[Contribution from the Chemistry Department of the Pennsylvania State University]

Carbonium Ions. IV. Deuterium Experiments with Triarylmethyl Cations[1]

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The effect of replacing hydrogen by deuterium has been investigated for the equilibrium, $Ar_3C\text{-}OH + H^+ = Ar_3C^+ + H_2O$. Four triarylmethyl cations were studied, each in a different concentration of sulfuric acid. The acid concentrations varied from 9 to 73% H_2SO_4. Nitric acid, 6%, was also studied. The data satisfactorily fit equations derived by an extension of Butler's treatment of deuterium exchange equilibria. In addition, the triphenylmethyl cation and its 4,4′,4″-trimethyl derivative do not undergo hydrogen-deuterium exchange in 35-50% H_2SO_4. The implications of this result are discussed.

Effect of Deuterium on R^+/ROH Equilibria.—Several groups of workers have investigated the effect of replacing H by D on the equilibrium represented by eq. 1.[2-4] For acetic acid, the equilibrium constant ($K = a_{HA}/(a_{A^-}a_{H^+})$) increased by a factor of 3.25 from 0% to 100 mole % D.[2] The value of K at intermediate mole percentages of D is correlatable with the values of K at 0% and 100% D by equations developed by Butler and coworkers.[4]

$$A^- + H^+ = HA \qquad (1)$$

We have now investigated eq. 2 in water–sulfuric acid solutions

$$H^+ + Ar_3C—OH = H_2O + Ar_3C^+ \qquad (2)$$

containing varying amounts of D in place of H. The data are summarized in Table I. Also the treatment of Butler[4] has been extended to reactions of the type of eq. 2.

It was assumed that replacing H by D does not affect activity coefficients so that activities can be set equal to concentrations. Equations 3 and 4 are equilibrium constant expressions. In eq. 5 and 6, the subscripts H and D refer to a system containing only H and one containing only D as the isotopic form of hydrogen. The mole fraction of D is given the symbol n. Equation 8 resulted from the combination of eq. 3, 4 and 7. Equation 9 resulted by combining eq. 5, 6 and 8. In obtaining eq. 10, we have used the expressions for the various concentrations which have been developed by Butler.[4]

$$K_1 = \frac{(R^+)(H_2O)}{(ROH)(H^+)} \quad (3) \qquad K_2 = \frac{(R^+)(D_2O)}{(ROD)(D^+)} \quad (4)$$

$$K_H = \frac{(R^+)_H}{(ROH)_H} = K_1(H^+)_H \quad (5)$$

$$K_D = \frac{(R^+)_D}{(ROD)_D} = K_2(D^+)_D \quad (6)$$

$$K_n = \frac{(R^+)}{(ROH) + (ROD)};\ \frac{1}{K_n} = \frac{(ROH)}{(R^+)} + \frac{(ROD)}{(R^+)} \quad (7)$$

$$\frac{1}{K_n} = \frac{(H_2O)}{K_1(H^+)} + \frac{(D_2O)}{K_2(D^+)} \quad (8)$$

$$\frac{1}{K_n} = \frac{(H^+)_H(H_2O)}{K_H(H^+)} + \frac{(D^+)_D(D_2O)}{K_D(D^+)} \quad (9)$$

$$1/K_n = (1/K_H)(1 - n)Q'(n) + (1/K_D)3.79nQ'(n) \quad (10)$$

$$\frac{K_D}{K_H} = \frac{3.79nQ'(n)}{(K_H/K_n) - (1 - n)Q'(n)} \quad (11)$$

The values $(H_2O) = (1 - n)^2$ and $(D_2O) = n^2$, which have been used in deriving eq. 10 and 11 are based on the assumption that the equilibrium constant for $H_2O + D_2O = 2HOD$ is the statistical value, 4. Values of 3.26,[5] 3.96[6] and 3.80[7] have been calculated for this equilibrium constant at 25° using statistical thermodynamics. No notice seems to have been taken of the discrepancy.[6,7] We chose to use the statistical value of 4 because the latest calculations[6,7] closely approach this value and because the choice simplifies the treatment.[8] In any event, the equations of Butler[4] and those derived herein are rather insensitive to variation in this equilibrium constant.

Equation 11 has been used to test the above treatment. Values of $Q'(n)$ were taken from the papers of Butler.[4] If values of (K_D/K_H), calculated from the experimental data from $n = 0$ to 1, are constant, eq. 10 and 11 are verified. The values in Table I show that the data fit eq. 10 and 11 with satisfactory precision. The most reliable data are those in 10 and 28% H_2SO_4 because in both cases 2 runs using different concentrations of alcohol gave close agreement. In 50% H_2SO_4, although 4 runs were conducted, values of (K_n/K_H) deviated by up to 0.2 between runs so that the data in 50% H_2SO_4 are less reliable. However, eq. 10 and 11 predict the interesting minimum observed in this acid concentration. The data in 73% H_2SO_4 and 6% HNO_3 were obtained from single runs so that individual points may be unreliable.

In the higher concentrations of H_2SO_4, no account has been taken of the effect of D replacing H on the equilibria between H_2SO_4, HSO_4^- and $SO_4^=$

Deuteration of the triarylmethanols, other than at the -OH group, was not a factor in these equilibrium shifts as indicated by experiments described in the next section.

H-D Exchange on Triarylmethyl Cations.—The triarylmethyl cations could conceivably lose a proton to form an uncharged base. For the triphenylmethyl cation, a reasonable electronic structure would be I. Structure I is similar to certain methylene free radicals for which evidence has recently appeared.[9]

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[1] Grateful acknowledgment is made of the support of this research by a grant from the National Science Foundation (G468).

[2] V. K. La Mer and J. P. Chittum, This Journal, **58**, 1642 (1936); S. Korman and V. K. La Mer, *ibid.*, **58**, 1396 (1936).

[3] P. Gross and A. Wischin, *Trans. Faraday Soc.*, **32**, 879 (1936).

[4] W. J. C. Orr and J. A. V. Butler, *J. Chem. Soc.*, 330 (1937); W. E. Nelson and J. A. V. Butler, *ibid.*, 958 (1938).

[5] A. Farkas, "Orthohydrogen, Parahydrogen, and Heavy Hydrogen," Cambridge Univ. Press, London, 1935, p. 181.

[6] H. Urey, *J. Chem. Soc.*, 568 (1947).

[7] I. Kirschenbaum, "Physical Properties and Analysis of Heavy Water," McGraw-Hill Book Co., New York, N. Y., 1951, p. 54.

[8] The calculated values apply to the gas phase; however, the correction to the liquid phase, which involves ratios of the vapor pressures of H_2O, D_2O and HOD, is small. For example, 3.80 is corrected to 3.81.

[9] W. E. Doering and A. K. Hoffmann, This Journal, **76**, 6162 (1954); J. Hine, *ibid.*, **72**, 2438 (1950); W. E. Parham and H. E. Reiff, Abstracts of the 127th meeting of the American Chemical Society, April 1955, p. 20-N.

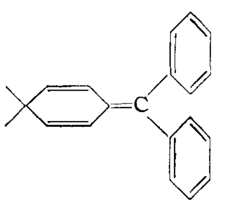
TABLE I

VARIATION IN K_n/K_K WITH VARIATION IN MOLE % DEUTERIUM

Mole % D	K_n/K_H	K_D/K_H (calcd. by eq. 11)
4,4′-Dimethoxytriphenylmethanol in 10% H_2SO_4 (av. of 2 runs)		
0	1.00	
10	1.01	
20	1.05	2.3
30	1.11	2.3
40	1.20	2.4
50	1.32	2.4
60	1.47	2.5
70	1.65	2.5
80	1.85	2.5
90	2.08	2.4
95	2.22	2.4
100	(2.40)[a]	2.4
4 Methoxytriphenylmethanol in 28% H_2SO_4 (av. of 2 runs)		
0	1.00	
10	1.02	
20	1.05	2.3
30	1.09	2.2
40	1.13	2.1
50	1.17	2.0
60	1.23	1.9
70	1.31	1.9
80	1.47	1.9
90	1.78	2.1
95	2.15	2.3
100	(2.30)[a]	2.3
Triphenylmethanol in 50% H_2SO_4 (av. of 4 runs)		
0	1.00	
10	0.88	
20	.85	1.3
30	.85	1.3
40	.87	1.4
50	.92	1.4
60	1.02	1.5
70	1.18	1.6
80	1.47	2.2
4,4′-Dinitrotriphenylmethyl chloride in 73% H_2SO_4 (1 run)		
0	1.00	
10	0.89	1.2
20	.85	1.3
30	.83	1.3
40	.80	1.2
50	.77	0.9
60	.74	.9
70	.71	.9
4,4′-Dimethoxytriphenylmethanol in 6% HNO_3 (1 run)		
0	1.00	
10	1.04	
20	1.09	2.6
30	1.16	2.6
40	1.23	2.5
50	1.33	2.5
60	1.46	2.5
70	1.68	2.6
80	2.06	2.9
90	2.53	3.0
98.5	2.60	2.6

[a] This value was obtained by extrapolation.

For the 4,4′,4″-trimethyltriphenylmethyl cation, a reasonable electronic structure for the hypothetical conjugate base would be II. Structure II is similar in structure to 1,4-dimethylene-2,5-cyclohexadiene (III), which recently has been shown to be stable enough to exist at elevated temperatures.[10]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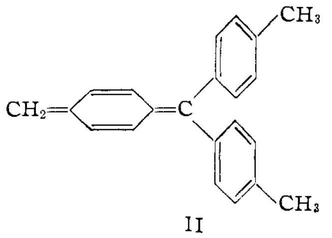
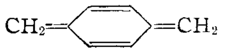


II



III

Hydrogen–deuterium exchange experiments were designed so as to be most favorable for exchange on the triphenylmethyl cation and its 4,4′,4″-trimethyl derivative. Since the rate of H–D exchange would increase with increasing concentration of cation and with increasing activity of bases to accept protons, a concentration of sulfuric acid was chosen in which the triarylmethanol would be 10–90% ionized to the triarylmethyl cation. Higher acid concentrations would not appreciably increase the concentration of cation and would only decrease the activity of the base or bases which must enter the transition state to accept the proton. Lower acid concentrations would probably lower the concentration of cation more than it would increase the activity of the proton-accepting bases.

No H–D exchange was observed in the triphenylmethyl cation when it was dissolved in 50% H_2SO_4 (95% deuterated) for six hr. at 25°. No H–D exchange was observed in the 4,4′,4″-trimethyltriphenylmethyl cation when it was dissolved in 40% H_2SO_4 (95% deuterated) for six hr. at 25°. The complete absence of exchange was demonstrated as follows. The triarylmethanol was reisolated through addition of the sulfuric acid solution to water or by carbon tetrachloride extraction from the deuterated sulfuric acid. The infrared absorption spectrum of the recovered triarylmethanol was measured in carbon tetrachloride solution. No difference could be detected in the region 2 to 12 μ between the original triarylmethanol and the triarylmethanol recovered from the attempted deuteration. In particular, no trace of C–D stretching vibration could be found at 4.3 μ at concentration in which the C–H bands absorbed 90% of the incident radiation.

We can thus conclude that structures such as I and II are not in equilibrium with the corresponding cations at 25°, not only in the concentrations of sulfuric acid at which measurements were taken, but probably in all other water–sulfuric acid mixtures.

Experimental

The preparation of the triarylmethanols and the method of measuring c_{R^+}/c_{ROH} has been reported.[11] In the equilib-

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[10] M. Szwarc, *Discs. Faraday Soc.*, **2**, 48 (1947).

[11] N. Deno, J. J. Jaruzelski and A. Schriesheim, THIS JOURNAL, **77**, 3044 (1955).

rium experiments, the deuterated sulfuric acid was made from 99.95% D_2O[12] and 97% sulfuric acid. To about 5 ml. of this deuterated acid was added one drop of an acetic acid solution of the triarylmethanol. The deuterated acid was successively diluted with water–sulfuric acid containing the same mole % H_2SO_4. The optical density was measured after the addition of each increment. All measurements were conducted at 25 ± 0.2°. In correcting for the change in stoichiometric concentration of triarylmethanol due to the dilution, it was assumed that the volumes were additive.

Acknowledgment.—This problem was called to our attention by Dr. R. W. Taft, Jr., and Dr. Lee Purlee, both of whom contributed in discussions of the derivation.

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[12] The D_2O was obtained from the Stuart Oxygen Company with authorization from the Atomic Energy Commission.

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The Reactions of 3-Phenyl-1-propylamine-1-^{14}C and 3-(*p*-Methoxyphenyl)-1-propylamine-1-^{14}C with Nitrous Acid[1]

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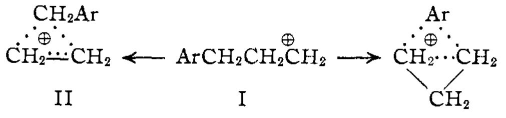
3-Phenyl-1-propylamine-1-^{14}C reacts with nitrous acid in aqueous solution to give hydrocinnamyl alcohol, benzylmethylcarbinol and allylbenzene. Under similar conditions, 3-(*p*-methoxyphenyl)-1-propylamine-1-^{14}C gives *p*-methoxyhydrocinnamyl alcohol, *p*-methoxybenzylmethylcarbinol and *p*-methoxyallylbenzene. A negligible amount of isotope-position rearrangement attends the formation of the above products. The course of the reactions of 3-aryl-1-propylamines with nitrous acid is discussed.

The tendency of the 3-aryl-1-propyl cations (I) to be converted into the bridged-carbonium ions II and III has been investigated as part of research[3] directed to the elucidation of the factors which determine the degree of rearrangement in carbonium ion-type reactions.



II I III

Ar = C_6H_5– or *p*-$CH_3OC_6H_4$–

The isotopic tracer technique was used to detect carbon-skeleton rearrangements and the primary amine–nitrous acid reaction was used for the irreversible generation of I.

The products of the reaction of 3-phenyl-1-propylamine with excess nitrous acid in aqueous solution were hydrocinnamyl alcohol (IV), benzylmethylcarbinol (V) and allylbenzene (VI), along with smaller amounts of organic nitrites and nitro compounds and a considerable amount of higher boiling material, which was probably nitroso secondary amine as found in similar reactions.[4] The absence of other isomeric phenylpropanols and phenylpropenes was demonstrated by comparison of infrared spectra with those of authentic samples of possible contaminants.

β-Phenylpropionitrile-1-^{14}C was prepared by the reaction of 2-phenylethyl bromide with sodium cyanide-^{14}C and was reduced with lithium aluminum hydride to 3-phenyl-1-propylamine-1-^{14}C. A solution of the active amine in dilute aqueous perchloric acid was treated with sodium nitrite at 50–55°. Inactive IV, V and VI were added to act as carriers; the products were separated by fractionation and yields calculated from the extent of isotopic dilution (*cf.* Table I).

TABLE I

PRODUCTS FROM THE REACTIONS OF 3-ARYL-1-PROPYLAMINES WITH AQUEOUS NITROUS ACID

	3-Phenyl-1-propylamine, 50–55°	3-(*p*-Methoxyphenyl)-1-propylamine, 60°
3-Aryl-1-propanol, %	30^a	27^a
1-Aryl-2-propanol, %	19^a	18^a
3-Arylpropene, %	12^a	13^a
Recovered amine, %	9	7.5

^{a} Obtained by isotope-dilution analysis.

The reaction of 3-(*p*-methoxyphenyl)-1-propylamine with excess nitrous acid in aqueous solution at 55° gave *p*-methoxyhydrocinnamyl alcohol (VII), *p*-methoxybenzylmethylcarbinol (VIII) and *p*-methoxyallylbenzene (IX), along with side products of the types mentioned earlier. The infrared spectra of the reaction products were essentially identical in all major respects with those of the corresponding authentic samples except for a strong absorption band at 6.4 μ in the spectrum of VII.

β-(*p*-Methoxyphenyl)-propionitrile-1-^{14}C was prepared by the reaction of 2-(*p*-methoxyphenyl)-ethyl *p*-toluenesulfonate with sodium cyanide-^{14}C, and was reduced to 3-(*p*-methoxyphenyl)-1-propylamine-1-^{14}C with lithium aluminum hydride. A solution of the active amine in excess dilute aqueous perchloric acid was treated with sodium nitrite

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[2] (a) National Science Foundation Predoctoral Fellow, 1952–1954; (b) Gates and Crellin Laboratories, California Institute of Technology.

[3] (a) J. D. Roberts, R. E. McMahon and J. S. Hine, THIS JOURNAL, **72**, 4237 (1950); (b) J. D. Roberts and R. H. Mazur, *ibid.*, **73**, 2509, 3542 (1951); (c) J. D. Roberts and C. C. Lee, *ibid.*, **73**, 5009 (1951); (d) J. D. Roberts, W. Bennett, R. E. McMahon and E. W. Holroyd, Jr., *ibid.*, **74**, 4283 (1952); (e) J. D. Roberts and G. R. Coraor, *ibid.*, **74**, 3586 (1952); (f) J. D. Roberts and J. A. Yancey, *ibid.*, **74**, 5943 (1952); (g) J. D. Roberts and C. M. Regan, *ibid.*, **75**, 2069 (1953); (h) J. D. Roberts and J. A. Yancey, *ibid.*, **75**, 3165 (1953); (i) J. D. Roberts and M. Halmann, *ibid.*, **75**, 5759 (1953); (j) J. D. Roberts, C. C. Lee and W. H. Saunders, Jr., *ibid.*, **76**, 4501 (1954).

[4] (a) D. W. Adamson and J. Kenner, *J. Chem. Soc.*, 838 (1934); (b) E. Linnemann, *Ann.*, **161**, 43 (1872).