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Analytical Applications of N-Bromophthalimide & N-Bromosaccharin: Direct Potentiometric & Visual Titrations of 3-Methyl-1-phenylpyrazol-5-one alone and in Its Lanthanide Complexes

C MOHANA DAS & P INDRASENAN*
Department of Chemistry, University of Kerala, Trivandrum 695 034

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N-Bromophthalimide (NBP) and N-bromosaccharin (NBSA) have been used for the direct potentiometric and visual titrations of 3-methyl-1-phenylpyrazol-5-one alone and in its lanthanide nitrate and perchlorate complexes of the general formulae, $[Ln(MPP)_3(NO_3)_3]$ and $[Ln(MPP)_6](ClO_4)_3$ (where Ln = La, Pr, Nd, Sm, Gd, Tb, Dy, Ho and Y, and MPP = 3-methyl-1-phenylpyrazol-5-one). The proposed titrimetric methods using NBP and NBSA are simple and elegant, and provide better methods for the determination of purity of these complexes.

Recently N-bromophthalimide (NBP) and N-bromosaccharin (NBSA) have been developed in our laboratory as fairly stable oxidimetric titrants in aqueous acetic acid medium[1,2]. The title investigation is in continuation of these studies.

The same apparatus which had been used earlier[1], was employed for the potentiometric method.

Standard solutions (~0.05 *N*) of NBP and NBSA were prepared and stored in amber coloured bottles as described earlier[1,2]. The lanthanide perchlorate and nitrate complexes of 3-methyl-1-phenylpyrazol-5-one (MPP) were prepared by the literature method[3] and their purities checked by estimating the lanthanide content gravimetrically[4]. The purity of MPP was determined by standard method[5]. Standard solutions of MPP and its complexes (~0.1 *N*) were prepared in 75% (v/v) aq acetic acid. For visual titrations methyl orange (2% aq) indicator was used.

In the potentiometric method, a measured aliquot (3-7 ml) of the sample solution (MPP or the complex) was diluted to 50 ml with 50% aq acetic acid in a titration cell and the resulting solution titrated with a standard solution of NBP or NBSA. Near the equivalence point addition of the titrant was restricted to 0.1 ml portions and the solution was stirred for ½ min before noting the steady potential. At the equivalence point a potential jump of about 200 mV was obtained for the addition of 0.1 ml of either of the oxidants.

In the visual method, an aliquot (5-10 ml) of the sample solution taken in an iodine flask was diluted to 100 ml with 50% aq acetic acid. After adding 2-3 drops of methyl orange indicator the solution was titrated with standard solution of NBP or NBSA until there was a distinct colour change from red to pale yellow. A blank titration was also carried out along with each determination and no blank correction was found necessary.

The results presented in Tables 1 and 2 indicate that both NBP and NBSA can be used as titrants for the determination of MPP and its lanthanide complexes with high accuracy and precision. During the reaction with MPP and its complexes, NBP and NBSA undergo reduction to yield phthalimide and saccharin, respectively[1,2]. MPP undergoes bromination to yield its dibromo derivative according to the reaction

$$C_{10}H_{10}ON + 2RNBr \rightarrow C_{10}H_8ONBr_2 + 2RNH_2$$

where RNBr is NBP or NBSA.

The success of these estimations with NBP and NBSA is due to the fact that the C-4 and N-2 of the pyrazolone nucleus have no substituents. The hydrogen atom at C-4 is easily replaced by the stronger electrophilic agent[6] such as bromonium ion, Br^+. It is observed that one mol of MPP consumes four equivalents (i.e. 2 mol) of oxidant (NBP or NBSA) in accordance with the above bromination reaction.

The position of the second bromine atom is found to be N-2 by the following procedure. It has been reported that N-bromoamines are obtained by the reaction of N-bromoimides with amines[7]. It has also been reported that N-haloamines are easily converted into halogen and amines whereas C-haloamines are not[8]. Accordingly, the bromine attached to N-2 of MPP is labile and liberates iodine from acidified potassium iodide. This is found true and hence MPP is dibrominated at C-4 and N-2 of the pyrazolone nucleus.

In view of the fact that one mol of MPP consumes 4 equivalents (2 mol) of NBP or NBSA, it is observed that each of the lanthanide nitrate complexes, where there are 3 MPP molecules, consumes 12 equivalents (6 mol) of oxidant, while each of the lanthanide perchlorate complexes, where there are 6 MPP molecules, consumes 24 equivalents (12 mol) of oxidant. The advantages of the proposed methods are (i) simplicity, (ii) ad-

Table 1—Determination of 3-Methyl-1-phenylpyrazol-5-one alone and in Its Lanthanide Complexes Using N-Bromophthalimide (Ten replicates)

Compound*	Potentiometric titration			Visual titration		
	Range studied (mmol)	St dev (μ mol)	Av. error (%)	Range studied (mmol)	St. dev (μ mol)	Av. error (%)
MPP	0.03-0.19	2.7	0.35	0.14-0.30	2.9	0.39
$[La(MPP)_3(NO_3)_3]$	0.01-0.03	2.4	0.34	0.04-0.08	1.6	6.35
$[Pr(MPP)_3(NO_3)_3]$	0.01-0.03	2.9	0.33	0.02-0.06	3.1	0.34
$[Nd(MPP)_3(NO_3)_3]$	0.01-0.04	1.3	0.32	0.04-0.10	2.3	0.31
$[Sm(MPP)_3(NO_3)_3]$	0.02-0.05	2.6	0.25	0.04-0.10	2.1	0.23
$[Gd(MPP)_3(NO_3)_3]$	0.02-0.04	2.8	0.27	0.04-0.08	2.2	0.20
$[Tb(MPP)_3(NO_3)_3]$	0.02-0.05	3.1	0.37	0.04-0.08	3.3	0.25
$[Dy(MPP)_3(NO_3)_3]$	0.02-0.04	2.3	0.17	0.04-0.08	3.4	0.30
$Ho(MPP)_3(NO_3)_3]$	0.02-0.04	1.7	0.23	0.04-0.08	3.3	0.28
$[Y(MPP)_3(NO_3)_3]$	0.02-0.04	3.0	0.26	0.04-0.07	2.7	0.21
$[La(MPP)_6](ClO_4)_3$	0.01-0.03	2.4	0.28	0.02-0.05	2.2	0.34
$[Pr(MPP)_6](ClO_4)_3$	0.01-0.03	4.0	0.34	0.02-0.05	1.7	0.22
$[Nd(MPP)_6](ClO_4)_3$	0.02-0.03	1.8	0.34	0.03-0.06	2.6	0.23
$[Sm(MPP)_6](ClO_4)_3$	0.02-0.03	2.7	0.23	0.03-0.06	2.1	0.18
$[Gd(MPP)_6](ClO_4)_3$	0.02-0.03	1.9	0.28	0.03-0.06	2.3	0.40
$[Tb(MPP)_6](ClO_4)_3$	0.02-0.03	2.7	0.18	0.03-0.06	2.8	0.27
$[Dy(MPP)_6](ClO_4)_3$	0.02-0.03	3.6	0.33	0.03-0.06	4.5	0.40
$[Ho(MPP)_6](ClO_4)_3$	0.02-0.04	2.4	0.24	0.04-0.07	2.2	0.19
$[Y(MPP)_6](ClO_4)_3$	0.02-0.05	2.6	0.22	0.04-0.08	2.5	0.21

*MPP = 3-Methyl-1-phenylpyrazol-5-one.

Table 2—Determination of 3-Methyl-1-phenylpyrazole-5-one alone and in Its Lanthanide Complexes Using N-Bromosaccharin (Ten replicates)

Compound*	Potentiometric titration			Visual titration		
	Range studied (mmol)	St. dev (μ mol)	Av. error (%)	Range studied (mmol)	St. dev (μ mol)	Av. error (%)
MPP	0.05-0.16	3.0	0.32	0.14-0.30	2.3	0.45
$[La(MPP)_3(NO_3)_3]$	0.04-0.05	2.2	0.21	0.04-0.08	1.6	0.38
$[Pr(MPP)_3(NO_3)_3]$	0.01-0.03	2.6	0.38	0.02-0.06	3.0	0.32
$[Nd(MPP)_3(NO_3)_3]$	0.01-0.04	2.3	0.20	0.04-0.10	1.0	0.24
$[Sm(MPP)_3(NO_3)_3]$	0.02-0.05	2.1	0.16	0.04-0.10	1.3	0.13
$[Gd(MPP)_3(NO_3)_3]$	0.02-0.04	2.4	0.18	0.04-0.08	2.3	0.32
$[Tb(MPP)_3(NO_3)_3]$	0.02-0.05	2.6	0.29	0.04-0.08	3.6	0.24
$[Dy(MPP)_3(NO_3)_3]$	0.02-0.04	2.5	0.20	0.04-0.08	2.9	0.27
$[Ho(MPP)_3(NO_3)_3]$	0.02-0.04	2.3	0.17	0.04-0.08	3.2	0.38
$[Y(MPP)_3(NO_3)_3]$	0.02-0.04	2.9	0.26	0.04-0.07	3.4	0.29
$[La(MPP)_6](ClO_4)_3$	0.01-0.03	4.1	0.34	0.02-0.03	2.5	0.24
$[Pr(MPP)_6](ClO_4)_3$	0.01-0.03	4.3	0.38	0.02-0.05	3.2	0.30
$[Nd(MPP)_6](ClO_4)_3$	0.02-0.03	2.9	0.25	0.03-0.06	3.1	0.27
$[Sm(MPP)_6](ClO_4)_3$	0.02-0.03	3.7	0.32	0.03-0.06	1.3	0.21
$[Gd(MPP)_6](ClO_4)_3$	0.02-0.03	2.1	0.16	0.03-0.06	2.0	0.23
$[Tb(MPP)_6](ClO_4)_3$	0.02-0.04	3.0	0.22	0.03-0.06	2.8	0.24
$[Dy(MPP)_6](ClO_4)_3$	0.02-0.03	3.3	0.28	0.03-0.06	3.6	0.36
$[Ho(MPP)_6](ClO_4)_3$	0.02-0.04	2.1	0.16	0.04-0.07	1.7	0.13
$[Y(MPP)_6](ClO_4)_3$	0.02-0.05	2.4	0.22	0.04-0.08	2.3	0.22

*MPP = 3-Methyl-1-phenylpyrazol-5-one.

dition of auxiliary agent such as KBr is not necessary, (iii) the dibrominated products are not precipitated in 50% aq acetic acid, and (iv) the reagents are stable solids and their solutions have better keeping quality. To the best of our knowledge the proposed methods are the first titrimetric methods for the determination of a number of MPP molecules in the lanthanide complexes.

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