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THE THERMAL DECOMPOSITION OF ALKALINE EARTH FORMATES

R. CANNING AND M. A. HUGHES
The School of Chemical Engineering, Bradford University, Bradford BD7 1DP (England)
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ABSTRACT

The thermal decomposition of alkaline earth formates has been studied. Experiments with single crystals, compacts and powders of strontium formate demonstrate that the method of sample presentation can affect the rate of decomposition.

For anhydrous calcium, strontium and barium formates, isothermal kinetic runs show that the decompositions follow the Erofeev law, $\ln(1-\alpha) = kt^n$; the measured activation energies were 199.4, 228 and 270 kJ/mol respectively.

INTRODUCTION

The thermal decomposition of metal formates is of importance where residues are obtained which have catalytic properties.

The pyrolysis of the formates gives rise to a diversity of products which vary with the nature of the cation of the starting salt. Thus, alkali metal salts give mainly the carbonate when heated at low temperatures but in all cases, except lithium[1], the oxalate results from conditions above 250°C. Alkaline earth formates can give[2] carbonates or oxides. Transition metal formates, which have been widely studied[2,3], give metal or oxide or a mixture of these two.

For the most part, previous work has been concentrated on the identification of solid products although some investigations into the gases evolved show that the situation is complex. In one study[2], where large samples (ca. 10 g) were taken, various mixtures of the following were detected: CO, CO_2, H_2, H_2O, HCO, $HCOOH$, CH_3COOH, CH_4 and CH_2COCH_3.

In a few cases, the kinetics of the decomposition of formates have been reported. Kornienko[3] showed that for the series manganese to copper the topokinetic equation due to Erofeev could account for the data. In the studies on nickel formate[4] and uranyl formate[5] the data obeyed a Prout–Tompkin equation.

In one study[6] of the thermal decomposition of calcium formate the reactant was presented as a compressed powder in a potassium bromide matrix. The kinetics were followed by changes in the optical densities of the several infrared bands. The first-order kinetics reported may reflect the way in which the material was presented. Thus, very fine crystallites dispersed in a matrix may nucleate individually and the reaction is controlled by a nucleation process where each particle can nucleate with equal probability; thus the reaction is not controlled by the overall geometry of the individual formate crystals.

The activation energy, reported as 217 kJ/mol, compared favourably with thermogravimetric analysis of the powder which gave $E = 197$ kJ/mol for isothermal runs and $E = 234.5$ kJ/mol for temperature programmed runs.

It is reasonable that the decomposition of other alkaline earth formates should provide a useful study where their behaviour is compared with that of the calcium salt. Furthermore, the study of formates in general, where the ligand is monodentate, may contribute to the understanding of the decomposition of more complicated salts.

EXPERIMENTAL

Materials

Samples of powdered magnesium, strontium and barium formates were obtained from K and K Laboratories; the calcium formate was from BDH.

Single crystals of the formates were grown according to the method described by Holden and Singer[7]. In the case of strontium formate, strontium carbonate (29.5 g) was dissolved in warm water (150 ml) containing 88% formic acid (18.5 ml). Seed crystals were isolated from the solution on evaporation and these were subsequently grown to give single crystals of approximately 70–250 mg. Single crystals of barium formate were grown in a similar manner to give 80 mg samples, but attempts to grow large crystals of calcium or magnesium formates were not successful.

Single crystals of orthorhombic strontium formate dihydrate and anhydrous barium formate were colourless.

Compacts of the powders were prepared as discs, 0.73 mm thick and 10 mm diameter. For strontium formate, the disc was made with 150–200 B.S. mesh powder compressed for five minutes at 7 tons per square inch pressure.

Analyses

The metal content of the compounds was found by direct titration with standard ethylenediaminetetraacetic acid to an eriochrome black T end point.

An attempt was made to analyse for formate by direct titration with potassium permanganate in alkaline conditions but the technique was unsatisfactory in the presence of the heavier alkaline earth metals. Therefore, the alkaline earth metal was exchanged for hydrogen by passing aliquots of the formate solution down Amberlite IR (12OH) cation exchange resin columns and the formic acid was collected quantitatively in excess caustic soda and was then titrated directly by the standardised permanganate.

TABLE 1

ANALYSIS OF ALKALINE EARTH FORMATES

Compound	*% found*		*% theory*
$Mg(HCO_2)_2.2H_2O$	formate	58.6	58.8
	Mg	16.2	16.2
$Ca(HCO_2)_2$	formate	69.1	69.2
	Ca	30.6	30.8
$Sr(HCO_2)_2.0.8H_2O$	formate	46.3	45.6
	Sr	46.2	46.8
$Ba(HCO_2)_2$	formate	39.5	39.6
	Ba	59.4	60.4

The strontium formate appeared to be slightly effluorescent which may account for the relatively poor analyses and we note that freshly prepared single crystals of this compound gave analyses which corresponded to the dihydrate. Single crystals of barium formate were found to be anhydrous like the original powder.

Apparatus and procedure

Thermogravimetric analysis (TG) was carried out on a Stanton Thermobalance, Model HT-M. The sample was held in a platinum crucible (height 7 mm, diameter 10 mm) and in each case 200 mg of powder sample, mesh size 150–200 B.S. was taken. The temperature of the sample was measured by a thermocouple placed in contact with the crucible and the signal from this thermocouple was lead to a Kent recorder (0–10 mV). For isothermal experiments the signal was read to greater accuracy by use of a Pye potentiometer (model 7596P).

All TG analyses were carried out in air with the alumina plug situated in the top of the furnace. Differential thermal analysis (DTA) was achieved on an apparatus constructed in this laboratory after Grimshaw et al.[8]. The apparatus was adapted to work with an inert atmosphere present by housing the analytical cell in a ceramic tube through which argon passed at 150 ml/min. The sample was placed in one half of the divided analytical cell and was open to the surrounding atmosphere, alumina was used as an inert reference material in the other half of the cell.

Samples were also decomposed in a furnace with an isoteniscope attachment. The gases were collected for analysis on an Orsat apparatus and any liquid condensate was titrated for acid content. Moisture in gases was determined by absorption and weighing.

RESULTS

The chemistry of the decompositions

Powders. The TG curves are presented in Figs. 1 and 2 as differential thermogravimetric curves in which the rate of weight loss (dw/dt) is plotted against temperature. The DTA curves are reported in the same diagrams for comparison purposes.

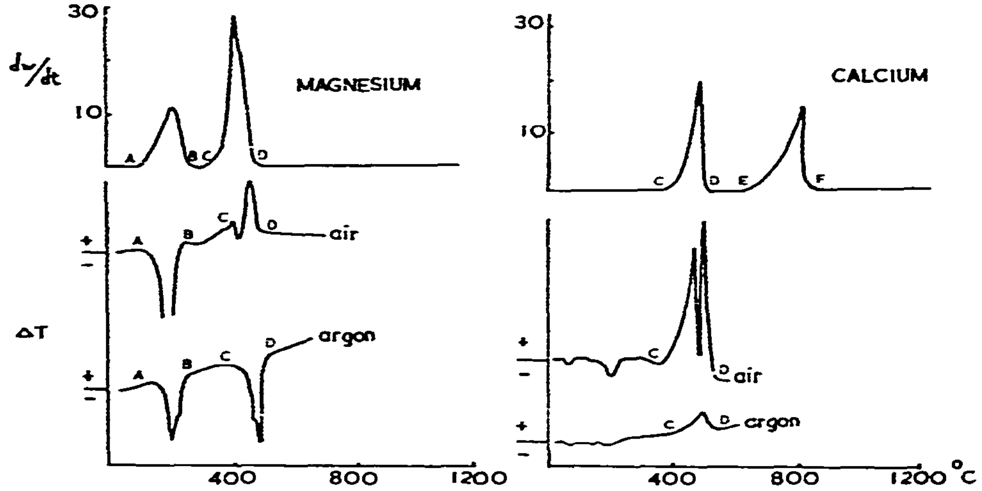


Fig. 1. Differential thermogravimetric curves (dw/dt) and thermograms (ΔT) for magnesium and calcium formates.

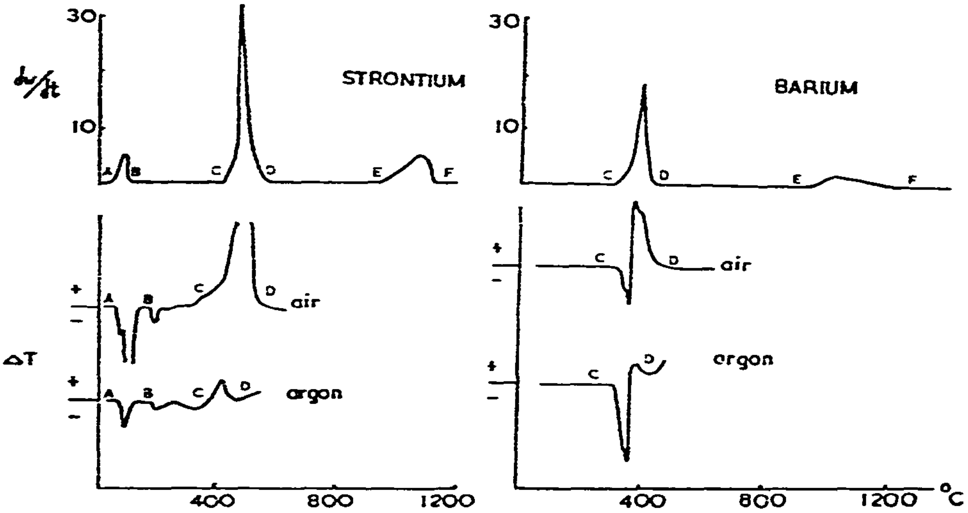


Fig. 2. Differential thermogravimetric curves (dw/dt) and thermograms (ΔT) for strontium and barium formates.

An analysis of the weight changes in the TG curves has been made and the results are given in Table 2.

In general, the DTA curves confirm the thermogravimetric analysis, thus the dehydration process is always indicated by an endothermic peak in the same temperature range as a weight loss of water indicated by TG. The decarboxylation process is more difficult to interpret for although a DTA signal appears in that temperature range corresponding to the thermogravimetric weight loss, the nature of the peak varies from exothermic to endothermic or a mixture of both; as in the case of oxalates, the primary decarboxylation may in itself be endothermic but the gaseous products react

TABLE 2

ANALYSIS OF THERMOGRAVIMETRY CURVES

Region of curve		*Change indicated by weight analysis*	*Observed % of theoretical wt. change*	
			in air	*in argon*
Fig. 1 magnesium formate				
A	B	dehydration $Mg(HCO_2)_2 \rightarrow Mg(HCO_2)_2$	98	97
C	D	decarboxylation $Mg(HCO_2)_2 \rightarrow MgO$	76	99
Fig. 1 calcium formate				
C	D	decarboxylation $Ca(HCO_2)_2 \rightarrow CaCO_3$	94	95
E	F	$CaCO_3 \rightarrow CaO$	99	99
Fig. 2 strontium formate				
A	B	dehydration $Sr(HCO_2)_2 . 1H_2O \rightarrow Sr(HCO_2)_2$	98	99
C	D	decarboxylation $Sr(HCO_2)_2 \rightarrow SrCO_3$	95	94
E	F	$SrCO_3 \rightarrow SrO$	100	98
Fig. 2 barium formate				
C	D	decarboxylation $Ba(HCO_2)_2 \rightarrow BaCO_3$	96	95
E	F	$BaCO_3 \rightarrow BaO$	99	99

further to give exothermic or endothermic effects. One example of this is where carbon monoxide is produced which subsequently gives carbon dioxide in oxidising atmospheres and this reaction is strongly exothermic; we expect that carbon monoxide is a primary produce of the decomposition of many formates.

Single crystals. Studies on the chemistry of the decomposition of single crystals have been confined to the formates of strontium and barium since these could be grown to a reasonable size. The DTG curves of the single crystals and a compact are given in Fig. 3. These curves show differences from the curves obtained with the powders. In the case of strontium formate, the single crystal is a dihydrate and consequently two stages now appear in the region of dehydration whereas only one existed for the powder. The most noticeable change is in the region of decarboxylation where for the single crystals of the strontium and barium salts the reaction was extremely fast and was sufficiently violent to cause mechanical loss of the sample from the crucible.

An important observation concerning single crystals is that if the crystal is large, *i.e.* ca. 0.5 g, the oxide is produced, but with smaller crystals, *i.e.* ca. 0.07 g, the decomposition followed that pattern found for powders in that carbonate was formed and subsequently decomposed at a much higher temperature to give the corresponding oxide. We were also able to show that compacts in disc form behaved in a similar way to large crystals and in the case of strontium formate a large compact gave the oxide directly. The fast reaction rate for single crystals reflects the exothermic character of the reaction leading to temperature rise and a violent autocatalytic decomposition.

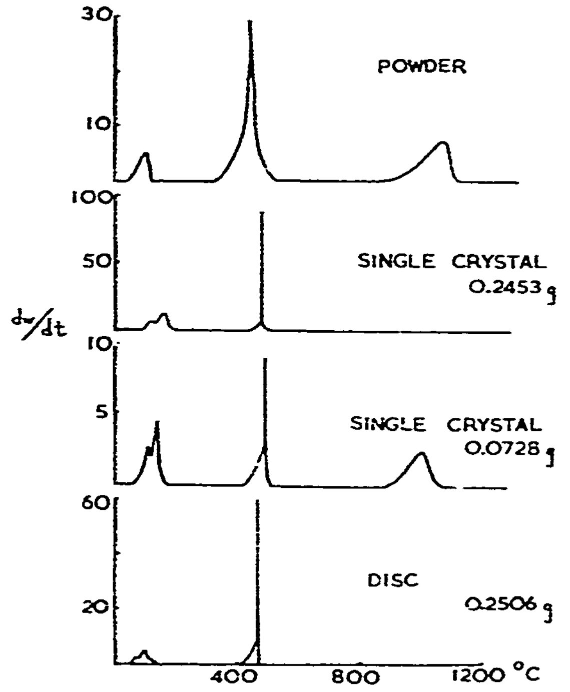


Fig. 3. Differential thermogravimetric curves for various preparations of strontium formate dihydrate.

Also the temperature rise must be so marked that the reaction $SrO + CO_2 \rightarrow SrCO_3$ lies well over to the left and precludes carbonate formation. There is no evidence to suggest that marked increases in temperature occur when powders are heated under isothermal conditions.

KINETICS OF DECARBOXYLATION

It has not been possible to make a study of the kinetics of the decarboxylation of single crystals or compacts because of the very fast reaction which occurred; in any case, the heat evolved would remove isothermal conditions. However, the kinetics of the reaction involving the calcium, strontium and barium formate powder have been investigated. In each case the reaction gave carbonate, unlike the reaction involving magnesium formate powder, which gave the oxide. For this reason magnesium formate was not studied further.

Isothermal conditions were employed, each salt being investigated at five different temperatures which had been selected from the TG experiment. In Fig. 4 we show typical α/t transformations at one temperature for each salt where α is the fraction decomposed and t is the time.

In order to investigate the kinetics of the strontium formate decomposition, the material was required to be anhydrous. For the first kinetic analysis, anhydrous formate was obtained by heating the powdered hydrate at 120 °C until constant weight was obtained. However, the decomposition curves were then quite different (curve

Sr*, Fig. 4) from those obtained with anhydrous barium and calcium formates. In particular the induction period was absent on the strontium formate curve and this suggests that the sample had already been nucleated during the dehydration process.

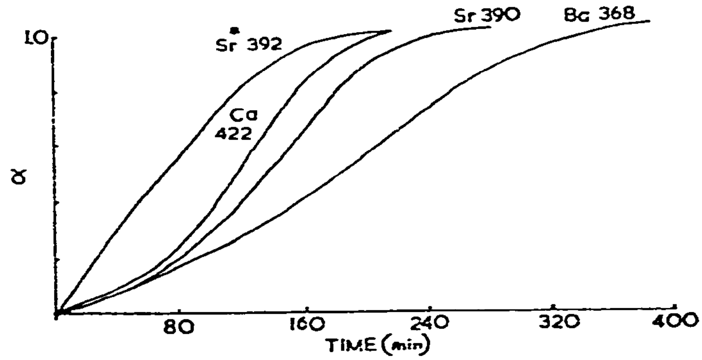


Fig. 4. Isothermal runs on the decomposition of anhydrous formates. Sr* strontium formate prepared by dehydration of the dihydrate.

Anhydrous strontium formate was prepared in another way by refluxing strontium carbonate with excess 100% formic acid and collecting the crystals which resulted from this procedure. The α/t plots obtained with this material now exhibited an induction period and were then similar to those for calcium and barium formates (curve Sr, Fig. 4).

Various topokinetic models have been suggested to explain solid state decompositions. The Erofeev equation[9]

$$\ln(1-\alpha) = e - kt^n$$

has been extensively used and in this instance the data gave a reasonable fit to the law where $n = 4$; the extent of the fit is shown in Fig. 5 where data for one temperature only is given. Other laws were tested but found to be unsatisfactory.

Values of log k, obtained from Fig. 5 type plots, were plotted against $1/T$ and this Arrhenius analysis gave activation energies as follows: calcium formate 199.4 kJ/mole, strontium formate 228 kJ/mol, and barium formate 270 kJ/mol. The result for calcium formate agrees well with that reported by Hartman and Hisatsune[6] ($E^{*} = 197$ kJ/mol).

DISCUSSION

The approaches which have been made to explain formate decompositions are several and reflect the complexity of the situation.

Kornienko[3] considers that two basic mechanisms operate to give the oxide or metal, *i.e.*

$$\text{(i)}\quad M(HCOO)_{2(s)} \rightarrow M_{(s)} + 2HCOO^{\circ}_{(g)}$$

$$\text{(ii)}\quad M(HCOO)_{2(s)} \rightarrow MO_{(s)} + HCOO^{\circ}_{(g)} + HCO^{\circ}_{(g)}$$

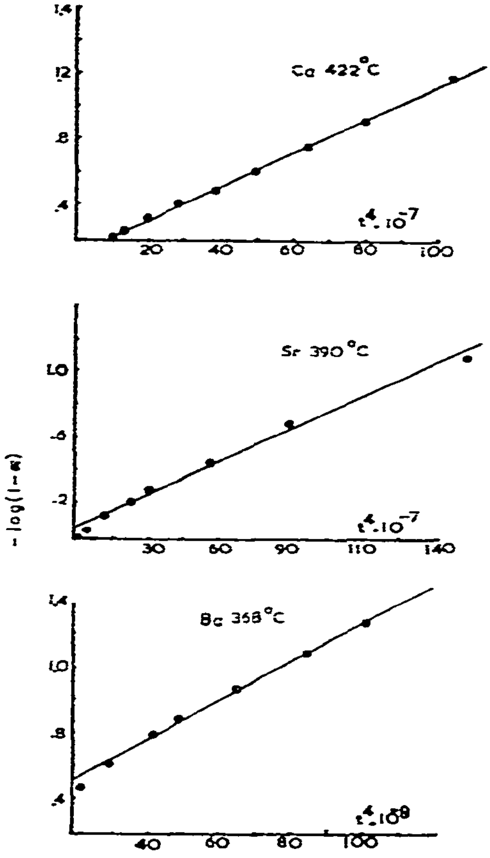


Fig. 5. Tests on data from Fig. 4 for goodness of fit to the Erofeev equation with $n = 4$.

In either case, the free radicals are subsequently removed from the crystal surface by recombination and breakdown. The approach accounts for the solid residues observed in the pyrolysis of transition metal formates.

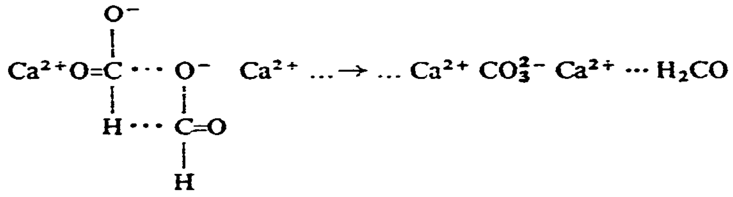
For the alkaline earth formates, a third possibility arises when carbonate is formed directly, *i.e.*

$$\text{(iii)}\quad M(HCOO)_{2(g)} \rightarrow MCO_{3(s)} + H^{\circ}_{(g)} + HCO^{\circ}_{(g)}$$

In many instances, formic acid is observed in the reaction products from formates, the acid may be subsequently dehydrogenated or dehydrated on the residue surface. In order to account for the latter, it has been suggested[5] that the C–H bond of the formate ion is ruptured to give a proton and the radical ion CO_2^{2-}, the reaction of the proton with formate ion then gives formic acid. Certainly the energy required to break the C–H bond, estimated at 317 kJ/mol in formaldehyde, is well above observed activation energies but it has been argued that in the reaction intermediate in the solid state, the formate ion could be a distorted formate ion and the energy required for C–H dissociation is lowered.

Hartman[6] dismissed the theory of C–H bond fission on the basis that the CO_2^- radical was not detected in e.s.r. experiments. The CO_2^{2-} radical, if formed by C–H bond fission would not be detected by e.s.r. techniques. Hartman suggests that in the crystal the formate ions move by about 1 Å toward each other and rotate to form the complex below which then breaks down directly to carbonate.

(3)



$$\ldots Ca^{2+}O{=}\overset{O^-}{\underset{H\cdots}{C}}\cdots \underset{\underset{H}{C=O}}{O^-}\;Ca^{2+}\ldots\rightarrow\ldots Ca^{2+}\,CO_3^{2-}\,Ca^{2+}\cdots H_2CO$$

The formaldehyde produced would decompose immediately into hydrogen and carbon monoxide. Unfortunately the crystal structure observed at room temperature, on which the explanation is founded, may not be appropriate to the heated material. It is also possible that the carbonate may be formed between the primary product oxide and carbon dioxide. Indeed, in further arguments we assume that oxide is the primary product from both transition metal formates and alkaline earth formates.

Kornienko calculated the free energies of the decomposition of formates by paths (i) or (ii) to give the following:

Formate of:	Mn^{2+}	Fe^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	
$\Delta G(i)_{298}$	667	570	516	408	611	kJ/mol
$\Delta G(ii)_{298}$	154	171	156.5	131	147	kJ/mol

The corresponding values for the alkaline earth salts have been calculated by a similar method:

	Ca^{2+}	Sr^{2+}	Ba^{2+}	
$\Delta G(i)_{298}$	790	829	801	kJ/mol
$\Delta G(ii)_{298}$	154	212	250	kJ/mol

(where an average $298\Delta S(i) = 76.6$ kJ/mole and $298\Delta S(ii) = 80.0$ kJ/mol). It is evident that in the two series of compounds a primary breakdown to the oxide is favoured.

The gaseous products of the reaction may account for other residues. Thus, carbon is formed by the Boudard reaction

$$2CO \rightarrow CO_2 + C$$

Carbon has been observed in the carbonate residues from the breakdown of the strontium and barium salts. There is also evidence[3] for carbon occurring in the oxides produced from transition metal formates.

An attempt was made to measure the free carbon content of the carbonate residues. In the case of strontium and barium carbonate less than 1% carbon was detected.

The carbonates are produced by reaction of oxide with carbon dioxide. The known stability[10] of carbonates may be taken as that temperature at which the carbon dioxide pressure reaches 1 atmosphere.

Carbonate	*Decomposition temperature (°C)*
$MgCO_3$	400
$CaCO_3$	900
$SrCO_3$	1280
$BaCO_3$	1360

It is apparent that in all cases, except magnesium, the carbonate residue resulting from the breakdown of the anhydrous formate would be stable. In the case of magnesium the decomposition range for the formate 340–450°C happens to coincide with that temperature region where appreciable dissociation of carbonate would occur. The residue from the experiment with air present (see Table 2) must be a mixture of oxide and carbonate.

There have been attempts by previous workers to correlate the decomposition temperature, or Arrhenius parameters for thermal decompositions, with atomic number[11], cation radius[12], or the heat of formation of the oxide[13]. There is not sufficient evidence available to describe with certainty the nature of the activated complex formed in oxalates, formates or other salts and many arguments are largely conjecture. However, if it is accepted that in the case of oxalates and formates a primary stage is the transfer of electrons from the acid radical to the metal ion then it is possible that the nature of the cation influences the decomposition. The acceleration of these electrons through conduction bands should be related to the ionisation potential. The data* (estimated from ref. 13) for certain divalent metal formates and oxalates may support this:

Cation type	Mn^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
activation energy dec. formate			95[4]	106[14]	199.4	228	270
activation energy dec. oxalate	182	161	138	140	310[15]		
2nd ionisation potential	1512	1642	1748	1958	1145	1061	965

In general, the greater the ionisation potential the greater the attracting force on the electron and the lower the activation energy.

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*Units are kJ/mol.

The absolute values for the ionisation potential are very much higher than observed activation energies. This is to be expected since the former measures the energy of removal of the electron to infinity, in salts this situation will not arise.

It should be noted that in making such correlations between activation energies and other parameters it is assumed that physical parameters of formates do not vary from salt to salt. This will not always be the case, only in this study we can presume the experimental conditions did not alter, *i.e.* standard mesh size powders were taken and the alkaline earth formates belong to the same crystal class being orthorhombic[16]. Crystal structures for other formates are not available.

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