

TABLE II  
 PRODUCTS OF PYROLYSIS OF THE ESTERS (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>CCOOR

Radical	CO <sub>2</sub> in gaseous products, %	Olefin products, %	Remarks
CH <sub>3</sub>	12	0	Gas contained 8% CO. 61.9% absorbed in H <sub>2</sub> O (formald.) and 18% satd. HC.
C <sub>2</sub> H <sub>5</sub>	46.7	41	Resid. satd. gas burned pale blue flame
<i>n</i> -C <sub>3</sub> H <sub>7</sub>	50	49.5	Vol. of gas equiv. to 80% dec.
iso-C <sub>3</sub> H <sub>7</sub>	46	53	83% decomposition
<i>n</i> -C <sub>4</sub> H <sub>9</sub>	40	40	Ester heated two days at 270-300°. Resid. gas air
iso-C <sub>4</sub> H <sub>9</sub>	47	47	Resid. gas burned pale blue flame; 84% dec.
<i>sec</i> -C <sub>4</sub> H <sub>9</sub>	50.7	41.1	8.2% gas burned pale blue flame
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	37	..	42.4% CO. Resid. gas air
$\beta$ -C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH <sub>2</sub>	76	..	1.7% CO. Residual gas air. 0.5 g. pyrolyzed. Gas coll. over Hg with trap to condense vol. liquids. 0.2 cc. liquid. Micro b. p. 143°. Index refr. at 25° 1.566. Styrene, b. p. 144°, index at 20°, 1.547

The tubes were heated to a constant temperature in a vapor-bath for twenty minutes to ensure thermal equilibrium and the manometer was read. The tube was then heated for one hour and any increase in pressure noted. Since the vapor pressure of the ester was constant, any increase in pressure was due to the gaseous products of

cracking. An increase of 1 mm. at 150-200° in a tube of 5 cc. capacity would correspond to approximately 0.003% decomposition of the ethyl, propyl and butyl esters.

Preliminary experiments made by heating tubes in the vapors of several boiling liquids showed the temperature ranges within which decomposition took place. To obtain the intermediate temperatures an apparatus was designed in which the tubes were heated by the vapor of a liquid boiling under a pressure that could be varied. For temperatures between 170 and 210°, nitrobenzene and between 145 and 179.5° *p*-cymene were used. If a tube showed no increase in pressure at the end of one hour, the temperature was raised five degrees. If the tube then showed an increase the temperature was dropped 2° and another reading made. It is believed that the temperatures of decomposition were measured to an accuracy of 2°. The cracking temperatures of the esters were as follows: CH<sub>3</sub> 196°, C<sub>2</sub>H<sub>5</sub> 188°, *n*-C<sub>3</sub>H<sub>7</sub> 169°, iso-C<sub>3</sub>H<sub>7</sub> 154°, *n*-C<sub>4</sub>H<sub>9</sub> 183°, *sec*-C<sub>4</sub>H<sub>9</sub> 163°, iso-C<sub>4</sub>H<sub>9</sub> 149°, C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub> 179° and C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>CH<sub>2</sub> 157°.

### Summary

1. The following esters of triphenylacetic acid were prepared: CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, *n*-C<sub>3</sub>H<sub>7</sub>, iso-C<sub>3</sub>H<sub>7</sub>, *n*-C<sub>4</sub>H<sub>9</sub>, *sec*-C<sub>4</sub>H<sub>9</sub>, *n*-C<sub>5</sub>H<sub>11</sub>, iso-C<sub>5</sub>H<sub>11</sub>, *n*-C<sub>6</sub>H<sub>13</sub>, C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub> and C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>CH<sub>2</sub>.

2. The temperatures at which the esters first began to show signs of decomposition when heated for one hour (the cracking temperatures) were determined.

3. The influence of a change in the radical present on the cracking temperatures is compared with another series of compounds containing the same radicals.

CAMBRIDGE, MASS.

RECEIVED AUGUST 2, 1933

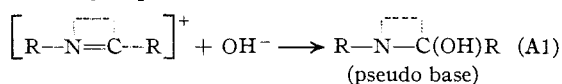
[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

## Pseudo Bases. IV. The Mechanism of Formation of Dimolecular Ethers from Pseudo Bases. The Aromatic Nature of Heterocyclic Compounds<sup>1</sup>

BY JOHN G. ASTON AND PERCIVAL A. LASSELLE

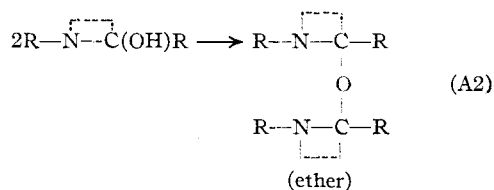
### Introduction

The pseudo basic systems in the quinoline series have long been known to yield dimolecular ethers by loss of a molecule of water from two molecules of the pseudo base. This reaction has been formally represented<sup>2</sup>



(1) Submitted in partial fulfillment of the requirements for the Ph.D. Degree.

(2) Hantzsch and Kalb, *Ber.*, **32**, 3109 (1899).



when  $\overset{\text{---}}{\text{N}}=\overset{\text{---}}{\text{C}}$  represents the quinoline nucleus.

It has been shown<sup>3</sup> that 1,2,5-trimethylpyrazinium hydroxide disappears slowly from its aqueous solution by a reaction of the second order with

(3) Aston, *THIS JOURNAL*, **53**, 1448 (1931).

respect to both the positive ion and the hydroxide ion. The product, which was too unstable to isolate, was presumably the dimolecular ether. In this case, as in the quinoline series, equilibrium in the pseudo basic system favored the ions of the quaternary (true) base. It therefore seemed of interest to determine the mechanism by which dimolecular ethers were formed from pseudo bases in the quinoline series in cases where the ethers had been actually isolated and analyzed. The present paper concerns the rate and mechanism of such reactions.

### Discussion of Results

Measurements of the rate of reaction of 1-methylquinolinium ion and hydroxide ion have been made by a conductivity method over a range of concentrations of 0.05 to 0.01 *N* with respect to either ion, and with the concentrations of the reactants at several ratios. These results show that the reaction is second order with respect to both the positive ion and the hydroxide ion, over the entire range of concentration. Similar measurements were made with 1,2-dimethylquinolinium hydroxide. The order of this reaction was also approximately second with respect to each of the ions. However, the rate was much slower, and for this reason the measurements were considerably less accurate due to increased error caused by precipitation of the ether on the electrodes and the solubility of the glass.

The specific reaction rate constant calculated for a reaction bimolecular with respect to the positive and negative ions, respectively, corrected for the Brönsted salt effect, was 710 for the 1-methyl- and 100 for the 1,2-dimethylquinolinium hydroxide at 25.00° (both in moles per liter per hour in 1 molal solution). In the same units the corresponding rate for 1,2,5-trimethylpyrazinium hydroxide was  $3.9 \times 10^5$ .

The formal heat of activation for the reaction in the case of 1-methylquinolinium hydroxide has been found to be 10,420 calories by measurement of the temperature coefficient.

Experiments with 1,2-dimethylpyrazolinium hydroxide and 1,2-dimethylpyridinium hydroxide showed that both of these bases were strong electrolytes. The conductivity of their solutions did not change appreciably on standing at 25.00°, thus showing that the rate of ether formation at 25.00° was negligible.

Hantzsch has shown that 1-methylpyridinium

hydroxide does not form the ether at an appreciable rate even on boiling.<sup>2</sup>

The only pseudo basic system in which the equilibrium is known to be largely in favor of the pseudo base is 1,2,2,5,5-pentamethyldihydropyrazinium hydroxide.<sup>3,4</sup> This compound does not form the dimolecular ether on heating above 80° in various solvents or on distillation.

In Table I, the pseudo basic systems are arranged in order of the decreasing aromatic properties of the parent ring, starting from the top, on the basis of the extent to which they exhibit the characteristic reactions of aromatic compounds. In column 2 is given the specific reaction rate constant of dimolecular ether formation,  $k_4$ , in moles per liter per hour in a one molal solution of each of the ions. In column 3 is recorded the position of equilibrium in the pseudo basic system as favoring mostly the ions of the quaternary base (*i. e.*, the system forms a strong electrolyte), or mostly the pseudo base. No intermediate cases are known.

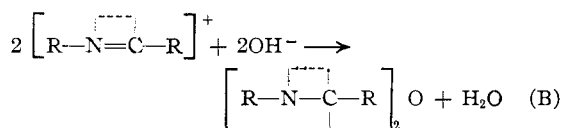
TABLE I  
SUMMARY OF PROPERTIES OF PSEUDO BASIC SYSTEMS

System	$k_4$	Equilibrium favors
1,2-Dimethylpyrazolinium	0	Ions
1-Methylpyridinium	0	Ions
1,2-Dimethylpyridinium	0	Ions
1-Methylquinolinium	$7.1 \times 10^2$	Ions
1,2-Dimethylquinolinium	$1.0 \times 10^2$	Ions
1,2,5-Trimethylpyrazinium	$3.9 \times 10^5$	Ions
5-Phenyl-10-methylacridinium	Base insol.	Pseudo base
1,2,2,5,5-Pentamethyldihydropyrazinium	0	Pseudo base

The rate of formation of ethers from the pseudo bases in the above list increases from zero in the pyrazolinium and pyridinium series where the equilibrium concentrations of pseudo base are small to a maximum at the pyrazinium series and falls to zero again at the dihydropyrazinium series where the equilibrium is largely in the direction of the pseudo base. The differences in rate are far too large to be due only to "steric" effects. The introduction of a methyl group in the 2 position of the quinoline system causes but a tenfold decrease in the rate whereas the effects observed are completely different in order of magnitude.

The following explanation of these effects fits all the facts observed. The net reaction of ether formation may be formulated as

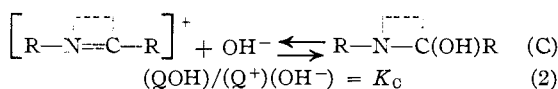
(4) Aston, *THIS JOURNAL*, **52**, 5254 (1930).



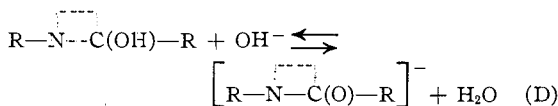
The rate of such a reaction would be given by

$$d\text{Q}^+/\text{dt} = -k'_1(\text{Q}^+)^2(\text{OH}^-)^2 \quad (1)$$

where  $\text{Q}^+$  is the concentration of the positive ion. This is as found. Since reaction through quadruple collision is unlikely, it has been suggested<sup>3</sup> that the small quantities of pseudo base in equilibrium reacted to yield the ether and shown that this would give rise to the observed fourth order constant. If this mechanism were correct, 1,2,2,5,5-pentamethyldihydropyrazinium hydroxide should yield the dimolecular ether at quite a measurable rate, since it exists mostly in the form of the pseudo base. Therefore this mechanism now seems untenable. It still seems likely that the first step is the rapid establishment of equilibrium (C). In all cases studied when the dimolecular ether is formed this is far to the left.



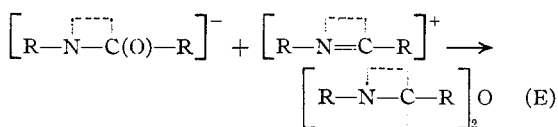
In equation (2) (QOH) is the concentration of pseudo base. The equilibrium



is also established rapidly for which

$$(\text{QO}^-)/(\text{QOH})(\text{OH}^-) = K_D \quad (3)$$

where (QO<sup>-</sup>) is the small but finite concentration of the alcoholate (or phenolate) negative ion on the right-hand side of equation D. The positive quaternary ion and the negative alcoholate ion then react slowly thus



the alcoholate ion having added to the quaternary positive ion to form the dimolecular ether in the same way that hydroxide ion adds to yield the pseudo base. The rate of this reaction is given by

$$\frac{d(\text{Q}^+)_{\text{total}}}{dt} = \frac{2d(\text{Q}^+)}{dt} = -2k_E(\text{Q}^+)(\text{QO}^-) \quad (4)$$

where  $d(\text{Q}^+)_{\text{total}}$  is the observed rate of disappearance of the quaternary ion, which is twice the rate of (E), because one mole of this ion is also used up

to form every mole of the alcoholate ion; substituting (2) in (3)

$$(\text{QO}^-) = K_D K_C (\text{Q}^+)(\text{OH}^-)^2 \quad (5)$$

substituting (5) in (4)

$$d(\text{Q}^+)_{\text{total}}/\text{dt} = -2k_E K_D K_C (\text{Q}^+)^2 (\text{OH}^-)^2 = -k'_1 (\text{Q}^+)^2 (\text{OH}^-)^2 \quad (6)$$

$$\text{where } k'_1 = 2k_E K_D K_C \quad (7)$$

There are then three distinct effects contributing to dimolecular ether formation, the equilibria in (C) and (D) and the rate of (E). It will be assumed that the specific reaction rate constant of (E) does not vary greatly from system to system. Any pseudo basic system which has but a small concentration of the quaternary ion and hydroxide ion at equilibrium can yield but very little of the alcoholate ion because although the concentration of pseudo base is large the hydroxide-ion concentration is small. The rate of reaction (E) thus becomes negligible. If the equilibrium favors the quaternary and hydroxide ions exclusively, there is insufficient pseudo base to yield the alcoholate ion and the rate of the dimolecular ether formation again becomes small.

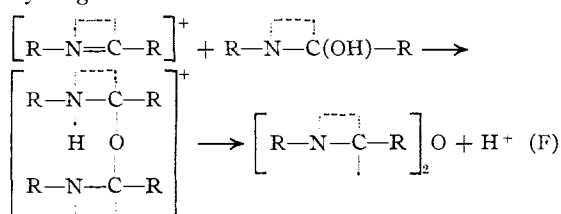
Thus pseudo basic systems with equilibria lying between the two extremes should yield ethers most rapidly. Since conjugation is presumably the factor influencing pseudo basic equilibria,<sup>3</sup> such a condition might be expected in heterocyclic systems with condensed nuclei in which the complete conjugation is partly destroyed as in the case of quinolinium hydroxides and acridinium hydroxides. However, 5-phenyl-10-methylacridinium hydroxide does not yield a dimolecular ether but this is because its pseudo base is so insoluble that it precipitates and shifts the equilibrium in favor of the insoluble pseudo base.<sup>5</sup> Nevertheless, the compound does yield an ethyl ether merely on boiling with ethyl alcohol, in which it is soluble.<sup>6</sup> The ethylate ion first produced by the action of the strong base reacts according to (E). We are thus led to believe that the pseudo basic systems in the pyrazole and pyridine series which do not form ethers have negligibly small concentrations of pseudo base in equilibrium with the ions. This is to be expected in view of the extreme aromatic nature of the rings which would lead to completely conjugated systems. On this view 1,2,5-trimethylpyrazinium hydroxide must contain a ring with only incomplete conjugation. This is reasonable. The

(5) Aston and Montgomery, *THIS JOURNAL*, **53**, 4298 (1931).

(6) Decker, *J. prakt. Chem.*, **45**, 195 (1891); *Ber.*, **35**, 3072 (1902).

pyridine ring is apparently completely conjugated; therefore the pyrazine ring, with one more unsaturated nitrogen atom, could hardly be supposed to have its partial valences fully satisfied.

It has been shown<sup>3</sup> that 1,2,5-trimethylpyrazinium hydroxide also forms the dimolecular ether by a second reaction simultaneous with the fourth order one already discussed. This reaction predominates in dilute solution and is second order with respect to the quaternary ion and first order with respect to the hydroxide ion. This reaction apparently proceeds by addition of the pseudo base to the positive ion with subsequent loss of hydrogen ion.



This mechanism has been shown to give rise to the correct order. Such an addition is apparently caused by the decreased conjugation in the ring. In cases where the conjugation is greater the rate of this addition is apparently too slow to be observed.

### Experimental

**Preparation of Materials.**—All of the quaternary iodides were crystallized from 95% alcohol and dried over phosphorus pentoxide in vacuo. In each case the purity was checked by analysis for iodine. In the case of 1,2-dimethylpyrazolinium iodide, carbon and hydrogen analyses were also made.

*Anal.* Calcd. for  $\text{C}_6\text{H}_9\text{N}_2\text{I}$ : C, 26.78; H, 4.05; I, 56.66. Found: C, 26.83; H, 4.13; I, 56.76.

Solutions of these salts were made up to any required concentration by diluting a weighed amount of salt to a known volume with conductivity water, the accuracy being at least 0.05%. In each case the solution of the salt was made up after the sodium hydroxide solution to bear a definite relation to the concentration of the latter.

The solutions of sodium hydroxide were made by dissolving distilled sodium in conductivity water. The resulting solution was weighed and the concentration calculated from measurements of density. The method was essentially that of Randall and Scalone.<sup>7</sup>

**Apparatus for Measuring Conductivities and Method.**—The bridge assembly and thermostat were those already described by the authors.<sup>8</sup> The reaction cell was of the same design as that shown in Fig. 1 of a previous paper.<sup>3</sup> The method was described in the same paper.

**Calculations.**—The method of calculating the results differed somewhat from that already

described. In the present paper it is assumed that the equivalent conductance of an electrolyte depends only on the ionic strength.

Any solution after mixing was formally considered as consisting of the quaternary hydroxide at a concentration equal to that of the quaternary ion when hydroxide ion was in excess and equal to that of the hydroxide ion when the quaternary ion was in excess. When the two were equal the concentration of quaternary base was taken equal to either one.

The equivalent conductance of the quaternary hydroxide was obtained at several ionic strengths from the extrapolated zero time values of the conductance in various runs, after subtracting the conductance of all the other electrolytes present. The values of the equivalent conductance of the other electrolytes were taken at the same ionic strength, from plots of the equivalent conductance against the square root of the ionic strength. The conductance data on the several quaternary salts were determined for this purpose and are given in Tables II and III.<sup>9</sup>

TABLE II  
CONDUCTIVITY OF 1-METHYLQUINOLINIUM IODIDE  
AT 25.00°

Concn. in Equivs. per liter	Equiv. cond.	Concn. in Equivs. per liter	Equiv. cond.
0.10541	82.03	0.022092	98.06
.095067	83.30	.0047395	106.18
.066750	87.75	.00057230	110.34
.037722	93.57	Extrapolated	113.00
.023288	97.67		

TABLE III  
CONDUCTIVITY OF 1,2-DIMETHYLQUINOLINIUM  
IODIDE AT 25.00°

Concn. in equiv. per liter	0.13402	0.10143	0.055207	0.047126	0.031985
Equiv. cond.	73.13	77.77	86.53	88.21	92.24

The specific reaction rate constant  $k'_1$  was calculated by the equation

$$\frac{dx}{dt} = \frac{d(Q^+)}{dt} = \frac{d(\text{OH}^-)}{dt} = -k'_1(Q^+)^2(\text{OH}^-)^2 \quad (8)$$

where  $x$  is the concentration of the quaternary base, and  $(Q^+)$  is the concentration of the quaternary ion. The concentration of quaternary base at any time after the start was determined by subtracting the portion of the specific conductance due to the other electrolytes from the total and substituting in the relation

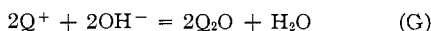
$$C = 1000\kappa/\Lambda_b \quad (9)$$

(9) The values of the equivalent conductance used for the other electrolytes were from the following sources: sodium iodide, Lasselle and Aston, *ibid.*, **55**, 3067 (1933); sodium hydroxide, Randall and Scalone, *ibid.*, **49**, 1491 (1927).

(7) Randall and Scalone, *THIS JOURNAL*, **49**, 1491 (1927).

(8) Lasselle and Aston, *ibid.*, **55**, 3067 (1933).

where  $\Lambda_b$ , the equivalent conductance of the quaternary base, was taken at the ionic strength of the solution from the data obtained from the extrapolated zero time values. Since the concentration of the quaternary base was required to compute the ionic strength at which to take the values of the equivalent conductance of the quaternary base and the other electrolytes, a method of successive approximations was employed. Having obtained the concentration of quaternary base, the total concentration of  $Q^+$  was determined by adding to it the concentration of any excess salt of the quaternary base; the total concentration of hydroxide ion was obtained by adding the concentration of any excess sodium hydroxide to that of the quaternary base. The differential coefficients in equation 8 refer to the rate of disappearance of the quaternary hydroxide by the net reaction



It was obtained directly from graphs in which the total resistance of the reacting solution was plotted against the time.

$$\kappa = C/R \quad (10)$$

where  $\kappa$  is the total specific conductance of the solution and  $C$  is the cell constant

$$\frac{d\kappa}{dt} = -\frac{C}{R^2} \frac{dR}{dt} \quad (11)$$

$$\kappa = \frac{\sum c_s \Lambda_s}{1000} + \frac{x \Lambda_b}{1000} \quad (12)$$

where  $c_s$  is the concentration of an electrolyte other than the quaternary base and  $\Lambda_s$  is the equivalent conductance of the same electrolyte. The summation is taken over all inert electrolytes;  $x$  and  $\Lambda_b$  are the concentration and equivalent conductance, respectively, of the quaternary base.<sup>10</sup>

By differentiation of (12) we get

$$\frac{d\kappa}{dx} = \left[ \sum \left( \frac{c_s}{1000} \frac{d\Lambda_s}{dx} \right) \right] + \left( \frac{x}{1000} \frac{d\Lambda_b}{dx} \right) + \frac{\Lambda_b}{1000} \quad (13)$$

If  $\mu$  is the ionic strength (in this case the total concentration of electrolyte)

$$\mu = x + \sum c_s; \quad d\mu = dx \quad (14)$$

and

$$\frac{d\Lambda}{dx} = \frac{d\Lambda}{d\mu} = \frac{d\Lambda}{d\sqrt{\mu}} \frac{1}{2\sqrt{\mu}} \quad (15)$$

whence

$$\frac{d\kappa}{dx} = \left\{ \left[ \sum \left( \frac{c_s}{1000} \frac{d\Lambda_s}{d\sqrt{\mu}} \frac{1}{2\sqrt{\mu}} \right) \right] + \left( \frac{x}{1000} \frac{d\Lambda_b}{d\sqrt{\mu}} \frac{1}{2\sqrt{\mu}} \right) \right\} + \frac{\Lambda_b}{1000} \quad (16)$$

(10) The concentration of the pseudo base and the negative alcoholate ion at equilibrium is assumed to be so small that no appreciable concentration of quaternary ion would be used up in forming them. The concentration of alcoholate ion would thus be too small to affect the conductance.

The various differential coefficients were obtained from the slope of plots of the equivalent conductance against the square root of the ionic strength for each of the electrolytes at the ionic strength of the solution. The value of the equivalent conductance of the base was taken at the same ionic strength from the plot for the quaternary base.

From the equation

$$\frac{dx}{dt} = \frac{d\kappa}{dt} \frac{dx}{d\kappa} \quad (17)$$

the value of  $dx/dt$  in equation (8) was then obtained immediately, both differential coefficients on the right-hand side being obtained from equations (11) and (16).

#### Data on 1-Methylquinolinium Hydroxide.—

Table IV gives the values of the equivalent conductance of 1-methylquinolinium hydroxide at several values of the ionic strength obtained from the extrapolated zero time measurements.<sup>11</sup> These results show that the base is a strong electrolyte.

TABLE IV  
CONDUCTIVITY OF 1-METHYLQUINOLINIUM  
HYDROXIDE AT 25.00°

Ionic strength	Equiv. cond.	Ionic strength	Equiv. cond.
0.1053	197.0	0.04408	208.9
.09519	199.9	.03767	209.7
.08641	201.1	.03515	211.1
.07553	203.6	.03355	211.5
.05409	207.3	.02326	214.1

The results at various times after mixing 1-methylquinolinium iodide and sodium hydroxide are given in Table V. To save space only typical results are included.<sup>12</sup> In column 1 is given the time in hours after mixing. Column 2 gives the rate of change of specific conductance in mhos per hour. Column 3 gives the specific conductance. Column 4 gives the rate of disappearance of the quaternary base in moles per liter per hour. Columns 5 and 6 give, respectively, the concentration of 1-methylquinolinium ion and hydroxide ion. Column 7 gives the value of  $k'_4$ , calculated by equation 8, and column 8 gives the value of  $k_4$  corrected to zero ionic strength according to the Brönsted theory by the equation

$$\log k_4 = \log k'_4 + 2\sqrt{\mu} \quad (18)$$

The extreme accuracy of the slopes of the resistance-time curves can be seen by inspection of

(11) In all the measurements soft glass cells were used. Except in the second series of measurements the cell was the actual one used in the case of 1,2,5-trimethylpyrazinium hydroxide.

(12) The complete data on this work are recorded in a Doctor's Thesis submitted by P. A. Lasselle to the Graduate School of The Pennsylvania State College, August, 1933.

TABLE V  
RATE OF CHANGE OF SPECIFIC CONDUCTANCE AT 25.00°  
AFTER MIXING 25 CC. OF  $x$  NORMAL 1-METHYLQUINOLIUM  
IODIDE AND OF  $y$  NORMAL SODIUM HYDROXIDE

Time	$-d\kappa/dt$	$\kappa \times 10^3$	$-dx/dt$	(Q <sup>-</sup> )	(OH <sup>-</sup> )	$k_1^0$	$k_1$
	$\times 10^3$		$\times 10^3$				
$x = 0.095067; y = 0.095323$							
1	1.720	145.04	0.8213	0.04686	0.04673	190	780
3	1.481	141.84	.7069	.04528	.04515	186	750
5	1.288	138.11	.6139	.04321	.04308	195	780
7	1.091	136.68	.5200	.04246	.04233	176	690
9	1.036	134.52	.4933	.04131	.04118	187	730
$x = 0.054063; y = 0.054117$							
1	.2438	86.19	.1136	.02706	.02708	229	665
5	.2330	85.25	.1086	.02660	.02662	234	680
9	.2280	84.32	.1063	.02612	.02614	250	720
$x = 0.10078; y = 0.050298$							
7	.4924	96.67	.2319	.04851	.02327	200	700
9	.4653	95.70	.2189	.04813	.02271	202	700
23	.3146	90.35	.1479	.04519	.01995	200	675
28	.2901	88.80	.1364	.04439	.01915	206	695
$x = 0.046911; y = 0.093864$							
3	.4259	124.56	.2011	.02246	.04593	205	685
7	.3709	122.97	.1751	.02176	.04523	195	650
9	.3567	121.52	.1682	.02102	.04449	208	690
$x = 0.037722; y = 0.037633$							
6	.0720	60.21	.03319	.01847	.01843	305	725
12	.0668	59.79	.03056	.01826	.01822	295	715
$x = 0.023288; y = 0.023244$							
50	.01142	37.48	.005194	.01121	.01119	350	700
85	.01112	36.88	.005062	.01092	.01090	378	750
Average 710							

curve (a) in Fig. 1, which is typical of those obtained in all the runs. The entire curve corresponds to only 1% reaction. The extreme accuracy is due to the fact that only changes of conductance are being measured on a single solution in the same cell.

In the dilute runs below 0.02 normal the values of  $k_1$  at the start were larger than those of the more concentrated runs and steadily fell until constant values were reached after the reaction had proceeded about 3%. In the case of the 0.01 normal solution the initial value was five times the constant values given in Table V. Only the constant values finally reached are given in Table V. This effect was not noticed in the more concentrated runs. These initially high values have been found to be due to one or both of two causes, (a) initial rate of solubility of glass which is greatly decreased in the latter part of the run due to coating of the walls with the insoluble ether, (b) slight increases in cell constant due to an observed coating of the electrodes with the insoluble ether. In all cases this precipitation caused a marked change in the ca-

capacity of the cell. However, it was shown that the resistance measurements were still accurate by demonstrating that they were independent of frequency.

The effect of soft glass on the conductance of solutions of sodium hydroxide was studied. It was found that the change of conductance of solutions of 0.02 normal and greater would correspond to an error of not more than 6 to 8% in  $k_1$  but for 0.01 normal solutions the error in  $k_1$  might be 30 to 40% when the glass is not coated with the insoluble ether.

The combined effect of material precipitated on the electrode and solubility of the glass was demonstrated as follows. An apparatus was made similar to that used in all our measurements except it was equipped with two pairs of mixing flasks. It was made entirely of Pyrex glass. Fifty cubic centimeters each of the 1-methylquinolinium iodide and sodium hydroxide to be mixed were placed in the respective flasks of each pair. First the contents of one pair of flasks were mixed and forced into the clean conductivity cell. The change of conductivity was followed for several hours until the values of  $k_1$  became constant. The cell was then emptied. The contents of the other pair of flasks were then mixed, yielding a solution identical with that at the start of the run just discontinued. The conductivity cell was rapidly rinsed once, taking care not to

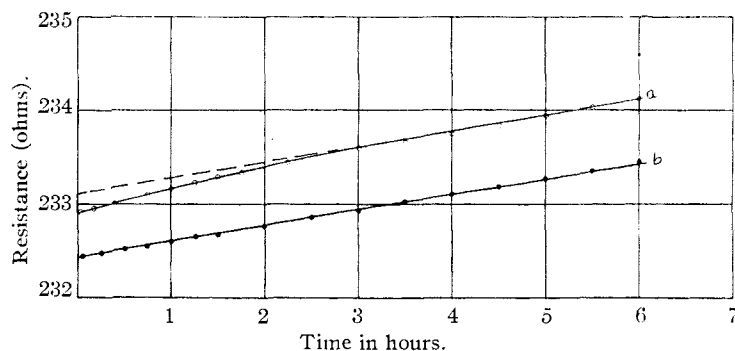


Fig. 1.—a = first filling; b = second filling.

shake, and filled with the new solution and the change of resistance again followed. The results are given in Table VI. Figure 1 gives a plot of these data.

If the initially high value of  $k_1$  were the result of a change in the observed conductance caused by an increase of cell constant, due to coating of the electrodes with a film of the ether, the cell constant must have become again constant when

TABLE VI  
RATE OF CHANGE OF SPECIFIC CONDUCTANCE AT 25.00°  
AFTER MIXING 25 CC. OF  $x$  NORMAL 1-METHYLQUINOLINIUM  
IODIDE AND OF  $y$  NORMAL SODIUM HYDROXIDE

First Filling							
$x = 0.035092; y = 0.035216$							
Time	$-\frac{d\kappa}{dt} \times 10^4$	$\kappa \times 10^4$	$-\frac{dx}{dt} \times 10^3$	(Q <sup>+</sup> )	(OH <sup>-</sup> )	$k_1'$	$k_1$
1	0.06130	57.17	0.02784	0.01759	0.01765	312	749
2	.05405	57.12	.2482	.01754	.01759	281	665
3	.04641	57.07	.02121	.01751	.01757	228	530
4	.04149	57.02	.01906	.01749	.01750	217	515
5	.03896	56.98	.01808	.01746	.01747	207	490
Second Filling							
2	.03936	57.26	.01808	.01760	.01762	202	475
4	.03925	57.18	.01803	.01756	.01758	202	475

constant values of  $k_1$  were finally reached. The second run therefore should not show the effect because the electrodes would already be coated to the maximum extent. Moreover, the initial values of the conductance in the second run should be lower because of the coated electrodes. The initial value after the second filling indicates that the deposit has not increased the cell constant as shown in Table VI, where it is seen that the slightly higher initial conductance after the second filling differs from that of the first filling by less than 0.2%, which is within the error of measuring out and mixing the two solutions. However, since the concentration changes only about 0.1% per hour a 0.05% increase in cell constant in the first hour would produce a 50% increase in the average rate constant over that period. Such a small change in cell constant is, as mentioned, less than the probable error of absolute measurement, but would be readily detectable in the rate, which involves only difference measurements on the same solution. Table VI and Fig. 1 show quite clearly that the initially high values of  $k_1$  are absent in the second run starting with coated electrodes. Thus, it is shown that the ether, when it coats the electrodes, does so only until a layer of a certain thickness is formed and thereafter has no further effect.<sup>13</sup>

(13) At the time when the cell constant is believed to have become constant, the change in the conductance is about 1% while the change in cell constant is only about 0.1 or 0.2% as may be seen from the results of the above experiment and the plot of these data shown in Fig. 1. Since  $dx/dt$  is computed on the assumption that the cell constant remains constant, the values obtained at the first of a run are in error due to the change with time of the cell constant while those values obtained after the cell constant has become constant are only in error by a percentage equal to the percentage change in the cell constant, *i.e.*, 0.2%. Values of  $k_1'$  calculated from the relation  $k_1' = -(dx/dt)/(Q^+)(OH^-)^2$  will also be in error due to the fact that the values Q<sup>+</sup> and OH<sup>-</sup> are both in error by a percentage equal to the percentage change in the cell constant. Thus if  $\epsilon$  is the percentage error in the cell constant, the percentage error in  $k_1'$  after the cell constant has become constant, is approximately  $-3\epsilon$ , *i. e.*, of the order of 1%.

In the second run the glass surface was coated with precipitate formed in the first run. This by decreasing the rate of solution of the glass may also have contributed to the more consistent results.

The values of the specific reaction rate constant in the special Pyrex cell are 29% lower than the constant obtained in the soft glass cell. However, with more concentrated solutions the results in both cases were identical. We believe that the difference was due in some way to the effect of the glass in using up alkali. If this is true our results in the case of dilute solutions are somewhat too high and the excellent check with the more concentrated ones is fortuitous. Perfect agreement is hardly to be expected in view of the high ionic strengths involved. However, if the reaction were actually fifth order, the constant computed as above in 0.017 normal solution would be one-third of that in the 0.05 normal solution. It thus seems impossible that the several irregularities just mentioned could cause any serious error in our interpretations of the results.

The results at 33.8° are given in Table VII.

TABLE VII  
RATE OF CHANGE OF SPECIFIC CONDUCTANCE AT 33.8°  
AFTER MIXING 50 CC. OF  $x$  NORMAL 1-METHYLQUINOLINIUM  
IODIDE AND OF  $y$  NORMAL SODIUM HYDROXIDE

$x = 0.055429; y = 0.055420$							
Time	$-\frac{d\kappa}{dt} \times 10^4$	$\kappa \times 10^4$	$-\frac{dx}{dt} \times 10^3$	(Q <sup>+</sup> )	(OH <sup>-</sup> )	$k_1'$	$k_1$
2	0.5511	102.01	0.2354	0.02721	0.02721	427	1259
4	.5065	100.99	.2163	.02677	.02677	418	1233
6	.4773	100.00	.2038	.02635	.02635	421	1242
9	.4140	98.68	.1768	.02578	.02578	380	1120
$x = 0.036006; y = 0.036006$							
2	.1318	68.19	.05505	.01789	.01789	536	1285
4	.1308	67.93	.05463	.01778	.01778	546	1309
6	.1093	67.69	.04555	.01768	.01768	468	1123
9	.09800	67.33	.04093	.01753	.01753	433	1038
Average 1201							

The agreement of the constants at the two concentrations shows that the order is the same as at 25.00°. For these the same type of soft glass cell was used. The formal heat of activation,  $Q$ , was calculated from the equation

$$2.303 \log_{10} \frac{k_2}{k_1} = \frac{Q}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

using the average value of  $k$  at each temperature. The value of  $Q$  thus found was 10,420 calories per mole.

**Data on 1,2-Dimethylquinolinium Hydroxide.**—Table VIII gives the values of the equivalent conductance of 1,2-dimethylquinolinium hydroxide at several values of the ionic strength obtained

TABLE VIII  
CONDUCTIVITY OF 1,2-DIMETHYLQUINOLIUM HYDROXIDE  
AT 25.00°

Ionic strength	0.1014	0.04712	0.02694	0.02242
Equiv. cond.	186.5	202.1	206.5	209.2

from the extrapolated zero time measurements. These results show that the base is a strong electrolyte.

TABLE IX  
RATE OF CHANGE OF SPECIFIC CONDUCTANCE AT 25.00°  
AFTER MIXING 25 CC. OF  $x$  NORMAL 1,2-DIMETHYLQUINO-  
LINIUM IODIDE AND OF  $y$  NORMAL SODIUM HYDROXIDE

Time	$x = 0.10143; y = 0.10139$		$(Q^+)$	$(OH^-)$	$k_1'$	$k_1$
	$-\frac{d\kappa}{dt} \times 10^4$	$\kappa \times 10^4$				
1	0.4310	149.19	0.2186	0.05050	0.05048	37 159
3	.3940	148.37	.1997	.05005	.05003	35 150
5	.3238	147.63	.1542	.04966	.04964	28 121
7	.2901	147.03	.1471	.04929	.04927	27 117
9	.2878	146.42	.1460	.04895	.04893	28 118
$x = 0.047126; y = 0.047126$						
1	.08196	74.12	.03906	.02352	.02352	137 372
10	.03641	73.65	.01734	.02326	.02326	63 168
30	.02313	73.12	.01102	.02300	.02300	42 114
45	.02055	72.79	.009794	.02284	.02284	39 104
70	.01406	72.36	.006698	.02261	.02261	29 78

The results at various times after mixing 1,2-dimethylquinolinium iodide and sodium hydroxide are given in Table IX, which corresponds to Table V. Only a few of our typical results are included. The values of the specific reaction rate constant on the more dilute run have practically reached a constant value. If the reaction were fifth order this value would be one-half of that in the concentrated run. We believe that our results indicate quite definitely a fourth order reaction. The irregularities are doubtless due to the solubility of the glass and the electrode effects already discussed. These effects would be much greater in the present case owing to the far slower reaction rate.

**Data on 1,2-Dimethylpyrazolinium Hydroxide and 1,2-Dimethylpyridinium Hydroxide.**—Equal volumes of a solution of the iodide and an equivalent solution of sodium hydroxide were mixed and the conductance determined at 25.00°. After subtracting the conductance due to the ions of

sodium iodide the equivalent conductance of the base was calculated by equation (9). The results obtained were regarded as being equal to the values of the equivalent conductance of the base alone at a concentration equal to the total electrolyte concentration (ionic strength) in the determination (equal to that of the equivalent solutions mixed).

1,2-dimethylpyrazolinium hydroxide

$$\mu = 0.02 \quad \Lambda = 225.3$$

$$\mu = 0.1 \quad \Lambda = 208.2$$

1,2-dimethylpyridinium hydroxide

$$\mu = 0.1052 \quad \Lambda = 204.1$$

No significant change of conductance with time at 25.00° was detected with 0.05 normal solutions of either of these bases. In more dilute solutions a small decrease traced directly to reaction of the alkali with the glass was observed. Thus neither of the bases yields a dimolecular ether at an appreciable rate.

### Summary

1. A method for the calculation of the instantaneous specific reaction rate constant of an ionic reaction from resistance-time plots has been outlined.
2. The rate of formation of dimolecular ethers from 1-methylquinolinium hydroxide and 1,2-dimethylquinolinium hydroxide has been measured by a conductance method at 25.00°. The measurements indicate a reaction second order with respect to the positive ion and second order with respect to hydroxide ion in either case.
3. Measurements at 33.8° on 1-methylquinolinium hydroxide yield a value of the formal heat of activation of 10,420 calories.
4. 1,2-Dimethylpyrazolinium and 1,2-dimethylpyridinium hydroxide do not yield ethers at 25.00°. Both bases are strong electrolytes.
5. The results are explained on the basis of the extent of conjugation in the heterocyclic nuclei.