

VINYL POLYMERIZATION

IX. Polymerization of Acrylonitrile by V^{5+} + Pinacol Redox System

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Synopsis.—Polymerization of acrylonitrile initiated by V^{5+} + Pinacol in sulphuric and perchloric acid media was studied in the temperature range 20°–30° C. The rates of polymerization and of V^{5+} disappearance were measured with respect to changes in $[M]$, $[V^{5+}]$, $[Pinacol]$, $[H^+]$ ionic strength, μ etc. Experimental evidence favoured the initiation by the free radical produced by the interaction of Pinacol with V^{5+} and the termination being linear by V^{5+} . The various rate parameters k , k_p/k_t and k_o/k_i and the activation parameters ΔE and ΔS^* were evaluated.

Only qualitative studies were made by Waters and co-workers¹ regarding initiation of vinyl polymerisation by V^{5+} + organic substrate redox system. Results on polymerization of Acrylonitrile with V^{5+} + Pinacol redox system in sulphuric and perchloric acid solutions at 20, 25, 30 and 35° C.; $\mu = 1.0$ M, 0.8 M and $[H^+] = 0.5$ M are now presented. Close similarity was observed in the kinetic results obtained in both the acid media and the rate parameters were almost identical.

EXPERIMENTAL

Reagents.—The various chemicals used in this investigation were of Analar grade. Doubly distilled deionised water was used for preparing all the solutions. Nitrogen (Indian Oxygen Co.) was purified by passing through Fieser's solution, Lead acetate solution and finally through distilled water.

Preparation and estimation.— V^{5+} stock solution (~ 0.4 M; $H^+ \sim 4$ M) was prepared by suspending ammonium meta vanadate in distilled water and adding concentrated H_2SO_4 or $HClO_4$ to it, while stirring. The $[V^{5+}]$ and $[H^+]$ of the stock solution were determined by vanadometry and alkali-metry respectively.

Kinetic measurements.—The thermostat was a large glass tank (dia. 12"; cap. 20 litres) provided with a stirrer and constant temperature ($\pm 0.1^\circ$ C.)

was maintained by a hot wire vacuum switch relay and a toluene regulator. The reaction vessel was a long pyrex tube (8" × 1") fitted with B-24 socket and cone and to the latter gas inlet and outlet tubes were fused. The reaction system consisting of Acrylonitrile (0.7539 M); Pinacol (0.075 M); sulphuric acid (0.5 M) and sodium bisulphate (0.3 M); perchloric acid (0.5 M) and sodium perchlorate (0.5 M) in the case of perchloric acid medium was deaerated by bubbling oxygen free nitrogen through the inlet tube for about 20–30 minutes and then thermostated at 30° C. V^{5+} (0.03 M) stock solution was then added to the reaction vessel through the outlet tube and then closed with a rubber gasket. Polymerization started without induction period as showed by the appearance of turbidity. The reaction was usually run for 20–30 minutes and then arrested by addition of Fe^{++} to the system. The precipitated poly (Acrylonitrile) was filtered off and the rate of polymerization, R_p was determined from the weight of the polymer sample; rate of V^{5+} disappearance, $-R_v$, was determined by estimating the excess Fe^{++} in the filtrate. Determination of chainlengths (n) of poly (Acrylonitrile) (0.1% solutions in dimethyl formamide) was done by viscometry, the relevant Mark-Houwink equation due to Stockmeyer and Cleland² being:

$$[\eta] = 2.43 \times 10^{-4} [\bar{M}_v]^{0.75} \text{ at } 25^\circ \text{ C.}$$

where $[\eta]$ = intrinsic viscosity and \bar{M}_v = viscosity number average molecular weight.

RESULTS AND DISCUSSION

Steady state rate was reached within 20 minutes in perchloric as well as sulphuric acid medium. Commencement of polymerization in the absence of oxygen within a few seconds as indicated by the appearance of turbidity and long induction periods (> 5 minutes) in the presence of oxygen were indicative that a free radical mechanism was operative.

(i) *Rate of polymerization, R_p .*—The rate was proportional to $[M]^2$ and $[Pin]$. The plots of R_p vs. $[M]^2$ (Fig. 1) and R_p vs. $[Pin]$ being linear with zero intercepts (Fig. 2) showed that the orders with respect to monomer and Pinacol were two and one respectively. Increase in $[V^{5+}]$ (0.03 to 0.1 N) decreased the rate (40%), the plots of $1/R_p$ vs. $[V^{5+}]$ (Fig. 4) being linear with intercepts on the ordinate. The rate increased with increase in $[H^+]$ at low acidities (< 1.5 M) but was independent of $[H^+]$ at high acidities (> 1.5 M) in both the acid media. This effect of $[H^+]$ on rate in the system under

study was not observed in systems, V^{5+} + lactic acid + AN and V^{5+} + cyclohexanol + AN studied by us.^{3, 4}

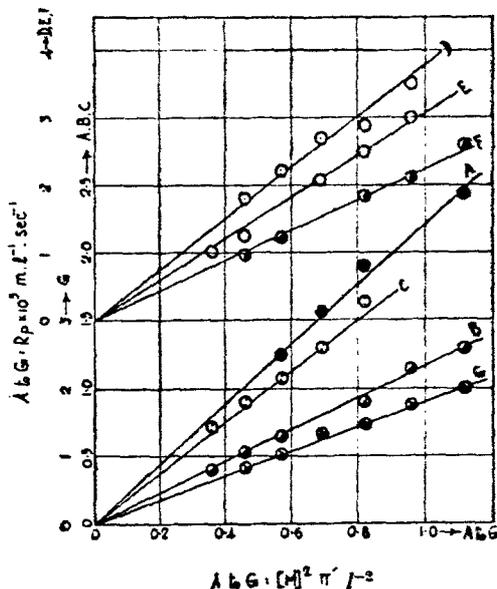


Fig. 1. Variation of R_p with $[M]^2$ at constant $[H_2SO_4] = 0.375$ M, $\mu = 0.4$ M and temperature 30° C.

- (A) $[V^{5+}] = 2.73 \times 10^{-2}$ N, $[pin] = 0.06$ M;
- (B) $[V^{5+}] = 2.43 \times 10^{-2}$ N, $[pin] = 0.03$ M;
- (C) $[V^{5+}] = 2.64 \times 10^{-2}$ N, $[pin] = 0.05$ M;
- (D) $[V^{5+}] = 2.47 \times 10^{-2}$ N, $[pin] = 0.1$ M;
- (E) $[V^{5+}] = 2.43 \times 10^{-2}$ N, $[pin] = 0.08$ M;
- (F) $[V^{5+}] = 4.38 \times 10^{-2}$ N, $[pin] = 0.08$ M;
- (G) $[V^{5+}] = 5.936 \times 10^{-2}$ N, $[pin] = 0.08$ M.

In sulphuric acid medium, the increase in $[HSO_4^-]$ (0.5 to 0.8 M) had practically no effect on the rate. For a four-fold increase of μ with $NaClO_3$, (0.4 to 1.6 M) a four-fold increase in R_p was noticed in H_2SO_4 medium; similarly, increasing μ with $NaHSO_4$ in H_2SO_4 (0.4 to 1.0 M) an equivalent increase in rate was noticed; in $HClO_4$ medium also increase in μ (0.4 to 1.0 M) gave an equivalent increase in rate.

(ii) *Rate of V^{5+} disappearance, $-R_v$.*— $[M]$ (0.6 to 1.0M) had no effect on the rate. $[V^{5+}]$ (0.03 to 0.1 N) increased the rate and plots of $-R_v$ vs. $[V^{5+}]$ were linear (Fig. 5) and the order with reference to $[V^{5+}]$ was unity. Increase in $[Pin]$ (0.02 to 0.12 M) increased the rate. Plots of $-R_v$ vs. $[Pin]$

[Pin] were linear at low [Pin] but tended to constancy at high [Pin] (Fig. 3) both in HClO_4 and H_2SO_4 . In the linear portion, the order with respect to [Pin] was unity. Increase in $[\text{H}^+]$ (0.2 to 0.75 M H_2SO_4 and HClO_4) had practically no effect on the rate (the same trend was noticed in the absence of Monomer also), indicating the protonated species, $\text{V}(\text{OH})_3^{2+}$, $\text{VO}\cdot\text{OH}^{2+}$,

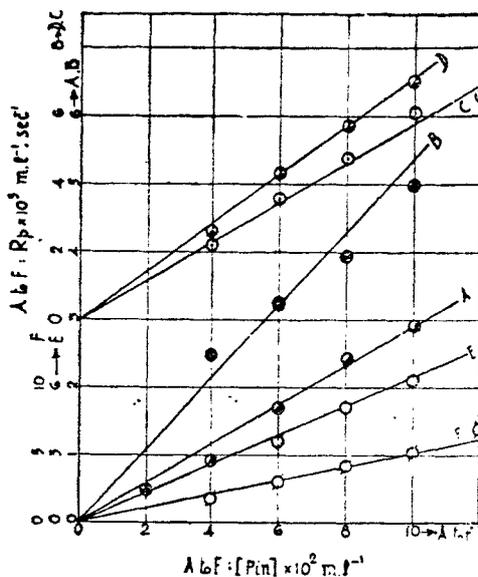


FIG. 2. Variation of R_p with [pin] at constant $[\text{H}_2\text{SO}_4] = 0.5 \text{ M}$, $\mu = 0.8 \text{ M}$ and $[\text{M}] = 0.7539 \text{ M}$.

- (A) $[\text{V}^{3+}] = 6.6 \times 10^{-2} \text{ N}$, 30° C. ;
 (B) $[\text{V}^{2+}] = 3.3 \times 10^{-2} \text{ N}$, 30° C. ;
 (C) $[\text{V}^{3+}] = 4.94 \times 10^{-2} \text{ N}$,
 (D) $[\text{V}^{5+}] = 4.17 \times 10^{-2} \text{ N}$,
 (E) $[\text{V}^{5+}] = 5.8 \times 10^{-2} \text{ N}$,
 (F) $[\text{V}^{5+}] = 6.6 \times 10^{-2} \text{ N}$,
35° C.

etc., were probably not the active oxidants in the two acid media studied. In perchloric acid medium a 3-fold increase in μ (0.54 to 1.73 M) increased the rate by 40%. But in H_2SO_4 medium, a constancy in rate with increase in μ as well as $[\text{HSO}_4^-]$ was observed. This showed that the bisulphate or sulphato complexes of V^{5+} were not active in H_2SO_4 medium.

(iii) *Chainlength measurements.*—Chainlengths increased with decrease in $[\text{V}^{5+}]$ and practically no change in chainlength was noticed when either $[\text{H}^+]$ (0.5 to 1.5 M) or [Pin] (0.6 to 0.12 M) was increased. A regular increase in chainlength was observed with increase in $[\text{M}]$ (0.06 to 1.0 M),

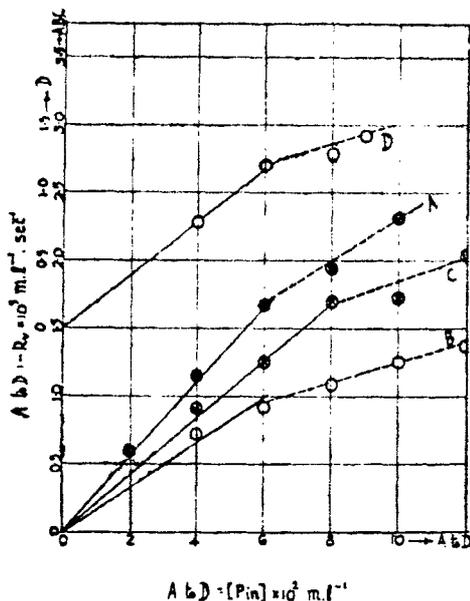
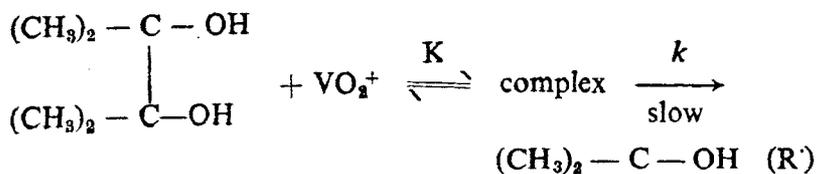


FIG. 3. Variation of $-R_p$ with $[pin]$ at constant $\mu = 0.8 \text{ M}$, $[M] = 0.7539 \text{ M}$ and temperature 30° C .

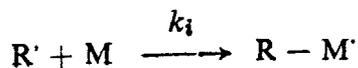
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|--------------------------------------------------|-----------------------------------------------|
| (A) $[V^{5+}] = 6.6 \times 10^{-2} \text{ N}$, | } $[\text{H}_2\text{SO}_4] = 0.5 \text{ M}$; |
| (B) $[V^{5+}] = 3.3 \times 10^{-2} \text{ N}$, | |
| (C) $[V^{5+}] = 4.96 \times 10^{-2} \text{ N}$, | |
| (D) $[V^{5+}] = 4.24 \times 10^{-2} \text{ N}$, | |

(iv) Kinetic scheme and rate expressions.—

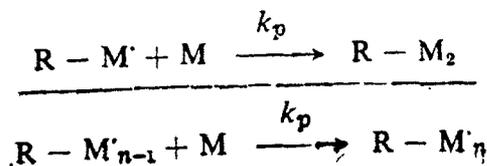
(1) Radical formation:



(2) Initiation:



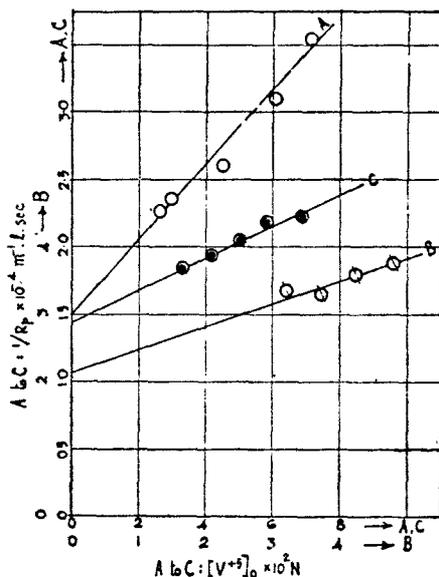
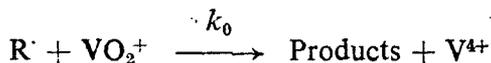
(3) Propagation:



(4) Linear termination:



and primary radical decomposition,

FIG. 4. Variation of $1/R_p$ with $[V^{5+}]$ at constant $[pin] = 0.08$ M.(A) $[H_2SO_4] = 0.55$ M, $\mu = 0.62$ M, $[M] = 0.9046$ M, 30° C.;(B) $[H_2SO_4] = 0.5$ M, $\mu = 0.8$ M, $[M] = 0.7539$ M, 30° C.;(C) $[H_2SO_4] = 0.5$ M, $\mu = 0.8$ M, $[M] = 0.7539$ M, 35° C.

Assuming stationary state concentration for micro and macro radicals the rate expressions obtained were:

$$R_p = \left(\frac{k_p}{k_t} \right) \frac{[M]^2 [Pin]}{\left\{ [M] + \left(\frac{k_0}{k_i} \right) [VO_2^+] \right\}} \quad (1)$$

$$-R_v = 2k [VO_2^+] [Pin] \quad (2)$$

$$n = \left(\frac{k_p}{k_t} \right) \left(\frac{[M]}{[VO_2^+]} \right). \quad (3)$$

The dependence of rate of polymerization (R_p) on $[M]^2$; $[Pin]$, $1/[V^{5+}]$ and the dependence of $-R_v$ on $[Pin]$, $[V^{5+}]$ and not on $[M]$, etc., were all

experimentally realised. These proportionalities do conform to the reaction scheme if termination is only by V^{5+} and not by mutual type or by primary radicals.

The observation of increase in R_p with $[H^+]$ at low acidities ($< 1.5 \text{ M}$) and that of no change in $-R_v$ with $[H^+]$ in that region may be understood in terms of catalysing effect of H^+ on the propagation step. The effect of μ on R_p may be due to the polar nature of the monomer.⁵ Acrylonitrile is capable of forming complexes with the cations as well as the anions of the added salts and thereby catalyse the propagation step.

V. *Evaluation of kinetic and energy parameters.*—The second order rate constant k evaluated (a) from the plots of $-R_v$ vs. $[V^{5+}]$ (Fig. 5; $k = 0.72 \times 10^{-3}$, 2.18×10^{-3} and 2.77×10^{-3} at 20° , 30° , and 35° C. in H_2SO_4 medium

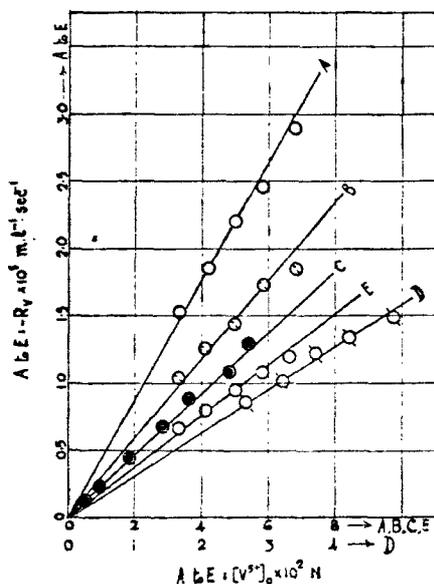


FIG. 5. Variation of $-R_v$ with $[V^{5+}]$ at constant $[M] = 0.7539 \text{ M}$ and $\mu = 0.8 \text{ M}$.

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|-----------------------------------------------------------------------------------------------------------|-------------------------|
| (A) $[\text{H}_2\text{SO}_4] = 0.5 \text{ M}$, $[\text{pin}] = 0.08 \text{ M}$, 35° C. ; | |
| (B) $[\text{H}_2\text{SO}_4] = 0.5 \text{ M}$, $[\text{pin}] = 0.08 \text{ M}$, | } 30° C. |
| (C) $[\text{H}_2\text{SO}_4] = 0.75 \text{ M}$, $[\text{pin}] = 0.05 \text{ M}$, | |
| (D) $[\text{H}_2\text{SO}_4] = 0.5 \text{ M}$, $[\text{pin}] = 0.08 \text{ M}$, | |
| (E) $[\text{H}_2\text{SO}_4] = 0.5 \text{ M}$, $[\text{pin}] = 0.04 \text{ M}$, | |

and 2.1×10^{-3} , 3.3×10^{-3} and 4.44×10^{-3} at 25° , 30° and 35° C. in HClO_4 medium respectively), and (b) from the initial slopes of $-R_v$ vs. $[\text{Pin}]$ (Fig. 3; $k = 2.185 \times 10^{-3}$ at 30° C. in H_2SO_4 and 2.0×10^{-3}

and 3.78×10^{-3} at 25° and 30° C. in HClO_4 medium respectively), agreed within limits of experimental errors, average values of k , $k_{av} = 0.72 \times 10^{-3}$, 2.18×10^{-3} and 2.77×10^{-3} l m.⁻¹ sec.⁻¹ at 20°, 30° and 35° C. in H_2SO_4 and 2.05×10^{-3} , 3.55×10^{-3} and 4.4×10^{-3} l m.⁻¹ sec.⁻¹ at 25°, 30° and 35° C. in HClO_4 medium respectively being obtained). k_p/k_t and k_0/k_i values were also computed from $1/R_p$ vs. $[\text{V}^{5+}]$ plots (Fig. 4; $k_p/k_t = 0.27$, 0.44 and 0.36 at 20°, 30° and 35° C. in H_2SO_4 and 0.22 and 0.21 at 25° and 30° C. in HClO_4 medium respectively. $k_0/k_i = 9.9$, 7.0 and 6.7 at 20°, 30° and 35° C. in H_2SO_4 medium and 13.58 and 10.4 at 25° and 30° C. in HClO_4 medium respectively). ΔE_k (8.8 K.cals./mole and 9.2 K.cals./mole in H_2SO_4 and HClO_4 medium respectively) and ΔS_k^* (-67.8 eu and -66.9 eu in H_2SO_4 and HClO_4 medium respectively) at 303.2° K. were evaluated.

The -ve entropy of activation was also obtained in the case of V^{5+} + cyclohexanol system. The ΔS_k^* ^{6,4} value in the presence and absence of Acrylonitrile for the system V^{5+} + cyclohexanol were found to be -11 eu and -17 eu respectively.

REFERENCES

1. Littler, J. S. and Waters, W. A. *J. Chem. Soc.*, 1959, Pp. 1300.
2. Stockmeyer, W. H. and Cleland, R. C. *J. Poly. Sci.*, 1955, 17, 473.
3. Saccubai, S. .. *Ph.D. Thesis*, January, 1958.
4. — and Santappa, M. .. *Die Mak. Chemie*, 1968, (in press).
5. Bamford, C. H., Jenkins, A. D. and Johnston *J. Poly. Sci.*, 1958, 31, 481.
6. Kemp, T. J. and Waters, W. A. *Proc. Roy. Soc.*, 1963, 274 A, 493.