composition should indicate in most cases the class to which the acid may be assigned.

The effects of double and triple bonds are assumed to be due to the additive actions of the valence directions making up these bonds. Fumaric acid is thus shown to be comparable in strength to an acid such as monochloroacetic and maleic acid to dichloroacetic.

BOSTON, April, 1911.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

POLARITY OF ELEMENTS AND RADICALS MEASURED IN TERMS OF A LOGARITHMIC FUNCTION OF THE IONIZATION CONSTANT.

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Introduction.

In recent years polarity of elements and radicals has been employed to explain many chemical behaviors. Since the overthrow of the dualistic theory, polarity has remained a rather indefinit term, one of "chemical instinct" rather than mathematical exactness. In 1901 W. A. Noyes and A. C. Lyon[1] made the following statement: "If we suppose, what seems not to be improbable, that all reactions involving the decomposition of molecules are preceded by an ionization of the parts of molecules, it would follow that elementary molecules as well may ionize into positive and negative parts." Ostwald[2] noted that certain groups and elements when substituted into acetic acid cause an increase or a decrease in its affinity constant. The former he called negative and the latter positive. Abegg,[3] in his article on "Valence and the Periodic System," stated that all elements are amphoteric, that is, exhibit positivity or negativity. He offers four criterions of polarity, ionization, hydrolysis, position in the periodic system, and finally the formula of the compound, in which case the maximum valence is the guide. This work supports the views of W. A. Noyes, referred to above. Finally, B. Flürscheim[4] has employed polarity in his studies of the distribution of affinity in the molecule of organic compounds. In a distinctly qualitative manner he has shown the value of the conception of polarity in interpreting certain properties of the organic molecule and it is in this branch of chemistry that polarity may be used most successfully in correlating chemical properties. In all these suggestions a more or less qualitative measure

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[1] THIS JOURNAL, 23, 460 (1901).

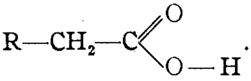
[2] *J. prakt. Chem.*, 31, 433 (1885); *Z. physik. Chem.*, 3, 170, 418 (1889). Also Nernst, "Theoretische Chemie," 6th Auflage, p. 510.

[3] *Z. anorg. Chem.*, 39, 330 (1904).

[4] *J. Chem. Soc.*, 95, 718 (1909); 97, 84 (1910).

of polarity has been implied. It is the purpose of this paper to discuss an exact definition for the terms positivity and negativity.

Definition of Positivity and Negativity.

In a general way, all elements and radicals will exhibit positivity if they cause hydroxyl ionization and negativity if they cause hydrogen ionization. But since some compounds do not appear to ionize appreciably this definition would have decided limitations. To overcome this difficulty, Ostwald suggested the use of an ionizing standard into which he substituted the element or radical. As referred to above, he chose acetic acid, but acetic acid is open to the objection that the negativity of negative groups is greatly magnified by the very negative carbonyl group—while the positivity of positive radicals is greatly decreased by the negativity of the carbonyl group. Hence a true relative quantitative comparison of the positivity and negativity of different radicals is impossible, using the standard, acetic acid. These facts may be easily seen if it is remembered that in using acetic acid as a standard we are in reality measuring the effect of different radicals upon the power of the carboxylic hydroxyl group to ionize hydrogen ions in the neighborhood of the strongly negative carbonyl group, as will be seen from the structural formula of substituted acetic acids,  $R—CH_2—C\begin{matrix}\nearrow O \\ \searrow O—H\end{matrix}$. Such a standard is also open to the objection that all elements and radicals cannot be easily substituted into it, but this objection will hold for nearly every standard that may be chosen.

With these points in mind, the author has chosen water as the most satisfactory standard into which different elements and radicals may be substituted in order to determine their polaric nature. In water we have the hydrogen and hydroxyl ionizations balanced, that is, water is an amphoteric electrolyte which possesses equal negativity and positivity. Further, when a hydrogen of water has been replaced by a radical we are free to determine its true negativity or positivity without the influence of other groups. Using this standard, we may obtain a quantitative comparison of the negativity or positivity of different radicals as well as of the same radical, since most radicals appear to be amphoteric.[1] Hence we may give the following definitions:

1. An element or radical possesses positivity if, when it is substituted for a hydrogen of water, it increases the hydroxyl ionization. It is therefore said to be positive.

2. An element or radical possesses negativity if, when it is substituted for a hydrogen of water, it increases the hydrogen ionization. It is therefore said to be negative.

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[1] See above references to W. A. Noyes and Abegg. C. Worth, Doctor's Thesis, Karlsruhe (1910).

In other words, a positive radical increases the affinity constant K*b* while a negative group increases the affinity constant K*a* for water. Since some elements and most radicals show a measurable positive and negative nature,[1] it will often be found that both K*a* and K*b* for water are increased by substitution of a radical for hydrogen.

Since the free energy change—rather than the total energy change—is the best measure of chemical affinity, the affinity constant K is chosen as the measure of positivity and negativity. For the decrease in free energy which accompanies any chemical reaction we have, according to the second law of thermodynamics, the expression $A = R\,T\,ln\,K$, in which

A is the free energy of ionization,
R is the gas constant,
T is the absolute temperature, and
K is the ionization constant (Ostwald's "affinity constant" = 100 K).

From this expression it is evident that the free energy of ionization is a logarithmic function of K, since R is a constant. Therefore positivity and negativity of groups must be measured in terms of the logarithmic function of K*b* or K*a*, respectively.

Since polarity is measured in terms of a logarithmic function of K, it is clear that it must vary with the temperature, since K varies with T. The expression by which K varies with the temperature is $d\,ln\,K = q\,\frac{dT}{RT^2}$, in which

K is the affinity constant,
q is the heat of ionization,
dT is the change of temperature, and
R is the gas constant.

If the integration is performed between given limits of temperature T_1 and T_2 with the assumption that q is constant over this range of temperature, the following expression is obtained:

$$ln K_2 - ln K_1 = \frac{q}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right).$$

By means of this equation, after measuring K_1 and K_2 at the temperatures T_1 and T_2, respectively, the value of q may be calculated without direct measurements and hence K may be calculated at any desired temperature, as restricted above. However, if q is not constant over the desired range of temperatures, the manner in which q varies with T must be determined and substituted in the differential equation and the latter integrated, when a perfectly general equation for the given substance will be obtained. With such an equation we have the means of determining how polarity varies with the temperature.

Since the affinity constant is chosen at the measure of polarity, the values given in the following tables will hold for those cases only where the mass law holds. In other words, the values are true for the radicals causing weak ionization in water solution at not too great concentrations. In the case of other solvents or strong electrolytes the polarity of a given radical must be determined under the given conditions of temperature, pressure, solvent and concentration.

Finally, this quantitative measure of polarity may be considered as made up of two factors which van't Hoff calls the direct space action and the indirect action (*i. e.*, through intervening carbon atoms) of radicals. This will be developed more fully later. Such a measure of polarity is justified from the standpoint that it will serve to correlate many isolated facts of organic chemistry, as will be shown in the following papers.

Explanation of the Following Tables of Polarity.

In the theoretical discussion, we found that the free energy of ionization was equal to $R\,T\,ln\,K$. A review of the following tables will show that the logarithm in this expression is minus in sign in the case of practically every organic compound. This means that an organic acid (base) will not of itself pass from unit concentration of the unionized form to unit concentration of its ions, but to cause this change work must be done on the acid (base). This work is equal to $R\,T\,ln\,K$. Obviously the greater the ionization of such an acid, the smaller will be the value of $R\,T\,ln\,K$. But, the greater the negativity (positivity) of a group substituted into water the greater will be its ionization. In the case of the organic compounds, therefore, those groups having the greatest polarity will give the smallest values for the free energy of ionization when substituted into water. Because of this fact, it seems better to define the negativity (Θ) and the positivity (ϕ) as equal to $-\frac{1000}{\log K}$. Thus the polaric constants Θ and ϕ are inversely proportional to the free energy of ionization and the value of the free energy of ionization in calories may be determined by multiplying $1/\Theta$ and $1/\phi$ by a RT (-1000), in which

a is the factor necessary to change the natural logarithm to the Brigg's logarithm (2.30258).

R is the gas constant (1.986 calories), and

T is the absolute temperature ($273 + 25$).

The use of such a quantitative measure of polarity and other reasons for choosing the free energy of ionization rather than the ionization constant as the measure of the same will be given in subsequent papers. Finally, no attempt has been made to determine the probable error in the constants Θ and ϕ, but that they are accurate enough for the purpose of generalization in the field of organic chemistry will be shown later

POLARITY OF ORGANIC RADICALS AT 25° IN WATER SOLUTION.

Name of radical.	*Formula of radical.*	K. K*a*	*Log* K.	*θ*.	*φ*.
I. Hydrocarbon radicals:					
Chloral hydrate.............	$CCl_3CHOH—$	$(K_a^{18°} =) 1.0 \times 10^{-11}$	—11.000	90:9	
Phenyl....................	$C_6H_5—$	1.3×10^{-10}	— 9.886	101.5	
o-Chlorophenyl............	$C_6H_4\overset{2}{(Cl)}—$	7.7×10^{-10}	— 9.113	109.8	
p-Chlorophenyl............	$C_6{}^4H_4\overset{4}{(Cl)}—$	4.1×10^{-10}	— 9.387	106.5	
p-Nitrophenyl.............	$(NO_2)C_6H_4—$	7.0×10^{-8}	— 7.155	139.7	
p-Cyanophenyl.............	$\overset{4}{(CN)}C_6H_4—$	1.3×10^{-8}	— 7.886	126.6	
II. Acyl radicals:					
Formyl (aldehyde radical)....	$HCO—$	2.14×10^{-4}	— 3.670	272.4	
Acetyl (ketone radical)......	$CH_3CO—$	1.86×10^{-5}	— 4.731	211.0	
Propionyl.................	$C_2H_5CO—$	1.45×10^{-5}	— 4.839	206.6	
n-Butyryl................	$C_3H_7CO—$	1.56×10^{-5}	— 4.807	208.0	
Isobutyryl................	$(CH_3)_2CHCO—$	1.60×10^{-5}	— 4.796	208.4	
n-Pentyl.................	$C_4H_9CO—$	1.60×10^{-5}	— 4.796	208.4	
Isopentyl.................	$(CH_3)_2CH : CH_2.CO—$	1.70×10^{-5}	— 4.770	209.6	
Trimethylacetyl	$(CH_3)_3C.CO—$	9.78×10^{-6}	— 5.010	199:6	
Capronyl..................	$CH_3(CH_2)_4CO—$	1.45×10^{-5}	— 4.839	206.3	
Oenanthyl.................	$CH_3(CH_2)_5CO—$	1.46×10^{-5}	— 4.836	206.7	
Capryl....................	$CH_3(CH_2)_6CO—$	1.44×10^{-5}	— 4.842	206.3	
Pelayonyl.................	$CH_3(CH_3)_7CO—$	1.12×10^{-5}	— 4.951	202.0	
III. Olefine unsaturated acyl radicals:					
Acrylyl...................	$CH_2=CH—CO—$	5.6×10^{-5}	— 4.252	235.0	
α-*β*-Pentenyl..............	$C_2H_5CH=CHCO$	1.48×10^{-5}	— 4.830	206.8	
β-*γ*-Pentenyl..............	$CH_3CH=CH.CH_2CO—$	3.35×10^{-5}	— 4.475	223.5	
γ-*δ*-Pentenyl..............	$CH_2=CH.(CH_2)_2CO—$	2.09×10^{-5}	— 4.680	213.2	

IV. Halogen substituted acyl radicals:				
α-Chlorobutyryl	$C_2H_5CHCl—CO—$	1.39×10^{-3}	— 2.857	350.0
β-Chlorobutyryl	$CH_3CHClCH_2CO—$	8.59×10^{-5}	— 4.066	246.0
γ-Chlorobutyryl	$CH_2O(CH_2)_3CO—$	3.0×10^{-5}	— 4.523	220.8
δ-Chlorovaleryl	$CH_2O(CH_2)_3CO—$	2.04×10^{-5}	— 4.689	213.0
α-Bromoacetyl	$CH_2BrCO—$	1.38×10^{-3}	— 2.860	349.5
β-Bromopropionyl	$CH_2BrCH_2CO—$	9.8×10^{-5}	— 4.009	249.3
γ-Bromobutyryl	$CH_2Br(CH_2)_2CO—$	2.6×10^{-5}	— 4.585	217.8
δ-Bromobutyryl	$CH_2Br(CH_2)_3CO—$	1.91×10^{-5}	— 4.719	212.0
Iodoacetyl	$CH_2ICO—$	7.5×10^{-4}	— 3.125	320.0
β-Iodopropionyl	$CH_2BrCH_2CO—$	9.0×10^{-5}	— 4.046	247.0
γ-Iodobutyryl	$CH_2Br(CH_2)_2CO—$	2.3×10^{-5}	— 4.638	215.3
δ-Iodovaleryl	$CH_2Br(CH_2)_3CO—$	1.71×10^{-5}	— 4.767	209.8
V. Hydroxy acyl radicals:				
α-Hydroxypropionyl	$CH_3CHOH.CO—$	1.38×10^{-4}	— 3.860	259.0
β-Hydroxypropionyl	$CH_2OHCH_2CO—$	3.1×10^{-5}	— 4.509	222.0
γ-Hydroxybutyryl	$CH_2OH(CH_2)_2CO—$	1.93×10^{-5}		
VI. Alkoxy acyl radicals:				
Methoxyacetyl	$CH_3O.CH_2.CO—$	3.0×10^{-4}	— 3.523	283.9
Ethoxyacetyl	$C_2H_5O.CH_2.CO—$	2.34×10^{-4}	— 3.631	275.2
VII. Carboxyl substituted acyl radicals:				
Malonyl (carboxy acetyl)	$HO_2C.CH_2CO—$	1.64×10^{-3}	— 2.785	359.2
Succinyl (β-carboxypropionyl)	$HO_2C.(CH_2)_2CO—$	6.7×10^{-5}	— 4.174	239.3
Glutaryl (γ-carboxybutyryl)	$HO_2C(CH_2)_2CO—$	4.7×10^{-5}	— 4.328	231.0
Adipyl (δ-carboxyvaleryl)	$HO_2C(CH_2)_3CO—$	3.7×10^{-5}	— 4.432	225.3
Pimelyl (ε-carboxycapronyl)	$HO_2C(CH_2)_4CO—$	3.23×10^{-5}	— 4.491	222.7
Suberyl (ξ-carboxyenanthyl)	$HO_2C(CH_2)_5CO—$	2.99×10^{-5}	— 4.524	220.8
Azelayl (η-carboxycaprylyl)	$HO_2C(CH_2)_6CO—$	2.5×10^{-5}	— 4.602	217.2
Sebacyl (θ-carboxypelayonyl)	$HO_2C(CH_2)_7CO—$	2.38×10^{-5}	— 4.624	216.0

POLARITY OF ORGANIC RADICALS AT 25° IN WATER SOLUTION (*Continued*).

Name of radical.	Formula of radical.		K.	Log K.	θ.	φ.
VIII. Carboxalkyl substituted acyl radicals:						
Carboxethyl acetyl..........	$C_2H_5O_2C.CH_2CO$—		4.51×10^{-4}	— 3.346	299.0	
Carboxethyl-β-propionyl......	$C_2H_5O_2C.(CH_2)_2CO$—		3.02×10^{-5}	— 4.520	221.0	
Carboxmethyl-β-propionyl....	$CH_3O_2C(CH_2)_2CO$—		3.23×10^{-5}	— 4.491	222.7	
Carboxethyl-ζ-enanthyl......	$C_2H_5O_2C(CH_2)_5CO$ —		1.46×10^{-5}	— 4.836	206.7	
Carboxethyl-θ-pelargonyl.....	$C_2H_5O_2C(CH_2)_7CO$—		1.43×10^{-5}	— 4.845	206.4	
IX. Aminoacyl radicals:						
Aminoacetyl................	NH_2CH_2CO—	Kb =	2.7×10^{-12}	—11.569		86.4
		Ka =	1.8×10^{-10}	— 9.745	102.6	
α-Aminopropionyl...........	$CH_3CH(NH_2)CO$—	Ka =	1.9×10^{-10}	— 9.721	102.7	
		Kb =	$5.1 = 10^{-12}$	—11.293		88.5
X. (N)-Alkylaminoacyl radicals:						
(N)-Methylaminoacetyl	$CH_3NH.CH_2CO$—	Ka =	1.2×10^{-10}	— 9.921	100.7	
		Kb =	1.7×10^{-12}	—11.770		85.0
(N)-Dimethylaminoacetyl....	$(CH_3)_2N.CH_2CO$—	Ka =	1.3×10^{-10}	— 9.886	101.2	
		Kb =	9.8×10^{-13}	—12.009		82.7
XI. (N)-Arylaminoacyl radicals:						
Anilino-α-propionyl..........	$CH_3CH(C_6H_5NH)CO$—		2.2×10^{-5}	— 4.658	214.8	
Anilino-β-propionyl..........	$C_6H_5NH—(CH_2)_2CO$—		4.0×10^{-6}	— 5.398	185.3	
o-Toluino-α-propionyl........	$CH_3\underset{2}{C_6H_4}NH—CH(CH_3)CO$—		3.9×10^{-5}	— 4.409	227.0	
o-Toluino-β-isobutyryl........	$CH_3\underset{2}{C_6H_4}NH.C(C_2H_5)_2CO$—		4.0×10^{-6}	— 5.398	185.3	
p-Toluino-α-propionyl........	$CH_3\underset{4}{C_6H_4}NH.CH(CH_3)CO$		7.0×10^{-6}	— 5.155	197.7	
p-Toluino-β-propionyl........	$CH_3\underset{4}{C_6H_4}NH.(CH_2)_2CO$ —		2.0×10^{-6}	— 5.699	175.4	
XII. (N)-Acetarylaminoacyl radicals:						
Acetanilino-α-propionyl......	$C_6H_5N(COCH_3)CH(CH_3)CO$—		1.25×10^{-4}	— 3.903	256.3	

Acetanilino-β-isobutyryl	$C_6H_5N(COCH_3)C(CH_3)_2—CO—$	2.9 × 10^{-5}	— 4.538	220.0
Aceto-*o*-toluino-α-propionyl	$CH_3\overset{2}{C_6H_4}N(COCH_3)CH(CH_3)CO—$	1.04 × 10^{-4}	— 3.983	251.0
Aceto-*o*-toluino-β-isobutyryl	$CH_3\overset{2}{C_6H_4}N(COCH_3)C(CH_3)_2CO—$	2.1 × 10^{-5}	— 4.678	213.7
Aceto-*p*-toluino-α-isobutyryl	$CH_3\overset{4}{C_6H_4}N(COCH_3)C(CH_3)_2CO—$	9.5 × 10^{-5}	— 4.022	248.4
Aceto-*p*-toluino-β-isobutyryl	$CH_3\overset{4}{C_6H_4}N(COCH_3)CH_2.CH(CH_3)CO—$	2.3 × 10^{-5}	— 4.638	215.2
XIII. Aromatic acid radicals:				
Benzoyl	$C_6H_5CO—$	6.9 × 10^{-5}	— 4.161	240.0
Phenylacetyl	$C_6H_5CH_2CO—$	5.3 × 10^{-5}	— 4.276	233.8
Phenyl-β-propionyl	$C_6H_5(CH_2)_2CO—$	2.3 × 10^{-5}	— 4.638	215.2
o-Toluyl	$CH_3\overset{2}{C_6H_4}CO—$	1.25 × 10^{-4}	— 3.903	256.4
m-Toluyl	$CH_3\overset{3}{C_6H_4}CO—$	5.1 × 10^{-5}	— 4.293	232.7
p-Toluyl	$CH_3\overset{4}{C_6H_4}CO—$	5.1 × 10^{-5}	— 4.293	232.7
Mesityl	$(CH_3)_2\overset{3,5}{C_6H_3}CO—$	4.8 × 10^{-5}	— 4.319	226.5
α-Naphthyl	$C_6H_4.C_4H_3CO—$	2.0 × 10^{-3}	— 2.699	374.6
β-Naphthyl	$C_6H_4C_4H_3CO—$	6.0 × 10^{-5}	— 4.222	236.6
Cinnamyl	$C_6H_5CH=CHCO—$	3.5 × 10^{-5}	— 4.456	224.6
Phenylpropiolyl	$C_6H_5C=C—CO—$	5.9 × 10^{-3}	— 2.959	337.7
o-Chlorobenzoyl	$Cl\overset{2}{C_6H_4}CO—$	1.32 × 10^{-3}	— 2.880	347.0
m-Chlorobenzoyl	$Cl\overset{3}{C_6H_4}CO—$	1.35 × 10^{-3}	— 2.810	355.5
p-Chlorobenzoyl	$Cl\overset{4}{C_6H_4}CO—$	9.3 × 10^{-5}	— 4.032	247.8
Salicyl	$HO\overset{2}{C_6H_4}CO—$	1.04 × 10^{-3}	— 2.983	325.0
m-Hydroxybenzoyl	$HO\overset{3}{C_6H_4}CO—$	8.33 × 10^{-5}	— 4.078	244.8
p-Hydroxybenzoyl	$HO\overset{4}{C_6H_4}CO—$	2.9 × 10^{-5}	— 4.538	220.2

POLARITY OF ORGANIC RADICALS AT 25° IN WATER SOLUTION (*Continued*).

Name of radical.	Formula of radical.		K.	Log K.	θ.	φ.
Phthalyl..................	$\overset{2}{\mathrm{H}}\mathrm{OOCC_6H_4CO}$—		1.21×10^{-3}	— 2.917	342.4	
Isophthalyl................	$\overset{3}{\mathrm{H}}\mathrm{OOCC_6H_4CO}$—		2.9×10^{-4}	— 3.538	282.6	
Terephthalyl...............	$\overset{4}{\mathrm{H}}\mathrm{OOCC_6H_4CO}$—		1.5×10^{-4}	— 3.824	261.5	
o-Nitrobenzoyl.............	$\overset{2}{\mathrm{N}}\mathrm{O_2C_6H_4CO}$—		6.3×10^{-3}	— 2.199	450.5	
m-Nitrobenzoyl............	$\overset{3}{\mathrm{N}}\mathrm{O_2C_6H_4CO}$—		3.45×10^{-4}	— 3.462	290.0	
p-Nitrobenzoyl.............	$\overset{4}{\mathrm{N}}\mathrm{O_2C_6H_4CO}$—		4.0×10^{-4}	— 3.398	294.0	
o-Aminobenzoyl............	$\mathrm{NH_2}\overset{2}{\mathrm{C}}\mathrm{_6H_4CO}$—	Ka =	1.06×10^{-5}	— 4.975	201.0	
		Kb =	1.38×10^{-12}	—11.860		84.3
m-Aminobenzoyl...........	$\overset{3}{\mathrm{N}}\mathrm{H_2C_6H_4CO}$—	Ka =	1.63×10^{-5}	— 4.788	209.0	
		Kb =	1.22×10^{-11}	—10.914		9.61
p-Aminobenzoyl...........	$\overset{4}{\mathrm{N}}\mathrm{H_2C_6H_4CO}$—	Ka =	1.21×10^{-5}	— 4.917	203.3	
		Kb =	2.33×10^{-12}	—11.633		86.0
(N) Methyl-*o*-aminobenzoyl...	$\overset{2}{\mathrm{C}}\mathrm{H_3NHC_6H_4CO}$—	Ka =	4.6×10^{-6}	— 5.337	187.0	
		Kb =	8.5×10^{-13}	—12.068		82.8
(N) Methyl-*o*-aminobenzoyl...	$\overset{3}{\mathrm{C}}\mathrm{H_3NHC_6H_4CO}$—	Ka =	8.0×10^{-6}	— 5.096	196.0	
		Kb =	1.10×10^{-11}	—10.959		91.3
(N) Methyl-*p*-aminobenzoyl...	$\overset{4}{\mathrm{C}}\mathrm{H_3NHC_6H_4CO}$—	Ka =	8.2×10^{-5}	— 5.036	198.4	
		Kb =	1.52×10^{-12}	11.818		84.5
XIV. Acyl radical of nitrogen:						
Nitroso...................	O = N—		4.5×10^{-4}	— 3.347	298.8	

XV. Basic radicals of nitrogen:			K*b*			
Ammonium................	NH_4—	=	1.87×10^{-5}	2— 4.728		211.4
Methylammonium...........	CH_3NH_3—		5.0×10^{-4}	— 3.301		302.8
Dimethylammonium.........	$(CH_3)_2NH_2$—		7.4×10^{-4}	— 3.131		319.0
Trimethylammonium........	$(CH_3)_3NH$—		7.4×10^{-5}	— 4.131		242.0
Ethylammonium............	$C_2H_5NH_3$—		5.6×10^{-4}	— 3.252		307.2
Propylammonium...........	$C_3H_7NH_3$—		4.7×10^{-4}	— 3.328		298.5
Isopropylammonium.........	$(CH_3)_2CHNH_3$—		5.3×10^{-4}	— 3.276		305.2
Isobutylammonium..........	$(CH_3)_2CH.CH_2NH_3$		3.1×10^{-4}	— 3.509		284.7
Isoamylammonium..........	$(CH_3)_2CH.(CH_2)_2NH_3$—		5.0×10^{-4}	— 3.301		302.8
Phenylammonium...........	$C_6H_5NH_3$—		4.6×10^{-10}	— 9.337		107.0
o-Toluylammonium..........	$\overset{2}{CH_3}.C_6H_4NH_3$—		3.3×10^{-10}	— 9.482		105.5
m-Toluylammonium.........	$\overset{3}{CH_3}C_6H_4NH_3$—		6.0×10^{-10}	— 9.222		108.3
p-Toluylammonium..........	$\overset{4}{CH_3}C_6H_4NH_3$—		2.0×10^{-9}	— 8.699		115.0
Phenylmethylammonium	$C_6H_5(CH_3)NH_2$—		7.4×10^{-9}	— 8.131		123.0
Urea......................	$NH_2CO.NH_3$—		1.5×10^{-14}	—13.824		72.2
Anilinoammonium...........	$C_6H_5NH.NH_3$—	Kb^{40} =	1.6×10^{-9}	— 8.796		125.0
Aminoammonium...........	$NH_2.NH_3$—		3.0×10^{-6}	— 5.523		180.8
Semicarbazine.............	$NH_2CO.NH.NH_3$—		2.7×10^{-11}	—10.569		94.6
Pyridine..................	$\underline{CH{=}CH{-}CH{=}CH{-}CH{=}N}H$—		2.28×10^{-9}	— 8.642		115.6
XVI. Acyl sulfur radicals:			K*a*			
Sulfurous..................	HOSO—		1.6×10^{-2}	— 1.796	557.0	

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.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

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.

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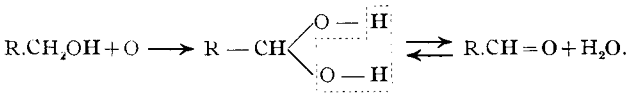
I. Mechanism of Dehydration of the Dihydroxy Form of Aldehydes and Ketones.

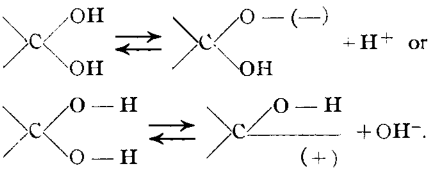
The quantitative measure of polarity developed in the previous paper may be applied to the reactions of aldehydes and ketones, so that useful generalizations may be drawn, as the following will illustrate. To apply this measure a neutral aldehyde or ketone is defined as a compound whose ionization constant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

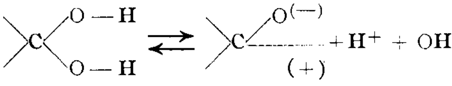


$$R.CH_2OH + O \longrightarrow R-CH\begin{matrix} O-H \\ O-H \end{matrix} \rightleftarrows R.CH=O + H_2O.$$

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:



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



If the hydrogen and hydroxyl ionization occur simultaneously in water