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A New Method For Estimating the Relative pK Values of Amines and Alcohols

by

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A New Method For Estimating the Relative pK Values of Amines and Alcohols*

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Linear free energy relationships were established between reaction rate constants of alcohols and amines with ethyl magnesium bromide in diethyl ether at 25°, and their pK values in terms of Bronsted equation, which are:

$$\text{for alcohols, } \log k = -0,09 \text{ pK} + 0,93 \quad (\text{at } 25^\circ\text{C})$$

$$\text{and for amines, } \log k = -0,07 \text{ pK} + 0,78 \quad (\text{at } 25^\circ\text{C})$$

From these equations, the relative pK values of amines and alcohols can be predicted by measuring their reaction rate constants with ethyl magnesium bromide in diethyl ether, at 25°C.

INTRODUCTION

The present work was undertaken in order to correlate the thermodynamic and kinetic acidities of amines, alcohols and 1-alkynes which are very weak acids and then propose a new method for determining very weak acidity constants, i.e. pK values.

Thermodynamic acidity deals with the position of equilibria between acids and their conjugate bases whereas kinetic acidity pertains to the rates at which acids donate protons to bases. In our work, the kinetic acidity of amines, alcohols and 1-alkynes were calculated by kinetic investigation of their reactions with ethyl magnesium bromide in diethyl ether, at 25°C. The reaction is a quantitative interaction of ethyl magnesium bromide, a Grig-

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nard reagent, with active hydrogen compounds and is known as Zerewitinoff reaction [1]. Their thermodynamic acidities, i.e. relative pK values were taken from McEwen's scale [2], which is the classic and still valuable thermodynamic acidity scale.

In the previous paper [3], we investigated the kinetics and mechanism of Zerewitinoff reaction between ethyl magnesium bromide and a number of amines, alcohols and 1-alkynes in diethyl ether at 25°C and found the second order rate constants with precision enough to establish some linear free energy relationships.

These correlations between thermodynamic and kinetic acidities are named as acidity-rate or Bronsted equations which are linear free energy relationships involving substituent effects. Bronsted equation provides for a linear relationship between $\log k$ (rate constant for kinetic processes involving proton transfer) and $\log K$ (the dissociation constant of the acid, $\text{pK} = -\log K$) [4, 5].

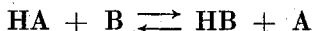
$$\log k = \alpha \log K + \log G$$

Parameters α and G are constants characteristic of the particular series of reactions; α is positive and smaller than unity when k and K are measured in the same solvent-base system.

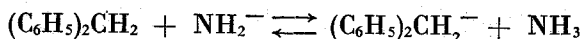
In this work, we investigated the validity of Bronsted equation for Zerewitinoff reaction in an aprotic solvent like diethyl ether and with very weak acids. Bronsted equation has already been investigated frequently for oxygen acids and in aqueous solutions or in amphiprotic solvent-water mixtures [6]. And then we proposed a new method for predicting the thermodynamic acidity of very weak oxygen and nitrogen acids depending upon kinetic measurements.

VERY WEAK ACIDITY AND THERMODYNAMIC ACIDITY SCALES

The strengths of acids may be studied only by measurements on equilibria involving at least two acids [7, 8].

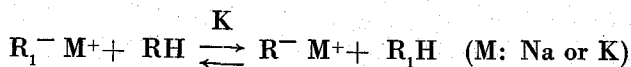


Commonly the solvent acts as one of the acids or bases in equilibria of this type. For fairly strong acids, measurable concentration of A are obtained when the base B is the solvent. For weaker acids, however, the conjugate base of the solvent must be used as B in order to transform a measurable concentration of HA to A. In the studies of very weak acids, HB should be very weak so that B will be strongly basic. For this reason, deprotonation of very weak acids can not be measured in water (except some alcohols acidic enough to be measured in water and fluoradene, the most acidic hydrocarbon), then the solvent, liquid ammonia is often used in studying very weak acids. Many hydrocarbons, such as diphenyl methane, react as acids toward potassium amide:



Another technique, that has been used in the study of very weak acids, involves a direct comparison of two acids by studying of the equilibrium between one and the conjugate base of the other in a solvent having negligible acidity.

Conant and Wheland [9] introduced and McEwen [2] developed the measurement of the equilibrium constants for dissociation of very weak acids by means of ion-pair equilibria:



In a classic paper, Conant and Wheland [9] ranked a number of very weak carbon acids in an acidity scale, which was later expanded and made more quantitative by McEwen [2]. In these studies, Na or K salts of carbon acids in ether or benzene in nitrogen atmosphere were prepared and treated with other carbon acids. The equilibrium constants between the two salts and the two carbon acids were estimated colorimetrically by observing the differences in color of two salts. An additional method for ranking of the carbon acids was carbonation, i.e. carbonation of the equilibrium mixture, isolation of the resulting carboxylic acids and determination of each acid present. These two techniques related the $\text{pK}'\text{s}$ of carbon acids to one another. Furthermore, the optical rotations of menthol and sodium methoxide in benzene differ and are easily determined. This technique allowed the aci-

dities of oxygen and carbon acids (and a few nitrogen acids) to be interrelated and a continuous acidity scale was constructed: McEwen's acidity scale (Table I). The pK of methanol was taken to be 16 [10]. McEwen pointed out that the p'Ks of acids between 18 and 37 have an error of ∓ 1 pK.

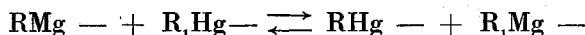
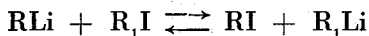
TABLE I

McEwen's acidity scale.

Compound	pK	Compound	pK
Methyl alcohol	16	Indene	21
Pyrrole	16.5	Diphenylamine	23
Benzyl alcohol	18	Fluorene	25
Ethyl alcohol	"	Aniline	27
Benzhydrol	"	p- Toluidine	"
Iso-propyl alcohol	"	p- Anisidine	"
Triphenyl carbinol	19	Xanthane	29
Ter-butyl alcohol	"	Phenyl xanthane	"
Ter-amyl alcohol	"	Diphenylbiphenylmethane	31
Menthol	"	Triphenyl methane	33
Acetophenone	"	Diphenyl α -naphthyl methane	34
Phenyl Fluorene	21	Diphenyl methane	35
α - Naphthyl fluorene	"	Diphenyl methyl ethylene	36
Phenyl acetylene	"	Cumene	37

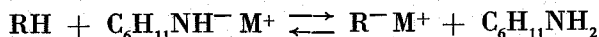
The acidity of acetylenic hydrocarbons which were not determined by McEwen, were measured by Gilman [11] with metalation method and the order of decreasing acid strength was given as phenyl acetylene > 1- heptyne > acetylene [12].

Other equilibria, like lithium-halogen interchange between lithium organic compounds and organoiodine derivatives by Appiequist and O'Brien [13] and organo mercury-organo magnesium compound exchange by Dessy and Salinger [14] were used to rank carbanions in order of relative stability.



A second thermodynamic acidity scale has been developed by Streitweiser and coworkers [15]. These authors measured the equilibrium constants between lithium or cesium cyclohexylamide and the carbon acid on the one hand and cyclohexylamine and

the lithium or cesium carbon salt on the other in cyclohexyl amine as solvent by spectroscopy.

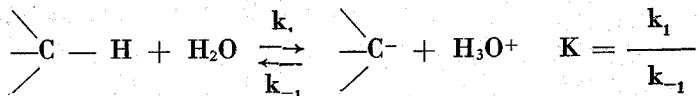


Examined pK values of carbon acids were based on 9- phenyl fluorene; its pK value was found to be 18,5 in aqueous solution.

Methods based on the equilibrium position became less practical as the acids became weaker. Nevertheless, the McEwen scale, in spite of its short comings has survived and has served as a point of departure for the other investigators [16]. However, it was found that the rates at which protons were transferred from carbon (kinetic acidity) would be measured somewhat more easily than equilibrium constants (thermodynamic acidity). In this paper, the rates at which protons were transferred from nitrogen and oxygen in very weak Bronsted acids were measured and after a connection between their thermodynamic and kinetic acidities has been examined, a new method for predicting the thermodynamic acidity of very weak nitrogen and oxygen acids was proposed, being independent of solvent as the property of a thermodynamic acidity scale [5].

In spite of a complete lack of such a correlation between thermodynamic and kinetic acidity of very weak oxygen and nitrogen acids, there are numerous good Bronsted relationships for oxygen acids in aqueous solution and some for carbon acids in aprotic solvents. In the following section, correlation of thermodynamic and kinetic acidity of the carbon acids are summarized; then some linear free energy relationships for nitrogen and oxygen acids will be proposed.

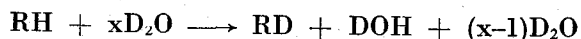
Pearson and Dillon [17] made the most comprehensive attempt on this correlation by collecting the data to relate between k_1 and K for proton transfer from carbon acids to water at 25°C.



A plot of $\log k_1$ versus $-\log K$ for the carbon acids gave a straight line but with considerable scatter.

Shatenshtein [18] introduced a procedure based on a Bronsted correlation between the rate of hydrogen exchange and the pK which is determined by the equilibrium method i.e. from McEwen's scale. Most studies were carried out with potassium dideutero amide ($K^+ND_2^-$) in deuteroammonia (ND_3).

An interesting correlation between rates and equilibria involving carbon acids was made by Dessy, et al [19]. These authors measured the rates of hydrogen-deuterium exchange of cyclopentadiene, acetophenone, phenyl acetylene and fluorene with deuterium oxide, catalyzed by 1M triethyl amine in dimethyl formamide.



The pK of cyclopentadiene was estimated to be 14-15 from the observation that sodium methoxide in methanol metalates cyclopentadiene whereas sodium phenoxide does not. This pK, taken together with those of McEwen and from the work of Shatenshtein, provided the data for the correlation.

Another correlation has been developed by Streitweiser [20] who have greatly extended the utility of Shatenshtein's approach, by measuring the rates of tritium exchange from tritiated hydrocarbons as catalyzed by lithium or cesium cyclohexylamide in cyclohexylamine. Cyclohexane is the weakest acid for which a pK value equal to 49 has been obtained. The Bronsted correlation used by Streitweiser and his coworkers is based on the rate of exchange observed in methanol with sodium methoxide and pK obtained by the equilibrium method with cesium cyclohexyl amide in cyclohexyl amine.

Cram [21] has combined information from equilibrium and kinetic measures of hydrocarbon acidity into a scale called the McEwen-Streitweiser-Applequist-Dessy (MSAD) pK scale. The reference compound was 9- phenyl fluorene with pK of 18,5 in aqueous sulfolane.

Although C—H acidity has been investigated experimentally and studied theoretically, X — H acidity (X: nitrogen, oxygen, etc.) has been studied only on protonation reactions. However,

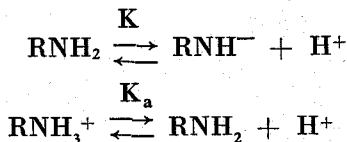
the acidity of about thirty-five alcohols were determined by Hine and Hine [22] with indicator method in isopropyl alcohol solution. Ballinger and Long [23] have determined the acid ionization constants of twelve simple alcohols by a conductivity procedure in water.

No acidity-rate relationship concerning Zerewitinoff reaction as in the case of other Grignard reactions has been given up to our work. Dessy [19] attempted at correlation of pK values and rate constants of substituted phenyl acetylenes in their Zerewitinoff reaction with ethyl magnesium bromide after having predicted the pK values of these acetylenes through the linear plot of hydrogen-detuerium exchange rate against known pK values of some acetylenes. Then he concluded that there is no linearity between Zerewitinoff reaction rate constants (in fact, relative reactivities based on half-times) of substituted acetylenes and their pK values. However examining the relevant data carefully, it is possible to conclude that there is a linearity between the relative reactivity of substituted phenyl acetylenes and their pK values.

CORRELATIONS BETWEEN THE RATE CONSTANTS AND THE RELATIVE ACIDITY OF AMINES, ALCOHOLS AND 1-ALKYNES CONCERNING ZEREWITINOFF REACTION

A. An Acidity-Rate Relationship Concerning the Reaction of Ethyl Magnesium Bromide with Amines in Diethyl Ether at 25°C.

The pK values of amines were taken from McEwen's scale [2]. But only a few nitrogen acids are found to be related to the other carbon and oxygen acids in this scale. pK values of amines in this scale, together with their pK_a values which are acidic dissociation constants of their conjugate acids, referring the following relationships



are given in Table 2.

TABLE 2

Relative acidity of amines, from Mc Ewen's scale [2] (pK) and dissociation constants of their conjugate acids (pK_a).

Amine	pK	pK _a
Diphenylamine	23	0.79
Aniline	27	4.63
p-Toluidine	27	5.08
p-Anisidine	27	5.34

It can be seen that the increase in pK values is in agreement with the increase in pK_a values. Taking this result as a departure point, the relative pK values of amines which were studied in Zerewitinoff reaction were found. The reaction rate constants of amines with ethyl magnesium bromide in diethyl ether at 25°C (k) and pK values of amines in McEwen's scale together with pK_a values of these amines are given in Table 3.

TABLE 3

The reaction rate constants of amines with ethyl magnesium bromide in diethylether at 25°C (k), their relative pK values and pK_a values.

Amine	k(10 ³ M ⁻¹ sec ⁻¹)*	pK	pK _a
Diethyl amine	11.2	33	10.98
N-ethyl aniline	20.0	27	5.11
Diphenyl amine	45.0	23	0.85
Aniline	24.6	27	4.65
Benzyl amine	15.1	31	9.34
n-Butyl amine	16.4	33	10.43
iso-Propyl amine	11.8	33	10.63

* From Table 4 of the previous paper [3].

We examined a correlation between these rate constants and pK values of amines. The linear plot of log of k values against pK values is shown in Figure 1 A. The correlation is good with no considerable scatter. The linear free energy relationship for this plot is as follows:

$$\log k = -0,09 \text{ pK} + 0,93 \quad (1)$$

This relationship and the others which will be given later were found by using the method of least-square adjustment.

However in acid or base catalyzed reactions, Bronsted equation, which correlates the rate constant (k) to the dissociation constant of acid or base (K),

$$\log k = \alpha \log K + \log G$$

is a linear free energy relationship and also valid by correlating the kinetic acidity to the thermodynamic acidity in the reactions that consume the acid or base, α is known as Bronsted slope and is always positive, with the magnitude between zero and 1,00. If $\log K$ is written instead of K in the equation (1), α is found to be 0,09 for the reaction of ethyl magnesium bromide with amines and it is seen to be agreed with the value of Bronsted slope.

Furthermore, the base strengths of amines, i.e. pK_a values are plotted against the Taft, σ^* values [24]. All of the aliphatic amines and all of the aromatic amines are approximately correlated

to a single line each by the equation $\log \frac{K}{K_0} = \rho^* \Sigma \sigma^* + H(n)$.

The quantity $\Sigma \sigma^*$ is the sum of polar substituent constants of the groups attached to the amino nitrogen, n is the number of hydrated $N^+—H$ groups in the ammonium ion and H is an empirical constant measuring the base strengthening effects of each hydrated $N^+—H$ groups. The values of the reaction constants, ρ^* and the hydration constant, H are the same for both the aliphatic and aromatic series. This result is found by Folkers and Runquist [25]. Hall [26] has already plotted the pK_a values of primary, secondary and tertiary aliphatic amines against the Taft σ^* values and found that each class of amine lay on a different line with slopes, i.e. ρ^* values -3,14, -3,23 and - 3,30 respectively and primary and secondary amines with a low degree of steric hindrance give the same linear plot. However Folkers and Runquist reported that the values of the reaction constants, ρ^* are equal to - 3,06 and - 3,08, almost equal values for aliphatic and aromatic amines respectively.

Consequently, the following linear free energy relationships for the dissociation of amines can be written as follow:

$$pK_a = - 3,07 \Sigma \sigma^* + \text{Constant} \quad (2)$$

On the other hand, we have found that plotting the rate constants of the reaction of ethyl magnesium bromide with amines (k) versus their Taft $\Sigma\sigma^*$ values gave a single line, represented by the equation:

$$\log k = 0,29 \Sigma\sigma^* - 2,14 \quad (3)$$

The Taft $\Sigma\sigma^*$ values for the amines and their reaction rate constants with ethyl magnesium bromide in diethyl ether at 25°C are given in Table 4 and the corresponding linear Taft plot is given in Figure 1B.

TABLE 4

The reaction rate constants of amines with ethyl magnesium bromide in diethyl ether at 25°C (k) and their Taft $\Sigma\sigma^*$ values.

Amine	$k(10^3 \text{ M}^{-1} \text{ sec}^{-1})^*$	$\Sigma\sigma^{*\ddagger}$
Diethyl amine	11.2	0.29
N-Ethyl aniline	20.0	0.99
Diphenyl amine	45.0	1.69
Aniline	24.6	1.58
Benzyl amine	15.1	1.20
n-Butyl amine	16.4	0.85
iso-Propyl amine	11.8	0.79

* From Table 4 of the previous paper [3].

$\ddagger \Sigma\sigma^*$ can be found by summing of polar substituent constants of the groups attached to amino nitrogen. H: + 0,49, C₂H₅: - 0,10, iso-C₃H₇: - 0,19, n-C₄H₉: - 0,13, C₆H₅: + 0,60 and C₆H₅CH₂: + 0,22

As a rule, in a Taft equation as well as in other linear free energy relationships; if electronwithdrawing substituents increase the rate of the reaction, the reaction constant, ρ^* ($\log k = \rho^* \Sigma\sigma^* + \text{Constant}$) is positive. In the above equation ρ^* is 0,29 and this indicates that the attack of amino nitrogen on ethyl magnesium bromide is nucleophilic. This result is in good agreement with the proposed mechanism [3] for the reaction of ethyl magnesium bromide with amines in diethyl ether.

Being the plot of $\log k$ versus $\Sigma\sigma^*$ and the plot of $\text{p}K_a$ versus $\Sigma\sigma^*$ are linear, the plot $\log k$ versus $\text{p}K_a$ would be linear. This can be shown as follow: Equation (2) is rewritten for $\Sigma\sigma^*$ as:

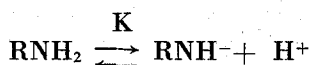
$$\Sigma\sigma^* = \frac{\text{pK}_a - \text{Constant}}{-3,07} \quad (4)$$

Substituting this $\Sigma\sigma^*$ value in equation (3), we have:

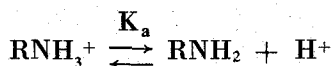
$$\log k = 0,29 \left(- \frac{\text{pK}_a - \text{Constant}}{3,07} \right) - 2,14$$

$$\log k = -0,09 \text{ pK}_a + \text{Constant} \quad (5)$$

From this it can be readily deduced that the reaction constants of two linear Bronsted plots, namely the plot of $\log k$ versus pK (1) and the plot of $\log k$ versus pK_a (5) for amines are the same, $\rho^* = -0,09$. As a consequence, the relative acidity of amines (pK) was found parallel to the acid strength of their conjugate acids (pK_a). Nevertheless, before attempting the correlation of reaction rate constants of amines with ethyl magnesium bromide, to their pK values; we have calculated some of these pK values by proposing this parallelism based on the qualitative agreement of pK and pK_a values of four amines. (See Table 2). Consequently, we proposed that the relative acidity of amines (K),



and the relative acidity of the conjugate acids of amines (K_a)



are the same and this fact could be deduced with the aid of a linear free energy relationship concerning a reaction consisting of a proton transfer from RNH_2 (and $\text{R}_1\text{R}_2\text{NH}$) (i.e. Zerewitinoff reaction).

B. An Acidity-Rate Relationship Concerning the Reaction of Ethyl Magnesium Bromide with Alcohols in Diethyl Ether at 25°C.

The reaction rate constants of alcohols with ethyl magnesium bromide in diethyl ether at 25°C (k) and pK values of alcohols in McEwen's scale are given in Table 5.

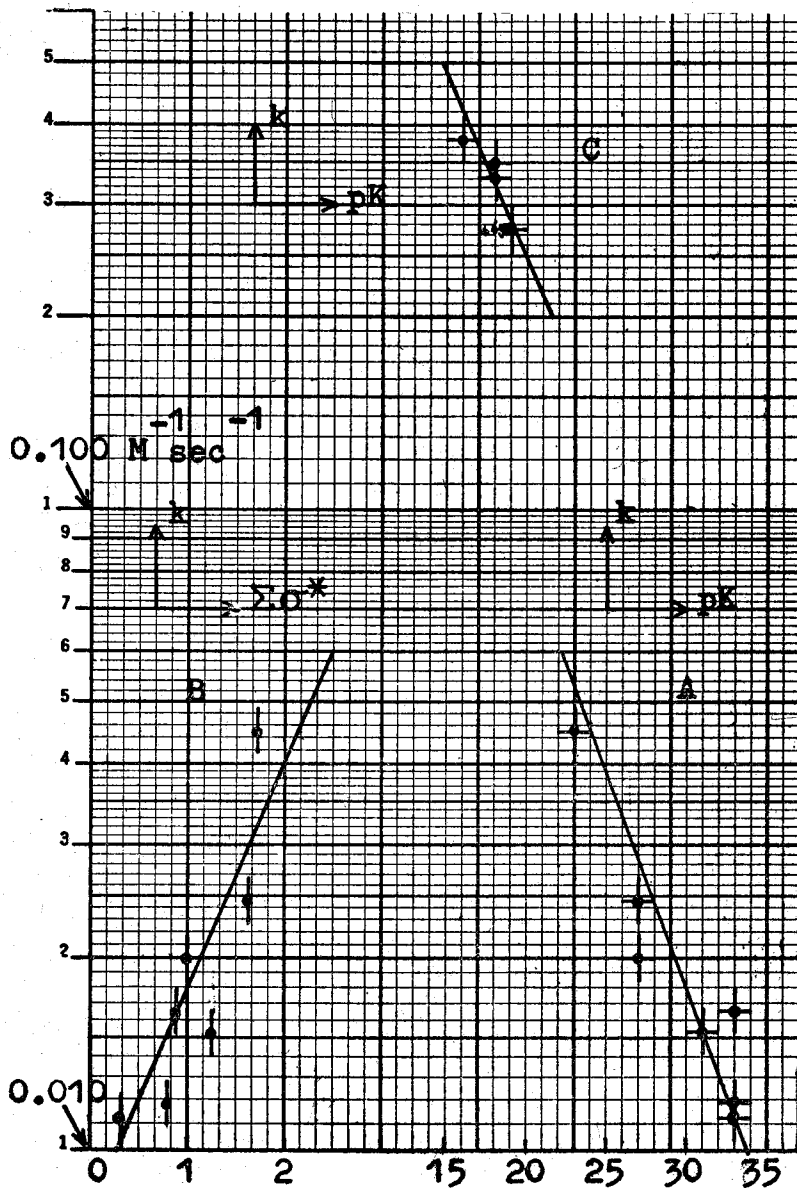


Figure 1. The plots of linear free energy relationships concerning Zerewitinoff reaction of ethyl magnesium bromide A: with amines, Brønsted plot of $\log k$ versus pK ; B: with amines, Taft plot of $\log k$ versus $\Sigma\sigma^*$ and C: with alcohols, Brønsted plot of $\log k$ versus pK .

TABLE 5

The reaction rate constants of alcohols with ethyl magnesium bromide in diethyl ether at 25°C (k) and their relative pK values.

Alcohol	k(10 ³ M ⁻¹ sec ⁻¹)*	pK
Methyl alcohol	377	16
Benzyl alcohol	347	18
Ethyl alcohol	335	18
t-Butyl alcohol	277	19

* From Table 7 of the previous paper [3].

The linear plot of log of k values against pK values is shown in Figure 1C; the linear free energy relationship for this plot is as follows:

$$\log k = -0,07 \text{ pK} + 0,78 \quad (6)$$

As alcohols are stronger very weak acids than amines and 1-alkynes, acidities of some alcohols could be measured in isopropyl alcohol [22] and those of only primary alcohols in water [23] by indicator and conductivity methods respectively, which are equilibrium methods. In this work, for measurement of the very weak acidity of alcohols, we developed a method involving the measurement of kinetic rate constants of ethyl magnesium bromide with alcohols in diethyl ether at 25°C — taking the initial concentrations lower than 30 mM and keeping the ionic strength constant [3] — and calculating the pK values from the equation (6).

C. An Acidity-Rate Relationship Concerning the Reaction of Ethyl Magnesium Bromide with 1-Alkynes in Diethyl Ether at 25°C.

The reaction rate constants of 1-alkynes with ethyl magnesium bromide in diethyl ether at 25°C (k) and their relative pK values are given in Table 6.

No attempt has been made for a Bronsted plot concerning 1-alkynes in this work, because it needs four or six points to have a suitable linear free energy relationship and accurate pK values of 1-alkynes are not available in the literature as explained below. However, the rate constants were found to increase in the

order of 1- hexyne, 1- heptyne and 1,7- octadyne qualitatively with the increasing acid strength.

TABLE 6

The reaction rate constants of 1- alkynes with ethyl magnesium bromide in diethyl ether at 25°C (k) and their relative pK values.

1- Alkyne	k(10 ³ M ⁻¹ sec ⁻¹)*	pK
1- Hexyne	0.6	24.0 ‡
1- Heptyne	1.0	22.5 §
1- Octyne	1.4	—
1,7- Octadyne	1.0	23.8 ‡

* From Table 8 of the previous paper [3].

‡ From Ref [19].

§ It's reported that the pK of 1- heptyne is higher, nearly 1,5 pK than phenyl acetylene's which is 21,0, in Ref [19].

Dessy [19] showed the linearity between pK values of phenyl acetylene, acetylene and 1- hexyne and their Taft σ^* constants. These results are given in Table 7.

TABLE 7

pK values and Taft σ^* constants of some 1- alkynes

1- alkyne	pK	σ^*
Phenylacetylene	21.0	+ 0.60
Acetylene	21.4	+ 0.49
1- Hexyne	24.0	— 0.13

The Taft σ^* constants for 1- hexyne and 1- heptyne are equal to — 0,13 [24]. So that 1- heptyne must have a pK of 24,0 or a value close to 24,0 which is 1- hexyne's pK value. But Gilman [11] found the order of phenylacetylene > 1- heptyne > acetylene for decreasing acidity which is reverse to the order given by Dessy. Furthermore in MSAD scale [21], the pK values of phenyl acetylene and acetylene are 18,5 and 25 respectively. Consequently, as no compatible and accurate pK values of 1- alkynes are present, no attempt for correlation of Zerewitinoff reaction rate constants of 1- alkynes to their acidities was made in our work.

THE PROPOSED METHOD FOR ESTIMATING THE RELATIVE pK
VALUES OF AMINES AND ALCOHOLS IN MC EWEN'S SCALE

For estimating the relative acidity of an amine, this is reacted with ethyl magnesium bromide in diethyl ether at 25 °C. The second order rate constant ($k \text{ M}^{-1} \text{ sec}^{-1}$) is calculated. But because of having two protons, a primary amine must be reacted with ethyl magnesium bromide in 1: 2 mol ratio. Then pK value of the amine relative to methyl alcohol, is calculated from the following equation:

$$\log k = - 0,09 \text{ pK} + 0,93$$

It was also shown that the relative acidity of amines (pK values) and the relative acidity of their conjugate acids (pK_a values) are the same. Taking the pK and pK_a value of an amine as reference (e. g. diphenyl amine, $\text{pK} = 23$ and $\text{pK}_a = 0,79$), the pK of another amine can be predicted by the following equation if its pK_a value is known:

$$\text{pK} - 23 = \text{pK}_a - 0,79$$

For estimating the relative acidity of an alcohol, this is reacted with ethyl magnesium bromide in diethyl ether at 25 °C. The second order rate constant ($k \text{ M}^{-1} \text{ sec}^{-1}$) is calculated under the following conditions: (1) The initial concentrations of reagents must be 15–30 mM. (2) At least five fold excess of HOMgBr (the solid product of the reaction of ethyl magnesium bromide with water) over the equivalent of reagents should be present in the reaction medium. Then pK value of the alcohol relative to methyl alcohol is calculated from the following equation:

$$\log k = - 0,07 \text{ pK} + 0,78$$

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ÖZET

Aminlerin ve alkollerin etil magnezyum bromürle dietil eterde 25°C de Zerewitinoff reaksiyonu hız sabitleri ile bağıl asitlikleri arasında lineer serbest enerji bağıntıları verilmiştir; k , $M^{-1}sn^{-1}$ cinsinden reaksiyon hız sabiti olmak üzere bu bağıntılar aminler için

$$\log k = -0,09 pK + 0,93 \quad (25^\circ C \text{ de})$$

ve alkoller için

$$\log k = -0,07 pK + 0,78 \quad (25^\circ C \text{ de})$$

dir. Bu iki bağıntı yardımıyla, aminlerin ve alkollerin bağıl pK değerleri, dietil eterde, 25°C de, etil magnezyum bromürle reaksiyon hız sabitleri ölçülerek bulunabilir.

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