We wish to acknowledge our indebtedness to Professor S. J. Bates of this Laboratory for much helpful advice and criticism during the course of this investigation.

Summary

The effects of added sodium dithionate and of added perchloric acid upon the activity coefficients of hydrochloric acid in aqueous solution were determined at 25° up to an ionic strength somewhat greater than unity.

The effects of these salts, which are of types not heretofore tested, are qualitatively the same as those of added chlorides of the alkali and alkaline earth elements. Thus, when added to a dilute solution of hydrochloric acid they cause its activity coefficient at first to decrease and then to increase with increasing ionic strength. The addition of perchloric acid increases the activity coefficient more than does that of any other electrolyte. In fact, the activity coefficient in these mixtures is greater than is that of pure hydrochloric acid at the same ionic strength.

The equation which has been found to hold for the effect of certain other electrolytes upon hydrochloric acid, namely, $\log \alpha = \log \alpha_0 + k(\mu - m)$ is closely followed by mixtures containing sodium dithionate and perchloric acid.

PASADENA, CALIFORNIA

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

The Rate of Addition of Methyl Esters to Trimethylamine[1]

BY LOUIS P. HAMMETT AND HELMUTH L. PFLUGER

We have found that the rate of methylation of trimethylamine to tetramethylammonium ion by the methyl ester of a carboxylic acid is determined by the strength of the acid in a fashion which is without parallel in recorded ester reactions but is very similar to the general acid catalysis equation of Brönsted.[2] The reaction in question: $RCOOCH_3 + N(CH_3)_3 \longrightarrow RCOO' + N(CH_3)_4^+$, is of the same type as those upon which depend the familiar preparative use of the esters of strong acids as alkylating agents; in fact, now that the work of Hantzsch[3] has shown that those acids which are strong, and of equal strength, in aqueous solution are of very different inherent strengths, it becomes apparent that the useful alkylating agents are precisely the esters of the strongest acids, the sul-

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[1] This article is based upon a dissertation submitted by Helmuth L. Pfluger to the Faculty of Pure Science of Columbia University in partial fulfilment of the requirements for the degree of Doctor of Philosophy, May, 1933. The material was presented at the Washington Meeting of the American Chemical Society, March, 1933.

[2] Brönsted and Pedersen, *Z. physik. Chem.*, **108**, 185 (1924). See the review by Kilpatrick and Kilpatrick; *Chem. Rev.*, **10**, 213 (1932).

[3] Hantzsch, *Z. Elektrochem.*, **29**, 221 (1923).

fates, the sulfonates, and, in the order of the strength of the corresponding acids, the halides. That carboxylic esters can accomplish a similar alkylation of tertiary amines was shown by Willstätter and Kahn,[4] who worked without solvent, and merely demonstrated the formation of a large yield of tetraalkylammonium salt. We have found that the reaction goes cleanly and at a suitable rate for measurement in methyl alcoholic solution at 100°.

Materials and Method

Methyl alcohol was synthetic methanol from the Commercial Solvents Corporation. It was dried by the method of Lund and Bjerrum[5] using magnesium in the presence of iodine, and distilled through a bulb stillhead in an all-glass apparatus, retaining only the first two-thirds of the distillate. The product had a density of 0.78691 at 25°, which was not altered by repetition of the treatment. We also tried the method of drying with aluminum amalgam recommended by Hartley and Raikes,[6] but found the co-distillation of mercury with the alcohol troublesome.

Trimethylamine was purchased as a 33% methyl alcohol solution and diluted directly with the purified methyl alcohol. Qualitative tests for primary and secondary amines were negative.

Esters were, in general, purified by extraction of an ether solution with aqueous sodium carbonate, drying over anhydrous sodium sulfate, and distilling through a Vigreux stillhead in an all-glass apparatus, retaining a portion of constant boiling point. *Methyl acetate* was extracted with calcium chloride brine without the use of ether, and then dried and distilled. Boiling points and saponification values were as follows: acetate, 58.9°, 99.6%; benzoate, 198°, 100.2%; *o*-toluate, 212.8°, 99.6%; *p*-toluate, 221°, 99.6%; *o*-chlorobenzoate, 235°, 99.7%; phthalate, 282.3°, 99.2%; *o*-nitrobenzoate, 288°, 99.5%. Free acid was found to be less than 0.01% in all cases except lactate. The *methyl lactate* purchased was a "practical" product and very impure, much of it distilling below 100°. A portion with a constant boiling point of 144.5° after two distillations was used for the velocity measurements. It was still impure, and probably contained a formic ester, as shown by a saponification value 3.75% too high, and by a direct test for formic acid with mercuric oxide in aqueous solution. *Methyl p-nitrobenzoate* was recrystallized from methyl alcohol and melted at 96.5° (corr.).

All materials were kept after purification in stoppered bottles in desiccators containing phosphorus pentoxide.

Method.—The reaction was followed quantitatively by determining the concentration of trimethylamine which remained after definite intervals of time. This was accomplished by steam-distilling the trimethylamine into standard acid and back-titrating with standard alkali. The reaction solutions were prepared by weighing out a suitable amount of ester either directly in a 50-cc. volumetric flask or by use of a small Bailey weight buret, then diluting to the mark with an approximately 0.2 molar solution of trimethylamine in methyl alcohol; 5 cc. of the mixed solution was pipetted into a 50-cc. volumetric flask half full of water (or methyl alcohol, if the ester was insoluble in water) to which 1 cc. of approximately 0.2 *N* hydrochloric acid had previously been added, and the flask was then filled with water up to the mark. This solution was used for the determination of the initial concentration of trimethylamine. The remainder of the reaction mixture was introduced into clean and dry Pyrex ampoules of 8 cc. capacity with the aid of a funnel drawn to a capillary, a small space being left in the ampoule for

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(4) Willstätter and Kahn, *Ber.*, **35**, 2757 (1902).

(5) Lund and Bjerrum, *ibid.*, **64**, 210 (1931).

(6) Hartley and Raikes, *J. Chem. Soc.*, 524 (1925).

expansion of the alcohol upon introduction into the hot bath. The ampoules, cooled by ice, were sealed and introduced into an oil thermostat which operated at 100 ± 0.03°. The time was recorded to the nearest minute.

When an ampoule was removed from the thermostat it was placed immediately in ice and the time was recorded. After cleaning it was opened, its contents were shaken into a small beaker, and 5 cc. was pipetted into an acid solution and diluted to 50 cc. exactly as with the initial reaction mixture.

For the determination of trimethylamine, the micro-Kjeldahl distillation method of Pregl[7] was used. Duplicate determinations were made on each ampoule and on the initial reaction mixture, using for each determination 10 cc. of the solutions diluted as above described. Twenty cc. of standard 0.01 N hydrochloric acid diluted to 50 cc. was contained in the receiver. After seven minutes distillation with the condenser immersed below the surface of the acid, followed by four minutes with the tip above the acid solution, the acid was boiled to remove carbon dioxide, and titrated with 0.01 N sodium hydroxide from a microburet, using methyl red indicator and a daylight lamp.

Precision.—That the reaction actually produced tetramethylammonium ion in large quantities was demonstrated with all the esters by qualitative test with the potassium bismuth iodide reagent of Kraut. This gives a red precipitate with both trimethylammonium and tetramethylammonium ions, and was therefore applied to a solution which had first been made alkaline and heated to remove the former. It is as a matter of fact difficult to imagine any reaction other than the formation of tetramethylammonium ion by which the quantity of trimethylamine measured by our method of analysis can decrease.

In the case of the nitro compounds a titanous chloride titration showed that no reduction of the nitro group by the alkaline alcoholic solution occurred, and colorimetric tests showed that only traces of nitrite ion were produced by splitting-off of the nitro group during the course of the reaction. In the case of the chlorobenzoate, no chloride ion could be found in the reaction mixture.

In further support of the unique course of the reaction is the failure to observe drifts in the bimolecular constants in nearly all of the reactions studied.

Two successive analyses of the same solution always agreed within three parts per thousand, and usually much better than this. Suitable experiments demonstrated that, within this precision, the operation of introduction into the ampoule and removal from it produced no errors; the distillation method gave figures in agreement with direct titration of a trimethylamine solution; there is no disappearance of trimethylamine when a methyl alcoholic solution is heated at 100° for one month.

Table I contains the detailed experimental data for two esters, methyl acetate and methyl benzoate. Except for the two nitrobenzoates, the precision and freedom from drift here exhibited is typical, as may be seen from the average deviations included in Table III. In the case of *p*-nitro-

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(7) Pregl, "Quantitative Organic Microanalysis," translated by Fyleman, P. Blakiston's Son & Co., Philadelphia, p. 94 ff.

benzoate, the much larger and entirely irregular scatter of the results probably arises from the difficulty of manipulation without loss of solutions in a volatile solvent of this not very soluble substance. In the case of *o*-nitrobenzoate, and in this case only, was there the sort of recognizable drift of the constants apparent in Table II. The constants for methyl

TABLE I

METHYL BENZOATE

Run 1. Initial concn. of ester, 0.6170 m. p. l.

Time, hrs.	0	122	144	178	310
Concn. of $(CH_3)_3N$	0.1928	0.06736	0.05560	0.04395	0.01699
$k \times 10^2$	....	1.593	1.624	1.593	1.593

Run 2. Initial concn. of ester, 0.5778 m. p. l.

Time, hrs.	0	119	139	305
Concn. of $(CH_3)_3N$	0.1935	0.07307	0.06275	0.02039
$k \times 10^2$	.....	1.619	1.628	1.616

METHYL ACETATE

Run 1. Initial concn. of ester, 0.5178 m. p. l.

Time, hrs.	0	144	210	224	320	390
Concn. of $(CH_3)_3N$	0.1962	0.1297	0.1094	0.1058	0.0846	0.0710
$k \times 10^3$	....	5.959	5.933	5.908	5.816	5.900

Run 2. Initial concn. of ester, 0.5021 m. p. l.

Time, hrs.	0	148	210	231	261
Concn. of $(CH_3)_3N$	0.1962	0.1300	0.1103	0.1055	0.0978
$k \times 10^3$	....	5.970	6.043	5.823	5.986

TABLE II

METHYL *o*-NITROBENZOATE

Run 1. Initial concn. of ester, 0.1873 m. p. l.

Time, hrs.	0	3.25	6	12	24
Concn. of $(CH_3)_3N$	0.1729	0.1441	0.1278	0.1022	0.0735
k	....	.3258	.3098	.2998	.2864

Run 2. Initial concn. of ester, 0.1413 m. p. l.

Time, hrs.	0	12	30.2	35.5
Concn. of $(CH_3)_3N$	0.1720	0.1162	0.0848	0.0795
k	....	.2991	.2722	.2675

TABLE III

	Alkylation constants	Ionization constants 25°	Ionization constants 99°	Hydrolysis constants
Acetate	0.00593 ± 0.00006	0.0000186	0.000011	100
p-Toluate	.0123 ± .0003	.000044	.000032	12.1
Benzoate	.01609 ± .00014	.000068	.000045	25.9
o-Toluate	.0166 ± .0003	.000135	.000058	....
Lactate	.0351 ± .0009	.000138	.....	968
o-Chlorobenzoate	.0727 ± .0014	.00132	.00042	49.5
p-Nitrobenzoate	.113 ± .013	.000396	.....	2690
Phthalate	.1243 ± .0017	.000654	.....	....
o-Nitrobenzoate	.33 (extrapolated)	.0065	.00161	148

lactate also show a drift if the actual initial concentrations of ester and amine are used in the calculation, a fact which we attribute to the impurity already mentioned. If, however, those concentrations found to exist after some five or ten per cent. of the ester has reacted are used as a starting point, the excellent agreement indicated by the average deviation shown is obtained.

Conclusions

The mean values of the rate constants of the nine carboxylic esters investigated in this research are arranged in Table III in the order of their magnitude. There are also included the dissociation constants[8] of the corresponding acids at 25°, and those reported by Schaller[9] for benzoic acid and its derivatives at 99°, and by Noyes[10] for acetic acid at 100°. These ionization constants are, of course, the values obtaining in aqueous solution.

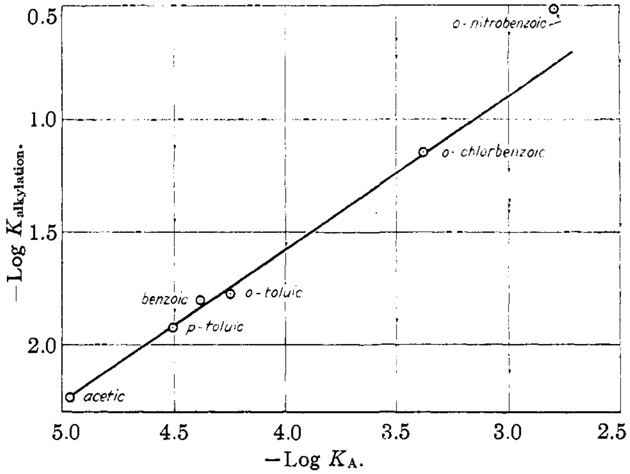

Fig. 1.

It is obvious that the rate of methylation of trimethylamine by these esters increases with increasing strength of the corresponding acid. But the relationship between reaction rate and acid strength is more than qualitative. Figure 1 contains a plot of the logarithm of the rate constant against the logarithm of the dissociation constant of the corresponding acid at either 100 or 99°, for all of the esters studied for whose acids dissociation constants at this temperature are available. The straight line whose equation is $\log k_v = 1.10 + 0.67 \log K_A$, where k_v is the velocity constant of the alkylation reaction, and K_A is the acid ionization con-

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(8) Where no specific references are given, the dissociation constants have been obtained from the "International Critical Tables." Attention is called, however, to an error in the order of magnitude given in these tables for the constant of benzoic acid.

(9) Schaller, *Z. physik. Chem.*, **25**, 497 (1898).

(10) Noyes, THIS JOURNAL, **30**, 335 (1908).

stant, fits these data excellently except in the case of *o*-nitrobenzoate. The deviation of almost 0.3 unit in this case requires further investigation.

In Fig. 2 the alkylation constants at 100° have been plotted against acid dissociation constants at 25°. This seems a more reasonable procedure than the estimation of temperature coefficients which are at present unknown. It is clear that there is a very definite advantage in the comparison of the alkylation velocity at 100° with the ionization constant of the acid at the same temperature, especially when ortho substituted benzoic acids are concerned. The fact that the latter have especially large temperature coefficients of ionization has been pointed out by Smallwood[11] and given a theoretical derivation.

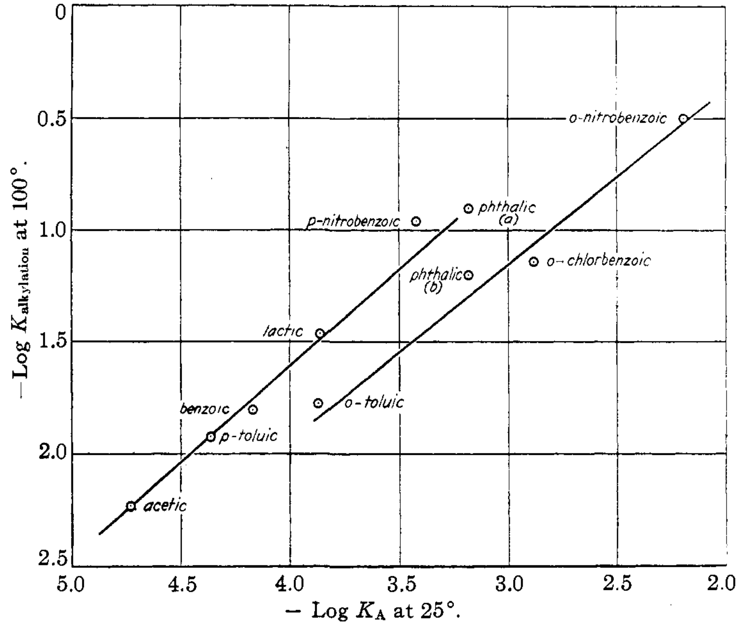

Fig. 2.

The acid with whose ionization constant the alkylation velocity of dimethyl phthalate is to be compared is of course the monomethyl ester of phthalic acid, and it is this constant which is listed in Table III. If the alkylation rate is plotted against this, the point (*a*) in Fig. 2 is obtained. Since, however, the dimethyl ester has twice the probability of reacting that a monomethyl ester would have, it is reasonable to divide the rate constant by two for comparison with the esters of monobasic acids. If this is done, point (*b*), which is in reasonable agreement with the other ortho substituted esters, is obtained.

We shall report later on the behavior of phenolic esters which do methyl-

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[11] Smallwood, THIS JOURNAL, **54**, 3048 (1932).

ate trimethylamine, but do not exhibit the same relation between rate and acid strength as that found for carboxylic esters, and upon the closely related problem inherent in the fact that we have here compared velocities in methyl alcohol solution with acid strengths in aqueous solution. This relation appears in the fact that carboxylic and phenolic acids are very differently affected by a change in solvent.[12]

Discussion

Because there is no universally valid relation between the rate of a chemical reaction and the equilibrium constant of the same or closely related reactions,[13] and because there is indeed no obvious reason to expect it, the existence of a simple and unique relation in this case presents a striking contrast which throws light on a number of important problems of reaction mechanism.

If one attempts to relate the velocity of the reaction of an ester with hydroxyl ion, *i. e.*, its alkaline hydrolysis, to the strength of the corresponding acid in the same way as we have done with the velocity of the reaction with trimethylamine, one obtains the complete lack of functional relationship exhibited by Fig. 3. The data[14] necessary are included in Table III. There is nevertheless this regularity in the large amount of existing data on hydrolysis velocities: that any substitution, of whatever electrochemical nature, in the immediate neighborhood of the carboxyl group tends to decrease the hydrolysis rate.[15] Whether the mechanism implied by the usual name "steric hindrance" is correct or not, the facts are that ethyl benzoate hydrolyzes only one-fourth as fast as ethyl acetate, though benzoic acid is almost four times as strong as acetic acid; and that alpha substituted aliphatic esters and ortho substituted aromatic esters hydrolyze less rapidly than unsubstituted esters of the same strength or esters containing the same substituent in a position further removed from the carboxyl group.

An important difference in principle between the reaction of an ester with a tertiary amine and its reaction with hydroxyl ion appears in the fact that the ester must in the first case break thus, $R_1COO\vdots R_2$, at the dotted line, both oxygens going with the acid radical, whereas the hydrolysis may go by two quite different mechanisms

$$R_1COO\vdots R_2 + OH' \longrightarrow R_2OH + R_1COO' \qquad (I)$$

$$R_1CO\vdots OR_2 + OH' \longrightarrow R_1COOH + {}'OR_2 \qquad (II)$$

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(12) Larsson, Dissertation, Lund, 1924.

(13) Adkins and Adams, THIS JOURNAL, **47**, 1368 (1925); Conant, *Ind. Eng. Chem.*, **24**, 470 (1932).

(14) These data are for the hydrolysis of ethyl esters, and are taken from Olsson's tables in which *k* for ethyl acetate is arbitrarily set at 100 [Olsson, *Z. physik. Chem.*, **133**, 233 (1928)] or calculated to the same scale from Kindler's tables [*Ann.*, **450**, 1 (1926); **452**, 90 (1927); **464**, 278 (1928)]. The use of ethyl esters is entirely justified by the well-demonstrated constancy of the ratio of the hydrolysis constants of ethyl and methyl esters [see Olsson, p. 240) and the wider range of data available for the ethyl esters.

(15) See for instance Kindler, *Ann.*, **464**, 278 (1928).

In the first case, the reaction may be called an alkylation of the hydroxyl ion, and in the second case an acylation, the acylation of ammonia to acetamide by methyl acetate being entirely analogous. It has been a much discussed problem for some thirty years whether the one or the other or both of these mechanisms agrees more closely with the facts.[16] If the hydrolysis mechanism were the alkylation represented by equation I, it is inconceivable that it should be more subject to steric hindrance than is the alkylation of trimethylamine. The existence of steric effects in the hydrolysis compared with their complete absence in the amine reaction is therefore strong evidence that the hydrolysis is an acylation proceeding according to equation II, the break occurring at a point in the molecule nearer the hindering groups than would be the case with the alkylation.

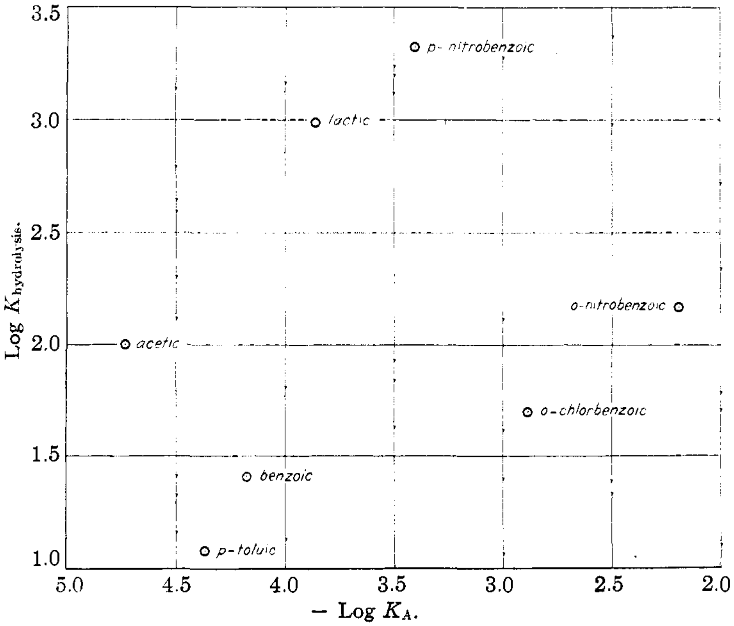


Fig. 3.

The previously existing evidence favors this mechanism for the hydrolysis of carboxylic esters, but it is directly applicable only to esters of secondary and tertiary alcohols. Holmberg[17] in 1912 pointed out that a Walden inversion can occur in the hydrolysis of an optically active alcohol whose activity depends upon an asymmetric carbinol carbon only if the hydrolysis is an alkylation, and follows mechanism I. Such an inversion has never been observed in the esterification and subsequent hydrolysis of a carboxylic ester.[16,17,18] On the other hand, the existence of an inversion

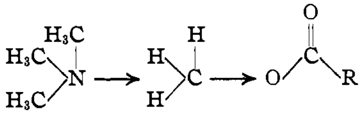
(16) Hückel and Frank, *Ann.*, **477**, 137 (1930).

(17) Holmberg, *Ber.*, **45**, 2997 (1912).

(18) Fischer, *Ann.*, **394**, 360 (1912); Verkade, *ibid.*, **477**, 287, 297 (1930).

in the hydrolysis of *p*-toluene sulfonic esters[19] of active alcohols proves that these do hydrolyze by mechanism I, a reasonable result because these esters of strong acids are in general active alkylating agents.[20] In further agreement is the fact that steric hindrances due to ortho substitution do not appear in the hydrolysis of substituted benzene sulfonic esters.[21]

With respect to detailed mechanism, it is profitable to consider the amine reaction as a substitution of trimethylamine for acetate ion, both amine and ion being bases in the Brönsted sense or molecules with lone electron pairs in the Lewis picture. Of the two widely discussed mechanisms for substitution reactions, the one dependent upon a preliminary dissociation of one reactant is here impossible. It would require either that the rate be independent of nature and concentration of the base or that it be proportional directly to the dissociation constant and inversely to the concentration of the acid ion produced. The hypothesis of a preliminary addition reaction on the other hand can be reconciled with the present result only by supposing that the rate of the addition is dependent upon the strength of a linkage which is to be broken in a further reaction of the addition compound. Recently, however, a theory of simultaneous addition and dissociation has been proposed on quantum mechanical grounds by London,[22] given quantitative application to simple reactions by Eyring and Polanyi,[23] and by Eyring and others,[24] and utilized qualitatively for more complex reactions by Polanyi[25] and others and by Olson.[26] Applied to the methylation of trimethylamine, one obtains the picture shown, in which the arrows represent the direction of motion. The reaction takes place by the approach of the nitrogen of the pyramidal trimethylamine molecule to the carbon of the methyl group on the side directly opposite to the oxygen atom. Simultaneously the oxygen and the accompanying acid radical recede from the carbon. If the kinetic energy of the approaching trimethylamine exceeds a certain minimum, the activation energy of the reaction, there is complete ejection of the acid ion, attachment of the trimethylamine, and rearrangement of the hydrogens on the methyl to new positions of equilibrium. The activation energy is dependent upon the energies of both the broken bond and the newly formed one, increases very rapidly with any deviation from linearity of ap-



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(19) Phillips, *J. Chem. Soc.*, **123**, 44 (1923); Kenyon, Phillips and Turley, *ibid.*, **127**, 899 (1925).

(20) Ferns and Lapworth, *J. Chem. Soc.*, **101**, 273 (1912).

(21) Demény, *Rec. trav. chim.*, **50**, 60 (1931).

(22) London, *Z. Elektrochem.*, **35**, 552 (1929).

(23) Eyring and Polanyi, *Z. physik. Chem.*, **B12**, 279 (1931).

(24) Eyring, THIS JOURNAL, **53**, 2537 (1931); Rollefson and Eyring, *ibid.*, **54**, 170 (1932); Eyring, *ibid.*, **54**, 3191 (1932); Kimball and Eyring, *ibid.*, **54**, 3876 (1932).

(25) Meer and Polanyi, *Z. physik. Chem.*, **B19**, 164 (1932); Bergmann, Polanyi and Szabo, *ibid.*, **B20**, 161 (1933).

(26) Olson, *J. Chem. Phys.*, **1**, 418 (1933).

proach,[23,24] and determines the reaction velocity provided steric factors are constant. One need only suppose that the energy of the bond between alkyl and acid radical is related to the strength of the corresponding acid to obtain a reasonable account of the existence if not of the exact form of a relation between velocity and acid strength. The equally probable dependence upon the strength of the reacting base is much more likely to be complicated by steric effects, and both base strength and spatial configuration are apparently factors in determining the rate of addition of different tertiary amines to a single alkyl halide.[27]

In further agreement with the demonstrated properties of the alkylation reaction, a Walden inversion must take place when the carbinol carbon is asymmetric[25,26] and variations in shape or size of the radical R can have no effect as such upon the velocity of a reaction which takes place at a point in the molecule so widely separated from R and so completely shielded from it.

The formal identity of the relation here found between acid strength and methylation rate with that found by Brönsted[2] between acid strength and the rate of a reaction subject to general acid catalysis suggests a fundamental similarity in the two reactions. It is therefore probable that the rate-determining step in the catalysis is a transfer of hydrogen ion from the acid HA to the weakly basic substrate S, entirely analogous to the transfer of methyl in the alkylation reaction $HA + S \rightleftarrows SH^+ + A'$, and that the further reaction of the ion SH^+ is by comparison extremely rapid. This is the interpretation of the catalysis suggested by Pedersen,[28] and it may be added that the mechanism of reaction just discussed casts considerable doubt upon the possibility of further dissection of the reaction, for instance, into the formation of an addition compound (HA, S), and its subsequent further reaction. Those predictions of a dependence upon base strength as well as upon acid strength and upon steric properties which were made for the alkylation reaction should be equally applicable to both acid and basic catalysis and should furnish a test of the usefulness of the interpretation.

Summary

It has been found that the rate of the alkylation of trimethylamine to tetramethylammonium ion by the methyl ester of a carboxylic acid is related to the strength of the acid by an equation of the same form as that which connects the rate of a reaction subject to general acid catalysis with the strength of the catalyst acid.

The complete absence of steric hindrances in this reaction compared with its predominance in ester hydrolysis shows that the mechanisms of the two reactions are different.

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[27] Preston and Jones, *J. Chem. Soc.*, **101**, 1930 (1912); Thomas, *ibid.*, **103**, 594 (1913).

[28] Pedersen, THIS JOURNAL, **53**, 18 (1931).

It is probable that the rate-determining step in the general acid and basic catalysis of Brönsted is a transfer of hydrogen ion from acid catalyst to substrate similar to the transfer of methyl in the alkylation reaction.

These results are in agreement with the theory of simultaneous addition and dissociation in substitution reactions.

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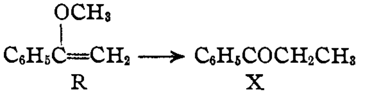
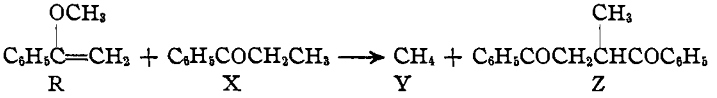
[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

The Kinetics of the Rearrangement of α-Methoxystyrene[1]

BY F. H. MACDOUGALL, WALTER M. LAUER AND MARVIN A. SPIELMAN[2]

Claisen[3] has shown that α-methoxystyrene undergoes on heating a molecular rearrangement with the formation of propiophenone. A recent investigation[4] of the process has revealed an unusual type of side reaction. The unchanged starting material (R) reacts with the rearrangement product (X); a molecule of methane (Y) is eliminated and 1,2-dibenzoylpropane (Z) results.


$$\underset{R}{C_6H_5\overset{OCH_3}{\overset{|}{C}}{=}CH_2} \longrightarrow \underset{X}{C_6H_5COCH_2CH_3} \qquad \text{I}$$


$$\underset{R}{C_6H_5\overset{OCH_3}{\overset{|}{C}}{=}CH_2} + \underset{X}{C_6H_5COCH_2CH_3} \longrightarrow \underset{Y}{CH_4} + \underset{Z}{C_6H_5COCH_2\overset{CH_3}{\overset{|}{C}}HCOC_6H_5} \qquad \text{II}$$

In connection with a study of the mechanism of this type of molecular rearrangement, it became desirable to know the order of the reaction and to gain as much information as possible about the unique condensation reaction (II). While the mixture of compounds resulting from reactions I and II does not lend itself to highly precise methods of analysis, nevertheless a technique was developed whereby its composition could be determined with a fair degree of accuracy.

Experimental Methods

The thermostat was an upright Pyrex tube, 16 × 40 cm. rounded at the lower end and closed at the top with an asbestos cover. The lower two-thirds was wrapped with an asbestos jacket. Within was suspended a cylindrical aluminum block, 4.5 × 9 cm., in which were drilled five holes. An 8 mm. hole through the center bore a glass supporting rod and symmetrically disposed about it were four cylindrical holes. The diameter

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(1) This paper is a portion of the thesis presented by Marvin A. Spielman to the Graduate Faculty of the University of Minnesota in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

(2) Dupont Research Fellow in Chemistry, 1932–1933.

(3) Claisen, *Ber.*, **29**, 2931 (1896); Claisen and Haase, *ibid.*, **33**, 3778 (1900).

(4) Lauer and Spielman, THIS JOURNAL, **55**, in press (1933).