Heated in a capillary tube, the monohydrate evolves gas rapidly at 175° (cor.) and increases in bulk about twentyfold. It shows a rotation of $[\alpha]^{24}\text{D}$ +22.3° (c 5, H_2O).

FERMENTATION DIVISION
NORTHERN REGIONAL RESEARCH LABORATORY[3]
PEORIA, ILLINOIS

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(3) One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Article not copyrighted.

Acid-catalyzed Hydrolysis of Ethyl Acetate

BY OGDEN R. PIERCE AND GEORGE GORIN

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In connection with other work done in this Laboratory, it was of interest to measure the rates of hydrolysis of ethyl acetate at 25° in aqueous acetone (70% by volume) with varying concentrations of hydrochloric acid as catalyst, and also to estimate the relative catalytic activities of trifluoroacetic and difluoroacetic acids. The results are reported in Table I, together with data from the literature from which interesting comparisons can be made. Each value determined in this investigation is the average of three or four determinations, and the degree of reproducibility is indicated by the indeterminate error of the mean.[1] The ester concentration was 0.2 M unless otherwise specified in the footnote.

TABLE I

Concn. catalyst, c, mole/l.	Medium	Cat. constant, k/c, $\times 10^5$, l. mole^{-1} sec.$^{-1}$
0.025 N HCl	70% acetone	4.24 ± 0.05
.05 N HCl[2]	70% acetone	4.27 ± .01
.1 N HCl	70% acetone	4.28 ± .04
.5 N HCl[3]	70% acetone	4.61
.1 N CF_3COOH	70% acetone	1.90 ± 0.02
.1 N HCl[4]	Water	10.8
.1 N CF_3COOH	Water	10.0 ± 0.1
.1 N CHF_2COOH	Water	6.09 ± 0.05
.1 N CCl_3COOH[5]	Water	10.7
.1 N $CHCl_2COOH$[6]	Water	6.30

It is seen that the reaction-rate constant divided by the concentration of catalyzing acid is constant within experimental error for 0.1, 0.05 and 0.025 N hydrochloric acid. This indicates that the rate is proportional to the concentration of catalyst within this concentration range. The catalytic constant is somewhat lower than the value previously found by Haskell and Hammett[3] in 0.5 N acid, and this is wholly analogous to the results reported for water, where the catalytic constant is 1.08 × 10^{-4} throughout the range 0.0002 to 0.1 N hydrochloric acid, and shows a 5% increase in 0.5 N acid.[4]

In 70% acetone at 0.1 N concentration, trifluoroacetic acid is less than half as effective as hydrochloric acid, and this must reflect the relative strength of these acids, although the relation is not linear. In water, a medium of much higher dielectric constant, the levelling effect of the solvent[7] makes the difference less marked; hydrochloric acid, trifluoroacetic acid and trichloroacetic acid all appear to be about equally strong. Even in water, however, difluoroacetic acid is weaker than any of these, and about as good a catalyst as dichloroacetic acid.

Experimental

Materials.—Ethyl acetate was a commercial C.P. product, which was purified according to Weissberger and Proskauer[8] and distilled through a 4-ft. helices-packed Todd column; the middle third boiled within 0.1° and was collected in three successive fractions which were employed interchangeably with no noticeable change in results. A portion of this product was purified again in the same way and a small center cut was collected at constant temperature. The results obtained with this preparation were the same as the rest within experimental error.

Trifluoroacetic acid was obtained from the Minnesota Mining and Mfg. Co. and distilled twice; a small center fraction was collected for use each time, and both preparations gave the same results: b.p. 70–71°, neut. equiv. 113.7 (calculated 114.0). Difluoroacetic acid was a laboratory preparation, redistilled from phosphorus pentoxide: b.p. 133.2°, neut. equiv. 95.6 (calculated 96.0).

Acetone was a C.P. product that was refluxed with potassium permanganate and distilled, the center four-fifths being retained for use. The "70% acetone" medium consisted of 70.0 ml. of acetone (54.9 ± 0.1 g.) per 100 ml. of solution.

Method.—Water and other reagents were first allowed to come to constant temperature. Two milliliters of ester was then placed in a weighed 100-ml. volumetric flask containing a little water, and the weight of the ester was determined by difference; the initial concentration of ester, a, was calculated from this weight. Water, acetone if desired, and appropriate amounts of acid were then added to the flask and the solution diluted to the mark. Immediately after mixing and at appropriate intervals thereafter 2.00-ml. aliquots were withdrawn, diluted to 20 ml. with water, and titrated with standard 0.01 N barium hydroxide to a phenolphthalein end-point. Zero time was taken as the instant at which the acid was added, and the titer at zero time was estimated by extrapolation. The concentration of catalyzing acid could thus be estimated directly, and the value compared to that calculated from the normality of the original solution and the dilution factor; an average of the two values was taken as the actual catalyst concentration. The amount of ester, x, hydrolyzed at any time, t, was calculated from the titer of barium hydroxide required in excess of the extrapolated zero-time titer. Measurements were made only in the interval to 50% reaction, so that the effect of the reverse reaction could be neglected. The reaction rate constant was then computed by means of the equation[9]

$$k = \frac{2.303}{t_2 - t_1} \log \frac{(a - x_1)}{(a - x_2)}$$

taking care to vary the intervals of time between successive measurements. Usually five or six values of k were obtained in each experiment, and the results averaged.

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(1) F. Daniels, *et al.*, "Experimental Physical Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1949, p. 357.

(2) G. Davies and D. P. Evans, *J. Chem. Soc.*, 339 (1940), reported 4.47 × 10^{-5} at 24.8° and correction to 25.0° using their value for the energy of activation gives 4.55 × 10^{-5}. In their experiments the ester concentration was 0.05 M and the medium contained about 1.5 ml. more water per 100 ml. of solution: the higher water content is sufficient to account for the difference in rates. The rate found by the present authors for 0.1 M ester in a medium containing about 1 ml. more water was 4.60 × 10^{-5}.

(3) V. C. Haskell and L. P. Hammett, THIS JOURNAL, **71**, 1284 (1949).

(4) H. M. Dawson and W. Lowson, *J. Chem. Soc.*, 2146 (1928).

(5) H. S. Taylor, *Medd. K. Vetenskapsakad. Nobelinst.*, **2**, No. 37, 1–18 (1913).

(6) H. M. Dawson and W. Lowson, *J. Chem. Soc.*, 1217 (1929).

(7) L. P. Hammett, "Physical Organic Chemistry," McGraw–Hill Book Co., Inc., New York, N. Y., 1940, p. 256.

(8) A. Weissberger and E. Proskauer, "Organic Solvents," Oxford University Press, 1935, p. 150.

(9) W. E. Roseveare, THIS JOURNAL, **53**, 1651 (1931). As pointed out in this article, the more popular alternative form of the equation, *i.e.*, $k = 2.303/t \log (a/a - x)$, gives greater statistical weight to the first measurements, which would be particularly undesirable in this case because the first titers are small differences between large numbers.

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DEPARTMENT OF CHEMISTRY
PURDUE UNIVERSITY
LAFAYETTE, INDIANA

N,N'-Dialkylethylenediamines by Reduction of Dialkyloxamides[1a,b]

BY LEONARD M. RICE, BERNARD H. ARMBRECHT, CHARLES H. GROGAN AND E. EMMET REID[2]

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Lithium aluminum hydride has proved to be an efficient agent for the reduction of acid amides to amines. It seemed to be of interest to try the reduction of N,N'-dialkyloxamides in which the two carbonyls are adjacent. This has been found to go smoothly and to give a good yield of a product which does not require extensive purification. There are several more or less satisfactory ways of preparing the N,N'-dialkylethylenediamines, but our method may prove useful in special cases, particularly for symmetrical alkyl-aryl compounds.

TABLE I

N,N'-DIALKYLETHYLENEDIAMINES, R—NH—CH_2CH_2—NH—R

R	Source	B.p., °C.	B.p., Mm.	Yield, %	d^{25}_{4}[e]	$n^{25}\text{D}$	Diphenylurea derivative, m.p., °C.
Ethyl[a]	Diacetate	148–150	760	50	0.804	1.4298	197–199[f]
Ethyl	Oxamide	148–150	760	53	.809	1.4296	197–199[f,g]
Butyl[b]	Dibutyrate	74–77	3	72	.811	1.4382	174–176[b,h]
Butyl	Oxamide	73–78	3	63	.811	1.4387	174–175[h]
Decyl[c]	Dicaprate	180–183	0.7	61	...	....	86–86.5[i,j]
Decyl[d]	Oxamide	184–190	1	56	...	....	85.5–86[i]

[a] W. R. Boon, *J. Chem. Soc.*, 307 (1947). [b] A. E. Frost, S. Chaberek and A. E. Martell, THIS JOURNAL, **71**, 3842 (1949). [c] F. Linsker and R. L. Evans, *ibid.*, **68**, 1432 (1946), recorded m.p. 0–2°, found, m.p. 28–30°. [d] Dihydrochloride. *Anal.* Calcd. for $C_{22}H_{48}N_2Cl_2$: C, 64.38; H, 11.70; N, 6.77; Cl, 17.15. Found: C, 63.71; H, 11.82; N, 6.79; Cl, 17.08. [e] ±0.005. [f] Mixed m.p. 196–197°. [g] *Anal.* Calcd. for $C_{20}H_{26}N_4O_2$: N, 15.81. Found: N, 16.02. [h] Mixed m.p. 174–176°. [i] Mixed m.p. 86–87°. [j] *Anal.* Calcd. for $C_{36}H_{58}N_4O_2$: N, 9.68. Found: N, 9.84.

In order to check the identity and purity of our products we also prepared them by the reduction of the isomeric diacylethylenediamines. As in the case of the substituted oxamides, the reduction proceeded evenly to give good yields of pure dialkylethylenediamines.

$$\begin{array}{l} RCH_2NHCOCONHCH_2R \searrow \\ \qquad\qquad\qquad\qquad\qquad\qquad RCH_2NHCH_2CH_2NHCH_2R \\ RCONHCH_2CH_2NHCOR \nearrow \end{array}$$

This has been done with three pairs of amides with the results shown in Table I in which the boiling points, density and refractive index all checked. The diphenylurea derivatives correspond in each set.

Experimental

The Dialkyloxamides.—These were conveniently prepared by adding ethyl oxalate to a slight excess of the amine in water or in alcohol. The melting points of the products were 176° for diethyl, 154° for dibutyl, and 123° for didecyl, which were in agreement with recorded values.[3,4] The ethylene bis-amides were materials from a previous investigation.[5]

General Procedure for Reduction.—In a two-liter, three-necked flask, fitted with a dropping funnel, sealed stirrer and a long reflux condenser closed with a drying tube, a solution of 15 g. of lithium aluminum hydride in 600 ml. of anhydrous ether was prepared. The bis-amide, 30 g. in the form of a well mixed ether slurry, was added to the hydride solution at such a rate that the ether refluxed at a moderate rate.

In some cases it was found that the use of a soxhlet extractor was more convenient, although there was no appreciable increase in yield. In either case when all of the reactants had been brought together the contents were vigorously stirred under reflux for four hours and then allowed to stand overnight. The reaction mixture was decomposed by the dropwise addition of water regulated at such a rate that the capacity of the condenser was not exceeded. After reflux had ceased, a 10-ml. excess of water was added and the mixture stirred an additional hour. The suspension was filtered and the residue was washed three times with 50-ml. portions of ether. The ethereal filtrate was dried over potassium hydroxide and the ether stripped off. Distillation in vacuum over a pellet of potassium hydroxide yielded the products as colorless liquids. The decyl compound solidified in the receiver. As these liquids are strong absorbants of CO_2, it was advisable to purge the apparatus with nitrogen.

GEORGETOWN UNIVERSITY MEDICAL CENTER
WASHINGTON 7, D. C.

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(1) (a) Presented at the Meeting of the American Chemical Society, Medicinal Section, Atlantic City, N. J., September 15, 1952. (b) Supported in part by a grant from the Geschickter Fund for Medical Research, Inc.

(2) Professor Emeritus, Johns Hopkins University, Baltimore 18, Md.

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Aluminum Monochlorodilaurate, a Non-thickener for Hydrocarbons[1]

BY KAROL J. MYSELS AND DORIS MAY CHIN[2]

RECEIVED JUNE 26, 1952

Aluminum difatty acid soaps, depending on the nature of the third substituent, show marked and as yet unexplained differences in their ability to increase the viscosity of hydrocarbon solvents. The hydroxy compounds are excellent thickeners and widely used in greases and flame warfare, while the alcoxy,[3] the cresoxy[3] and perhaps the carboxy[4]

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(1) Based upon the M.S. thesis of D.M. Chin, University of Southern California, Los Angeles 7, California, August, 1950, and presented in part before the Division of Colloid Chemistry during the 118th Meeting of the American Chemical Society at Chicago, Illinois.

(2) Colgate-Palmolive-Peet Fellow 1949–1950.

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