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KINETICS AND MECHANISM OF PERSULPHATE POLYMERIZATION OF ACRYLONITRILE IN THE PRESENCE OF CHLORIDE IONS

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The kinetics and mechanism of polymerization of acrylonitrile were studied using potassium persulphate as an initiator. The parameters varied were the pH of the medium, and initiator and monomer concentrations. The effect of the chloride ions on the reaction rate was also investigated and it was observed that the chloride ions retarded the rate of polymerization. Further, the reaction was found to be sesquimolecular in order.

Introduction

During the past 20 years the kinetic studies of polyacrylonitrile have assumed a position of prime importance in the field of high polymers. The kinetics of acrylonitrile polymerization initiated by potassium persulphate,¹⁻⁴ the kinetics of solution polymerization of acrylonitrile,⁵ and the photochemical initiation of polymerization of acrylonitrile by persulphate⁶ has been studied.

The present investigation was designed to observe the effect of pH, maintained by H₂SO₄ or HCl, on the rate of acrylonitrile polymerization initiated by potassium persulphate. The two mineral acids were selected with a view to determining the effect of sulphate or chloride ions under similar hydrogen ion concentrations. The choice of monomer was due to its great industrial importance in the preparation of synthetic fibres.

Experimental

Materials.—The following chemicals were used. Acrylonitrile (B.D.H.), potassium persulphate (E. Merck), sulphuric acid (B.D.H. Analar), hydrochloric acid (B.D.H. Analar), sodium chloride (May & Baker), sodium hydroxide (May & Baker).

Acrylonitrile was further purified by distillation under reduced pressure in order to remove inhibitor. The purity of the middle fraction was checked by measuring its physical constants (d_4^{25} 0.8001, n_D^{25} 1.3885). These values agreed with those reported by Blout and Hokenstein.⁷

Procedure.—In order to investigate the kinetics and mechanism of polymerization three para-

eters, i.e. pH of the medium, initiator concentration and monomer concentration, were varied in turn keeping the other two constant. Further, the effect of chloride ions on the rate was studied. The rate was followed dilatometrically. Before degassing the reaction mixtures, the pH values were measured by means of a Cambridge pH-meter. The variation in pH was made with the addition of HCl and NaOH or H₂SO₄ and NaOH. The reaction mixture at the required pH value was filled in bulb B (Fig. 1) which was then attached to a high vacuum line. The solution was degassed by at least two cycles of freezing, pumping to 10⁻⁵ mm and melting. While the solution was frozen in B, the stop-cock S₁ was closed and the apparatus was detached from the vacuum line. Dilatometer was filled by inverting the bulb B and after closing stop-cock S₂ it was detached at the point A from the bulb B.

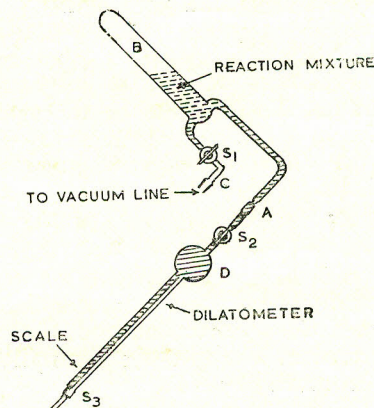
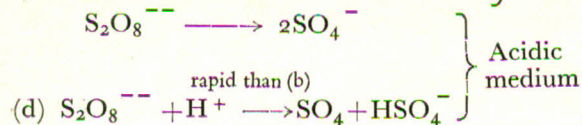
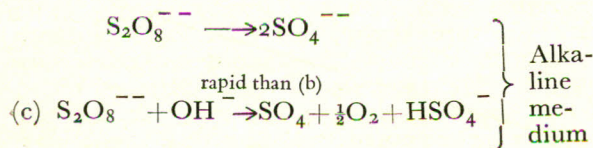
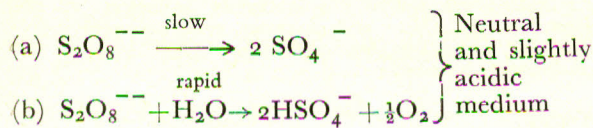


Fig. 1.

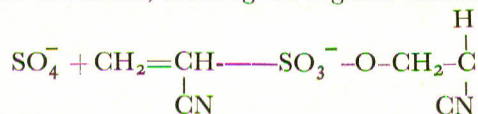
The dilatometer, previously calibrated, was then placed in the thermostat set at $32 \pm 0.1^\circ\text{C}$. The induction period was measured from the interval between the time of placing of dilatometer in thermostat and the first appearance of contraction in the capillary of the dilatometer. After determining the induction period the stop-cock S_2 was opened and the polymer formed was filtered, washed and dried at 110°C to a constant weight for the determination of molecular weights.

Results and Discussion

Potassium persulphate decomposes in various media according to the following reactions.⁸



The sulphate radical ion formed possesses an unpaired electron and therefore exhibits the extreme reactivity, characteristic of free radicals. In the presence of monomer the sulphate radical ion probably initiates the polymerization by adding to the monomer, forming an organic radical ion:



In polymerization the rate of propagation R_p and termination R_t are given by the well-known equations:

$$R_p = K_p M C \quad (1)$$

$$R_t = K_t C^2 \quad (2)$$

where K_p and K_t are the specific rates of propagation and termination respectively, C the monomer radical concentration and M the monomer concentration. The rate of consumption of the monomer is given by

$$-\frac{dM}{dt} = R_i + R_p$$

$$\text{or } -\frac{dM}{dt} = R_i + K_p C M \quad (3)$$

where R_i is the rate of initiation. For the very long chain formation the rate of initiation R_i could be neglected as compared to R_p . In the steady state

$$R_i = R_t = K_t C^2 \quad (4)$$

$$\text{Hence } C = \left[\frac{R_i}{K_t} \right]^{\frac{1}{2}} \quad (5)$$

Substituting the value of C in the equation (3) we get

$$-\frac{dM}{dt} = R_i + K_p M \left[\frac{R_i}{K_t} \right]^{\frac{1}{2}} \quad (6)$$

The value of R_i in the case of catalysed polymerization is given by

$$R_i = K_i M B \quad (7)$$

where B is initiator concentration. By ignoring the first factor, equation (6) reduces to the form

$$-\frac{dM}{dt} = K_p M \left[\frac{K_i B M}{K} \right]^{\frac{1}{2}} \quad (8)$$

$$-\frac{dM}{dt} = K_p \left[\frac{K_i}{K_t} \right]^{\frac{1}{2}} B^{0.5} M^{1.5} \quad (9)$$

$$\frac{1}{\sqrt{a-er}} = \frac{1}{\sqrt{a}} + \frac{1}{2} K B^{0.5} t \quad (10)$$

On integrating equation (9)

where a is the initial monomer concentration.

When $-dM/dt$ is plotted against 1.5th power of the monomer as well as against the square root of initiator concentration, straight lines are to be expected. Figures 2 and 3 show these facts in accordance with the kinetic equation (9).

Dependence of Specific Rate on pH.—The specific rates of polymerization at pH from 0 to 8 are given in Table 1. The rate is found to be maximum at pH 7 (Fig. 2), but it decreases with the increase or decrease of pH. In alkaline medium the reaction (c) dominates over reaction (b). Consequently, the sulphate radical ion formation in reaction (a) decreases and the rate falls. In strongly acidic medium decomposition of the persulphate leads to Caro's acid and reaction (d) dominates over reaction (b). Hence the formation of sulphate radical

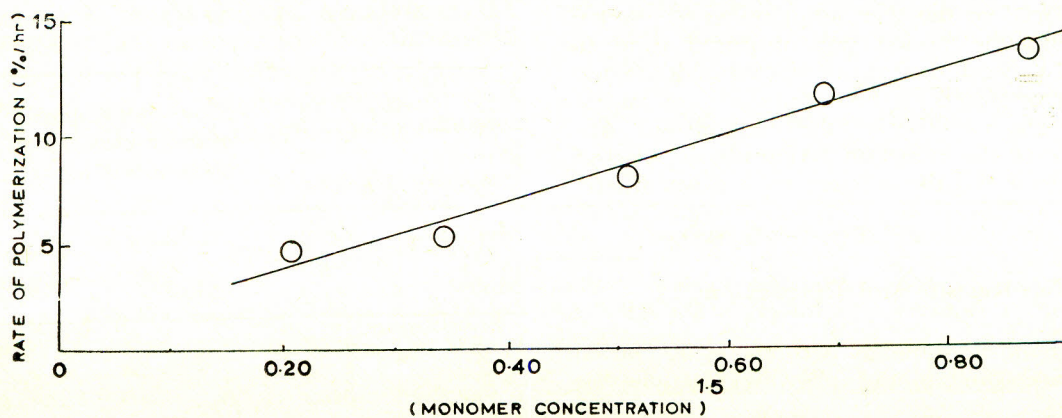


Fig. 2.

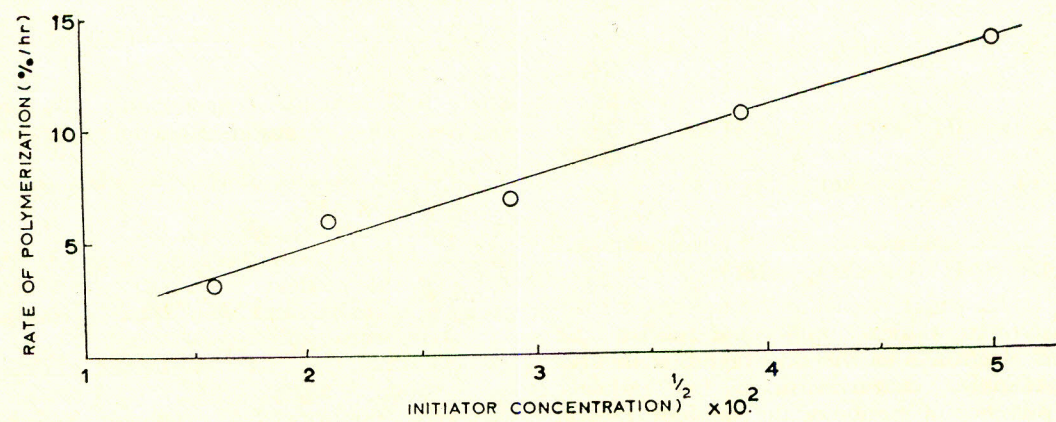


Fig. 3.

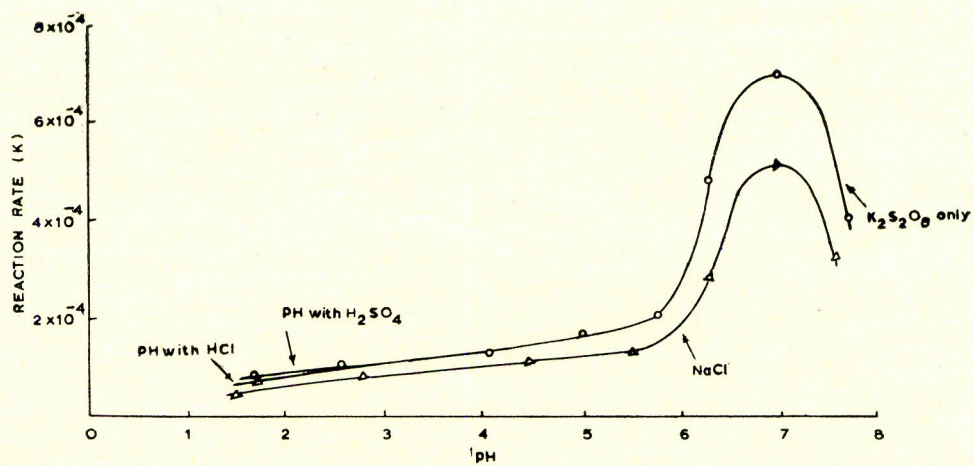


Fig. 4.

TABLE 1.—DEPENDENCE OF THE REACTION RATE CONSTANT ON pH AND CHLORIDE IONS.

Acrylonitrile = 0.8831 M.
 Initiator ($K_2S_2O_8$) = 3.08×10^{-3} M.
 NaCl = 0.25 M.

pH of the reaction mixture	pH maintained with		
	H ₂ SO ₄ and NaOH	HCl and NaOH	HCl and NaOH in presence of NaCl
	$10^4 \times K$ litre mole ⁻¹ sec ⁻¹	$10^4 \times K$ litre mole ⁻¹ sec ⁻¹	$10^4 \times K$ litre mole ⁻¹ sec ⁻¹
1.75	0.78	0.62	0.53
2.60	1.02	0.94	0.70
4.10	1.26	1.26	0.92
5.0	1.68	1.68	1.10
5.8	2.02	2.02	1.60
6.3	4.80	4.80	2.90
7.0	6.93	6.93	5.17
7.7	4.15	4.15	2.90

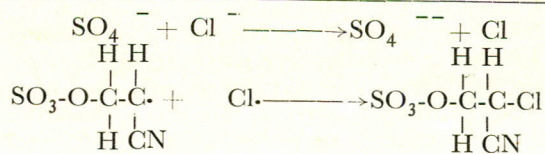
ions decreases which results in the fall of the reaction rate. At or below pH 3 the specific rate decreases when the pH is maintained with HCl instead of H₂SO₄ shown in Fig. 4.

In order to determine the decrease of rate in case of HCl, the effect of chloride ions on the rate of polymerization was further investigated.

The inhibitory effect of chloride ions may be explained from the view point of the removal of both the active species by interaction with a chloride ion. This may be illustrated as follows:

TABLE 2.—RATE DEPENDENCE ON MONOMER AND INITIATOR CONCENTRATIONS AT pH 7.0 AND 32°C.

Monomer (M) Mole/l	Rate average/hr	Rate dependence on initiator concentration.	
		Initiator (B) Mole/l	Rate average/hr
0.3532	4.77	2.5×10^{-4}	3.03
0.49448	5.27	4.3×10^{-4}	5.97
0.63576	8.04	8.3×10^{-4}	6.87
0.77704	11.91	1.5×10^{-3}	10.62
0.91812	13.65	2.5×10^{-3}	13.82



References

1. R.G.R. Bacon, *Trans. Faraday Soc.*, **42**, 140 (1946).
2. L.B. Morgan, *ibid.*, **42**, 169 (1946).
3. T. Alfrey, C.G. Overberger and S.H. Pinner, *J. Am. Chem. Soc.*, **75**, 4221 (1953).
4. W.S. Heinaman, M.S. Thesis, University of Delaware, June 1950.
5. Thomas, Greason and Pellion, *Proc. Roy. Soc., A* **24**, 43 (1957).
6. F.S. Dainton, P.H. Seaman and D.G.L. James, *J. Polymer Sci.*, **34**, 209 (1959).
7. Blout, Mark and Hokenstein, *Monomers* (Interscience Publishers, New York, 1949), p. 16.
8. F.A. Bovey, I.M. Kolthoff, A.I. Medalia and E.J. Meehan, *High Polymers* (Interscience Publishers, New York, 1955), vol. ix, p. 67.