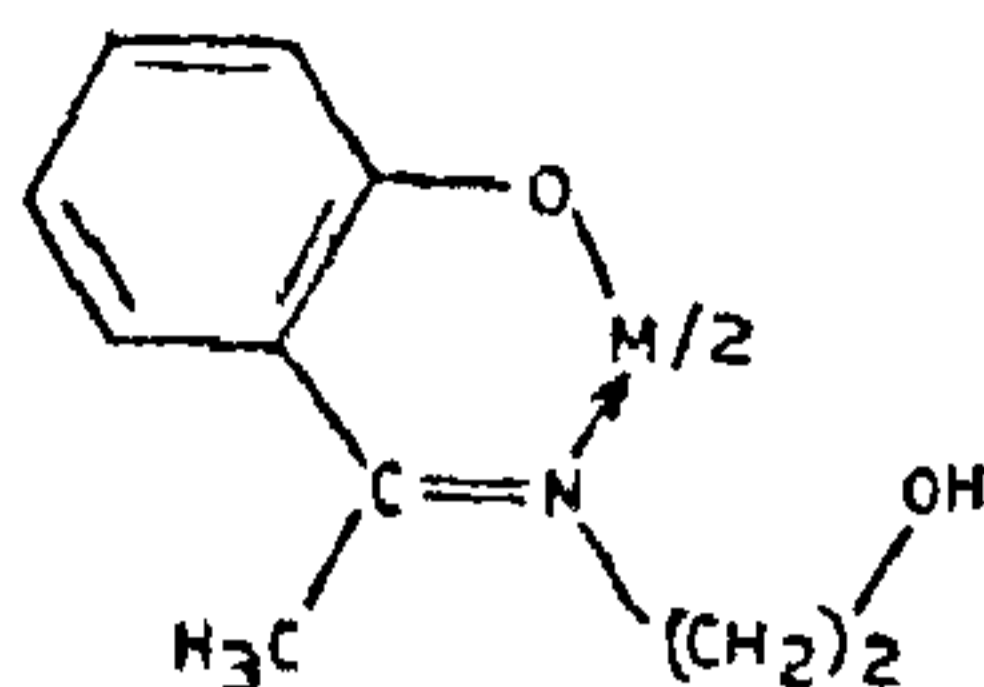


metal chelates may be represented by the structure shown in Fig. 1.



WHERE M = Ni(II) Cu(II) OR Pd(II)  
BUT WHEN M = VO(II) ONE MOLECULE OF H<sub>2</sub>O  
IS ALSO COORDINATED TO IT

FIG. 1. Metal chelates of N-hydroxyethyl,  $\alpha$ -methyl, 2-hydroxybenzylideneimine schiff base.

The authors are thankful to U.G.C., New Delhi, for award of fellowship to one of them (PKK).

Department of Chemistry,  
University of Jodhpur,  
Jodhpur, July 18, 1977.

D. C. SEHGAL,  
P. K. KANUNGO,  
R. K. MEHTA.

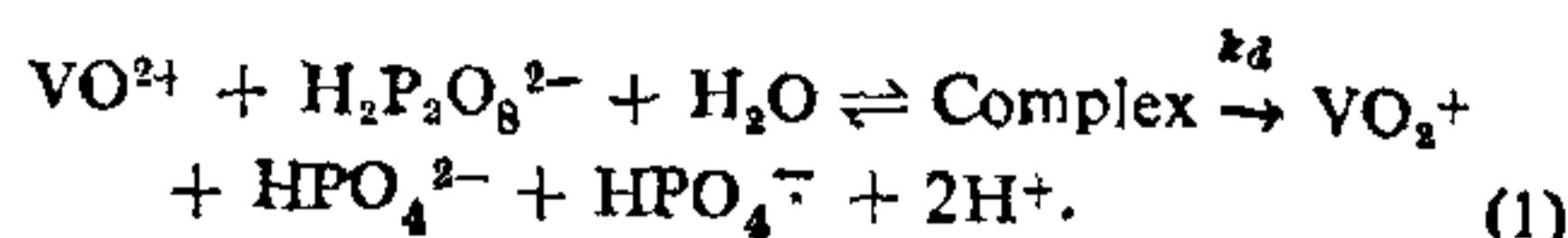
1. Cotton, F. A. and Wilkinson, G., *Advanced Inorganic Chemistry*, 1966, p. 881.
2. Siconi, L., *J. Inorg. Nucl. Chem.*, 1961, 19, 73.
3. Yamada, S., *Coordin. Chem. Rev.*, 1966, 1, 415.
4. Poddar, S. N., Ghosh, S. and Das, A. K., *J. Indian Chem. Soc.*, 1976, 53, 788.
5. Selbin, J., *Chem. Rev.*, 1965, 65, 165.
6. Dasch, L. W. and Hanninen, U. E., *J. Am. Chem. Soc.*, 1950, 72, 3673.

### VINYL POLYMERIZATION INITIATED BY PEROXYDIPHOSPHATE—VANADYL ION REDOX SYSTEM

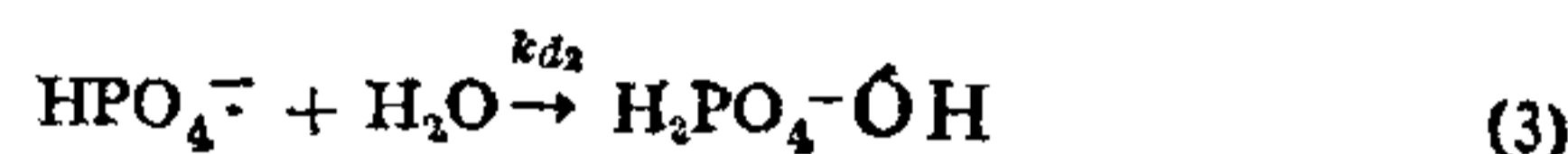
STUDIES involving peroxydiphosphate for the initiation of vinyl polymerization have been undertaken by us in order to evaluate the use of this compound as a suitable water-soluble initiator. Our preliminary investigation<sup>1</sup> with peroxydiphosphate—Ag<sup>+</sup> redox system revealed some interesting features and it was shown that peroxydiphosphate can function as initiator in the presence of H<sup>+</sup> and suitable reducing agents.

In the present investigation, we report some of the important aspects of another redox system, peroxydiphosphate—VO<sup>2+</sup>, for the initiation of vinyl polymerization. Edwards *et al.*<sup>2</sup> studied the oxidation of vanadyl ion by peroxydiphosphate and showed that the reaction proceeds *via* complex formation and a free-radical mechanism. It is also evident<sup>3</sup> that V<sup>5+</sup> alone, in the absence of a reducing agent, cannot initiate the polymerization of a vinyl monomer. Hence the

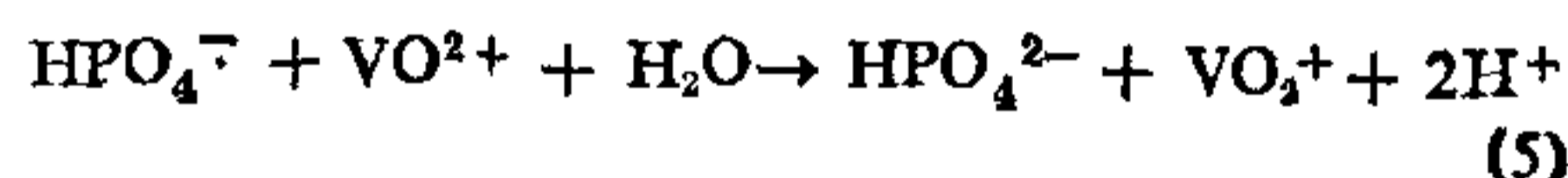
primary radical-producing reaction can be indicated<sup>3</sup> as follows;



This would result in the formation of HPO<sub>4</sub><sup>·-</sup> as the only active initiating species. HPO<sub>4</sub><sup>·-</sup> by itself can initiate the polymerization of the vinyl monomer or it can react with water producing  $\dot{\text{O}}\text{H}$ , a second initiating species<sup>1</sup>.



It is not possible to get reactive metal ion intermediate in this system. But in the case of PP—Ag<sup>+</sup> (PP = peroxydiphosphate) redox system, Ag<sup>2+</sup> formed as the active intermediate would react with water producing  $\dot{\text{O}}\text{H}$  and regenerating Ag<sup>+</sup>. In PP—Co<sup>2+</sup> redox system<sup>4</sup> also, a similar reactive intermediate is formed. In addition to the fact that no reactive metal ion intermediate is formed, V<sup>5+</sup> formed in the radical-producing step can act as a linear terminator. Termination by the metal ion in its quadrivalent state would also be expected since both oxidative and reductive termination of polymer radicals<sup>5-9</sup> by metal ions are possible. Partial destruction of the initiating species by the reaction of the following type,



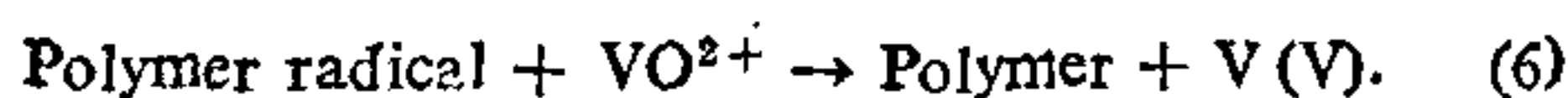
would also be expected.

Experiments were carried out under the conditions, [PP] = 1.5–3.0 × 10<sup>-4</sup>M, [VO<sup>2+</sup>] = 2.5–25 × 10<sup>-3</sup>M, [Acrylonitrile] = 0.1519–0.9112M and pH = 1.95 (using phosphate buffer) at 25°C under deaerated conditions. Vanadyl sulphate is E. Merck sample. Other experimental details are the same as described previously<sup>1</sup>.

Summarising the important observations of the present study, PP—VO<sup>2+</sup> redox pair initiated the polymerization of acrylonitrile efficiently. A transition in order, with respect to vanadyl ion, 0.5 order at low [VO<sup>2+</sup>] (0.0025–0.005M) and 0.1 to zero order at high [VO<sup>2+</sup>] (0.005–0.025M) was noticed. Over the wide range of [VO<sup>2+</sup>] (0.0025–0.025M), only a first order variation with respect to monomer was observed. A half-order dependence on PP at low [VO<sup>2+</sup>] (0.005M) changed into 0.9 order dependence at high [VO<sup>2+</sup>] (0.025M). A three-fold increase in hydrogen ion concentration and a two-fold increase in ionic strength did not result in any change in the

rate of polymerization. Increase in temperature led to an increase in the rate of polymerization unlike the case of PP-Ag<sup>+</sup> redox system.

The above experimental findings indicate that at low concentration of the metal ion, mutual termination takes place exclusively and as the metal ion concentration increases, termination by vanadyl ion or V<sup>5+</sup> also sets in. As the order tends toward zero with respect to VO<sup>2+</sup> at high [VO<sup>2+</sup>], it is probable that termination by vanadyl ion takes place.



The operation of both mutual and linear terminations would explain the transition in order, with respect to the metal ion.

Since the radical-producing step leads to the formation of the phosphate radical ion only, without any reactive metal ion intermediate and also the initiating species would be destroyed by reaction (5), one would expect PP-VO<sup>2+</sup> redox system to be less effective than PP-Ag<sup>+</sup> redox system. But the reverse is found to be true. This may be due to the ease of oxidation of vanadyl ion relative to Ag<sup>+</sup>, giving rise to a higher value of  $k_d$  and hence the rate of polymerization.

Studies involving various PP-reducing agent redox systems are in progress in developing the efficiency of PP as a water-soluble initiator.

Dept. of Physical Chemistry,  
University of Madras,  
A.C. College Campus,  
Madras 600 025. July 22, 1977.

S. S. HARIHARAN,  
A. MEENAKSHI.

1. Hariharan, S. S. and Meenakshi, A., *J. Polym. Sci., Polym. Lett.*, 1977, 15, 1.
2. Anderson, M., Edwards, J. O., Green, A. A. Sr. and Wiswell, M. D. Sr., *Inorg. Chim. Acta*, 1969, 3:4, 655.
3. Saccubai, S., *Ph.D. Thesis*, Madras University, January 1968.
4. Hariharan, S. S. and Meenakshi, A., Unpublished results.
5. Dainton, F. S. and Seaman, P. H., *J. Polym. Sci.* 1959, 39, 279.
6. Collinson, E., Dainton, F. S., Smith, D. R., Trudel, G. J. and Tazuke, S. (in Part), *Discussions Faraday Soc.*, 1960, 29, 188.
7. Watanabe, M. and Kiuchi, H., *J. Polym. Sci.*, 1962, 58, 103.
8. Cavell, E. A. S. and Meeks, A. C., *Polymer*, 1967, 8 (2), 79.
9. Viswanathan, S. and Santappa, M., *J. Polym. Sci., Polym. Lett.*, 1968, 6, 629.

### VAN ECK AND COOK METHOD FOR THE EVALUATION OF THE FORMATION CONSTANT OF METAL CARBONYLS

THE formation constant of some mononuclear and substituted mononuclear carbonyl complexes have been evaluated using a relation derived from Van Eck<sup>1</sup> and Cook equations<sup>2</sup>. The formation constant of four binuclear carbonyl complexes have also been calculated.

Van Panthaleon Van Eck<sup>1</sup> gave an empirical relation between the formation constant of the metal carbonyls and their ionization potential, viz.,

$$\log K = 1.25 I - 4.2. \quad (1)$$

D. Cook<sup>2</sup> correlated the stretching frequency of the carbonyl group in metal carbonyls with the ionization potential,

$$\nu_{C=O} = 29.20 I + 1409 \quad (2)$$

K,  $\nu_{C=O}$  and I are the formation constant, stretching frequency of the carbonyl group and ionization potential respectively. The combination of equations (1) and (2) gives the following relation,

$$\log K = 0.042 \nu_{C=O} - 64.428. \quad (3)$$

Equation (3) has been utilized by many workers<sup>3-6</sup> to evaluate the formation constant of various metal carbonyls with their stretching frequency and is found in good agreement with the experimental values. In the present work we have evaluated the formation constant of some mononuclear and substituted mononuclear carbonyl complexes and the data are shown in Tables I and II respectively. Table I also contains the formation constant of four binuclear carbonyl complexes, viz., Mn<sub>2</sub>(CO)<sub>10</sub>, Cr<sub>2</sub>(CO)<sub>10</sub>, Re<sub>2</sub>(CO)<sub>10</sub> and W<sub>2</sub>(CO)<sub>10</sub>. A plot of log K vs.  $\nu_{C=O}$  gives a straight line in accordance with equation (3). Although the experimental values of the formation constants of these metal carbonyls are not available in literature, the result can be verified in an indirect way. Thus from Table I it is evident that Ni(CO)<sub>4</sub> > Co(CO)<sub>4</sub><sup>-</sup> > Fe(CO)<sub>4</sub><sup>-2</sup> are isoelectronic and their formation constants follow the order Ni(CO)<sub>4</sub> > Co(CO)<sub>4</sub><sup>-</sup> > Fe(CO)<sub>4</sub><sup>-2</sup>. This is due to the fact that a negative charge on the metal atom favours the shift of electrons from the metal d-orbital to antibonding \* orbital or carbon in CO group, thus decreasing the triple bond character in CO which decreases the bond strength and hence the stretching frequency of the carbonyl group and the formation constant also decreases. The formation constant of Ni > Co > Fe is in agreement with the Irving William<sup>6</sup> series. Similarly a positive charge on the metal atom is reluctant to back-bond formation and hence the formation constant increases in this case. In Table II, of the substituted metal carbonyls of Fe, Mn, Cr and V are isoelectronic and have a general formula [C<sub>6</sub>H<sub>5</sub>M(CO)<sub>5</sub>] wherein, is the formal