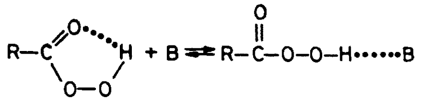
A 'Double Reciprocal' Analysis of Calorimetric Data for Simultaneous Determination of Equilibrium Constants and Enthalpies of Complex Formation: Intermolecular Hydrogen Bonding in Peroxy Acid–Oxygen Base Complexes in Carbon Tetrachloride

By Jože Škerjanc,* Aleksander Regent, and Božo Plesničar*
(Department of Chemistry, University of Ljubljana, 61000 Ljubljana, Yugoslavia)

Summary A 'double reciprocal' ($1/\Delta H$ *vs.* $1/B_0$) analysis has been used in a calorimetric study of hydrogen bonding in some peroxybenzoic acid–oxygen base complexes in carbon tetrachloride; the calculated enthalpy change per mole of hydrogen-bonded complex is sensitive to the acidity of the peroxy acid as well as the basicity of the oxygen base.

Various methods for the simultaneous determination of K and ΔH_0 have been reported;[1] however, the double reciprocal analysis used in this paper seems to be preferable to some of the previous methods. We illustrate the application of this method to peroxy acid–oxygen base complex formation [equation (1)].†


(1)

---

† Peroxybenzoic acids exist in 'inert' solvents exclusively in the form of intramolecular hydrogen bonded chelates (W. H. T. Davison, *J. Chem. Soc.*, 1951, 2456; R. Kavčič, B. Plesničar, and D. Hadži, *Spectrochim. Acta*, 1967, A **23**, 2483). Oxygen bases disrupt the chelate ring to form intermolecularly hydrogen bonded adducts (B. Plesničar, R. Kavčič, and D. Hadži, *J. Mol. Struct.*, 1974, **20**, 457).

The formation of the 1 : 1 complex, C, from the acid, A and the base, B, is represented by the equilibrium constant, $K(\mathrm{a})$ [equation (2)], where parentheses denote the activity

$$K(\mathrm{a}) = (\mathrm{C})/\{(\mathrm{A})(\mathrm{B})\} \qquad (2)$$

of A, B and C. Since the activities of these species are usually not known, this thermodynamic equilibrium constant is approximated by the conventional constant, K, defined by equation (3), where square brackets denote the equilibrium analytical concentrations. Equation (3) can also be

$$K = [\mathrm{C}]/\{[\mathrm{A}][\mathrm{B}]\} \qquad (3)$$

expressed in terms of the initial concentrations of the acid, $\mathrm{A_0}$, and the base, $\mathrm{B_0}$, in the reaction mixture [equation (**4**)]

$$K = [\mathrm{C}]/\{(\mathrm{A_0} - [\mathrm{C}])(\mathrm{B_0} - [\mathrm{C}])\} \qquad (4)$$

The following treatment of data is suitable for experiments in which the base is in excess. If the experimentally determined enthalpy of mixing of acid with base, calculated per mole of A which is initially present, is ΔH and that calculated per mole of C which is formed is ΔH_0 then $\Delta H_0/\Delta H$ [equation (5)] will tend to unity with increasing

$$\Delta H_0/\Delta H = \mathrm{A_0}/[\mathrm{C}] \qquad (5)$$

extent of reaction (1). Obviously, from calorimetric measurements we can determine directly only ΔH. Therefore, ΔH_0 must be determined by an appropriate method. Combination of equations (4) and (5) leads to equation (6)

$$1/\Delta H = 1/\Delta H_0 + 1/\Delta H_0[1/K + \mathrm{A_0}(1 - \Delta H/\Delta H_0)](1/\mathrm{B_0}) \qquad (6)$$

This equation is essentially the same as that reported by Bolles and Drago,[2] although written in another form with another definition of ΔH. The simplest way of obtaining ΔH_0 is that described by Arnett *et al.*,[3] *e.g.* to determine K by spectroscopic measurements and then calculate ΔH_0 from equation (6) knowing ΔH for various values of $\mathrm{A_0}$ and $\mathrm{B_0}$. Since we were not able to determine K of equation (1) spectroscopically with a reasonable degree of accuracy, another procedure was needed. Inspection of equation (6) shows that the slope of a plot of $1/\Delta H$ *vs.* $1/\mathrm{B_0}$ is determined by the expression in the square brackets. If the initial concentration of the acid, $\mathrm{A_0}$, is low enough, the product $\mathrm{A_0}(1 - \Delta H/\Delta H_0)$, which is always smaller than $\mathrm{A_0}$, becomes negligible in comparison with $1/K$. This suggests that the plot of $1/\Delta H$ *vs.* $1/\mathrm{B_0}$ should be almost linear. The extrapolation of the curve to $1/\mathrm{B_0} = 0$, where the correction term $\mathrm{A_0}(1 - \Delta H/\Delta H_0)$ becomes zero, should yield $1/\Delta H_0$ as the intercept and $1/(K\Delta H_0)$ as the initial slope.

Although this data analysis scheme is new in calorimetric studies, it is in principle analogous to double reciprocal plots introduced in some earlier studies (studies of adsorption isotherms, the Lineweaver–Burke plot in enzyme kinetics). Since such plots are prone to experimental errors, the applicability of the method was carefully tested. The pair 4-chlorophenol and *NN*-dimethylacetamide in $\mathrm{CCl_4}$ has been chosen for this purpose. The equilibrium constant for this system is relatively high, and so it was necessary to perform measurements at low acid concentration to satisfy the above mentioned condition. The calorimetric results were obtained by mixing 4·00 ml of 0·001 M 4-chlorophenol in $\mathrm{CCl_4}$ with 2·00 ml of *NN*-dimethylacetamide in $\mathrm{CCl_4}$, the concentration of which was progressively raised from 0·01 to 0·08 M. A good linear relationship between $1/\Delta H$ and $1/\mathrm{B_0}$, correlation coefficient > 0.99 (eight experimental values), supports the present data treatment method. Linear regression of the experimental data gave

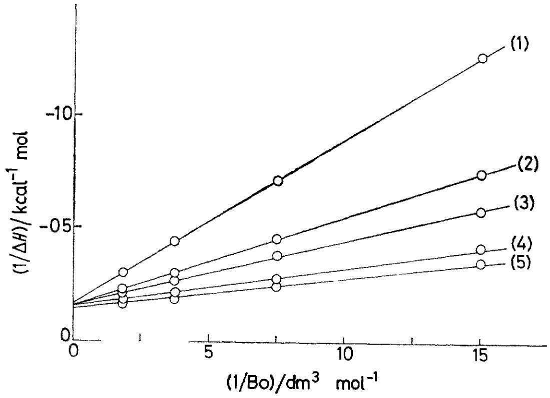


FIGURE. Inverse plot of the enthalpy of complex formation of peroxybenzoic acids with various oxygen bases in $\mathrm{CCl_4}$ at 25 °C. (1) *p*-chloroperoxybenzoic acid–THF, (2), *p*-chloroperoxybenzoic acid–DMF, (3), *p*-t-butylperoxybenzoic acid–DMAA, (4) *p*-chloroperoxybenzoic acid–DMAA, (**5**) *m*-chloroperoxybenzoic acid–DMAA.

TABLE. Calorimetric (equilibrium constants and enthalpies of complex formation) results for hydrogen bonded complexes of substituted peroxybenzoic acids with acceptor bases in carbon tetrachloride

Peroxy acid–acceptor base	K/l mol^{-1} [a]	$-\Delta H_0$/kcal mol^{-1} [a]	pK_a	$\Delta\delta_{\mathrm{OOH}}$/p.p.m. [b]
p-t-Butylperoxybenzoic acid–DMAA	4·0 ± 0·5	6·3 ± 0·1	>8[c]	
m-Chloroperoxybenzoic acid–DMMA	9·9 ± 0·5	7·1 ± 0·1	7·60[c]	
p-Chloroperoxybenzoic acid–DMMA	8·5 ± 0·5	6·6 ± 0·1	7·67[c], −0·36[d]	2·48 ± 0·05
p-Chloroperoxybenzoic acid–DMF	6·0 ± 0·5	6·0 ± 0·1	−1·5[e]	2·25 ± 0·05
p-Chloroperoxybenzoic acid–THF	2·3 ± 0·5	5·8 ± 0·1	−2·02[f]	0·99 ± 0·07

[a] Calorimetric measurements were carried out at 25 °C in a commercial LKB 100700 2 batch microcalorimeter with gold reaction cells. Into the larger compartment of the reaction cell 4·00 ml of 0·02 M peroxy acid in $\mathrm{CCl_4}$ was introduced, and into the smaller one 2·00 ml of base in the same solvent. The concentrations of base were 0·2, 0·4, 0·8 and 1·6 M. The reference cell was charged with 4·00 ml of $\mathrm{CCl_4}$ and 2·00 ml of the same base solution. Thus the enthalpy of dilution of the base was corrected for. Separate experiments showed the enthalpy of dilution of the peroxy acid to be negligible. No decomposition of peroxy acids under these conditions was detected. [b] $\Delta\delta_{\mathrm{OOH}} = \delta_{\mathrm{OOH}}\,(\mathrm{base}) - \delta_{\mathrm{OOH}}\,(\mathrm{CCl_4})$, solutions of *p*-t-butylperoxybenzoic acid (8%). [c] Data from J. F. Goodman, P. Robson, and E. R. Wilson, *Trans. Faraday Soc.*, 1962, **58**, 1846. [d] M. Liler 'Reaction Mechanisms in Sulfuric Acid and Other Strong Acid Solutions,' Academic Press, London, 1971. [e] P. Haake, R. D. Cook, and G. H. Hurst, *J. Am. Chem. Soc.*, 1967, **89**, 2650. [f] E. M. Arnett, E. J. Mitchel, and T. S. S. R. Murty, *J. Am. Chem. Soc.*, 1974, **96**, 3875.

$\Delta H_0 = (7{\cdot}6 \pm 0{\cdot}1)$ kcal mol^{-1} and $K = (205 \pm 20)$ l mol^{-1}, values which are in close agreement with those reported by Drago and Epley: $\Delta H_0 = (7{\cdot}3 \pm 0{\cdot}1)$ kcal mol^{-1} and $K = (207 \pm 25)$ l mol^{-1}.[4]‡

The enthalpies of complex formation for some substituted peroxybenzoic acids with oxygen bases are presented in the Figure. For all pairs studied good straight lines are observed in the inverse plot. First-order regression analysis of the data yielded the values for ΔH_0 and K in the Table. ΔH_0 values are sensitive to the acidity of the peroxy acid as well as the basicity of the oxygen base. Deshielding of OOH protons in n.m.r. spectra of peroxy acids in basic solvents (as compared with CCl_4 solutions) also correlates well with ΔH_0. A progressive reduction of reaction rates together with increasing enthalpies of activation for oxidation of cyclohexene with t-butylperoxybenzoic acid, when going from less basic to more basic solvents, also parallels the trend in ΔH_0 values. (CCl_4, $k_2 = 37{\cdot}5 \times 10^{-4}$ l mol^{-1} s^{-1}, $\Delta H^{\ddagger} = 10{\cdot}4$ kcal mol^{-1}; tetrahydrofuran, THF, $k_2 = 2{\cdot}80 \times 10^{-4}$ l mol^{-1} s^{-1}, $\Delta H^{\ddagger} = 14{\cdot}6$ kcal mol^{-1}; *NN*-dimethylformamide, DMF, $k_2 = 1{\cdot}61 \times 10^{-4}$ l mol^{-1} s^{-1}, $\Delta H^{\ddagger} = 15{\cdot}5$ kcal mol^{-1}; *NN*-dimethylacetamide, DMAA, $k_2 = 0{\cdot}80 \times 10^{-4}$ l mol^{-1} s^{-1}, $\Delta H^{\ddagger} = 16{\cdot}4$ kcal mol^{-1}; rate constants refer to 20 °C; kinetics were followed iodometrically, standard deviations in k_2, $\pm 3\%$). All these results strongly suggest that the strength of the intermolecular association between the peroxy acid and base is the major factor influencing the kinetics of oxidation with peroxy acids of olefins,[5] and most probably acetylenes[6] and sulphides[5b] as well, when oxygen bases are used as solvents.

We thank the Research Council of Slovenia for financial support of this work, and Mrs. A. Pohl for skilful technical assistance.

(*Received*, 13*th June* 1980, *Com.* 645.)

---

‡ 1 cal = 4·184 J.

[1] For a review, see: L. Lamberts, *Ind. Chim. Belg.*, 1971, **36**, 347.

[2] T. F. Bolles and R. S. Drago, *J. Am. Chem. Soc.*, 1965, **87**, 5015.

[3] E. M. Arnett, L. Joris, E. Mitchell, T. S. S. R. Murty, T. M. Garrie, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, 1970, **92**, 2365.

[4] R. S. Drago and T. D. Epley, *J. Am. Chem. Soc.*, 1969, **91**, 2883.

[5] (a) P. Renolen and J. Ugelstad, *J. Chim. Phys.*, 1960, **57**, 1976; (b) R. Curci, R. A. DiPrete, J. O. Edwards, and G. Modena, *J. Org. Chem.*, 1970, **35**, 740; (c) R. Kavčič and B. Plesničar, *ibid.*, p. 2033; (d) V. G. Dryuk, *Tetrahedron*, 1976, **32**, 2855.

[6] K. M. Ibne-Rasa, R. H. Pater, J. Ciabattoni, and J. O. Edwards, *J. Am. Chem. Soc.*, 1973, **95**, 7894.