endo derivative decreased by more than 120 kcal. The latter result was to be expected from simple steric consideration. An analysis of the bond indices reveals at this point that the observed differences are produced both by a *steric inhibition for the endo derivative* and *a σ participation for the exo derivative* (Figure 1). However, even the *exo* derivative appears to be less stable than his analog with a 2–6 CC distance of 2.4 Å indicating that the closing of the cyclopropane ring (σ assistance) occurs later in the process. These results are tentatively interpreted as in the Figure 1 where the *exo* derivative appears to react faster and its transition state involves more σ participation than the *endo* position whose reactivity is inhibited by steric hindrance. Similarly, the formation of a new bond, C–Y, to form the product is more favorable in the *exo* position. In a very nucleophilic medium the quenching of the carbonium occurs very fast and before any extensive rearrangement of the ^{14}C occurs whereas in a less nucleophilic medium the longer life of the protonated nortricyclene permits the tautomeric rearrangement of the protons. In this case, a complete scrambling of the hydrogen and the carbon atoms may occur.

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The Oxibase Scale and Displacement Reactions. XVII. The Reaction of Nucleophiles with Ethyl Tosylate and the Extension of the Oxibase Scale[1]

R. E. Davis, R. Nehring,[2a] W. J. Blume,[2b] and C. R. Chuang[2c]

Contribution from the Department of Chemistry, Purdue University, Lafayette, Indiana 47906. *Received January 23, 1968*

Abstract: The rate constants of ten nucleophiles reacting with ethyl tosylate have been measured in aqueous solution. From these rate constants the oxibase scale parameters for ethyl tosylate have been obtained; α = 1.48 and β = 0.03 at 25° in water. The nucleophilic constants of several nucleophiles have been obtained for the temperature range of 0–100° in water. The uses of the oxibase scale are extended to include the energetics of isotopic exchange reactions as well as the relationship between the oxidation potential and the basicity.

The tosylate group, $^{-}OSO_2C_6H_4CH_3$-*p*, is an often used leaving group to study structure–reactivity effects in physical-organic chemistry. In the present study ethyl tosylate has served as the substrate for ten nucleophiles in aqueous solution (see section I below).

The data of McCleary and Hammett[3] on the S$_N$2 reaction of water, hydroxide, and halide ions with ethyl *p*-toluenesulfonate (or ethyl tosylate) were determined in 60% aqueous dioxane (by volume) at 50°. Edwards[4] computed α to be 1.68 and β to be 0.014. However, the plot[5] of E^{-1} log (k/k_0) *vs.* H/E has a large amount of scatter. The scatter is due to several factors; an important factor is the requirement of accurate pK_a values of the halide ions. A second problem is that kinetic data in dioxane–water at 50° should not necessarily correlate well the thermodynamic values in water[7] at 25° or with empirical kinetic constants[8] obtained in water at 25°.

In parts II and III, the oxibase scale is extended as the result of theoretical work to cover the temperature range of 0–100° in water. Further theoretical work on the oxibase scale relates the parameters to more fundamental properties of the reacting species.

Results

I. The Present Investigation. The use of the oxibase scale on ethyl tosylate in pure water at 25° has been made so that the substrate can be used as a convenient substrate for determining the kinetic *E* values of the mercaptoethylamine and other nucleophiles (see the following paper).

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(1) Paper XVI: R. E. Davis in "Inorganic Sulphur Chemistry," G. Nickless, Ed., Elsevier Publishing Co., The Netherlands, in press.

(2) (a) Postdoctoral Fellow, 1962–1963. (b) Undergraduate Research Thesis Student, 1963–1964. (c) Taken in part from the Ph.D. Thesis, August 1967.

(3) H. R. McCleary and L. P. Hammett, *J. Amer. Chem. Soc.*, **63**, 2254 (1941).

(4) J. O. Edwards, *ibid.*, **76**, 1540 (1954).

(5) The equation now called the oxibase scale[6] is

$$\log (k/k_0) = \alpha E + \beta H \qquad \text{(i)}$$

with

$$X^- + AY \xrightarrow{k} AX + Y^-$$

$$H_2O + AY \xrightarrow{k_0} AOH + Y^- + H^+$$

$$E \equiv \epsilon^0 + 2.60 \text{ V}$$

$$2X^- \rightleftharpoons X_2 + 2e^- \quad \epsilon^0$$

$$X^- + H^+ \rightleftharpoons HX \quad pK_a$$

$$H \equiv pK_a + 1.74$$

A plot can be prepared from (i) by dividing by *E*.

$$E^{-1} \log (k/k_0) = \alpha + \beta(H/E) \qquad \text{(ii)}$$

(6) R. E. Davis in "Survey of Progress in Chemistry," A. Scott, Ed., Academic Press, New York, N. Y., 1964, pp 189–238.

(7) The same problem of using nucleophilic data obtained in one solvent at one temperature with data in other solvents at different temperatures is wide spread. Lack of data forces such correlations to be tried, nevertheless.

(8) C. G. Swain and C. B. Scott, *J. Amer. Chem. Soc.*, **75**, 141 (1953).

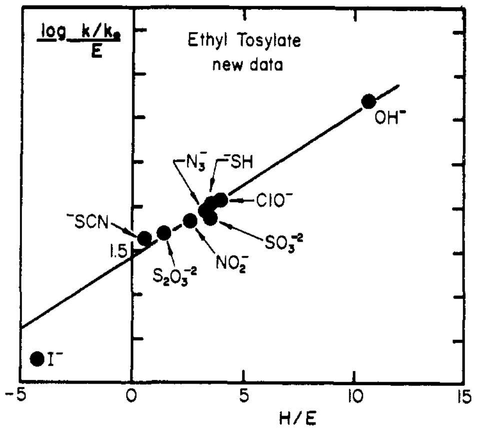

Figure 1. Oxibase scale plot of the data on ethyl tosylate at 25°. Divisions on the E^{-1} log (k/k_0) axis are 0.10 unit each. The points for NO_2^-, N_3^-, and ClO^- have been placed on the line and the E value computed. Note that the value of $k_0(k_{H_2O})$ is included in each ratio of k/k_0. Therefore, all ten data points are used.

Using the general rules,[6] an *a priori* estimate of the two substrate constants (α and β) can be made. The methylene carbon is only slightly positive due to the electronegativity of the adjacent oxygen. Therefore, β will be small and positive. The E of the tosylate group is low.[9] An estimate from the data of Hammett[3] on the rates of displacement of tosylate ion on the ethyl halides formed allows an estimate of E as about 0.6 ± 0.2 V. This E value is quite uncertain but at least it allows a prediction concerning the α of ethyl tosylate. Using the solubility product of silver sulfate and of silver tosylate in water at 25°, a value of $E = 0.50 \pm 0.05$ V can be estimated for the tosylate anion.[9a] The leganion order[9] would predict an α of 1.5 (see eq 18). Experimentally the value has been determined to be 1.48 in pure water at 25°. The experimental data are presented in Table I.

The oxibase scale plot of $E^{-1} \log (k/k_0) = \alpha + \beta(H/E)$ is presented in Figure 1. The correlation is satisfactory. The values of E reported for the nucleophiles in Table II for nitrite, hydrosulfide, azide, and hypochlorite must be considered to be accurate for ethyl tosylate as a substrate but subject to verification using other substrates. Using the E and H values[6] of hydroxide, thiosulfate, sulfite, iodide, thiocyanate, and water the α of ethyl tosylate is 1.48 and the β is +0.03.

II. The *E* and *H* Values at Other Temperatures.[10] The E value was defined[5] as the oxidative dimerization relative to that of water. Initially,[4] the potential values were those listed by Latimer at 25°. The standard oxidation potential at a temperature, $\epsilon^0(t)$, can be related to the ϵ^0 at 25° using

$$\epsilon^0(t) = \epsilon^0 + \left(\frac{\partial \epsilon^0}{\partial T}\right)(t - 25) + \frac{1}{2}\left(\frac{\partial^2 \epsilon^0}{\partial T^2}\right)(t - 25)^2 \quad (1)$$

which is a Taylor expansion equation. Accurate thermodynamic data are available on seven nucleophiles; these data are listed in Table III. From these data the $\epsilon^0(t)$ values have been computed. The E value is defined as $\epsilon^0 + 2.60$ V at 25°; the value of 2.60 V is the negative of the value arbitrarily assigned[5] for the process

$$2H_2O \rightleftharpoons H_4O_2^{2+} + 2e^- \quad (2)$$

Table I. Reaction of Nucleophiles with Ethyl Tosylate in Aqueous Solution at 25.00 ± 0.01°

Nucleophile	M[a]	pH[b]	k_1, sec^{-1} [c]	k_2, M^{-1} sec^{-1} [d]
H_2O	55.5	4.0	6.38×10^{-6}	1.15×10^{-7}
	55.5	5.2	6.40×10^{-6}	1.16×10^{-7}
	55.5	7.0	6.39×10^{-6}	1.15×10^{-7}
	55.5	6.8[e]	6.48×10^{-6}	
	55.5	7.0[f]	6.44×10^{-6}	
	55.5	7.0[g]	6.39×10^{-6}	
	55.5	7.0[h]	6.28×10^{-6}	
NaOH	0.0600		1.16×10^{-5}	1.23×10^{-4}
	0.0918		1.78×10^{-5}	1.25×10^{-4}
	0.168		2.83×10^{-5}	1.24×10^{-4}
	0.180		2.89×10^{-5}	1.22×10^{-4}
	0.221		3.43×10^{-5}	1.20×10^{-4}
$Na_2S_2O_3$	0.598	8.54	3.37×10^{-5}	8.60×10^{-4} [i]
	0.0854	8.56	4.31×10^{-5}	
	0.169	8.56	7.45×10^{-5}	
	0.199	8.57	8.60×10^{-5}	
Na_2SO_3	0.0729	6.75	3.09×10^{-5}	
	0.0844	9.14	5.41×10^{-5}	
	0.107	6.75	4.88×10^{-5}	1.13×10^{-3} [j]
	0.123	9.14	7.45×10^{-5}	1.11×10^{-3} [j]
NaN_3	0.0993	8.74	1.39×10^{-5}	1.15×10^{-4} [k]
	0.149	8.74	1.76×10^{-5}	1.50×10^{-4}
	0.192	8.90	2.06×10^{-5}	1.48×10^{-4}
NaClO	0.0250	10.7	2.89×10^{-5}	0.90×10^{-3} [k]
	0.0250	10.7	3.26×10^{-5}	1.04×10^{-3}
	0.0125	10.0	1.84×10^{-5}	0.96×10^{-3}
	0.0475	11.2	4.95×10^{-5}	0.90×10^{-3}
NaSH[l]	0.0400	11.4	3.40×10^{-5}	1.60×10^{-3} [k]
	0.0641	10.74	5.87×10^{-5}	1.63×10^{-3}
	0.0985	10.55	9.00×10^{-5}	1.70×10^{-3}
	0.0984	11.4	9.02×10^{-5}	1.70×10^{-3}
KI	0.0676	8.56	8.06×10^{-6}	6.54×10^{-5} [k]
	0.100	8.55	1.29×10^{-5}	6.50×10^{-5}
	0.153	8.60	1.63×10^{-5}	6.50×10^{-5}
	0.187	8.55	1.84×10^{-5}	6.48×10^{-5}
KSCN	0.0992	6.75	9.77×10^{-6}	6.84×10^{-5} [k]
	0.0998	8.50	9.78×10^{-6}	6.82×10^{-5}
	0.1521	8.50	1.64×10^{-6}	6.50×10^{-5}
$NaNO_2$	0.155	6.75	1.84×10^{-5}	1.55×10^{-4} [k]
	0.155	8.37	1.83×10^{-5}	1.55×10^{-4}
	0.157	9.80	1.80×10^{-5}	1.50×10^{-4}

[a] Molarity. [b] pH ± 0.01 using dilute buffer solutions of phosphates. Ionic strength, 0.1. [c] Observed first-order rate constant: $-d[EtOTs]/dt = k_1[EtOTs]$. [d] Second-order rate constant computed from k_1 after correction for the water reactions; rate $= k_2[EtOTs][N] + k_0[EtOTs][H_2O] + k[EtOTs][OH^-]$. The value of k_2 is about that at infinite dilution except for the data on hydroxide ion. [e] Pure water, no buffer present. Initial pH. [f] Sodium perchlorate added to very dilute pH 7.0 phosphate buffer. Ionic strength $\mu = 0.03$. [g] See *f*, $\mu = 0.07$. [h] $\mu = 0.14$, see *f*. [i] Slope of the line using the four points. [j] Five second-order rate constants computed at each pH. [k] Second-order rate constant computed at each concentration of the nucleophile. [l] Added as $Na_2S \cdot 9H_2O$.

Table II. E_x Values Computed from k_x, α, and β of Ethyl Tosylate

Nucleophile	E	H
NO_2^-	1.97	5.09
SH^-	2.60	8.70
N_3^-	1.95	6.46
ClO^-	2.43	9.04

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(9) (a) R. E. Davis, *J. Amer. Chem. Soc.*, **87**, 3010 (1965); paper VI. (b) Some misunderstanding has arisen using the E value of the legate (leaving group) anion to predict the α value of the substrate. Methyl iodide is quite sensitive to the oxibase scale values of the attacking nucleophile; the α is almost 3.0. Since iodide ion, the legate anion, is so easily oxidized, this means that the substrate methyl iodide is, therefore, very sensitive to the E value of the nucleophile.

(10) Parts II and III of this paper are discussed in greater detail in ref 2c.

Table III. Standard Oxidation Potentials of Various Nucleophiles

X	Reaction	ϵ^0 (25°), V[a]	$d\epsilon^0/dT$, mV/deg[a]	$d\epsilon^0/dT^2$, (μV/deg)^2 [a]	ϵ^0 (0°),[b] V	ϵ^0 (50°), V	ϵ^0 (75°), V	ϵ^0 (100°), V
H_2	$H_2 \rightleftharpoons 2H^+ + 2e^-$	0	0	0	0	0	0	0[c]
S^{2-}	$2S^{2-} \rightleftharpoons S_2^{2-} + 2e^-$	0.480	0.93		0.457	0.503	0.526	0.550
$S_2O_3^{2-}$	$2S_2O_3^{2-} \rightleftharpoons S_4O_6^{2-} + 2e^-$	−0.080	1.11		−0.108	−0.052	−0.024	0.003
I^-	$2I^- \rightleftharpoons I_2 + 2e^-$	−0.5355	0.148	5.965	−0.537	−0.530	−0.521	−0.508
Br^-	$2Br^- \rightleftharpoons Br_2 + 2e^-$	−1.087	0.478		−1.099	−1.075	−1.063	−1.051
Cl^-	$2Cl^- \rightleftharpoons Cl_2 + 2e^-$	−1.3595	1.260	5.454	−1.389	−1.326	−1.290	−1.250
SO_4^{2-}	$2SO_4^{2-} \rightleftharpoons S_2O_8^{2-} + 2e^-$	−2.01	1.26		−2.04	−1.98	−1.94	−1.92
F^-	$2F^- \rightleftharpoons F_2 + 2e^-$	−2.87	1.83	5.34	−2.91	−2.82	−2.77	−2.72

[a] A. J. de Bethune and N. A. S. Loud, "Standard Aqueous Electrode Potentials and Temperature Coefficients at 25°C," C. A. Hampel, Publishing Co., Skokie, Ill., 1964. [b] All values computed using eq 1. [c] Standard.

The ϵ^0 of (2) would also vary with temperature; however, since no data are available it is convenient to eliminate the value of 2.60 from the oxibase scale. Thus at 25°

$$\log (k_1/k_0) = \alpha E_1 + \beta H_1 = \alpha(\epsilon_1 + 2.60) + \beta H_1 \quad (3)$$

and

$$\log (k_2/k_0) = \alpha(\epsilon_2 + 2.60) + \beta H_2 \quad (4)$$

then

$$\log (k_1/k_2) = \alpha(\epsilon_1 - \epsilon_2) + \beta(H_1 - H_2) \quad (5)$$

In eq 5 another nucleophile (with a rate constant k_2 on the substrate) would serve as the standard. Then eq 5 can serve as a more general oxibase scale from 0 to 100° using the ϵ and H values at the proper temperature (See Table IV). In eq 5 it will be assumed that α and β are independent of temperature until accurate kinetic data are available to test this hypothesis.

Table IV. H Values of Selected Nucleophiles as a Function of Temperature[a]

Nucleophile	0°	25°	50°	75°	100°
CN^-	11.66	10.97	10.4	9.92	9.52
S^{2-}	15.41	14.04	13.86	13.1	12.3
SO_4^{2-}	3.43	3.74	4.06	4.41	4.8
F^-	4.76	4.90	5.13	5.39	5.68

[a] Data have been obtained from J. Bjerrum, G. Schwarzenbach, and L. G. Sillen, "Stability Constants," Part II, The Chemical Society, London, 1958.

The K_a values of the nucleophile would vary as

$$\ln K_a = \frac{-\Delta H^\circ}{RT} + \frac{\Delta C_p}{R} \ln T + \frac{\Delta S^\circ - \Delta C_p}{R} \quad (6)$$

In Table V, the pK_a values are listed. Since H is defined as pK_a + log [H_2O], the log [H_2O] term will vary as the density of water varied from 0 to 100°. The variation of the density is about 4%, thus log [H_2O] varies from 1.744 to 1.728 and 0 to 100°. To a good approximation log [H_2O] is constant and a value of 1.74 will be used.

III. The Relationship of the Oxibase Scale to the Properties of the Nucleophiles. For an acid, HL, the following cycle may be written[11]

$$\begin{tikzcd}
H^+(aq) + L^-(aq) \arrow[rr, "\Delta G_5"] \arrow[d, "\Delta G_1"] & & HL(aq) \\
H^+(g) + L^-(g) \arrow[dr, "\Delta G_2"'] & & HL(g) \arrow[u, "\Delta G_4"'] \\
& H(g) + L(g) \arrow[ur, "\Delta G_3"'] &
\end{tikzcd}$$

Likewise

$$\begin{tikzcd}
H^+(aq) + L^-(aq) \arrow[rr, "\Delta G_{10}"] \arrow[d, "\Delta G_1 = \Delta G_6"'] & & 0.5H_2(aq) + 0.5L_2(aq) \\
H^+(g) + L^-(g) \arrow[dr, "\Delta G_2 = \Delta G_7"'] & & 0.5H_2(g) + 0.5L_2(g) \arrow[u, "\Delta G_9"'] \\
& H(g) + L(g) \arrow[ur, "\Delta G_8"'] &
\end{tikzcd}$$

Thus

$$\Delta G_5 - \Delta G_{10} = \Delta G_3 - \Delta G_8 + \Delta G_4 - \Delta G_9 \quad (7)$$

$$\Delta G_5 - \Delta G_{10} = \Delta H_3 - \Delta H_8 + T(\Delta S_3 - \Delta S_8) + \Delta G_4 - \Delta G_9 \quad (8)$$

or

$$1.364\text{p}K_a - 23.06\epsilon^0 = D_{HL} - 0.5[D_{H_2} + D_{L_2}] + T(\Delta S_3 - \Delta S_8) - \Delta G_4 + \Delta G_9 \quad (9)$$

since $\Delta G_{10} = -n\mathfrak{F}\epsilon^0 = -23.06\epsilon^0$, $\Delta H_3 = -D_{HL}$, $\Delta H_8 = -0.5[D_{H_2} + D_{L_2}]$ at 25°.

The terms on the left of the equation are the pK_a value (a base term) and the oxidation term. They are related to the bond dissociation enthalpies, the entropies (ΔS_3 and ΔS_8) and the solvation terms (ΔG_4 and ΔG_9) of the neutral species. If one restricts one self to L = F, Cl, Br, I, OH, SH, SeH, and TeH, enough data are available so that D_{HL} and D_{L_2} are known. Likewise enough structural data are known so that the entropies (ΔS_3 and ΔS_8) can be computed in the gas phase using the standard methods of statistical mechanics.

For example, $\Delta S_3 - \Delta S_8$ for a monoatomic L case is given by

$$\Delta S_3 - \Delta S_8 = 1.5R \ln m_{HL} - 0.75R \ln m_{H_2} - 0.75R \ln m_{L_2} + R \ln (I_{HL}/1) - 0.5R \ln (I_{H_2}/2) - 0.5R \ln (I_{L_2}/2) \quad (10)$$

when R is the gas constant, m is the mass, and I is the moment of inertia.

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[11] Part III of this paper is a further development of the work of McDaniel. See D. H. McDaniel and A. Yingst, *J. Amer. Chem. Soc.*, **86**, 1334 (1964). In that paper the entropy terms ($\Delta S_3 - \Delta S_8$) and the solvation terms ($\Delta G_4 - \Delta G_9$) were neglected. In part III of this present study, these terms are computed.

Table V. Thermodynamic Functions of Some Selected Nucleophiles and Their pK_a Values at Different Temperatures (0–100°) for the Reaction Scheme $HX^{-n+1} \rightleftharpoons H^+ + X^{-n}$

Nucleophile, X^{-n}	$\Delta H°$, kcal/mol	ΔC_p, cal/(mol deg)	$\Delta S_0°$, cal/(mol deg)	a[a]	b[b]	c[c]	pK_a 0°	25°	50°	75°	100°
CN^-	12.81	−8.91	42.60	2.7995 × 10³	4.4841	−11.2562	9.92	9.23	8.66	8.18	7.78
S^{2-}	−12.63	84.68	−499.25	−2.7595 × 10³	−42.619	127.608	13.68	12.90	12.12	11.36	10.60
SO_4^{2-}	12.34	−58.46	306.92	2.6962 × 10³	29.420	−79.848	1.69	2.00	2.32	2.67	3.04
F^-	15.55	−62.44	331.03	3.3988 × 10³	31.424	−85.986	3.02	3.16	3.39	3.65	3.94
Cl^-	−20.74	10.07	−84.86	−4.5324 × 10³	−5.066	20.744	−8.2	−7.0	−6.0	−5.16	−4.44

[a] $\Delta H°_0/2.303R$. [b] $-\Delta C_p/R$. [c] $(-\Delta S°_0 - \Delta C_p)/2.303R$.

Table VI. Parameters for the Diatomic Molecule, HL, and the Value of $\Delta S_3 - \Delta S_8$[a]

Molecule H-L	$M_L \times 10^{24}$ g	$M_{H-L} \times 10^{24}$ g	$r_H \times 10^8$ cm	$r_L \times 10^8$ cm	$d_{H-L} \times 10^8$ cm $r_H + r_L$	Obsd	Reaction	$\Delta S_3 - \Delta S_8$,[b] cal/(mol deg)
H-H	1.674	3.348	0.37	0.37	0.74[c]	0.74		
H-F	31.54	33.22	0.28	0.709	0.989	0.918	$0.5H_2(g) + 0.5F_2(g) \rightleftharpoons HF(g)$	1.763
H-Cl	58.87	60.54	0.28	0.991	1.274	1.27	$0.5H_2(g) + 0.5Cl_2(g) \rightleftharpoons HCl(g)$	2.668
H-Br	132.68	134.36	0.28	0.140	1.420	1.42	$0.5H_2(g) + 0.5Br_2(g) \rightleftharpoons HBr(g)$	3.228
H-I	210.71	212.39	0.28	1.333	1.613	1.61	$0.5H_2(g) + 0.5I_2(g) \rightleftharpoons HI(g)$	3.642

[a] Bond distances taken from L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 225. [b] At 298°K and 1 atm. [c] All values in this column are calculated.

Table VII. Parameters on Diatomic Nucleophiles and the Value of $\Delta S_3 - \Delta S_8$

H_2X	<HXH, θ, deg	d_{H-X}, Å	Moments of inertia × 10⁴⁰ g cm² I_A	I_B	I_C	H_2X_2	<HXX, θ, deg	Dihedral, ω, deg	d_{HX}, Å	d_{XX}, Å	Moments of inertia × 10⁴⁰ g cm² I_A	I_B	I_C
H_2O[a]	104.45	0.958	1.023	1.921	2.944	H_2O_2[e]	100	90	0.97	1.48	2.826	33.38	33.43
H_2S[b]	92.2	1.334	2.692	3.097	5.788	H_2S_2[f]	105	102	1.33	2.05	5.276	120.44	121.48
H_2Se[c]	91.0	1.460	3.419	3.631	7.049	H_2Se_2[g]	106	101	1.47	2.19	6.555	324.70	325.91
H_2Te[d]	89.5	1.67	4.636	4.628	9.264	H_2Te_2[g]	102	100	1.67	2.59	8.837	723.37	724.89

[a] S. Weisbaum, Y. Beers, and G. Herrmann, *J. Chem. Phys.*, **23**, 1601 (1955). [b] H. C. Allen, Jr., and E. K. Plyer, *ibid.*, **25**, 1132 (1956). [c] A. W. Jache, P. W. Moser, and W. Gordy, *ibid.*, **25**, 209 (1956). [d] K. Rossman and J. W. Straley, *ibid.*, **24**, 1276 (1956). [e] P. A. Giguere and V. Schomaker, *J. Amer. Chem. Soc.*, **65**, 2025 (1943), and W. R. Busing and H. A. Levy, Proceedings of the American Crystallography Association Meeting, Milwaukee, Wis., June, 1958. [f] P. Stevenson and J. Y. Beach, *J. Amer. Chem. Soc.*, **60**, 2872 (1938). [g] L. R. Maxwell and V. M. Mosley, *Phys. Rev.*, **57**, 21 (1940).

For L = OH, SH, SeH, or TeH, the entropy difference becomes

$$\Delta S_3 - \Delta S_8 = 0.25R[\ln \frac{8\pi^3 kT}{h^2} + 1] + 0.25R \ln \frac{(I_A I_B I_C)^2{}_{HL}}{(I_A I_B I_C)_{L_2}(I)_{H_2}{}^2} \quad (11)$$

The parameters are listed in Table VI. The values of $\Delta S_3 - \Delta S_8$ are also listed. In Tables VII and VIII the data are presented on diatomic nucleophiles.

Table VIII

Reaction scheme $0.5H_2(g) + 0.5L_2'(g) \xrightarrow{\Delta S_3 - \Delta S_8} HL'(g)$	$\Delta S_3 - \Delta S_8$, cal/(mol deg)
$0.5H_2(g) + 0.5HO\text{-}OH(g) \longrightarrow H_2O(g)$	3.937
$0.5H_2(g) + 0.5HS\text{-}SH(g) \longrightarrow H_2S(g)$	8.797
$0.5H_2(g) + 0.5HSe\text{-}SeH(g) \longrightarrow H_2Se(g)$	6.130
$0.5H_2(g) + 0.5HTe\text{-}TeH(g) \longrightarrow H_2Te(g)$	6.695

In Table IX the necessary basicities, potentials, bond energies, and enthalpy changes are reported. Unfortunately the $\Delta G_4 - \Delta G_9$ terms are either hard to obtain with any accuracy or else they are unknown. To a good approximation, the solvation free energies of the neutral molecules H_2, L_2, and HL ought be such that $\Delta G_4 - \Delta G_9$ would be close to zero. As a test of this approximation, a plot has been prepared of 1.364pK_a − 23.06ϵ *vs.* $D_{HL} - 0.5(D_{H_2} + D_{L_2}) + T(\Delta S_3 - \Delta S_8)$ at 25° (see Figure 2). The line is quite straight with a least squares slope of 1.04, which could be compared to a slope of 1.00 expected if $\Delta G_4 - \Delta G_9$ is always zero.

However, the data can be used to obtain the $\Delta G_4 - \Delta G_9$ terms. These are listed Table X. The large negative value of HF (−5.55) would reflect the hydrogen bonding of neutral water to the neutral HF molecule as it creates structure within the water. On first principles one would expect that the value of $\Delta G_4 - \Delta G_9$ for H_2O would be exactly equal to zero (rather than −0.1 kcal/mol) since H_2O and H_2O_2 are supposed to be hydrogen bonded in water to the same extent.[12] The larger values for HI and HTeH probably reflect the decreased electronegativity of I and Te coupled with the increase in hydrophobic character of these large atoms.

Application of These Relationships to Prediction of Free Energies of Displacement Reactions. As seen

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(12) L. Pauling, "The Nature of the Chemical Bond," 3rd, ed, Cornell University Press, Ithaca, N. Y., 1960, p 225.

Table IX. Values of Basicities, Oxidative Coupling Potentials, Bonding Energies, and Entropy Changes for the Molecule HL

HL	pK_a[a]	ϵ^0, V[b]	I,[c,d] kcal/mol	II,[d,e] kcal/mol	$1.364pK_a - 23.06\epsilon$, kcal/mol	I + II
HF	3.16	−2.87	64.20	0.526	70.275	64.726
HCl	−7.0	−1.3595	22.10	0.796	21.798	22.896
HBr	−9	−1.087	12.35	0.963	12.785	13.313
HI	−9.5	−0.5355	1.25	1.086	−0.614	2.336
HOH	15.7	−0.94	41.9	1.17	43.2	43.1
HSH	6.92	0.32	3.55	2.62	2.0	6.2
HSeH	3.73	0.61	−8.0	1.82	−7.9	−6.2
HTeH	2.64	0.89	−11.0	1.99	−17.3	−9.0

[a] $HL(aq) \rightarrow H^+(aq) + L^-(aq)$. [b] $L^-(aq) \rightarrow 0.5L_2(aq) + e^-$. [c] $I = D_{H-L} - 0.5(D_{H-H} + D_{L-L})$. [d] M L. Huggins, *J. Amer. Chem. Soc.*, 75, 4123 (1953). [e] $II = T(\Delta S_3 - \Delta S_8)$.

Table X. Calculation of Solvation Free Energy Differences

HL	$\Delta G_4 - \Delta G_9$, kcal/mol	HL	$\Delta G_4 - \Delta G_9$, kcal/mol
HF	−5.5	HOH	−0.10
HCl	1.1	HSH	4.2
HBr	0.53	HSeH	1.7
HI	2.95	HTeH	8.2

from eq 9, the oxibase scale values are related to fundamental properties of the nucleophile, L^-, its acid (HL) and its dimer, L_2. Hence one can ask if the oxibase scale can predict the free energies of displacement reactions as well.

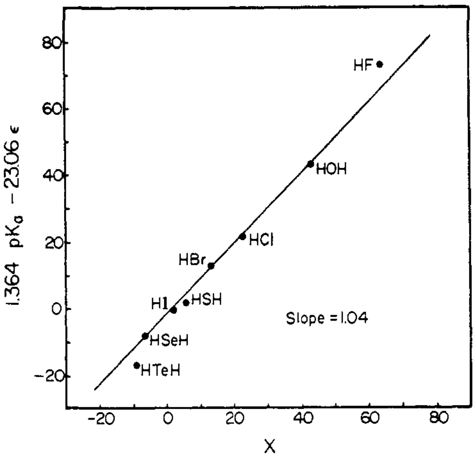

Figure 2. A test of an approximation of the exact eq 9 by assuming $\Delta G_9 - \Delta G_4$ is zero. Equation 9 as exact predicts a slope of 1.00, $X = D_{HL} - 0.5(D_{H_2} + D_{L_2}) + T(\Delta S_3 - \Delta S_8)$.

Consider the general system

$$X^- + AY \underset{k_2}{\overset{k_1}{\rightleftharpoons}} AX + Y^- \tag{12}$$

$$H_2O + AY \xrightarrow{k_{10}} AOH + Y^- + H^+ \tag{13}$$

$$H_2O + AX \xrightarrow{k_{20}} AOH + X^- + H^+ \tag{14}$$

then

$$\log (k_1/k_{10}) = \alpha_1 E_x + \beta_1 H_x \tag{15}$$

and

$$\log (k_2/k_{20}) = \alpha_1 E_y + \beta_2 H_y \tag{16}$$

or

$$\log K = \log (k_1/k_2) = \alpha_1 E_x + \beta_1 H_x - \alpha_2 E_y - \beta_2 H_y + \log (k_{10}/k_{20}) \tag{17}$$

The ratio of $\log (k_1/k_2)$ is proportional to the free energy, ΔG, of the reaction. It is a function of the oxidation potential of E_x and the negative value of the E_y potential[9] (which is therefore a reduction term).

If A is a simple primary alkyl group, then using the experimental (or empirical) data[9] on the relationship between α and E,

$$\alpha_1 \cong 1 + E_y \tag{18}$$

$$\alpha_2 \cong 1 + E_x \tag{19}$$

Then the equation becomes

$$\log (k_1/k_2) = E_x - E_y + \beta_1 H_x - \beta_2 H_y + \log (k_{10}/k_{20}) \tag{20}$$

In Figure 3 an experimental energy relationship is given between H–Y and CH_3–Y, both covalent compounds. If we assume that $G_{CH_3Y} = cG_{HY} + d$ (c and d being constants), we see that the $\log (k_{10}/k_{20})$ term is related to the H_Y and H_X values. Thus in general

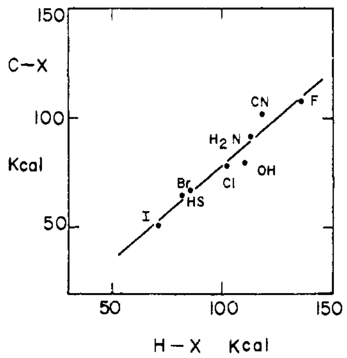

Figure 3. Plot of the bond strength of the carbon-X in the ethyl derivative *vs.* the bond strength in kcalories/mole for the hydrogen-X compound: T. L. Cottrell, "The Strengths of Chemical Bonds," 2nd ed, Butterworths Scientific Publishers, Ltd., London, 1958.

$$\log (k_1/k_2) = f(E_x, E_y, H_x, H_y) \tag{20}$$

the ΔG of the reaction is related to the E values and the H values. Hence the oxibase scale can in aliphatic carbon systems predict not only the $\Delta G^{\ddagger}$ but also the ΔG of the reaction. The constants, c and d, remain a problem.

It is to be noted that (17) predicts a ΔG of zero for $CH_3I + {}^*I^- \rightleftharpoons CH_3I^* + I^-$; yet, a $\Delta G^{\ddagger}$ for k_I can be computed using (15). Note that for the isotopic exchange reaction $\alpha_1 = \alpha_2$, $\beta_1 = \beta_2$, $E_x = E_y$, $H_x = H_y$, and $k_{10} = k_{20}$. Equation 17 then becomes

$$\log K = \log (k_1/k_2) = \alpha_1 E_x - \alpha_1 E_x + \beta_1 H_x - \beta_1 H_x + \log (k_{10}/k_{10}) = 0 \quad (21)$$

and the free energy (neglecting isotope effects) is equal to zero.

Presently a theoretical treatment for the system

$$2X^- + Y_2 \rightleftharpoons X_2 + 2Y^- \quad (22)$$

is being done. The free energy of reaction 22 is related to the difference in E values between X^- and Y^-. While several assumptions are necessary, it is possible to derive the free energy of (22) using the oxibase scale and the assumed mechanism

$$X^- + Y_2 \rightleftharpoons XY + Y^- \quad (23)$$

$$X^- + XY \rightleftharpoons X_2 + Y^- \quad (24)$$

The assumations needed are those that relate the α and β values of Y–Y, X–Y, and X–X to the E and H values of Y and X. While derivation of thermodynamic equations from purely kinetic principles is considered most unorthodox, further extensions of the oxibase scale is being made and will be reported in other papers.

Conclusion

The oxibase scale works quite well for ethyl tosylate. Using these α and β values or the new E and H values the predictive ability of the oxidase scale is increased. Further work is in progress to show the further utility and the limitations of the oxibase scale. It is suggested that the oxibase scale be used to discuss rates and equilibria in systems in which covalent bonds are broken and/or formed. Thus far we have only used the oxibase scale in reactions with substrates having reactive center atoms in the first and second row of the periodic table such as C, O, N, and S. While limiting the possible generalizations of the oxibase scale, these restrictions appear to be necessary.

Experimental Section

Kinetic Measurements. All kinetic experiments were made on a calibrated Beckman DU spectrophotometer using 1.00 ± 0.003 cm quartz cells in a brass thermostated block (±0.01° NBS). All solutions were prepared in aqueous phosphate, carbonate, or borate buffers in deionized distilled water. Variation of buffer strength had little effect on the second-order rate constants. All flasks, solvents, and solutions were kept under pure nitrogen. Kinetic measurements were made using a thermostated spectrophotometer. The wavelength was set usually at 275 mμ. Measurement of pH were made using E-2 glass electrodes with a Beckman Model G meter. Stock solutions were prepared (in deoxygenated buffer solutions) using a Cahn microbalance.

The rate constants were estimated from properly constructed graphs and then computed from the data using a McBee computer to obtain a least-square fit.

EDTA at $4-6 \times 10^{-4}$ M had no effect upon the rates. Variation of the lot and the amount of the buffers produced no strange results; therefore, we conclude metal ions have little or no catalytic role in the reactions.

Materials. Eastman Kodak Yellow Label ethyl tosylate was distilled in vacuum, bp 127° (2.5 mm). Ethyl tosylate was then recrystallized three times from ethanol. The melting point was 35.0–35.3°. Distilled water was passed over a well-washed, mixed-bed, ion-exchange column.

All salts were reagent or used as standardized solutions (NaOH, NaOCl). Sodium hydroxide solutions were standardized against potassium hydrogen phthalate. The sodium hypochlorite was prepared from a solution of HOCl and HgO by neutralization with standard base.[13] The solution was then analyzed.[14]

Products of the Reactions. Products studies of the reactions were performed in aqueous solutions of ethyl tosylate and the nucleophiles in pH buffer solutions. The conditions were as close as conveniently possible to the conditions reported in Table **II**. Typically, 25 mg of ethyl tosylate was dissolved in 2.5 ml of methanol or tetrahydrofuran and diluted to 50 ml with a Borax buffer solution 0.100 M in the nucleophile (X^-). Analysis was made after reaction by direct vpc analysis on the aqueous solution with an ion flame detector. In all cases the ethyl-X derivative was detected and analyzed by direct calibration with known solutions of ethyl-X. Yields of ethyl-X were 94–102% in all cases except when X^- was $^-$OCl. Further work is in progress on the product studies of $^-$OCl and on other such anions as well (J. Louis, studies in progress).

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(13) N. G. Lordi and J. Epsetein, *J. Amer. Chem. Soc.*, **80**, 509 (1958).

(14) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," 3rd ed, The MacMillan Co., New York, N. Y., 1958, p 597.