borohydride monoetherate.[2,5] The inflection expected for the monoetherate at mole ratio 1.00 was observed between mole ratios 0.96 and 1.02.

Reaction at Reduced Temperature.—At −80° the reaction is slow, in one experiment 0.03 mole of diborane for each mole of lithium amide being absorbed in 12 hours, while under similar conditions but at −45°, the reaction is complete within several hours. At −65° the reaction appears to cease after absorption of approximately one-half mole of diborane, but whether this indicates a stepwise reaction or results from coating of the sample could not be determined, as duplication proved difficult.

Discussion

The simplicity of the stoichiometry and the absence of side reactions when the reaction is carried out under controlled conditions suggest a simple process. By analogy to the behavior of diborane toward lithium hydride to give lithium borohydride[2] it might be expected a borine group would add to an electron pair of the amide ion.

$$^1/_2B_2H_6 + LiNH_2 = LiH_3BNH_2 \qquad (2)$$

Displacement of the weak acid, aminoborine, by the stronger acid, borine, would then result in the products observed.

$$LiH_3BNH_2 + {}^1/_2B_2H_6 = LiBH_4 + BH_2NH_2 \qquad (3)$$

An alternate, but less probable, process which could lead to the observed products is the addition of a second borine to the product of reaction (2)

$$LiH_3BNH_2 + {}^1/_2B_2H_6 = LiBH_3NH_2BH_3 \qquad (4)$$

followed by the displacement of the weak acid, aminodiborane, by the stronger acid, borine

$$LiBH_3NH_2BH_3 + {}^1/_2B_2H_6 = LiBH_4 + B_2H_5NH_2 \qquad (5)$$

and the decomposition of the aminodiborane

$$B_2H_5NH_2 = BH_2NH_2 + {}^1/_2B_2H_6 \qquad (6)$$

Although every effort was made to detect the presence of aminodiborane, a fairly stable substance under the conditions of the reaction,[6] and to isolate the lithium salt $LiH_3BNH_2BH_3$, which by analogy to the corresponding sodium salt[7] $NaH_3BNH_2BH_3$ ought to be stable, no support for this alternate process could be obtained.

The reaction between lithium amide and diborane provides a convenient method for the preparation of polymeric aminoborine, a substance heretofore available only by the decomposition of aminodiborane.[8]

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St. Louis University
St. Louis 4, Missouri

The Kinetics of Hydrolysis of Acetyl Chloride in Acetone–Water Mixtures

By George Zimmerman and Ching Yuan

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A number of careful studies of the kinetics of hydrolysis and alcoholysis of acid halides have been made recently[1-8]; in several instances for relatively low concentrations of water (or alcohol) in a non-reacting solvent, the reaction was second order with respect to water (or alcohol) and first order with respect to acid halide.[2,5,7] A termolecular mechanism has been proposed[2,5] and is consistent with the observed low activation enthalpies and entropies. Hudson and co-workers[1-3] have shown that several independent mechanisms are required to account for the kinetic behavior of benzoyl chloride hydrolysis over a wide range of water concentrations in several solvents. Using conductometric methods, we have measured the rate of hydrolysis of acetyl chloride dissolved in acetone containing 1 to 5% of water. The results seem to fit well into and to substantiate the above picture.

Experimental.—Acetyl chloride was purified carefully as recommended by Fieser,[9] and stored in a special buret in an atmosphere of dry nitrogen; from this the CH_3COCl could be added to dry acetone[10] in the absence of moisture or to the various acetone–water mixtures. The conductance cell used was a modified "pipet type" cell,[11] of 12 ml. volume and with a cell constant of 0.253 cm.$^{-1}$. A conventional a.c. bridge circuit[12] using a Leeds and Northrup 1000-cycle oscillator and a cathode ray oscilloscope as the current detector was employed. The cell had such a small capacitance that relatively little precision was to be gained by capacitance balancing. For a given run the acetone–water mixture was brought to bath temperature, approximately the desired amount of CH_3COCl was added and mixed (in about 8 seconds; zero time taken halfway through), the cell rinsed, filled, and mounted in the bath (in about 1 min.). The remaining mixture was sealed and kept in the bath for at least 24 hr., in order that the reaction proceed to completion. Part was then titrated with standard base to obtain the exact initial concentration of CH_3COCl, and part was used for an infinite-time conductance measurement. All runs were carried out with a sufficiently large ratio, concn. of H_2O/concn. of CH_3COCl, that first-order kinetics were observed over a wide range of reaction. For a given acetone–water mixture the dependence of conductance on the concentration of reaction products was found by measuring the conductance of a completely reacted solution at various dilutions (with the same water–acetone mixture). Actually, over the range of reaction studied in most runs, the conductance was so close to being a linear function of the concentration of products that it was assumed exactly so. In this case (for a first-order reaction) a plot of $\log(L_\infty - L_t)$ against t (L_t = measured conductance at time, t) should be a straight line with a slope of $k'/2.303$ (k' = pseudo first-order rate constant).[13]

Results.—Figure 1 shows $[\log(L_\infty - L_t) + 5]$ plotted against t for two typical runs and justifies to within 2–3% the assumptions made in the kinetic analysis. Table I summarizes data for the runs of interest; in a few cases (with smaller ex-

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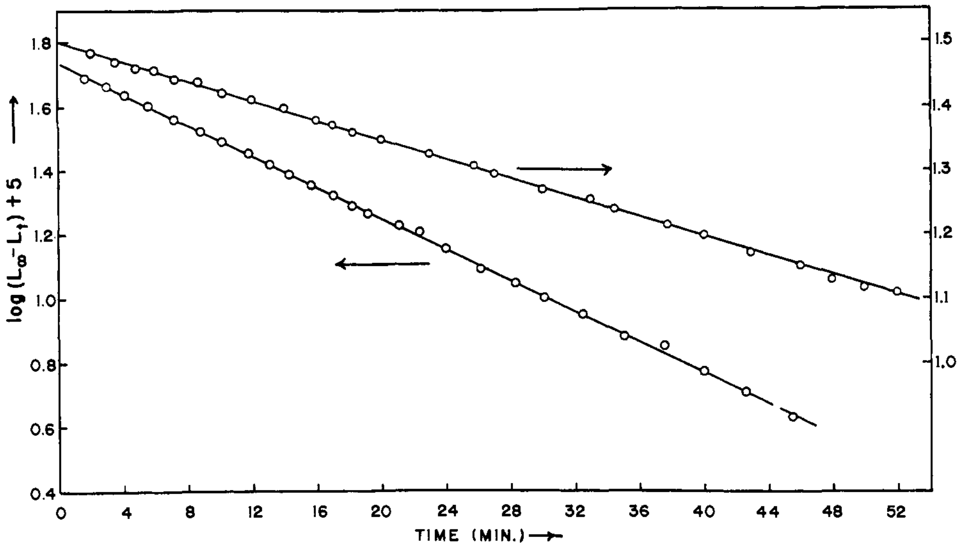

Fig. 1.

TABLE I

VARIATION OF THE FIRST-ORDER CONSTANT WITH WATER CONCENTRATION[14]

Solvent composition, volume % of H_2O	Concn. of H_2O, moles/liter of soln.	Initial concn. of CH_3COCl, moles/liter of soln.	$\frac{m_{H_2O}}{m_{CH_3COCl}}$	k' (min.$^{-1}$ × 10^2) ± 5%
0.99	0.547	0.01976	27.6	1.73
1.48	.817	.01430	57.1	3.25
1.77	.978	.01149	85.1	4.56
1.77	.974	.06688	14.6	4.74
1.89	1.048	.01966	53.3	4.72
1.89	1.046	.04894	21.4	5.04
1.96	1.084	.01730	62.7	5.26
2.79	1.55	.02322	66.8	11.2
3.47	1.92	.01832	104.8	15.9
5.12	2.83	.02098	124.9	40.1
1.77	0.98	.02388	41.0	5.64
1.77	0.98	.02376	41.2	5.58

cesses of H_2O) initial slopes were taken, when there was a slight noticeable curvature in the line of points. In Fig. 2, log k' is plotted against log m_{H_2O} (m = initial molarity); least squares analysis gives a slope of 1.92 ± 0.07 (or 1.98 ± 0.04 if the most divergent point is omitted), showing a second-order dependence on water in the concentration range studied. The true third-order constant, k, is $4.82 \pm 0.24 \times 10^{-2}$ min.$^{-1}$ l.^{2} moles^{-2} (or $4.63 \pm 0.22 \times 10^{-2}$ with the same point omitted). From the results for $m_{H_2O} = 0.98$ at the two temperatures shown in Table I, $\Delta H^{\ddagger} = 7.6 \pm 0.3$ kcal./mole and $\Delta S^{\ddagger} = -49.2$ e.u. (at 24.8°).

The present data are neither extensive nor precise enough to permit any further conclusions, but the slight suggestion of curvature in the points of Fig. 2 allows for the possibility of finding an order smaller than 3 at still smaller water concentrations. As the results stand, they confirm (for this system) the mechanism discussed by Swain[5] and by Archer and Hudson.[2] For 5% (by volume) of H_2O in acetone at 25° one can compare the third-order constant and activation enthalpy for CH_3COCl (7.83×10^{-4} sec.$^{-1}$ l.^{2} moles^{-2} and 7.6 kcal./mole) and C_6H_5COCl (7.18×10^{-6} sec.$^{-1}$ l.^{2} moles^{-2} and 11.73 kcal./mole)[2]. One might expect this sort of relation because of resonance stabilization of the initial state of C_6H_5COCl.

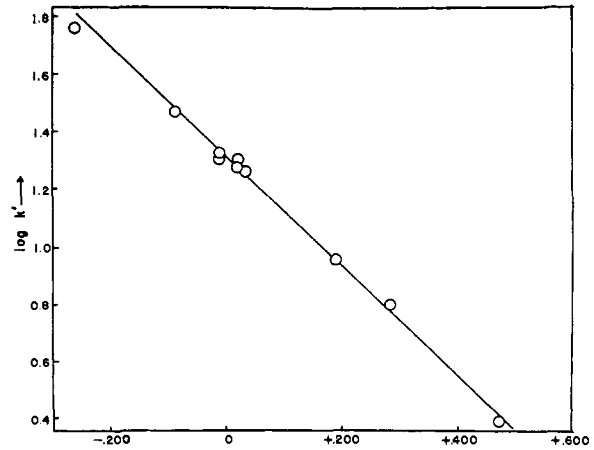

Fig. 2.

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[14] The last two runs are for 29.2 ± 0.1°; all others for 24.8 ± 0.1°.