

EMPIRICAL RELATIONSHIPS BETWEEN ACTIVATION PARAMETERS AND SUBSTITUENT  
CONSTANTS FOR STYRENE BROMINATION

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Although the isokinetic relationship is usually regarded as a necessary condition for a linear free energy relationship (1), numerous reactions do not satisfy this requirement at all. We shall show here that non-isokinetic behaviour is not contradictory, theoretically, with the existence of linear free energy relationships at several temperatures.

The activation parameters for the bromination of para-substituted styrenes in MeOH containing NaBr (Table I) were calculated from the second-order rate constant  $k_{Br_2}$  for addition of molecular bromine, which itself was extrapolated from the over-all experimental constants  $k_g$  measured at different NaBr concentrations (2,3). Although  $\log k_{Br_2}$  (or  $\Delta G^\ddagger$ ) is linearly related to  $\sigma^+$  at all the temperatures investigated and although  $\rho$  varies linearly with  $T^{-1}$ , the reaction is neither isokinetic nor isoentropic nor isoenthalpic. Besides, neither  $\Delta H^\ddagger$  nor  $\Delta S^\ddagger$  vary linearly with  $\sigma^+$  (Figure 1). However, the fact that  $\Delta G^\ddagger$  is a linear function of  $\sigma^+$ , i.e. :

$$[1] \quad \Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger = A\sigma^+ + B$$

does not necessarily imply that  $\Delta H^\ddagger$  and  $T\Delta S^\ddagger$  are linear functions of  $\sigma^+$ . One may in fact assume that  $\Delta H^\ddagger$  and  $T\Delta S^\ddagger$  are, for example, of the form :

$$[2] \quad \begin{array}{l} a) \quad \Delta H^\ddagger = A_1\sigma^+ + B_1 + f(\sigma^+) \\ b) \quad T\Delta S^\ddagger = A_2\sigma^+ + B_2 + f(\sigma^+) \end{array}$$

where  $f(\sigma^+)$  would be a function common to  $\Delta H^\ddagger$  and  $T\Delta S^\ddagger$ , so that :

$$[3] \quad \Delta G^\ddagger = (A_1 - A_2)\sigma^+ + (B_1 - B_2) = A\sigma^+ + B$$

Equations [2] could also be of the form :  $\Delta H^\ddagger = f(\sigma^+)$  and  $T\Delta S^\ddagger = A_2\sigma^+ + B_2 + f(\sigma^+)$  or vice versa

**TABLE I :** Experimental values of the activation parameters for the addition of molecular bromine to styrenes (p-R-C<sub>6</sub>H<sub>4</sub>-CH=CH<sub>2</sub>) in methanol-NaBr.

R( $\sigma^+$ )	$\Delta H^\ddagger$ (kcal/mole)	$\Delta S^\ddagger$ (e.u.)	$\Delta G^\ddagger$ (298 K) (kcal/mole)
p-MeO (-0.778)	5.29 ± 0.30	-10.83 ± 1.17	8.52
p-Me (-0.311)	5.91 ± 0.13	-19.08 ± 0.30	11.60
p-F (-0.073)	6.05 ± 0.16	-23.58 ± 0.40	13.07
H (0.00)	6.68 ± 0.61	-21.56 ± 1.95	13.11
p-Cl (+0.114)	10.28 ± 0.30	-12.17 ± 1.10	13.91
p-Br (+0.150)	8.64 ± 0.15	-18.50 ± 0.35	14.15

1.- DEPENDENCE OF  $\Delta H^\ddagger$  ON  $\sigma^+$  : The experimental points tend to fall on a branch of a hyperbola of the form :

$$[4] \quad \Delta H^\ddagger = \frac{a_0 + a_1\sigma^+}{a'_0 + a'_1\sigma^+} = \frac{b_0 + b_1\sigma^+}{b_2 + \sigma^+}$$

where  $b_2 \neq 0$  since  $\Delta H^\ddagger$  must remain finite when  $\sigma^+ = 0$  (R-H). Coefficients  $b_1$  were calculated using a classical mathematical method (4) and lead to the curve :

$$[5] \quad \Delta H^\ddagger = 5.29 \frac{(\sigma^+ - 0.243)}{(\sigma^+ - 0.197)}$$

which is in excellent agreement with the rate data (Figure 1).

2.- DEPENDENCE OF  $T\Delta S^\ddagger$  ON  $\sigma^+$  : Considering the expression of  $\Delta H^\ddagger$ ,  $T\Delta S^\ddagger$  must be of the form :

$$[6] \quad T\Delta S^\ddagger = A_2\sigma^+ + B_2 + \frac{a_0 + a_1\sigma^+}{a'_0 + a'_1\sigma^+} \equiv \frac{b'_0 + b'_1\sigma^+ + b'_2(\sigma^+)^2}{b_2 + \sigma^+}$$

Calculation of coefficients  $b'_1$  and  $b_2 = a'_0/a'_1$  (4) at T = 298 K leads to the expression :

$$[7] \quad T\Delta S^\ddagger = -5.707 \left[ \frac{-0.234 + 1.184 \sigma^+ + (\sigma^+)^2}{\sigma^+ - 0.197} \right]$$

This curve is also in good agreement with the experimental data (Figure 1).

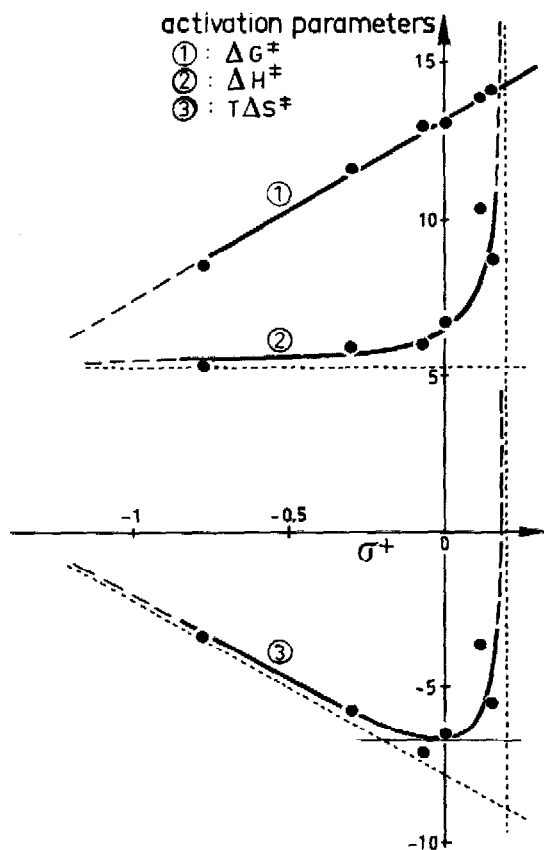


Figure 1.- Substituent dependence of  $\Delta H^\ddagger$ ,  $T\Delta S^\ddagger$  and  $\Delta G^\ddagger$  ( $T = 298$  K) for the molecular bromination of styrenes in methanol-NaBr. (●: experimental points; full lines: calculated curves from [5], [7] and [9]).

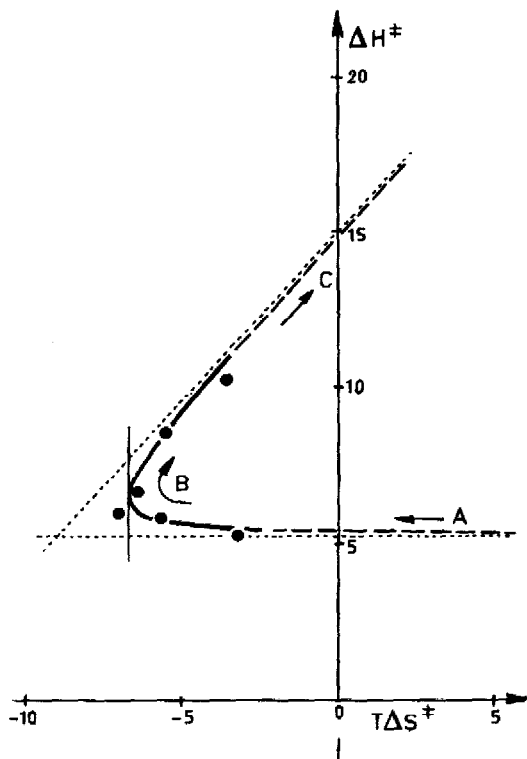


Figure 2.- Calculated  $\Delta H^\ddagger$  vs  $T\Delta S^\ddagger$  ( $T = 298$  K) curve for the molecular bromination of styrenes in methanol-NaBr. (●: experimental points; ABC: calculated curve (increasing  $\sigma^+$ )).

3.- DEPENDENCE OF  $\Delta G^\ddagger$  ON  $\sigma^+$  : From [5] and [7] we obtain equation [8] :

$$[8] \quad \Delta G^\ddagger = 5.707 (\sigma^+ + 2.299) \frac{(\sigma^+ - 0.199)}{(\sigma^+ - 0.197)}$$

which obviously simplifies to :

$$[9] \quad \Delta G^\ddagger = 5.707 \sigma^+ + 13.120$$

The good agreement between [9] and the experimental equation [10], i.e. :

$$[10] \quad \Delta G_{\text{exp}}^\ddagger = 5.992 \sigma^+ + 13.290 \text{ (correlation coefficient} = 0.997)$$

supports the hypothesis that there is a function common to  $\Delta H^\ddagger$  and  $T\Delta S^\ddagger$ .

4.-  $\Delta H^\ddagger$  AS A FUNCTION OF  $T\Delta S^\ddagger$  : The curve  $\Delta H^\ddagger$  vs  $T\Delta S^\ddagger$  plotted from the calculated curves [5] and [7] satisfactorily accounts for the experimental points (Figure 2). This clearly shows that these points are not to be plotted on two "straight-lines" (the one for the electron-donating and the other for the electron-attracting substituents) as one might think on the basis of the experimental values only.

In the case of styrene bromination, the empirical relationships for  $\Delta H^\ddagger$  and  $T\Delta S^\ddagger$  are valid for the six para-substituted styrenes and the medium studied. The function  $f(\sigma^+)$  common to  $\Delta H^\ddagger$  and  $T\Delta S^\ddagger$  (or  $\Delta S^\ddagger$ ) for other derivatives could be more complicated although  $\Delta G^\ddagger$  is expected to remain a linear function of  $\sigma^+$ .

#### REFERENCES

- (1) See for example, O. EXNER, Progress in Physical Organic Chemistry, vol. 10, Edited by A. Streitwieser and R.W. Taft, Wiley, New York, 1973, p. 411, and references therein.
- (2) J.E. DUBOIS and M. MARIE de FICQUELMONT-LOIZOS, to be published.
- (3) M. MARIE de FICQUELMONT-LOIZOS, Doctoral Thesis, Paris, 1973, N° C.N.R.S., AO 8355, and references therein.
- (4) In equations [5] and [7] the value of 0.197 in the denominator is the arithmetic mean of the values 0.1966 and 0.1981 actually found for  $\Delta H^\ddagger$  and  $T\Delta S^\ddagger$ . The other constants in these equations have been modified accordingly.