

Relationship between Thermodynamical Parameters of Activated Complexes and Initial Reactants in the Reaction of Peroxides with Amines

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ABSTRACT: The linear dependence between heats of formation and entropies of initial reactants on the one hand and the corresponding thermodynamical parameters of activated complexes on the other hand was obtained for the

reaction of peroxides with amines. This relationship allows one to estimate such parameters for other similar reactions of amines with peroxides. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 641–642, 2003

INTRODUCTION

At present the mixtures of peroxides with amines as a class of reduction–oxidation systems are widely used for initiating the processes of radical polymerization. During the reaction between amines and peroxides, free radicals are easily generated under low temperatures. Such radicals act as effective initiators by the interaction of anions with these free radicals. Reaction of chain growth termination in the solution cage is then excluded before the desired degree of conversion. Sometimes during the choice of appropriate initiators, *a priori* estimation of thermodynamical and kinetic parameters (without experiments) is possible on the basis of structure analysis of reactants. We may apply quantum-chemical computational methods to solve this problem. *Ab initio* approximations are effective for calculations of potential energy barriers of only small molecules. Application of semiempirical methods for examination of these barriers is not, in general, acceptable. So we propose a way of useful estimation of thermodynamical and kinetic parameters of the reaction between amines and peroxides.

THEORETICAL

To determinate free activation energy ΔF^* , one must add activation entropy ΔS^* , which is calculated by

statistical methods with rough accuracy. Free activation energy of the reaction of peroxides with amines is determined as follows:

$$\Delta F^* = \sum \Delta F_{bc} - \sum \Delta F_{br} \quad (1)$$

where $\sum \Delta F_{bc}$ is a sum of free activation energy of the activated bonds in the activated complex, $\sum \Delta F_{br}$ is a sum of free energy of bonds of the initial reactants, which are changed during the reaction. Taking into account that free energy

$$\Delta F_r = \sum \Delta F_{br} + \sum \Delta F_{b'r'} \quad (2)$$

where $\sum \Delta F_{b'r'}$ is free bond energy (fixed both in reactants and activated complexes). Then,

$$\Delta F_c = \sum \Delta F_{bc} + \sum \Delta F_{b'r'} \quad (3)$$

It is postulated that free activation energy of the activated complex is a linear function of free energy of reactants. Then, taking into account that $\Delta F = \Delta H - T\Delta S$, we obtain the following relationships: $\Delta H_c = \alpha \Delta F_r$ (Figure 1) and $\Delta S_c = \beta \Delta S_r$ (Figure 2).

RESULTS AND DISCUSSION

On the basis of experimental data on activation energies (E) and preexponents (A) for the reactions of amines with peroxides on one side and theoretical studies of their ΔH_c , ΔS_c , ΔH_r , and ΔS_r on other side, we can determine next values:

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$$\Delta H^* = E + RT(T = 298K) \quad (4)$$

$$\Delta S^* = R[\ln A - \ln(kT/h)] \quad (5)$$

$$\Delta H_c = \Delta H^* + \Delta H_r \quad (6)$$

$$\Delta S_c = \Delta S^* + \Delta S_r \quad (7)$$

Values of ΔH_r and ΔS_r may be obtained by experiments as well. All our calculations were performed by the PM3 method.¹

Our statistical treatments lead to the following equations with linear dependences:

$$\Delta H_c = ((0.98 + (-) 0.02)) \Delta H_r + 11.44 + (-) 1.58$$

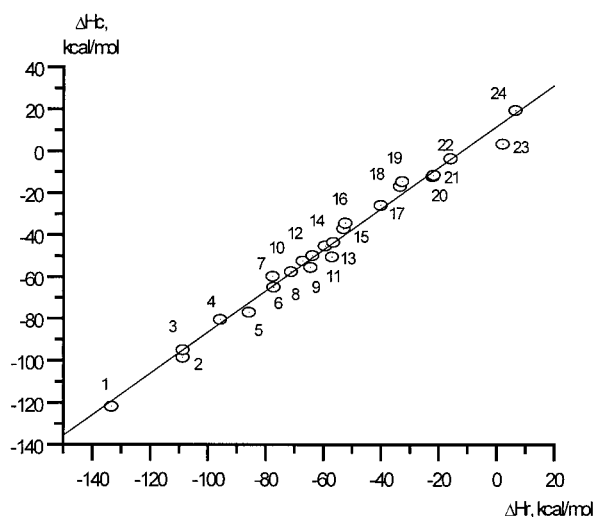


Figure 1 Dependence of values of ΔH_c on ΔS_r for peroxide reaction with amine. Key: (1) *p*-CH₃O-PB + cyclo-C₄H₈NH; (2) PB + (C₂H₅)₂NCH₂CH₂OH; (3) PB + (C₂H₅)₂NCH₂CH(CH₃)OH; (4) PB + *p*-CH₃C₆H₄N(CH₂)₂CH=CH₂; (5) PB + (*n*-C₄H₉)₂NH; (6) C₆H₅C(CH₃)₂OOH + cyclo-OC₄H₈NH; (7) PB + (C₂H₅)₂NCH₂CH(CH₃)OH; (8) PB + (C₂H₅)₃N; (9) *p*-VH₃O-PB + (C₆H₅)₂NH; (10) PB + (C₂H₅)₂NH; (11) PB + cyclo-C₅H₁₀NH; (12) C₆H₅C(CH₃)₂OOH + (C₂H₅)₃N; (13) PB + cyclo-C₄H₈NH; (14) PB + *p*-CH₃C₆H₄N(CH₃)₂; (15) C₆H₅C(CH₃)₂OOH + (C₂H₅)₂NH; (16) C₆H₅C(CH₃)₂OOH + cyclo-C₅H₁₀NH; (17) C₆H₅C(CH₃)₂OOH + (C₂H₅)₃N; (18) C₆H₅C(CH₃)₂OOH + (C₂H₅)₂NH; (19) C₆H₅C(CH₃)₂OOH + cyclo-C₅H₁₀NH; (20) PB + C₆H₅CH₂NH₂; (21) PB + C₆H₅N(CH₃)₂; (22) PB + C₆H₅NHCH₃; (23) *p*-NO₂-PB + (C₆H₅)₂NH; (24) PB + (C₆H₅)₂NH.

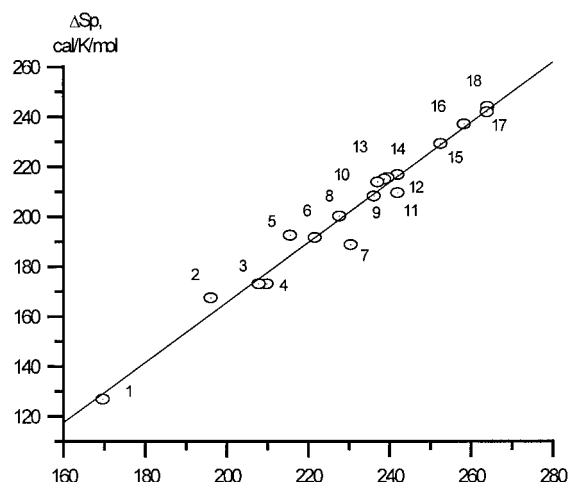


Figure 2 Dependence of values ΔS_c on the sum of ΔS_r for peroxide reaction with amine: Key: (1) C₆H₅C(CH₃)₂OOH + cyclo-C₅H₁₀NH; (2) C₆H₅C(CH₃)₂OOH + (C₂H₅)₃N; (3) PB + cyclo-C₄H₈NH; (4) PB + cyclo-C₅H₁₀NH; (5) C₆H₅C(CH₃)₂OOH + (C₂H₅)₂NH; (6) [C₆H₅C(O)O-]₂ + C₆H₅CH₂NH₂; (7) PB + (C₂H₅)₃N; (8) [*p*-CH₃C₆H₄C(O)O-]₂ + cyclo-C₄H₈NH; (9) [*p*-CH₃OC₆H₄C(O)O-]₂ + cyclo-C₄H₈NH; (10) PB + (C₂H₅)₂NCH₂CH₂OH; (11) PB + (C₆H₅)₂NH; (12) PB + *p*-CH₃C₆H₄N(CH₃)₂; (13) PB + (C₂H₅)₂NCH₂C(CH₃)HOH; (14) PB + (C₂H₅)₂NCH₂CH₂OH; (15) [*p*-ClC₆H₄C(O)O-]₂ + (C₆H₅)₂NH; (16) [*p*-CH₃C₆H₄C(O)O-]₂ + (C₆H₅)₂NH; (17) PB + *p*-CH₃C₆H₄N(CH₃)₂; (18) [*p*-CH₃OC₆H₄C(O)O-]₂ + (C₆H₅)₂NH.

$$R = 0.9937 \quad (8)$$

$$\Delta S_c = ((1.20 + (-) 0.05)) \Delta S_r + 74.57 + (-) 11.47$$

$$R = 0.9754 \quad (9)$$

where R is a correlation coefficient.

If values of ΔH_r and ΔS_r are known for reactants, the values of ΔH_c and ΔS_c for the activated complex and its activation parameters are simply obtained as a difference between activated and initial states.

Experimental parameters of activation energies (E) and preexponents ($\ln A$) were taken from the handbook.²

References

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