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UTILITY OF KINETIC ANALYSIS IN THE DETERMINATION OF REACTION MECHANISM

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Thermal analysis has a long and prominent role in the characterization of materials, including polymeric materials. Kinetic studies in one form or another have often been employed in an attempt to assess stability, predict lifetime, establish degradation pathway, or project suitable processing conditions. The results of such studies have often formed the basis for the proposal of the 'mechanism' of reaction. This despite the fact that the reaction being observed is often unknown or is not a single process but rather several parallel or consecutive events. This latter is particularly true for 'variable temperature kinetics'. The utility/value of such exercises is marginal at best and contributes nothing to an understanding of the mechanism of any of the reactions involved.

Keywords: *activated complex structure, activation parameters, thermal methods in kinetic studies, kinetics, thermogravimetry*

Introduction

Kinetic studies of one kind or another, some genuine some not, are widely utilized in the characterization of thermally-induced events in a variety of materials, most particularly polymeric materials. Such studies provide information that may be useful for a variety of purposes particularly for comparisons within a series of similar materials, for quality control, to predict suitable process conditions, or to project an expected use lifetime [1]. All of these are valuable in their own right and when used with proper care can have great utility. However, when attempts are made to project modes of reaction based on such studies the results are rarely of much consequence. In the best case, mischief often results and in the worst, downright misrepresentation can occur.

Discussion

The mechanism of reaction is a detailed description of the molecular events which correspond to progress along the reaction coordinate, i.e., molecular changes, atom reorganizations, which account for the transformation of reactants to products. The essential feature of any mechanism is the structure of the rate-determining activated complex. Since an activated complex exists in a transition state energy level and is exceedingly short-lived (one vibrational lifetime), it cannot be observed spectroscopically or trapped chemically. Therefore, its structure must be established by indirect methods. Intermediates present may be characterized by direct spectroscopic observation or trapped with a suitable reagent to form a stable structure which may be fully characterized and from which the structure of the intermediate may be deduced. For polymers in the melt either of these approaches may present a challenge. Before any mechanism study is initiated, the reaction itself must be detailed. In particular, the products of reaction must be rigorously identified. Sometimes not so obviously, the identity of the reactants must also be known, i.e., the reactants must be pure materials. Questions to be answered include: is the reaction concerted or stepwise?; are intermediates present?; etc.

Kinetics are facts: concentration (or some suitable representation of concentration – absorbance, peak area, mass change, etc.) and time data. That is, kinetics reflect the change in concentration of a reactant (or product) species as a function of time. This is usually observed under a carefully controlled set of conditions. To obtain a reliable rate constant (the constant which converts the concentration, time proportionality to an equality), the temperature at which the reaction is observed must be controlled within very narrow limits. The rate constant is one of the quantities useful in characterizing a reaction. Another is the rate law, the expression which describes the rate of change in concentration as a function of time. This expression is a product of the rate constant and molar concentrations raised to appropriate powers. For a particular reactant the exponent for its concentration in the rate law is referred to as the reaction order for that species. The overall order for the reaction is the sum of the exponents in the rate law. It should be noted that there

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is no necessary relationship between order and the observed stoichiometry of reaction, i.e., order must be determined experimentally. Further, there is no relationship between order and the molecularity of the reaction. Molecularity refers to the number of reactant species which come together to form the rate-determining activated complex for reaction and is apparent only from a knowledge of the mechanism of reaction, i.e., a knowledge of the structure of the activated complex.

It has been asserted that, 'kinetic studies, in one guise or another, have historically made the greatest contribution to the elucidation of reaction mechanisms' [2]. Why is this so? The simple direct answer is that the temperature dependence of the rate constant reveals something about activated complex structure. This is usually expressed in terms of the activation parameters for the reaction. The enthalpy of activation, $\Delta H^{\neq}$, provides a reflection of the height of the barrier to reaction while the entropy of activation, $\Delta S^{\neq}$, reflects the shape of the same barrier, i.e., it reflects the relative order in the activated complex (transition state energy level) *vs.* that in reactants (ground state energy level). In the absence of matrix effects, $\Delta S^{\neq}$ would be negative for a unimolecular decomposition reaction (often observed for polymer degradation) and positive for a bimolecular addition reaction. Both the sign and magnitude of $\Delta S^{\neq}$ provide useful information about the structure of the activated complex. Both of these parameters may be readily extracted if the rate constant for reaction can be determined at several temperatures. This is most reliably done using an isothermal technique, i.e., by determining the rate constant at several fixed, well-defined temperatures [3]. Then a plot of $\ln k/T$ (where k is the rate constant and T the absolute temperature) *vs.* $1/T$ yields a slope of $-\Delta H^{\neq}/R$ (where R is the gas constant, 1.9872 cal mol^{-1} K^{-1} or equivalent). The activation entropy, $\Delta S^{\neq}$ may then be calculated at any given temperature from the expression

$$\Delta S^{\neq}/R=\ln k-\ln(k/h)-\ln T+\Delta H^{\neq}/RT$$

and since (k/h) is the ratio of the Boltzman and Planck constants, it may be rewritten as

$$\Delta S^{\neq}/R=\ln k-23.760-\ln T+\Delta H^{\neq}/RT$$

For a variety of reasons, usually having to do with temperature control or other reaction variables, it is common practice to plot $\ln k$ *vs.* $1/T$. The slope of this plot is $-E_a/R$ where E_a is the Arrhenius activation energy. This quantity approximates $\Delta H^{\neq}$ (the difference is given by RT for a simple first order process; at room temperature this represents approximately 600 cal mol^{-1} – for many experiments the limits of temperature control contribute a larger error). Because the isothermal technique is somewhat tedious and time consuming, a number of variable temperature techniques for the determination of E_a have been developed [4, 5]. For a single, well-defined process, this approach works quite well [6]. However, the value of E_a obtained for processes involving many reactions occurring simultaneously (as is often the case for the degradation of many materials, including polymers, both natural and products of synthesis) is of limited utility. It may be used in a limited way for comparisons among lots of materials, etc., but is no value for the determination of mechanism since no particular reaction can be identified. The rather lax reporting of 'activation energies' for such processes has contributed much to the somewhat controversial acceptance of variable temperature techniques. It is not the methods which are at fault but rather the uses to which they have been put. As noted above, for a well-defined reaction, any of the variable temperature appoaches can provide acceptable values for E_a. However, it is simply not creditable to report or discuss an activation energy or mechanism for a process involving multiple reactions occurring simultaneously.

Conclusions

Kinetic studies are an essential component of any mechanism study. The activation parameters derived from such studies provide information about activated complex structure (the molecular species present in the transition state – the highest energy level on a two-dimensional reaction coordinate diagram or an area in phase space on a three-dimensional reaction potential plot). This is the most crucial information required for the formulation of mechanism. For kinetic studies to have validity they must be carried out for a well-defined, single reaction. Finally, kinetic studies are an important component, but only one component, of a mechanism study. Alone kinetic studies rarely provide a complete description of the mode of reaction. Information from kinetic studies must be combined with information derived from a variety of other techniques to permit a meaningful description of molecular/atomic events which correspond to the conversion of reactants to products.

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Dedication

This paper is dedicated to the memory of Professor David Dollimore who always approached a discussion of kinetics with relish. We will miss his enthusiasm, his dedication to thermal analysis, his gentle wisdom, and his friendship.

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