The constants Θ and ϕ given in these tables are for the solvent water at 25°. The data from which they were calculated were taken from "Affintatmessungen an schwachen Säuren and Basen," by H. Lunden.

The author wishes to express his thanks and appreciation to Dr. E. W. Washburn for his criticisms and suggestions.

APPLICATION OF POLARITY MEASURED IN TERMS OF A LOGARITHMIC FUNCTION OF THE IONIZATION CONSTANT. I. THE USE OF POLARITY IN THE EXPLANATION OF THE REACTIONS OF ALDEHYDES AND KETONES.
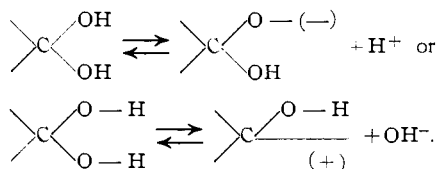
BY C. G. DERICK.

I. Mechanism of Dehydration of the Dihydroxy Form of Aldehydes and Ketones.

The quantitative measure of polarity developed in the previous paper may be applied to the reactions of aldehydes and ketones, so that useful generalizations may be drawn, as the following will illustrate. To apply this measure a neutral aldehyde or ketone is defined as a compound whose ionization constant lies in the order 10^{-14} at 25° for water solutions. The acid or basic aldehyde must therefore have Ka or Kb greater than 9.99×10^{-14}.

In the explanation of the formation of aldehydes and ketones from primary or secondary alcohols, respectively, the following mechanism is usually employed:

$$R.CH_2OH + O \longrightarrow R - CH \diagup_{O - H}^{O - H} \rightleftarrows R.CH = O + H_2O.$$
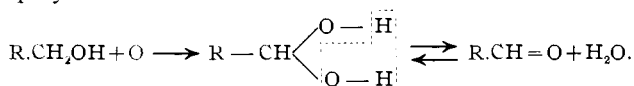
The mechanism of the spontaneous dehydration may be explained as follows for neutral aldehydes or ketones. These substances in the dihydroxy forms are amphoteric, ionizing thus:

$$\diagup C \diagdown_{OH}^{OH} \rightleftarrows \diagup C \diagdown_{OH}^{O - (-)} + H^+ \text{ or}$$

$$\diagup C \diagdown_{O-H}^{O-H} \rightleftarrows \diagup C \diagdown_{(+)}^{O-H} + OH^-.$$

But if the above ionization occurs upon the same carbon atom, we have:

$$\diagup C \diagdown_{O-H}^{O-H} \rightleftarrows \diagup C \diagdown_{(+)}^{O^{(-)}} + H^+ + OH^-$$
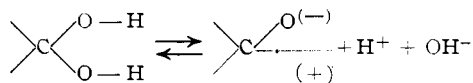
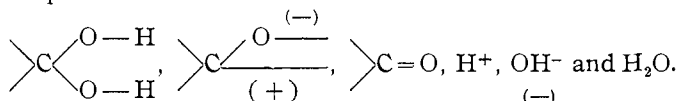If the hydrogen and hydroxyl ionization occur simultaneously in water

solution, the concentration of at least one of the ions must be reduced
to that of water under the given conditions due to the reaction

$$H^+ + OH^- \rightleftharpoons H_2O.$$
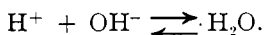
There would be left in solution $>C\begin{smallmatrix}O-H\\O-H\end{smallmatrix}$ and the ion $>C\begin{smallmatrix}O\overset{(-)}{-}\\(+)\end{smallmatrix}$, but
since upon isolation we obtain the aldehyde or ketone in the form $>C=O$,
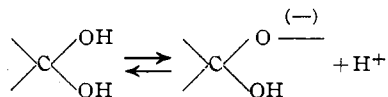we know that another equilibrium is present, namely,

$$>C\begin{smallmatrix}O\overset{(-)}{-}\\(+)\end{smallmatrix} \rightleftharpoons >C=O.$$
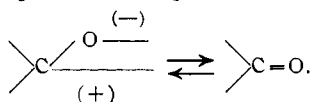
Therefore a water solution of an aldehyde contains at least the following
molecular species:

$$>C\begin{smallmatrix}O-H\\O-H\end{smallmatrix}, \quad >C\begin{smallmatrix}O\overset{(-)}{-}\\(+)\end{smallmatrix}, \quad >C=O, \; H^+, \; OH^- \text{ and } H_2O.$$

Obviously the active form of the aldehyde is $>C\begin{smallmatrix}O\overset{(-)}{-}\\(+)\end{smallmatrix}$ and the mecha-
nism of the dehydration of the dihydroxy forms of aldehyde and ketones
is easily explained.

This explanation may be tested in the following manner: It was
shown under the measure of polarity that negative groups increased the
H^+ ionization and decreased the OH^- ionization of a given amphoteric
electrolyte. The effect of substitution of negative groups into neutral
aldehydes or ketones must be to increase the hydrogen and decrease the
hydroxyl ionizations. If such substitution decreases the concentration
of the hydroxyl ionization to that of water under the given conditions,
the dihydroxy form should be completely stable and give the following
equilibrium in solution:

$$>C\begin{smallmatrix}OH\\OH\end{smallmatrix} \rightleftharpoons >C\begin{smallmatrix}O\overset{(-)}{-}\\OH\end{smallmatrix} + H^+$$

If the negativity of the molecule is not sufficiently great to prevent the
tendency of the OH^- ionization becoming greater than that of water,
then the following equilibria must exist in solution:

$$>C\begin{smallmatrix}O-H\\O-H\end{smallmatrix} \rightleftharpoons >C\begin{smallmatrix}O\overset{(-)}{-}\\O-H\end{smallmatrix} + H^+,$$

$$>C\begin{smallmatrix}OH\\OH\end{smallmatrix} \rightleftharpoons >C\begin{smallmatrix}O\overset{(-)}{-}\\(+)\end{smallmatrix} + (H^+ + OH^-), \; H^+ + OH^- \rightleftharpoons H_2O,$$

$$\diagup C \diagup \overset{(-)\cdot}{\underset{(\div)}{O---}} \rightleftharpoons \diagup C = O.$$
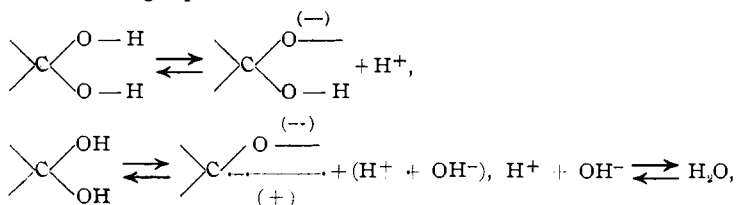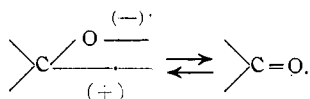
In such a case the aldehyde or ketone must exist mainly in the inactive form, $> C = O$, and its water solution will have $Ka > Kb$ or Ka for aldehydes $> Ka$ for water. This is apparently the case in formaldehyde and acetaldehyde, which give $Ka^\circ = 0.7$ and 1.4×10^{-14}, respectively, while that of water at zero degrees is 0.12×10^{-14}. This shows that the negativity of the molecule is predominant, so that the tendency to ionize H^+ is greater than that to give the hydroxyl ion, OH^-, yet the negativity is not sufficient to reduce the tendency to produce hydroxyl ions, OH^-, to that of water under the same conditions.

In the case of chloral hydrate, however, the negativity, $\Theta_{18^\circ} = 134$, for chlorine of the molecule is sufficient to reduce the tendency of the production of hydroxyl ions to that of water under the same conditions. Hence the aldehyde is stable in the dihydroxy form and is a much stronger acid than formaldehyde, since it gives the following equilibrium in water:
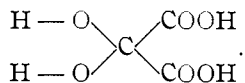
$$CCl_3C \diagdown \overset{O-H}{\underset{H \diagdown O-H}{}} \rightleftharpoons \diagup C(Cl_3).C \diagdown \overset{O---(-)}{\underset{\underset{H}{|} \diagdown OH}{}} + H^+$$
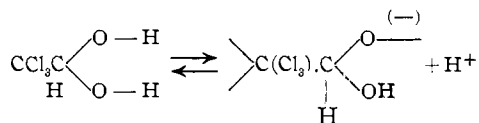
$Ka^\circ = 0.4 \times 10^{-11}$ and $Ka^{18^\circ} = 1 \times 10^{-11}$ for chloral hydrate, bearing out the above conclusions.

If we choose groups of greater negativity than chlorine and substitute them into neutral aldehydes or ketones, the dihydroxy form should be stable. In the paper on the measure of polarity Θ is defined as proportional to $I/\log K$. If we compare carbonic and hypoiodous acids we find for Θ_{18°, $HOOC : Cl = 1/6.516 :: 1/7.422 = 1.138 : 1$. It is seen that the carboxyl group is more negative than chlorine, yet the accuracy of this ratio may be questioned.[1] Hence the substitution of the carboxyl group into neutral aldehydes and ketones should make the dihydroxy form stable at ordinary temperature. In the case of glyoxalic acid, $\left(\overset{H-O}{\underset{H-O}{}} \diagdown C-COOH \atop H \right)$, we have the hydrogen of formaldehyde substituted by the strongly negative carboxyl group and the dihydroxy form of the aldehyde is stable, so stable toward dehydration that all attempts to dehydrate it have resulted in its complete decomposition. The same facts are true concerning mesoxalic acid,

$$\overset{H-O}{\underset{H-O}{}} \diagdown C \diagdown \overset{COOH}{\underset{COOH}{}} .$$

[1] J. Walker, Z. physik. Chem., 49, 82 (1904); 51, 708 (1905); 57, 600 (1906).

The ionization constants of these two acids at $25°$ are 5×10^{-4} and 5×10^{-3}, respectively.

From acetic and formic acids, we find from the tables of polarity that Θ for the acetyl and aldehyde radicals is 211 and 272.4, respectively. By comparing the normal paraffin acids it will be seen that hydrogen and methyl radicals have a small positive effect, so that the true negativity of the carbonyl radical would be greater than 272.4. Thus, if carbonyl groups are substituted into a neutral aldehyde or ketone, the dihydroxy form would be more stable since the carbonyl radical is much more negative than the chlorine radical (Θ_{18} for HC $= O$: Cl $= 272.4$: 134.5). The dihydroxy form of diethyl mesoxalate,

$$
\begin{array}{c}
\text{HO} \diagdown \quad\quad \overset{O}{\diagup} \\
\quad\quad C \diagdown C \diagdown OC_2H_5 \\
\text{HO} \diagup \quad C \diagdown OC_2H_5 \\
\quad\quad\quad \diagdown O
\end{array}
$$

is stable below $58°$.

These illustrations serve to show the connection between polarity and the form in which certain grouping of atoms may exist. They also serve as an indication of the conditions under which certain forms of compounds may be isolated.

II. Oxime, Hydrazone and Semicarbazone Formations.

A quantitative measure of polarity furnishes us with a means of stating generalization in place of endless detail. This fact is well illustrated by the additive reactions of aldehydes and ketones.

Ammonia is represented as adding to an aldehyde as follows:

$$
\diagup\diagdown C=O \rightleftarrows \diagup\diagdown C \overset{(-)}{\diagup}\overset{O——}{\underset{+}{\rule{0pt}{1em}}} + H-\underset{H}{\overset{H}{N}}-H + \rightleftarrows \diagup\diagdown C \overset{O-H}{\underset{NH_2}{}}
$$

In the case of hydroxylamine, phenylhydrazine and semicarbazine and an aldehyde the reaction is written in the following ways:

$$
\text{(I)} \diagup\diagdown C=O \rightleftarrows C \overset{(-)}{\underset{(+)}{\overset{O——}{\rule{0pt}{1em}}}} + \overset{H}{\underset{H}{\diagdown N}}-R \longrightarrow \diagup\diagdown C \overset{O-H}{\underset{N\,H\,R}{}} \longrightarrow > C=N.R+H_2O,
$$

$$
\text{(II)} \quad \diagup\diagdown C = O + H_2 N.R \rightleftarrows \diagup\diagdown C = N.R+H_2O.
$$

Unquestionably, I is the correct reaction since we are dealing with substituted ammonias and it is the same NH_2 group which reacts in every case as in NH_3. That hydroxylamine, semicarbazine, phenylhydrazine, hydrazine, ethylamine and methylamine are substituted ammoniums possessing a similar NH_2 group is seen by the following scheme:

φ.

$\begin{array}{l} H \\ \diagdown \\ \diagup NH - H \\ H | \end{array}$ 211.4

$\begin{array}{l} H \\ \diagdown \\ \diagup NH - OH \\ H | \end{array}$ < 211.4

$\begin{array}{l} H \\ \diagdown \\ \diagup NH - NHCONH_2 \\ H | \end{array}$ 94.6

$\begin{array}{l} H \\ \diagdown \\ \diagup NH - NHC_6H_5 \\ H | \end{array}$ 125.0

$\begin{array}{l} H \\ \diagdown \\ \diagup NH - NH_2 \\ H | \end{array}$ 180.8

$\begin{array}{l} H \\ \diagdown \\ \diagup NH - C_2H_5 \\ H | \end{array}$ 307.2

$\begin{array}{l} H \\ \diagdown \\ \diagup NH - CH_3 \\ H | \end{array}$ 302.8

Taking ammonium as unity, the relative positivity is:

$NH_4 : NH_3.NH.CONH_2 : NH_3.NHC_6H_5 : NH_3.NH_2 : NH_3C_2H_5 : NH_3CH_3 =$
$1 : 0.447 : 0.592 : 0.855 : 1.452 : 1.433.$
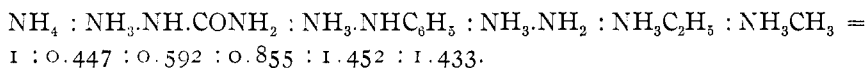
It will be noted that those molecules whose positivity is less than that of ammonia will add to neutral aldehydes or ketones and dehydration will spontaneously follow the addition, while those molecules which are more positive than ammonia add to neutral aldehydes and ketones producing stable hydroxy addition products. For example, methyl and ethyl amines add to formaldehyde, giving $H-C \diagup{O-H} \diagdown{NHCH_3}$ and $HC \diagup{O-H} \diagdown{NHC_2H_5}$.

Hence we may state the following general principle:

Neutral aldehydes or ketones will add ammonia or substituted ammonias, by one of the carbonyl unions breaking, thus liberating a free bond on the oxygen and carbon. The ammonia hydrogen adds to the oxygen and the amine residue to carbon through nitrogen. If the substituted ammonia is less positive than ammonia, the addition product will dehydrate, giving a double union between the carbonyl carbon and the ammonia nitrogen. In other words, it is the aldehyde (ketone) ion, $\diagup{C}\diagup{O\,(-)}{}{(+)}$, which is the chemically active form of aldehydes and ketones and to it the ammonias add.

It is interesting to note that when two positive amine groups ($\phi = 211.4$) unite, one becomes negative while the other remains positive.

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[1] For the meaning of ϕ see previous article.

The fact that the nitrogen atoms have different polarity is proven from the ionization constants of ammonia and hydrazine, the former gives $K_b^{25°} = 1.87 \times 10^{-5}$ while for the latter we have $K_b^{25°} = 3 \times 10^{-6}$. From the previous work upon polarity it is evident that the second NH_2 radical in hydrazine behaves as a negative group, since it reduces the ionization of ammonia. The fact that when two like atoms combine one must be positive while the other is negative was first suggested by W. A. Noyes[1] from the reaction between chlorine and ammonia.

In the case of negative aldehydes and ketones, the less positive the substituted ammonia which adds, the more chance that it will give a stable hydroxy addition product. The work of R. S. Curtiss[2] upon the substituted amine addition products of dimethyl mesoxalate bears out this deduction. He has been able to isolate in the hydroxyl form addition products of the above ester with aniline ($\phi = 107$) and urea ($\phi = 72.2$), while attempts to isolate a similar compound with ammonia ($\phi = 211.4$) have failed.

Similarly, with aldehydes and ketones possessing an excess of positivity within the molecule, it should be easier to isolate the hydroxy addition products of substituted ammonias the more positive the substituted ammonia.

URBANA, ILL.,
April 21, 1911.

APPLICATION OF POLARITY MEASURED IN TERMS OF A LOGARITHMIC FUNCTION OF THE IONIZATION CONSTANT. II. SCALE OF COMBINED INFLUENCE OF SUBSTITUTION IN ORGANIC COMPOUNDS.

BY C G. DERICK.
Received May 15, 1911.

Michael,[3] following the idea of van't Hoff that the atoms in a molecule act upon each other through direct union (through space) or indirectly through intermediate atoms, states[4] "if we number a certain atom in any fatty compound with a normal carbon chain by the figure 1, our present knowledge of the combined mutual influence between this atom and the others in the molecule is expressed by the following scale of combined influence, the number indicating the degree of removal and the extent of influence decreasing in the order given: 2–3–5–6–4–7–(9–10–11)–8. It is to be strongly emphasized that the effect of any atom in the position 2 or 3 is *far greater* than that of any similar atom less closely connected,

[1] THIS JOURNAL, 23, 460 (1901).
[2] Ibid., 31, 1053 (1909).
[3] J. prakt. Chem., [2] 60, 331; Ber., 39, 2138, 2780; 40, 141.
[4] THIS JOURNAL, 32, 999 (1910).