

# VINYL POLYMERIZATION

## VIII. Photopolymerization of Vinyl Monomers by Azidopentamminecobalt (III) Chloride

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### ABSTRACT

A systematic study of the kinetics of photopolymerization of vinyl monomers initiated by the complex azidopentamminecobalt (III) chloride in aqueous solution has been made. The determinations of monomer disappearance, complex disappearance, chainlengths of polymers, obtained against the different variables like light intensity, concentrations of monomer, light absorption fraction, etc., have been made. A kinetic mechanism proposed for the overall reaction is discussed in the light of the experimental results and certain rate constants have also been evaluated.

### I. INTRODUCTION

PHOTOLYSIS<sup>1,2</sup> of cobaltamine complexes led to redox decomposition yielding free radicals from ligands with the reduction of cobalt (III) to cobalt (II). Adamson,<sup>1</sup> Endicott and Hofmann<sup>2</sup> showed cobaltous ion formation from a number of cobalt (III) complexes when irradiated. Possibility of photo initiation by azidopentamminecobalt (III) complex was first reported by the authors.<sup>3</sup> Recently, Delzenne<sup>4</sup> also observed photoinitiation of acrylamide polymerization by halogenopentamminecobalt(III) complexes. In the present paper a systematic study of the kinetics of vinyl polymerization, photoinitiated by azidopentamminecobalt (III) chloride is reported. The vinyl monomers employed were methyl methacrylate (MMA), methylacrylate (MA) and acrylonitrile (AN). The polymerization was conducted at  $\lambda = 365 \text{ m}\mu$ . It was hoped that this study might throw more light on the primary photochemical act, subsequent dark reactions involved in the photolysis of azidopentamminecobalt (III) complex and their role in polymerization reaction.

### II. EXPERIMENTAL

Experimental set up and determinations of monomer disappearance, light intensity, chainlengths (poly (MMA)) etc., were described in Part I

of the series.<sup>5</sup> The azido complex was prepared by the method described by Linhard<sup>6</sup> and the rate of complex disappearance during polymerization was followed spectrophotometrically using a Beer's law calibration curve at  $\lambda = 303 \text{ m}\mu$ . The monomers methyl methacrylate, methylacrylate and acrylonitrile were used free of the inhibitors with a 5% solution of sodium hydroxide and then with water and finally distilled under reduced pressure in an atmosphere of nitrogen and stored at 5° C.

A typical experiment is described below in brief and the procedures for various measurements are given. The reaction system, vinyl monomer—azidocomplex—perchloric acid in aqueous solution at  $\text{pH} \approx 2$  was introduced into a reaction cell (capacity 75 ml.) and deaerated by passing nitrogen purified from oxygen. The reaction cell was then mounted inside a thermostat, maintained at  $35 \pm 0.1^\circ \text{C}$ . by the use of a toluene regulator and a hot wire vacuum switch relay (Gallenkamp), in the path of the monochromatic light beam and the reaction cell was irradiated for 20–30 minutes. The precipitated polymer was then filtered off, dried and weighed for rate of monomer disappearance and chainlength determination. The filtrate was used for following the rate of complex disappearance. The fraction of light absorbed ( $k_a$ ) by the cobalt complex in the reaction mixture was calculated from the absorbancies. For measurement of chainlength, the polymers were purified by reprecipitation with methanol from their solutions in benzene for poly (MMA) and poly (MA) and dimethyl formamide for poly AN, and the viscosities of 0.1% solutions of poly (MMA), poly (MA) in benzene and a 0.1% solution of poly (AN) in dimethyl formamide measured in a viscometer thermostated to  $\pm 0.01^\circ \text{C}$ ., in a viscometric bath designed for precision viscometry. Chainlengths were computed from the measured viscosities by using Mark-Houwink type relationships between limiting viscosity number and molecular weights of polymers:

$$[\eta] = 1.282 \times 10^{-4} M^{0.7143} \text{ at } 35^\circ \text{C. for poly (MA).}^7$$

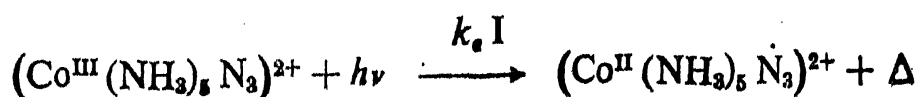
$$[\eta] = 2.43 \times 10^{-4} M^{0.66} \text{ at } 25^\circ \text{C. for poly AN.}^8$$

$$n = 2.81 \times 10^3 [\eta]^{1.32} \text{ at } 25^\circ \text{C. for poly (MMA).}$$

### III. KINETIC SCHEME

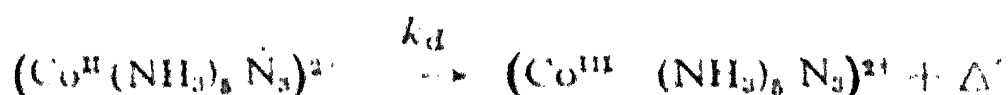
The following kinetic scheme explains the experimental results:

(1) Light Absorption:



$k_e$  is the light absorption fraction by the complex,  $I$  is the light intensity,  $\Delta$  term refers to the excess energy which may be dissipated to the surrounding medium.

(2) Dark Back Reaction:



(3) Decomposition of the Complex:



(4) Initiation:  $\dot{\text{N}}_3 + \text{M} \xrightarrow{k_i} \dot{\text{M}}$

(5) Propagation:  $\dot{\text{M}} + \text{M} \xrightarrow{k_p} \text{M}_2 \dots \text{etc.}$

(6) Termination: (a) Mutual:  $\text{M}_n + \text{M}_m \xrightarrow{k_t} \text{M}_{m+n}$

(b) Radical  $\dot{\text{N}}_3$ :  $\text{M}_n + \dot{\text{N}}_3 \xrightarrow{k_{t_1}} \text{polymer}$

(c) By complex:  $(\text{Co}(\text{NH}_3)_5\dot{\text{N}}_3)^{2+} + \text{M}_n \xrightarrow{k_{t_2}} \text{Polymer}$

#### IV. RESULTS AND DISCUSSION

Initiation of vinyl polymerization by azidopentamminecobalt (III) chloride was under deaerated conditions photochemical in nature, not thermal, and with dissolved  $\text{O}_2$  in the system long induction periods were observed indicating that the reaction was free radical in nature. The steady state was reached in about 15 minutes with  $\approx 20-30\%$  and  $\approx 40\%$  conversions of the monomer and complex respectively. A photochemical after effect for about 24 hours characteristic of MMA was noticed.<sup>9</sup> In the absence of monomer, evolution of nitrogen and decolorization of the complex took place. Polymerization was also noticed in diffused daylight and in sun light. It was evident from our studies that irradiation of the azido-complex led only to redox decomposition. There was no evidence for aquated product, *i.e.*  $(\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}^{\text{II}})^{2+}$ .

(a) Rate of Monomer Disappearance

Making the usual assumptions for stationary state kinetics for micro and macro-radicals and also assuming constancy of  $k_p$  and  $k_t$  with chain growth, on the basis of mutual termination

$$-\frac{d[M]}{dt} = \frac{k_p}{k_t^{\frac{1}{2}}} \left( \frac{k_s}{k_s + k_d} \right)^{\frac{1}{2}} k_e^{\frac{1}{2}} I^{\frac{1}{2}} [M]$$

the above expression may be derived. Rate of monomer disappearance was proportional to the unit power of monomer concentration for all the monomers (MMA, MA and AN) (Fig. 1) and square root of light absorption

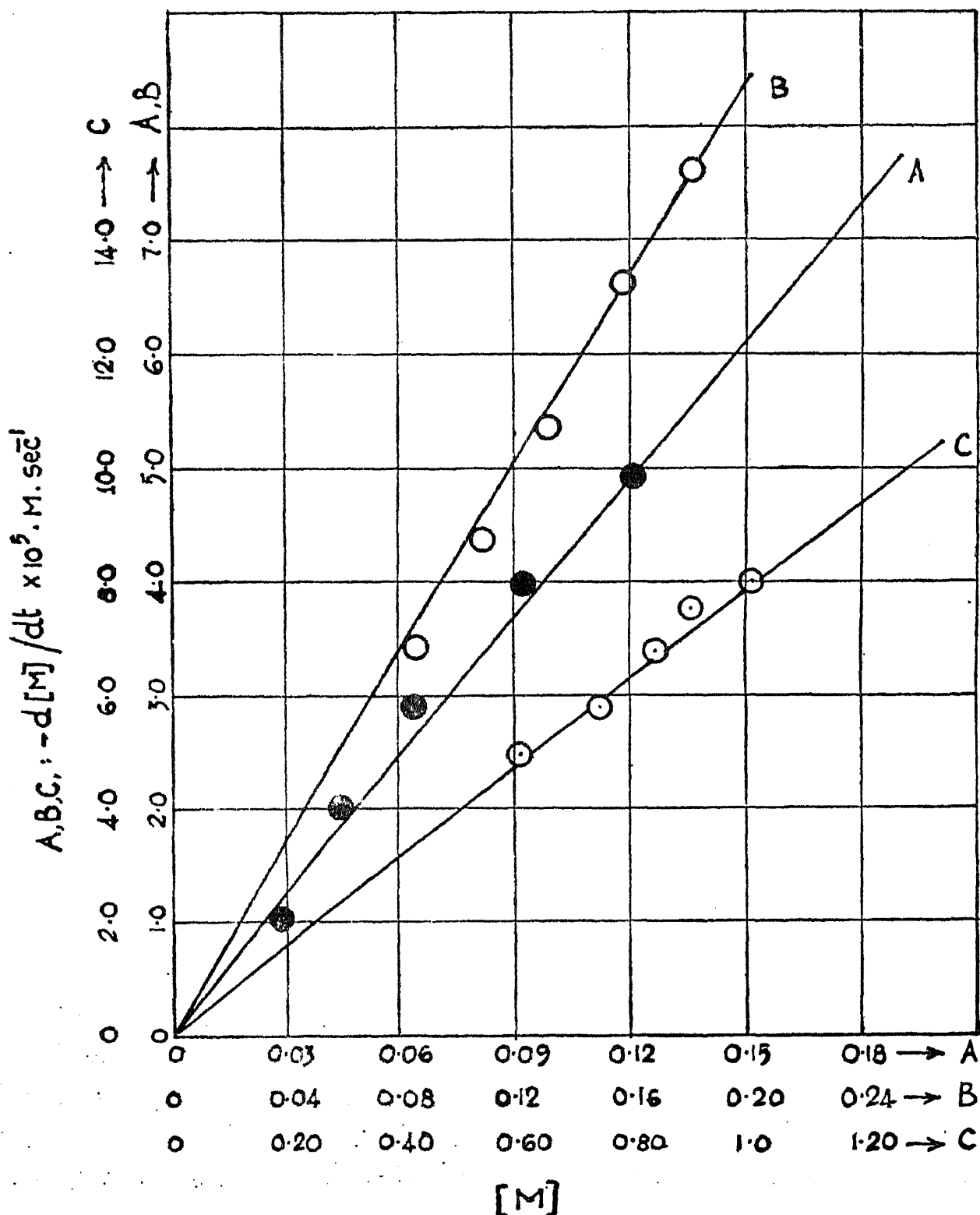


FIG. 1. Plots of  $-d[M]/dt$  vs.  $[M]$ . (A) MMA, (B) AN, (C) MA.

fraction and square root of the incident light intensity for all the monomers (MMA, AN, MA). The experimental results clearly showed that termination was only mutual type. Termination by azide radical would require a dependence of  $[M]^2$  and zero exponent values for  $k_e$  and I. Termination by the complex would require a dependence of unit power of  $k_e$  and I. The absence of nitrogen evolution during polymerization indicated that all the azide radicals were consumed for initiation.

(b) *Rate of Complex Disappearance*

The expression for the rate of complex disappearance under conditions of mutual termination of polymer radicals

$$\frac{-d[C]}{dt} = \left( \frac{k_s}{k_s + k_d} \right) k_e I$$

may be derived. The quantum yield for the complex disappearance,  $\phi_C$ , would be equal to  $k_s/(k_s + k_d)$ . The rate of complex disappearance was proportional to the first power of  $k_e$  and I and independent of monomer concentration for all the monomers (MA, AN, MMA) (Fig. 2).

(c) *Chainlengths*

On the basis of mutual termination, the expression for chainlength would be

$$n = \frac{k_p}{k_t^{1/2}} [M] \left( \frac{k_s + k_d}{k_s k_e I} \right)^{1/2}$$

Chainlengths were found to be proportional to the first power of monomer concentration and inversely proportional to the square root of  $k_e$  and I. It may be seen that the experimental results do not agree with the other modes of termination, *i.e.*, by azide radical or complex molecule. Azide radical termination would require a square dependence on  $[M]$  and inverse dependence on  $k_e$  and I whereas termination by complex would require zero exponent values for  $k_e$  and I.

(d) *Rate Constants ( $k_p/k_t^{1/2}$ )*

The rate constants  $k_p/k_t^{1/2}$  were evaluated from slopes of the plots of  $-d[M]/dt$  versus  $k_e^{1/2}$  or  $I^{1/2}$  or  $[M]$  and assuming  $k_s/(k_s + k_d) = \phi_C$ .  $\phi_C$  was evaluated by the ratio  $(-d[C]/dt)/k_e I$ . Our values of  $k_p/k_t^{1/2}$ , namely, 1.188, 1.221, 0.340 respectively for MMA, MA and AN, were in good agreement with those of ferric ion pairs<sup>10,11</sup> (1.1 for MMA) anthraquinone

sulfonates<sup>12</sup> (1.253 for MMA and 1.103 for MA) and dye reducing system<sup>13</sup> (1.403 for MMA, 1.19 for MA and 0.05 for AN) as photoinitiators of vinyl polymerization.

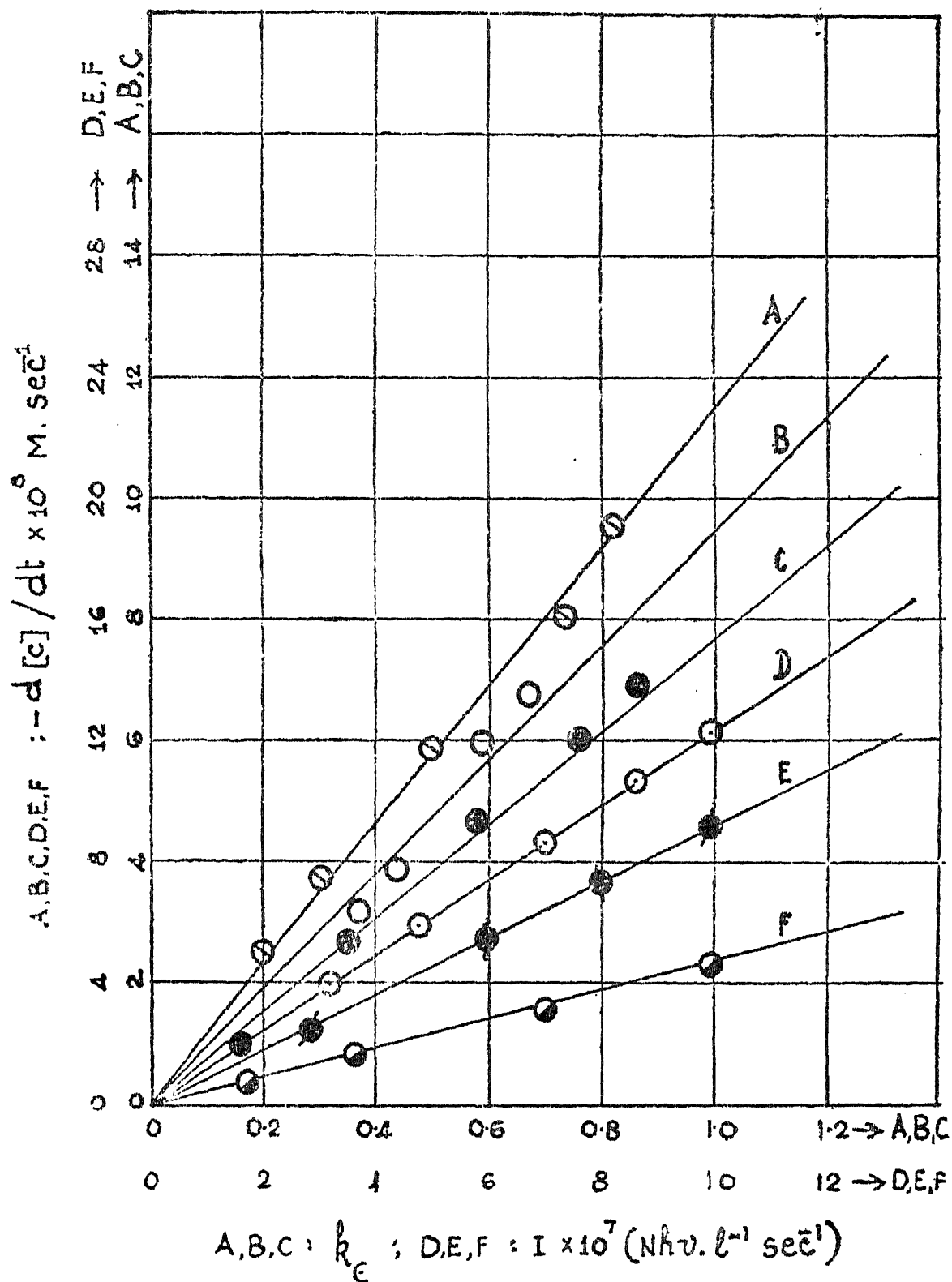


FIG. 2. Plots of  $-d[C]/dt$ . vs.  $k_e$ . (A) MMA, (B) MA, (C) AN. Plots of  $-d[C]/dt$  vs.  $I$ . (D) MMA, (E) MA, (F) AN.

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