Some Properties of Heterolytic Bond Dissociation Energies and Their Use as Molecular Parameters for Rationalizing or Predicting Reactivity

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Three sets of heterolytic bond dissociation energies, $D(R^+–X^-)$, with R = H, CH_3, Et, *n*-Pr, *i*-Pr, *n*-Bu, *i*-Bu, *s*-Bu, and *t*-Bu and X = H, Cl, and Br, have been calculated from available thermochemical data. These three sets as well as other sets reported earlier exhibit a number of properties that are reminiscent of the relevant ionization potentials, namely: (1) any two series are linearly dependent on each other; (2) they are linearly related to the relevant ionization potentials; (3) they can be correlated with kinetic and physical data; (4) they behave like additive substituent constants. The $D(R^+–H^-)$ parameters exhibit the largest range of the structural effect, i.e., 164.4 kcal/mol, from R = H to R = *t*-Bu. This means that the $D(R^+–H^-)$ parameters are the most sensitive to structural variation in R and therefore have been chosen to demonstrate the possibility of using heterolytic bond dissociation energies as additive alkyl substituent constants. For example, the ionization potentials of aldehydes and ketones and of alcohols and ethers are representable by the equations $IP(R_1R_2C{=}O) = 0.615[10^{-2}\sum D(R^+–H^-)] + 5.808$ ($r = 0.985$) and $IP(R_1R_2O) = 0.746[10^{-2}\sum D(R^+–H^-)] + 5.376$ ($r = 0.990$), where R_1 and R_2 = hydrogen or alkyl. Kinetic data can be represented by one of the following three equivalent equations: $E_a = aD(R^+–H^-) + b$; $\ln k = aD(R^+–H^-)/RT + \ln A + b/RT$; $\Delta H^{\ne} = aD(R^+–H^-) + b$. Other data which have been related to IP(R)'s and/or $\sigma_I(R)$ constants can be alternatively represented by the $D(R^+–H^-)$ parameters; also, e.g., Charton's υ_{SR} constant is related to the $D(R^+–H^-)$'s by the regression equation $1/\upsilon_{SR} = 1.212[10^{-2}D(R^+–H^-)] - 2.264$ ($r = 0.983$). The findings of this work appear to strengthen the conclusion arrived at in a previous paper that "a given set of kinetic (or physical) data can be represented by several alternative self-consistent but, nevertheless, arbitrary ways".

Homolytic bond dissociation energies, $D(R–X)$, are molecular parameters which have found wide utility in rationalizing reactivity.[1] In the field of free-radical chemistry in particular the usefulness of these thermochemical data is even greater since $D(R–X)$'s form the basis for empirical[2,3] or semiempirical[4] calculations of activation energies. Homolytic bond dissociation energies, however, show little variation with respect to the structure of R in RX. For example, the range of the structural effect, RSE, in $D(R–Br)$ for the series R = CH_3, Et, *n*-Pr, *i*-Pr, *n*-Bu, *i*-Bu, *s*-Bu, and *t*-Bu is only 3 kcal/mol.[5] Beauchamp et al.[6,7] have defined a new thermochemical parameter as the enthalpy change of the gas-phase reaction (eq 1). This

$$R^+ + X^- \rightarrow R–X \qquad (1)$$

parameter, which is called heterolytic bond dissociation energy, HtBDE, $D(R^+–X^-)$, appears to be much more sensitive to structural variation of the alkyl R than the corresponding $D(R–X)$ parameter. The RSE for the above-mentioned series in $D(R^+–Br^-)$ is 71.5 kcal/mol, compared to 3 kcal/mol in $D(R–Br)$. It therefore appeared interesting to examine the possibility of using heterolytic bond dissociation energies to rationalize reactivity, given that $D(R^+–X^-)$ values can be readily accessible from existing thermochemical data, by eq 2, where IP(R) is the

$$D(R^+–X^-) = D(R–X) + IP(R) - EA(X) \qquad (2)$$

gas-phase ionization potential of the free radical R and EA(X) is the electron affinity of the atom or the free radical X.

Table I. Heterolytic Bond Dissociation Energies (kcal/mol) Used in Correlations

R	$D(R^+–H^-)$	$D(R^+–Cl^-)$	$D(R^+–Br^-)$[b]
H	399.3	333.3	323.6
CH_3	312.2	227.1	219.3
Et	272.6	190.3	183.4
n-Pr	265.9	184.1	177.3
n-Bu	264.4	181.2	175.3
i-Bu	264.4	181.2	175.3
i-Pr	249.9	171.0	164.5
s-Bu	247.5	167.7	161.7
t-Bu	234.9	156.0	147.8
Ph	294[a]		
$CH_2{=}CH$	290.2		
$CH_2{=}CHCH_2$	255.3		
$PhCH_2$	233.5		

[a] Estimated from IP(Ph) = 212 kcal/mol by using the regression equation $D(R^+–H^-) = 1.159IP(R) + 48.932$.

[b] The following are data used in calculations of $D(R^+–X^-)$'s. IP(R) (kcal/mol): H, 313.48; CH_3, 226.81; Et, 193.16; *n*-Pr, 186.71; *n*-Bu, 184.63; *i*-Bu, 184.63; *i*-Pr, 174.03; *s*-Bu, 170.80; *t*-Bu, 159.74. $\Delta H_f{}^\circ{}_{298}$ (R·) (kcal/mol): H, 52.1; CH_3, 34.0; Et, 25.7; *n*-Pr, 20.7; *i*-Pr, 17.6; *n*-Bu, 15.7; *i*-Bu, 13.7; *s*-Bu, 12.6; *t*-Bu, 6.8, taken from ref 8. $\Delta H_f{}^\circ$ (RCl) (kcal/mol): CH_3, −20.55; Et, −26.1; *n*-Pr, −31.0; *i*-Pr, −33.6; *n*-Bu, −35.1; *s*-Bu, −38.6; *t*-Bu, −43.7. $\Delta H_f{}^\circ$ (RBr) (kcal/mol): CH_3, −9.1; Et, −15.2; *n*-Pr, −20.5; *i*-Pr, −23.5; *n*-Bu, −25.6, *s*-Bu, −28.94; *t*-Bu, −31.88. $\Delta H_f{}^\circ$ (X) (kcal/mol): Cl, 28.92; Br, 26.74. $\Delta H_f{}^\circ$ (RH) (kcal/mol): *n*-Pr, −24.83; *n*-Bu, −30.36; *i*-Bu, −32.41, taken from ref 9. EA(X) (kcal/mol): Cl, 83.2; Br, 77.4; H, 18.4, taken from ref 5. $D(H–X)$ (kcal/mol): Cl, 103.01; Br, 87.48, taken from ref 11. IP(R) (kcal/mol): vinyl, 206.3; allyl, 186.0 186.01; benzyl, 167.57. $D(R–H)$ (kcal/mol): vinyl, 102.31; allyl, 87.82, calculated from data which were from ref 8. $D(Ph-CH_2–H)$ 84.3 kcal/mol, taken from ref 10.

The purpose of this paper is to report some properties of HtBDE, to describe some correlations between $D(R^+–X^-)$ and various kinetic and physical data, to compare HtBDE with other parameters used for the same purpose, and finally to suggest the use of these parameters for predicting reactivity.

Three sets of $D(R^+–X^-)$'s have been calculated, i.e., those with R = H, CH_3, Et, *n*-Pr, *i*-Pr, *n*-Bu, *i*-Bu, *s*-Bu, and *t*-Bu and X = H, Cl, and Br. The values of these parameters are summarized in Table I and were calculated by using thermochemical data taken from the appropriate

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[1] E.g.: Russell, G. A. In "Free Radicals"; Kochi, J. K., Ed.; Wiley: New York, 1973; p 275.

[2] Trotman-Dickenson, A. F. *Chem. Ind.* (*London*) **1965**, 379.

[3] Spirin, Y. L. *Russ. J. Phys. Chem.* (*Engl. Transl.*) **1962**, *36*, 636.

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[5] "Handbook of Chemistry and Physics", 54th ed.; Chemical Rubber Publishing Co.: Cleveland, OH, 1973–1974; p F-211.

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Table II. Correlation of Activation Energies with Heterolytic Bond Dissociation Energies, $D(R^+-X^-)$[a]

reaction	regression eq	correl coeff	R in correl data[b]	ref[c]
1, $RBr + I^- \rightarrow RI + Br^-$	$E_a = -0.079_5D(R^+-Br^-) + 33.510$	0.980	1-3, 5, 6, 8	i
2, $RBr + Cl^- \rightarrow RCl + Br^-$	$E_a = 0.054D(R^+-Br^-) + 27.455$	0.979	1-3, 5, 6	i
3, $RBr + Br^{*-} \rightarrow RBr^* + Br^-$	$E_a = -0.116D(R^+-Br^-) + 38.902$	0.993	1, 5, 6, 8	i
4, $RBr + S_2O_3^{2-} \rightarrow RS_2O_3^- + Br^-$	$E_a = -0.084D(R^+-Br^-) + 34.124$	0.995	1, 2, 5, 6	i
5, $RH + CD_3\cdot \rightarrow R\cdot + CHD_3$	$E_a = 0.077D(R^+-H^-) - 9.336$	0.974	1, 2, 4, 6-8	ii
6, $CH_4 + R\cdot \rightarrow CH_3\cdot + RH$	$E_a = -0.080D(R^+-H^-) + 39.389$	0.976	1-4, 6, 8	ii
7, $RH + CH_3\cdot \rightarrow R\cdot + CH_4$	$E_a = 0.073D(R^+-H^-) - 8.043$	0.998	1, 2, 6, 8	ii
8, $RH + CH_3O\cdot \rightarrow R\cdot + CH_3OH$	$E_a = 0.090D(R^+-H^-) - 17.183$	0.997	1, 2, 6, 8	iii
9, $RH + Br\cdot \rightarrow R\cdot + HBr$	$E_a = 0.137D(R^+-H^-) - 24.402$	0.998	1, 2, 6, 8	iv
10, $RBr \rightarrow R'_{ene} + HBr$	$E_a = 0.360D(R^+-Br^-) - 12.308$	0.993	2-6, 8	v
11, $RCl \rightarrow R'_{ene} + HCl$	$E_a = 0.327D(R^+-Cl^-) - 5.159$	0.978	2-8	v

[a] E_a and $D(R^+-X^-)$ in kcal/mol. [b] CH_3 = 1; Et = 2; *n*-Pr = 3; *n*-Bu = 4; *i*-Bu = 5; *i*-Pr = 6; *s*-Bu = 7; *t*-Bu = 8. [c] Data taken from the following sources. (i) Streitwieser, A., Jr. *Chem. Rev.* **1956**, *56*, 571. (ii) Gray, P.; Herod, A. A.; Jones, A. *Ibid.* **1971**, *71*, 247. (iii) Zavitsas, A. A. *J. Am. Chem. Soc.* **1972**, *94*, 2779. (iv) Poutsma, M. L. In "Free Radicals"; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. II, p 159. (v) See ref 14.

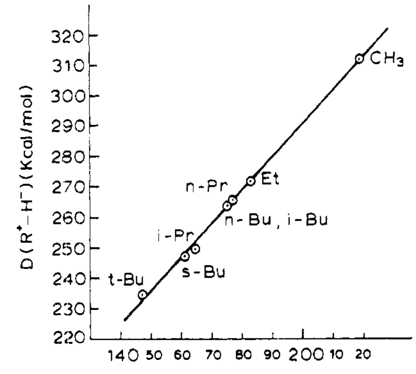

Figure 1. Plot of the heterolytic bond dissociation energies for the process $R^+ + H^-$ against the respective parameters for the process $R^+ + Br^-$.

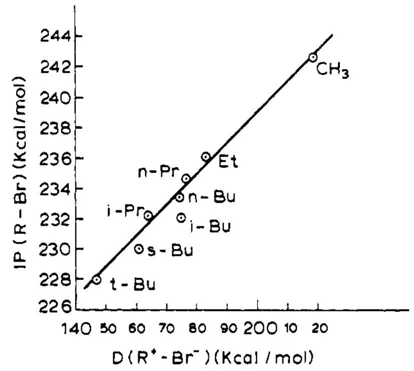

Figure 2. Plot of the gas-phase ionization potentials of a series of RBr against the respective heterolytic bond dissociation energies.

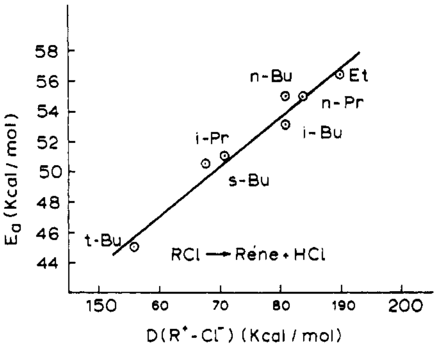

Figure 3. Activation energies for the gas-phase unimolecular decomposition of a series of alkyl chlorides plotted against the respective heterolytic bond dissociation energies.

sources.[5,8-11] These particular sets have been chosen because the idea originally was to try to correlate kinetic data from reactions in which C-H, C-Cl, and C-Br bonds were broken, respectively.

From an examination of eq 2 it becomes obvious that the "individuality" of $D(R^+-X^-)$ is mainly due to the IP(R) term, whereas the other two terms contribute almost equally throughout the series of RX. This is so because the RSE in the $D(R-X)$'s is small as compared to the respective RSE value of the IP(R)'s. It should be noted, however, that the range of the structural effect in the $D(R^+-X^-)$'s appears to be larger than the respective RSE value of the IP(R)'s, i.e., 67.08 kcal/mol.[12] Thus from the available data the RSE values specifically are as follows (in kcal/mol): X = NH_2, 70.1;[12] X = Cl, 71.1; X = Br, 71.5; X = CH_3, 73.0;[12] X = I, 73.1;[12] X = H, 77.3 (all from R = CH_3 to R = *t*-Bu). In some instances the $D(R^+-X^-)$ values are very close to those of the IP(R). This is due to the accidental (approximate) canceling of the $D(R-X)$ and EA(X) terms in eq 2, e.g., in the case of RCl.

It has already been noted[12] that heterolytic bond dissociation energies are linearly related to the respective IP(R)'s. Heterolytic bond dissociation energies, in general, appear to behave like the relevant ionization potentials; i.e., there exists linearity between any two series of $D(R^+-X^-)$ just as in the IP(R-X) series[12,13] (e.g., Figure 1). Thus, $D(R^+-H^-)$ and $D(R^+-Cl^-)$ are related to $D(R^+-Br^-)$ through the regression relationships (3) and (4).

$$D(R^+-H^-) = 1.101D(R^+-Br^-) + 70.724 \quad (r = 0.999) \quad (3)$$

$$D(R^+-Cl^-) = 1.007D(R^+-Br^-) + 5.528 \quad (r = 0.999) \quad (4)$$

The analogy between $D(R^+-X^-)$'s and IP's seems to go even further. For example, we notice that HtBDE's for RBr are linearly related to the respective IP(R-Br) (Figure 2 and regression relationship (5)). $D(R^+-X^-)$'s are also linearly related to the respective $\sigma_I(R)$ parameters.

$$IP(R-Br) = 0.209D(R^+-Br^-) + 196.944 \quad (r = 0.988) \quad (5)$$

It therefore appeared probable that kinetic and physical data that have been correlated with IP(R)'s[12] could be

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correlated with the relevant HtBDE.

Activation energies for the gas-phase reaction (eq 6)[14]

$$\text{R-Cl} \rightarrow \text{R}'_{\text{ene}} + \text{HCl} \qquad (6)$$

are plotted against the HtBDE that corresponds to the bond that is being broken, $D(\text{R}^+\text{-Cl}^-)$, in Figure 3. The points fall very nearly on a straight line. Results from similar correlations are summarized in Table II. In this table are given the reaction, the regression equation, the correlation coefficient, the number and the kind of the data points in the correlation, and the reference to the source of the data. The correlated data in Table II are from reactions which involve one of the three cases of bond breaking, namely, C–H, C–Cl, and C–Br, and the correlation is done respectively with the $D(\text{R}^+\text{-H}^-)$, $D(\text{R}^+\text{-Cl}^-)$, and $D(\text{R}^+\text{-Br}^-)$ parameters. The data in Table II are exactly the same as those used in the correlations with IP(R)[12] and/or $\sigma_I(\text{R})$.[15] Therefore, another analogy between HtBDE and IP's is observed.

The regression equations are of the form given by eq 7. Applying the same method which has been used to analyze the E_a vs. $\sigma_I(\text{R})$[15] correlations, one can readily show that eq 7 can be recast to eq 8 and 9, where a and b are the

$$E_a = aD(\text{R}^+\text{-X}^-) + b \qquad (7)$$

$$\ln k = aD(\text{R}^+\text{-X}^-)/RT + \ln A + b/RT \qquad (8)$$

$$\Delta H^{*} = aD(\text{R}^+\text{-X}^-) + b \qquad (9)$$

coefficients of the linear regression equation, A is the Arrhenius preexponential factor, and the rest of the symbols have their usual meanings. Equation 7 is of an Evans–Polanyi type and formally analogous to the one that relates activation energies for hydrogen abstraction by free alkyl radicals with relevant homolytic bond dissociation energies.[16] It should be noted that the E_a vs. $D(\text{R-H})$ relationship[16] can be put in forms analogous to eq 8 and 9.

The successful correlation of kinetic data with HtBDE indicates that the latter parameters are of a broader scope than originally meant, i.e., as a measure of carbenium ion affinity for a given charged nucleophile in the gas phase. Actually $D(\text{R}^+\text{-X}^-)$'s could be viewed as substituent constants, specific for a particular bond that is being broken. These constants most probably reflect the electrical effects of the substituent R, as they are modulated by the corresponding effects of its partner X.

It has been observed that the data in Table II can be correlated with any $D(\text{R}^+\text{-X}^-)$ parameter. In order to demonstrate this, a second group of sets of kinetic and physical data have been correlated with the $D(\text{R}^+\text{-H}^-)$ parameters, because these parameters exhibit the largest RSE value, namely, 164.4 kcal/mol, from $D(\text{H}^+\text{-H}^-)$ to $D(t\text{-Bu}^+\text{-H}^-)$. Table III summarizes these correlations. It must be mentioned that the same data have been correlated with IP(R) and/or $\sigma_I(\text{R})$ parameters.[12,15] Again, the close analogy between heterolytic bond dissociation energies and IP(R)'s becomes apparent from the fact that $D(\text{R}^+\text{-H}^-)$ parameters behave like additive substituent constants, just like the IP(R)'s.[12] Thus the gas-phase first ionization potentials of aldehydes and ketones correlate with the sum of the two $D(\text{R}^+\text{-H}^-)$ parameters that correspond to the two alkyls, or hydrogen and alkyl, attached to the carbonyl group. Notice that a total of nine sub-

Table III. Correlation of Physical and Kinetic Data with $D(\text{R}^+\text{-H}^-)$ Parameters

process	regression eq[a]	r	R or R_1 and R_2 in correl data[b]	ref[c]
1, $R_1R_2O \rightarrow R_1R_2O^{+}\cdot + e^-$	$\text{IP}(R_1R_2O) = 0.746[10^{-2}\,\Sigma D(\text{R}^+\text{-H}^-)] + 5.376$	0.990	see Figure 5	i
2, $R_1R_2S \rightarrow R_1R_2S^{+}\cdot + e^-$	$\text{IP}(R_1R_2S) = 0.659[10^{-2}\,\Sigma D(\text{R}^+\text{-H}^-)] + 4.763$	0.979	1, 2; 1, 3; 1, 4; 2, 2; 2, 3; 3, 3; 4, 4	i
3, $R_1R_2C{=}O \rightarrow R_1R_2C{=}O^{+}\cdot + e^-$	$\text{IP}(R_1R_2CO) = 0.615[10^{-2}\,\Sigma D(\text{R}^+\text{-H}^-)] + 5.808$	0.985	see Figure 4	i
4, $RBr \rightarrow RBr^{+}\cdot + e^-$	$\text{IP(RBr)} = 0.826[10^{-2}D(\text{R}^+\text{-H}^-)] + 7.958$	0.986	2-9	i
5, $RI \rightarrow RI^{+}\cdot + e^-$	$\text{IP(RI)} = 0.611[10^{-2}D(\text{R}^+\text{-H}^-)] + 7.606$	0.975	2-9	i
6, $AcOR + OH^- \rightarrow AcO^- + ROH$	$E_a = -6.138[10^{-2}D(\text{R}^+\text{-H}^-)] + 27.542$	0.960	2-9	ii
7, $HCO_2R + OH^- \rightarrow HCO_2^- + ROH$	$E_a = 2.035[10^{-2}D(\text{R}^+\text{-H}^-)] + 3.226$	0.976	2-4, 7	iii
8, $Ph_3CH + RLi \rightarrow Ph_3CLi + RH$	$\log k_r = -3.218[10^{-2}D(\text{R}^+\text{-H}^-)] + 10.053$	0.985	2, 5, 10-13	iv
9, $RN{=}NR \rightarrow R\cdot + RN_2\cdot$	$E_a = 19.005[10^{-2}D(\text{R}^+\text{-H}^-)] - 0.692$	0.984	2, 3, 5-9	v
10, $RCONR_1R_2 \xrightarrow{H_2O} RCO_2H + R_1R_2NH$	$\upsilon_{NR_1R_2} = -1.282[10^{-2}\Sigma D(\text{R}^+\text{-H}^-)] + 8.399$	0.999	2, 2; 2, 3; 3, 3; 4, 4; 7, 7	vi
11, $R'COSR \xrightarrow{H_2O} R'CO_2H + RSH$	$1/\upsilon_{SR} = 1.212[10^{-2}D(\text{R}^+\text{-H}^-)] - 2.264$	0.983	2-9	vii
12, $R'CO_2R \xrightarrow{H_2O} R'CO_2H + ROH$	$1/\upsilon_{OR} = 3.185[10^{-2}D(\text{R}^+\text{-H}^-)] - 6.689$	0.989	3-9	viii

[a] IP's in eV and $D(\text{R}^+\text{-H}^-)$'s in kcal/mol. [b] H = 1; CH_3 = 2; Et = 3, n-Pr = 4; n-Bu = 5; i-Bu = 6; i-Pr = 7; s-Bu = 8; t-Bu = 9; Ph = 10; $CH_2{=}CH$ = 11; $CH_2{=}CHCH_2$ = 12; $PhCH_2$ = 13. [c] Data taken from the following sources. (i) See ref 8. (ii) Jones, R. W. A.; Thomas, J. D. R. *J. Chem. Soc. B* **1966**, 661. (iii) Leimm, R.; Korte, R.; Laaksonen, E.; Lehmuskoski, U. *Suom. Kemistil. B* **1946**, *19*, 93; *Chem. Abstr.* **1947**, *41*, 5370*d*. (iv) Relative reactivities at $(\text{RLi})_i = 0.10$ F: West, P.; Waack, R.; Purmort, J. T. *J. Am. Chem. Soc.* **1970**, *92*, 840. (v) Reference 14. (vi) Charton, M. *J. Org. Chem.* **1977**, *42*, 3535. (vii) Charton, M.; Charton, B. I. *Ibid.* **1978**, *43*, 1161. (viii) Charton, M. *Ibid.* **1977**, *42*, 3531.

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(14) Benson, S. W.; O'Neal, H. E. *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.* **1970**, *No. 21*.

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(16) Reference 2.

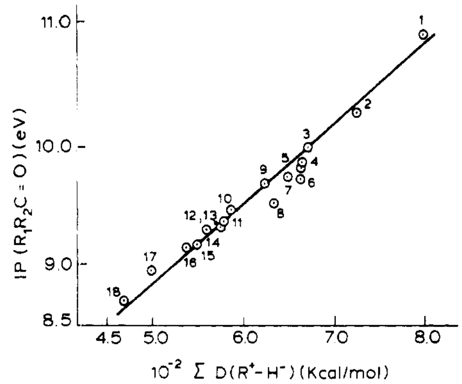

Figure 4. First gas-phase ionization potential of aldehydes and ketones plotted against the sum of the heterolytic bond dissociation energies for the process $R^+ + H^-$ that correspond to the two alkyls (or hydrogen and alkyl) attached to the carbonyl group: (1) H, H; (2) H, CH_3; (3) H, Et; (4) H, *n*-Pr; (5) H, *n*-Bu; (6) H, *i*-Bu; (7) H, *i*-Pr; (8) H, *t*-Bu; (9) CH_3, CH_3; (10) CH_3, Et; (11) CH_3, *n*-Pr; (12) CH_3, *n*-Bu; (13) CH_3, *i*-Bu; (14) CH_3, *i*-Pr; (15) CH_3, *t*-Bu; (16) *n*-Pr, *n*-Pr; (17) *i*-Pr, *i*-Pr; (18) *t*-Bu, *t*-Bu.

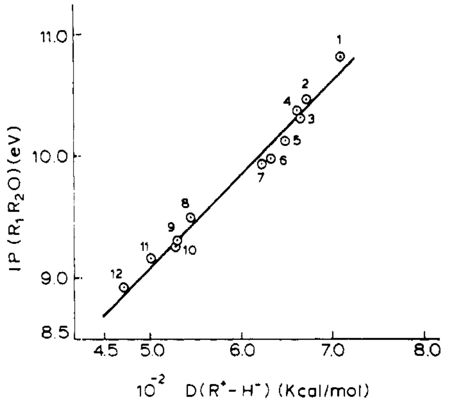

Figure 5. First gas-phase ionization potential of alcohols and ethers plotted as in Figure 4: (1) H, CH_3; (2) H, Et; (3) H, *n*-Pr; (4) H, *n*-Bu; (5) H, *i*-Pr; (6) H, *t*-Bu; (7) CH_3, CH_3; (8) Et, Et; (9) *n*-Pr, *n*-Pr; (10) *n*-Bu, *n*-Bu; (11) *i*-Pr, *i*-Pr; (12) *t*-Bu, *t*-Bu.

stituents are involved in the correlation (Figure 4). Similarly, the ionization potentials of alcohols and ethers and of thiols and thioethers (e.g., Figure 5) are representable by the same way. Charton's steric parameters υ_{OR},[17] υ_{SR},[18] and $\upsilon_{NR_1R_2}$[19] exhibit the same dependence on $D(R^+–H^-)$ as on IP(R)[12] or $\sigma_I(R)$[15] (see relevant entry in Table III and Figure 6.

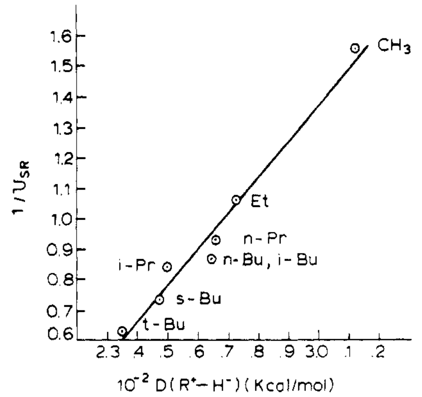

Figure 6. The inverse of Charton's steric parameter, υ_{SR}, plotted against the respective $D(R^+–H^-)$ parameter.

We propose the use of $D(R^+–H^-)$ parameters as substituent constants for representing kinetic and physical data. Kinetic data can be represented by either eq 7, 8, or 9. This representation is alternative to the ones in terms of IP(R)[12] or $\sigma_I(R)$[15] and can be used for predictive purposes. It is felt that the correlations reported in this paper strengthen the conclusion that was arrived at in a previous work,[15] namely, that "a given set of kinetic (or physical) data can be represented by several alternative self-consistent but, nevertheless, arbitrary ways".

Finally, it can be said that as soon as accurate values of electron affinities of series of radicals such as R·, RO·, RS·, etc. will become available, they can make possible the calculation of series of useful $D(R^+–X^-)$ parameters. For example, the availability of the series of EA(R·)'s could make accessible the $D(M^+–R^-)$ parameters, where M is, e.g., an alkali metal, that are very much needed in main-group organometallic chemistry.

Concluding Remarks

Heterolytic bond dissociation energies exhibit a number of properties that make them analogous to the respective ionization potentials or the relevant ionization potentials of free radicals. The most remarkable of these properties are (1) that there is a linear dependence between any two series, (2) that they correlate with kinetic and physical data, and (3) that they behave like additive substituent constants. Correlations between physical or kinetic data and heterolytic bond dissociation energies may be an arbitrary way of representing such data but may also be useful in predicting reactivity.

Registry No. H_2, 1333-74-0; HCl, 7647-01-0; HBr, 10035-10-6; CH_4, 74-82-8; CH_3Cl, 74-87-3; CH_3Br, 74-83-9; EtH, 74-84-0; EtCl, 75-00-3; EtBr, 74-96-4; *n*-PrH, 74-98-6; *n*-PrCl, 540-54-5; *n*-PrBr, 106-94-5; *n*-BuH, 106-97-8; *n*-BuCl, 109-69-3; *n*-BuBr, 109-65-9; *i*-BuH, 75-28-5; *i*-BuCl, 513-36-0; *i*-BuBr, 78-77-3; *i*-PrCl, 75-29-6; *i*-PrBr, 75-26-3; *s*-BuCl, 78-86-4; *s*-BuBr, 78-76-2; *t*-BuCl, 507-20-0; *t*-BuBr, 507-19-7; PhH, 71-43-2; $CH_2{=}CH_2$, 74-85-1; $CH_2{=}CHCH_3$, 115-07-1; $PhCH_3$, 108-88-3.

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