

of the dimerization of *I*, appreciable in protic media, is negligibly small. The dimerization of *II* can also be neglected. The initial product of the combination of *I* and *II*, itself an alkoxy anion *III*, would normally acquire a second proton either from its surrounding media or on subsequent workup; instead, in the aprotic media, it releases its remaining proton for reuse and eventually acquires both missing protons on subsequent workup. Accordingly, a minimal supply of protons may service a very large number of anion radicals.

In support of the above, it will be noted in Table I that the formal addition of a source of protons (5% H<sub>2</sub>O) appreciably lowered (to about 5) the *rac* preference. This figure is still very considerably greater than the "neutral" media value of 1.2 in the earlier protic media studies.

To insure the results did not reflect an equilibrium situation, *i.e.* that step *a*) was truly irreversible, the reaction was carried out in the presence of preformed *meso*-pinacol (Entry 10, Table I). The preformed pinacol would be expected to yield either or both the anion *III* and dianion *IV*; if either of these collapsed to its components *I* and/or *II*, the final *rac/meso* ratio would be expected to be previously observed value of greater than 7. If it did not so collapse, the ketone present should itself go in essentially quantitative yield to pinacol in this 7 : 1 *rac/meso* ratio, which, allowing for the unchanged *meso*-pinacol, would lead to a calculated *rac/meso* value of 1.27. This figure is in excellent agreement with the observed value of 1.25.

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#### INFLUENCE OF COMPETITIVE ADSORPTION OF WATER AND FUEL ON THE ACTIVITY OF ANODES IN FUEL CELLS

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Tungsten carbide has proved to be an acid-insoluble relatively inexpensive solid material with high activity for the anodic oxidation of hydrogen and formaldehyde in acid fuel cells<sup>1,2</sup>. On the other hand the activity for the conversion of carbon monoxide and methanol is very low<sup>2</sup>. Adsorption properties might be a reason for this different behavior. This assumption is tested by comparing the activities of tungsten carbide and Raney platinum and by investigating the adsorption of water and several simple fuels at these catalysts.

## EXPERIMENTAL

## Activity Measurements

The catalytic activities of tungsten carbide and Raney platinum were obtained by potentiostatic measurement of current densities at 350 mV and 70°C in a half-cell arrangement. Test electrode, counter electrode (carbon) and reference electrode (autogenous hydrogen electrode<sup>3</sup>) were deposited in a vessel with a 6 molar solution of the fuel in 3N-H<sub>2</sub>SO<sub>4</sub>.

The platinum electrode was prepared in the form of a porous disk of 1.3 cm<sup>2</sup> by compacting a mixture of gold powder, forming the electrode skeleton, and powdered Raney platinum-aluminium alloy. Subsequently, the aluminium was dissolved by treating the disk with KOH solution.

The tungsten carbide electrode was prepared from powders. The macroporosity was achieved by adding substances that could be removed after pressing the mixture to disks of 1.8 cm<sup>2</sup>. The microporosity was given by the method of preparation which determined the size of the crystallites as could be ascertained by X-ray analysis. The conversion of gaseous fuels was tested with a bubble electrode, where graphite felt was used as a support for the finely dispersed catalyst.

The surface of the tungsten carbide was measured by a dynamic BET-method<sup>4,5</sup>. The surface of the platinum was determined from hydrogen charging curves obtained by a potentiodynamic method<sup>6</sup>. The given current densities refer to the surfaces evaluated in this manner.

## Adsorption Measurements

Adsorption isotherms at room temperature and 70°C respectively were obtained at powders of tungsten carbide and Raney platinum by volumetric adsorption from the gas phase in a conventional high vacuum and gas handling system. Isothermic heats of adsorption were evaluated from the isotherms. The heat of adsorption of formaldehyde at tungsten carbide was determined by gas chromatography. Depolymerised polyoxymethylene was dosed in a helium carrier stream and conducted over a column of granulated tungsten carbide, held at temperatures between 80 and 120°C.

## RESULTS

Table I shows that tungsten carbide is as active for the conversion of formaldehyde as Raney platinum. But it has a markedly lower activity for the oxidation of formic acid and methanol. These results were reproduced with several different electrodes. Comparisons of the hydrogen

TABLE I

Current Densities (mA m<sup>-2</sup>) for the Anodic Oxidation at 70°C and a Potential of 350 mV in 3N-H<sub>2</sub>SO<sub>4</sub>

Fuel	Tungsten carbide	Raney platinum
6M-CH <sub>3</sub> OH	4.9 · 10 <sup>-2</sup>	5.1
6M-HCOOH	2.1	33.2
6M-CH <sub>2</sub> O	6.8	7.8
H <sub>2</sub> (1 at)	23.0	7.4

conversion are rather arbitrary because the current densities at gas electrodes of the type used here presumably depend on transport processes.

The values given in Table II refer to a relatively high coverage which is close to the actual conditions at working electrocatalysts. Heats of adsorption for hydrogen at tungsten carbide and platinum and for carbon monoxide at platinum were not evaluated from the isotherms because in the selected temperature region the measurements have proved to be performed at the ascending part of the isobar. This indicates an activated adsorption, which is however often found to be not reversible in this case.

The heats of adsorption for water and formic acid are lower at platinum than at tungsten carbide. This result could be expected from rules which correlate the heats of adsorption to the heats of oxide formation<sup>7</sup>. Unexpected is the relatively high value for methanol at platinum which however agree rather well with results found by adsorption from sulfuric acid solution by Bagot-skii and coworkers<sup>8</sup>.

### DISCUSSION

Observations indicate that electrocatalytic oxidations of several simple organic molecules occur with a similar mechanism<sup>9,10</sup>. The catalytic surface reaction demands the simultaneous chemisorption of carbonaceous and oxygen species. The active oxygen species will probably be formed from chemisorbed water. Assuming that the adsorptivity of  $\text{SO}_4^{2-}$  ions is rather low<sup>8</sup> the concentration of the surface species will be conditioned by competitive adsorption of water and fuel. As the measured isotherms indicate to follow a Langmuir mechanism, relative coverages at constant bulk concentrations may be described by the Langmuir-Hinshelwood displacement isotherm in the simplified form:

$$C_{\text{ads,f}}/C_{\text{ads,w}} = k_1 \cdot \exp [-(\Delta H_{\text{ads,f}} - \Delta H_{\text{ads,w}})/RT]. \quad (1)$$

The equation relates differences of the relative concentrations at the surface to differences of the heats of adsorption, if solutions of different fuels with equal bulk concentrations are compared and differences of the frequency factors are neglected. The influence of the surface concentrations of the reacting molecules on the current density may be described by a simple kinetic equation:

TABLE II  
Heats of Adsorption ( $\text{kcal mol}^{-1}$ )

Adsorbate	Tungsten carbide	Raney platinum
$\text{H}_2\text{O}$	-15	-4
CO	-4	<sup>a</sup>
$\text{H}_2$	<sup>a</sup>	<sup>a</sup>
HCOOH	-9	-4
$\text{CH}_3\text{OH}$	-2	-12
$\text{CH}_2\text{O}$	-10	-

<sup>a</sup> Activated adsorption.

$$i = k_{11} C_{\text{ads},r}^{\alpha} C_{\text{ads},w}^{\beta} \exp(\gamma F\phi/RT). \quad (2)$$

The factors  $\alpha$  and  $\beta$  account for the reaction orders,  $\gamma$  is an empiric factor<sup>8</sup>. At constant overpotential and temperature the activity is influenced mainly by the concentration of the reactants at the surface, if the same rate determining step holds for the oxidation of the three derivatives of methane at the same catalyst.

From Table II the conclusion can be drawn that in a fuel cell the surface of tungsten carbide is strongly covered with water because of its relatively high heat of adsorption. With the values of Table II and the above equations the prediction can be made that the oxidation rate should depend on the ability of the fuel to displace water and to cover an adequate part of the catalyst surface.

At Raney platinum we have the inverse situation. Because of the low heat of adsorption for water the surface is strongly covered with the fuel. Here the activity should be higher for a less strongly adsorbed fuel which allows an adequate coverage with water. The results in Table I agree with these predictions.

Besides the energetics of adsorption the type of adsorption may be important in the formation of active oxidable surface species. The relatively high heat of adsorption for methanol at platinum may be explained by the formation of a surface complex bound at two points (*via* C and O). Such a structure was proposed by Kubelková, Schürer and Jirů for methanol at silver from infrared spectroscopic investigations<sup>11</sup>.

#### CONCLUSION

Tungsten carbide and Raney platinum show accordances as well as deviations in their activities for the conversion of simple fuels. Such a behaviour may be easily understood if an important role of adsorbed states in electrocatalytic processes is assumed. Adsorption complexes at electrocatalysts may be often studied successfully with methods which are usual in catalytic research. Although these informations are achieved at simplified conditions of gas phase adsorption, where the complications of electrocatalysis brought about by electrolyte and potential are avoided, they should nevertheless be valuable for a deeper understanding of surface reactions in electrocatalysis, *e.g.* in fuel cells.

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