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Binary and ternary pyrotechnic systems of Mn and/or Mo and BaO_2 and/or SrO_2.
Part 3. Kinetic aspects

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Abstract

Kinetic parameters for the reactions occurring in the binary pyrotechnic systems of manganese, molybdenum, BaO_2 and SrO_2 have been derived from the results of thermal analysis experiments and from temperature–time profiles recorded during combustion. Activation energies derived from thermal analysis results are in the range 70–720 kJ mol^{-1}, and values derived from temperature profiles are much lower (3–40 kJ mol^{-1}) and support suggestions that reactions at high temperatures are controlled by diffusion processes.

INTRODUCTION

The binary and ternary pyrotechnic systems of manganese, molybdenum, BaO_2 and SrO_2 have been studied in detail using thermal analysis [1] and by recording temperature–time profiles during combustion [2].

Hill et al. [3, 4] studied combustion of the Mo/BaO_2, Fe/BaO_2 and S/BaO_2 systems. They found good agreement between the observed linear burning rates for the Fe/BaO_2 system and those calculated from the shapes of the temperature profiles, and fair agreement for the Mo/BaO_2 system. Improved correlation between observed and calculated burning rates was achieved for the 80% $Fe/KMnO_4$ system by greater control over materials and experimental conditions. Kinetic analysis of the temperature profiles gave low values for the activation energy (13–33 kJ mol^{-1}) and a thermal conduction mechanism was proposed to account for the burning rate.

The theory and method of analysis of temperature profiles (excess temperature U against time t) has been developed by Boddington et al. [5–8]. An outline of the procedure is given below.

The rise time t_r, or the related S factor ($t_r = 1/S$) from the Hill analysis [3, 4], is obtained from the slope of a plot of ln U against t over the early

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rise portion of the profile. The choice of t_r has a marked influence on the derived kinetic parameters. Similarly, the decay time t_d may be determined from the slope of a plot of ln U versus t over the cooling section of the temperature profile. This decay time is generally much greater than the rise time and hence has only a small influence on the analysis.

The power function G [5–8] given by

$$G = (U/t_d) + (dU/dt) - t_r(d^2U/dt^2)$$

is calculated from the original profile and the derivative curves using the esitmated values of t_r and t_d. The value for the extent of reaction α is given in the Hill treatment [3, 4] by

$$\alpha = \theta - t_r(d\theta/dt)$$

where $\theta = U/U_{max}$ and, in the Leeds treatment, from the partial areas under the curve of G versus t.

The rate equation is assumed to be of the form

$$d\alpha/dt = k(1-\alpha)^n = A\exp(-E_a/RT)(1-\alpha)^n \quad (1)$$

where n is the "order" of the reaction and A and E_a are the conventional Arrhenius parameters. In the Hill treatment the rate equation is rewritten as

$$h(\alpha) = \ln(d\alpha/dt) - n\ln(1-\alpha) = -(E_a/RT) + \ln A$$

Various values of n are selected and the linearity of the plots of $h(\alpha)$ versus $1/T$ is examined. E_a and ln A values are then determined from the slope and intercept, respectively.

In the Leeds treatment [5–8], the values of G are proportional to $d\alpha/dt$

$$G = U_{ad}(d\alpha/dt)$$

so the rate equation may be written as

$$G = U_{ad}A(1-\alpha)^n\exp(-E_a/RT)$$

The measured quantities are values of G_i and α_i at temperatures T_i. U_{ad} may be obtainable independently from the profiles. The unknowns were thus n, A and E_a. The values of n, A and E_a are then adjusted so that the sum of the squares of the differences

$$\Sigma\,\{(G_{exp})_i - (G_{calc})_i\}^2$$

is a minimum.

Extraction of kinetic information from thermal analysis results is an active, although controversial, field. There are many methods, of varying degrees of complexity, for analyzing experimental data. The Borchardt and Daniels [9] method is closely related to the Hill method used in the analysis of temperature profiles (see above). The Borchardt and Daniels method makes the same assumptions as in eqn. (1) above. Values of the rate coefficients, $k = (\mathrm{d}\alpha/\mathrm{d}t)/(1-\alpha)^n$, are calculated from the thermal analysis curve. For DSC, the DSC response is proportional to $\mathrm{d}\alpha/\mathrm{d}t$ and the partial area under an exotherm or endotherm is a measure of α. As in the Hill method, a value for n has to be selected by trial and error.

The k values obtained in this way are used in a conventional Arrhenius plot of $\ln k$ versus the reciprocal of the corresponding temperature.

EXPERIMENTAL

Materials

The materials used were those as used in Parts 1 and 2 of this series [1, 2]. The four binary pyrotechnic system Mn/BaO_2, Mo/BaO_2, Mn/SrO_2 and Mo/SrO_2 were studied in detail. Compositions are stated as percentages by mass of the fuel.

APPARATUS

Two thermal analysis techniques were available, differential scanning calorimetry (DSC) and thermogravimetry (TG). Experimental details and full results are given in ref. 1. Details of the apparatus and procedure for measurement of temperature profiles during combustion are given in ref. 2.

Data treatment

Temperature profiles for various compositions for all four binary systems were recorded as described in ref. 2. Profiles were generally sigmoidal. Despite attempts to standardize the measurement procedure, the reproducibility of the recorded temperature profiles of all four binary systems was not particularly good.

The original temperature profiles were smoothed using a 12-point cubic spline program. Results of analyses of individual temperature profiles were averaged. The derivatives required in the analysis were obtained using the Savitsky–Golay method (with 9 points) [10]. The α,t and α,T curves for the same profile obtained by the Leeds and by the Hill treatments were similar but not identical. Optimization of the fit of the results to the G function was done using two BMDP [11] routines: (i) a linear regression BMDP1R, and (ii) a non-linear regression BMDP3R.

The shapes of the temperature profiles were affected by composition, compaction, particle size of the fuel and by the presence of various additives [2]. Exceptions to the regular sigmoidal temperature profiles were recorded in all four systems, especially in compositions near to the end of the range which supported combustion.

The diameter d of the thermocouple wire used has a pronounced effect

[5–8] on the response of the thermocouple to the rapid passage of the burning front and hence the amplitude and shape of the temperature profiles recorded. The use of the thinnest thermocouple wire available (0.05 mm diameter) produced temperature profiles with considerable noise due to mechanical movement of the thermocouple during combustion. Values of the parameters derived from temperature profiles were thus corrected [5–8] to the values expected for a thermocouple wire of negligible diameter.

RESULTS AND DISCUSSION

Thermal analysis

Extraction of kinetic parameters from thermal analysis results is not appropriate unless the thermal analysis curves are relatively simple. The thermal analysis traces (DSC and TG) obtained [1] were examined for suitability and the Borchardt and Daniels method [9] was applied to, (i) the oxidation of manganese (TG Fig. 1, curve b), (ii) the oxidation of molybdenum (DSC Fig. 1, curve a), (iii) the reaction of 40% Mn/BaO_2 (DSC Fig. 2, curve a), (iv) the reaction of 40% Mn/SrO_2 (DSC Fig. 2, curve c), (v) the reaction of 50% Mo/BaO_2 (DSC Fig. 2, curve b). No suitable exothermic response was obtained during thermal analysis of

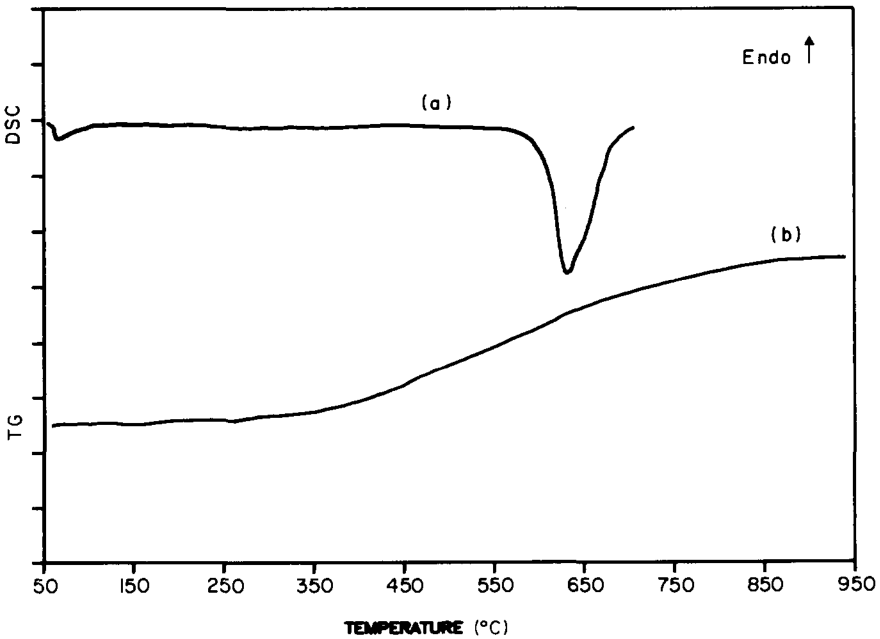

Fig. 1. Thermal analysis of the fuels in O_2 at 20°C min^{-1}. Curve a, DSC curve for Mo powder; curve b, TG curve for Mn powder.

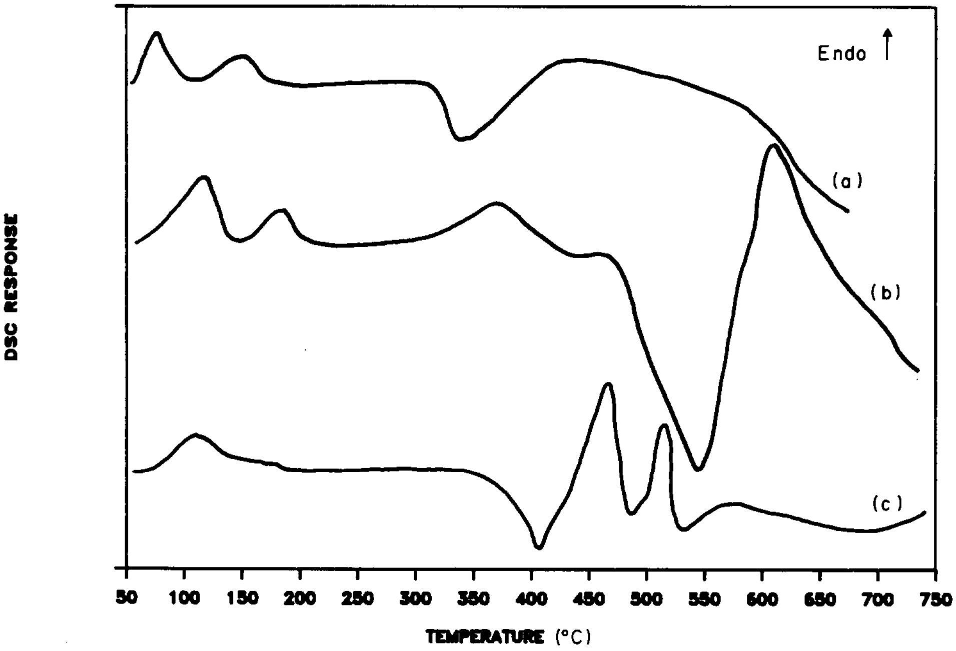

Fig. 2. Thermal analysis of binary pyrotechnic systems in N_2 at 20°C min^{-1}. Curve a, 40% Mn/BaO_2; curve b, 50% Mo/BaO_2; curve c, 40% Mn/SrO_2.

TABLE 1

Nonisothermal kinetic analysis (Borchardt and Daniels method) of thermal analysis traces

System	T_{ign} (K)	n	E_a (kJ mol^{-1})	ln$A$ (min^{-1})	r
Mn	525[a]	0.5	33.4 ± 0.2	−2.73 ± 0.08	0.99
		1.0	37.1 ± 0.2	−2.06 ± 0.11	0.99
		2.0	44.3 ± 0.3	−0.72 ± 0.18	0.98
Mo	815[a]	0.5	299 ± 4	34.72 ± 0.05	0.99
		1.0	242 ± 4	26.64 ± 0.26	0.98
		2.0	333 ± 2	39.54 ± 0.12	1.00
40% Mn/BaO_2	550	0.5	422 ± 3	82.89 ± 0.07	1.00
		1.0	236 ± 7	43.84 ± 0.35	0.97
		2.0	426 ± 7	83.71 ± 0.23	1.00
40% Mn/SrO_2	600	0.5	459 ± 2	105.07 ± 0.02	1.00
		1.0	434 ± 9	99.20 ± 0.19	0.99
		2.0	716 ± 10	166.76 ± 0.21	0.99
50% Mo/BaO_2	740	0.5	67.8 ± 1.6	4.49 ± 0.28	0.93
		1.0	84.2 ± 2.1	7.34 ± 0.36	0.92
		2.0	117.0 ± 3.1	13.04 ± 0.55	0.91

[a] Onset of oxidation.

Mo/SrO_2 compositions [1]. Where several exothermic responses were observed in a DSC trace, only the first exotherm was analyzed.

The results of application of the Borchardt and Daniels method [9] are summarized in Table 1. E_a values for manganese are significantly lower than those for molybdenum and this is consistent with the observation that manganese is more readily oxidized by O_2 in the TG than molybdenum. E_a values for the manganese systems were, however, higher than for the one molybdenum system, and did not differ significantly with change in oxidant.

Combustion

The temperature profiles for all compositions of the four binary systems were analyzed as described above. The effect of the value of the order of reaction n on the derived kinetic parameters for 20% compositions of three systems and 40% Mo/SrO_2 is shown in Table 2.

The relationship between the activation energy, calculated using n equal to unity, and composition is shown in Figs. 3 and 4 for the two manganese and the two molybdenum systems, respectively. The values for the Mn/BaO_2 and Mn/SrO_2 systems are more similar to each other than either is to the curve for the Mo/BaO_2 system. Reaction is more likely to be controlled by the properties of the metal and its oxidation product than by the properties of the oxidant.

The results obtained using the Leeds approach [5–8] are shown in Table 3.

The Hill approach requires selection of a value for the apparent order of reaction n before the Arrhenius parameters E_a and A are derived. The Leeds approach optimizes all three parameters. The values of n obtained from the Leeds analysis (Table 3) are generally low (0.1–0.7). Considering only the 20% Mn/SrO_2 system as an example (with $t_r = 0.020$ s), the value of n was 0.65 and E_a was 20.3 ± 1.6 kJ mol^{-1} (Table 3). The Hill treatment (Table 2) for the same composition gave values of E_a from 5 to 32 kJ mol^{-1} as n was increased from 0.5 to 2.0. Using $n = 0.65$, the value

TABLE 2

Kinetic parameters for binary compositions (Hill approach)

System	$n = 0.5$		$n = 1$		$n = 2$	
	E_a (kJ mol^{-1})	A (s^{-1})	E_a (kJ mol^{-1})	A (s^{-1})	E_a (kJ mol^{-1})	A (s^{-1})
20% Mn/BaO_2	5.9 ± 0.9	73 ± 5	11.1 ± 1.3	170 ± 10	21.4 ± 2.3	1000 ± 50
20% Mo/BaO_2	3.0 ± 1.2	32 ± 1	5.5 ± 1.3	54 ± 8	10.4 ± 1.7	148 ± 15
20% MN/SrO_2	4.8 ± 1.5	26 ± 3	11.7 ± 2.1	114 ± 50	31.6 ± 0.3	4390 ± 100
40% Mo/SrO_2	8.4 ± 3.7	74 ± 30	10.8 ± 3.1	125 ± 50	17.6 ± 2.4	456 ± 130

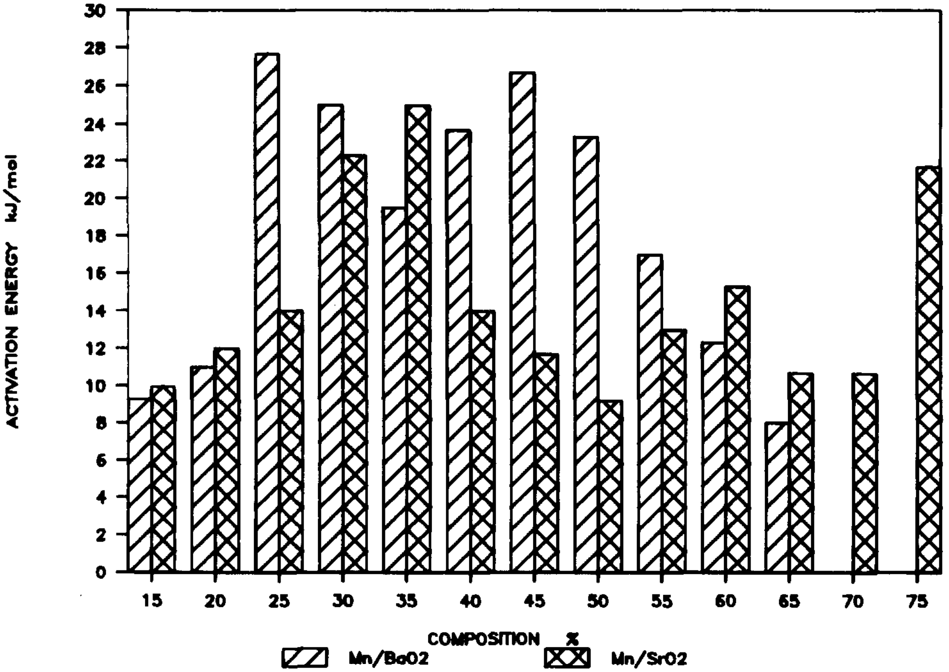

Fig. 3. Effect of composition on activation energy for the binary systems with Mn as fuel.

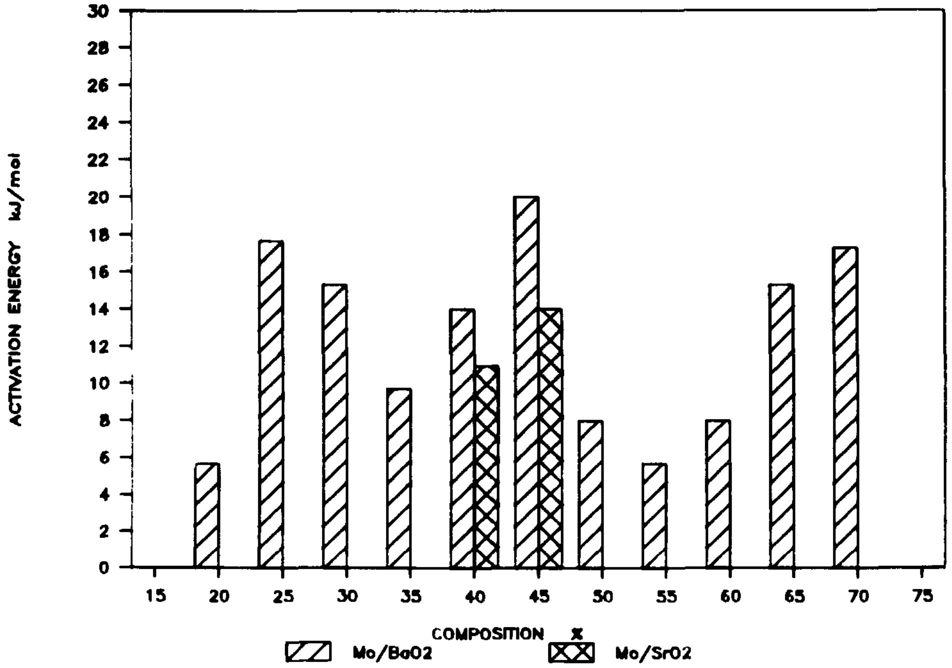

Fig. 4. Effect of composition on activation energy for the binary systems with Mo as fuel.

TABLE 3

Kinetic parameters using the Leeds treatment

System	BMDP[a]	$a \times 10^3$	b	n	E_a (kJ mol^{-1})	A (s^{-1})
20% Mn/BaO_2	L	169.8	1501 ± 143	0.38 ± 0.02	12.5 ± 3.2	107.6
	NL	344.9 ± 32.0	1864 ± 86	0.65 ± 0.03	15.5 ± 0.7	218.6 ± 20.2
20% Mo/BaO_2	L	122.5	2245 ± 83	0.18 ± 0.01	18.7 ± 0.7	74.6
	NL	139.5 ± 8.6	2595 ± 79	0.20 ± 0.01	21.6 ± 0.6	85.0 ± 5.2
20% Mn/SrO_2	L	2214.0	2823 ± 252	0.57 ± 0.05	23.5 ± 2.1	1264.4
	NL	1585.0 ± 407.0	2445 ± 186	0.65 ± 0.05	20.3 ± 1.6	905.2 ± 232.4
40% Mo/SrO_2	L	183.6	4000 ± 111	0.13 ± 0.01	33.2 ± 1.0	118.0
	NL	282.1 ± 61.7	4530 ± 271	0.15 ± 0.02	37.7 ± 2.2	181.3 ± 39.7

[a] L, linear; N, non-linear.

of E_a was 13.9 ± 1.4 kJ mol^{-1}. This is fair agreement considering the sensitivity of the value of E_a to the values of n and t_r, the considerable data processing involved and, in the Hill approach, the choice of temperature range to be regarded as linear in the Arrhenius plot.

Only a few published values of activation energies of reactions in the BaO_2 or SrO_2 pyrotechnic systems were found. Hogan and Gordon [12] measured an activation energy of 155 kJ mol^{-1} for the ignition of the Mg/BaO_2 system and Yoshinaga et al. [13] reported an ignition energy of between 44 and 49 kJ mol^{-1} for various compositions of the Mo/BaO_2 system. Hill et al. [3, 4], calculated an activation energy of 24 kJ mol^{-1} for the Fe/BaO_2 system, while Spice and Staveley reported [14] a value of about 200 kJ mol^{-1} for the pre-ignition reaction in the same system. Values reported for activation energies derived from temperature profiles are generally low, e.g. Boddington et al. [5–8] reported E_a values of 8–15 kJ mol^{-1} for different compositions of the W/$K_2Cr_2O_7$ system which were attributed to rate control by diffusion processes. The activation energies derived from the temperature profiles of the 20% compositions of three of the binary systems, and the 40% Mo/SrO_2 system, using both the Hill and Leeds approaches have similarly low values.

The values for the activation energy corrected to negligible thermocouple wire diameter, relative to the values for the "standard" 0.10 mm diameter thermocouple were 5% higher for the Mn/BaO_2 system, 17% higher for the Mo/BaO_2 system and 1% higher for both the Mn/SrO_2 and Mo/SrO_2 systems.

In the plot of activation energy versus composition for the Mn/BaO_2 system (Fig. 3), the lowest values were recorded for the 15 and 65% manganese compositions at the extremes of the range which supported combustion and which have reasonably slow burning rates and low maximum temperatures. A comparison of values of activation energy, burning rate and maximum excess temperature with the composition of the Mn/BaO_2 system shows that the three quantities follow the same pattern of behaviour, i.e. compositions with high burning rates burn at higher temperatures and have higher activation energies. There is also a pattern of double maxima, one at low percentage fuel and the other at high percentage fuel. The behaviour of the Mn/SrO_2 system was similar.

The variations of activation energy, burning rate and maximum temperature for the Mo/BaO_2 system with composition were smaller than for the Mn/BaO_2 system. Since only two compositions of the Mo/SrO_2 system burnt, no trends were discernible.

The applicability of the Arrhenius equation, and hence the significance of the parameters E_a and A, in reactions involving solid reactants has been debated in the literature without a generally agreed conclusion being reached. Arrhenius parameters are routinely derived from the thermal analysis, but the significance of these parameters is sometimes questionable. The Arrhenius parameters derived from analysis of temperature profiles generally imply higher reaction rates at low temperatures than are actually observed. Boddington et al. [8] proposed the use of a modified Arrhenius equation in describing the behaviour of pyrotechnic systems, which takes the form

$$k^{-1} = k_{AR}^{-1} + (BT^m)^{-1}$$

where B is the diffusion coefficient and

$$k_{AR} = A_{AR} \exp(-E_{AR}/RT)$$

and A_{AR} and E_{AR} should, in principle, be determinable from thermal analysis experiments. At high temperatures, k_{AR} is very large, so that $k_{TPA} \approx BT^m$.

In Table 4, the Arrhenius parameters for the 40% composition of the Mn/SrO_2 system, derived from the temperature profile recorded during the combustion of this mixture, are compared with those derived from the thermal analysis of the same mixture [1]. Figure 5 is a plot of the rate coefficients derived using the classical Arrhenius equation and kinetic data from the temperature profile and thermal analysis of 40% Mn/SrO_2, with the rate coefficient determined using the above modified equation. From the results shown, in the range 600–1500 K, $m = 1.75 \pm 0.02$, $B = (1.35 \pm$

TABLE 4

Comparison of kinetic parameters for 40% Mn/SrO_2 when $n = 1$

Thermal analysis		Temperature profile analysis	
E_a (kJ mol^{-1})	A (s^{-1})	E_a (kJ mol^{-1})	A (s^{-1})
434 ± 9	$(2.0 \pm 0.3) \times 10^{42}$	13.9 ± 1.5	1379 ± 100

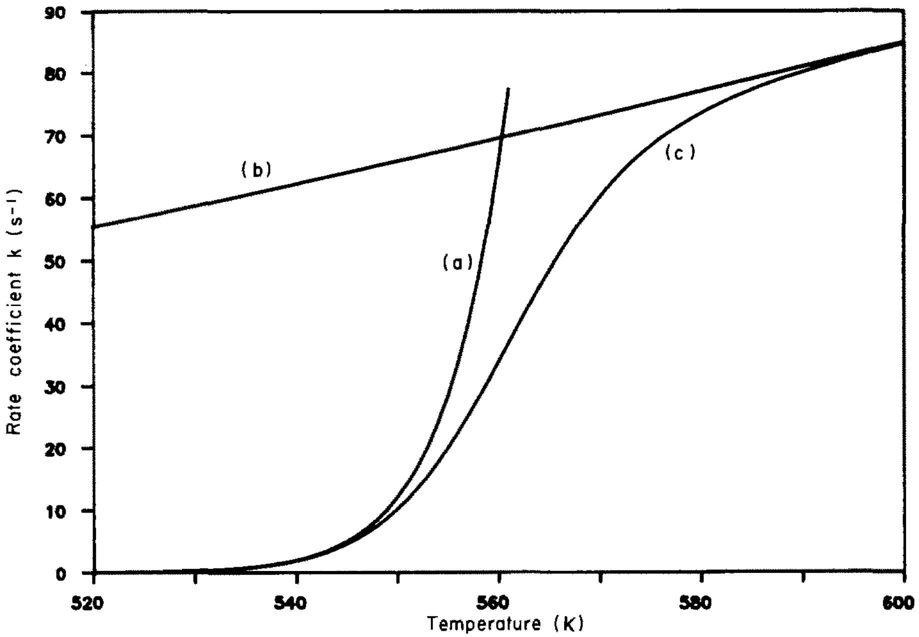

Fig. 5. Temperature dependence of rate coefficients for the 40% Mn/SrO_2 composition. Curve a, kinetic data from thermal analysis; curve b, kinetic data from temperature profile; curve c, modified Arrhenius equation (see text).

0.08) $\times 10^{-3}\ s^{-1}\ K^{-1.75}$ and $r = 0.99$. For the 50% $W/K_2Cr_2O_7$ system, Boddington et al. [8] found $m = 1.35$ and $B = 12.2 \times 10^{-3}\ s^{-1}\ K^{-1.35}$.

CONCLUSIONS

Values of activation energies derived from temperature profiles were all low (3–40 kJ mol^{-1} depending on the system and the assumptions made) and support the suggestion [6] that reaction at high temperatures is controlled by diffusion processes. Activation energies derived from thermal analysis results were considerably higher (70–720 kJ mol^{-1}).

Of all the binary systems the Mn/SrO_2 system burnt with the fastest rate ($\approx$12 mm s^{-1} for the 70% and 75% Mn compositions). The composition which burnt with the slowest rate but still with reliable combustion (i.e. combustion did not fail), was the 65% Mn/BaO_2 composition ($\approx$1.7 mm s^{-1}). In Table 5 the burning rates for a common mass composition and common mole ratios for the four binary systems are compared.

Based on the mass percent of fuel or on the common mole ratio, the binary systems can be placed in order of decreasing burning rate as follows: $Mn/SrO_2 > Mn/BaO_2 > Mo/BaO_2 > Mo/SrO_2$.

Similar comparisons of maximum excess temperature values for the four systems are made in Table 6.

Besides the compositions of the Mn/BaO_2 system which melted the thermocouple wire (25–45% Mn), the two molybdenum containing

TABLE 5

Comparison of burning rates (mm s^{-1})

Basis of comparison	Mn/BaO_2	Mo/BaO_2	Mn/SrO_2	Mo/SrO_2
40% fuel	6.6 ± 0.4	4.6 ± 1.0	7.5 ± 1.0	2.3 ± 0.1
Mol ratio 4:1	7.7 ± 0.6	4.6 ± 1.0	10.1 ± 1.6	—
Mol ratio 2:1	7.1 ± 0.4	4.2 ± 0.3	7.1 ± 1.3	2.3 ± 0.1

systems burned with higher temperatures than the two manganese containing systems.

Figures 3 and 4 show how the activation energy E_a values (based on a reaction order of $n = 1$) for the Mn/BaO_2 system are generally greater than those for the Mo/BaO_2 system. The E_a values are also higher for the

TABLE 6

Comparison of maximum excess temperature (°C) values

Basis of comparison	Mn/BaO_2	Mo/BaO_2	Mn/SrO_2	Mo/SrO_2
40% Fuel	>1760	1536 ± 82	1323 ± 45	1526 ± 19
Mol ratio 4:1	1156 ± 28	1536 ± 82	901 ± 17	—
Mol ratio 2:1	1436 ± 92	1687 ± 87	1291 ± 63	1526 ± 19

TABLE 7

Comparison of activation energies (kJ mol^{-1}) assuming $n = 1$

Basis of comparison	Mn/BaO_2	Mo/BaO_2	Mn/SrO_2	Mo/SrO_2
40% Fuel	23.8 ± 3.0	13.8 ± 3.0	13.9 ± 1.5	10.8 ± 3.1
Mol ratio 4:1	16.7 ± 1.0	13.8 ± 3.0	15.2 ± 4.6	—
Mol ratio 2:1	19.4 ± 5.3	17.5 ± 2.9	11.6 ± 1.2	10.8 ± 3.1

TABLE 8

Comparison of heat outputs Q (kJ per mol oxidant)

Basis of comparison	Mn/BaO_2	Mo/BaO_2	Mn/SrO_2	Mo/SrO_2
40% Fuel	169 ± 4	140 ± 4	125 ± 14	126 ± 6
Mol ratio 4:1	174 ± 8	140 ± 4	129 ± 17	—
Mol ratio 2:1	136 ± 2	115 ± 5	137 ± 16	126 ± 6

TABLE 9

Summary of trends within the four binary systems

Parameter	Decrease→
v_{obs}	$Mn/SrO_2 > Mn/BaO_2 > Mo/BaO_2 > Mo/SrO_2$
U_{max}	$Mo/BaO_2 > Mo/SrO_2 > Mn/BaO_2 > Mn/SrO_2$
E_a	$Mn/BaO_2 > Mn/SrO_2 \approx Mo/BaO_2 > Mo/SrO_2$
Q	$Mn/BaO_2 > Mo/BaO_2 > Mn/SrO_2 \approx Mo/SrO_2$

mid-range compositions (25–55% fuel) than the values for the Mn/SrO_2 system. There is little difference between the E_a values for the Mn/SrO_2 and Mo/SrO_2 systems but the Mo/SrO_2 system has a limited range of compositions which sustain combustion. The E_a values for the 40 and 45% Mo/BaO_2 compositions are greater than the two E_a values for the 40 and 45% Mo/SrO_2 compositions.

The comparison of E_a values for the binary systems in Table 7 shows that the Mn/BaO_2 system has the highest activation energy for similar mass proportions of fuel and for similar mole ratios.

There is little difference between the heat outputs ($Q = cU_{ad}$) [2] for the two BaO_2 systems and for the two SrO_2 systems (over the limited range of compositions of the Mo/SrO_2 system). However, the comparison of Q values for the systems with the same fuel shows that the two SrO_2 systems have greater heat outputs than the two BaO_2 systems, i.e. Mn/SrO_2 has generally greater Q values than the Mn/BaO_2 system, especially for low fuel compositions, and Mo/SrO_2 has greater Q values for its two compositions which sustain combustion than the corresponding compositions of Mo/BaO_2. Q values are given in Table 8.

Table 9 summarizes the trends in the four binary systems with respect to the parameters burning rate (v_{obs}), maximum excess temperature (U_{max}), activation energy (E_a) and heat output (Q). The closest correlation is thus between E_a and Q.

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