(*a*) lactic aldehyde and mandelic aldehyde in the presence of water, at 100°, rearrange to acetol and benzoyl carbinol, respectively; (*b*) lactic aldehyde does not undergo this rearrangement at ordinary temperature; (*c*) mandelic aldehyde, the aromatic analogue of lactic aldehyde, not only undergoes this rearrangement to benzoyl carbinol at ordinary temperature in the presence of water and dilute sulfuric acid, but this transformation also takes place at 0°; (*d*) mandelic aldehyde undergoes rearrangement to benzoyl carbinol even in the presence of water and dilute ethyl alcohol, both at ordinary temperature and at 0°; (*e*) mandelic aldehyde undergoes rearrangement to benzoyl carbinol with the water vapor of the atmosphere. In conclusion we wish to thank Mr. J. E. Day, of this laboratory, for the analysis of the benzoylformaldehyde acetal prepared by us.

COLUMBUS, OHIO.

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

CATALYSIS ON THE BASIS OF WORK WITH IMIDO ESTERS: A CONTRIBUTION TO THE PROBLEM OF SAPONIFICATION AND ESTERIFICATION.

BY JULIUS STIEGLITZ.

Received May 16, 1913.

The well-known explanation of the accelerating (catalytic) effect of acids on the saponification of esters by water assumes that the complex oxonium ion[1], formed by the ester with the hydrogen ion of the catalyzer, is the chief[2] reacting component of the ester which is saponified by the

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[1] Stieglitz, *Report of the Congress of Arts and Science*, St. Louis, **4**, 278 (1904); *Am. Chem. J.*, **39**, 29, 166, 402 (1908), and later articles. See also Bredig and Walton, *Z. Elektrochem.*, **9**, footnote, p. 118 (1903), and *Ibid.*, **10**, 586 (1904); Acree and coworkers, *Am. Chem. J.*, **37**, 410; **38**, 258 (1907), etc.; and Goldschmidt, *Z. physik. Chem.*, **60**, 728 (1907) and later articles. Closer examination of Lapworth's theory shows that it was not in conflict with the laws of equilibrium (cf. Lapworth, *Proc. Chem. Soc.*, **24**, 101, 152 (1908)), as was unfortunately concluded in the discussion of his theory by the present author (*Loc. cit.*, p. 424), but the criticism of the assumptions of the theory for the other reasons given appears justified and Lapworth himself later withdrew his theory. (See Fitzgerald and Lapworth, *J. Chem. Soc.*, **93**, 2165 (1908).)

[2] Questions concerning the rôle of non-ionized ionogens in reactions of this type have been brought to the fore in recent years, especially by Goldschmidt and Acree. Goldschmidt first suggested the possible activity of non-ionized acids in catalysis (*Z. physik. Chem.*, **29**, 118 (1899)). The present author first demonstrated with imido esters that the non-ionized molecules of an ionogen are active as well as its anions (Schlesinger's Dissertation, University of Chicago, 1905; *Am. Chem. J.*, **39**, 167 (1908)), where the general importance of the results both for organic and inorganic compounds was emphasized; finding, however, that the molecules react with velocities very much smaller than those of the ions, he considered the molecules capable only of very slow parallel reactions (see applications of this idea, THIS JOURNAL, **32**, 229 (1910) and

water. The equation expressing this hypothesis mathematically

$$-\frac{dC_{\text{Ester}}}{dt} = K_v \times C_{\text{Ester ion}} \times C_{\text{HOH}} \qquad (1)^{[1]}$$

goes over into the ordinary equation representing the empirical relations

$$-\frac{dC_{\text{Ester}}}{dt} = K_{\text{sap.}} \times C_{\text{Ester}} \times C_{\text{HOH}} \times C_{\text{H}^+} \qquad (2)$$

without any further assumption, by the simple application of the law of chemical equilibrium to the system.[2] For the reversed action of esterification the parallel assumption that the complex oxonium ion of the organic acid[2] is the reacting component esterified by the alcohol present is expressed in the equation for the velocity of the action

his "Qualitative Analysis," Vol. I, p. 83, "Chemical Activity of Non-ionized Molecules"), and consequently failed to consider salt molecules as active in the rapid catalysis of imido esters by bases or acids. Acree first recognized that the non-ionized salt molecules of a catalyzed substance might be *more reactive* than its ions and consequently might be the seat of accelerated reactions depending on salt formation—a most important contribution to the theory of catalysis (Acree and Johnson, *Am. Chem. J.*, **37**, 410 (1907)) which corrected the most serious omission in the author's own view. Acree and Johnson, on the basis of their general theory of the activity of non-ionized ionogens in catalytic reactions, were also the first to suggest a possible small share of the oxonium salt molecules in esterification and saponification (*Ibid.*, **38**, 329 (1908)); in their work of that period they failed to recognize, however, the facts indicating actual parallel reactions *of moment* of ions and molecules in these cases. More recently Acree has brought valuable contributions both on the subject of parallel reactions of ions and non-ionized ionogens in catalysis (a private communication to this effect was received by the author in October, 1910) and on that of the activity of non-ionized catalyzing agents, including in his studies work of his own as well as reinterpretations of the earlier work of several other investigators, including some of that of the present author. Goldschmidt was the first to publish a measurement of the parallel reactions of hydrogen ions and non-ionized acids (*Z. physik. Chem.*, **70**, 629 (1910)). According to Acree (*Am. Chem. J.*, **48**, 367 (1912)), his general theory of parallel activity of non-ionized forms and ions of acids, bases and salts forecasted Goldschmidt's discoveries. For further publications on this subject see Acree (*Loc. cit.*); Stieglitz (THIS JOURNAL, **34**, 1687 (1912); Goldschmidt (*Z. physik. Chem.*, **81**, 30 (1912), and *Z. Electrochem.*, **17**, 684 (1911)); Bredig (*Ibid.*, **18**, 535 (1912)); Snethlage (*Ibid.*, p. 539); and Acree (*Am. Chem. J.*, **49**, 116 (1913)). In regard to the "salt-effect" see Arrhenius (*Z. physik. Chem.*, **1**, 126 (1887)); Euler (*Ibid.*, **32**, 348 (1900)); Stieglitz (*Am. Chem. J.*, **39**, 178 (1908)); Acree (*Ibid.*, **38**, 496 (1907) and **41**, 474 (1909)), and further papers by the same and other authors. See Goldschmidt and Ude (*Z. physik. Chem.*, **60**, 728 (1907)) and Fitzgerald and Lapworth (*Loc. cit.*) as to the role of water as an oxonium-forming oxide. These various secondary factors in esterification and saponification, as well as Armstrong and Worley's interesting discussion of these catalyses from the point of view of the hydrate theory (*Proc. R. Soc. A.*, **87**, 604 (1912) and papers referred to therein), will not be discussed here but will receive attention in later articles in connection with the experimental data on imido esters.

[1] The symbols have the customary significance.

[2] Stieglitz, *Loc. cit.*

$$-\frac{dC_{\text{Acid}}}{dt} = \mathbf{K}'_{v} \times C_{\text{Ac. Ox. Ion}} \times C_{\text{HOR}} \qquad (3)$$

and this leads in the same way to the empirical equation

$$-\frac{dC_{\text{Acid}}}{dt} = K_{\text{est.}} \times C_{\text{Acid}} \times C_{\text{HOR}} \times C_{\text{H}^+}. \qquad (4)$$

Exactly the same result as to the relation of the theoretical and the empirical equations would be obtained mathematically if in esterification we assume that the action is one of the oxonium ion of the *alcohol*[1] on the organic acid, rather than of the alcohol on the oxonium ion of the organic acid, and if, in saponification, we assume that the oxonium ion of water acts on the ester, rather than that the water reacts with the oxonium ion of the ester. In other words, the *mathematical* relations for the formation of oxonium ions and their decomposition in the reversible reaction

$$\text{RCOOR}' + \text{HOH} + \text{H}^+ \rightleftarrows \text{RCOOH} + \text{R}'\text{OH} + \text{H}^+ \qquad (5)$$

cannot alone determin[2] with which oxide, in either of the reversible reactions, the hydrogen ion combines to form a reactive oxonium salt and ion. On the basis of our work on the velocity of decomposition of imido esters by water in the presence of acids it has seemed most probable[3] that in *saponification* the complex oxonium ion of the organic *ester*, in *esterification* the oxonium ion of the organic *acid* are primarily involved—that is, in either case, *the organic acid or its derivative forms the reacting complex ion.* Important direct evidence confirming this view has been found in the consideration of the formation of amidines from imido esters by the action of ammonia and amines, reactions which are accelerated by acid and which are altogether analogous to saponification and esterification.[4] The amidine formation has the advantage that the affinity constants of all the bases involved are known, which is not the case for the oxonium bases. When acid is added to a mixture of imido ester and ammonia (or amine) it is divided between the bases according to:

$$\text{C}_6\text{H}_5\text{C}(:\text{NH}_2\text{Cl})\text{OCH}_3 + \text{NH}_3 \rightleftarrows \text{C}_6\text{H}_5\text{C}(:\text{NH})\text{OCH}_3 + \text{NH}_4\text{Cl} \qquad (6)$$

and we have

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[1] See in particular Goldschmidt's important researches, which led him to the conclusion that esterification is due to such an action (*Loc. cit.*, and later articles).

[2] However, Goldschmidt based his conclusions as to the activity of the oxonium ions and salts of alcohols in esterification on the mathematical analysis of the secondary factors of the action.

[3] Stieglitz, *Loc. cit.*; Fitzgerald and Lapworth, *Loc. cit.*; Acree, *Am. Chem. J.*, 48, 371 (1912).

[4] Address before the American Chemical Society, Dec., 1907; see *Science*, May 15, 1908, p. 773. Dissertation of Miss Blunt, University of Chicago, 1907. Stieglitz, *Am. Chem. J.*, 39, 61 (1908) and THIS JOURNAL, 32, 228 (1910).

$$\frac{C_{\text{Im. Est. Ion}} \times C_{NH_3}}{C_{\text{Im. Est.}} \times C_{NH_4^+}} = \frac{k_{\text{aff. est.}}}{k_{\text{aff. amm.}}}. \qquad (7)$$

Stieglitz and Katherine Blunt[1] found that the velocity of the main[2] action by which amidine is formed may be expressed quantitatively on the basis of the assumption that the velocity of the action is proportional to the concentration of the imido ester cation (always very minute, as the imido ester is by far the weaker base) and to the concentration of ammonia:

$$C_6H_5C(:NH_2^+)OCH_3 + NH_3 \longrightarrow C_6H_5C(NH_3^+):NH + HOCH_3 \qquad (8)$$

and

$$-\frac{dC_{\text{Im. Est.}}}{dt} = K_v \times C_{\text{Im. Est. Ion}} \times C_{NH_3}, \qquad (9)$$

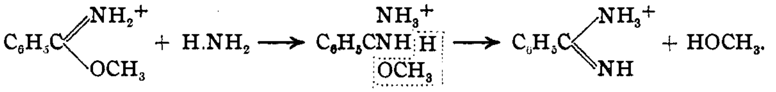
equations which correspond in every detail with those representing the saponification of esters and the esterification of acids according to the views of the author discussed above. It is evident,[2] by considering equation (7) that if a constant is obtained according to equation (9), one would also be obtained for

$$-\frac{dC_{\text{Im. Est.}}}{dt} = K'_v \times C_{\text{Im. Est.}} \times C_{NH_4^+}, \qquad (10)$$

representing the reaction

$$C_6H_5C(:NH)OCH_3 + NH_4^+ \longrightarrow C_6H_5C(:NH)NH_3^+ + HOCH_3. \qquad (11)^3$$

It is thus again evident that the purely mathematical relations do not enable us to distinguish between the alternative hypotheses for the formation of amidines. Preparative[4] organic chemistry, however, gives us a decisive answer to our problem in a rather simple fashion. If amidine formation is the result of the action of *ammonia* on the imido ester cation (equations 8 and 9), the action will start with the absorption of ammonia at the double bond between the carbon and nitrogen atoms and end with the loss of alcohol from the intermediate product:



$$C_6H_5C\begin{matrix}\nearrow NH_2^+\\ \searrow OCH_3\end{matrix} + H.NH_2 \longrightarrow C_6H_5\overset{NH_3^+}{\underset{OCH_3}{CNH\,H}} \longrightarrow C_6H_5C\begin{matrix}\nearrow NH_3^+\\ \searrow NH\end{matrix} + HOCH_3. \qquad (12)$$

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[1] A secondary very slow formation of amidine by the action of ammonia on the imido ester occurs, Stieglitz, This Journal, 32, p. 229.

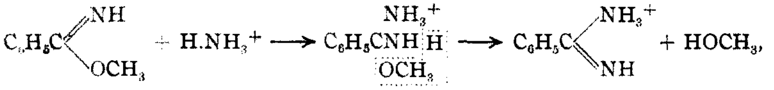
[2] Stieglitz, *Loc. cit.*, and This Journal, 32, 228 (1910). *Vide* Goldschmidt and Sunde, *Ber.*, 39, 711 (1906); Goldschmidt and Udby, *Z. phys. Chem.*, 60, 728 (1907); Acree, *Am. Chem. J.*, 39, 302 (1908) and Fitzgerald and Lapworth, *J. Chem. Soc.*, 93, 2163 (1908). Stieglitz, *Am. Chem. J.*, 39, 51, attempted to distinguish between the alternative possibilities by an hypothesis as to the mechanism of esterification.

[3] Acree made this kind of assumption for the formation of oximes by hydroxylamine in the presence of acid (*Am. Chem. J.*, 38, 308 (1907)). Later he pointed out (*Ibid.*, 39, 302 (1908)) that his data would agree equally well with the assumption that hydroxylamine (not its cation) reacts with the oxonium ion of acetone.

[4] As distinguished from physico-organic chemistry.

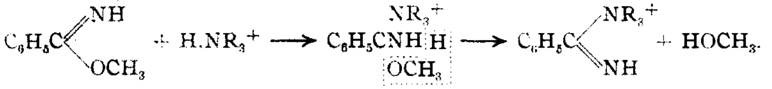
This is an instance of the well-known path by which the transformation of esters, acid amides, organic acids, aldehydes, ketones, nitriles and other unsaturated organic compounds is considered to take place as the result of a vast mass of cumulative evidence.[1] It is plain that amidine formation, according to this theory, should also be possible if we substitute a *primary* amine, H.NHR, or a *secondary* amine, $H.NR_2$, for the ammonia (see equation 12). A *tertiary* amine should, however, be incapable of forming an amidine by this series of reactions.

On the other hand, if amidine formation is the result of the action of the *ammonium ion* on the free imido ester, as expressed in



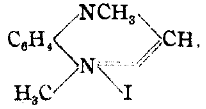
$$C_6H_5C\begin{matrix}\diagup NH\\ \diagdown OCH_3\end{matrix} + H.NH_3^+ \longrightarrow C_6H_5\overset{NH_3^+}{\underset{OCH_3}{CNH\,H}} \longrightarrow C_6H_5C\begin{matrix}\diagup NH_3^+\\ \diagdown NH\end{matrix} + HOCH_3, \quad (13)$$

then we should have amidine formation proceeding quite as smoothly by the action of a salt of a *tertiary amine*, through its ion HNR_3^+, on the imido ester. We should have, for instance:



$$C_6H_5C\begin{matrix}\diagup NH\\ \diagdown OCH_3\end{matrix} + H.NR_3^+ \longrightarrow C_6H_5\overset{NR_3^+}{\underset{OCH_3}{CNH\,H}} \longrightarrow C_6H_5C\begin{matrix}\diagup NR_3^+\\ \diagdown NH\end{matrix} + HOCH_3. \quad (14)$$

Fully alkylated ammonium salts of amidines, prepared in a different way, are known[2] in the case of the anhydro bases. We have, for instance,



I find that Pinner[3] has already answered the question whether salts of tertiary amines form amidines to the effect that *salts of tertiary amines do not form amidines* with imido esters, those of primary and secondary amines do. This result taken in conjunction with the velocity experiments agrees unequivocally with the theory that amidine formation is the result of the action of *ammonia* or of an *amine* on the imido ester ion[4] and disposes of the possibility that it is the product of the action of *ammo-*

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[1] The validity of the conclusion reached below is independent of the question of the correctness of this or of any other theory of the *structural mechanism* of the reactions. There should be no gap, however, between physico-organic and preparative and structural organic results and the conclusions reached are therefore put into a form satisfying the results obtained in both fields of investigation.

[2] E. Fischer and Rigaud, *Ber.*, 34, 936 (1901).

[3] "Imidoaether," pp. 86, 89 (1901). Miss Souther is examining the action of imido esters other than those used by Pinner in regard to amidine formation with salts of amines in order to verify his conclusions, which have now assumed particular importance. Attempts will also be made to prepare fully alkylated open chain amidine salts.

[4] The role of the non-ionized salt is not included in the present consideration but will be discussed in a later paper in connection with experimental data.

nium ions (or salt) on the free imido ester. It thus confirms the views previously held by the author.

The results reached may, with a very strong probability of reliability of the conclusions that follow, be applied to the many analogous actions, such as the saponification of esters and the esterification of organic acids: they make it extremely probable that in these fundamental reactions, of the possible alternative hypotheses, the one is correct which assumes that we have an action of an hydroxide, water or alcohol (corresponding to an amine) *on the oxonium ion of the ester or of the organic acid.* The same stages of absorption of the hydroxide at the double bond of the C:O group, followed by the loss of alcohol or water to form the organic acid or ester, should be assumed.[1]

Besides shedding some light on the theory of catalysis, the conclusion reached has an important bearing on another physico-chemical principle of general importance. In all the reactions studied by the author and his collaborators, acids have been found to accelerate actions in which a *weaker* base is converted into a *stronger*,[2] no doubt as the result of the loss of free energy involved in the union of the acid with a stronger base.[3] The conclusion just developed agrees in every respect with this general principle. Even in the reversible saponification of an ester and esterification of an organic acid, in the presence of an acid, we find, in the saponification, the salt of the *weaker ester oxonium base* forming the salt (ion) of the *stronger alcohol oxonium base* and in the reversed action of esterification the salt of the weaker *organic acid* oxonium base again forms the salt of the stronger *ester* oxonium base.[4] The theory formulated by Goldschmidt[5] would require the salt of the stronger *alcohol* oxonium base to be converted into the salt of a weaker base, the *ester*. Similarly, Acree's first formulation[6] of the formation of oximes in acid solution would require the hydroxylammonium ion, the ion of a relatively strong base, to go over into the ion of the oxime, a relatively weak base, in an action accelerated by acids. The later interpretation, suggested as an alternative possibility, assumed the transformation of the ion of the exceedingly weak oxonium base of the ketone into the ion of the much stronger base, the oxime. This would conform with the general principle laid down and is now confirmed by the examination of the behavior of the salts of tertiary amines toward imido esters.

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[1] Stieglitz, *Am. Chem. J.*, 39, 60 (1908).

[2] For the application of this general principle to these reactions, see Stieglitz, *Ibid.*, pp. 59–61, and THIS JOURNAL, 32, 225 (1910).

[3] *Mutatis mutandis* a similar rule holds for the action of bases. Stieglitz, *Am. Chem. J.*, 39, 60 (1908).

[4] Stieglitz, *Ibid.*

[5] See footnote 2, p. 1774.

[6] *Loc. cit.*