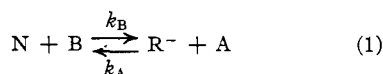


[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Calculation of Base Rate Constants from Acid Rate Constants

BY SAMUEL H. MARON¹ AND VICTOR K. LA MER

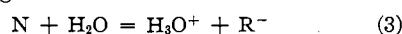
For the protolytic equilibrium



where N is acid substrate which ionizes to yield a proton to a base, B is base (proton acceptor), R⁻ is conjugate base of N, and A is conjugate acid of B, the equilibrium constant, K, is given by

$$K = \frac{k_B}{k_A} = \frac{[R^-][A]}{[N][B]} \quad (2)$$

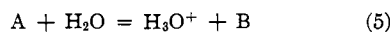
However, the ionization constant of N, K_N, corresponding to the reaction



is given by

$$K_N = \frac{[R^-][H_3O^+]}{[N]} \quad (4)$$

while the ionization constant of A, K_A, corresponding to the reaction



is given by

$$K_A = \frac{[B][H_3O^+]}{[A]} \quad (6)$$

Dividing now (4) by (6)

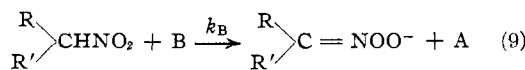
$$\frac{K_N}{K_A} = \frac{[R^-][H_3O^+]}{[N]} \frac{[A]}{[B][H_3O^+]} = \frac{[R^-][A]}{[N][B]} = K \quad (7)$$

by eq. (2). And hence

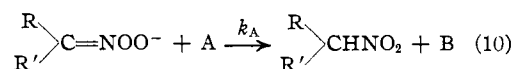
$$\frac{K_N}{K_A} = \frac{k_B}{k_A} \quad (8)$$

Knowing any three of the four constants K_N, K_A, k_B, k_A in (8), the fourth may be calculated. It is proposed to apply these equations to the prototropic isomerization of nitroparaffins to calculate k_B from available values of K_N, K_A, and k_A.

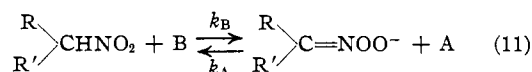
The primary and secondary nitroparaffins are acids which react with bases (defined in the general sense of Brönsted²) to yield an aci-nitroparaffin ion and a conjugate acid³ according to the general scheme



The mechanism of this reaction has been discussed before.⁴ Again, the reisoimerization of aci-nitroparaffin to the nitro form has been shown to be, under the proper conditions, a reaction between the aci-nitroparaffin ion and an acid⁵ (in the general sense) according to the scheme



If (9) and (10) be combined, we have the equilibrium condition:



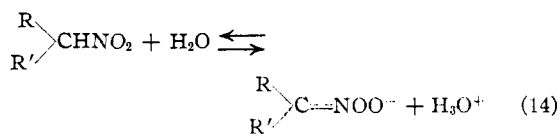
with equilibrium constant

$$K = \frac{\left[\begin{array}{c} R \\ \diagdown \\ \text{C} \\ \diagup \\ R' \end{array} = \text{NOO}^- \right] [A]}{\left[\begin{array}{c} R \\ \diagdown \\ \text{C} \\ \diagup \\ R' \end{array} \text{CHNO}_2 \right] [B]} = \frac{k_B}{k_A} \quad (12)$$

Equation (12) is exactly analogous to equation (2), and hence it follows from (8) that

$$K = \frac{k_B}{k_A} = \frac{K_N}{K_A} \quad (13)$$

where K_N is according to (3) and (4) the constant for the nitroparaffin dissociation



and

$$K_N = \frac{\left[\begin{array}{c} R \\ \diagdown \\ \text{C} \\ \diagup \\ R' \end{array} = \text{NOO}^- \right] [H_3O^+]}{\left[\begin{array}{c} R \\ \diagdown \\ \text{C} \\ \diagup \\ R' \end{array} \text{CHNO}_2 \right]} \quad (15)$$

while K_A is the ionization constant of the acid used and is defined by equations (5) and (6).

The ionization constants K_N of the nitro forms of nitromethane and nitroethane can be obtained from some measurements of Junell.⁶ Junell determined what he terms the "scheinbare Dissoziationskonstante" of these two substances by

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(2) Brönsted, *Chem. Rev.*, **5**, 231 (1928).

(3) Pedersen, *Det. Kgl. Videnskab. Selskab. Math.-fys. Medd.*, **12**, 1 (1932) (in English); Junell, *Z. physik. Chem.*, **141A**, 71-90 (1929); Dissertation, University of Uppsala, Sweden, 1935; *Arkiv Kemi*, **11B**, No. 27 (1934); *ibid.*, **11B**, No. 34 (1934); Reitz, *Z. physik. Chem.*, **176A**, 363-387 (1936).

(4) Maron and La Mer, *THIS JOURNAL*, **60**, 2588 (1938).

(5) Junell, (a) *Arkiv Kemi*, **11B**, No. 30 (1934); (b) *Svensk Kem. Tid.*, **46**, 125-136 (1934); (c) Dissertation, Uppsala, 1935; (d) Maron and La Mer, *THIS JOURNAL*, **61**, 692 (1939).

(6) Junell,³ Dissertation, pp. 114-124.

determining at high pH 's the total concentration of aci form and calculating the ratio

$$K'_N = [H_3O^+] [\text{aci form}] / [\text{nitro form}] \quad (16)$$

The highest H_3O^+ concentration used for the nitromethane measurements was 1.41×10^{-9} , while the highest concentration of H_3O^+ for nitroethane was 5.38×10^{-9} . Now, since the ionization constant of aci-nitromethane is given by Junell⁷ as 6×10^{-4} while that of nitroethane has been shown to be 4.1×10^{-5} ,⁸ it follows that the ratios of aci ion to aci acid at equilibrium must be

$$\frac{[R^-]}{[R\ H]} = \frac{6 \times 10^{-4}}{1.41 \times 10^{-9}} = 4.3 \times 10^5 \text{ for nitromethane}$$

and

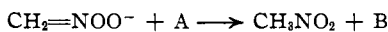
$$\frac{[R^-]}{[R\ H]} = \frac{4.1 \times 10^{-5}}{5.38 \times 10^{-9}} = 7.6 \times 10^3 \text{ for nitroethane}$$

From these ratios it is seen that compared to the concentrations of aci ion present the concentrations of aci acid are negligible, and hence (16) is essentially

$$K'_N = \frac{[H_3O^+][R^-]}{[N]} = K_N \quad (17)$$

the ionization constants of the nitro forms. For nitromethane Junell reports from five measurements $K_N = (2.6 \pm 0.2) \times 10^{-11}$, while for nitroethane he gives as a result of four measurements $K_N = (2.7 \pm 0.2) \times 10^{-9}$. These are the values of K_N employed in all calculations.

Table I gives the observed quantities and calculations for nitromethane at 0°. Columns (1), (2) and (3) give the acids used, their ionization constants, and the rate constants, respectively, for the reaction (10)



These data are due to Junell.⁷ Column (4) gives the equilibrium constant K calculated by Eq. (13), while column (5) gives the rate constant, k_B , calculated by (12) for the reaction: $CH_3NO_2 + B \rightarrow CH_2=NO_2^- + A$ where B is the conjugate base of the particular acid.

It is possible to compare several of the calculated values of k_B with observed results. Although no rate data are available for 0°, kinetic measurements are extant for the reaction with the bases H_2O , monochloroacetate, and acetate ions at several temperatures, so that extrapolation to 0° and comparison with the calculated constants are possible. The data available for this purpose are summarized in Table II. A

(7) Junell, Dissertation, ref. 3.

(8) Maron and Shedlovsky, THIS JOURNAL, 61, 753 (1939).

TABLE I
CALCULATIONS ON NITROMETHANE: Temp., 0.0°C. $K_N = 2.6 \times 10^{-11}$

Acid	K_A obsd.	k_A obsd.	K_N/K_A	k_B calcd.	k_B obsd.	K calcd.	k_B obsd./ k_A obsd.	K_N/k_B	Base	p	q	$\log (q/p \times K_A)$
H_2O^+	55.5	4500(?)	4.96×10^{-12}	2.24×10^{-9}	1.4×10^{-9} (extr.)	3.11×10^{-12}	83.6	8.65	H_2O	1	1	-8.65
$CH_2Cl-COOH$	3.32×10^{-2}	2800	7.83×10^{-10}	2.12×10^{-6}	1.74	$CH_2Cl-COO^-$	1	2	-5.98
CH_2Cl-CH_2COOH	1.53×10^{-3}	800	1.70×10^{-8}	1.36×10^{-6}	1.1×10^{-6} (extr.)	1.38×10^{-8}	1.88×10^{-3}	5.17	$CH_2Cl-CH_2COO^-$	1	2	-5.17
CH_2Cl-CH_2COOH	8.0×10^{-5}	290	3.25×10^{-7}	9.43×10^{-6}	4.33	$CH_2Cl-CH_2COO^-$	1	2	-4.33
CH_2COOH	1.70×10^{-6}	150	1.53×10^{-6}	2.30×10^{-4}	2.1×10^{-4} (extr.)	1.40×10^{-6}	1.86×10^{-6}	4.47	CH_2COO^-	1	2	-3.94
$COO^-(CH_2)_2COOH$	2.4×10^{-6}	80	1.07×10^{-5}	8.56×10^{-4}	3.67	$COO^-(CH_2)_2COO^-$	1	4	-3.67
$(CH_2)_2ASOOH$	5.7×10^{-7}	210	5.02	$(CH_2)_2ASOO^-$	1	2
$H_2PO_4^-$	4.1×10^{-8}	50	6.34×10^{-4}	3.17×10^{-2}	7.11	HPO_4^{2-}	2	3	-1.98
H_2O	2.1×10^{-17}	1.91×10^{-4} (calcd.)	1.24×10^5	16.7	OH^-	1	1	+2.38

TABLE III
CALCULATIONS ON NITROETHANE: Temp., 0.0°C. $K_N = 2.7 \times 10^{-9}$

Acid	K_A obsd.	k_A obsd.	K calcd.	k_B calcd.	Base	p	q	$\log (q/p \times K_A)$	$\log (k_B/q)$	$\log (k_A/p)$
H_2O^+	55.5	150	4.86×10^{-11}	7.3×10^{-9}	H_2O	1	1	1.74	-8.14	2.18
$CH_2ClCOOH$	1.53×10^{-3}	3.8	1.77×10^{-5}	6.7×10^{-4}	CH_2ClCOO^-	1	2	-2.51	-5.47	0.58
CH_2ClCH_2COOH	8.0×10^{-5}	1.62	3.38×10^{-5}	5.46×10^{-5}	$CH_2ClCH_2COO^-$	1	2	-3.80	-4.56	$.21$
CH_2COOH	1.7×10^{-6}	0.67	1.59×10^{-4}	1.06×10^{-4}	CH_2COO^-	1	2	-4.47	-4.28	$.174$
$COO^-(CH_2)_2COOH$	2.4×10^{-6}	.42	1.12×10^{-3}	4.71×10^{-4}	$(CH_2)_2(COO^-)_2$	1	4	-5.02	-3.55	$.377$
$(CH_2)_2ASOOH$	5.7×10^{-7}	.99	4.74×10^{-2}	4.69×10^{-2}	$(CH_2)_2ASOO^-$	1	2	-5.94	-2.63	$.004$
$H_2PO_4^-$	4.1×10^{-8}	.18	6.59×10^{-2}	1.18×10^{-2}	HPO_4^{2-}	2	3	-7.11	-2.41	-1.046
H_2O	2.1×10^{-17}	3.1×10^{-7} (calcd.)	1.28×10^{-8}	39.1 (obsd.)	OH^-	1	1	-16.7	1.59

TABLE II
RATE CONSTANTS FOR THE REACTION

Temp.	$\text{CH}_3\text{NO}_2 + \text{B} \xrightarrow{k_B} \text{CH}_2=\text{NOO}^- + \text{A}$	
	k_B	Reference
H_2O		
49.91	8.8×10^{-7}	Junell ³
59.93	2.5×10^{-6}	Junell ³
69.85	6.8×10^{-6}	Junell ⁵⁰
69.85	7.4×10^{-6}	Reitz ³
$\text{CH}_2\text{ClCOO}^-$		
11.2	5.1×10^{-5}	Reitz ³
20.0	1.50×10^{-4}	Pedersen ³
25.0	2.35×10^{-4}	Reitz ³
35.0	7.71×10^{-4}	Reitz ³
CH_3COO^-		
11.0	8.7×10^{-4}	Reitz ³
20.0	2.69×10^{-3}	Pedersen ³
22.0	3.22×10^{-3}	Pedersen ³
25.0	4.55×10^{-3}	Reitz ³
35.0	1.38×10^{-2}	Reitz ³

plot of $\log k_B$ vs. $1/T$ and extrapolation to 0° yields the constants given in column (6) of Table I. The agreement between calculated and observed results, columns (5) and (6), is good.

In case of the acid H_3O^+ the procedure was reversed and k_A calculated from the values of k_B at 0° measured by Maron and La Mer.⁴

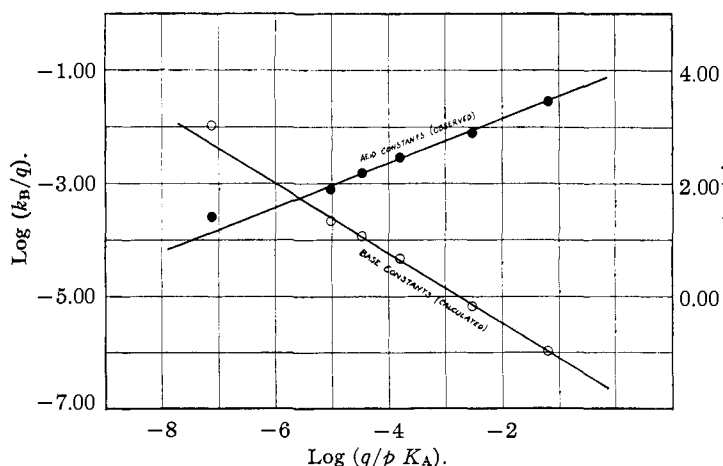
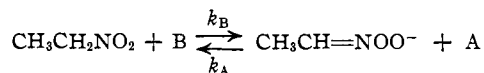


Fig. 1.—Plot of $\log k_B/q$ and $\log k_A/p$ vs. $\log (q/p K_A)$ for nitromethane at 0° .

It is possible to make the comparison between observed and calculated constants in two other ways, namely, by calculation of K and K_A from observed data. From equation (13), $K = k_B/k_A$. Using the observed values of k_A and k_B given in columns (3) and (6) of Table I, $K_{\text{obsd.}}$ have been calculated and are given in column (7). These values are to be compared with those given

in column (4), and calculated from $K_{\text{calcd.}} = K_N/K_A$. The agreement again is good. And, finally, also by equation (13), $K_A = K_N k_A/k_B$; values of K_A thus calculated are given in column (8), and again show as good agreement with the observed values of K_A in column (2) as can be expected.

Table III gives the results of similar calculations for nitroethane. These calculations are again based on Junell's values for k_A , and on his value of $K_N = 2.7 \times 10^{-9}$ for nitroethane. Columns (1), (2) and (3) have the same significance as before except that now the reaction involved is



while columns (4) and (5) give the calculated equilibrium constants of the reaction ($K_{\text{calcd.}}$) and the rate constants for the forward reaction (k_B). Unfortunately no extended data on the forward reaction are available to permit comparison of calculated and observed results in this case. The only value of k_B available at 0° is $k_{\text{OH}^-} = 39.1$ and due to Maron and La Mer,⁴ but no k_A observed is known to permit a calculation of k_B . Hence again the procedure was reversed and the known value of k_{OH^-} was used to calculate the value of $k_{\text{H}_2\text{O}}$ in column (3).

However, a test of the calculated values of k_B can be obtained in another way. Junell showed that for both nitromethane and nitroethane a plot of $\log k_A/p$ vs. $\log (qK_A/p)$ is essentially linear, as would be expected if the Brönsted relation $\log k_A/p = \log G_A + \alpha \log (q/p K_A)$ were obeyed. p and q are the statistical factors to correct the respective measured acid and base constants K_A and K_B to a uniform basis (see ref. 1). The values assigned p and q are given in Tables I and III. On theoretical grounds it may be anticipated that a plot of $\log k_B/q$ vs. $\log q/p K_A$ should also yield a straight line but with slope $= -\beta$ and y intercept $= \log G_B$. Further $\alpha + \beta$ should equal unity. The plot of both $\log k_A/p$ and $\log k_B/q$ vs. $\log q/p K_A$ for nitromethane at 0° is shown in Fig. 1. The expected linearity for $\log k_B/q$ vs. $\log q/p K_A$ is verified. Whenever a point is off the curve, the discrepancy is traceable to the corresponding value of k_A , which is also off

the curve. Further, from this plot we obtain nitromethane $G_B/G_A = 1.98 \times 10^{-7}/0.82 \times G_A = 8200$, $G_B = 1.98 \times 10^{-7}$, $\alpha = 0.39$ and $10^4 = 2.4 \times 10^{-11}$, as against the observed value $\beta = 0.62$, and hence $\alpha + \beta = 0.39 + 0.62 = 1.01$ as against the expected sum of unity.

A similar plot for nitroethane is shown in Fig. 2. Again the linear relation is obtained between $\log k_B/q$ and $\log q/pK_A$. In this case $G_A = 32$, $G_B = 1.05 \times 10^{-7}$, $\alpha = 0.36$, $\beta = 0.65$ and $\alpha + \beta = 0.36 + 0.65 = 1.01$.

From the deductions of this paper may be derived another very interesting and quite general relationship. For reactions of the type discussed here, and which lead to an equilibrium, we have in general

$$k_A/p = G_A(q/pK_A)^\alpha \text{ and } k_B/q = G_B(p/qK_B)^\beta$$

where $K_B = 1/K_A$, *i. e.*, the ionization constant for the base conjugate to A. With these equations we obtain finally for $\log k_B/k_A$

$$\log k_B/k_A = [1 - (\alpha + \beta)] \log q/p + \log \frac{G_B}{G_A} - (\alpha + \beta) \log K_A \quad (18)$$

But $k_B/k_A = K$ and $(\alpha + \beta) = 1$. Hence

$$\log \frac{k_B}{k_A} = \log K = \log \frac{G_B}{G_A} - \log K_A \quad (19)$$

However, according to (8) $\log K + \log K_A = \log K_N$. Therefore

$$\log K_N = \log G_B/G_A$$

and

$$K_N = G_B/G_A \quad (20)$$

According to (20) the ratio G_B/G_A should be the ionization constant of the substrate involved in the basic reaction. This relation can be tested easily by utilizing the values of G_B and G_A found at 0° for nitromethane and nitroethane. For

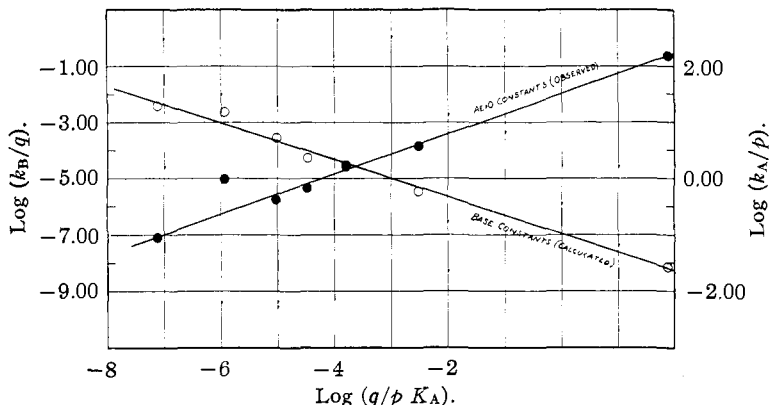


Fig. 2.—Plot of $\log k_B/q$ and $\log k_A/p$ vs. $\log (q/pK_A)$ for nitroethane at 0° .

of $K_N = 2.6 \times 10^{-11}$. Similarly, for nitroethane $G_B/G_A = 1.05 \times 10^{-7}/32 = 3.3 \times 10^{-9}$ as against the experimental value $K_N = 2.7 \times 10^{-9}$. Considering the uncertainties in drawing the straight lines in Figs. 1 and 2 the agreement is satisfactory.

Summary

1. Equations are deduced for calculating rate constants from certain kinetic and thermodynamic data.

2. These equations are applied to calculate the base rate constants for the isomerization of nitromethane and nitroethane to the aci forms.

3. Wherever comparison between calculated and observed values is possible, the agreement is good.

4. The calculated constants obey the Brönsted relation ($\log k_B/q = G_B(p/qK_B)^\beta$).

5. An equation is derived relating acid strength of the substrate to the constants G_A and G_B in the Brönsted equations. The equation is shown to be valid for the cases discussed.

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