

We note that the reaction of $\text{Ni}_2(\text{acac})_6$ with ligand (Ib) yields mononuclear pentacoordinated $\text{Ni}(\text{acac})(\text{salenR}_2)$ which readily forms octahedral adducts (III) with monodentate donors⁵. No evidence for dinuclear species has been obtained with this ligand. The difference in the behaviour of Ia and Ib can be rationalized on the basis of structure (II). In this structure the salenR_2 ligand occupies three facial positions of an octahedron. The flexible $-(\text{CH}_2)_3-$ chain makes this possible⁶. On the other hand salenR_2 can only span meridional positions⁷ (as in III) due to relative shortness of the $-(\text{CH}_2)_2-$ chain. It cannot span facially.

Financial assistance given by Department of Atomic Energy, Government of India, is gratefully acknowledged.

References

1. BULLEN, G. J., MASON, R. & PAULING, P., *Inorg. Chem.*, **4** (1965), 456.
2. GRADON, D. P., *Coord. Chem. Rev.*, **4** (1969), 1.
3. NAKAMOTO, K., *Infrared spectra of inorganic and coordination compounds* (Wiley-Interscience, New York), 1970, 247.
4. JORGENSEN, C. K., *Acta Chem. scand.*, **9** (1955), 1362.
5. BALUNDGI, R. H. & CHAKRAVORTY, A., *Inorg. Chim. Acta*, **8** (1974), 261.
6. DI VAIRA, M. & ORIOLI, P. L., *Inorg. Chem.*, **5** (1967), 490.
7. SACCONI, L., ORIOLI, P. L. & DI VAIRA, M., *J. Am. chem. Soc.*, **87** (1965), 2059; ORIOLI, P. L., DI VAIRA, M. & SACCONI, L., *J. Am. chem. Soc.*, **88** (1966), 4383; TEWARI, R., SRIVASTAVA, R. C., BALUNDGI, R. H. & CHAKRAVORTY, A., *Inorg. nucl. Chem. Lett.*, **9** (1973), 583.

Chemical Oscillations in Mn^{2+} -catalysed Belousov-Zhabotinskii Reaction in Orthophosphoric Acid Medium

K. PRASAD*, G. S. P. VERMA, A. PRASAD & V. B. DHAR

Department of Chemistry, Ranchi University, Ranchi 834008

Received 22 April 1976; accepted 19 June 1976

The occurrence of Belousov-Zhabotinskii reaction in orthophosphoric acid medium is reported for the first time. The existence of two alternate mechanisms for the observed chemical oscillations in this system is suggested.

OSCILLATORY reaction between potassium bromate, malonic acid, and cerous/ceric ion in sulphuric acid medium has received considerable attention¹⁻⁶. In this reaction malonic acid may be replaced by a number of organic substances containing active methylene group which can be easily brominated by enol mechanism⁷. The catalyst, the

cerous/ceric ion, can also be replaced by a number of metal ions capable of existing in two valence states differing by one electron only and having their E_0 values between 0.9 and 1.6 (ref. 7). However, no alternative to sulphuric acid medium for this reaction has, as yet, been reported. In this paper we report our observations on chemical oscillations in orthophosphoric acid medium. The work is all the more significant in view of chemical oscillations found in biological systems containing enough of phosphate group.

Potassium bromate (Baker analysed), manganous sulphate (S. Merck/GR), malonic acid (Riedel, extrapure) and orthophosphoric acid (E. Merck/GR) were used as such.

Procedure—The reaction was followed potentiometrically using bright Pt wire as indicator electrode and SCE as reference. Potassium chloride was found to inhibit oscillations and so a very dilute solution of KCl (0.002M) was taken in the calomel electrode. The two half cells were connected with the help of potassium sulphate agar agar bridge. The e.m.f. of the system was determined using direct reading potentiometer (Titricomat, ILM LABOR, GDR). To a solution containing orthophosphoric acid, malonic acid and manganous sulphate equilibrated at $35^\circ \pm 0.1^\circ$, was added a solution of potassium bromate also equilibrated at this temperature. The bright Pt indicator electrode was inserted in the vessel and e.m.f. recorded at varying time intervals. The results are plotted in Fig. 1.

The oscillation in the present system is found to be qualitatively different from that found in sulphuric acid medium. The total oscillatory state of the system can be divided into three parts (Fig. 1). The oscillatory states from A to B and from C to D are similar to that found in Belousov-Zhabotinskii reaction system in sulphuric acid medium. These states are characterized by a slight increase in time period with time.

The state from B to C is unique. It shows alternate long and short periods, $L_1, S_1; L_2, S_2; \dots$. L_i, S_i , suggesting that the system has two alternate cyclic routes by which it reaches the autocatalytic state signalled by a sudden rise of e.m.f. of the system. The shorter time period is associated with shorter amplitude whereas the longer time period is associated with longer amplitude. These amplitudes can be related to the difference between the upper and lower critical [bromide ion] limits^{8,9}. Thus it seems that the two alternative routes are having two pairs of critical [bromide ion] limits under two different conditions. More work is required to elucidate this point.

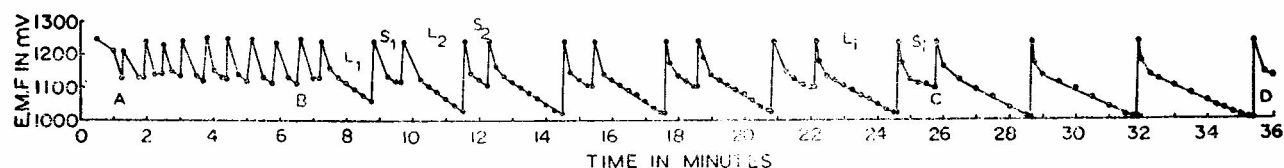


Fig. 1—Plot of e.m.f. against time at 35° ($[\text{Malonic acid}] = 0.032M$, $[\text{KBrO}_3] = 0.044M$, $[\text{MnSO}_4] = 0.0008M$ and $[\text{H}_3\text{PO}_4] = 8.4N$)

*To whom correspondence regarding the paper may be made.

The state, C to D, is highly sustained with nearly constant amplitude. Oscillations lasted for nearly 2 hr (only a part of which is shown in Fig. 1). One may have some doubt that sulphate ion obtained from manganous sulphate or potassium sulphate in the agar agar bridge may have caused oscillations. But this is negated by the fact that Rastogi and coworkers^{5,6} could not obtain oscillations in cerium and manganese catalysed Belousov-Zhabotinskii reaction when sulphuric acid concentration was less than 0.4N.

The authors express their thanks to Prof. H. C. Mishra, Head of the Department of Chemistry, Ranchi University, for facilities.

References

1. NOYES, R. M. & FIELD, R. J., *Annual Review of Physical Chemistry*, **25** (1974), 95.
2. NICOLIS, G. & PORTNOW, J., *Chem. Rev.*, **73** (1973), 365.
3. DEGN, H., *J. chem. Educ.*, **49** (1972), 302.
4. FARADAY SYMPOSIUM, *Discussion on physical chemistry of oscillatory processes* (Faraday Division of the Chemical Society, London), 1975.
5. RASTOGI, R. P. & YADAVA, K. D. S., *Indian J. Chem.*, **12** (1974), 687.
6. RASTOGI, R. P., YADAVA, K. D. S. & PRASAD, K., *Indian J. Chem.*, **12** (1974), 974.
7. VAVILIN, V. V., GULAK, P. V., ZHABOTINSKII, A. M. & ZAIKIN, A. M., *Izv. Acad. Nauk, SSSR, Ser Khim.*, **11** (1968), 2618.
8. NOYES, R. M., FIELD, R. J. & KÖRÖS, E., *J. Am. chem. Soc.*, **94** (1972), 1394.
9. FIELD, R. J., KÖRÖS, E. & NOYES, R. M., *J. Am. chem. Soc.*, **94** (1972), 8649.

Graph Theoretical Interpretation of Existence of Large Catacondensed Rings

SADHAN BASU

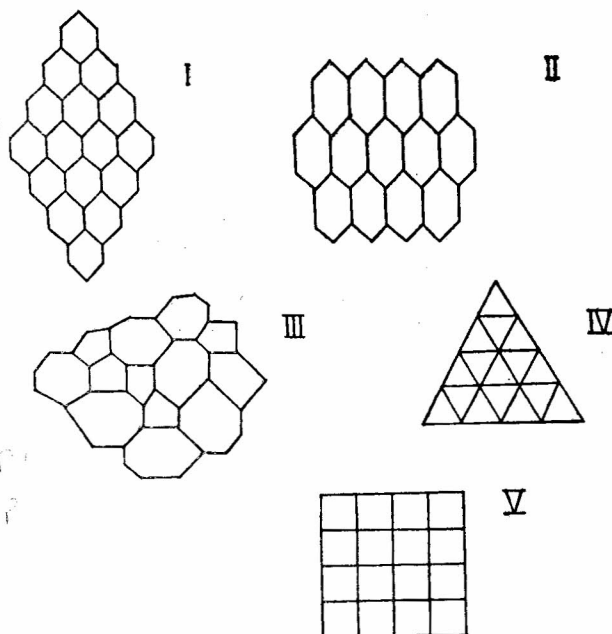
Department of Chemistry, University College of Science
Calcutta 700009

Received 23 August 1976

From graph theoretical considerations it has been shown that only three-, four- and six-membered rings can give extended catacondensed planar structures. Catacondensed structures from five- or seven-membered rings, if they exist, should be non-planar.

IT is well known that benzene rings can fuse together to form catacondensed hydrocarbons (I) which can be synthesized by various chemical means¹. When this fusion extends to infinity we get graphite which have unique electrical and magnetic properties. Catacondensed systems containing fused five (II) and seven (III) membered rings have also been prepared, but in these cases fusion has not proceeded very far, and large systems obtainable from six-membered ring systems have not been prepared². It has often been asked if graphite-like structure could be prepared with five- and seven-membered ring systems and if they will have unique electrical and magnetic properties as distinct from normal graphite.

We may analyse the possibility of such systems mathematically from the graph theoretical con-



siderations³. Let us consider a system of the type (I). Let us assume there are n_v vertices (occupied by atoms), n_e edges (represented by bonds) and n_f faces bounded by edges. Let ρ be the number of edges at each vertices which is evidently different from the ρ^* which gives the boundary edges. If n_b be the number of vertices at the boundary, we have

$$\frac{n_b}{n_v} \rightarrow 0 \text{ as } n_v \rightarrow \infty \quad \dots(1)$$

If the number of edges at each vertices is ρn_v and the boundary edges is ρn_b then

$$\rho n_v - \rho n_b < 2n_e < \rho n_v \quad \dots(2)$$

where n_e is the total number of edges in the graph. This may be written as

$$\frac{\rho}{2} - \frac{\rho}{2} \frac{n_b}{n_v} < \frac{n_e}{n_v} < \frac{\rho}{2} \quad \dots(3)$$

We, thus, conclude that

$$\frac{n_e}{n_v} \rightarrow \frac{\rho}{2} \text{ as } n_v \rightarrow \infty \quad \dots(4)$$

Now each edge lies on the boundary of just two faces. So there are $n_f - 1$ faces with ρ^* boundary edges and the face f_∞ has n_b boundary edges, same as the number of boundary vertices. This leads us to conclude that

$$2n_e = (n_f - 1)\rho^* + n_b$$

or

$$\frac{n_f}{n_v} = \frac{2}{\rho^*} \frac{n_e}{n_v} + \frac{1}{n_v} - \frac{1}{\rho^*} \frac{n_b}{n_v} \quad \dots(5)$$

As $n_v \rightarrow \infty$ we get

$$\frac{n_f}{n_v} \rightarrow \frac{\rho}{\rho^*} \quad \dots(6)$$

The Eulers equation³ for planar graph states

$$1 + \frac{n_f}{n_v} = \frac{n_e}{n_v} + \frac{2}{n_v} \quad \dots(7)$$