Ionization Potentials of Alkaline-earth Monohydroxides

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Summary The ionization potentials of CaOH, SrOH, and BaOH have been determined, from a Second Law procedure applied to the results of an electrostatic probe study of the chemistry of the reactions of Ca, Sr, and Ba in flames, to be 5·90 ± 0·1, 5·55 ± 0·1, and 5·25 ± 0·1 ev, respectively.

PREVIOUS evidence on the behaviour of Ca, Sr and Ba additives in $H_2 + O_2 + N_2$ flames points to the importance, *inter alia*, of the following balanced reactions:[1]

$$M(OH)_2 + H \rightleftharpoons MOH + H_2O \qquad (I)$$

$$MOH + H \rightleftharpoons MO + H_2 \qquad (II)$$

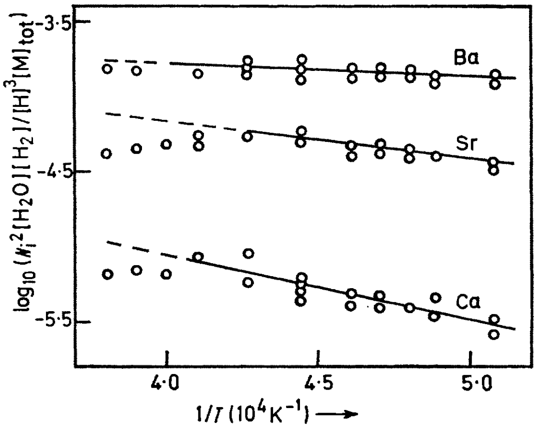
$$MO + H \rightleftharpoons MOH^+ + e^- \qquad (III)$$

Our current study of this system by means of the rotating single probe technique for total positive ion concentrations,[2] N_1, not only provides quantitative support for (I)—(III) but also applies, for the first time, now well understood flame chemistry procedures to the determination of unknown ionization potentials. This is illustrated here for the hydroxides, MOH, of Ca, Sr, and Ba.

For fuel-rich $H_2 + O_2 + N_2$ flames (Na D-line reversal temperatures in the range 1900—2700K), all the additive, $[M]_{tot}$, 1 ms (or less) downstream of the reaction zone is present in the gas phase, and MOH^+ the principal positive ion. Further, for insignificant or low ionization, $[M]_{tot} = [M(OH)_2]$ to a good approximation; this requires $[M]_{tot}$ to be sufficiently high (aqueous alkaline-earth salt solution spray additive > decimolar strength), T not too high

(< 2500K) and [H] as low as possible (*i.e.* in a given flame, well downstream from the reaction zone, as near to its equilibrium value as conveniently practicable). In these circumstances,

$$N_I^2[H_2O][H_2]/[H]^3[M]_{tot} = K_I K_{II} K_{III} \quad (1)$$



FIGURE

where [H] is the measured value of [H] in the *presence* of M. (Alkaline-earth metals are now known to be catalysts for H atom recombination at the level of $[M]_{tot}$ used in these experiments.[3]) Thus Second Law plots for (1) (Figure) should be straight lines, from the slope of which the enthalpy, ΔH^0_{2300}, of the overall reaction

$$M(OH)_2 + 3H \rightleftharpoons MOH^+ + e^- + H_2O + H_2 \quad (IV)$$

may be determined. Such plots are very satisfactory smooth lines, particularly when the sensitivity of such functions to [H]—let alone $[H]^3$—is borne in mind. (The downward curvature at high temperatures is fully accountable for in terms of breakdown of the required condition of low ionization.) Values of ΔH^0_{2300} for Ca, Sr, and Ba of 77, 46, and 17 kJ mol^{-1}, respectively, are deduced. These results, when suitably reduced to OK and combined with the dissociation energies of H_2, H–OH and HO–MOH (data from refs 1b and 4), yield ionization potentials for CaOH, SrOH, and BaOH of 5·90 ± 0·1, 5·55 ± 0·1, and 5·25 ± 0·1, respectively.

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[2] R. Kelly and P. J. Padley, *Trans. Faraday Soc.*, 1970, **66**, 1127.

[3] D. R. Jenkins, Thornton Research Centre, personal communication, 1969.

[4] JANAF Thermochemical Tables (Dow Chemical Company, Midland, Michigan, 1961).