Journal of the Less-Common Metals, *170* (1991) 191-198

Hydrolysis of lanthanide dicarbides: rates of reaction with water

I. J. McColm and **T. A. Quigley***
Department of Industrial Technology, University of Bradford, Bradford, BD7 1DP (U.K.)

D. R. Bourne
Science Department, Accrington Technical College, Accrington (U.K.)

(Received December 8, 1990)

Abstract

The kinetics of the reaction between liquid water and nine lanthanide dicarbides and YC_2 have been investigated by monitoring the gas evolved into a constant volume apparatus. The ratio of volume of gas evolved to that predicted was found to be consistent at 0.51 for wholly trivalent dicarbides, but rose to 0.66 for the light lanthanides containing Ln^{IV} components. Only linear kinetics were observed with the linear reaction rate constant K_L in the range 0.44 cm cm^{-2} min^{-1} for LuC_2 to 6.9 cm cm^{-2} min^{-1} for CeC_2. Over the limited temperature range 283-303.5 K it was possible to estimate activation energies for four of the dicarbides and the values ranged from 48.5 kJ mol^{-1} for the heavy, hard carbides to 150 kJ mol^{-1} for the light, soft, Ln^{IV}-containing members. The variation of K_L and E across the series is discussed in terms of M-C_2 bond energies, 4f-band electron density and the hardness of these dicarbides.

1. Introduction

Our previous attempts [1] to rectify the lack of data concerning the hydrolysis reaction rate constants of lanthanide dicarbides concentrated on investigating the reaction occurring in mild conditions. Mild in this context is defined by Anderson *et al.* [2] and was introduced to limit the secondary reactions between the reaction product gases, acetylene and hydrogen. Such reactions are catalysed by the metallic surface of the reactant dicarbide. In the previous work [1], the low vapour pressures did not lead to information about the fundamental reaction, as shown by the negative activation energies that were measured. This paper reports rate data found when using small arc-melted beads of the lanthanide dicarbides hydrolysed in liquid water.

In order to use the data comparatively, the consistency of the gaseous product volume evolution had first to be established since resorting to liquid water moved the conditions well away from those defined as mild. This was particularly true since the reaction had to be monitored by measurement of the pressure increase in a constant volume apparatus. This was achieved and the reactivities of LnC_2 phases have been found and compared to similar data for related phases. How the

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*Present address: British Gas Research Department, Kinross, Fife, U.K.

0022-5088/91/$3.50

reaction rate constant changes as a function of f-electron density, surface energy as revealed by hardness measurements, and the C_2^{n-} size change are discussed in the light of these new data.

2. Experimental details

All the preparative, characterisation and hydrolysis measurement techniques have been fully described before [1-3]. The samples of dicarbide used here were small beads taken from the same material used in [1].

3. Results

The overall hydrolysis reaction of trivalent and tetravalent lanthanide dicarbides can be summarised by eqns. (1) and (2):

$$M^{III}C_2 + 3H_2O = M(OH)_3 + C_2H_2 + \tfrac{1}{2}H_2 \qquad (1)$$

$$M^{IV}C_2 + 4H_2O = M(OH)_4 + C_2H_2 + H_2 \qquad (2)$$

Even using the mild conditions defined by Anderson *et al.* (2), hydrogen is removed from the product gases by several reactions, a few of which are summarised by eqn. (3):

$$\left.\begin{array}{l} C_2H_2 + H_2 = C_2H_4 \\ C_2H_2 + 2H_2 = C_2H_6 \\ 2C_2H_2 + H_2 = C_4H_6 \\ nC_2H_4 = \text{solid wax} \end{array}\right. \qquad (3)$$

In liquid water, because of catalysis on each layer of freshly revealed carbide surface, reactions such as those in (3) leading to product gas removal do occur as the results in Table 1 show.

However, for the purposes of this work, the results in Table 1 indicate a consistent pattern of H_2 and C_2H_2 removal from the V_o/V_e ratio. The V_o/V_e ratios were found by assuming that all the dicarbides were 100% trivalent and so eqn. (1) was relevant. For those that undoubtedly are wholly trivalent it is clear that constant hydrogen and acetylene removal occurs to produce the V_o/V_e ratio of 0.51 ± 0.02. The high V_o/V_e values for the light lanthanide trio CeC_2, PrC_2 and NdC_2 show the effect of the Ln^{4+} content of these materials, a fact previously noted [4], and used to explain the larger than expected C–C bond length in CeC_2 [5].

For such a comparative study as this, using a constant volume apparatus and monitoring the gas pressure rise, a constant V_o/V_e ratio is necessary. This assumes that hydrogen and acetylene are removed from the evolved gas by reaction at the dicarbide surface as they are being evolved; the constancy of V_o/V_e is therefore a good indication that this is happening. However in the case of those dicarbides

TABLE 1

Volumes of gas evolved from the reaction of lanthanide dicarbides with water at 20 °C compared to those expected from eqn. (1) in the text

Sample	Observed volume V_o (cm^3)	Calculated volume V_e (cm^3)	V_o/V_e
LaC_2	2.3	4.5	0.51
CeC_2	3.5	5.3	0.66
PrC_2	1.4_9	3.1	0.62
NdC_2	3.2	5.4	0.59
GdC_2	1.9_5	3.7	0.50
DyC_2	2.6	5.0	0.51
HoC_2	2.1	4.3	0.49
ErC_2	2.3	4.5	0.52
LuC_2	2.5	4.7	0.53

TABLE 2

Linear reaction rate constants for the reaction of LnC_2 phases in liquid water at 20 °C

Dicarbides	V_o/V_e	K_L ("cm" cm^{-2} min^{-1})
LaC_2	0.51	0.60 ± 0.08
CeC_2	0.66	6.90 ± 0.08
PrC_2	0.62	2.22 ± 0.08
NdC_2	0.59	3.11 ± 0.08
GdC_2	0.50	1.43 ± 0.08
DyC_2	0.51	1.11 ± 0.08
HoC_2	0.49	0.97 ± 0.08

having the Ln^{4+} component the extra volume of gas evolution that this implies must be adjusted through the V_o/V_e ratio and accordingly in Table 2 these rates are K_L observed multiplied by the factor $0.51/(V_o/V_e)_o$.

Table 2 contains the linear rate reaction constants after making these adjustments. Linear reaction kinetics are always observed, at least for the first 40 min, for which period of time the reaction was usually followed. The increase in manometric height (cm) was tracked for this time interval because it was found that over that period the 20–30 mg reaction bead did not suffer a reduction in surface area great enough to influence the results. However, when the temperature at which the reaction was studied was increased beyond 30–35 °C the volume of gas evolved became erratic as polymerisation reactions removed variable volumes of product gases. Above 40 °C the reaction rates appeared to decrease because of this effect which was the main reason why only four samples were able to be studied confidently to see how the linear reaction rate varied with temperature.

TABLE 3

Activation energies for the hydrolysis reaction of four lanthanide dicarbides

Dicarbide	Temperature (K)	K_L ("cm" cm^{-2} min^{-1})	Activation energy (kJ mol^{-1})
GdC_2	283	0.7	
	293	1.4	48.5
	297	1.7_4	
	303.5	2.8	
LaC_2	293	0.68	
	298.7	2.0	110.8
	304.5	3.75	
NdC_2			150
HoC_2			32.0

The most notable feature of the results presented in Table 2 is that compared with the reaction between LnC_2 and water vapour [1]; the rates of reaction are some 100 times faster and linear kinetics are always observed.

The way the reaction rate increased as the temperature is raised is shown for four dicarbides in Table 3.

4. Discussion

The hundredfold increase in reaction rates when water is the medium instead of water vapour has already been noted. Another difference between the water vapour and liquid water results is that the reaction rates reach a maximum for the middle members of the series GdC_2/DyC_2 when the reactant is a low pressure of water vapour, whilst in water, following a large increase in rate from LaC_2 to CeC_2, there is a monotonic decrease to LuC_2. It seems possible then that in water the reaction being studied is the fission of the M–C_2 bonds since the supply of H_2O molecules at the dicarbide surface is not limited as in the water vapour case. Diffusion through any product layer should not be rate-controlling since any product is severely disrupted, first by the excess of water, and then by the rapid production of gas bubbles on the surface. Thus water molecules on the bead surface are present in high concentration and reaction ensues producing the hydroxide product and H^+ ions which diffuse along the surface to combine with other H^+ ions to produce the H_2 gas or with surface C_2^{2-} ions to produce acetylene. As the V_o/V_e values show, the acetylene and hydrogen molecules do combine to produce reduction products and polymers, particularly at higher temperatures. The water vapour reactions, [1], appear to be controlled by retention of H_2O molecules on the hydroxide product and diffusion through to the reactive surface, hence the mainly negative activation energies that were observed in the vapour phase experiments [1]. The rate-determining features of the dicarbides when reacting with liquid water can be sought in the areas of the M–C_2 bond strengths, the mean cationic charge density, the surface energy, and the linear size of the C–C bond in the dicarbide. Considering now some of these features: Filby and Ames [6] have determined the M–C_2 dissociation energies by studying exchange reactions in the vapour phase of reactions of the type in eqn. (4):

$$CeC_2(g) + La(g) \rightleftharpoons LaC_2(g) + Ce(g) \tag{4}$$

Their results are given in Table 4.

If the reverse of the dissociation energies is the bond energy, then M–C_2 bonds in NdC_2 and PrC_2 are less stable than in LaC_2 and the increased hydrolysis reaction rates might be expected but CeC_2 would then be completely anomalous. The bond model used to describe these compounds has C_2^{n-} units bound by a pair of electrons in a 2pσ-bonding level and two unpaired electrons in 2pπ-bonding levels. Ionisation of Ln to Ln^{3+} then results in the occupation of two of the three electrons in the bonding π levels and the third e^- into the antibonding level where it increases overall bonding in the system by interaction with metal s, d and f orbitals in a delocalised metallic band. However, the increased electron density in the antibonding levels increases the size of the C_2^{n-} unit compared to the C_2^{2-} anion found in CaC_2. This size effect occurs as several neutron diffraction studies have shown [7–9]. The higher oxidation state present in CeC_2, PrC_2 and NdC_2, as the evolved gas volumes in Table 1 show, compared to LaC_2, GdC_2 *etc.* then leads to longer C–C bond lengths and greater overall size of the C_2^{n-} units. Some of our neutron diffraction data confirm this [5, 9], see Table 5. Presumably increased size of C_2^{n-} means greater availability at the surface for H^+ reaction and of course higher overall mean cation charge $Ln^{(3+\delta)+}$ makes the $Ln^{(3+\delta)+} + H_2O \rightarrow H^+ +$ Ln–OH reaction proceed faster. The observed peak to CeC_2 in the reaction rates and the steady decline in reaction rate through PrC_2, NdC_2 to GdC_2 and on to LuC_2, might then be explained. The fact that reaction rates for YC_2 are close to the GdC_2, DyC_2 values when the overall X-ray unit cell size and C–C distance of these three dicarbides is so close, and all contain only Ln^{3+} species, helps to support the C_2^{n-} size explanation.

The pendulum and Vickers hardness values of the dicarbides both show a variation, [3], that mirrors the reaction rate data. This is shown in Fig. 1. The soft

TABLE 4

Gaseous rare earth dicarbide dissociation energies (after [6])

Dicarbide	D^0(M–C_2) (kJ mol^{-1})	K_L at 20 °C ("cm" cm^{-2} min^{-1})
LaC_2	669 ± 12	0.60
CeC_2	677 ± 8	6.90
PrC_2	631 ± 12	2.22
NdC_2	602 ± 12	3.11

TABLE 5

Some C–C bond lengths as obtained from neutron diffraction experiments

Dicarbide	C–C (nm)	Reference
CaC_2	0.119	[7, 8]
YC_2	0.1275	[7, 8]
	0.1288	[9]
UC_2	0.134	[7, 8]
	0.132_2	[5]
LaC_2	0.130	[7, 8]
	0.1284	[14]
CeC_2	0.1283	[7, 8]
	0.1297	[9]
PrC_2	0.129_4	[7, 8]
NdC_2	0.130_2	[9]
TbC_2	0.129_1	[7, 8]
HoC_2	0.127_9	[7, 8]
	0.128_5	[9]
ErC_2	0.127_5	[14]
LuC_2	0.127_6	[7, 8]
ThC_2	0.1304	[5]

dicarbides CeC_2, PrC_2, NdC_2 are the most hydrolytically reactive and reaction rates for the wholly $Ln^{3+}C_2$ species follow a decrease in the reaction rate as the hardness increases along the series.

The limited activation energy data add a little to differentiating the two groups of dicarbides and their changed rate controlling mechanisms. The two light, soft lanthanides examined have E values in excess of 100 kJ mol^{-1} whilst the two heavy lanthanide dicarbides examined have values of 48.5 (GdC_2) and 32.0 kJ mol^{-1} (HoC_2) which are significantly different. Independent data from two early studies of the UC_2 + liquid water reaction [10, 11] give two differing values at 30.7 and 54.3 kJ mol^{-1} but these have a mean value close to the GdC_2 value found here to infer the general indication of the same rate-controlling step in the overall reaction between the heavy, hard dicarbides and UC_2.

In the water vapour reactivity study, [1], GdC_2 was the one specimen that produced a positive activation energy in the 10–30 °C temperature range with a value of 86 kJ mol^{-1} being obtained. This indicates, as already assumed, that a different rate-controlling mechanism is active in the water vapour reaction.

The fairly clear demarcation of the two groups of dicarbides in terms of their K_L, E and hardness values, requires an explanation outside the gradual changes expected from a consideration of the way cell volumes and atomic number increases steadily across the lanthanide series. Gschneidner [12] has suggested a potential explanation through his model suggesting two types of f-electrons in the lanthanide metals, the 4f-band and 4f-atomic electrons. The model has been used to consider dicarbide results before [4]. The 4f-atomic are 4f-electrons associated

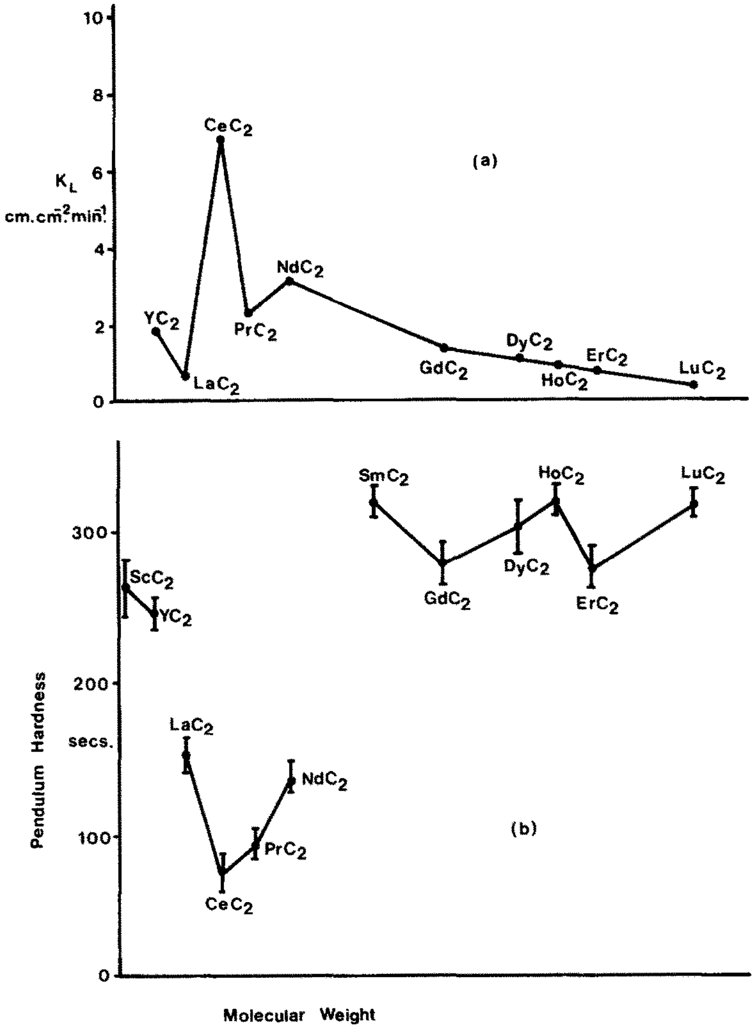

Fig. 1. (a) The variation of linear reaction rate constant, K_L, for the hydrolysis reaction of lanthanide dicarbides compared with (b) the pendulum hardness of polished and protected surfaces of lanthanide dicarbides. The soft and fast reacting low molecular weight dicarbides are clearly indicated.

with the trivalent metals and ions and vary in number from zero for La and Y, to 14 for Lu and they account for normal magnetic susceptibilities. The 4f-band electron arises because the lowest of the empty energy levels, 14 for La and 1 for Tm, lie very close to the Fermi level, and this is partially occupied by conduction electrons. These 4f-band electrons vary from 0.7 e^- for light lanthanides to 0.1 or less for heavy lanthanides; they contribute to the bonding and thus influence the melting points and heats of sublimation. From an analysis of these two physical properties, Gschneidner estimated the fractional 4f-electron concentration in the valence band and their effective contributions. The full 4f-band contribution to the bonding is, however, only realised if there is sufficient overlap between wavefunctions of the neighbouring atoms. Hence because of the rapid radial decrease with increasing atomic number, it is unlikely that the full f contribution will be realised for the heavy lanthanides. On consideration of a function $R_m - R_{4f}$, where R_m is the radius of the metal and R_{4f} is the radius of the 4f orbital, it is suggested that this is a measure of the relative overlap of the 4f wavefunction, the smaller the $R_m - R_{4f}$ value the greater the overlap. The inverse of this function represents the variation of the 4f contribution to bonding for lanthanide metals. In the aligned C_2^{n-} model of Atoji and Medrud [13] it is possible to extend the metal picture to the dicarbides through covalent interactions between the C_2–$2p\pi^*$ antibonding orbitals and the metallic s–p–d–f-band electrons. Physically larger C_2^{n-} species aid this overlap and increase the electron density of 4f-band electrons, especially if the $2p\pi^*$ level has a greater electron density from a higher oxidation number associated with $Ce^{3.6+}$ etc. Increased 4f-band density leads to decreased stability as Gschneidner has shown and so the increased hydrolysis reaction rates for CeC_2, PrC_2, NdC_2 are expected. The vapour phase M–C_2 bond energies given in Table 4 will not reflect the band contribution to bonding which is a function of the solid state.

In conclusion the reaction rate data gathered from this research are further support for the concept of 4f-band electron density and its effect on reactivity. This relationship was not obvious in the previous water vapour studies [1] because the overall reactivity was masked by the retention properties for H_2O molecules on the surface of the solids.

The reactivity of lanthanide solid solutions, particularly those that have cubic structures, will be reported in a further publication in the light of the model so far suggested.

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