

TABLE I

| Name                         | Formula  | m.p.<br>(°C) | Yield | % of N |       | % of C |       | % of H |       |
|------------------------------|--|--------------|-------|--------|-------|--------|-------|--------|-------|
|                              |  |              |       | Found  | Calc. | Found  | Calc. | Found  | Calc. |
| 1. R- <i>p</i> -Bromoanilide | C <sub>16</sub> H <sub>11</sub> N <sub>2</sub> O <sub>2</sub> Br | >360         | 88%   | 7.85   | 8.16  | 55.66  | 55.97 | 2.98   | 3.20  |
| 2. R- <i>o</i> -Phenetide    | C <sub>18</sub> H <sub>16</sub> N <sub>2</sub> O <sub>3</sub>    | 244          | 83%   | 8.86   | 9.09  | 69.87  | 70.13 | 4.85   | 5.19  |
| 3. R-2:5-Xylidide            | C <sub>18</sub> H <sub>16</sub> N <sub>2</sub> O <sub>2</sub>    | 321          | 90%   | 9.42   | 9.58  | 73.60  | 73.97 | 5.12   | 5.47  |
| 4. R- <i>m</i> -Anisidide    | C <sub>17</sub> H <sub>14</sub> N <sub>2</sub> O <sub>3</sub>    | 296          | 90%   | 9.60   | 9.52  | 69.13  | 69.38 | 4.43   | 4.75  |
| 5. R- <i>p</i> -Anisidide    | C <sub>17</sub> H <sub>14</sub> N <sub>2</sub> O <sub>3</sub>    | 325          | 91%   | 9.50   | 9.52  | 68.97  | 69.38 | 4.56   | 4.75  |

where R stands for 2-quinolone-3-carboxy-

taken in a round bottomed flask and the mixture heated to very gentle ebullition with an air condenser. After one hour the mixture was cooled and 50 ml of ethanol was added. The crystals of the dianilide which separated was filtered and the filtrate concentrated in a china dish over a steam bath. The product obtained was recrystallised from petroleum ether, m.p. 115° C, yield (30%). Found: N, 3.86%; C, 39.33%; H, 3.48%; C<sub>11</sub>H<sub>12</sub>NO<sub>3</sub>I requires N, 4.19%; C, 39.63%; H, 3.60%.

*Ethyl malon-p-phenetidate*.—This was prepared similarly from *o*-phenetidine and ethyl malonate; yield (41.6%), m.p. 44° C. Found: N, 5.84%; C, 61.68%; H, 6.43%; C<sub>13</sub>H<sub>17</sub>O<sub>4</sub>N requires N, 5.58%; C, 62.15%; H, 6.77%.

*Condensation of o-aminobenzaldehyde with ethyl malon-p-iodoanilate: formation of 2-quinolone-3-carboxy-p-iodoanilide*.—Ethyl malon-p-iodoanilate (0.33 g), *o*-aminobenzaldehyde (0.12 g) and two drops of piperidine were heated on a steam bath for 3 hours. The mass was then washed with hot water (15 ml) and filtered. The product was insoluble in most of the common organic solvents. It was repeatedly washed with hot ethanol, m.p. > 360° C, yield (82%). Found: N, 6.92%; C, 48.98%; H, 2.46%; C<sub>16</sub>H<sub>11</sub>N<sub>2</sub>O<sub>2</sub>I requires N, 7.11%; C, 49.23%; H, 2.82%.

Using the same experimental conditions, the following 2-quinolones were prepared. Melting point, percentage yield and analytical results are given in Table I.

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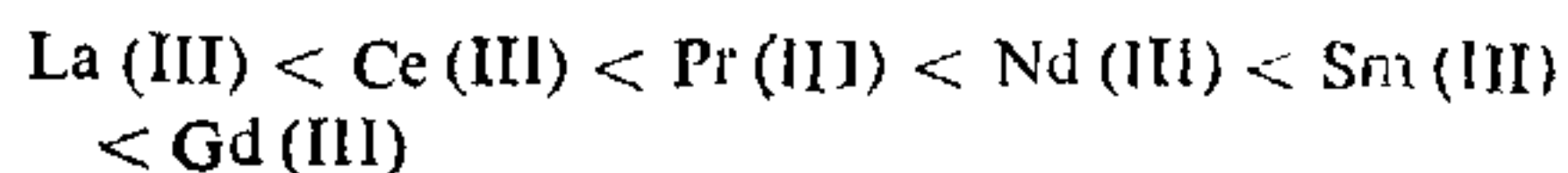
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#### STABILITY CONSTANTS OF SOME TRIVALENT METAL-ION COMPLEXES OF N-BENZOYL-ACETONEANTHRANILIC ACID

IN this communication we are giving the dissociation constants of the ligand derived from benzoyl-acetone and anthranilic acid, and the formation constants of its complexes with La (III), Ce (III), Pr (III), Nd (III), Sm (III) and Gd (III) which have been determined potentiometrically (0.1 M NaClO<sub>4</sub>) at 30 ± 0.1° C. The sequence of stability constants was found,



All the chemicals used were either B.D.H. AnalaR or Reidel reagents. The ligand N-Benzoyl-acetoneanthranilic acid (abbr. H<sub>2</sub>BA) was synthesised by the method of Pfeiffer *et al.*<sup>1</sup>. Calvin-Bjerrum pH-titration technique<sup>2,3</sup> as modified by Irving and Rossotti<sup>4</sup> was used for stepwise formation constant of the complexes. The ionic strength of the solution was maintained constant by NaClO<sub>4</sub> (0.1 M) solution. All the measurements were carried out at 30 ± 0.1° C.

In the case of H<sub>2</sub>BA, the formation curve extends upto  $\bar{n}_0 \approx 2.0$  indicating that two protons respectively from carboxylic and phenolic hydroxyl groups are dissociated. The values of dissociation constants as obtained by interpolation at half  $\bar{n}_0$  values method and interpolation at various  $\bar{n}_0$  values were found to be 9.81 and 6.20,

TABLE I  
Stability constants of trivalent metal complexes of  $H_2BA$

Temperature =  $30 \pm 0.1^\circ C$   $\mu = 0.1 M NaClO_4$

|                 | A     | B     | C     | D*    | E*    | F     |
|-----------------|-------|-------|-------|-------|-------|-------|
| <b>La (III)</b> |       |       |       |       |       |       |
| log $K_1$       | 7.14  | 7.18  | 7.13  | 7.14  | 7.14  | 7.14  |
| log $K_2$       | 3.84  | 3.80  | 3.83  | 3.86  | 3.84  | 3.83  |
| log $\beta_2$   | 10.98 | 10.98 | 10.96 | 11.00 | 10.98 | 10.97 |
| <b>Ce (III)</b> |       |       |       |       |       |       |
| log $K_1$       | 8.56  | 8.59  | 8.58  | 8.56  | 8.56  | 8.57  |
| log $K_2$       | 5.29  | 5.25  | 5.30  | 5.30  | 5.29  | 5.29  |
| log $\beta_2$   | 13.85 | 13.84 | 13.88 | 13.86 | 13.85 | 13.86 |
| <b>Pr (III)</b> |       |       |       |       |       |       |
| log $K_1$       | 8.90  | 8.94  | 8.88  | 8.90  | 8.90  | 8.90  |
| log $K_2$       | 5.65  | 5.61  | 5.68  | 5.70  | 5.65  | 5.66  |
| log $\beta_2$   | 14.55 | 14.55 | 14.56 | 14.60 | 14.55 | 14.56 |
| <b>Nd (III)</b> |       |       |       |       |       |       |
| log $K_1$       | 9.20  | 9.26  | 9.18  | 9.21  | 9.20  | 9.21  |
| log $K_2$       | 5.75  | 5.70  | 5.80  | 5.82  | 5.75  | 5.76  |
| log $\beta_2$   | 14.95 | 14.96 | 14.98 | 15.03 | 14.95 | 14.97 |
| <b>Sm (III)</b> |       |       |       |       |       |       |
| log $K_1$       | 9.90  | 9.96  | 9.86  | 9.88  | 9.91  | 9.89  |
| log $K_2$       | 6.42  | 6.40  | 6.45  | 6.40  | 6.42  | 6.42  |
| log $\beta_2$   | 16.32 | 16.36 | 16.31 | 16.28 | 16.33 | 16.31 |
| <b>Gd (III)</b> |       |       |       |       |       |       |
| log $K_1$       | 11.18 | 11.20 | 11.16 | 11.20 | 11.18 | 11.18 |
| log $K_2$       | 7.94  | 7.90  | 7.98  | 7.98  | 7.95  | 7.95  |
| log $\beta_2$   | 19.12 | 19.10 | 19.14 | 19.18 | 19.13 | 19.13 |

A = Interpolation at various  $\bar{n}$  values ; B = Interpolation at half  $\bar{n}$  values ; C = Correction term ; D = Successive approximation ; E = Convergence formulae ; F = Average values.

\* Most suitable methods in this case.

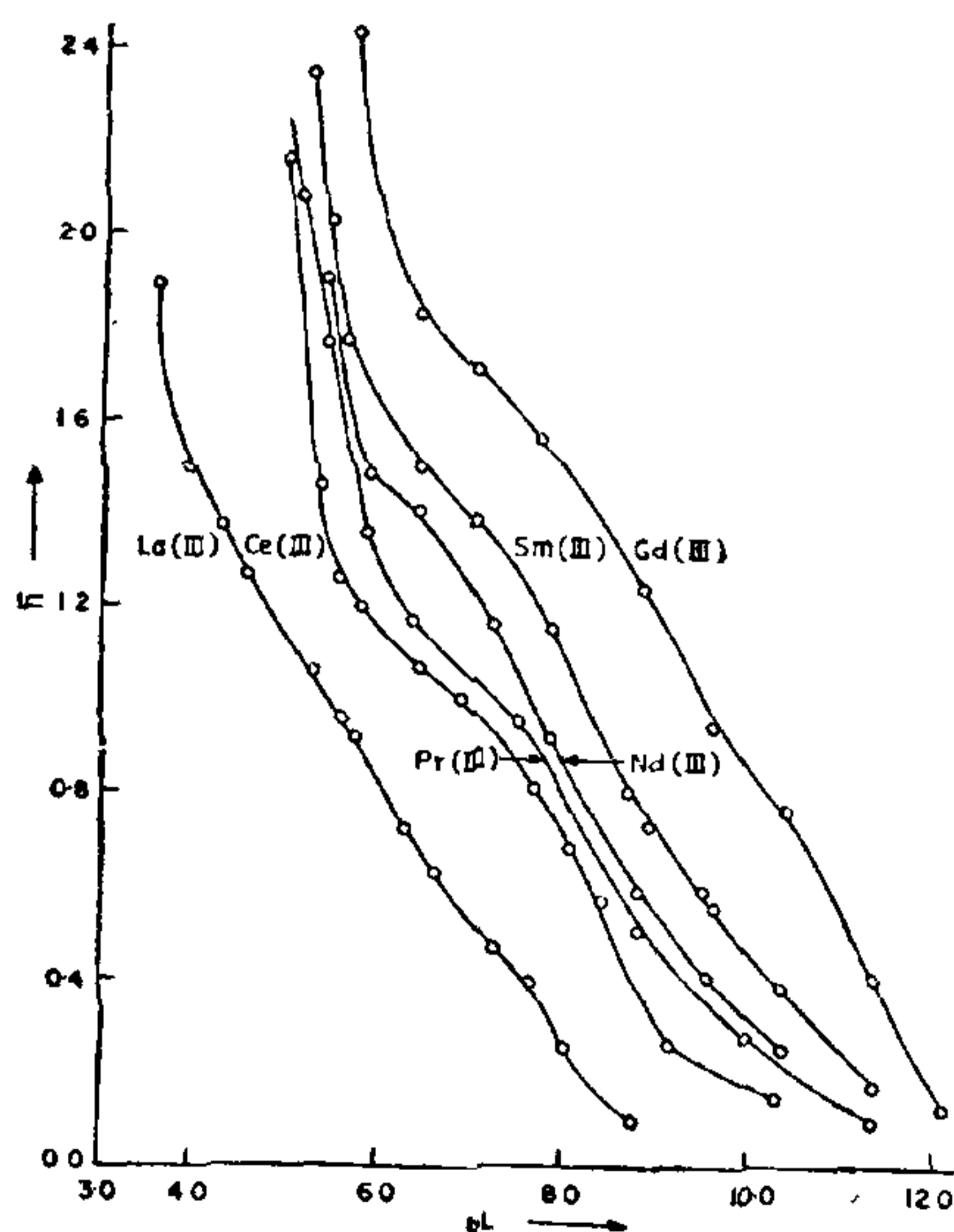
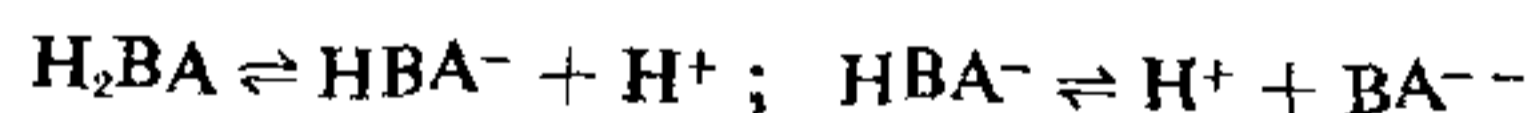


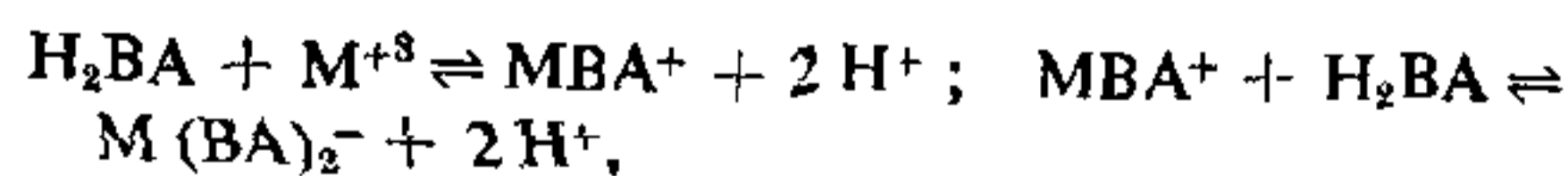
FIG. 1. Formation curves of trivalent metal- $H_2BA$  complexes.

The formation curves (Fig. 1) of all metal-ligand systems attain maxima at  $\bar{n} > 1.5$  which indicate that both 1:1 and 1:2 complexes are formed. The values of log  $K_1$  and log  $K_2$  were obtained from the formation curves at  $\bar{n} = 0.5$  and  $\bar{n} = 1.5$ , respectively. The values of these constants were refined by different computational methods<sup>5</sup> and are shown in Table I.

$H_2BA$  being a tridentate neutralizes two equivalents of the base to yield two buffer regions in its potentiometric equilibrium,



when 1:5 mixtures of ligand and the metal are titrated against standard alkali, the systems show inflections at lower buffer region indicating complexation. The complex equilibria may be represented by the equations,



La (III), Ce (III), Pr (III), Nd (III), Sm (III), and Gd (III) having  $4f^0$ ,  $4f^1$ ,  $4f^2$ ,  $4f^3$ ,  $4f^5$  and  $4f^7$  electrons possess ionic radii, 1.061, 1.034, 1.013, 0.995, 0.964 and 0.938 Å, respectively. The stability of the complexes of the metals, having similar electronic configuration increases with

decreasing ionic size. The same trend has also been observed in the present case.

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### CATALYTIC ACTIVITY OF OXIDE SPINELS: DECOMPOSITION OF ISOPROPYL ALCOHOL

THE catalytic activity of spinels of the type  $MgM_2O_4$  ( $M = Al, Fe, Cr$ ) has been investigated for a variety of reactions like methanation of carbon monoxide<sup>1</sup>, oxidation and dehydrogenation of hydrocarbons<sup>2,3</sup>. The catalytic properties of spinels are much dependent on their structure. In oxidation reactions, the position of the trivalent metal ion could significantly influence the reactivity of the catalyst<sup>4</sup>. Of the compounds  $MgAl_2O_4$ ,  $MgCr_2O_4$  and  $MgFe_2O_4$ , the first two are normal spinels, while  $MgFe_2O_4$  is partly an inverse spinel. The purpose of the present study is to compare the activity and selectivity of the spinels in the decomposition of isopropyl alcohol in terms of the structural changes of the spinels and changes in conductivity type.

The spinels were prepared by the coprecipitation of hydroxides from the respective nitrates (BDH AR) at an optimum pH. They were then dried at 100° C and calcined at 850° C for 24 hours. The spinel formation in each case was checked by TGA, DTA and X-ray analyses. The BET ( $N_2$ ) surface areas of the samples  $MgAl_2O_4$ ,  $MgCr_2O_4$  and  $MgFe_2O_4$  were found to be 49.5, 19.8 and 18.3  $m^2/g$  respectively. Isopropyl alcohol (BDH AR) was distilled before use and its purity checked by chromatograph.

The activity of the catalysts for the decomposition of isopropyl alcohol was determined in a fixed bed flow type reactor<sup>5</sup>. The gaseous products were analysed using Orsat's gas analyser and liquid products were estimated with a vapour phase chromatograph (Varian, 1800).

For the catalyst  $MgCr_2O_4$  both dehydrogenation and dehydration reactions took place, while on  $MgAl_2O_4$  only dehydration was observed to the complete exclusion of dehydrogenation with traces of condensation product, namely, diisopropyl ether (< 0.5 mole %). The catalyst  $MgFe_2O_4$  was predominantly dehydrogenating. The dehydration product, namely, water, in this case was very small (< 1 mole %). Contact time vs concentration plots were made for dehydrogenation and dehydration reactions on the catalysts and from the initial slopes, the corresponding rates of reaction were calculated. These rates were used to make Arrhenius plots from which energies of activation were calculated. Table I shows the kinetic parameters for the decomposition of isopropyl alcohol on different catalysts studied.

TABLE I

*Kinetic parameters for the decomposition of isopropyl alcohol*

| Catalyst    | Rate of dehydrogenation (moles $sec^{-1} m^{-2}$ ) | Rate of dehydrogenation moles ( $sec^{-1} m^{-2}$ ) | Activation energy kcal/mole |             | Frequency factor $min^{-1} m^{-2}$ |                    |                       |
|-------------|--|---|-----------------------------|-------------|------------------------------------|--------------------|-----------------------|
|             |  |   | Dehydrogenation             | Dehydration | Dehydrogenation                    | Dehydration        |                       |
| $MgCr_2O_4$ | 285° C   | 0.19  | 0.03                        | 11.99       | 16.10                              | $6.3 \times 10^6$  | $4.8 \times 10^8$     |
|             | 310° C   | 0.32  | 0.06                        |             |                                    |                    |                       |
|             | 330° C   | 0.46  | 0.10                        |             |                                    |                    |                       |
| $MgFe_2O_4$ | 290° C   | 0.47  | ..                          | 7.14        | ..                                 | $1.74 \times 10^3$ | ..                    |
|             | 310° C   | 0.52  | ..                          |             |                                    |                    |                       |
|             | 335° C   | 0.74  | ..                          |             |                                    |                    |                       |
| $MgAl_2O_4$ | 220° C   | ..  | 0.14                        | ..          | 29.38                              | ..                 | $4.66 \times 10^{12}$ |
|             | 235° C   | ..  | 0.37                        |             |                                    |                    |                       |
|             | 250° C   | ..  | 0.83                        |             |                                    |                    |                       |