ammonia, and in this respect the latter possesses a distinct advantage over either an aqueous or organic medium in carrying out the alkylation reactions studied in this investigation. By using the alkyl *p*-toluenesulfonates and alkyl sulfates as alkylating agents, this advantage is combined with the facts that the alkylations are capable of being carried out at atmospheric pressure, and that the final product as obtained directly from the reaction mixture is in a high state of purity. The latter presents a serious problem when alkylating with the alkyl halides, due to the difficulty in separating them from the desired product by fractionation. This is especially true in the case of the alkylacetylenes.

The preparation of *i*-propylacetylene by means of *i*-propyl sulfate represents, as far as is possible to ascertain, the first direct method for the synthesis of this compound. Investigations will be continued along this line in an attempt to synthesize various branched chain alkyl acetylenes by means of the appropriate alkyl sulfates.

Summary

The alkylation of acetylene, phenol and alcohols has been accomplished by means of the alkyl esters of *p*-toluenesulfonic acid and sulfuric acid in liquid ammonia.

It has been found that the yields are increased considerably by increasing the molal ratio of compound alkylated to ester used, the best yields resulting when this ratio was 2:1.

i-Propyl sulfate has been employed for the synthesis of the corresponding branched chain alkyl acetylene.

A modified method for the preparation of *n*-butyl *p*-toluenesulfonate has been described.

A convenient method has been given for the synthesis of *n*-propyl and *i*-propyl sulfates.

NOTRE DAME, INDIANA RECEIVED JUNE 7, 1937

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, FORDHAM UNIVERSITY]

Equilibria in Protium Oxide–Deuterium Oxide Mixtures

BY WILLIAM H. HAMILL

Ionization of a Weak Acid in H_2O–D_2O.—The dissociation equilibrium expression for a weak acid in aqueous medium of normal isotopic composition is expressed satisfactorily in the conventional manner: $K = (H^+)(A^-)/(HA)$. For isotopic mixtures an apparent equilibrium constant ($K_{ap.}$) is defined in terms of all isotopically variable molecular species involved in the component equilibria. In general, for the isotopically distinct reactants A_i, B_i, ... and products X_i, Y_i, ... this is (1) and becomes (2) for a weak monobasic acid.

$$\frac{(\Sigma X_i)^x(\Sigma Y_i)^y \ldots}{(\Sigma A_i)^a(\Sigma B_i)^b \ldots} \equiv K_{ap.} \qquad (1)$$

$$\frac{(H_3O^+ + H_2DO^+ + HD_2O^+ + D_3O^+)(A-)}{(HA + DA)(H_2O + HDO + D_2O)} \equiv K_{ap.} \cong K_2 \qquad (2)$$

In terms of equilibria (3) to (7) of Table I, where $R = HDO/H_2O$, equation (2) is simply resolved and becomes (8a). An exchange constant of the

$$\frac{(H_3O^+)(A^-)(1 + K_3R + K_3K_4R^2 + K_3K_4K_5R^3)}{(HA)(H_2O)(1 + K_6R)(1 + R + R^2/K_7)} = K_{ap.} = K_8 \qquad (8a)$$

type K_6 ordinarily can be determined by experiment or from spectroscopic data, or indirectly as appears below. The evaluation of K_3, K_4, K_5 depends upon a knowledge of $K_{ap.}$ for H_2O–D_2O mixtures. K_3 can be determined at small deuterium concentrations where R is very small and (8a) becomes approximately

$$\frac{K_{HA}(1 + K_3R)}{(1 + K_6R)(1 + R + R^2/K_7)} = K_8 \qquad (8b)$$

In the limit for deuterium oxide the product $K_3K_4K_5$ is obtained since (8a) becomes

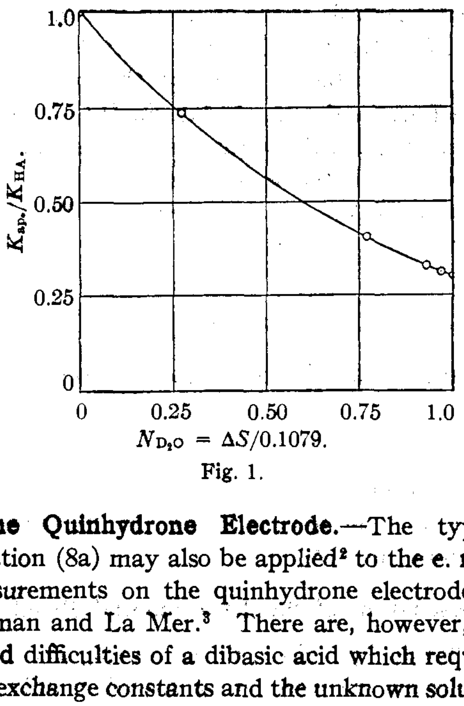
$$K_3K_4K_5K_7/K_6 = K_{DA}/K_{HA} \qquad (8c)$$

TABLE I

$H_3O^+ + HDO = H_2DO^+ + H_2O$;	$(H_2DO^+) = K_3R(H_3O^+)$	(3)
$H_2DO^+ + HDO = HD_2O^+ + H_2O$;	$(HD_2O^+) = K_3K_4R^2(H_3O^+)$	(4)
$HD_2O^+ + HDO = D_3O^+ + H_2O$;	$(D_3O^+) = K_3K_4K_5R^3(H_3O^+)$	(5)
$HA + HDO = DA + H_2O$;	$(DA) = K_6R(HA)$	(6)
$H_2O + D_2O = 2HDO$;	$K_7 = 3.27$	(7)
$QH_2 + HDO = QHD + H_2O$;	K_9	(9)
$QHD + HDO = QD_2 + H_2O$;	K_{10}	(10)
$H_2DO^+ + D_2O = D_3O^+ + H_2O$;	$K = K_4K_5K_7$	(12a)
$H_3O^+ + D_2O = HD_2O^+ + H_2O$;	$K = K_3K_4K_7$	(12b)
etc.		

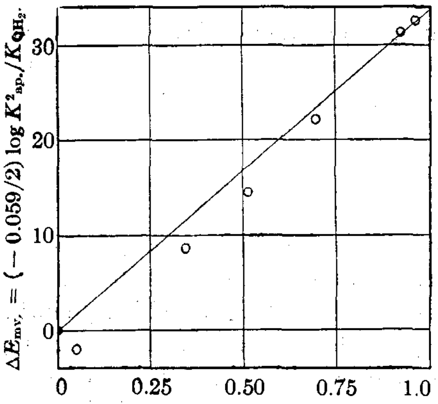
K_4 is obtained readily at intermediate H_2O–D_2O concentrations. It is clear that K_6 is the only variable at constant temperature which is required to fix the ratio K_{DA}/K_{HA}.

Acetic Acid.—Such calculations have been performed with the conductance data for acetic acid of La Mer and Chittum.[1] Their log $K_{ap.}$ *vs.* N_{D_2O} is sufficiently linear to permit accurate interpolation of $K_{ap.}$ at small heavy water concentrations. An experimental determination of K_6 for acetic acid is lacking but it can be determined simultaneously with K_3 from 8b. Equilibrium constants have the following values: $K_3 = 0.93$, $K_4 = 0.344$, $K_5 = 0.138$, $K_6 = 0.475$. These values will be used hereafter as required. Calculated and observed values of $K_{ap.}$, compared in Fig. 1, agree satisfactorily. In all graphs circles are experimental, curves are calculated.



$N_{D_2O} = \Delta S/0.1079$.
Fig. 1.

The Quinhydrone Electrode.—The typical equation (8a) may also be applied[2] to the e. m. f. measurements on the quinhydrone electrode by Korman and La Mer.[3] There are, however, the added difficulties of a dibasic acid which requires two exchange constants and the unknown solubilities of quinone and hydroquinone (QH_2) for the mixtures H_2O-D_2O. By disregarding variations in the solubilities and by applying a pseudo exchange constant,[4] (8a) may be applied to the calculation of $K_{ap.}$ for the mixtures H_2O-D_2O. In Fig. 2, 0.030 log K^2_{ap}/K_{QH_2} is in fair agreement with observed increments in e. m. f. The failure of this equation to account for the experimental minimum may be due to the unavoidable simplifications involved.



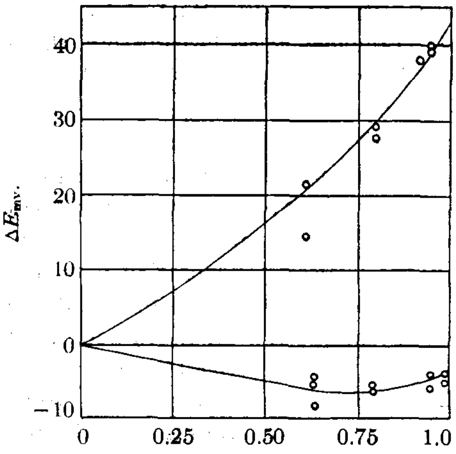
$N_{D_2O} = \Delta S/0.1079$.
Fig. 2.

The Hydrogen Electrode.—The behavior of the hydrogen electrode[5] in H_2O-D_2O can also be described by analogous treatment.

$$\frac{(H_3O^+ + H_2DO^+ + HD_2O^+ + D_3O^+)^2}{(p_{H_2} + p_{HD} + p_{D_2})(H_2O + HDO + D_2O)^2} = K_{ap.}$$

$$\frac{(1 + K_3R + K_3K_4R^2 + K_3K_4K_5R^3)^2}{(1 + 0.309R + 0.0292R^2)(1 + R + R^2/K_7)^2} = K_{ap.}/K_{H^+}{}^{6}$$

The ratio K_{ap}/K_{H^+} approaches 0.76 in the limit as compared to the experimentally extrapolated value of 0.77. The behavior of this ratio in terms of e. m. f. *vs.* N_{D_2O} is a good description of the experimental curve (Fig. 3). The behavior of



$N_{D_2O} = \Delta S/0.1079$.
Fig. 3.

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(1) La Mer and Chittum, THIS JOURNAL, 58, 1642 (1936).

(2) Equation (1) has better justification for practical rather than for theoretical reasons. Although this expression seems to correspond to the one obtained by La Mer and Chittum,[1] it does not appear to bear any simple relation to the electrode reactions to be considered below for which the experimental apparent equilibrium constants are of the type $K^a_A K^b_B \ldots K^n_N$, where $a + b + \ldots n$ is the number of faradays for the electrode reaction which has A, B, ... N isotopic variations. Empirically, however, (1) satisfactorily describes these e. m. f. measurements without requiring any obviously empirical constant.

(3) Korman and La Mer, THIS JOURNAL, 58, 1396 (1936).

(4) Since $K_{ap.}$ for this dibasic acid includes the term $(QH_2 + QHD + QD_2) = (1 + K_9R + K_9K_{10}R^2)$, by (9) and (10) Table I, it is first necessary to assume $(1 + K_9R + K_9K_{10}R^2) = (1 + AR)^2$. Hydroquinone may then be treated as a monobasic acid (QH) for which $K_{QH}/K_{QD} = 3.84$ and $A = K_4 = 0.55$.

(5) Abel, Bratu and Redlich, *Z. physik. Chem.*, **A173**, 353 (1935).

(6) The requisite equilibrium constants were taken from Farkas' "Light and Heavy Hydrogen," Cambridge University Press, London, 1935, pp. 180 ff.

the hydrogen electrode in alkaline media may be described similarly once the exchange constant for the hydroxyl ion has been evaluated from the e. m. f. data. This constant has the value K = 0.348. Calculated and experimental values, in good agreement, are compared in the upper curve of Fig. 3.

Hydrogen Ion Equilibria.—The following expression (9a) is of considerable interest. It is

$$\frac{(\mathrm{H_2OD^+ + HDOD^+ + D_2OD^+})(\mathrm{H_2O})}{(\mathrm{H_2OH^+ + HDOH^+ + D_2OH^+})(\mathrm{HDO})} = K_{\mathrm{ap.}} = K_9 \tag{9a}$$

$$\frac{(K_3 + K_3K_4R + K_3K_4K_5R^2)}{(1 + K_3R + K_3K_4R^2)} = K_9 \tag{9b}$$

readily converted to (9b) and $K_{\mathrm{ap.}}$ is seen to have the limiting values $K_9 = K_3 = 0.93$ in H_2O and $K_9 = K_5 = 0.138$ in D_2O. This equilibrium has been expressed in the simplified manner of (10).[6,7] In accordance with the considerations above, however, K_{10} must be considered the limiting value in D_2O of an apparent constant and is not to be confused with (11) which is a true equilibrium expression (if the existence of H_3O^+, etc., be granted).

$$\frac{(\mathrm{D^+})(\mathrm{H_2O})}{(\mathrm{H^+})(\mathrm{HDO})} = K_{10} = 0.141 \tag{10}$$

$$\frac{(\mathrm{D_3O^+})}{(\mathrm{H_3O^+})}\frac{(\mathrm{H_2O})^3}{(\mathrm{HDO})^3} = K_3K_4K_5 = 0.044 \tag{11}$$

The various equilibria involved in the conductance of strong acids[8] are readily evaluated. In addition to the fundamental equilibria (3, 4, 5) there are the equilibria (12), Table I.

The author is grateful to Prof. V. K. La Mer for helpful criticism.

Summary

Upon the basis of the assumed existence of the ions H_3O^+, H_2DO^+, HD_2O^+ and D_3O^+ it is possible to describe consistently the behavior of conductance and e. m. f. data in H_2O–D_2O mixtures in terms of the various isotopic equilibria.

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[7] Hamill and La Mer, *J. Chem. Phys.*, **4**, 395 (1936).

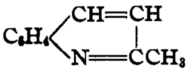
[8] Baker and La Mer, *ibid.*, **3**, 406 (1935).

NEW YORK, N. Y. RECEIVED JUNE 1, 1937

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF STANFORD UNIVERSITY]

Claisen Type Condensations with Quinaldine and Related Ammono Ketone Ethers

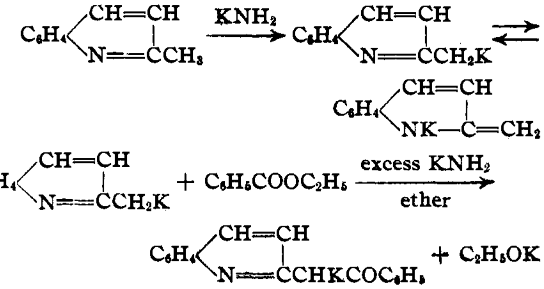
BY F. W. BERGSTROM AND ALAN MOFFAT

Quinaldine,  $C_6H_4\langle CH{=}CH / N{=}CCH_3$ (a cyclic ammono ketone ether), has long been known to undergo many of the reactions of an aquo ketone, in which one of the two groups attached to carbonyl is methyl. Previous work bearing out this statement has been reviewed briefly in earlier articles,[2] where it was shown that quinaldine and other 2-alkylquinolines react with the alkali amides in liquid ammonia to form salts which can be alkylated. In the present investigation, it will be shown that quinaldine and many related compounds undergo the Claisen condensation with aromatic esters in the presence of potassium amide. Quinaldine and lepidine (an expanded ketone ether of the ammonia system (Ingold) or a vinylog of quinaldine (Fuson)) are known to react with diethyl oxalate in absolute ether in the presence of potassium ethylate[3] to form quinaldine and lepidine oxalic esters. Another possible Claisen condensation of this type occurs when quinaldine reacts with diethyl phthalate, in the presence of sodium metal.[4]

Discussion of the Experimental Results

2-Phenacylquinoline (ω-benzoylquinaldine, α-quinolylacetophenone) is prepared readily and in fairly good yield by the action of potassium quinaldyl on one equivalent of ethyl benzoate in absolute ether, preferably in the presence of an excess of amide. The reaction follows the equations

(1)



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[1] Presented at the Pittsburgh meeting of the American Chemical Society, September, 1936.

[2] Bergstrom, THIS JOURNAL, **53**, 3027, 4065 (1931).

[3] Wislicenus and Kleisinger, *Ber.*, **42**, 1141 (1909).

[4] Eibner and Lange, *Ann.*, **315**, 346 (1901).