

Influence of α -Naphthol Chelate Complex of Cu(II) on Potassium Monopersulphate Decomposition and Vinyl Polymerization of Acrylonitrile in Solution

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ABSTRACT: The catalytic influence of various Cu(II) salts and Cu(II)-chelate complexes of certain phenols and naphthols on potassium monopersulphate decomposition and vinyl polymerization of acrylonitrile has been investigated in aqueous medium. From the knowledge of the comparative rate data, the CuSO_4/α -naphthol chelate complex was chosen for a detailed study of the kinetic aspects of acrylonitrile polymerization. The polymerization was studied at various concentrations of the reacting components and over a temperature range of 35—50°C. The rate of polymerization was found to be

$$R_p = K[\text{Cu(II)}]^{0.169}[\alpha\text{-N}]^{0.512}[\text{KHSO}_5]^{1-1}[\text{AN}]^{1-1}$$

The overall activation energy was computed to be 3.118 kcal mol⁻¹ (13.03 kJ mol⁻¹) and other thermodynamic parameters were evaluated. From the kinetic results and spectrophotometry studies on the interaction of KHSO_5 and α -naphthol with Cu(II), the mechanism of KHSO_5 decomposition and initiation of acrylonitrile polymerization are suggested.

KEY WORDS Chelate Complex / α -Naphthol Effect / Copper Sulfate Effect / Monomer Effect / KHSO_5 Effect / Acid Effect / Solvent Effect / Complex Initiation /

The prominence of peroxygen compounds such as organic peroxides, hydroperoxides and inorganic peroxy salts is attributed to their ample applications as free-radical initiators and/or curing agents for polymers and resin industries. The choice of a peroxygen compound depends on its activity in regard to its decomposition reaction initiation. Apart from other reaction conditions, a trace of metal salt as an impurity causes a facile homolysis of the peroxobridge due to induced activity.¹⁻⁷

The catalytic effect of variable valency transition metal salts which are prominent in this regard, on the decomposition of peroxy compounds, is based on a known reaction scheme

according to which the metal ion present both in the lower and higher oxidation states is catalytically effective.^{1,2} For this reason in the free radical polymerization of vinyl and diene monomer, these salts are widely used along with organic peroxides and hydroperoxides and peroxy salts as components of redox pairs. Sheldon *et al.*⁸ noticed that the participation of a given metal ion in a free radical process is strongly influenced by factors such as the kind of ligand bound to the metal ion and the presence of complexing agents in the reaction system. Barton and coworkers⁹⁻¹¹ noticed similar observations during their investigation on the effects of certain copper salts on cumene hydroperoxide (CHP) decomposition and vinyl polymerization. The rate of CHP de-

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composition was strongly affected by the addition of complexing agents such as amino alcohols. Indicator *et al.*^{12,13} in the decomposition of *t*-butyl hydroperoxide (*t*-BHP) noticed the rate of decomposition to be highly accelerated by the addition of a metal-acetylacetonate complex and the nature of the reaction path to be free-radical so that vinyl polymerization was effectively initiated. Recently Samal and coworkers¹⁴⁻¹⁷ noted interesting behaviour on the part of the acidic peroxy salt, potassium monopersulphate. The ability of this compound to initiate free-radical polymerization is enhanced by the addition of metal salts. With some metal ions such as copper(II), the catalytic action depends on the nature of the anion bound to it. The authors, during the course of this study, observed that with Cu(II), Fe(III) and Cr(III) salts, when the reaction mixture was quenched with 0.1 (M) hydroquinone solution and the reaction vessels were allowed to stand in an ice bath, many polymers were produced, even though initially the formation of homopolymer was less. Especially with Cu(II)SO₄ this effect was pronounced. It was thus considered that hydroquinone and other quinones, phenols and naphthols which behave as ideal inhibitors and retarders of free-radical polymerization may change in their characteristics, when coupled with Cu(II). Our interest has thus been directed to evaluate the influence of various Cu(II)-salts and Cu(II)/phenols couples on potassium monopersulphate decomposition and vinyl polymerization, and also in carrying out selective graft copolymerization onto chelate forming polymers, using KHSO₅ as the initiator. The present report is concerned with the effects of Cu(II)-salts and the Cu(II)/ α -naphthol couple on KHSO₅ decomposition and radical polymerization of acrylonitrile.

EXPERIMENTAL

A Potassium monopersulphate solution (0.129 M) was prepared in distilled water and

kept cool. The strength of the stock-solution was determined by estimating the percentage of active oxygen with cerimetry. Acrylonitrile was purified by standard procedures. All other reagents such as CuSO₄, Cu(OAc)₂, Cu(NO₃)₂, CuCl₂, phenol, nitrophenols, cresols, hydroquinone, resorcinol, catechol, pyrogallol, salicylaldehyde, α -naphthol and β -naphthol, sulfuric acid, ferrous ammonium sulphate, ceric ammonium sulphate, *ortho*-phenanthroline were of BDH (AR) grade and used after purification by standard methods. The polymerization experiments for the control and activated system and rate measurement along with other rate parameters were performed similarly to our previous communication,¹⁸ as follows.

The polymerization experiments for all sets were carried out in specially designed glass vessels with B_{24/29} standard joints and inlet and outlet tubes for passing oxygen free nitrogen. The reaction vessels containing known concentrations of monomer, CuSO₄, and α -naphthol were deaerated by passing purified nitrogen, sealed carefully by rubber caps and thermostated at the experimental temperature. A requisite amount of the initiator solution was carefully injected through the rubber caps and mechanically stirred to ensure homogeneous mixing of the components. The vessels were carefully observed from the outside with a high power telescope to detect the appearance of turbidity in the reaction mixture. The polymerization reactions were carried out for various times and arrested by the addition of a known excess of Fe(II), which spontaneously consumed the unreacted KHSO₅. A similar procedure was used for the reference experiments.

The precipitated polymers were filtered, washed repeatedly with water and absolute alcohol, dried to constant weight at 60°C. From the weights, the conversion percentage and rate of polymerization (R_p) were calculated. For all kinetic aspects the rate was calculated. From the filtrate the rate of

KHSO₅ consumption was determined by estimating the unconsumed Fe(II) with cerimetry and spectrophotometrical measurements, using [Fe(II)orthophenanthroline] ferroin as the indicator.

The intrinsic viscosity $[\eta]$ of the purified polymers was determined using an Ubbelohde type suspended level dilution viscometer in DMF at 30°C and the average molecular weight of the polymer was calculated from the following relationship.¹⁹

$$[\eta] = 3.335 \times 10^{-4} M_v^{0.72}$$

RESULTS AND DISCUSSION

Aqueous polymerization of acrylonitrile was carried out using KHSO₅ as the initiator with Cu(II) salts and Cu(II)/phenol couples as catalysts. Prior to a detailed kinetic study involving the Cu(II) sulphate/ α -naphthol/KHSO₅ system, the polymerization was carried out with KHSO₅ alone, KHSO₅ coupled with CuSO₄, Cu(OAc)₂, Cu(NO₃)₂, and CuCl₂ separately and KHSO₅ coupled with individual phenols under identical reaction conditions. The results of this preliminary study are recorded in Tables I—III. No polymer precipitated with Cu(II)/phenol couples in the absence of KHSO₅, even though the reaction mixture was maintained by a thermostat for 48 h.

Table I. Rates of polymerization (R_p) for various Cu(II)-salt catalysed polymerizations of acrylonitrile initiated by KHSO₅. [KHSO₅] = 0.0129 M; [Cu(II)] = 0.02 M; [AN] = 0.754 M; temp = 50°C

Salt	$10^5 \times R_p$
	ml ⁻¹ s ⁻¹
Control	1.67
CuSO ₄	2.52
Cu(NO ₃) ₂	2.33
CuCl ₂	7.11
Cu(OAc) ₂	11.99

From Tables I—III, it is quite evident that with CuSO₄, which has a feeble activating influence on the course of potassium mono-

Table II. Rates of polymerization (R_p) under the influence of various phenols in the polymerization of acrylonitrile initiated by KHSO₅. [KHSO₅] = 0.0129 M; [phenol] = 0.0015 M; [AN] = 0.754 M; temp = 50°C

Phenols	$10^5 \times R_p$
	ml ⁻¹ s ⁻¹
Control	1.67
Phenol	1.35
<i>o</i> -(Cl)Phenol	0.87
<i>p</i> -Cresol	2.34
<i>p</i> -(NO ₂)Phenol	0.81
<i>o</i> -(NO ₂)Phenol	0.91
Catechol	3.66
Resorcinol	9.92
Hydroquinone	4.68
Pyrogallol	9.45
Salicylaldehyde	0.81
<i>m</i> -(OH)Benzaldehyde	3.85
α -Naphthol	4.89
β -Naphthol	4.92

Table III. Rate of polymerization (R_p) catalysed by various Cu(II)-phenol couples in the polymerization of acrylonitrile initiated by KHSO₅. [KHSO₅] = 0.0129 M; [Cu(II)] = 0.02 M; [phenol] = 0.0015 M; temp = 50°C; [AN] = 0.754 M

Phenol	$10^5 \times R_p / \text{ml}^{-1} \text{s}^{-1}$			
	CuSO ₄	Cu(NO ₃) ₂	CuCl ₂	Cu(OAc) ₂
Phenol	5.67	6.22	1.71	10.27
<i>o</i> -(Cl)Phenol	3.39	3.42	5.25	12.00
<i>p</i> -Cresol	10.12	9.52	5.23	13.61
<i>o</i> -(NO ₂)Phenol	2.53	2.57	1.50	10.34
<i>m</i> -(NO ₂)Phenol	—	2.22	4.03	11.54
<i>p</i> -(NO ₂)Phenol	2.87	3.28	5.14	12.64
Catechol	10.42	12.03	4.87	13.34
Resorcinol	18.03	16.82	8.97	15.40
Hydroquinone	14.65	8.52	7.02	14.06
Salicylaldehyde	8.89	13.40	5.04	13.32
<i>m</i> -(OH)Benzaldehyde	10.46	10.75	6.03	11.81
Pyrogallol	15.38	15.48	4.91	16.08
α -Naphthol	9.41	10.63	5.92	14.25
β -Naphthol	10.05	11.77	5.09	12.47

persulphate decomposition, the addition of resorcinol, hydroquinone, pyrogallol, α -naphthol, β -naphthol, and *p*-cresol greatly activates the rate of KHSO_5 decomposition and hence the rate of initiation of polymerization. From our investigation with α -naphthol it was found that,

$$R_p(\text{KHSO}_5/\text{CuSO}_4/\alpha\text{-N}) > [R_p(\text{KHSO}_5) + R_p(\text{KHSO}_5/\text{CuSO}_4) + R_p(\text{KHSO}_5/\alpha\text{-N})].$$

Further, CuSO_4 alone has poor activation, α -naphthol, moderate activation and CuSO_4/α -naphthol couple, pronounced activation effects on the rate of polymerization (R_p) which is about six times greater than the non-catalyzed system.

The feeble activation by CuSO_4 might be due to Cu(II) which, though a poor oxidising agent, in conjunction with KHSO_5 , behaves as a reducing agent and undergoes oxidation to Cu(III) . The oxidation of Cu(II) to Cu(III) is extremely difficult from the stand point of energy. It is expected that Cu(II) is converted to Cu(I) and the net reaction yields sufficient oxygen which is an ideal retarder of radical polymerization. All these reactions proceed through the intermediate formation of a tran-

sient complex, as evident from Figure 1. A similar complex formation has been observed by several other workers^{3-6,9-11} in hydroperoxide decomposition by transition metal salts as catalysts. The visible spectra of CuSO_4/α -naphthol couple are also shown in Figure 1(c). The high R_p value with CuSO_4/α -naphthol couple may probably be attributed to the high rate of production of initiating radicals generated by the facile homolysis of the initiator bound by the transition complex of Cu(II) - α -naphthol, where the internal energy is transferred to the initiator.

The polymerization was studied at various concentrations of the reaction components to establish the relationship between catalytic influence and mole-ratios of the donor-acceptor entities.

(i) Effects of α -Naphthol Concentration

Time conversion curves are plotted in Figure 2 for varying concentrations of α -naphthol (5×10^{-5} — 15×10^{-3} M) at fixed concentrations of CuSO_4 (0.002 M), KHSO_5 (0.0129 M), AN (0.754 M) at 40°C . From Figure 2, it is clear that the conversion per-

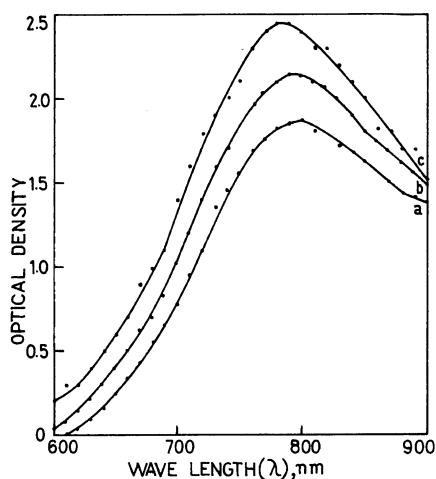


Figure 1. Visible spectra of (a) $[\text{CuSO}_4]=0.02$ M, (b) $[\text{CuSO}_4]=0.02$ M + $[\text{KHSO}_5]=0.0129$ M, (c) $[\text{CuSO}_4]=0.02$ M + $[\alpha\text{-N}]=0.05$ M.

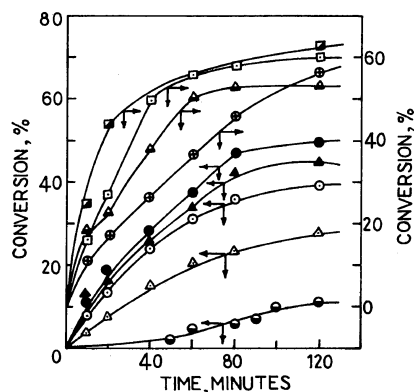


Figure 2. Variation in conversion % with time. (a) Effects of α -naphthol concentration: $[\text{KHSO}_5]=0.0129$ M; $[\text{CuSO}_4]=0.002$ M; $[\text{AN}]=0.754$ M; temp = 40°C . Plots: (●) $[\alpha\text{-N}]=0.00005$ M; (△) $[\alpha\text{-N}]=0.0005$ M; (○) $[\alpha\text{-N}]=0.002$ M; (●) $[\alpha\text{-N}]=0.01$ M; (▲) $[\alpha\text{-N}]=0.015$ M. (b) Effects of organic solvents: $[\text{KHSO}_5]=0.0129$ M; $[\text{CuSO}_4]=0.002$ M; $[\alpha\text{-N}]=0.01$ M; $[\text{AN}]=0.754$ M; temp = 40°C . Plots: (⊕) [acetic acid]=10%; (▲) [formic acid]=10%; (□) [acetone]=10%; (■) [Ethanol]=10%.

centage increases in the range of α -naphthol concentration 5×10^{-5} — 10×10^{-3} M but beyond which, it decreases. For a specific reaction time the rate of polymerization (R_p) was estimated at various concentrations of α -naphthol (2.5×10^{-6} — 10×10^{-3} M) where R_p increases steadily. The plot of $\log R_p$ vs. $\log [\alpha\text{-N}]$ was linear with a slope of 0.512 (Figure 6). The enhancement of % conversion and rate of polymerization with increase in α -naphthol concentration may be attributed to the resultant increase in concentration of the Cu(II)– α -N complex which enables the initiator KHSO_5 to undergo a spontaneous cleavage to produce initiating radicals very quickly. The depression of % conversion beyond a particular α -naphthol concentration (10×10^{-3} M) may account for its radical trapping and interaction with growing polymer radicals. The inhibition and retardation of radical polymerization by α -naphthol was reported in our previous publication.²⁰ Here we suggest that α -naphthol coupling with Cu(II)SO₄ acts both as activator and retarder, being dependent on concentration.

(ii) Effects of CuSO₄ Concentration

Time conversion curves are plotted in Figure 3 at various concentrations of CuSO₄ (2×10^{-6} — 4×10^{-2} M) and at fixed concentrations of KHSO₅ (0.0129 M), α -naphthol (0.01 M), and AN (0.754 M) at 40°C. The initial rate of polymerization and maximum conversion were found to increase by raising the concentration of CuSO₄ from 2×10^{-6} M to 0.02 M but then a decrease was noted.

The rate of polymerization (R_p) increased with increasing concentration of CuSO₄ (5×10^{-7} — 20×10^{-3} M). A plot of $\log R_p$ vs. $\log [\text{Cu(II)}]$ was linear with a slope of 0.169 (Figure 6). The increase in rate with increasing Cu(II) ions in the above range may be attributed to increasing catalysis since an appropriate molar ratio of Cu(II) to α -naphthol in the solution favors the formation of an activated complex which actively interacts

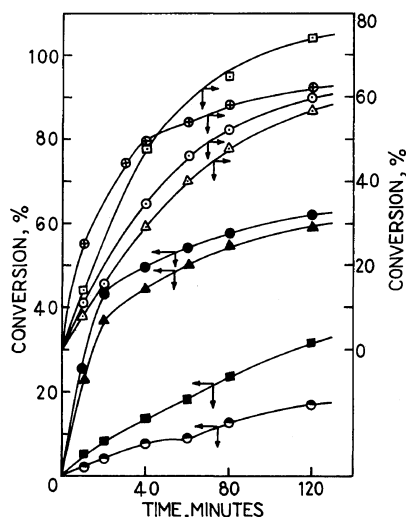


Figure 3. Variation in conversion % with time. (a) Effects of CuSO₄ concentration: $[\text{KHSO}_5]=0.0129$ M; $[\alpha\text{-N}]=0.01$ M; $[\text{AN}]=0.754$ M; temp = 40°C. Plots: (●) $[\text{CuSO}_4]=2 \times 10^{-6}$ M; (■) $[\text{CuSO}_4]=2 \times 10^{-5}$ M; (▲) $[\text{CuSO}_4]=4 \times 10^{-2}$ M. (b) Effects of mineral acid concentration: $[\text{KHSO}_5]=0.0129$ M; $[\text{CuSO}_4]=0.02$ M; $[\alpha\text{-N}]=0.01$ M; $[\text{AN}]=0.754$ M; temp = 40°C. Plots: (⊕) Control; (○) $[\text{H}^+]=0.3$ M; (△) $[\text{H}^+]=0.6$ M; (□) $[\text{H}^+]=1.2$ M.

with the peroxo bridge orbital, resulting in rupture of the O–O bond in a sequential fashion. This in turn influences the rate of the initiation of polymerization.

The dependence of rate on the 0.169 power of $[\text{Cu(II)}]$ and 0.512 power of $[\alpha\text{-N}]$ indicates that the catalysed decomposition of KHSO₅ and polymerization of acrylonitrile is caused by the intermediate formation of a 1:3 complex between Cu(II) and α -N. An increase in temperature has a positive effect on the rate.

(iii) Effects of Monomer Concentration

The rate of polymerization (R_p) increases with an increase in the concentration of acrylonitrile (0.1508—1.056 M) at fixed concentrations of CuSO₄ (0.02 M), α -N (0.01 M) and KHSO₅ (0.0129 M) in the temperature range of 35°C—50°C. A plot of R_p vs. $[\text{AN}]$ was linear passing through the origin (Figure 5). Figure 5 includes a double logarithmic plot of

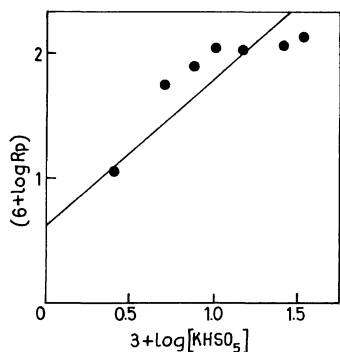


Figure 4. Variation in R_p with $[KHSO_5]$: $[CuSO_4]=0.02$ M; $[\alpha-N]=0.01$ M; $[AN]=0.754$ M; temp = 40°C .

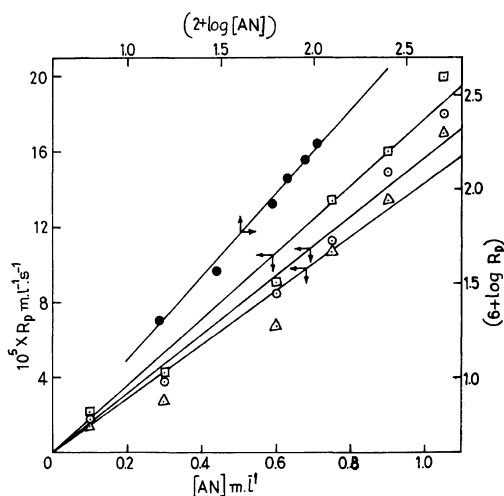


Figure 5. Variation in R_p with [Monomer] at various temperatures. $[KHSO_5]=0.0129$ M; $[CuSO_4]=0.02$ M; $[\alpha-N]=0.01$ M. Plots: (a) $[AN]$ vs. $10^5 \times R_p$, (Δ) temp = 35°C ; (\circ) temp = 40°C ; (\square) temp = 50°C . (b) (\bullet) $(2 + \log [AN])$ vs. $(6 + \log R_p)$ at 40°C .

the rate vs. $[AN]$ with unity slope which indicates first order dependence of rate on monomer concentration. An increase in temperature enhances the value of R_p slowly in the above mentioned range. Thus the termination rate is proportional to monomer concentration in aqueous medium and is independent of polymer concentration in the colloidal phase.

(iv) *Effects of $KHSO_5$ Concentration*

The initial rate of polymerization and maxi-

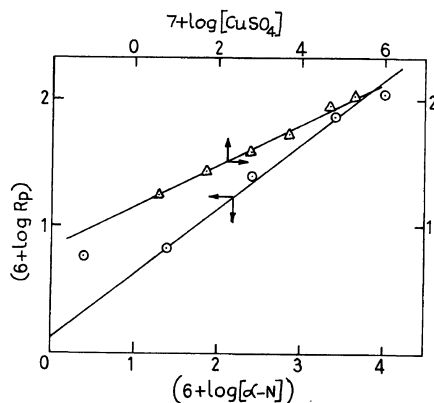


Figure 6. Variation in R_p with $[\alpha\text{-naphthol}]$ and $[CuSO_4]$: $[KHSO_5]=0.0129$ M; $[AN]=0.754$ M; temp = 40°C . Plots: (\circ) $(6 + \log [\alpha-N])$ vs. $(6 + \log R_p)$ at $[CuSO_4]=0.02$ M. (Δ) $(7 + \log [CuSO_4])$ vs. $(6 + \log R_p)$ at $[\alpha-N]=0.01$ M.

imum conversions increased steadily with increasing concentration of the initiator, $KHSO_5$. The polymerization rate, R_p increased with increased concentration of $KHSO_5$ (2.5×10^{-3} — 35×10^{-3} M) at fixed concentrations of $CuSO_4$ (0.02 M), $\alpha-N$ (0.01 M), and AN (0.754 M). The increase was not very pronounced at higher concentrations. Plots of R_p vs. $[KHSO_5]$ and $\log R_p$ vs. $\log [KHSO_5]$ (Figure 4) indicate the overall rate to be first order dependent on initiator concentration. This, however, deviates from the normal half order dependence of the rate on initiator concentration in conventional free-radical polymerization. This deviation may be attributed to complexation of the initiator with $Cu(II)$ ion in $Cu(II)\text{-}\alpha\text{-N}$ complex, resulting in selective stereochemical initiation involving a *cis*-attack on the bound monomer.

(v) *Effects of Mineral Acid*

The addition of mineral acid ($6N\text{-}H_2SO_4$) to the reaction mixture decreased the initial rate of polymerization and maximum conversion, but at high H^+ ion concentration (1.2 M), the rate was low for 40 min, followed

by an increase (Figure 3). This might be due to changes in the thermodynamic stability of the Cu(II)/ α -naphthol complex, the entity responsible for active catalysis. This was not noticed in our previous communication with AgNO₃/KHSO₅ couple.¹⁴

(iv) Effects of Organic Solvents

The addition of 10% (v/v) water miscible organic solvents such as acetone, ethanol, acetic acid and formic acid to the reaction mixture containing CuSO₄ (0.02 M), α -naphthol (0.01 M), KHSO₅ (0.0129 M), and AN (0.754 M) at 40°C retarded the initial rate and maximum conversion (Figure 2). The retardation of the reaction in the presence of these solvents may be attributed to (i) solvation of Cu(II) ions causing its complex forming ability with α -naphthol to lessen and the net effect in a reduction in the activity of the complex catalysis so that the peroxy orbital undergoes decomposition; (ii) simultaneous oxidation of the additives by KHSO₅, causing the optimum concentration of the initiating radicals in the immediate vicinity of the monomer to be reduced. The oxidation of compounds such as ethyl alcohol to ethyl acetate and acetic acid to glycolic acid has been established,²¹ (iii) premature termination of growing polymer chains resulting from activity transfer to these solvents. All these possibilities may apply in the present case.

Arrhenius Interpretation and Evaluation of Thermodynamic Parameters

An Arrhenius interpretation (Figure 7) was made of the polymerization reactions in the tricomponent system Cu(II)/ α -N/KHSO₅ at appropriate molar-ratios in the temperature range of 35–50°C. From the slope of the plot, the overall activation energy (E) was calculated as 3.118 kcal mol⁻¹ (13.03 kJ mol⁻¹). The value of E was used to evaluate various thermodynamic parameters at 40°C such as standard entropy of activation (ΔS^\ddagger), standard enthalpy (ΔH^\ddagger), standard free-energy (ΔF^\ddagger)

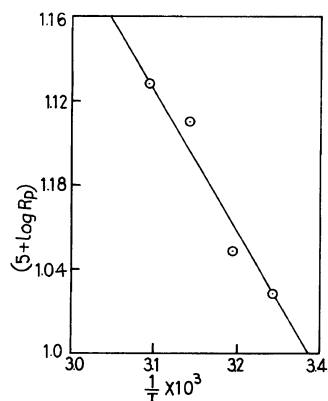


Figure 7. Arrhenius plot for acrylonitrile polymerization initiated by Cu(II)/ α -N/KHSO₅ system.

Table IV. Values of E and other thermodynamic parameters at 40°C

E	$-\Delta S^\ddagger$	ΔH^\ddagger	ΔF^\ddagger	$-\log \beta$
kJ mol ⁻¹	J mol ⁻¹ K ⁻¹	kJ mol ⁻¹	kJ mol ⁻¹	
13.03	287.44	15.63	105.61	17.62

of the polymerization and the overall stability constant (β) for the transient intermediate (Table IV).

The values in Table IV reveal the fact that the low activation energy of 3.118 kcal mol⁻¹ (13.03 kJ mol⁻¹) indicates the reaction to be feasible even at room temperature and a number of free-radical species are at once produced to initiate the reaction. The O–O bond energy in KHSO₅ is about 34 kcal mol⁻¹ and should be thermally catalyzed to undergo decomposition at elevated temperature. However, at low temperature, the molecule decomposes due to excess energy released by the Cu(II)- α -naphthol interaction.

The negative value of the entropy of activation $\Delta S^\ddagger = -287.4$ J mol⁻¹ K⁻¹ indicates the reaction to be thermodynamically feasible and is a controlled reaction that proceeds smoothly in the direction of the free radical path. Further, since ΔH^\ddagger and ΔF^\ddagger are directly related to E and ΔS^\ddagger , their values in the

present reaction show the system to be a novel initiating system.

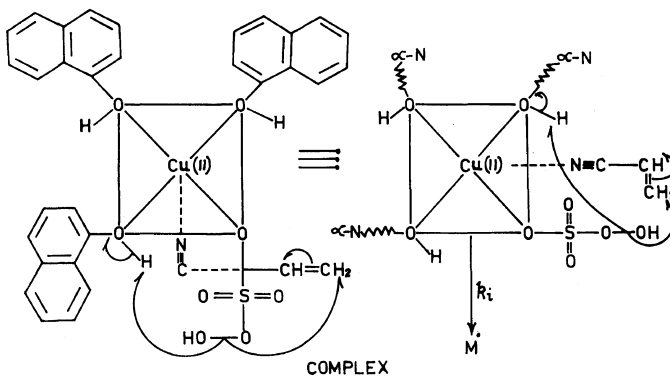
Mechanism of Polymerization

The polymerization of acrylonitrile initiated by the system Cu(II)/ α -N/KHSO₅ is characteristic of heterogenous polymerization. From the proportionalities obtained between measured parameters and variables, the rate of polymerization was found to be $R_p = K[AN]^{1.1} [KHSO_5]^{1.1} [Cu(II)]^{0.169} [\alpha-N]^{0.512}$. The proportionality of rate to the 1st power of initiator deviates from a simple path involving the decomposition of KHSO₅ to generate two radicals (OH· and ·OSO₃⁻) followed by initiation. Rather, a complex initiation mechanism is involved. The mode of initiator decomposition and chain initiation and termination mechanism of polymerization involving the tricomponent activator system Cu(II)/ α -N/KHSO₅ can be interpreted as proceeding through a novel catalytic path induced by the transient 1 : 3, Cu(II)- α -N, complex where ab-

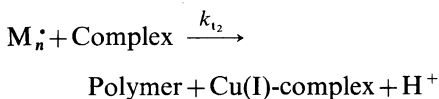
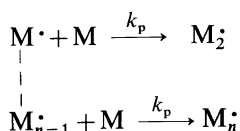
straction of an H-atom of the chelating OH group at α -naphthol in the complex by the initiator takes place followed by attack of OH· on the monomer. The initiation is a surface catalysis with adequate energy transfer from the complex to the initiator molecule. The SO₄⁻ part of initiator is converted to HSO₄⁻ ions. Termination is caused by the Cu(II)-complex. According to this interpretation, an increase in concentration of the radical donor and acceptor at the activation site should accelerate the rate and this has been found to be the case, where an increase in the KHSO₅ and AN concentrations enhances the value of R_p .

1. (a) $Cu(II) + 3\alpha-N \xrightleftharpoons{\beta_1} \text{Complex-I.}$
- (b) $\text{Complex-I} + KHSO_5 \xrightleftharpoons{\beta_2} \text{Complex-II.}$
- (c) $\text{Complex-II} + AN \longrightarrow \text{Transient complex.}$

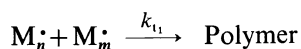
2. Initiation:



3. Propagation:



4. Termination:



The ligand bound transient complex initiation in a concerted path involving participation of the monomer molecules at the immediate vicinity seems tenable since generated free-radicals are spontaneously consumed. The

concerted generation-consumption criteria in the driving force in the complex catalysed peroxide decomposition and vinyl polymerization.

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