Activation Energies of Hydrogen Atom Abstractions from Alkanes by Free Radicals

By **R. R. Baldwin** and **R. W. Walker,*** Department of Chemistry, University of Hull, Hull HU6 7RX

Activation energies for the gas phase reaction X + RH = HX + R where X is an atom or free radical and RH is an alkane conform to equation (i) where $\sigma^*_{XCH_2}$ is the Taft parameter for the group XCH_2 in aliphatic systems undergoing reaction in aqueous solution at 25 °C.

$$E = 12{\cdot}2 - 7{\cdot}2\sigma^*_{XCH_2} + 0{\cdot}55\Delta H + \Delta H^2/(40 + 2{\cdot}2|\Delta H|) \qquad \text{(i)}$$

Calculated activation energies for X = Cl and particularly for X = CF_3 differ significantly from the experimental values, and possible explanations have been given. With substrates (HY) other than alkanes, thermochemical data and Arrhenius parameters are less accurately known, but within experimental error the activation energies are generally consistent with the above equation, indicating that the electronegativity of Y has little influence on the activation energy. For the substrates H_2S and HCl, the experimental activation energies are significantly lower than the calculated values.

THE activation energies of hydrogen-atom abstractions from alkanes by free radicals are influenced not only by the enthalpy changes in the reactions, but also by the electronegativity of the attacking radical.[1] For instance, in the reactions of H atoms with methane and with the tertiary C–H in isobutane, the difference between $E_1 = 11{\cdot}9$ [2] and $E_2 = 7{\cdot}0$ [3] kcal mol^{-1} arises from the difference in the enthalpies of the reactions of *ca.* 13 kcal mol^{-1}. However, E_3 is only 3·8 [4] kcal mol^{-1} in contrast to $E_1 = 11{\cdot}9$, even though $\Delta H_3 = +2$ and $\Delta H_1 = 0$.

$$\begin{array}{lllr}
 & & \Delta H/\text{kcal mol}^{-1} & \\
H + CH_4 & = H_2 + CH_3 & 0 & (1)\\
H + HCMe_3 & = H_2 + Me_3C & -13 & (2)\\
Cl + CH_4 & = HCl + CH_3 & +2 & (3)
\end{array}$$

Clearly, this large difference in activation energy can be related to the difference in the electronegativity of the two abstracting atoms. These effects have been recognised for a long time, but little attempt has been made to quantify them. Usually, activation energies have been related to the enthalpy change by one of the Evans–Polanyi relationships such as (4). The approximately straight lines obtained when E is plotted against ΔH for each radical X attacking a series of similar substrates RH give specific values for the constants C and α. If D(R–H) is not known, equation (4) can be modified to (5).

$$E = C + \alpha\Delta H \qquad (4)$$

$$E = \alpha[D(R\text{–}H) + \beta] \qquad (5)$$

The activation energies for attack of I, NF_2, Br, CF_3, and Me at primary, secondary, and tertiary C–H bonds in alkanes and at the aldehydic C–H bond in acetaldehyde have been treated in this way by Trotman-Dickenson *et al.*[5] Reasonably straight lines were obtained for each radical, giving $\alpha_{NF_2} = 0{\cdot}90$, $\alpha_I = 0{\cdot}97$, $\alpha_{Br} = 0{\cdot}86$, and $\alpha_{Me} = \alpha_{CF_3} = 0{\cdot}49$. Many similar values of α for

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[1] A. F. Trotman-Dickenson, *Adv. Free Radical Chem.*, 1965, **1**, 1.

[2] R. W. Walker, *J. Chem. Soc.* (*A*), 1968, 2391.

[3] R. R. Baker, R. R. Baldwin, and R. W. Walker, *Trans. Faraday Soc.*, 1970, **66**, 2812.

[4] J. H. Knox and R. L. Nelson, *Trans. Faraday Soc.*, 1959, **55**, 937.

[5] P. Cadman, C. Dodwell, A. J. White, and A. F. Trotman-Dickenson, *J. Chem. Soc.* (*A*), 1971, 2967.

these and other radicals are in the literature.[6-8] This paper examines the relationship between the activation energies and a well established measure of polar character used in solution kinetics. For two reasons, discussion will be mainly restricted to reaction (6) where X = H,

$$\mathrm{X + RH = XH + R} \qquad (6)$$

O, OH, MeO, Me, Et, I, Cl, Br, CF_3, and CCl_3 and R = Me, Et, Pr^i, and Bu^t. (a) The polar character of RH will be approximately constant, so that the only significant change in polarity will be caused by variation in X. (b) The C–H bond dissociation energies are less well known for compounds other than alkanes.

Relationship between E *and* ΔH.—Figure 1 shows a plot of E against ΔH for the various species X reacting with RH. All values of E have been obtained using the simple Arrhenius equation $k = Ae^{-E/RT}$ and they refer to attack at the weakest C–H bond in RH. Suitable corrections have been made where the experimental results give an overall value of E by assuming that all primary C–H bonds in ethane, propane, and isobutane are identical.[3]

Values of C–H bond dissociation energies at 25 °C have been mostly taken from Kerr's tabulation.[8] First, over the whole range of radicals, the relationship between E and ΔH is best represented by a curve rather than a straight line; at high values of ΔH the gradient approaches unity, whereas at low ΔH the gradient approaches zero. Secondly, for each X, there is a particular relationship between E and ΔH. It is difficult to find a simple equation to fit the points in Figure 1, but the full lines are drawn according to equation (7) for

$$E = \mathrm{C_X} + 0{\cdot}55\Delta H + \Delta H^2/(40 + 2{\cdot}2|\Delta H|) \qquad (7)$$

different values of $\mathrm{C_X}$. The change in curvature in the lines is very similar to that observed for each radical X. The choice of the constants in equation (7) will be discussed later.

$\mathrm{C_X}$ May be regarded as the activation energy when the reaction of X with a hydrocarbon is thermoneutral. This situation arises with Me + CH_4 and nearly so with H + CH_4, but usually is hypothetical. The value of $\mathrm{C_X}$ decreases as the electronegativity of the radical increases, the halogen, CCl_3, and O radicals having the lowest values of $\mathrm{C_X}$ and H, Me, and Et the highest.

Relationship between $\mathrm{C_X}$ *and* σ^*.—The electronegativity of a free radical X can be related to the parameter for the group X, $\sigma^*_{\rm X}$, first introduced by Taft.[9,10] To find a parameter that expresses only the polar character of a substituent group X in aliphatic reactions in solution, data from several reactions must be combined so as to cancel any resonance or steric effects. Ingold[11] first catalysed hydrolyses of esters are so similar that resonance and steric effects should cancel if the ratio of the rate constants is taken. As the polar effect of X will be unimportant in the acid-catalysed hydrolysis, the ratio will be dependent only on the polar effect which influences the base-catalysed reaction. Taft[9,10] suggested that the polar effect of a substituent X, as manifested in the ester XCO_2R, was given by equation (8). Sub-

$$\sigma^*_{\rm X} = [\log (k/k_0)_{\rm B} - \log (k/k_0)_{\rm A}]/2{\cdot}48 \qquad (8)$$

scripts A and B refer to acid and base catalysis, respectively, and k_0 is the rate constant for X = Me so that $\sigma^*_{\rm X}$ for Me is by definition zero. The factor of 2·48 was included by Taft so that the values of $\sigma^*_{\rm X}$ were approximately equal to the Hammett σ values.[12] A complete definition of $\sigma^*_{\rm X}$ should refer to temperature, the nature

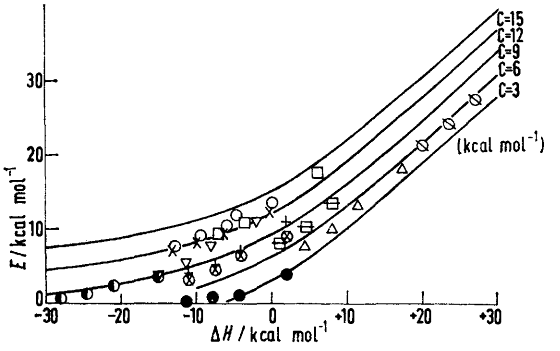

FIGURE 1 Plot of E against ΔH for X + RH (refs. in Table 2). ×, X = H; ○, X = Me; □, X = Et; △, X = Br, ●, X = Cl; +, X = MeO; ⦰, X = I; ⊗, X = O;[7] ⊟, X = CCl_3; ▽, X = CF_3; and ◐, X = OH

suggested that the mechanisms of the acid- and base- of R, and to the solvent. However, the values of $\sigma^*_{\rm X}$ are relatively insensitive[9,10] to these variables if (a) the variation in temperature is small (most $\sigma^*_{\rm X}$ values have been determined between 20 and 30 °C), (b) R is a hydrocarbon residue such as Me, Et, or cyclohexyl, and (c) aqueous organic solvents are used.†

The use of $\sigma^*_{\rm X}$ has achieved undoubted empirical success in correlating the reactivities of aliphatic compounds in solution, but Taft's procedure has been criticised.[10,13] In particular, doubts have been expressed about whether the role of the solvent is the same in the acid- and the base-catalysed reactions so that the steric effects involving inhibition of solvation will not completely cancel. Further experimental work is necessary to resolve these difficulties, but there is little doubt that the $\sigma^*_{\rm X}$ values do give at least a semi-quantitative estimate of the polar character of the group X in the environment of the solution.

Table 1 shows a selection of the available[9,10] values of $\sigma^*_{\rm X}$, obtained mostly from the rates of hydrolysis and

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† In pure water, the $\sigma^*_{\rm X}$ values are somewhat different, particularly when H bonding is important.

[6] J. H. Knox, 'Advances in Chemistry Series,' no. 76, vol. II (Amer. Chem. Soc.), 1968, p. 1.

[7] J. T. Herron and R. E. Huie, *J. Phys. Chem.*, 1969, **73**, 3327.

[8] J. A. Kerr, *Chem. Rev.*, 1966, **66**, 465.

[9] R. W. Taft, jun., *J. Amer. Chem. Soc.*, 1952, **74**, 3120; 1953, **75**, 4231.

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[11] C. K. Ingold, *J. Chem. Soc.*, 1930, 1032.

[12] L. P. Hammett, 'Physical Organic Chemistry,' McGraw-Hill, New York, 1940, ch. 7.

[13] J. Shorter, *Chem. in Britain*, 1969, **5**, 269.

alcoholysis of esters XCO_2R where R = Me, Et, cyclohexyl, and benzyl, in 60% acetone, methanol, ethanol, and in 85% aqueous ethanol, or cyclohexanol at 25 and 30 °C.

Unfortunately, the correlation between σ^*_X and C_X cannot be tested directly, as σ^*_X values for X = I, Br, Cl, O, OH, and MeO are not available, though values of $\sigma^*_{CH_2X}$ are. However, Taft established that (except in the case of alkyl groups) the value of σ^* for the group X was reduced by a nearly constant factor of 2·8 when the group X in the ester is replaced by XCH_2. Consequently any relationship between σ^*_X and C_X can be tested by plotting C_X against $\sigma^*_{XCH_2}$. Figure 2 shows that a relatively good straight line is obtained, apart from the point relating to the CF_3 radical. The linearity is particularly encouraging in view of the potential inaccuracies in both C_X and $\sigma^*_{XCH_2}$. The value of $\sigma^*_{CCl_3CH_2}$ has not been determined and that for $\sigma^*_{CCl_3}$ divided by 2·8 has been used in the plot. The value for C_{CF_3} would lie much nearer the line if the older value[14] of $D(CF_3–H)$ = 102 kcal mol^{-1} is taken, but the more recent[8] value of 106 kcal mol^{-1} has been used in Figure 1 to obtain C_{CF_3}. Figure 2 gives the best line as equation (9). Combination of equations (7) and (9) gives (10).

TABLE 1

Selected values of σ^*_X[9, 10]

X	σ^*_X	X	σ^*_X
CCl_3	2·65	ICH_2	0·85
$ClCH_2$	1·05	$HOCH_2$	0·56
$ClCH_2CH_2$	0·385	$MeOCH_2$	0·52
$BrCH_2$	1·00	Me	0·00
CF_3CH_2	0·92	Et	−0·10
$CF_3(CH_2)_2$	0·32	Bu^t	−0·30

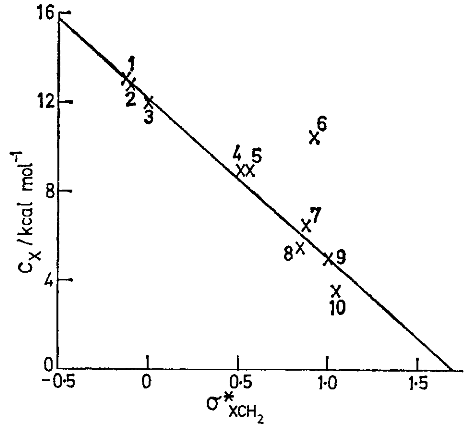

FIGURE 2 Plot of C_X against $\sigma^*_{XCH_2}$. 1, X = Et; 2, X = Me; 3, X = H; 4, X = MeO; 5, X = OH; 6, X = CF_3; 7, X = CCl_3; 8, X = I; 9, X = Br; and 10, X = Cl

$$C_X = 12{\cdot}2 - 7{\cdot}2\sigma^*_{XCH_2} \qquad (9)$$

$$E = 12{\cdot}2 - 7{\cdot}2\sigma^*_{XCH_2} + 0{\cdot}55\Delta H + \Delta H^2/(40 + 2{\cdot}2|\Delta H|) \qquad (10)$$

E Can thus be calculated for the reaction of any radical X with a hydrocarbon from a knowledge of $\sigma^*_{XCH_2}$ (or σ^*_X) and the enthalpy change of the reaction. Table 2 compares the calculated values of *E* from equation (10) with the experimental values; unfortunately neither $\sigma^*_{XCH_2}$ nor σ^*_X values for O atoms are available. The agreement is poorest with the Cl and CCl_3 radicals which is to be expected as their points in Figure 2 are furthest from the mean line. The Cl radical represents the extremes of low activation energy and highest electronegativity and the simple treatment may require modification. The large discrepancies with CF_3 radicals have no obvious explanation, if the current value of $D(CF_3–H)$ is accepted.

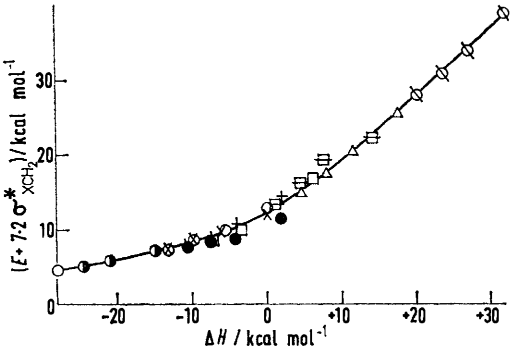

FIGURE 3 Plot of $(E + 7{\cdot}2\sigma^*_{XCH_2})$ against ΔH for X + RH. ×, X = H; ○, X = Me; □, X = Et; △, X = Br; ●, X = Cl; +, X = Me; ⊘, X = I; ⊟, X = CCl_3; and ◑, X = OH

The consistency of the treatment can be strikingly demonstrated as follows. As $7{\cdot}2\sigma^*_{XCH_2}$ represents the reduction in the activation energy, due to the electronegativity of X, relative to the equivalent reaction where X = H, a plot of $E + \sigma^*_{XCH_2}$ should give a common line, as shown in Figure 3. The Cl points again do not give a very good fit; the CF_3 points have not been plotted. The constant 0·55 in equation (10) represents the gradient of the line at $\Delta H = 0$. The term $\Delta H^2/(40 + 2{\cdot}2|\Delta H|)$ gives the curve the correct shape and approaches a value of 0·45 ΔH at very high values of ΔH, when the relationship (11) holds. The excellent agreement shown

$$E = C_X + \Delta H \qquad (11)$$

in Table 2 and Figure 3 suggests that the values of ΔH and *E* for the radical reactions, and the values of σ^*_X and $\sigma^*_{XCH_2}$ are now quite accurately known.

Thermodynamic Considerations of Equation (10).—Equation (10) may be rewritten in the form (12), and the

$$2{\cdot}48\sigma^*_X = \log\,(k_B k_{0A}/k_A k_{0B}) \qquad (12)$$

velocity constants can be expressed using the standard thermodynamic equation (13). Accepting the Taft

$$k = (\boldsymbol{k}T/h)\exp\,(\Delta S^‡/R)\exp\,(\Delta H^‡/RT) \qquad (13)$$

assumption that all the entropy effects and steric strain effects cancel, then σ^*_X for alkali-catalysed hydrolyses

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[14] G. O. Pritchard, H. O. Pritchard, H. I. Schiff, and A. F. Trotman-Dickenson, *Trans. Faraday Soc.*, 1956, **52**, 849.

TABLE 2

Comparison of experimental and calculated activation energies

RH	ΔH	E_{calc}	E_{exp}	Ref.
	kcal mol^{-1}			
H + RH				
CH_4	−0·2	12·1	11·9	2
C_2H_6	−6·2	9·5	9·7	3
C_3H_8	−9·7	8·5	8·3	3
i-C_4H_{10}	−13·2	7·5	7·0	3
Me + RH				
CH_4	0	12·9	12·8 14·3	1,15
C_2H_6	−6·0	10·4	10·4	15
C_3H_8	−9·5	9·2	9·0 †	15
i-C_4H_{10}	−13·0	8·2	7·5	15
CMe_4	−4·7	10·9	12·0	16
Et + RH				
CH_4	+6·0	17·1	17·7	17
C_2H_6	0	13·0		
C_3H_8	−3·5	11·2	10·2 †	18
i-C_4H_{10}	−7·0	10·0	8·8 †	18
Br + RH				
CH_4	+17·5	18·7	18·2	19
C_2H_6	+11·5	13·4	13·2	20
C_3H_8	+8·0	10·5	10·0	20
i-C_4H_{10}	+4·5	7·9	7·5	20
Cl + RH				
CH_4	+1·8	5·6	3·8	4
C_2H_6	−4·2	2·5	1·0	21
C_3H_8	−7·7	1·4	0·7	4
i-C_4H_{10}	−11·2	0·4	0·2	4
MeO + RH				
CH_4	+2·0	9·7	11·0	22
C_2H_6	−4·0	6·6	7·1	23
C_3H_8	−7·5	5·4	5·0 †	23
i-C_4H_{10}	−11·0	4·3	3·9 †	23
I + RH				
CH_4	+33·0	34·5	33·7	24
C_2H_6	+27·0	28·7	27·6	24
C_3H_8	+23·5	25·3	24·4	24
i-C_4H_{10}	+20·0	22·1	21·9	24
OH + RH				
CH_4	−15·0	3·2	3·8	25
C_2H_6	−21·0	2·0	2·4	25
C_3H_8	−24·5	1·4	1·2	25
i-C_4H_{10}	−28·0	1·0	0·4	25
CCl_3 + RH				
CH_4	+14·0	16·5	21·6 ‡	26
C_2H_6	+8·0	11·4	13·4	27
C_3H_8	+4·5	8·8	10·3	27
i-C_4H_{10}	+1·0	6·5	7·9	27
CF_3 + RH				
CH_4	−2·0	4·6	11·3	28
C_2H_6	−8·0	2·3	7·5	14
C_3H_8	−11·5	1·4	5·1	14
i-C_4H_{10}	−15·0	0·5	3·6	29

† Corrected to give E for attack at the weakest C–H bond.[3]

‡ Hautecloque [26] gives the pre-exponential factor for $CCl_3 + CH_4$ as $10^{12\cdot1}$ l mol^{-1} s^{-1} which is 10^2—10^3 too high by comparison with similar values for other reactions. If the pre-exponential factor is reduced by this amount, using the velocity constant at the mean temperature of 300 °C, E = 13·7 – 16·4 kcal mol^{-1} in good agreement with the calculated value.

is given by equations (14) and (15) where $\Delta(\Delta H^{\ddagger})$

$$2{\cdot}48\sigma^*_{X} = (\Delta H^{\ddagger}_{A} - \Delta H^{\ddagger}_{0A}) - (\Delta H^{\ddagger}_{B} - \Delta H^{\ddagger}_{0B})/2{\cdot}303RT \quad (14)$$

$$= \Delta(\Delta H^{\ddagger})/2{\cdot}303RT \quad (15)$$

represents the reduction in the energy barrier to reaction relative to the reaction with X = Me, as a result of the polar effects associated with X. The value of $\Delta(\Delta H^{\ddagger})$ is then given by equation (16), or using the relationship $\sigma^*_{X} = 2{\cdot}8\sigma^*_{XCH_2}$, by equation (17).

$$\Delta(\Delta H^{\ddagger}) = 5{\cdot}71RT\sigma^*_{X} \quad (16)$$

$$\Delta(\Delta H^{\ddagger}) = 16{\cdot}0RT\sigma^*_{XCH_2} \quad (17)$$

At 298 K, $\Delta(\Delta H^{\ddagger})$ will be equal to $9{\cdot}5\sigma^*_{XCH_2}$ kcal mol^{-1}. The factor of 9·5 is somewhat greater than the value of 7·2 kcal mol^{-1}, obtained from the gradient in Figure 2 which represents the reduction in activation energy (relative to X = H) in the gas phase reactions. The difference is not large and may be due to cumulative experimental errors and to the non-cancellation of entropy effects, but in any event the polar effects due to the group X would not be expected to manifest themselves in exactly the same quantitative manner in the gas phase and in solution because of the completely different environments. Indeed it is surprising that the two values are so close. The apparent agreement may result from cancellation of opposing trends. In solution, ion–dipole interactions are involved so that changes in the electronegativity of X should be more important than for free radical reactions. However, the lower dielectric constant of the gas phase will tend to make variations in the electronegativity of X more important than in solution, hence causing cancellation of the opposing effects.

Extension to Other Substrates.—Extension of the treatment to consider reactions of the type (18) where Y is

$$X + HY = HX + Y \quad (18)$$

not an alkyl substituent but a polar group such as a halogen atom, HCO, MeO, or $MeCOCH_2$, is complicated by the effect of the polarity of Y on the activation energy. Further, the bond dissociation energies in these

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[15] A. F. Trotman-Dickenson, 'An Introduction to Free Radicals,' Methuen, London, 1959, p. 34.

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[24] J. H. Knox and R. G. Musgrave, *Trans. Faraday Soc.*, 1967, **63**, 2201.

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[28] W. G. Alcock and E. Whittle, *Trans. Faraday Soc.*, 1965, **61**, 244.

[29] R. E. Dodd and J. W. Smith, *J. Chem. Soc.*, 1957, 1465.

compounds are less accurately known than in hydrocarbons, and only a limited number of activation energies for these reactions have been determined experimentally. The existing data suggest that equations similar to (9) and (10) will apply, modified slightly to account for the polar effects of the Y group.

For a preliminary treatment, it is assumed that the polar effects of X and Y can be treated independently. As earlier, $7{\cdot}2\sigma^*_{\mathrm{XCH_2}}$ has been added to the experimental values of the activation energy to allow for the varying electronegativity of X. If ΔH is the sole factor affecting the activation energy, the plot of $E_{\mathrm{exp}} + 7{\cdot}2\sigma^*_{\mathrm{XCH_2}}$ against ΔH should give the same line as that found when the substrate is a hydrocarbon. The plot is shown in Figure 4; the full line is not drawn through the points, but is defined by equation (19) which gives the electro-

$$E = 12{\cdot}2 + 0{\cdot}55\Delta H + \Delta H^2/(40 + 2{\cdot}2|\Delta H|) \quad (19)$$

negativity-corrected activation energies when the substrate is a hydrocarbon. Points are plotted for HY = H_2, H_2O, H_2S, HCl, HCHO, MeCOMe, and MeOH, and the points include values for X = H, OH, Cl, Br, I, Me, and Et, which represent a wide range in polarity. Within experimental error, many of the points fit the line. The experimental value of 3·0 kcal mol^{-1} used for $E_{\mathrm{H+HCHO}}$ (point A) is clearly too small (*cf.* E for H reacting with the tertiary C–H bond in i-C_4H_{10} is 7·0 kcal mol^{-1}). Also the value for $E_{\mathrm{Et+H_2}} = 14{\cdot}1$ kcal mol^{-1} appears a little low (point B). Accepting $E_{\mathrm{H+C_2H_6}} = 9{\cdot}7$ and $\Delta H = -6$ kcal mol^{-1}, the $E_{\mathrm{Et+H_2}} = 15{\cdot}7$ which almost fits the line. The points for HY = H_2S and HCl appear to be systematically low and it is unlikely that the cause is simply experimental error. For the other compounds HY there is little evidence that the electronegativity of Y influences the activation energy to any extent. Consequently, there should be only a minute effect on activation energy when various alkyl groups are used as Y, which confirms the assumption made earlier that the polar character of different alkanes is approximately constant. Apart from the points for HY = HCl and H_2S, there is a general tendency for the points in Figure 4 to lie *ca.* 1 kcal mol^{-1} below the line, and if this is a genuine effect, a better general relationship between E and ΔH for non-alkanes will be given by equation (20).

$$E = 11{\cdot}5 - 7{\cdot}2\sigma^*_{\mathrm{XCH_2}} + 0{\cdot}55\Delta H + \Delta H^2/(40 + 2{\cdot}2|\Delta H|) \quad (20)$$

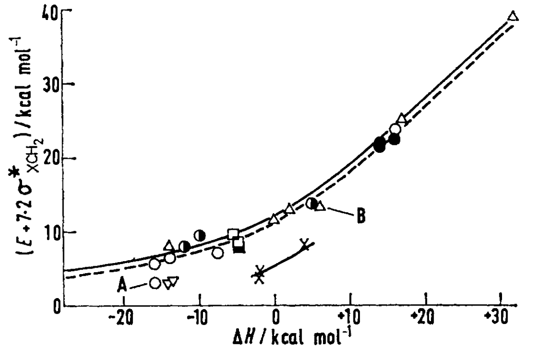

FIGURE 4 Plot of $(E + 7{\cdot}2\sigma^*_{\mathrm{XCH_2}})$ against ΔH for X + HY. △, HY = H_2;[2,30-32] ○, HY = HCHO;[33-37] □, HY = MeCOMe;[38] ■, HY = MeCOEt;[39] ×, HY = HCl;[40-42] ●, HY = H_2O;[3,43] ▽, HY = H_2S;[44,45] and ◑, HY = MeOH.[46-49] Point A, H + HCHO; and Point B, Et + H_2. Full line defined by $E = 12{\cdot}2 + 0{\cdot}55\ \Delta H + \Delta H^2/(40 + 2{\cdot}2|\Delta H|)$. Dashed line defined by $E = 11{\cdot}5 + 0{\cdot}55\ \Delta H + \Delta H^2/(40 + 2{\cdot}2|\Delta H|)$

This equation will not apply for H_2S and HCl. Although the high electronegativity of the Cl atom might explain a reduction in the activation energy for reactions of X + HCl, the electronegativity of the groups OH, HCO, MeCO, and MeO clearly has little effect on activation energy. Further discussion is premature until more accurate thermochemical and kinetic data are available.

We are indebted to Dr. J. Shorter for several helpful discussions.

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