Hydrogen-Deuterium Equilibration Reaction Catalysed by Graphite-Potassium Compounds

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Summary The activity pattern of the series of graphite–potassium compounds for the H_2–D_2 equilibration reaction was found to be $C_{24}K > C_{36}K \geqslant C_8K$-hydride $\gg C_8K \sim 0$.

THE H_2-D_2 equilibration reaction catalysed by caesium graphite has been previously studied.[1] We now report the activity pattern of the 1st, 2nd, and 3rd stage potassium–graphite compounds, C_8K, $C_{24}K$, $C_{36}K$ and the hydro-

genated compound of C_8K which has the approximate composition $C_8KH_{2/3}$ (C_8K-hydride).[2]

For all the experiments, 'spectroscopic grade' natural graphite was used. C_8K, $C_{24}K$, and $C_{36}K$ were synthesised by the "dual-furnace" method.[3,4] A neutron diffraction study on C_8K and $C_{24}K$ proved that a single-stage compound could be synthesised by the above method.[5] C_8K-hydride was synthesised from C_8K by direct reaction with H_2 and D_2 at 70—80 °C.

Kinetic measurements were carried out in a standard closed circulating system containing each compound synthesised from 0·3 g of graphite. A 1 : 1 mixture of H_2 and D_2 was introduced into the system (total pressure 6 cm Hg) and the extent of reaction was determined by periodically analysing the HD composition in the gas phase by gas chromatography.

All of the reactions gave straight lines when plotted as simple first-order reactions. In order to estimate the characteristic activity of each compound, the effect of hydrogen chemisorption on the reaction rate was rigorously examined. The first-stage compound, C_8K, was found to be inactive, but with increasing amounts of hydrogenation at 70—80 °C, the activity at 0 °C increased to reach a saturation value equal to that of the C_8K-hydride. The activity of $C_{24}K$ and $C_{36}K$, on the other hand, did not vary with the amount of chemisorption. Values of the first-order rate constant at 0 °C are shown in the Table.

TABLE

First-order rate constant for the H_2–D_2 equilibration reaction over potassium graphites[a]

	k_1 (h^{-1}) at 0°C		
Original graphite	0	$C_{24}K$	1·23 ± 0·05
C_8K	<0·01	$C_{36}K$	0·34 ± 0·01
		C_8K-hydride	0·17 ± 0·01

[a] Catalytic amount: each compound was synthesised from 0·3 g of graphite.

The activation energies of the compounds $C_{24}K$, $C_{36}K$, and C_8K-hydride are 7·5, 6·3, and 6·0 kcal mol^{-1}, respectively.

The first-stage compound, C_8K, does not show catalytic activity, but this cannot be interpreted in terms of either surface area or electronic properties. Below 100K, a marked amount of hydrogen sorption takes place on $C_{24}K$, whereas on C_8K, the amount of sorption is negligible. A correlation of this distinctive low-temperature sorption behaviour with the observed activity pattern is being attempted.

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