External diffusion limitations in initiator decomposition in heterogeneous media*

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The process of initiator decomposition in media, where it has a limited solubility will be influenced by external diffusional limitations. A theoretical framework has been built up to analyse such a process. An experimental investigation of AIBN decomposition has been undertaken and it is shown how falsified kinetics may result in the presence of diffusional effects. A method for extracting intrinsic kinetic information for both single bond and multibond initiators has been demonstrated.

Keywords Diffusion limitations; initiator decomposition; heterogeneous media; solubility; kinetics

INTRODUCTION

Studies in initiator decomposition kinetics are of great pragmatic significance since the decomposition of initiator and subsequent initiation are important steps in the kinetics of polymerization. Several efforts have been made in the past[1-4], where the solvent and viscosity effects on the kinetics of decomposition have been studied. Studies have been conducted with reference to both multibond initiator systems (such as azobisisobutyronitrile, which undergo simultaneous scission of two C–N bonds) and single bond initiator systems (such as *p*-nitrophenylazotriphenyl methane (NAT), which undergo scission of C–N bonds in a sequential manner).

Diffusional effects occurring in the case of a one bond initiator have recently been comprehensively studied by Kulkarni and Mashelkar[5]. Here a single bond initiator such as NAT decomposes to yield fragments which undergo a cage recombination process. This is a diffusion controlled process. Kulkarni and Mashelkar[5] elucidated the role of diffusional resistance in such cases by proposing the concept of 'microviscosity'. In a recently published study, Rafikov *et al.*[6] observed a fourfold decrease in the rate constant of AIBN at 71.2°C with an increase in the viscosity of the dimethylformamide (DMF)–glycerol blends from 0.5 to 20 cP. AIBN is a multibond initiator and hence the viscosity of the medium should have no effect on the decomposition kinetics. In view of this, the results of Rafikov *et al.*[6] indicating a rapid decrease in the rate of decomposition of AIBN with an increase in the viscosity of DMF–glycerol blends over a narrow range appeared surprising.

Our studies on the decomposition kinetics of AIBN at higher concentration of glycerol revealed some interesting features[7]. The initiator is only sparingly soluble in the medium and the rate of evolution of nitrogen remained constant and did not fit into a first order rate equation. Since the initiator is not completely soluble in the medium, the concepts of a homogeneous chemical reaction cannot be applied. Indeed, the overall decomposition process is now controlled by three steps: (a) dissolution of the initiator in the solvent; (b) decomposition of dissolved initiator; and (c) desorption of nitrogen out of the medium. Limited solubility of the initiator thus imposes external diffusion limitations. To our knowledge, no such studies with relevant framework for analysis have appeared in the literature in the past.

In this paper, we will develop a theoretical framework to model such a reaction system and provide experimental data to verify the model. Apart from resolving the apparent conflict arising out of the observations of Rafikov *et al.*[6] this study may be helpful in providing a basis for the analysis of initiator decomposition in solvent–non-solvent systems or in systems where the initiator has limited solubilities.

THEORETICAL FRAMEWORK

Consider decomposition of an initiator such as AIBN in a medium in which it is sparingly soluble. The overall process now consists of dissolution of AIBN particles in the medium followed by decomposition of the species, which is in solution. It can be assumed that the main diffusional resistance lies in a thin film around the particle. The mass transfer coefficient for the dissolution step is denoted by k_s. The rate of dissolution (which is a mass transfer controlled process) is given by

$$R = k_s a_p (C^* - C_b) \qquad (1)$$

where R denotes the rate of dissolution process, where a_p denotes the area of the particles per unit volume, C^* denotes the solubility in the solution and C_b, the bulk concentration at any instant of time.

The initiator dissolved in the medium then undergoes decomposition, which is a first order reaction. The rate of decomposition is given by

$$R = k C_b \qquad (2)$$

where k denotes the first order rate constant. At steady

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state the rate of dissolution and rate of decomposition would be identical. Eliminating C_b from equations (1) and (2) we obtain

$$\frac{C^*}{R} = \frac{1}{k_s a_p} + \frac{1}{k} \tag{3}$$

If we assume that the initiator particle is spherical with diameter d_p, density ρ_p and that the total mass of particles per unit volume is m, then

$$a_p = \frac{6m}{\rho_p d_p} \tag{4}$$

Substitution of this value of a_p in equation (3) results in

$$\frac{C^*}{R} = \left[\frac{\rho_p d_p}{6m}\right]\frac{1}{k_s} + \frac{1}{k} \tag{5}$$

The value of the mass transfer coefficient for dissolution step k_s is determined by the molecular diffusion coefficient (D) and the hydrodynamics. The influence of hydrodynamics will be determined by the stirrer design and speed as well as the geometry of the reactor. A number of correlations exist in literature which correlate k_s with the parameters mentioned above. The correlation presented by Levins and Glastonbury[8] has been extensively used. This correlation is given as

$$\frac{k_s d_p}{D} = 2 + 0.47\left[\frac{{d_p}^{4/3} e^{1/3} \rho}{\eta}\right]^{0.62}\left[\frac{d_I}{d_T}\right]^{0.17}\left[\frac{\eta}{\rho D}\right]^{0.36} \tag{6}$$

Here e denotes the energy supplied per unit mass, ρ is the density of the solution, η is the viscosity of the solution, d_I is the diameter of the impeller and d_T denotes the diameter of the vessel.

In the above equation the first term denotes the contribution from molecular diffusion and the second term represents the influence of convection on the mass transfer process. Equations (5) and (6) together represent a model for initiator decomposition in a well stirred reactor. However, when power inputs are low, e.g. as in the laboratory studies (wherein a magnetic stirrer device is used), the contribution of the convective term is negligible. Under such conditions the mass transfer coefficient is predominantly governed by molecular diffusion and given as

$$k_s = \frac{2D}{d_p} \tag{7}$$

Combining equations (5) and (7), we have

$$\frac{C^*}{R} = \frac{\rho_p {d_p}^2}{12Dm} + \frac{1}{k} \tag{8}$$

According to equation (8), under otherwise identical conditions, if the overall rate of reaction is studied as a function of the initiator loading (m), a linear plot would result when $\left(\frac{C^*}{R}\right)$ is plotted against $\left(\frac{1}{m}\right)$.

The treatment is strictly applicable to multibond initiators, such as AIBN, wherein the decomposition constant is independent of the diffusional resistances in the homogeneous medium[5].

There exists another class of initiators wherein the decomposition does not occur by simultaneous scission of two C–N bonds but by a sequential mechanism. In such a case the mechanism of decomposition of the initiator in a homogeneous medium can be expressed as:

$$\begin{tikzcd} \text{Initiator} \arrow[r, shift left, "k_1"] & (\text{cage } 1) \arrow[l, shift left, "k_{-1}"] \arrow[r, "k_d"] \arrow[d, "k_\beta"] & \text{free radicals} \\ & (\text{cage } 2) + \text{small molecules} & \end{tikzcd} \tag{9}$$

Following Pryor and Smith[4] it can be demonstrated that in such a case the overall rate could then be deduced as:

$$\frac{C^*}{R} = \frac{1}{k_1} + \left(\frac{k_{-1}}{k_1}\right)\left(\frac{1}{k_d + k_\beta}\right) + \frac{1}{k_s a_p} \tag{10}$$

It is evident that in such a case both external (k_s) and homogeneous phase (k_d) diffusional limitations play a role.

EXPERIMENTAL

Decomposition of AIBN was followed by the nigrogen evolution technique. The apparatus consisted of a jacketed vessel connected to a gas burette by a capillary and had provision for purging nitrogen. The experimental procedure was slightly modified to eliminate certain drawbacks of the techniques used earlier.

A known quantity of solvent under investigation was taken in the jacketed vessel and was brought to the temperature of experiment. Nitrogen was then bubbled through the solvent, which was magnetically stirred. Flushing of nitrogen was stopped after half an hour. The liquid level in the gas burette was adjusted to zero and a weighed quantity of the initiator was introduced into the vessel. The volume of nitrogen evolved and burette temperature were noted at definite time intervals. The amount of initiator decomposed at the end of time was calculated from the rate of nitrogen evolution. Each experiment was repeated three times to confirm the reproducibility of the results.

Solubility of AIBN

Solubility of AIBN (C^*) was determined by spectrophotometry. To ascertain that a change of medium composition does not introduce an error in measurement, absorbance of AIBN as a function of AIBN concentration was studied in media of varying glycerol concentrations in which the initiator was completely soluble. It was observed that a change in the composition did not affect the molar extinction coefficient of AIBN.

The medium in which solubility of AIBN was to be determined was thermostated to the desired temperature. An excess of AIBN was added. The heterogeneous mass was stirred magnetically in an inert atmosphere. Aliquots were removed at various time intervals and filtered through the sintered disc funnels of specific porosity. The filtrate was quidkly transferred to the u.v. cell and the absorbance at 28 000 cm^{-1} was recorded. Concentration

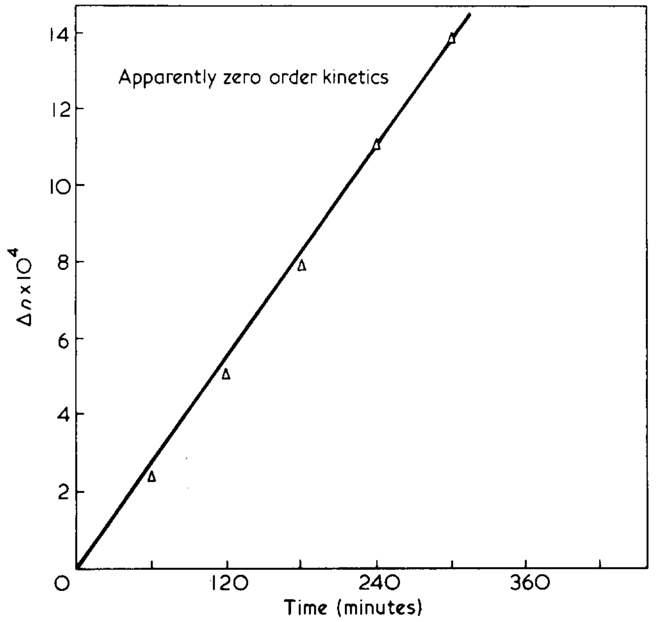

Figure 1 Apparently zero order kinetics of heterogeneous phase decomposition of AIBN (at 71.2°C in DMF/glycerol blend, 20/80)

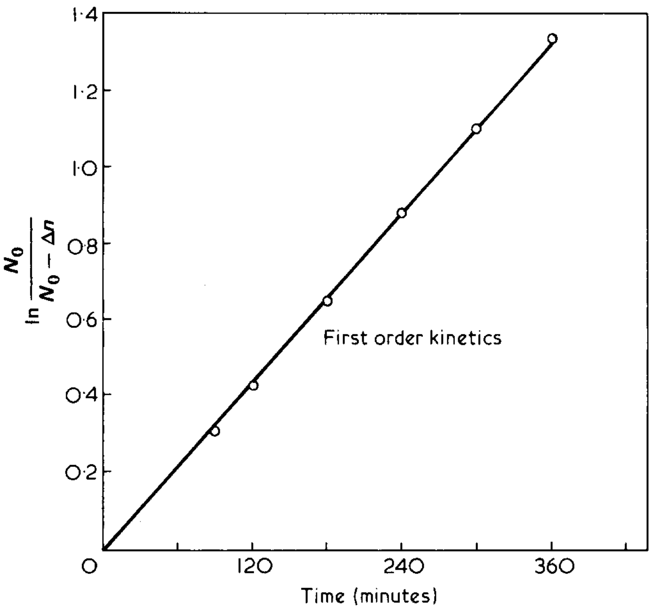

Figure 2 First order kinetics of homogeneous phase decomposition of AIBN (at 71.2°C)

and hence solubility of AIBN was then calculated from the knowledge of molar extinction coefficients.

RESULTS AND DISCUSSION

It is apparent from the theoretical framework presented in the earlier section that in the presence of external diffusional limitations, when the pseudo-steady-state assumption could be made, the reactant concentration in the bulk would be kept at a constant value. Therefore the rate of decomposition will be constant. Thus the nitrogen evolution process will be such that the rate would be independent of time. Alternatively, in the total absence of external diffusional limitations, the process is truly kinetically controlled and therefore with the assumption of first order kinetics we should have a linear plot when $\ln\left[\frac{N_0}{N_0-\Delta n}\right]$ is plotted vs. t, where N_0 is the number of moles of AIBN at the start of the experiment and Δn is the number of moles decomposed up to the time t.

Figures 1 and *2* show two such plots for two cases. The first figure corresponds to the DMF–glycerol blend, where the external diffusional limitations play an important role. Here Δn vs. t gives a linear plot showing that the rate is constant. The second figure shows initiator decomposition in pure DMF, where there are no external diffusional limitations and the rate changes in such a way that the process is a first order one. It is interesting to note here that when an experimenter observes a constant rate of decomposition, lack of appreciation of the presence of external diffusion limitations could give an erroneous impression of a kinetically controlled zeroth order reaction, although in practice the reaction may be kinetically a first order reaction, as in the case of the DMF–glycerol blend studied by us.

In order to isolate the intrinsic kinetic rate constant from the observed reaction rates, the overall rate of decomposition was studied as a function of loading and composition of the DMF–glycerol blends. *Figure 3* shows a plot of reciprocal rate of decomposition vs. reciprocal loading. As per the predictions of equation (8), a plot of $\frac{C^*}{R}$ vs. $\frac{1}{m}$ should be linear with slope $\frac{\rho_p d_p^2}{12D}$ and the intercept equal to the reciprocal of the intrinsic rate constant k_1. It can be seen from *Figure 3* that the trend predicted by equation (8) is borne out.

It is worth while to check the approximate magnitude of individual parameters. The particle size (d_p) of initiator used was of the order of 1 mm. The density (ρ_p) was 1 g cm^{-3}. Based on the data presented in *Figure 3* it is seen that the slope equals $\frac{\rho_p d_p^2}{12D}$ and substituting the values of ρ_p and d_p we have $D=2\times10^{-6}$ cm^2 s^{-1}. There is no reliable information in the literature on the diffusion coefficient of AIBN in viscous media such as DMF–glycerol blends. However, based on the existing literature,

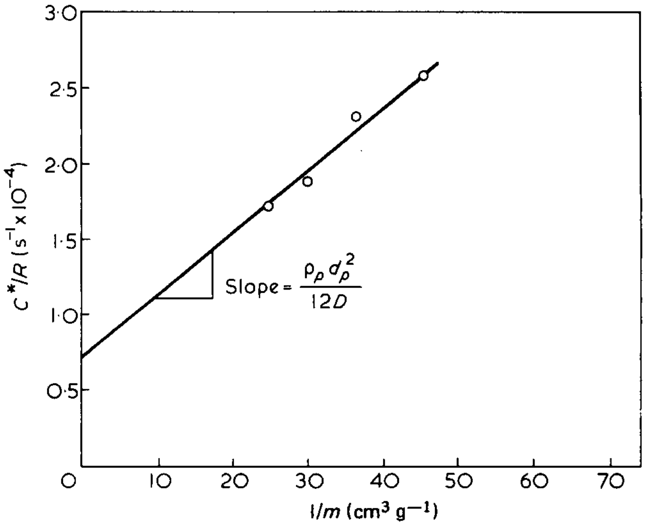

Figure 3 Effect of loading on the rate of decomposition of AIBN in heterogeneous phase (at 71.2°C in DMF/glycerol blend, 20/80)

Table 1 Evaluation of intrinsic rate constant from observed rates of decomposition of AIBN in viscous media

Medium	Solubility C^* (g mol cm^{-3})	R R (g mol cm^{-3} s^{-1})	η(cP)	k_1 (s^{-1})
DMF/glycerol				
100/0				6.20×10^{-5}
20/80	9.09×10^{-5}	6.76×10^{-9}	18.6	1.60×10^{-4}
15/85	6.76×10^{-5}	5.38×10^{-9}	25.0	2.77×10^{-4}
5/95	4.84×10^{-5}	3.64×10^{-9}	31.4	3.46×10^{-4}

(Temperature = 71.2°C)

a value of 10^{-6} cm^2 s^{-1} could be anticipated. Thus the order of magnitude estimated appears to be reasonable.

We now evaluate the intrinsic rate constant (k_1) for decomposition of AIBN in various DMF–glycerol blends. This could be easily done with the help of equation (8), if we had recourse to the exact values of diffusivity of AIBN in different blends. In the absence of such information, the following procedure was used.

For fixed values of ρ_p, d_p and m, equation (8) becomes:

$$\frac{C^*}{R} = \frac{\alpha}{D} + \frac{1}{k_1} \tag{11}$$

where α is a constant. There is strong evidence in the literature[5,8,9] which shows that for such viscous media, diffusivity varies as $\eta^{-2/3}$ or

$$\frac{D}{D_{\text{ref}}} = \frac{\eta_{\text{ref}}^{2/3}}{\eta^{2/3}} \tag{12}$$

where D_{ref} and η_{ref} denote the diffusivity in and viscosity of the reference system. Then from equation (11), we get

$$\frac{C^*}{R} = \left[\frac{\alpha}{D_{\text{ref}}\eta_{\text{ref}}^{2/3}}\right]\eta^{2/3} + \frac{1}{k_1} \tag{13}$$

Using the system DMF/glycerol (20/80) as the reference medium, the bracketed term in equation (13) could be considered to be a constant at a given temperature. The value of intrinsic rate constant can then be determined from the knowledge of solubility and observed reaction rate. Such calculations were done for all the solutions studied in this work. The data are summarized in *Table 1*. It is observed that there is an increase in the kinetic rate constant with increase in glycerol concentration. This represents the true influence of glycerol on the intrinsic rate constant.

CONCLUSION

A theoretical framework has been built up on the basis of which the kinetics of decomposition of a multibond initiator can be studied in viscous media in the presence of external diffusion limitations. The possibility of obtaining falsified kinetic data has been emphasized. An experimental study of AIBN decomposition in the presence of external diffusion limitations has been conducted and with the help of the model developed, the intrinsic kinetics has been deduced.

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