

fair. The maximum error is found to be approximately 5% for even series and about 10% for odd series. The average error is found to be 4.47% for alkanes and 0.69% for alkenes.

Comparison of experimental and calculated values of Heats of Melting for n-alkenes :

For comparing the heats of melting for *n*-alkenes no distinction has been made for the flexibility of long chains having odd and even number of carbon atoms for calculating the values of heats of melting. These values show good agreement with experimental⁸ values (Fig. 2). The data shows that the per cent error is both negative and positive at random.

From the break up of the contributions towards ΔH_m it can be seen that the maximum contribution arises out of the partition function due to the introduction of gas like holes and is approximately 80% of the total value. Moreover, the gas like partition function becomes asymptotic beyond a certain value of *N*, the number of carbon atoms. The stepwise variation observed in the values of ΔH_m in the odd-even numbered carbon atom chains is reproduced.

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Deelectronation Mechanism of Hydrazine by Mn^{3+}

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OXIDATION of hydrazine by different monodeelectronators¹⁻⁴ has been studied extensively, but with contradictory reports. The oxidative mechanism of most of the deelectronations has been reported to vary with the working conditions like the concentration of acid, order of addition of reagents and temperature etc.

While Huang and Spence⁵ reported Mo(VI) acting as dideelectronator in pH range 1.2-3.2 in the oxidation of hydrazine, Mishra and Sinha¹ established Mo(VI) as the monodeelectronator in 1*N* H₂SO₄ medium. Prasad and Kumar² reported V(V) acting as monodeelectronator in the oxidation of hydrazine, when V(V) solution was added to

hydrazine and they proposed intermediates, N₂H₃, N₂H₂ and N₂H. Contradictory results have been reported in the oxidations of hydrazine by monodeelectronators^{3,4}, Ce(IV) and Fe(CN)₆³⁻.

Mn³⁺ is found to be very strong deelectronator⁶ and has been used for kinetic studies of the oxidations of hydroxylamine^{7a} and hydrazine^{7b} in perchloric acid. In the present communication we have reported the studies on oxidation of hydrazine in 9*N* H₂SO₄ with Mn³⁺. It is found that hydrazine undergoes four electron change in one electron steps.

Experimental

Manganous sulphate, potassium permanganate, sulphuric acid and hydrazine sulphate used in this study were B. D. H. Analar.

Mn³⁺ was prepared by the oxidation of Mn²⁺ by MnO₂ in acidic medium as described by Ubbelohde⁸. In 9*N* H₂SO₄ Mn³⁺ was quite stable for 24 hours and was standardised with a solution of ferrous ammonium sulphate (B. D. H. Analar). For oxidation study, the titration was broken up in different independent stages as described by Gyani and Prasad⁹. A number of cells were arranged in series. In each cell equal amount of M/40 reductant (10 ml) and increasing amounts of oxidant (M/10) were added.

The potential of each cell was recorded after 1 hour, 3 hours, 6 hours, 9 hours and 12 hours of the addition of oxidant. The readings taken after 1 hour and 12 hours and after heating the mixture for 2 hours at 90° and subsequent cooling for 24 hours are given in Table 1. The exact volume of oxidant at which sharp inflexions (Fig. 1) were observed are recorded in Table 1.

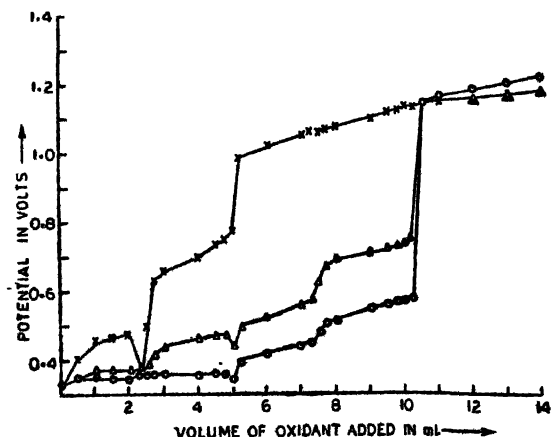


Fig. 1

TABLE 1—POTENTIOMETRIC TITRATION DATA OF THE OXIDATION OF HYDRAZINE BY Mn^{3+}

Cell: 10 ml M/40 Hydrazine sulphate, Medium: 9N H_2SO_4 ; Oxidant: M/10 Mn^{3+} solution.

Storage time for attaining equilibrium at room temperature	Position of inflexion in ml	Nature of inflexion
1 hr.	2.5	very sharp sharp
	5.1	
12 hrs.	2.5	sharp sharp sharp sharp
	5.1	
	7.5	
	10.3	
Solution heated for 2 hrs. at 90° and cooled		
24 hrs.	5.1	medium sharp medium sharp sharp
	7.5	
	10.4	

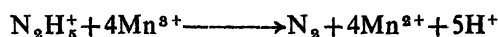
Results and Discussions

Four sharp inflexions at 2.5, 5.1, 7.5 and 10.3 ml of oxidant were observed at room temperature as expected, 10 ml of M/40 hydrazine solution on reacting with 2.5 ml of M/10 Mn^{3+} solution gave a colourless species which initiated vinyl polymerisation. This may be N_2H_3 (hydrazyl) radical¹. Since, the solution is colourless, it is expected that no species of manganese of higher oxidation state than Mn^{3+} is present and thus only species present in solution capable of initiating polymerisation may be the oxidised form of hydrazine.

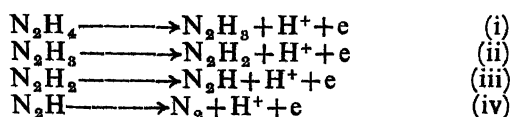
In the oxidation of hydrazine¹⁰ by copper(II), in spite of the low redox potentials of copper(II)-copper(I) couple, aquo copper(II) is found to oxidise N_2H_3 to N_2H_2 . Formation of N_2H_3 is cited in many cases and supported in literature^{11,12}.

The mixture, 10 ml of M/40 hydrazine solution and 5 ml of M/10 Mn^{3+} solution, probably gave a species diimide (N_2H_2), which was inferred from the reduction of fumaric acid by the above species to succinic acid⁵.

The observed stoichiometry of the overall reaction can be given as



The complete deelectronation of hydrazine can be represented by the following one electron step equations:



On heating the solution for two hours at 90° and storage for 24 hours, the first inflexion (i) vanished which may be due to the short life of the hydrazyl radical. All the other inflexions are found to be

less sharp, but the position does not change to any significant extent.

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Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Pd(II), Cd(II), UO_2^{2+} and VO^{2+} complexes of o-(2-pyrrolideneimino)benzoic acid and 3-(2-pyrrolideneimino)propionic acid

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O-(2-PYRROLIDENEIMINO)BENZOIC acid (H_2PB) and 3-(2-pyrrolideneimino)propionic acid (H_2PP) derived from pyrrole-2-carboxaldehyde and anthranilic acid or β -alanine are structurally similar and are expected to behave as biprotic tridentates. They for solid complexes with Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Pd(II), Cd(II), UO_2^{2+} and VO^{2+} .

Chemicals and apparatus used in the investigations are the same as reported earlier¹.

Preparation of H_2PB and H_2PP (Pfeiffer's Method²):

A mixture of alcoholic solution of pyrrole-2-