Kinetics of the Gas-phase Reactions $MOH^+ + e^- \rightleftarrows M + OH$ or $MO + H$ ($M = Ca$ or Sr)

By A. N. Hayhurst* and D. B. Kittelson
(*Department of Chemical Engineering, Pembroke Street, Cambridge* CB2 3RA)

Summary Ionization of alkaline earths in flames is not at equilibrium, the principal ion (MOH^+ for an alkaline earth M) is produced by the reverse of either of the two processes in the title, with activation energies slightly less than endothermicities, and recombination is bimolecular with a large rate constant (*ca.* 10^{-7} particle^{-1} ml s^{-1}) displaying a negative temperature coefficient.

A premixed flame provides a flow system for the study of fast gas-phase reactions without interference from surfaces. The atmospheric pressure flames used here were steady laminar ones of H_2, O_2, and N_2 with well defined temperatures (1820—2570 K) and velocities. To them were added traces ($\leqslant$0·1 p.p.m.) of Ca or Sr, which exist [1,2] principally as the mono- or di-hydroxide, but also with free atoms and smaller amounts of monoxide present.

The ions in these flames were found mass spectrometrically[3] to be M^+ and MOH^+ for an alkaline earth M, with $[MOH^+] \gg [M^+]$; the free electron was also present. The rapid equilibration (1)[4] enables the ratio of the ion

$$M^+ + H_2O = MOH^+ + H \qquad (1)$$

currents due to M^+ and MOH^+ to be used as a relative measure of [H] at the point where the flame is sampled into the mass spectrometer.

The total concentration of positive ions rose rapidly in the first 5 mm of the burnt gases (measured from the reaction zone). In cooler flames (*ca.* 1800 K) this increase was followed by a gentle decrease, but in hotter ones (*ca.* 2500 K) the rise continued very slowly. The rate of production of ions in the region close to the reaction zone was proportional to the amount of alkaline earth added. In the cooler flames, the total positive ion concentration displayed a maximum, I, when the rates of production and disappearance of ions are necessarily equal. The value of I was found to vary (as also did its location along the flame axis), when $[M]_0$, the total concentration of alkaline earth present in every form, was altered. This dependence fitted well to the expression: $[M]_0\gamma^3 = AI^2(1 + B\gamma + C\gamma^2)$ where A—C are constants for a given flame and γ is the ratio of [H] at the point of maximum ion concentration to that for equilibrium at the particular flame temperature. This indicates that ions are produced by the forward steps of either one or both of the processes (2) and (3) as already

$$M + OH \overset{k_2}{\rightleftarrows} MOH^+ + e^- \qquad (2)$$

$$MO + H \overset{k_3}{\rightleftarrows} MOH^+ + e^- \qquad (3)$$

suggested.[5-7] In addition, ions must recombine by the reverse reactions, as the alternative three-body process involving the less abundant ion M^+ is too slow. Both processes (2) and (3) must operate with reactions (4)—(7) in

$$M + H_2O = MOH + H \qquad (4)$$

$$MOH + H_2O = M(OH)_2 + H \qquad (5)$$

$$M + H_2O = MO + H_2 \qquad (6)$$

$$H_2 + OH = H_2O + H \qquad (7)$$

equilibrium.[1,8] Either (2) or (3) is equally likely to operate.

The measured concentrations of H, M^+, and MOH^+ at different points along several flames have been fitted using standard numerical procedures to differential equations arising theoretically from the above reaction mechanism. As the equilibrium constants of (1) and (4)—(7) are known, the only unknown parameters are the forward and backward velocity constants for (2) and (3). In fact the experimental data fitted well to the differential equation for the total rate of production of ions, and 'least squares' fits gave these rate constants in each flame studied for Ca and Sr. Such a procedure depends on (2) and (3) not being equilibrated.

Rate constants were derived on the assumption that (2) and (3) were each in turn solely operative. Those for the reactions producing ions were fitted to the Arrhenius expression, $A \exp(-E/RT)$. Values of A and E for k_2 and k_3 are given in the Table. Activation energies are slightly less than endothermicities, which is consistent with the negative temperature coefficients derived below for recombination. Also for both metals, the forward step of (3) requires a smaller P than (2), suggesting (3) as more likely for ion-production.

No distinction can be made between the values of the rate constants for recombination in (2) and (3). At 2000 K the recombination coefficient was $1{\cdot}2 \times 10^{-7{\cdot}0\pm0{\cdot}4}$ (Ca) and $7{\cdot}0 \times 10^{-8{\cdot}0\pm0{\cdot}4}$ (Sr) particle^{-1} ml s^{-1}. If these are taken to vary with temperature to the power η, $\eta = -1{\cdot}9 \pm 2{\cdot}7$ for Ca and $= -2{\cdot}7 \pm 2{\cdot}0$ for Sr. These recombination coefficients compare well with values for similar processes, *e.g. ca.* $3{\cdot}8 \times 10^{-7}$ particle^{-1} ml s^{-1} for dissociative recombination of H_3O^+ with electrons[9] at 2000 K. Although these values are larger than any for reactions between neutral species, the time constants for (2) and (3) are large enough for them not to be equilibrated in a flame. This arises from the small concentrations of alkaline earths used here and is in contrast with earlier theories[7] of equilibrium ionization.

Values of activation energy E, *pre-exponential factor* A *and steric factor* P *on the assumption that either reaction* (2) *or* (3) *is the sole ion-producing process. For each metal the percentage errors in* A_2, A_3, *and steric factors are the same.*

Metal	Ca	Ca	Sr	Sr
Rate constant	k_2	k_3	k_2	k_3
A/(particle^{-1} ml s^{-1})	$1{\cdot}3 \times 10^{-x}$	$2{\cdot}4 \times 10^{-x}$	$1{\cdot}3 \times 10^{-x}$	$2{\cdot}1 \times 10^{-x}$
x	$10^{+0{\cdot}6}_{-3{\cdot}4}$	$11^{+0{\cdot}6}_{-3{\cdot}4}$	$10^{+1{\cdot}1}_{-1{\cdot}4}$	$11^{+1{\cdot}1}_{-1{\cdot}4}$
P[a]	0·23	0·012	0·23	0·0095
E/(kJ mol^{-1})	130^{+38}_{-136}	58^{+38}_{-136}	102^{+56}_{-58}	63^{+56}_{-58}
ΔH_{2300}/(kJ mol^{-1})[b]	166 ± 15	94 ± 15	138 ± 15	99 ± 15

[a] Estimated on the basis of collision diameters given in ref. 1.

[b] Derived from observations on (1).

(*Received, 7th January* 1972; *Com.* 020.)

[1] D. H. Cotton and D. R. Jenkins, *Trans. Faraday Soc.*, 1968, **64**, 2988.

[2] D. H. Cotton and D. R. Jenkins, *Trans. Faraday Soc.*, 1971, **67**, 730.

[3] A. N. Hayhurst and T. M. Sugden, *Proc. Roy. Soc.*, 1966, *A*, **293**, 36; A. N. Hayhurst, F. R. G. Mitchell, and N. R. Telford, *J. Mass Spec. and Ion Phys.*, 1971, **7**, 177; D. B. Kittelson, Ph.D. Thesis, University of Cambridge, 1971.

[4] A. N. Hayhurst and D. B. Kittelson, *Nature Phys. Sci.*, 1972, **235**, 136.

[5] K. Schofield and T. M. Sugden, 10th Intern. Symp. on Combustion, The Combustion Institute, Pittsburgh, 1965, p. 589.

[6] D. E. Jensen, *Combustion and Flame*, 1968, **12**, 261.

[7] R. Kelly and P. J. Padley, *Trans. Faraday Soc.*, 1971, **67**, 1384.

[8] K. Schofield and T. M. Sugden, *Trans. Faraday Soc.*, 1966, **62**, 566.

[9] R. Kelly and P. J. Padley, *Trans. Faraday Soc.*, 1970, **66**, 1127; A. N. Hayhurst and N. R. Telford, *Nature Phys. Sci.*, 1972, **235**, 114.