can be expected to be considerably more basic than the ground state molecules[30] and the relative magnitudes of the basicities should be valid.

It is of interest to compare the predicted position of protonation in the ground and triplet states of the various molecules. It is seen that, in most cases, this has changed in the excited state, usually going to the position which is least active in the ground state. This is a consequence of the intramolecular charge transfer on excitation to a higher energy state.[31]

The relative basicities within the series are also interesting. It is seen that in every case where there is more than one methyl-substituted isomer (the di-, tri- and tetramethylbenzenes) the most basic and least basic members of the group exchanged relative position. In the case of the tetramethylbenzenes there was a complete reversal of order. Thus this series of molecules constitutes an example of the intramolecular charge-transfer phenomenon which occurs on excitation together with its attendant profound influence on the relative reactivities of the unique position in each molecule as well as on the series itself.

Conclusion

A refined inductive treatment of methyl-substituted π-electronic systems has been presented and applied to the calculation of the basicities of the methyl-substituted benzenes. When the localization energy approximation was corrected to allow for different type centers in the molecules, the agreement with experiment for ground state basicities was excellent. Basicities for these molecules in their first excited triplet state were also predicted.

It was shown that by application of a correction to the localization energies, Ehrenson's inductive results, which used a simpler model, could be improved to give good agreement with experiment.

It is anticipated that the method of calculation and the methyl group inductive parameters employed in this work can be used to predict correctly reactivities and other properties of other systems, including those which have methyl substitution on heteroatoms.

Acknowledgment.—We wish to thank Illinois Institute of Technology for a generous contribution of Univac 1105 computing time. P. G. L. wishes to thank the National Institutes of Health for a research grant which helped make this work possible.

(30) In order to bring the triplet state basicities in line with those of the ground state, an entropy difference of greater than 100 e.u. at 0° for reaction in the different states would be required. It is unlikely that even the solvation changes which would be expected to accompany the electronic reorganization could cause such an entropy change.

(31) For a graphic discussion of such effects in small systems see M. Kasha in "Comparative Effects of Radiation," John Wiley and Sons, Inc., New York, N. Y., 1960, p. 72.

[CONTRIBUTION FROM ARGONNE NATIONAL LABORATORY, ARGONNE, ILL.]

Kinetics of Hydrolysis of Acetals in Protium and Deuterium Oxides[1]

BY MARTIN KILPATRICK

RECEIVED NOVEMBER 1, 1962

The acid-catalyzed hydrolysis of ethylene acetal (2-methyl-1,3-dioxolane) and dimethyl acetal (1,1-dimethoxyethane) has been studied over the temperature range 0–40°. The experimental results can be represented within the experimental accuracy by a two-parameter Arrhenius equation and the ratio of the velocity constants in deuterium oxide to protium oxide is dependent on the difference in the energies of activation. The ratio $k^{\mathrm{DCl}}_{\mathrm{H_2O}}/k^{\mathrm{HCl}}_{\mathrm{H_2O}}$ decreases with increasing temperature for both acetals and is in qualitative agreement with theoretical calculations.

In 1940, Kilpatrick and Riesch[2] reported briefly that the experimental energy of activation for the hydrolysis of acetals for the temperature range 0–40° varied with temperature, the decrease with increasing temperature being -33 calories per degree for diethyl acetal, -7 calories per degree for ethylene acetal and essentially zero for dimethyl acetal. Changing the medium by the addition of salts did not appreciably change the experimentally determined energy of activation, although the electrolyte effect on the rate was of considerable magnitude. The sensitivity of these reactions to hydrogen ion varies in the ratio 1:20:100 for ethylene, dimethyl and diethyl acetals so that at 0° one can obtain accurate second-order constants by the dilatometric method up to 0.01 M HCl for diethyl, 0.1 for dimethyl and 1.0 for ethylene acetal. At 40° the convenient concentration of strong acids is reduced by a factor of 200 and directly determined velocity constants are less reliable owing to the basicity of the acetal or to acidic impurities. By using the two-thermostat method and assuming the pre-exponential factor in the Arrhenius equation to be constant over a temperature interval, experimental energies of activation can be determined without an accurate knowledge of the hydrogen ion concentration.

Earlier experiments were also attempted in the solvent D_2O by microdilatometric and interferometric techniques, but the limited supply of deuterium oxide prevented the completion of sufficient accurate determinations for publication. The ample supply of D_2O at the Argonne Laboratories has afforded an opportunity to complete this work on a macro scale and the results are reported here. A limited number of experiments has also been carried out at 25° spectrophotometrically as a check on the reliability of the dilatometric method.

Experimental

Ethylene acetal was prepared from acetaldehyde and ethylene glycol in the presence of $CaCl_2$, the upper layer separated and washed with a saturated solution of calcium chloride and dried over $CaCl_2$. After further drying with K_2CO_3 to prevent acid-catalyzed decomposition, the product was distilled and finally fractionated and the fraction boiling between 82.5 and 83.0° at 760 mm. was used for the measurements.

Dimethyl acetal was purified by fractional distillation of commercial samples after treating with K_2CO_3 and that fraction distilling between 63.5 and 64.0° at 760 mm. was used.

Various preparations of acetals were used in the course of the work and all gave kinetic results agreeing within 2%. The samples were tested periodically for acidity by adding 0.5 ml. to 50 ml. of carbon dioxide-free water containing brom thymol blue.

In some cases the acetals were tested on the vapor phase chromatograph and found to be better than 99% pure. The purity was also checked for decomposition by ultraviolet absorption measurements for acetaldehyde, the decomposition product. During the course of the work it was found necessary to keep the

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(1) Based on work performed in part under the auspices of the U. S. Atomic Energy Commission.

(2) M. Kilpatrick and L. C. Riesch, "Handbuch der Katalyse," Vol. 1, Julius Springer, Vienna, Austria, 1940, p. 258.

TABLE I

VELOCITY CONSTANTS FOR ETHYLENE ACETAL HYDROLYSIS

Temp., °C.	k_2, solvent H_2O Obsd. average	k_2, solvent H_2O Calcd. (eq. 1)	k_2, solvent D_2O Obsd.	k_2, solvent D_2O Calcd. (eq. 2)	$k_{2\,D_2O}^{DCl}/k_{2\,H_2O}^{HCl}$ Obsd.	$k_{2\,D_2O}^{DCl}/k_{2\,H_2O}^{HCl}$ Calcd. (eq. 3)
0.00	0.0004215	0.0004254				
5.00	.0009001	.0008840	0.002601	0.002608	2.890	2.949
10.00	.001805	.001791	.005239	.005197	2.902	2.902
15.00	.003551	.003540	.01012	.01012	2.850	2.858
20.00	.006806	.006835	.01905	.01924	2.799	2.815
25.00	.01289	.01291	.03590	.03582	2.785	2.775
30.00	.02417	.02410	.06548	.06534	2.709	2.736
35.00	.04268	.04329	.1163	.1169	2.724	2.700
40.00	.07734	.07734	.2062	.2052	2.666	2.604

acetals in tightly stoppered bottles to prevent the formation of acetic acid.

Hydrochloric acid was prepared as constant boiling acid by the method of Bonner and Titus[3] and the corresponding D-compound was prepared by a similar method. The starting material was a DCl solution prepared from the hydrolysis of benzoyl chloride in deuterium oxide.[4] The resulting product was analyzed by titration with standard caustic. An HCl sample distilled at 748 mm. was 20.248 weight % and a DCl sample distilled at 747 mm. was 17.578%.[5]

Protium and Deuterium Oxide.—In most of the experiments the water was prepared by redistillation from alkaline permanganate and the purity checked by conductivity. The deuterium oxide was treated in similar fashion and analyzed spectrophotometrically by a modification of the method of Crespi and Katz.[6] The starting material was 99.6% D_2O.

The course of the reaction was followed dilatometrically, the apparatus and method of calculation being similar to that used by Kilpatrick and co-workers.[7]

The concentration of the dilute acids was checked before and after reaction by a TTT1 titrator (manufactured by Radiometer, Copenhagen, Den.) which permitted an accurate determination of very dilute acids with small amounts of standard NaOH.

The first-order velocity constants determined dilatometrically for an initial concentration of acetal of 0.11 molar were converted to second-order constants (k_2) by dividing by the concentration of HCl or DCl and where necessary were extrapolated to zero electrolyte concentration. The second-order velocity constants are given in liters mole^{-1} sec.$^{-1}$.

Results

The experimental data for ethylene acetal given in Table I can be represented by the two-parameter Arrhenius equation for the 70 experiments in the solvent H_2O.

$$k_2 = 2.024 \pm 0.074 \times 10^{14} \exp\left(\frac{-22{,}088 \pm 21}{RT}\right) \quad (1)$$

and for the 20 experiments in D_2O

$$k_2 = 2.410 \pm 0.120 \times 10^{14} \exp\left(\frac{-21{,}587 \pm 28}{RT}\right) \quad (2)$$

which yield the following expression for the ratio of the two constants.

$$k_{2\,D_2O}^{DCl}/k_{2\,D_2O}^{HCl} = 1.191 \exp(501/RT) \quad (3)$$

The agreement between the average observed and the calculated constants at each temperature is shown in Table I. Equation 1 compares favorably with our earlier equation

$$k_2 = 2.29 \times 10^{14} \exp(-22{,}145/RT)$$

and with the recently published values[8] of A and E

$$k_2 = 2.75 \times 10^{14} \exp(-22{,}250/RT)$$

The corresponding equations for the hydrolysis of dimethyl acetal for 73 experiments in H_2O and 35 in D_2O are

$$k_2 = 1.540 \pm 0.075 \times 10^{13} \exp\left(\frac{-22{,}814 \pm 27}{RT}\right) \quad (4)$$

$$k_2 = 1.796 \pm .0.213 \times 10^{16} \exp\left(\frac{-22{,}293 \pm 66}{RT}\right) \quad (5)$$

and

$$k_{2\,H_2O}^{DCl}/k_{2\,H_2O}^{HCl} = 1.166 \exp(521/RT) \quad (6)$$

A comparison between the average of the experimental values at each temperature and the calculated values is given in Table II.

TABLE II

COMPARISON OF THE VELOCITY CONSTANTS FOR DIMETHYL ACETAL HYDROLYSIS

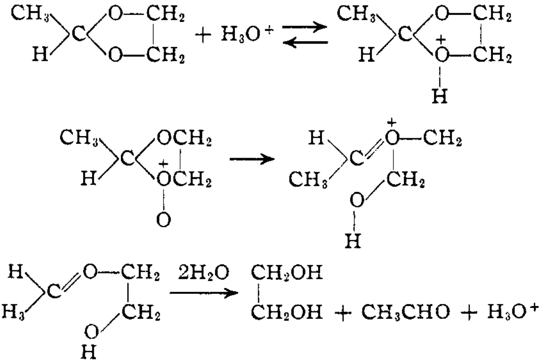
Temp., °C.	k_2, solvent H_2O Obsd. average	k_2, solvent H_2O Calcd. (eq. 4)	k_2, solvent D_2O Obsd. average	k_2, solvent D_2O Calcd. (eq. 5)	$k_{2\,D_2O}^{DCl}/k_{2\,H_2O}^{HCl}$ Obsd. average	$k_{2\,D_2O}^{DCl}/k_{2\,H_2O}^{HCl}$ Calcd. (eq. 6)
0.00	0.008658	0.008502				
5.00	.01825	.01810	0.05480	0.05414	3.003	3.000
10.00	.03701	.03750	.1079	.1097	2.915	2.942
15.00	.07573	.07580	.2207	.2195	2.914	2.897
20.00	.1472	.1496	.4390	.4264	2.982	2.852
25.00	.2893	.2897	.7809	.8103	2.700	2.810
30.00	.5555	.5447	1.518	1.509	2.733	2.770
35.00	.9915	1.0070	2.748	2.748	2.772	2.731
40.00	1.838	1.826	4.956	4.915	2.691	2.704

Discussion

From the results it is evident that the reaction is faster in D_2O than in H_2O and the experimentally measured energy of activation for the over-all reaction is 500 calories lower for the reaction in D_2O than in H_2O.

It is now generally accepted that the mechanism of these reactions involves a pre-equilibrium transfer to the substrate followed by a unimolecular slow decomposition of the conjugate acid (A-1 mechanism in the nomenclature of Ingold).

To illustrate, for ethylene acetal



or, in general

$$S + H_3O^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \{S\cdot H_3O\}^+ \xrightarrow{k_s} \text{products}$$

where $k_s << k_{-1}$ and equilibrium is maintained at all times. The velocity constant is given by

$$k_2 = (k_1/k_{-1})k_s = k_s/K_{SH^+}$$

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[3] W. D. Bonner and H. C. Titus, *J. Am. Chem. Soc.*, **52**, 633 (1930).

[4] H. C. Brown and C. Groot, *ibid.*, **64**, 2223 (1942).

[5] K. E. Holmberg, *Acta Scand.*, **14**, 1660 (1960).

[6] H. L. Crespi and J. J. Katz, *Anal. Biochem.*, **2**, 274 (1961).

[7] M. Kilpatrick and E. F. Chase, *J. Am. Chem. Soc.*, **53**, 1732 (1931); L. C. Riesch and M. Kilpatrick, *J. Phys. Chem.*, **39**, 561 (1935); P. M. Leininger and M. Kilpatrick, *J. Am. Chem. Soc.*, **61**, 2510 (1939).

[8] P. Salomaa and A. Kankaanpera, *Acta Chem. Scand.*, **15**, 871 (1961).

and the rate ratio for the solvent D_2O to H_2O

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

The ratio $k_s^{\mathrm{D}}/k_s^{\mathrm{H}}$ 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 $\{S\cdot H_3O\}^+$ and $\{S\cdot D_3O\}^+$. Qualitatively, $\{S\cdot D_3O\}^+$ is a weaker acid than $\{S\cdot H_3O\}^+$ which accounts for the faster rate in D_2O.

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

$$R_2OH^+ + H_2O \rightleftarrows H_3O^+ + R_2O$$

yield a value[10]

$$K_{\mathrm{H}}/K_{\mathrm{D}} \approx 2.2$$

For the hydrolysis of acetals Bunton and Shiner[11] calculate values for $k_{\mathrm{D_2O}}/k_{\mathrm{H_2O}}$ of 1.7 and 2.5 for their covalent and electrostatic models, respectively. The change in the ratio $k_{2\mathrm{D_2O}}^{\mathrm{DCl}}/k_{2\mathrm{H_2O}}^{\mathrm{HCl}}$ 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.

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

(10) A. Willi, private communication.

(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 BF_3 or NbF_5 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 $AlCl_3$–HCl,[3] with $AlBr_3$–HBr,[4,5] and with BF_3–HF[6] 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 BF_3 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 Luborsky[7] used the conductance method to determine the equilibrium constant of the reaction

$$\mathrm{Ar} + \mathrm{HF} \rightleftarrows \mathrm{ArH}^+ + \mathrm{F}^- \qquad (1)$$

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

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(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).

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