{F}^-})\{L_t - b\} = D\{L_t - b\} \quad (20)$$

$\Lambda_{\text{ArH}^+\text{BF}_4^-}$ may be evaluated from the data of Kilpatrick and Luborsky.⁷ Proceeding as before, one obtains

$$\{1 - (D/K_c')b + (D/K_c')L_\infty\} \ln \frac{L_\infty - L_0}{L_\infty - L_t} - (D/K_c')(L_t - L_0) = k_0 t \quad (21)$$

On plotting the left-hand side of 21 vs. time, straight lines passing through the origin were found at all hydrocarbon concentrations, and the values of k_0 thus obtained are given in the last column of Tables II and III. In making the calculation for the experiments with NbF_5 , $\Lambda_{\text{ArH}^+\text{NbF}_6^-}$ was assumed equal to $\Lambda_{\text{ArH}^+\text{BF}_4^-}$; k_0 was not significantly altered if $\lambda_{\text{SbF}_6^-}^0$ as given by Kilpatrick and Lewis¹² was used instead of $\lambda_{\text{BF}_4^-}^0$.

The isomerization in the presence of a co-acid—for prehnitene in the presence of BF_3 , for example—may then be written as



That ii will go nearly completely to the right in these kinetic runs where tetramethylbenzene is in excess over BF_3 is indicated by the vapor pressure and conductance measurements of Kilpatrick and Luborsky.^{7,13}

When the rate constant for the isomerization of durene at 20° in the presence of excess BF_3 is calculated from the single measurement reported by McCaulay and Lien⁶ at 0° by making use of the apparent energy of activation, the value found is $(7.9 \pm 2.6) \times 10^{-3} \text{ min.}^{-1}$, which may be compared with $k_0 = 6.0 \times 10^{-3} \text{ min.}^{-1}$ in Table III.

The Isomerization in HF with KF Added.—If the reactive species in isomerization is a protonated form, a reduction in rate upon addition of KF is to be expected, since 1 will be displaced toward the left. And as shown in Table II and Fig. 6, a decrease in k_{obs} is found.

A further test of eq. 7 is made in the same manner as before. For these solutions

$$1000L_t = \{[\text{PH}_2^+] + [\text{IH}_2^+]\} \Lambda_{\text{ArH}^+\text{F}^-} + [\text{K}^+] \Lambda_{\text{KF}} \quad (23)$$

and since $[\text{K}^+] \Lambda_{\text{KF}} = 1000L_{\text{KF}}$, which was measured prior to introduction of the hydrocarbon

$$1000\{L_t - L_{\text{KF}}\} / \Lambda_{\text{ArH}^+\text{F}^-} = [\text{PH}_2^+] + [\text{IH}_2^+] \quad (24)$$

and it follows that

$$[\text{F}^-] = 1000\{L_t - L_{\text{KF}}\} / \Lambda_{\text{ArH}^+\text{F}^-} + [\text{K}^+] \quad (25a)$$

and setting $L_{\text{KF}} = M$ and $[\text{K}^+] = m_{\text{KF}} = N$, one has

$$[\text{F}^-] = D\{L_t - M\} + N \quad (25b)$$

Then proceeding as before, one obtains

$$\{1 - M(D/K_c') + N/K_c' + (D/K_c')L_\infty\} \ln \frac{L_\infty - L_0}{L_\infty - L_t} - (D/K_c')(L_t - L_0) = k_0 t \quad (26)$$

Plots of the left-hand side of 26 vs. time proved linear, and the values of k_0 obtained are given in Table II.

Discussion

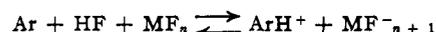
The experiments here reported support the mechanism of isomerization proposed by McCaulay and

(12) M. Kilpatrick and T. J. Lewis, *J. Am. Chem. Soc.*, **78**, 5186 (1956).

(13) F. E. Luborsky, Ph.D. Thesis, Illinois Institute of Technology, 1952.

Lien⁶ and given for the case of prehnitene in HF with BF_3 by eq. 22. The role of the pre-equilibrium 22i in controlling the rate is clearly revealed in Fig. 6 in which k_{obs} calculated by Guggenheim's method is shown for the series of experiments at an initial prehnitene concentration of 0.013 *m* and with various ratios of BF_3 , NbF_5 or KF to prehnitene. For these experiments k_{obs} rises from less than 2 to more than 4 times $10^{-3} \text{ min.}^{-1}$, but k_0 calculated by eq. 14, 21 or 26 remains constant at $(5.3 \pm 0.4) \times 10^{-3} \text{ min.}^{-1}$. The results shown in Fig. 6 may be compared with those of Schubert and Latourette¹⁴ on the decaylation of 2,6-dimethylacetophenone in strong sulfuric acid; here also the reactive species is the protonated substrate which constitutes an appreciable fraction of the stoichiometric concentration.

It can be seen from Tables II and III and Fig. 5 and 6 that the effects of BF_3 and NbF_5 on the rate of isomerization are within experimental error the same. This must mean that both co-acids are practically completely converted to anion



when there is present an excess of base Ar as strong as prehnitene or durene. Since the abilities of BF_3 and NbF_5 to form complexes with the fluoride ion are quite different, as shown, for example, by the much greater conductance of NbF_5 than of BF_3 in anhydrous HF, it should be possible to demonstrate a difference in catalytic effectiveness by choosing a more weakly basic reactant than prehnitene or durene.

The energy of activation found for the isomerization of the tetramethylbenzenes in the present study (16.5 kcal. per mole) is greater than that found for the isomerization of *p*-xylene by McCaulay and Lien (12 kcal.). The difference is in the expected direction since there are two methyl groups *ortho* or *para* to the added proton in the reactive cations of prehnitene and durene, and one in that of *p*-xylene; hence the former are expected to be the more stable.

In the dilute solutions used in the kinetic runs, durene and prehnitene appear to undergo over-all protonation to nearly the same extent; the average of the experimental values of K_c found for durene is 1.0×10^{-4} , and that for prehnitene at molalities < 0.03 (*i.e.*, over the same range) is 1.2×10^{-4} ; *cf.* Fig. 4. Prehnitene has two positions from which the methyl group of the cation can make a 1,2-shift; durene four. It is consequently surprising that durene and prehnitene isomerize at the same rate, within experimental error, in anhydrous HF. There are, however, grounds for believing that the carbon atom in each reactive position in prehnitene may have an inherent basicity about twice that of the carbon atom in each reactive position in durene. Ehrenson¹⁵ has recently calculated the equilibrium constant for proton attachment at an individual nuclear carbon atom in a methylbenzene (k_i) relative to that for attachment at the 2-position of *p*-xylene (k_s) chosen as standard. He has considered both nuclear carbon atoms bonded to a methyl group, and those bonded to a hydrogen atom. For attachment of a proton at a reactive position in durene, $k_i/k_s = 116$, in prehnitene, 211; if this is indeed the case, the equality in rate is understandable.

It might be asked if there was conversion of prehnitene into durene, and of durene into prehnitene, during the reaction of either to yield isodurene as final product. The conductance method is not suited to test this possibility, which was not considered likely.

(14) W. M. Schubert and H. K. Latourette, *J. Am. Chem. Soc.*, **74**, 1829 (1952).

(15) S. Ehrenson, *ibid.*, **83**, 4493 (1961).

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF SOUTHERN CALIFORNIA, LOS ANGELES 7, CALIF.]

The Electrical Conductance of Aqueous Sodium Chloride in the Range 300 to 383°^{1a}

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Values of equivalent conductance are tabulated at 300, 320, 345, 360, 370 and 373° for orthobaric liquid solutions, and at 360, 370, 373, 378 and 383° for solutions at densities of 0.591, 0.525, 0.447 and 0.399 g./cc., at compositions in the range $2\text{--}30 \times 10^{-4}$ molal. Limiting equivalent conductances and dissociation constants are obtained by Shedlovsky's method. The orthobaric liquid phase limiting equivalent conductance is depressed in the vicinity of the critical point. Neither hydrolysis nor the existence of triple ions appears to have a significant effect on the conductances reported.

Several investigations have been made of the electrical conductance of aqueous solutions of electrolytes at elevated temperatures,^{2–5} but most of these have not approached the critical temperature closely. Noyes and co-workers² studied the conductances of many electrolytes—including sodium chloride—up to 306° (T_c (water) is 374°). Fogo, Benson and Copeland^{3b} have measured the conductance of sodium chloride in the supercritical region 378–393° at solution densities from 0.2 to 0.4 g./cc. The present paper gives our results on the conductance of aqueous sodium chloride between 300 and 383°.

Experimental

Apparatus.—The conductance cell and the related equipment to permit its use at elevated temperatures and pressures have been described previously.^{3b,6,7}

To permit use of the cell with a two-phase system, a platinum disk was attached to the cell wall near the interior electrode, between the interior electrode and the diaphragm. The disk was notched at two points on the perimeter to permit passage of solution and vapor when the cell is oscillated. The disk succeeded in making the cell constant independent of the solution volume when the meniscus is between the disk and the diaphragm. For studying the conductance of water, an auxiliary cylindrical electrode was attached to the inner electrode to decrease the cell constant.

The cell volume was determined from the weight of water required to fill the cell at room temperature. The cell constant was determined by comparison with a Jones-type glass cell, using dilute hydrochloric acid. The glass cell was calibrated with 0.01 *N* potassium chloride. Both cell constant and cell volume were redetermined whenever the cell was altered in any way. Corrections were made to the cell constant and volume to allow for the expansion of the cell material with temperature. At the highest temperature these corrections amounted to about -0.3% and $+1.0\%$, respectively.

Because of the design of the cell, solutions were introduced with a glass syringe, equipped with a Pyrex needle. In order to have a constant mean density of solution in the cell for a series of salt concentrations the syringe was equipped with a calibrated, adjustable plunger stop, which permitted resetting of the syringe volume to within 0.1%.

(1) (a) This work has been supported by a contract from the United States Office of Naval Research; (b) Taken in part from the Ph.D. thesis presented by D. Pearson to the Graduate School (1960).

(2) A. A. Noyes, *et al.*, Publication No. 63, Carnegie Institution of Washington, Washington, D. C., 1907. Parts of this report are published in: *J. Am. Chem. Soc.*, **26**, 134 (1904); **30**, 335 (1908); **31**, 987 (1909); **32**, 159 (1910); *Z. physik. Chem.*, **46**, 323 (1903); **70**, 335 (1910).

(3) (a) A. C. Swinnerton, G. E. Owen and J. F. Corwin, *Discussions Faraday Soc.*, **8**, 172 (1949); (b) J. K. Fogo, S. W. Benson and C. S. Copeland, *J. Chem. Phys.*, **22**, 212 (1954).

(4) I. M. Rodnyanskii and I. S. Galinker, *Doklady Akad. Nauk S. S. S. R.*, **105**, 115 (1955).

(5) E. U. Franck, *Z. physik. Chem. (Frankfurt)*, **8**, 92, 107, 192 (1956).

(6) J. K. Fogo, C. S. Copeland and S. W. Benson, *Rev. Sci. Instr.*, **22**, 765 (1951).

(7) J. K. Fogo, S. W. Benson and C. S. Copeland, *J. Chem. Phys.*, **22**, 209 (1954).

For some of the experiments, the cell was sealed while under partial vacuum, both to eliminate most non-condensable gas from the vapor phase and to avoid solution-air contact. The cell was clamped in a specially constructed steel box, from the exterior of which the cell could be sealed after the box had been evacuated nearly to the vapor pressure of water. It was determined that the loss of water vapor from the cell during this operation was negligible.

The pressure gage and the thermocouples used were calibrated only by observing the filling points of solutions of various mean densities in the cell. The temperatures and pressures observed at each filling point have all been within 0.8° and 40 p.s.i. of the values interpolated from steam table data.⁸ The discrepancies were normally less than half of these figures, indicating no serious errors in either measurement.

Electrolyte Solutions.—Water was prepared either by careful distillation or by rapid distillation followed by passage through an ion-exchange column packed with Amberlite MB-2 resin. All water had a specific conductance at 25° of less than 10^{-6} ohm⁻¹ cm.⁻¹. Reagent grade sodium chloride was dried to constant weight, but was not otherwise purified. Sodium chloride solutions in the range $2\text{--}30 \times 10^{-4}$ molal were prepared by weight.

To determine the effect of dissolved air on the conductances at high temperature, a few samples of both water and salt solutions were de-aerated. De-ionized water was placed in a 500-cc. flask equipped with electrodes, thermometer well, insealed gas bubbling tube, and connections for partial evacuation and for sampling. Connections were made with Tygon tubing which did not contact the liquid. As nitrogen or helium was bubbled through the sample into a partial vacuum (water vapor pressure), the conductance change was followed. The 25° specific conductance of water reached $6.2\text{--}8.3 \times 10^{-8}$ ohm⁻¹ cm.⁻¹ (theoretical: 5.5×10^{-6} for pure water), indicating that the de-ionized water contained very little non-volatile, ionizable impurity. To prepare de-aerated sodium chloride solutions, salt crystals were added to de-aerated water. The solution was then further de-aerated. Solution concentrations were determined from the 25° conductance using the data obtained from gravimetrically prepared solutions, with appropriate solvent corrections.

De-aerated water and solutions were transferred to the conductance cell under a helium blanket in such a way that solution-air contact was avoided. Quickly, the cell side-arm assembly was screwed on, the cell was mounted in the vacuum box and the box was evacuated to the vapor pressure of water. The cell was then sealed.

Conductance Measurements.—Before each run, the 25° conductance of a solution was determined—either the sample in the high temperature cell, when its volume was sufficient, or a separate sample in a conventional glass cell.

Experiments were performed in the general manner described previously.^{3b,6} The cell was first heated to 300°, where measurements were made of the pressure, temperature and liquid phase resistance. These were repeated until the measurements became constant, except for small mutually consistent drifts with time. Between measurements the cell contents were stirred by rocking the oven in 180° oscillations. The cell was then heated to 320° and the measurements were repeated.

The cell was then heated to the filling temperature—345, 360, 370 or 373°. As the filling temperature was approached, the heating rate was reduced to nearly zero, in order to provide

(8) J. H. Keenan and F. G. Keyes, "Thermodynamic Properties of Steam," John Wiley and Sons, Inc., New York, N. Y., 1936.