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A STUDY OF RAPID REDOX INITIATION BY REACTION CALORIMETRY *

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ABSTRACT

The rate of radical formation, ρ_i, obtained by using a rapid redox system based on *t*-butyl hydroperoxide, vanadium(IV) and ascorbic acid was studied under emulsion polymerization conditions using a calorimetric reactor.

The rate of radical formation was found to follow the expression:

$$\rho_i = k[VO^{2+}][(CH_3)_3COOH]$$

with $k = 139$ l mol^{-1} s^{-1} at 50°C and an activation energy of 94 kJ mol^{-1}.

Under weakly acidic conditions (pH 3–5) and in the presence of an excess of ascorbic acid, the five-valent vanadium formed in the redox reaction was immediately reduced back to VO^{2+}. Under these conditions, a rapid pseudo first order reduction of the hydroperoxide could be maintained at low vanadium concentrations. Using redox systems of this kind, emulsion polymerizations can be carried out at closely controlled rates of initiation.

INTRODUCTION

Both practically and scientifically, it may be of great interest to perform emulsion polymerization processes at controlled initiation rates. This can be done by using rapid redox initiator systems and continuously feeding one of its rate-determining components to the reactor. The other components of the redox system should be present in the reactor from start. If the redox system is sufficiently rapid, the rate of initiation would be proportional to the rate at which the rate determining component is fed to the reactor. In the design of safe and dependable initiator systems of this type, methods to study the kinetics of such systems under as near practical conditions as possible would be most valuable.

This paper reports on the use of a calorimetric reactor to study the decomposition kinetics of a redox initiator system based on *t*-butyl hydro-

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peroxide, vanadium(IV) and ascorbic acid. The rate constant governing the primary radical formation was determined under normal emulsion polymerization conditions. In the actual experiments, the hydroperoxide was pumped into the reactor as an aqueous solution. Its rate of reaction was inferred from the decrease in polymerization rate observed after interrupting the feed of the hydroperoxide. By considering the dynamic properties of this reactor the kinetics could be studied under conditions giving very high rates of initiation. These experiments were carried out using vinyl chloride (VCM) as the monomer. This monomer was chosen because its rate of emulsion polymerization during stage II would be proportional to the square root of the rate of initiation [1,2].

THE CALORIMETRIC REACTOR

The experiments were carried out in a 200 cm^3 reactor, similar in construction to that described in ref. 3. The reactor was equipped with an efficient stirrer, a thermistor-based sensor for measuring interior reactor temperature and a small heater for calibration purpuses. Peltier coolers were mounted on the reactor exterior. The hydroperoxide solution was introduced via a rubber membrane fitting situated in the bottom flange of the reactor. The feed rate was controlled by a precision syringe pump.

During the experiments, the reactor was completely submerged in a well-thermostated water bath, which served as the thermal reference. By running a constant electrical current through the Peltier coolers, the autoclave content was always kept at a slightly lower temperature than that of the thermal reference. This insured that neither the monomer nor the water condensed on the reactor lid, which would have influenced the reactor's heat flow properties [3].

The reactor was operated as a passive calorimeter, i.e. the power generated in the autoclave in excess of that generated by the stirrer was inferred from the increase in the autoclave temperature. The properties of the calorimeter were modelled by eqn. (1), which expresses the heat balance over the autoclave (1a) and the temperature sensor (1b):

$$P_A = \theta_A \cdot K_{A,R} + C_A \cdot \frac{d\theta_A}{dt} \tag{1a}$$

$$\theta_A K_{A,S} = \theta_S K_{A,S} + C_S \cdot \frac{d\theta_S}{dt} \tag{1b}$$

where P_A symbolizes the thermal power generated in the autoclave, θ represents temperature, C total heat capacity and K total heat transfer coefficients for the exchange of heat between different parts of the reactor system. The subscripts indicate the following: A, autoclave; R, reference bath; S, temperature sensor.

Eliminating θ_A from eqn. (1) results in eqn. (2)

$$P_A = K_{A,R}\left(\theta_S + \left(\frac{C_S}{K_{A,S}} + \frac{C_A}{K_{A,R}}\right) \cdot \frac{d\theta_S}{dt} + \frac{C_S}{K_{A,S}} \cdot \frac{C_A}{K_{A,R}} \cdot \frac{d^2\theta_S}{dt^2}\right) \tag{2}$$

The heat flow properties of the reactor can thus be described by two time constants, $C_S/K_{A,S}$, $C_A/K_{A,R}$ and the total heat transfer coefficient, $K_{A,R}$. These parameters vary slightly with choice of experimental conditions: e.g. with stirring speed, liquid volume in the reactor and liquid viscosity. Thus, the reactor was calibrated between each experiment. Calibration was done by generating a square-shaped power pulse in the reactor's electrical heater. The response, θ_S, was then fitted to eqn. (2) by a curve fitting procedure. In this work, the individual experiments were of such short duration that variations in the heat transfer properties during an experiment could be safely neglected.

The total thermal power, P_A, developed in the reactor during a polymerization experiment consists of three individual power terms, and can be expressed thus:

$$P_A = P_{CHEM} + P_{PHYS} + P_{AGIT} \tag{3}$$

where, P_{CHEM} represents the power associated with chemical reactions, P_{PHYS}, the power associated with physical processes (e.g. mass transfer between phases) and P_{AGIT}, the power associated with agitation.

Because of the short reaction time used in this work, the last two terms of eqn. (3) can be regarded as constant and can be included in the base-line correction. If the power associated with the reactions of the initiator system is neglected, the rate of polymerization can be calculated as

$$R_P = -\frac{P_A}{\Delta H_p} \tag{4}$$

where ΔH_p is the enthalpy of polymerization.

The reactor system contained a data recording system, which sampled the temperature, θ_S, at constant time intervals (usually 1 s^{-1}). From this data, P_A was calculated using eqn. (2). The validity of eqn. 2 was tested in experiments where electrical power pulses of different shapes were generated in the internal heater. These tests showed that first order reactions with half-lives down to about 10 s could be studied with reasonable accuracy.

THEORY

According to Ugelstad and Hansen [1], emulsion polymerization of vinyl chloride under interval II conditions (the total particle number, N, is constant and liquid monomer is present as a separate phase) obeys the following equation

$$R_p = \left(\frac{k_p[\mathrm{M}]_p}{N_A}\right)\rho_i^{1/2} \cdot \left(\frac{V_p}{2k_t^*} + \frac{N}{2k_d}\right)^{1/2} \tag{5}$$

where k_p, k_t^* and k_d are the rate constants for propagation, termination and for desorption of radicals from the particles, $[\mathrm{M}]_p$ the monomer concentration in the particles, N_A Avogadro's number, ρ_i the rate of radical formation and V_p the total volume of particles. The rate constant for radical desorption has been expressed as

$$k_d = k_d' \cdot \left(\frac{N}{V_p}\right)^{2/3} \tag{6}$$

where k_d' should be independent of particle size.

During interval II, k_p, k_t^*, k_d' and N are constant. If the change in conversion is small, as was the case in the present experiments, $[\mathrm{M}]_p$ and V_p can also be regarded as constant, and eqn. (5) simplifies to

$$R_p = C_1 \cdot \rho_i^{1/2} \tag{7}$$

where C_1 is a constant.

The rate of radical formation by a redox couple can be written

$$\rho_i = k[\mathrm{Red}][\mathrm{Ox}] \tag{8}$$

where [Red] and [Ox] are the concentrations of the reducing and oxidating components of the redox system. If [Red] is kept constant, ρ_i varies with time by the following:

$$\rho_i = k[\mathrm{Red}][\mathrm{Ox}]_{t=0} \exp(-k[\mathrm{Red}]t) \tag{9}$$

where k[Red] can be considered as a pseudo first order rate constant.

Substituting eqn. (9) into eqn. (7) and taking logarithms gives

$$\ln(R_p) = \text{constant} - \frac{k[\mathrm{Red}]t}{2} \tag{10}$$

The rate constant, k, can thus be calculated from the slope of the line obtained when $\ln(R_p)$ is plotted as a function of time.

EXPERIMENTAL

The reactor was charged with 100 cm^3 of a PVC seed latex which had been treated to remove the initiator and all catalytically active metal ions remaining in the latex after its preparation. The latex was stabilized by sodium lauryl sulphate (SLS). After oxygen removal by evacuation, degassed aqueous solutions of $\mathrm{VOSO_4 \cdot 5H_2O}$ and ascorbic acid were added. The initial concentration of ascorbic acid was 0.01 $\mathrm{mol/l^{-1}}$ water. The reaction mixture was brought to pH 4.7 by adding an acetic acid/sodium acetate buffer. The total acetate content of the reaction medium was 0.05 M. Finally, freshly distilled VCM was added in an amount giving a VCM/PVC ratio of about 4. When the reactor reached a constant temperature, it was calibrated. The kinetic experiments were then started by feeding an aqueous solution of *t*-butyl hydroperoxide into the reactor at constant speed. As the rate of polymerization reached a steady state value, the hydroperoxide feed was stopped and the decrease in polymerization rate was followed by recording the signal, θ_S, from the temperature sensor as a function of time. Several experiments could be carried out in succession until the VCM/PVC ratio fell below 2/3. Experiments were carried out at 40, 50 and 60 °C and at various concentrations of VO^{2+}. The hydroperoxide feed rate was also varied. Its maximum value was 10^{-3} mmol $\min^{-1}$, corresponding to a maximum ρ_i-value of about 1.7×10^{-4} mmol s^{-1} and per litre water.

RESULTS

An example of the experimental results obtained is given in Fig. 1. This figure reproduces a recorder trace from a normal analogue recorder, showing

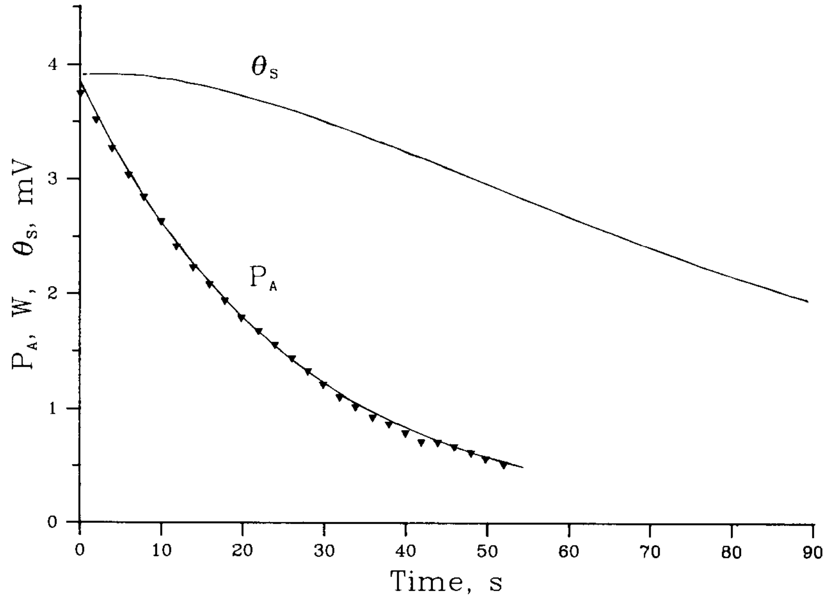

Fig. 1. The recorder trace of the θ_S-signal (undotted curve) obtained during the 90 s interval following the interruption of the feed of *t*-butyl hydroperoxide (the rate determining component of the initiator system) to the reactor. The triangles show data of P_A at two-seconds intervals, calculated from the θ_S-signal using eqn. (2). The P_A-values were calculated from data obtained by sampling the θ_S-signal at a frequency of 1 s^{-1} by a microcomputer. The curve representing $P_A(t)$ is a least square fit of the P_A data to a first order reaction kinetics (cf. Fig. 2).

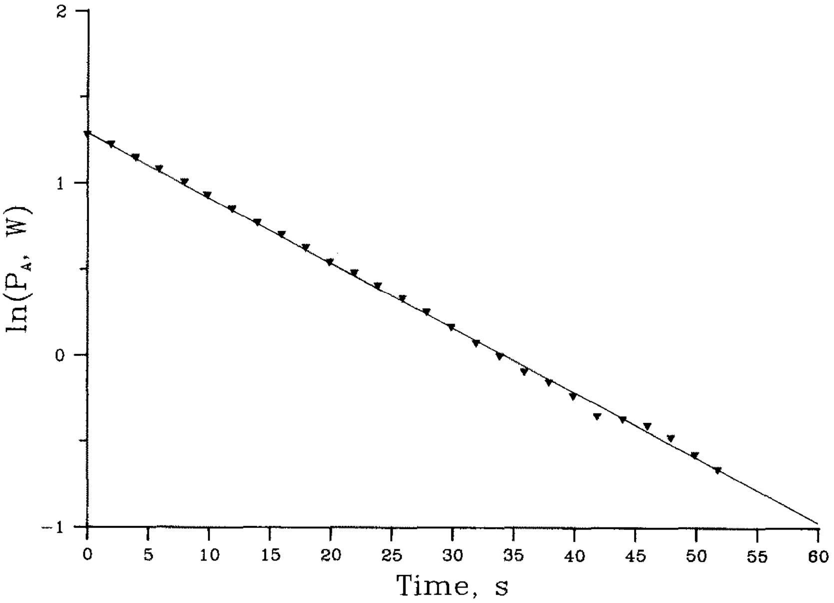

Fig. 2. A first order plot of the P_A-data in Fig. 1. The line was obtained by linear regression of the data points.

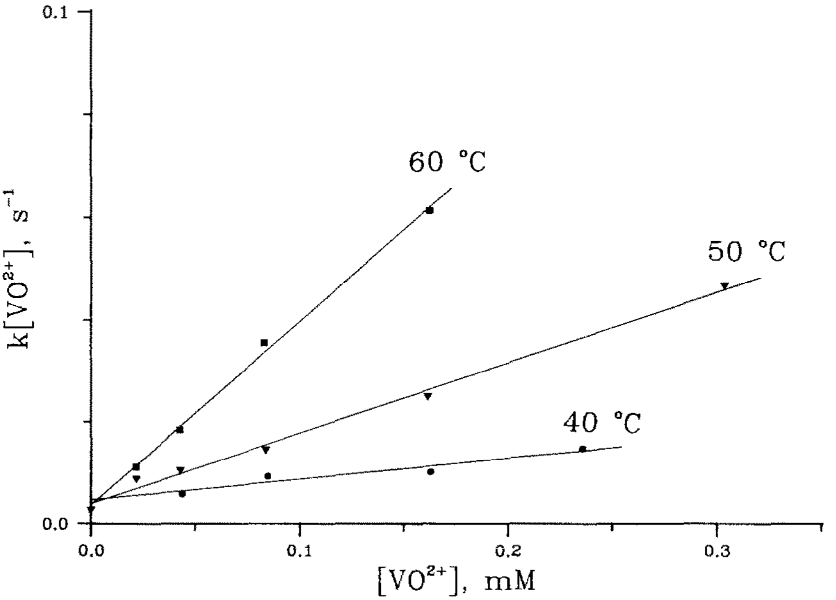

Fig. 3. The pseudo first order rate constant $k[\mathrm{VO}^{2+}]$ (cf. eqn. (9)) for the reduction of *t*-butyl hydroperoxide by vanadium(IV) at pH 4.7, as a function of the concentration of vanadium at (● 40 ° C, ▼ 50 ° C, and ■ 60 ° C).

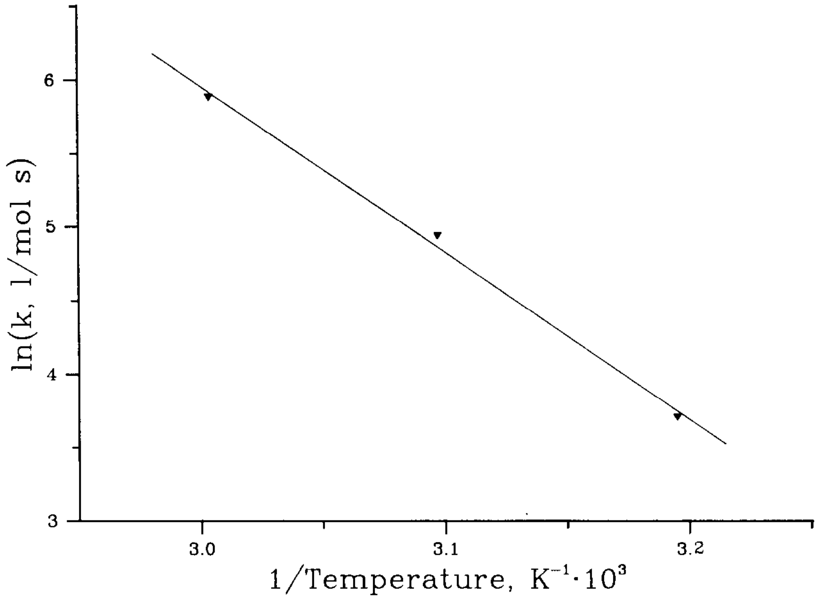

Fig. 4. An Arrhenius plot of the second order rate constant, k, of eqn. (10) as calculated from the data of Fig. 3.

how θ_S varied with time after interrupting the hydroperoxide feed. It also shows data for P_A (cf. eqn. (3)) calculated according to eqn. (2) using θ_S-values sampled by a micro-computer at intervals of 1 s^{-1}. Figure 2 shows a logarithmic plot of the P_{CHEM} versus time data of Fig. 1 and a least square fit of the data. Figure 3 gives half-life time data at 40, 50 and 60 °C as determined at different concentrations of vanadium. Figure 4, finally, gives the temperature dependence of the second order rate constant for the redox couple as defined by eqn. (8).

DISCUSSION

Methodology

The calorimetric reactor used in this work showed a rather slow response. Its dynamic properties would be mainly determined by the largest time constant of eqn. (2), $C_A/K_{A,R}$, which had a value of about 80 s. Despite this slow response, it was possible to study reactions with half-lives down to about 10 s (cf. Figs. 1 and 2) implying that eqn. (2) modelled the heat flow properties of the reactor quite well.

The use of eqn. 10 for the determination of rate constants for radical formation presupposed that eqn. (5) was valid under the experimental conditions used. As was recently shown (ref. 2), eqn. (5) accurately modelled vinyl chloride polymerization under stage II conditions, particularly with SLS as emulsifier and at moderate conversions. The results presented here indicate that vinyl chloride can be used to probe the rate of radical formation. This is due to the rapid exchange in this system of radicals between the polymerizing polymer particles (a high value of k'_d). The transport of radicals obviously was sufficiently rapid to allow the number of radicals per particle to reach its steady state value in a time period much shorter than the half-life of the redox reaction studied.

The redox system

As seen in Fig. 2, the rate data fitted quite well to a first order reaction, which in this case had a $t_{1/2}$-value of about 18 s. Also, at the other conditions employed, the reaction was found to behave as a pseudo first order reaction. This implies that the concentration of VO^{2+}-ions was constant during these reactions. That is, the VO_2^+-ions formed by reaction with the hydroperoxide was immediately reduced back to the valence state of IV by the ascorbic acid. The ascorbic acid was always present in excess of the amount of hydroperoxide. A separate spectrophotometric study using the stopped flow technique confirmed that the reaction between ascorbic acid and vanadium(IV) was indeed a very rapid one and much more rapid than the reaction between vanadium(IV) and the hydroperoxide at the concentration used in the polymerization experiments.

The results of Fig. 3 show that the reaction was also first order with respect to vanadium. As can be seen, however, the data was not extrapolatable back to the origin. A separate experiment carried out in the absence of vanadium confirmed that radicals were also formed by an apparantly non-catalyzed reaction. It is possible that this slow reaction was due to: (a) the presence of impurity amounts of other catalytically active metal ions, (b) the formation of radicals in a direct reaction between ascorbic acid and the hydroperoxide, or (c) thermal decomposition of an impurity peroxide present in the hydroperoxide.

The results in Figs. 3 and 4 suggest that the initiator system studied follows the same kinetics within the temperature range from 40 to 60 °C at all vanadium concentrations tested. The pH dependence of the redox system has not been studied in detail. It is clear, however, that the system can be used in a fairly wide pH range. It is only at pH values where the vanadium forms oxo hydroxy complexes that the activity starts to decrease. Experiments have shown, however, that the system retains some activity even at fairly high pH. Thus, in going from pH 4 to 9, the pseudo first order rate constant decreased, but not more than by a factor of 10.

CONCLUSIONS

This work has shown that reaction calorimetry can be used to study the kinetics of rapid redox initiator systems. Emulsion polymerization of vinyl chloride is a suitable model system as the rate of polymerization with this system is directly proportional to the square root of the rate of initiation.

This work has also shown that *t*-butyl hydroperoxide, in combination with ascorbic acid and small amounts of vanadium(IV), can give reproducible redox systems which are capable of generating radicals in pseudo first order reactions with half lives down to ten seconds.

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