Hydrolysis of lanthanide dicarbides: rates of reaction with water vapour

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Abstract

The kinetics of the reaction between water vapour and nine of the lanthanide dicarbides, YC_2 and UC_2 have been investigated by gravimetric and gas evolution techniques. Mild conditions were used with water vapour pressures in the range $5.8-16.6 \times 10^2$ N m⁻² and temperatures from 4.0-48 °C. Over 90% of the reactions studied showed linear kinetics with the remainder following parabolic rates. Linear reaction rate constants lie in the range $0.34-18.1 \times 10^{-2}$ mg cm⁻² min⁻¹ depending on the carbide, temperature and pressure. For any given temperature and water vapour pressure the rate constant increased in the series from LaC₂ to DyC₂ and then decreased in the series DyC₂ to LuC₂, suggesting that the light lanthanides are least reactive. YC₂ had rate constants close to those of GdC₂, whilst UC₂ reacted some 50 times more slowly. In general, at any given water vapour pressure, in the range studied, the rate constant decreased with increasing temperature – a behaviour leading to negative values for the activation energy. From the activation energies a mechanism controlled by water adsorption on the product layers is postulated which suggests that the data do not give a true picture of LaC₂ + H₂O reactions. Increasing the water vapour pressure always increases the reaction rate constants. The results are discussed in the light of data from UC₂ and CaC₂.

1. Introduction

Much data exist on the hydrolysis reaction of lanthanide dicarbides [1-15] which is almost exclusively concerned with the distribution of gaseous products as expressed in eqns (1) and (2).

$$MC_{2} + (3+x)H_{2}O \rightarrow M(OH)_{3+x} + C_{2}H_{2} + \frac{1}{2}(1+x)H_{2}$$

$$C_{2}H_{2} + H_{2} \rightarrow C_{2}H_{4}$$

$$C_{2}H_{4} + H_{2} \rightarrow C_{2}H_{6}$$

$$C_{2}H_{2} + C_{2}H_{2} \rightarrow C_{4}H_{4} \ etc.$$

$$C_{2}H_{2} + 3H_{2} \rightarrow 2CH_{4}$$

$$C_{2}H_{4} + 4H_{2} \rightarrow C_{3}H_{8} + CH_{4}$$

$$(1)$$

$$(2)$$

Whilst the primary gaseous products are, as expressed in eqn. (1), acetylene and hydrogen, the secondary reactions, some of which are represented by eqns (2), are

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responsible for the variable products so frequently reported from studies where vigorous conditions involving acid solutions were used. Anderson et al. (10) have shown that a consistent distribution of product can be obtained when mild conditions involving water vapour only are used. Typical distributions of product are presented in ref. 10. Clark et al. [16] have shown for lanthanide dicarbides that, as the temperature is raised to 40 °C, the total of C₂ hydrocarbons remains as high as 99.3% of the evolved hydrocarbons, as long as low water vapour pressures are employed; this only drops to 93.5% at 100 °C. Thus in order to study the hydrolysis behaviour quantitatively there appear to be limitations to the range of conditions that can be used. For consistency, and to maintain the production of acetylene as the major gaseous product, whilst achieving constant volumes of hydrogen removal from the product gases of eqn (1), mild conditions, where the sample temperature is kept below 50 °C and the water vapour pressure below 2×10^3 N m⁻², are required. This is particularly true if reaction (1) is to be monitored by measuring gas pressure changes in a constant volume system. However if the reaction is to be studied thermogravimetrically then this is not so important except that too vigorous conditions may result in hydrocarbon waxes coating the samples as the reactions in eqns. (2) proceed. Taking these practical limitations into account the first stage of this quantitative study was done thermogravimetrically before a gas volume method was developed. The reasons for the investigations were to probe the nature of the $M-C_2$ bond in the dicarbides by means of reaction rate data, and to obtain data prior to a study of the effects of solid solution formation between pairs of lanthanide dicarbides on the rates of hydrolysis and, in particular, to examine the changes in reactivity brought about by crystal structure change from the usual tetragonal form of LnC₂ phases to the stabilised cubic solid solutions that have been reported [17, 18]. It was felt that a comparative study across the lanthanide series should first be made using small, freshly prepared, arc cast beads of the dicarbides.

Quantitative studies of the hydrolysis rates of lanthanide carbides in any media do not appear to be available but some visual observations have been made by Svec [7]. He noted that: "the rate of reaction in water was slow but was reasonably high in 1.0M HCl. Since many of the heavier rare earths react even more slowly than lanthanum carbide, the hydrolysis of carbides was carried out routinely in 1.0M acid".

Because of their use in the nuclear power industry the 5f series of carbides has been more fully examined with respect to hydrolysis rates and dissolution characteristics [1, 5, 20–23]. Most of the published work concerns UC and ThC, but some data on UC₂ are available from both thermogravimetric and gas evolution studies [19, 20, 5]. In all these reported cases the temperatures used were in excess of 50 °C and the water vapour pressures had been greater than 3.9×10^3 N m⁻² which are outside that condition suggested as "mild". Albrecht and Koehl [19, 20] found linear rates of reaction for UC₂ from 50 to 2000 °C in water and water vapour with UO₂ being the only solid product. Linear rate constants were in the range 2.6×10^{-6} to 1.9×10^{-4} mg cm⁻² min⁻¹ from 50 to 975 °C. An activation energy of 35.7 KJ mol⁻¹ was found. Bradley *et al.* [1, 2], whilst studying the reaction of UC in water, did comment on the marked increase in the rate of reaction with temperature, whilst also noting that the product distribution of H₂ and CH_4 was not altered, a fact in marked contrast to the LnC₂ phases as the results from Anderson *et al.* [10] show. Other quantitative observations have been made, for example Kempter [5] made the statement: "the U₂C₃ does not react with water even at 75 °C, and UC does shows no visual attack below 50 °C but at 100 °C the reaction became violent". In the same set of observations UC₂ was thought to be hydrolysed about ten times faster than UC. From these experiments suggestions were made that higher hydrocarbon waxes may be responsible for the low temperature inhibition and the difference between UC and UC₂ may reflect the relative strengths of the M-C bonds. Other investigators have attempted more quantitive appraisals of UC, notably Hori [21, 22] and Schurenkamper [23] where the activation energy, for what appeared to be a linear rate process, was found to be between 54.5 and 60.0 KJ mol⁻¹. Temperature had only a slight influence on the rate, and reactions in water were faster than in water vapour.

These are the available data with which any results for lanthanide dicarbides may be compared, in particular the linear kinetics for UC₂ hydrolysis at 50 °C observed by Albrecht [20]. From observation of the relative stabilities of LnC₂ and UC₂ when exposed to ambient conditions, reaction rates greater than 2.6×10^{-6} mg cm⁻² min⁻¹ at 50 °C for the LnC₂ phases might be expected.

Much of the data collected in this study, and now reported, was obtained thermogravimetrically using water vapour as the reagent to attack single arcmelted beads of near hemispherical shape when the gaseous product distribution was of little concern. Subsequently a water manometric method was tried whereby consistent gas products and gaseous volumes were required and in order to achieve this the reaction was limited to the range of conditions previously described as "mild".

The reaction rate data obtained are given later and show both linear and parabolic behaviour. The majority of reactions showed a linear rate for at least 300 min, a behaviour consistent with a massive volume increase in the product phase which is further broken down by the gaseous reaction products and so allows the access of water molecules to new surfaces. When parabolic behaviour was observed the light lanthanide dicarbides LaC_2 , CeC_2 and PrC_2 were usually involved. Examination of the specimen bead in such cases showed a thin adherent coating, passive even to dilute acids.

The temperature behaviour of the rates is not constant for all the lanthanide carbides but the rates were observed to decrease as the temperature was increased within the pressure range used for the thermogravimetric method, while at the higher vapour pressures involved in the manometric apparatus the reaction rate constant increased with temperature but there is a temperature above which a further increase results in a decrease in the rate constant. At any given temperature in the range studied there is an increase in the reaction rate constant from LaC_2 to DyC_2 followed by a decrease to LuC_2 in the dicarbide series.

2 Experimental details

The dicarbides were prepared and characterised as described previously [17]. For thermogravimetric investigations of the hydrolysis reaction a C.I. Elec-

tronics mark IIB microbalance was built into a vacuum gas-handling system and connected to a Rikadenki multispeed chart recorder. The specimens were small arc-melted beads weighing approximately 100 mg. Each bead was weighed and the dimensions determined using a micrometer and a microscope with a scale eyepiece. After determining the radius and height of the bead its surface was cleaned by a 3 s immersion in HCl followed by acetone washes and then put into the aluminium bucket of the balance which already contained CCl₄ to protect the sample. The specimen bucket had to be of sufficient size to provide a fit for the arcmelted bead and also to contain all the solid reaction products which showed a large volume increase relative to the dicarbide. After taring the whole apparatus was evacuated and the reaction chamber brought to the desired temperature by circulating water at the required temperature or by immersing the chamber in a thermostatted enclosure. After approximately 30 min the apparatus was isolated from the vacuum system and water vapour admitted from a saturated CuSO₄ solution kept at a fixed temperature in order to maintain a chosen constant water vapour pressure.

Pressure monitoring was achieved by means of a manometer attached to the balance head. The specimen temperature from 0-60 °C was maintained by immersing the balance down-tube in a large-volume narrow-necked Dewar flask containing a large body of water at the required temperature. During a 20 h period the temperature change was only +1 °C which gave a negligible change over the 300-600 min time period of the average experiment. Only the weight change data over the first 300 min were used to calculate the reaction rates. One of the reasons for this was to avoid the complication caused by the large surface area reaction product acting as a water adsorption medium and so producing weight gains not associated with the reaction of the LnC_2 surface. Preliminary experiments, when the reaction was stopped at various times and the system evacuated to remove adsorbed water, showed that this effect was not noticeable until approximately 600 min had elapsed. Using this technique reasonably consistent values for the reaction rate constant could be achieved; some of the repeat results are given in Table 1.

The all-glass water manometer system was modified to that shown in ref. 23, where a double-walled water manometer and reaction vessel were maintained at a constant temperature by pumping water around the hollow walls using a Shandon constant temperature circulator. The water vapour pressure of the reaction was known from the temperature of the water reservoir at the base of the sample tube. As the reaction proceeded the increased pressure in the apparatus from the C_2H_2 and H₂ was observed as a depression of the water level in the manometer side arm by using a cathetometer with cross-wires focused on the water meniscus. A typical experiment involved sealing a small arc-melted bead of 25 mg mass with an iron rod in a vacuum in a Pyrex glass bulb. This bulb was suspended within the hollow glass vacuum-tap at the top of the reaction tube by a magnet at the outside. The sample tube and manometer were then evacuated and allowed to come to equilibrium; it usually took about 2 h to reach at this stage. After equilibration the magnet was removed, the bulb fell into the reaction vessel, broke and hydrolysis began. From this point the increase in the water level was noted. Specimen temperatures were maintained by immersing the reaction tube in a water bath main-

Sample	Temperature (°C)	$\frac{K_{\rm L}}{(\times 10^{-2}{\rm mgcm^2min^{-1}})}$	$\frac{\text{Mean } K_{\text{L}}}{(\times 10^{-2} \text{ mg cm}^2 \text{ min}^{-1})}$
LaC ₂	20	0.59 0.48 0.52	0.53 ± 0.06
NdC ₂	24.5	0.51 0.82 0.65 0.77	0.69±0.18
GdC ₂	14.5	5.2 6.6 6.2	6.0 ± 0.8
GdC ₂	24.5	6.0 4.6 5.6	5.4 ± 0.8

Reproducibility of the linear reaction rate constant $K_{\rm L}$ for water vapour at a pressure of 11×10^2 N m⁻²

tained at the required temperature. This technique was not as easy to perform as the gravimetric method for water vapour experiments but became indispensable in a later study when the hydrolysis reaction in liquid water was studied.

The rate data were obtained as either a weight increase over time for a unit surface area of dicarbide bead (mg cm⁻² min⁻¹) or as a height decrease in the water column with time for unit surface area: (cm cm⁻² min⁻¹). Three to seven runs per sample were done in order to obtain the average values quoted in the results. The maximum deviation was generally found to be within $\pm 15\%$ in a series of seven samples of each dicarbide. Where a rate constant in a series of experiments was found to be beyond the $\pm 15\%$ deviation an obvious experimental anomaly was observed; for example beads cracking open during the experiment to reveal fresh surfaces; a shiny impervious wax appearing as a surface layer; or variations in water vapour pressure occurring due to physical changes of temperature or leaks in the apparatus. These results were then ignored in subsequent considerations.

3. Results

3.1. Thermogravimetric results

More than 90% of the experiments showed linear increases in weight for times up to 300 min after the reaction began; Fig. 1 shows some of the traces obtained. About 10% of the experiments produced parabolic curves, often when the reaction rates were unusually slow and the samples involved were usually



Fig. 1. Plot of weight gain against time for some lanthanide dicarbides hydrolysed in water vapour at 14.5 °C and a pressure of 11×10^2 N m⁻².

 LaC_2 , CeC_2 and PrC_2 . For all the parabolic rate cases, visual examination of the specimen bead showed a thin adherent coat of shiny reaction product, which was passive even to dilute acids. The abnormality of the parabolic behaviour is emphasized by the fact that dicarbides showing this behaviour also produced repeatable linear behaviour in other experiments. Thus it was concluded that the reaction leading to linear kinetics was typical for this series of carbides and comparative data are collected in Table 2.

From the rate constants in Table 2, under the mild reaction conditions pertaining, at any temperature studied, the enhanced reactivity of GdC_2 and DyC_2 is apparent. With the exception of CeC₂ there is a rise in reactivity as the f-electron content of the lanthanide rises to the middle of the series and then there is a steady decrease in the reaction rate towards the end of the series to LuC₂. In general the heavy lanthanide dicarbides are increasingly more reactive than the light members of the series as the temperature is raised at these low water vapour pressures. Albrecht and Kohl's [19] linear rate data for UC₂ fall in the range 1.9×10^{-2} to 2.6×10^{-3} mg cm⁻² min⁻¹, as shown in Table 7, but the lowest temperature covered by that study was 50 °C when the rate was 2.64×10^{-3} mg cm⁻² min⁻¹. Since the vapour pressures used are not comparable in the two studies it is not possible to conclude absolutely that the lanthanide dicarbides react some 20 to 400 times more rapidly than UC_2 . The comparative data show that the decreasing reaction rate as the temperature is raised for LnC₂ phases is not paralleled by UC₂ when the vapour pressure exceeds 32×10^2 N m⁻². This clearly indicates, as further data, given later support, that the important step in the LuC₂ reaction involves the availability of water molecules at the surface of the sample.

Linear rate constants $K_{\rm L}$ for the reaction of lanthanide dicarbides with water vapour at temperatures up to 40 °C determined using the thermogravimetric technique. The water vapour pressure was maintained at 11×10^2 N m⁻²

Dicarbide	K_{1} (×10 ² mg cm ⁻² min ⁻¹) at temperature (°C)									
	10	14.5	18	20	24.5	28	30	40		
LaC	1.6	0.99	0.54	0.53	1.75	_		Very slow		
CeC,	8.3	2.0	1.1	0.41	2.2		_	_ ·		
PrC,	5.7	1.2	_	0.13	1.0	_	0.5			
NdČ,	8.2	1.9	1.6	0.73	0.69	_	_			
GdC,	10.3	6.0	5.2	3.2	5.4	_	Very slow	_		
DyC ₂	16.3	8.0	7.8	7.0	4.3		4.7	Very slow		
HoC,	9.6	6.3	5.9	5.7	3.6	-	_	0.34		
ErC ₂	7.0	6.0	6.4	5.0	3.3	2.7	2.1	—		
LuC,	4.0	2.9	3.1	2.8	1.9	-	_	_		
YC ₂		7.0		_	_		_	_		

TABLE 3

Parabolic rate constant K_p for the reaction of water vapour with lanthanide dicarbides as determined gravimetrically at a vapour pressure of 11.0×10^2 N m⁻²

Dicarbide	$K_{\rm p}$ ((×10 ² mg cm ⁻²) ² min ⁻¹) at temperature (°C)								
	10	14.5	16	18	20	24.5			
LaC	5.61	5.34	*	*	*	*			
CeC,	52.3	32.2	_	14.6	13.0	8.57			
PrC ₂	*	8.81	_		10.59	0.69			
NdC ₂	*	2.20		*	*	0.09			
GdC,	487	*	333	*	*	91			
DvC ₂	*	395.9		*	*	179.1			
HoC	*	*	_	*	*	*			
ErC	*	*	_	*	*	*			
	*	*	-	*	*	*			

*Parabolic rates not found, linear only.

-, No study made.

Those reactions that showed parabolic behaviour quite clearly confirm both the trends noted so far for the LnC_2 water vapour reaction, namely maximum rates for GdC₂ or DyC₂ and steady decreasing rate constants for increased reaction temperature when vapour pressure is held constant at 11.0×10^2 N m⁻². These data are shown in Table 3.

The sensitivity of the linear reaction rate constant to changes in water vapour pressure are tabulated in Table 4.

Sample	$K_{\rm L}$ (×10 ² mg cm ⁻² min ⁻¹) at water vapour pressure (×10 ² N m ⁻²)								
	5.8	8.55	11.0	12.3	13.6	15.6			
LaC ₂	1.3		0.99			_			
CeC_2	1.9		2.0			_			
PrC ₂	0.6	_	1.2		_	_			
NdC ₂	0.6	_	1.9		—				
GdC_2	3.1	4.2	6.6		10.2	_			
DyC_2	4.5		8.2		_				
HoC ₂	2.7		6.8	7.0	_				
ErC ₂	3.5		6.0		_	7.7	8.3		
LuC ₂	1.2	_	3.1	5.3	_	_			
YC ₂	_	_	7.0	18.3	_				

The effect of water vapour pressure on lanthanide dicarbide hydrolysis at 14.5 °C



Fig. 2. Linear reaction rate constant $K_{\rm L}$ and reduced rate constant $K'_{\rm L}$ as a function of water vapour pressure at 14.5 °C for GdC₂ and ErC₂ hydrolyses.

The results show that as the water vapour pressure is increased within the range defined as mild, the reaction rate constant is increased. The data points for the $GdC_2 + H_2O(g)$ reaction at 14.5 °C are plotted in Fig. 2 and show a markedly non-linear relationship. On the same figure there appears to be a linear increase in K_L with water vapour pressure for the $ErC_2 + H_2O(g)$ reaction. In order to extend the vapour water pressures to high values, attention was directed to the manometric method.

3.2. Manometric results

The dicarbides examined in this way are listed in Table 5; the data show that the vapour pressure was extended to 16.6×10^2 N m⁻² and the reaction temperature was also increased to 48 °C. In order to compare the results from the two methods more directly the K_L values from the thermobalance experiments were recalculated from plots of $\Delta m/m$, against time, where *m* is the initial mass of the sample bead whilst K_L from the manometric method were obtained from plots of $\Delta h/h$, where *h* was the final height of the water column. The final water column height is proportional to the initial mass of the starting bead. The units for these reduced K_L are then cm⁻² min⁻¹. The results in Table 5 now emphasise the sharp increases in the rate when more water molecules are available, but in general the increase is nonlinear conforming to the GdC₂-H₂O reaction of Fig. 2. Once again it is apparent that even at the higher water vapour pressure there is a temperature above which the rate of reaction does not increase. Indeed at 48 °C and 16.6×10^2 N m⁻² water pressure the reaction of HoC₂ is so slow as to leave the bead unchanged after 16 h.

4. Discussion

Consistent increases in the reaction rates with increasing temperature can only be observed if increased vapour pressures, beyond those defined as mild [10], are used in the experiments. This implies that with a good coverage of the surface with water molecules the rate constant will increase with increasing temperature. A closer look at the linear rate constants, particularly at their variation with temperature at a constant water vapour pressure, reveals three regions of behaviour for the dicarbides studies. At a low pressure of 11×10^2 N m⁻² these regions are:

(i) from 10 to 20 °C where the rate decreases as the temperature increases;

(ii) from 20 to 28 °C where the rate remains constant or increases; and

(iii) above about 25-28 °C where the rate decreases sharply as the temperature increases.

For these ranges it has been possible to make Arrhenius type plots even though insufficient data points were available to get precise activation energy data. As the figures in Table 6 show, negative activation energies have been found for some of these temperature regions. Negative activation energies are not commonly encountered and so there is little data with which to compare the values in Table 6. Svec *et al.* [24, 25] have studied the reaction of periodic group II metals with water

Sample	Method	Temperature	Water vapour	K. (munomater	Reduced rate constan	It
			$(\times 10^2 \mathrm{Mm^{-2}})$	× 10^{-2} cm cm ⁻² min ⁻¹ ; microbalance: × 10^{-2} mg cm ⁻² min ⁻¹)	$K_{\rm L}/h$ (×10 ⁻³ cm ⁻²)	$\frac{K_{\rm L}}{M_{\rm c}}$ $\frac{K_{\rm L}}{(\times 10^{-4} {\rm min^{-1}})}$
LaC2	Manometer	25	16.1	5.1	3.3×10^{-3}	
		30	16.1	8.4	3.6×10^{-3}	I
	Microbalance	24.5	11.0	1.8	I	2.6×10^{-4}
		14.5	5.8	1.3	1	1.4×10^{-4}
PrC,	Manometer	14.5	16.1	2.9	2.3×10^{-3}	1
I		26.0	16.1	4.8	2.5×10^{-3}	I
		33.5	16.1	6.5	2.5×10^{-3}	I
	Microbalance	14.5	11.0	1.2	Ι	2.7×10^{-4}
		14.5	5.8	0.64	ŀ	1.4×10^{-4}
		24.5	11.0	1.0	I	1.7×10^{-4}
DyC_2	Manometer	26.0	16.1	1.2	7.9×10^{-3}	I
		33.5	16.1	20	1.5×10^{-2}	I
		14.5	12.4	$K_{\rm p} = 186$	I	
	Microbalance	14.5	11.0	§.0	I	5.1×10^{-4}
		14.5	5.8	3.3	1	3.5×10^{-4}
		24.5	11.0	4.3	I	4.6×10^{-4}
		30.0	11.0	4.7	1	5.3×10^{-4}
		15.0	11.0	$K_{\rm p} = 395$	ł	I
HoC_2	Manometer	14.5	16.1	8.8	3.3×10^{-3}	*
		29.0	16.1	18.1	12.6×10^{-3}	I
		42.0	16.6	$K_{\rm n} = 1.01$	ŀ	I
		48.0	16.6	Too slow to detect	Ι	I
	Microbalance	14.5	11.0	6.3	1	1.3×10^{-3}
		14.5	5.8	2.7	1	3.9×10^{-4}
		24.5	11.0	0.48	l	5.2×10^{-4}
		4.0	11.8	0.34	I	0.44×10^{-4}

Manometric and gravimetric reaction rate data for some lanthanide dicarbides

TABLE 5

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Material	$P_{\rm H_2O}$	Activation energy $(kJ mol^{-1})$ at temperature (°C)						
	$(\mathbf{N} \mathbf{m}^2 \times 10)$	10-20	20-30	20-50	40-66	41-56	56-66	
LaC,	11.0	- 84	+ 193	_	_	_		
CeC,	11.0	-195	+275	_	_	—	_	
PrC,	11.0	-256	+ 326	_	_	_	_	
NdC ₂	11.0	-154	± 0		_	_	_	
GdC,	11.0	-77	+86	_		-	_	
DyC,	11.0	-40	- 76	_	_	-	_	
HoC,	11.0	-32	- 76	_	-	~	_	
ErC,	11.0	-24	-65	-	_	-	_	
LuC ₂	11.0	-24	-64			~		
Ca [24]	23-120	_	<u> </u>	-31.4 ± 1.2		-	_	
Sr [24]	22.5-67.5		_	_	21.7 ± 0.3	-		
Ba [25]	22.5			_		± 0		
Ba	41.5	_	-	_		-21.3 ± 1.2	-	
Ba	71.5		_	_	_	Not linear	_	
Ba	71.5		-	_		-	-39.7 ± 4.2	

Activation energies found for the reaction of water vapour with lanthanide dicarbides in this work and for alkaline earth metals elsewhere

vapour in a temperature range similar to that used here, but at the higher vapour pressure of 120×10^2 N m⁻². Logarithmic rate processes were found for calcium and parabolic rate processes for barium and strontium. In all cases the rate constants decreased with increasing temperature thus gives the negative activation energies.

The dependence of the rate constants on water vapour pressure in the temperature range 20-50 °C suggested that the inward diffusion of water molecules, through the cracked reaction product layer of Ca(OH)₂, is the ratecontrolling step. Thus when the temperature was increased the water molecules obtained sufficent energy to break away from the product layer at the surface and return to the gas phase. This leads to a decrease in the diffusion rate of H₂O through to the metal surface and overall to a decrease in reaction rate with temperature and the apparent negative activation energies. In this way the negative activation energies can be related to heats of desorption of H_2O from $M(OH)_2$ surfaces. Svec's data are presented along with this LnC_2 data in Table 6. At 11×10^2 N m⁻² water pressure throughout the first region, 10-20 °C, all the LnC₂ + H₂O(g) reactions have negative activation energies and Svec's explanation may apply throughout with the rate of reaction being controlled by the absorption and retention of water molecules at the product surface. Under identical conditions the apparent water activity at the dicarbide-hydroxide interface is significantly decreased for the light lanthanides CeC_2 , PrC_2 and NdC_2 ; these are the carbides in which the lanthanide has detectably higher oxidation states, all having some Ln⁴⁺. This will lead to a larger volume of the reaction products containing $Ln(OH)_3 + Ln(OH)_4$ which will inhibit the diffusion of water molecules to the reaction interface. It is notable that those carbides with only oxidation state three for the lanthanide show a steady increase in activation energy from LaC_2 to LuC_2 following the steady decrease in unit cell volume for these dicarbides.

The change to positive activation energies for the lighter lanthanides in the second temperature range may be indicative of faster reaction rates for these dicarbides rather than the $K_{\rm L}$ values peaking at GdC₂/DyC₂ as results shown in Tables 2 and 3 indicate.

A simplified scheme expressed by eqns. (3) and (4) leads to a possible explanation of the positive and negative activation energies found in the second temperature range.

$$H_2O(g) + surface \rightleftharpoons_{K_1}^{K_1} H_2O(ads)$$
 (3)

$$MC_2 + 3H_2O(ads) \stackrel{K_3}{\Longrightarrow} M(OH)_3 + C_2H_2 + \frac{1}{2}H_2$$
(4)

Rate constants K_2 and K_3 will increase as the temperature is raised and, at approximately 20 °C, the reaction rate K_3 for the lighter lanthanide dicarbides is faster than the water retention rate process K_1 and so it dominates and the reaction rate constant K_3 now increasing with temperature shows the positive activation energy. As the temperature is raised the process with rate constant K_2 increases more rapidly and the overall rate will decrease leading to the onset of region (iii) around 30 °C. If, for the heavier lanthanide dicarbides (DyC₂-LuC₂), K_3 does not increase so rapidly then the overall reaction has an apparent negative activation energy throughout all these temperature regions. The marked changes in K_L with increased water vapour pressures, Table 4, do support such a mechanism which leaves open the question of determining the actual rate constants and activation energies for the reaction expressed in eqn. (1). Clearly an excess of water molecules must be ensured by carrying out the reactions in liquid water but first an appraisal of the product distribution from such an "un-mild" procedure must be assessed; the results from such a study will be reported in a following publication.

From the arguments so far proposed the question arises as to why the dicarbides around the middle of the series appear to have either the greatest ability to retain water molecules, or for the H_2O to diffuse more rapidly to the reacting interface as the K_1 data now indicate.

The absence of anything other than a trivalent state would seem to be part of the answer and possibly a cation size relationship since K_L for the YC₂ reaction is close to those for GdC₂ and HoC₂ and these cations are almost the same size.

It seems from these data that no clear view can be obtained on the role of the $M-C_2$ bond in the process and that, to achieve this aim, reactions in water using the manometric apparatus will have to be studied. Before this can be done a careful assessment of the distribution of the gaseous products will have to be made to see if such vigorous reaction conditions seriously disturb the gaseous volumes implied by eqns. (1) and (2). Finally it is worth considering the general magnitude of the K_L

constants in terms of the rather sparse data on related systems. Engle [26] quotes a $K_{\rm L}$ value for UC₂ of 1.5×10^{-2} mg cm⁻² min⁻¹ in air saturated with water vapour at 50 °C. This emphasizes the trend that increasing the water vapour pressure considerably increases the reaction rate when comparing Albrecht's [19] 50 °C results for UC₂ using the lower vapour pressure given in Table 7. It can be seen that $K_{\rm L}$ is approximately 15 times lower.

The values of K_L for UC₂ found by Albrecht are all in excess of those found here for LnC₂ reactions but the conditions used here were so much milder. Some samples of UC₂ prepared here and examined gravimetrically produced the reaction rates shown in Table 7 which are in the range expected by extrapolating the Albrecht data to these much milder conditions. Hence taking a value of 6×10^{-4} cm⁻² min⁻¹ at 11.0×10^2 N m⁻² water vapour pressure and 20 °C for UC_2 this is a some 50 to 100 times slower rate than for lanthanide dicarbides. It is again not possible to ascribe this difference either to M-C₂ bond strength differences or to H₂O retention and diffusion differences in the two systems. The calcium dicarbide water vapour reaction has been investigated [27] but unexpectedly, as far as this study goes, the reaction only follows parabolic kinetics and therefore we have few data from LnC_2 systems with which to compare it. It was not found to be possible to prepare small well-shaped beads of CaC₂ in this work in order to make direct comparisons as was done for UC2. Therefore taking Tagawa's extreme values for K_p at 11.4×10^2 N m⁻² water vapour pressure to be 5.5 and 0.11×10^{-2} (mg cm⁻²)² min⁻¹ in the range 20–25 °C, and examining the parabolic rate constants occasionally found in this study, we see a range of faster rates from 0.09 to 179×10^{-2} (mg cm⁻²)² min⁻¹. This may imply a more rapid rate for $LnC_2 + H_2O(g)$ reactions arising from the lower M-C₂ bond strengths, but it is more likely to indicate the greater affinity for water molecules with a surface of $Ln^{3+}(OH)_3$ than one of $Ca^{2+}(OH)_2$. The heats of water desorption, implied by the negative activation energies in Table 6, do suggest that at 20 °C, Ca(OH)₂ has only 50% of the retention ability of $Ln(OH)_3$ hydrolysis products.

TABLE 7

Material	Water vapour pressure (×10 ² N m ⁻²)	Temper- ature (°C)	$\frac{K_{\rm L}}{(\rm mg\ cm^{-2}\ min^{-1})}$	$K_{\rm p}$ ((mg cm ⁻²) ² min ⁻¹)
UC ₂ [20]	37.6	50	264×10^{-3}	_
		150	3.96×10^{-2}	_
		200	1.92×10^{-1}	-
UC ₂ (here)	11.0	14.5	7.1×10^{-4}	
2.		20	5.8×10^{-4}	_
CaC ₂ [27]	11.5	20-25		(100) plane 5.55×10^{-2} (110) 0.24×10^{-2} (111) 0.11×10^{-2}

Rate constants for the reaction of UC2 and CaC2 with water vapour determined gravimetrically

From this discussion it can be seen that, in general, the data obtained here for the $LnC_2 + H_2O(g)$ reaction have K_L or K_p constants not out of line with the related systems of UC₂ and CaC₂.

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