

irregularities are present only at the bottom of the F-region. In this study, spread-F configurations at the time of onset are divided into three groups: range, complex and frequency. The range group consists of two types of configurations, one wherein spreading is present only at the low frequency end of the F-layer trace with clear cut foF2 cusps and the other wherein spreading is present over the entire frequency range of the F-layer trace. The frequency group represents the configuration wherein spreading exists only at and around the critical frequency of the F-region. Configurations which do not fall either into range or frequency group are taken as complex.

It can be clearly seen from Fig. 1 that there is considerable scatter (100–140 km) in the values of  $h'F$  at the time of onset of spread-F irrespective of season and the type of spread-F configuration. This behaviour, which is very much similar to the one we have observed recently<sup>10</sup> for high sunspot activity conditions, establishes the absence of any particular threshold height for the bottom of the F-region for the onset of equatorial spread-F. In an earlier study, we have found that there is no particular threshold height for the bottom of the F-region for the sustenance of equatorial spread-F.<sup>11</sup> It is therefore concluded that the onset and sustenance of equatorial spread-F does not uniquely depend on the height of the F-region. Any theoretical study of equatorial spread-F has to take into account this feature.

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### CIS-CHLORO-AQUO-TETRAMMINECOBALT(II) SULPHATE AS A PHOTOINITIATOR OF VINYL POLYMERIZATION

MOGGI<sup>1,2</sup> *et al.* studied the photobehaviour of *cis*-[Co(NH<sub>3</sub>)<sub>4</sub>(H<sub>2</sub>O)Cl]<sup>2+</sup> complex at 254 nm and 313 nm and observed that irradiation of the aqueous solutions of the complex resulted in photo-redox and photoaquation reactions. The photoredox products were identified as Co(II), NH<sub>3</sub>, H<sub>2</sub>O and chlorine atom, whereas the photoaquation was due to replacement of Cl<sup>-</sup> ligand in the complex by H<sub>2</sub>O. However the photobehaviour of this complex at longer wavelengths was not known. The present investigation was undertaken to follow the photobehaviour of this complex at light of  $\lambda = 365$  nm and also to explore the role of this complex as a photoinitiator of vinyl polymerization. For the first time the present study reports some interesting aspects of photopolymerization of acrylamide initiated by the *cis*-[Co(NH<sub>3</sub>)<sub>4</sub>(H<sub>2</sub>O)Cl]<sup>2+</sup> complex at  $\lambda = 365$  nm in nitric acid medium at 30°C.

The *cis*-[Co(NH<sub>3</sub>)<sub>4</sub>(H<sub>2</sub>O)Cl]<sup>2+</sup> complex prepared<sup>3</sup> in pure condition showed absorption maximum at  $\lambda = 360$  nm and 520 nm. The rate of disappearance of monomer,  $-d[M]/dt$ , was determined bromometrically, the rate of complex disappearance,  $-d[C]/dt$ , spectrophotometrically and the light intensity,  $I$ , by ferrioxalate actinometry<sup>4</sup>. The formation of photo-redox products at  $\lambda = 365$  nm was evident since an aliquot of the irradiated solution of the complex in concentrated HCl showed the characteristic absorption of Co(II) ion at 690 nm. Analysis of the irradiated solution also revealed that the rates of Co(III) disappearance and Co(II) production were not equal implying the presence of photoaquation reaction. With the *cis*-[Co(NH<sub>3</sub>)<sub>4</sub>(H<sub>2</sub>O)Cl]<sup>2+</sup> complex, in the presence of vinyl monomers like methyl methacrylate, acrylonitrile, acrylamide etc. photoinitiation of vinyl polymerization was also observed.

We summarize below the results of acrylamide polymerization photoinitiated by *cis*-[Co(NH<sub>3</sub>)<sub>4</sub>(H<sub>2</sub>O)Cl]<sup>2+</sup> complex at  $\lambda = 365$  nm in aqueous nitric acid medium at 30°C. 1. The reaction was definitely photochemical in nature since polymerization started almost immediately without any induction period in the presence of light. 2. Polymerization was also observed in the presence of sun light. 3. No thermal polymerization was observed upto 50°C. 4. The steady state was attained in about 45 minutes with 20% conversion of monomer and all experiments were

conducted at this time interval. 5.  $-d[M]/dt$  was proportional to  $[M]^{3/2}$ ,  $[C]^2$  and  $I^{1/2}$  (Fig. 1). 6.

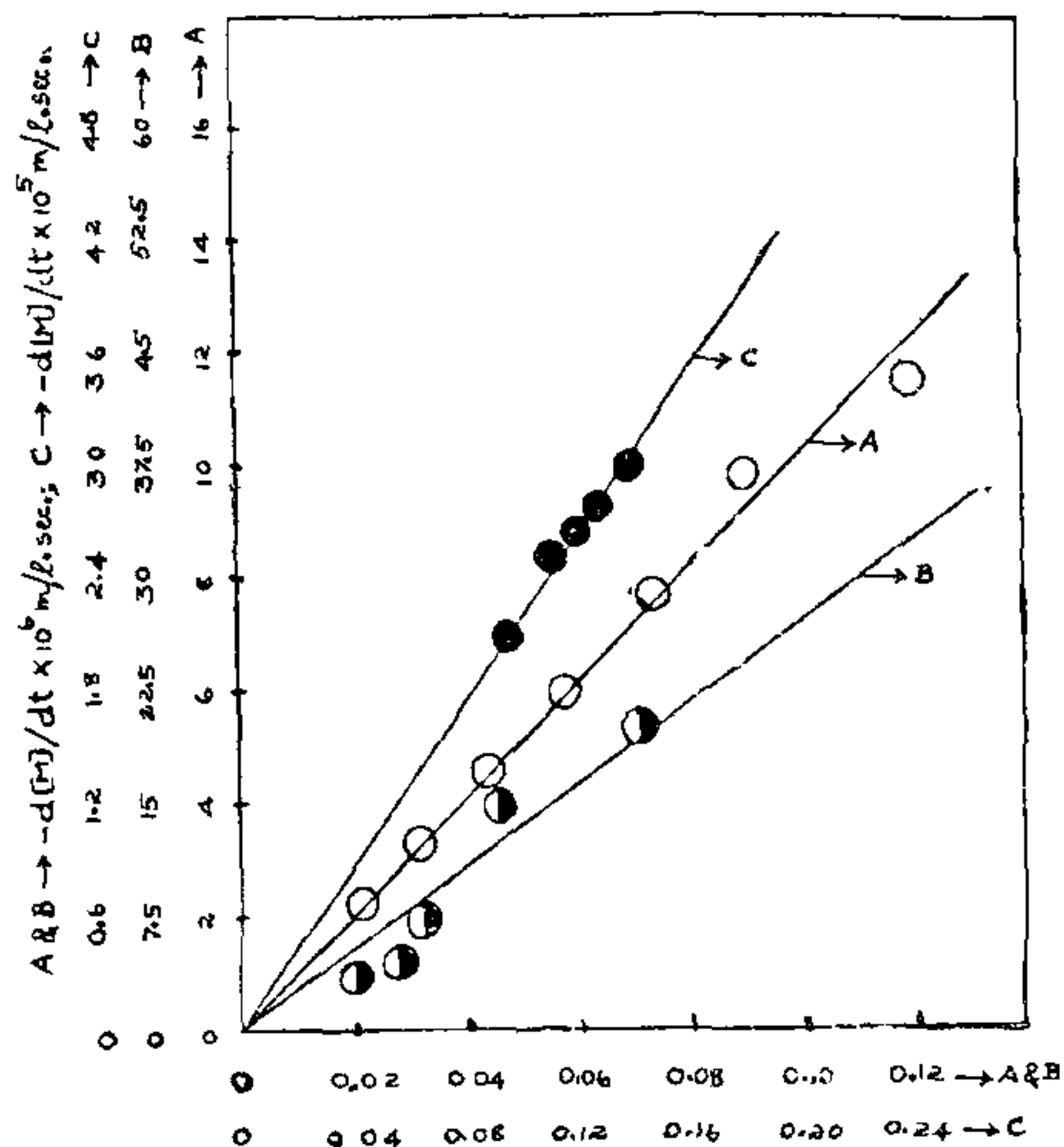
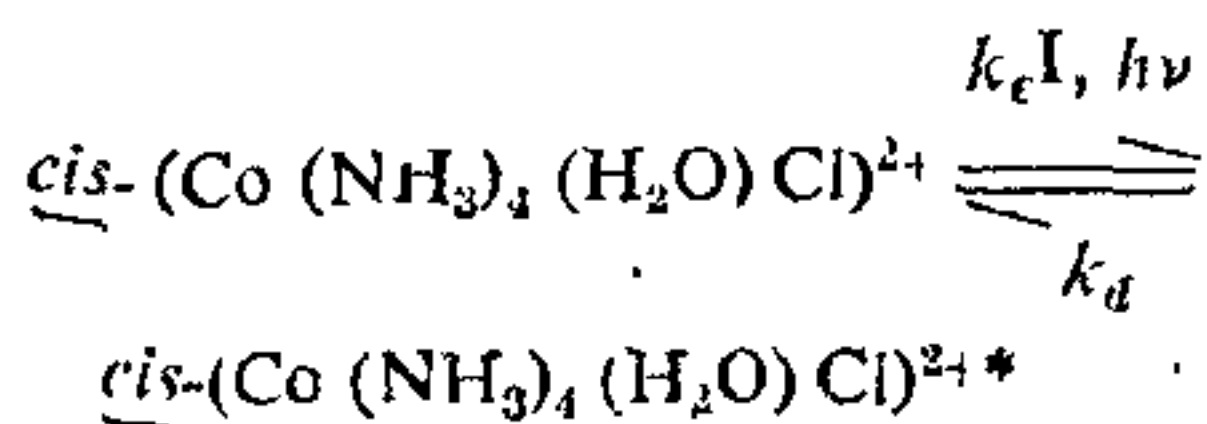


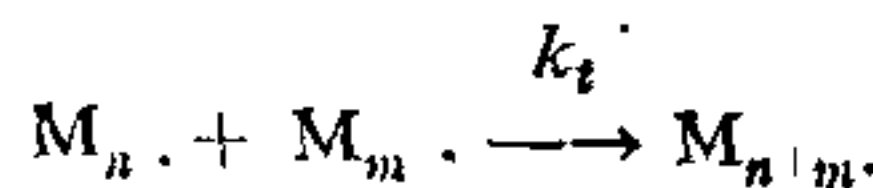
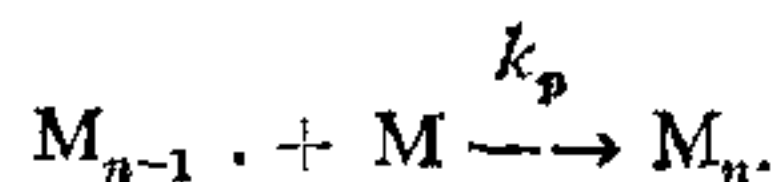
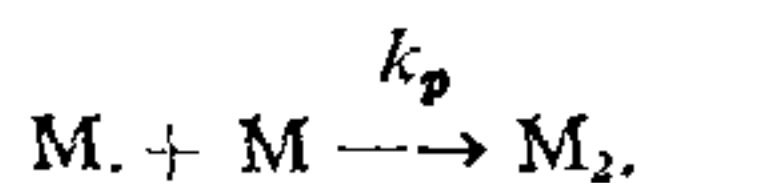
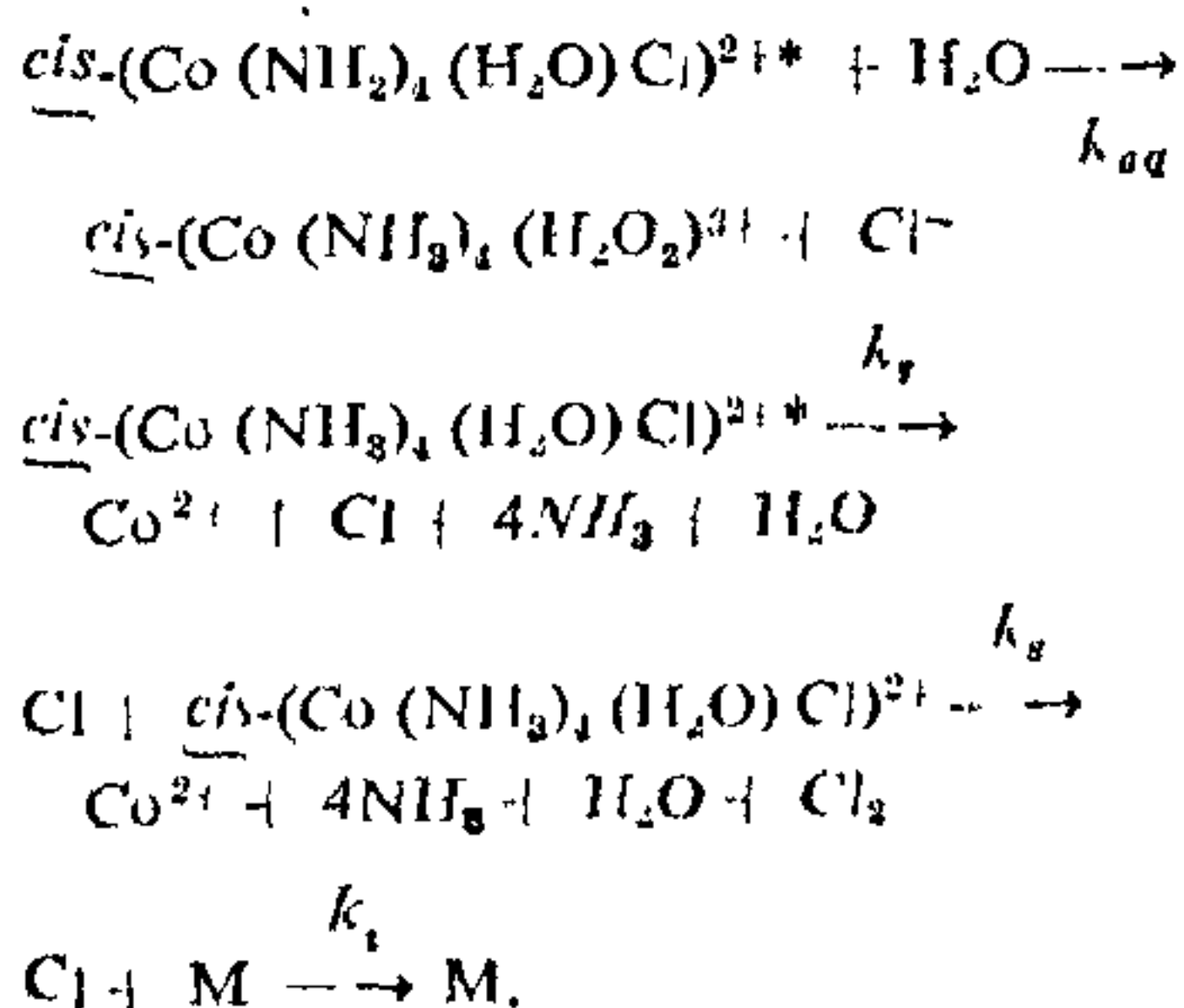
FIG. 1. (A) Rate of monomer disappearance vs. (Monomer concentration)<sup>1.5</sup>, (B) Rate of monomer disappearance vs. square root of complex concentration, (C) Rate of monomer disappearance vs. square root of light intensity.

A :  $[M]^{1.5} (\text{mole}^{-1})^{1.5}$ , B :  $[C]^{0.5} \times 10^2 (\text{mole}^{-1})^{0.5}$   
C :  $I^{0.5} \times 10^4 (\text{Nh } \nu, \text{ l}^{-1} \text{ s}^{-1})^{0.5}$ .

$-d[C]/dt$  was directly proportional to the first powers of  $[C]$  and  $I$ . The following reaction scheme *prima facie* may account for the experimental observations



where  $k_e$ , the light absorption fraction of the complex was proportional to  $[C]$  employed in our studies.

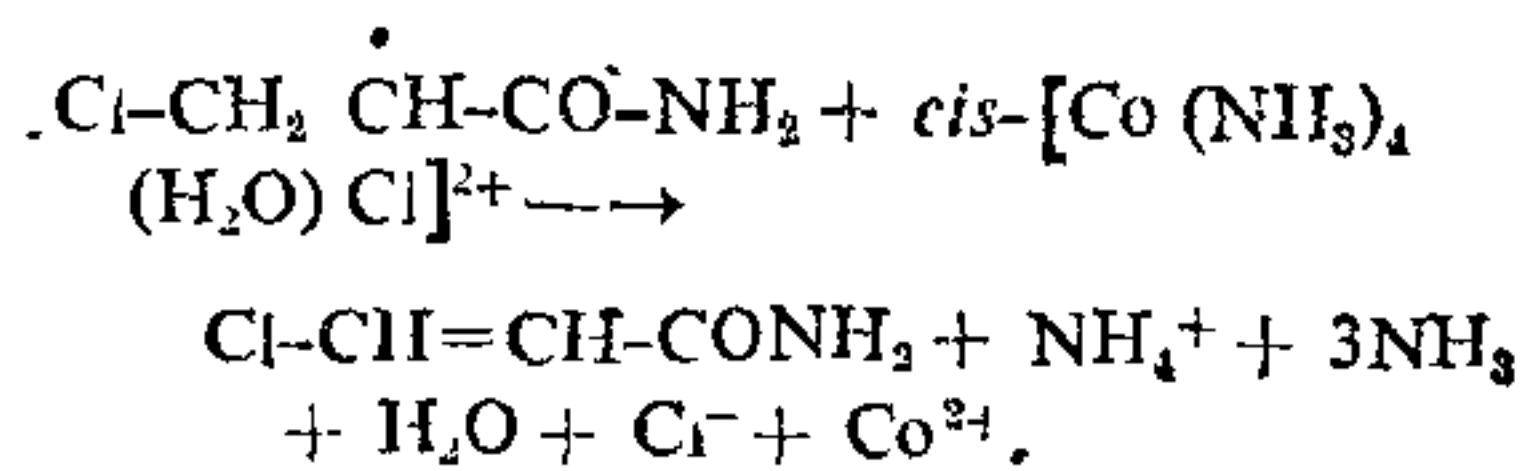


Assuming the steady state conditions for free radicals, the following rate expressions are derived.

$$-d[M]/dt = k_p/k_t^{1/2} \left\{ k_i \left( \frac{k_r}{k_r + k_d + k_{aa}} \right) \left( \frac{k_e I}{k_s [C] + k_i [M]} \right) \right\}^{1/2} [M]^{3/2} \quad (1)$$

$$-d[C]/dt = \left( \frac{k_r}{k_r + k_d + k_{aa}} \right) \left( \frac{2k_s [C] + k_i [M]}{k_s [C] + k_i [M]} \right) k_e I \quad (2)$$

The decreasing trend in the polymerization rates observed when complex concentrations were,  $[C] > 3.5 \times 10^{-3} \text{ M}$  may be attributed to the oxidative termination of polymer radicals by the complex such as



The polymerization rates also decreased with increase of  $[\text{H}^+]$  from  $5 \times 10^{-2}$  to  $0.6 \text{ gm ion lit}^{-1}$ , which may be attributed to increase of photoaquation reaction catalysed by hydrogen ion with decrease of redox products<sup>3</sup>. This suggests that the aquated product, namely  $\text{cis}-(\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2)^{3+}$ , is a poor initiator. Further work is in progress.

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