high value (about 8·2) given in the literature as an average for the total saliva of sheep[4] the formation of brushite is unexpected. It seems likely that the pH of the saliva from all glands is not identical, but unfortunately the localities of the two samples from the same jaw are unknown.

Whitlockite has not previously been found in animal dental calculus. The principal constituent of dental calculus from the horse is calcite[5,6], while samples from dog, ferret and hamster contain poorly crystalline apatite and sometimes small amounts of calcite[6]. In human dental calculus the formation of whitlockite is related to the presence of magnesium in the precipitating fluid, the magnesian whitlockite showing a characteristic shift of the diffraction lines compared with β-tricalcium phosphate. The diffuseness of the whitlockite lines in the patterns from sheep calculus makes it difficult to discern a similar shift. However, ignition (1,000° C for 1 h) of Scottish samples 2 and 3 gave magnesian whitlockite containing about 10 atomic per cent magnesium, indicating a significant magnesium content of the original material.

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Selective Poisoning of Catalytic Activity

A recent investigation[1] has shown that the exchange reaction between alkylbenzenes and deuterium may provide a useful method of investigating changes in the catalytic activity of evaporated metal films subjected to thermal sintering. One of the most suitable alkylbenzenes for this purpose is p-xylene because it contains only two different kinds of hydrogen atoms—the six in the methyl groups and the four on the benzene ring. Nickel films laid down on a glass substrate at 0° C will catalyse the exchange of the first six hydrogen atoms (reaction I) about five times faster than the exchange of the remaining four (reaction II) at 0° C. Pre-sintering such nickel films for 30 min at 200° C before use reduces their activity for reaction I by a factor of about 600 but has an even more drastic effect of about 10^5 on the rate of reaction II. The earlier work did not establish whether these marked changes of catalytic activity on sintering were due solely to the influence of temperature on the films or whether contamination, and consequent poisoning of the films, had occurred by gas evolved from the reaction vessel. Because of this uncertainty, we have now carried out a series of experiments on the influence of carbon monoxide as a poison for reactions I and II.

Films, prepared as previously described[1], were subjected to the following treatment at 0° C: (1) admission of 10 mm of deuterium for 5 min; (2) evacuation for 40 sec; (3) admission of a known pressure of carbon monoxide with a 10-fold excess of deuterium for 15 min; (4) evacuation for 40 sec and then used as catalysts for the exchange of 1 mm of p-xylene and about 23 mm of deuterium. This complicated procedure was designed to ensure that the small quantities of carbon monoxide admitted would be adsorbed by displacement of deuterium only on the sites giving the greatest heat of adsorption and not merely randomly on the surface. The main features of the results for the rates of exchange at 0° C are summarized in

Table 1. The figures in the fourth column were obtained from surface area data for similarly prepared nickel films[2] and an assumption of 7 $Å^2$ for the mean area of each nickel atom; they represent the maximum coverage of the surface if all carbon monoxide admitted was adsorbed and retained. The rate k_0 is the initial rate of disappearance of p-xylene-d_0 and corresponds to reaction I; k_6, the initial percentage rate of conversion of p-xylene-d_6 to products with more deuterium atoms, is a measure of the rate of reaction II. The rates quoted for experiments G, H and J were obtained by extrapolation of Arrhenius plots for rates at higher temperatures and each plot yielded an activation energy of about 20 kcal/mole for reaction I.

Table 1

Exp.	Weight of film (mg)	Molecules CO admitted ($\times 10^{17}$)	Approximate ratio of molecules of CO admitted to surface Ni atoms	k_0 (%/min)	k_6 (%/min)
A	10·5	0	0	50	8
B	12·3	1·2	0·04	60	13
C	16·7	1·6	0·04	45	3
D	10·8	2·0	0·07	18	0·05
E	10·9	2·8	0·10	21	0·02
F	11·1	5·1	0·18	1·8	$< 2 \times 10^{-3}$
G	11·8	8·1	0·27	0·03	$< 3 \times 10^{-5}$
H	8·8	16	0·65	0·02	$< 2 \times 10^{-6}$
J	8·5	160	7	$\sim 3 \times 10^{-4}$	—

Two runs were carried out on films laid down with the glass walls of the reaction vessel maintained at 200° C (after baking at 450° C) and the results were identical with those obtained previously[1] for films laid down at 0° C and presintered for 30 min at 200° C. Detailed rates for these experiments are not reported but were similar (about twice as fast) to those for experiment G.

It is convenient to discuss the results on the assumption that all carbon monoxide admitted in experiments B–H is adsorbed. A comparison of B and C with A suggests that the sites first covered by carbon monoxide are not important for the catalysis of either reaction. Presumably, the heat of adsorption of the hydrocarbon is too large on these sites, amounting to some 4 per cent of the surface, to permit easily reversible adsorption to occur. Experiments C and D show that adsorption of carbon monoxide on the next 3–6 per cent of the surface cuts down the rate of reaction II by more than a factor of 100 but only reduces the rate of reaction I by a factor of three. This is clear evidence that certain active centres on the nickel films are required to catalyse the exchange of the hydrogen atoms on the benzene ring of p-xylene and that these centres are selectively poisoned by carbon monoxide. A drastic reduction in the rate of reaction I is only obtained when more than 25 per cent of the surface is covered, indicating that some 20 per cent of the sites on the surface are efficient centres for this reaction.

We believe that the nickel films laid down with the glass maintained at 200° C will be substantially free of contamination. Such films, or films pre-sintered for 30 min at 200° C, contain practically no active centres for reaction II and very few for reaction I. It seems evident that thermal treatment, like poisoning by carbon monoxide, completely eliminates the centres for reaction II and also destroys most of the sites on which reaction I occurs as well. A possible explanation is that metastable metal atoms on the films are necessary to form the π-bonded adsorbed hydrocarbon intermediates[1,3] which are believed to be involved in the mechanism of the exchange reactions of the alkylbenzenes.

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