4. Klingenberg,H. G., Moese J. R., Fischer G., Porta J. and Sadjak A., *Zen. Tralbl. Bakieriol. Parsitenkd. Intektio. Nskr. Hyg. Erste.. Abt. Org. Reihe B. Hyg. Praeu. Med.*, 1975, **162**, 146.

5. Klingenberg,H. G., Moese J. R., Fischer G., Porta J. and Sadjak A., *Zen. Tralbl. Bakieriol. Parsitenkd. Intektio. Nskr. Dyz. Abt. Orig. Reihe. B. Hyg. Praeu. Med.*, 1975, **161**, 137.

6. Birnberger A. C., Birnberger K. L., Eliasson S. G. and Simpson P. C., *J. Nemotol.Chem.*, 1971, **18**, 1291.

PHOTOPOLYMERIZATION OF N,N'—METHYLENE BISACRYLAMIDE BY POTASSIUM TRISOXALATOCOBALTATE (III)

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COBALTIC ion has got sufficiently large redox potential and in its complexes it undergoes both photoredox and photoaquation processes by light absorption. Photodecomposition of a number of complexes has been studied by Adamson[1]. Potassium trisoxalatocobaltate (III) complex has been reported to possess a redox quantum yield of 0.25 at a wavelength of $\lambda = 365$ nm[2]. A different value was also reported by Copestake and Uri[3], who have also studied the photodecomposition of $Co(Ox)_3^{3-}$. Photoaquation reaction was not reported[4] in the case of $Co(Ox)_3^{3-}$. Potassium trisoxalatocobaltate (III) was used as a photoinitiator for methyl methacrylate[5], acrylamide[6], and acrylonitrile[7] polymerization and also as a thermal initiator by Biswas *et al*[8]. We present the results of photopolymerization of N,N'-methylene bisacrylamide initiated by potassium trisoxalatocobaltate (III) at $\lambda = 365$ nm in aqueous perchloric acid medium at 30°C. N,N'-methylene bisacrylamide is chosen for the study to observe the effect of substitution on amido 'nitrogen' of acrylamide unit. The second acrylamide unit would be present as pendent group along the polymer chain and hence the polymer should have unsaturation. The symmetrical structure leads to resonance stabilization of the radical. $CH_2 > NH-CO-CH-CH_2R$ (where R = the initiating radical) which may decrease the rate

The complex was prepared as reported[9]. The primary oxalate radical for initiation of polymerization was obtained by the photodissociation of $Co(C_2O_4)_3^{3-}$ complex at $\lambda = 365$ nm. Since oxalate anion is a

strongly chelating ligand, photoaquation will not occur in the complex during irradiation. The rate of monomer disappearance, $-d[M]/dt$ was determined gravimetrically as the polymer precipitated, the rate of complex disappearance, $-d[C]/dt$ spectrocalorimetrically by measuring its absorption at 420 nm and the light intensity, I, by ferrioxalate actinometry[10].

We summarise below the results of photopolymerization of N,N'-methylene bisacrylamide initiated by potassium trisoxalatocobaltate (III) complex at $\lambda = 365$ nm in aqueous perchloric acid medium. (1.) The steady state was attained in 40 min. and all the experiments were conducted at this time interval. (2.) The presence of dissolved oxygen in the system caused long induction periods. (3.) The reaction was photochemical in nature under deaerated conditions since no thermal polymerization occurred upto 40°C for a period of over 12 hr (4) $-d[M]/dt$ was proportional to $[M]$, $[C]^{1/2}$ and $[I]^{0.33}$ (figure 1). (5.) The dependence of the rate of monomer disappearance on the first power of monomer concentration was valid below 2×10^{-2} mol/l. When the monomer concentrations above 2×10^{-2} mol/l were used, the rate of monomer disappearance exhibited a decreasing trend as shown in figure 1, Plot A. (6.) The dependence of the rate of monomer disappearance on the square root of complex concentration was valid below 1.2×10^{-3} mol/l. Beyond this concentration of complex, the rate of monomer disappearance also showed a decreasing
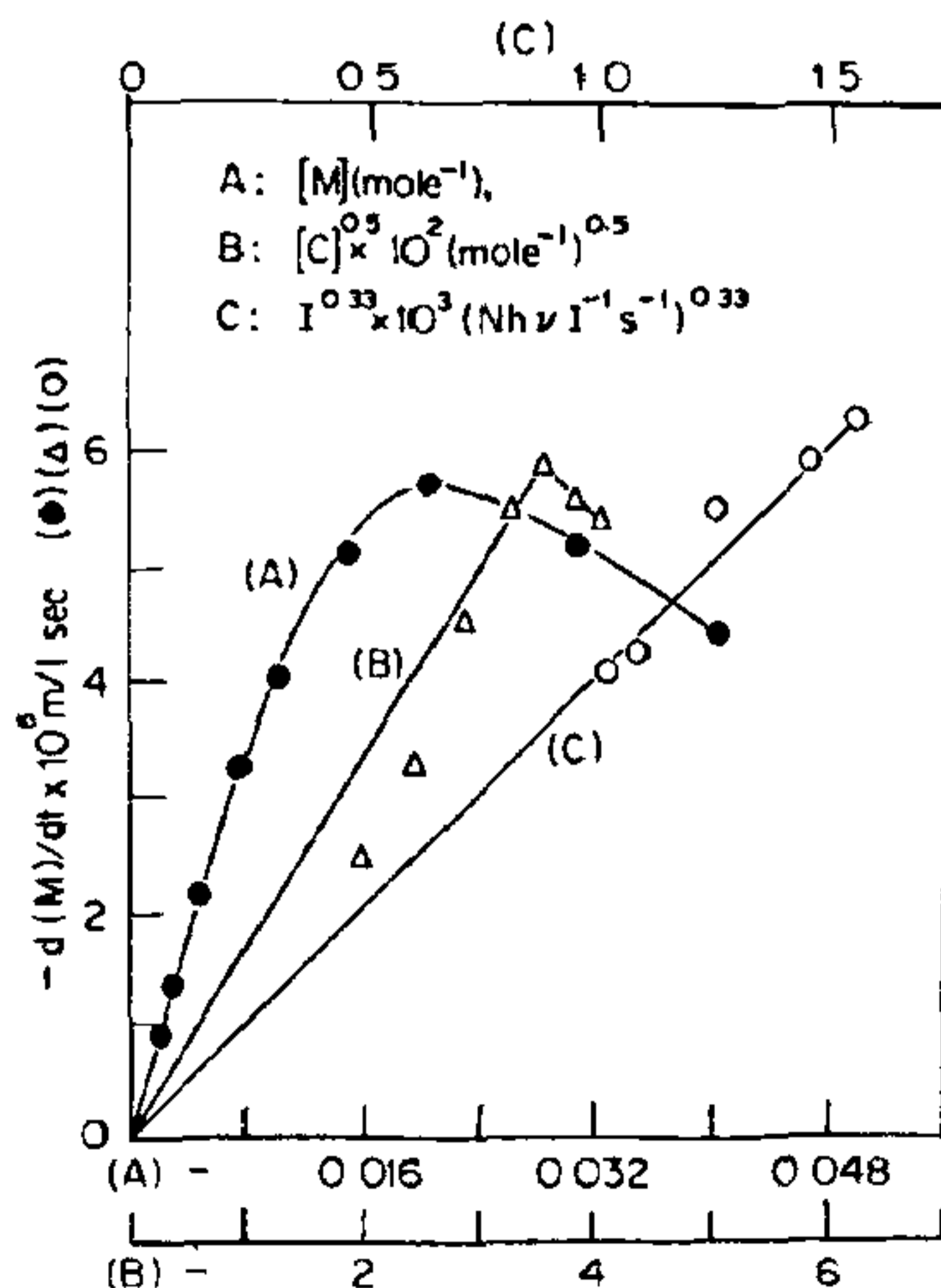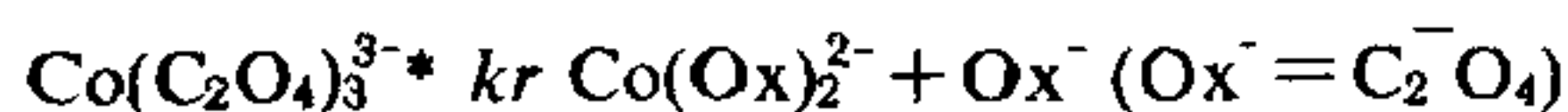

Figure 1. Rate of monomer disappearance vs A. monomer concentration, B. square root of complex concentration, C. light intensity.

trend as shown in figure 1, Plot B. (7.) The dependence of $-d[M]/dt$ on $[I]^{0.33}$ may be due to practical limitations. Hsiachen[11] observed a light intensity dependence of 0.4, in the study of photopolymerization of acrylamide in *ethylene glycol* sensitized by thiazine dyes with triethanolamine. (8.) $-d[C]/dt$ was directly proportional to the first power of $[C]$ and $[I]$.
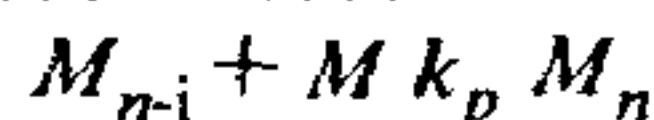
The following reaction scheme prima facie may account for the experimental observation.

$$Co(C_2O_4)_3^{3-} \xrightarrow[k_\epsilon l]{hv} Co(C_2O_4)_3^{3-*}$$

$$[C] \xrightarrow{} [C]^*$$
$$\;k_d\;$$
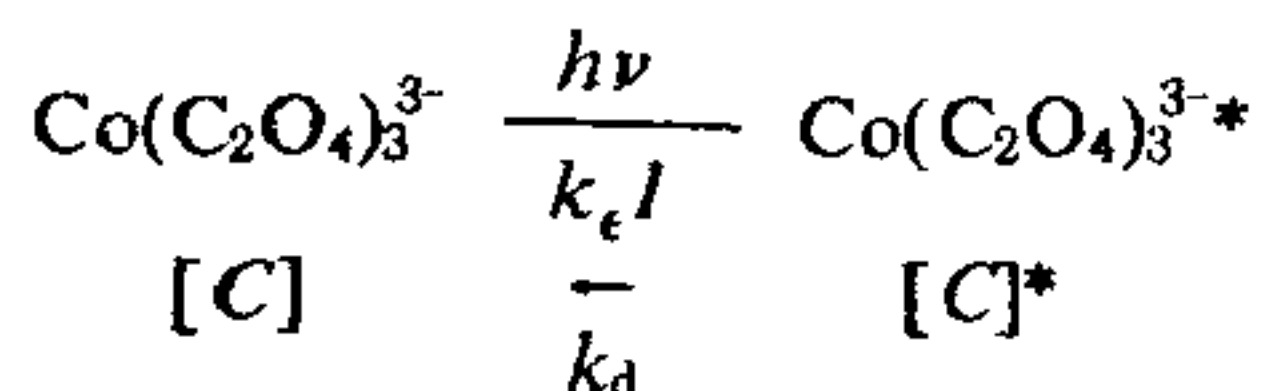
$Co(C_2O_4)_3^{3-*}$ was the excited complex and k_d, the rate constant for the dark back reaction of the excited complex.

$$Co(C_2O_4)_3^{3-*} \; kr \; Co(Ox)_2^{2-} + Ox^- \; (Ox^- = C_2^- O_4)$$

$$Co(C_2O_4)_3^{3-} + Ox^- \; k_s \; Co^{2+} + 3\,Ox^{2-} + 2\,CO_2$$

$$Ox- + M \; k_i \; M.$$

$$M. + M \; k_p \; M_2.$$
$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots$$
$$M_{n-i} + M \; k_p \; M_n$$

$$M_n + M_m \; k_t \; M_{n \cdot m}$$

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

$$d[M]/dt = \frac{k_p}{k_t^{1/2}} \; \frac{k_r k_\epsilon l}{k_r + k_d}^{1/2} \; [M]$$

$$-d[C]/dt = \frac{k_r}{k_r + k_d}[C]I$$

We have noticed that the rate of monomer disappearance, $-d[M]/dt$ and the rate of complex disappearnace, $-d[C]/dt$ increased with increasing hydrogen ion concentration. This might be explained by considering protonation of one of the oxalato ligands in $Co(Ox)_3^{3-}$ followed by the production of hydrogen atoms in acidic solutions[12].
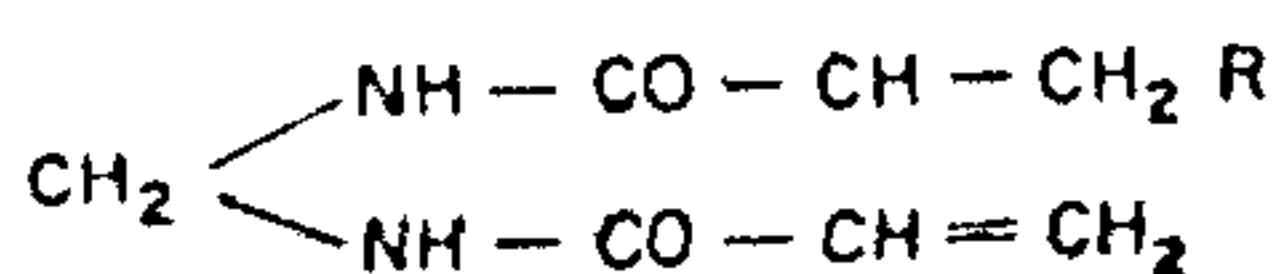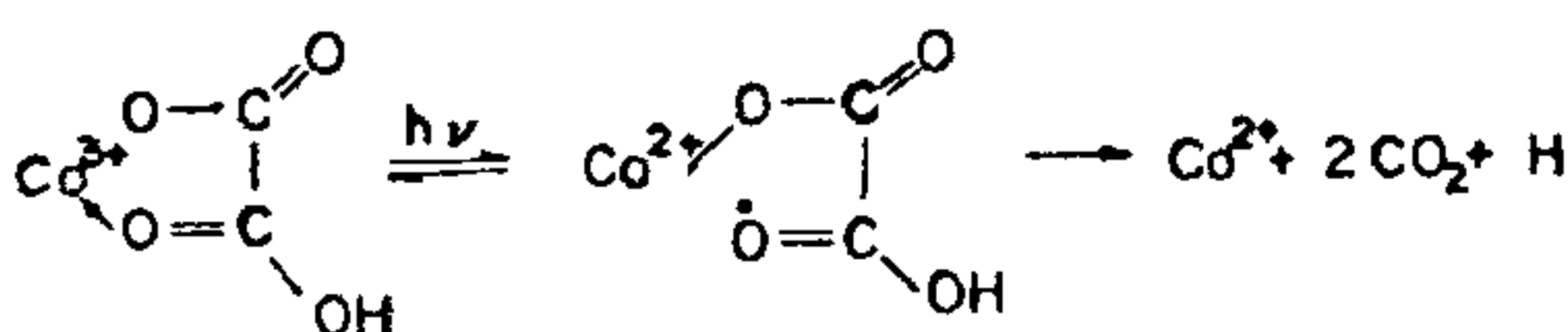
These hydrogen atoms account for the increased rate of polymerization. Our observations in this regard coincide with that of Shaik Mahaboob *et al*[7].

1. Adamson, A. W., *Discuss Faraday Soc.*, 1960, **29**, 163.
2. Porter, G. B., Doering, J. G. W. and Karanka, S., *J. Am. Chem. Soc.*, 1962, **84**, 4027.
3. Copestake, T. B., and Uri, N., *Proc. R. Soc. (London).*, 1955, **A228**, 252.
4. Bunton, C. A., Carter, J. H., Llewellyn, D. R., Odell, A. L. and Yisi, S. Y., *J. Chem. Soc.*, 1964, 4622.
5. Ghosh, P., Mukherjee, A. R. and Palit, S. R., *J. Polym. Sci.*, 1964, **A2**, 2817.
6. Takemura, F., Sagakuchi, K. and Tsuji, Y., *Nippon Kagaku Kaishi*, 1973, 4, 819, *Chem. Abstr.* 1973, 79, p. 79217.
7. Shaik Mahaboob, Natarajan, L. V. and Anwaruddin, Q., *J. Macromol. Sci.-Chem.*, 1978, **A12**, 971.
8. Biswas, A. M. and Mukherjee, A. R., *Indian J. Chem.*, 1966, **4**, 160.
9. Palmer, W. G., *Exp. Inorg. Chem.*, Cambridge Univ. Press, London, 1954, p. 550.
10. Hatchard, G. C., and Parker, C. A., *Proc. R. Soc. (London).*, 1956, **A235**, 518.
11. Catherine S. Hsiachen, *J. Polym. Sci.*, 1965, **A3**, 1155.
12. Eaton, D. R., and Stuart, S. R., *J. Phys. Chem.*, 1968, **72**, 400.

AN IMPROVED SYNTHESIS OF CHALCONES USING TRIETHYL BENZYL AMMONIUM CHLORIDE (TEBA)

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BASE catalysed condensation[1] of appropriate acetophenones and benzaldehydes in aqueous ethanolic medium has been most commonly adopted for obtaining chalcones of desired substitution patterns, though there are other methods available for their preparation[2], largely because of the simplicity of this method and ready accessibility of starting materials with a wide variety of substitution patterns. Benzaldehydes are normally taken in slight excess, to make up for their consumption by the accompanying Cannizzaro reaction, during the course of condensation.