

**Figure 4.** Schematic description of the hydrophobic hydration in the alkaline hydrolyses of neutral esters (A) and cationic esters (B).  $\angle$  indicates water molecules and their ordered arrangement reflects the iceberg structure. The region covered by  $\angle$  indicates the iceberg structure of water.

of the interionic reactions between oppositely charged species. Thus, the anionic macroions would increase  $\Delta V_h^*$  in this case, as was found earlier.<sup>3</sup>

Now, we discuss the  $\Delta V_h^*$  and  $\Delta S_h^*$  terms. As is shown schematically in Figure 4, the term  $\Delta V_h^*$  with PMVA would be negative, because the cationic macroions and the negatively charged (for eq 1) or neutral (eq 2) activated complex stabilize the large iceberg structure more than the reactant esters. For example, for the hydrolyses of neutral esters, an attraction between a hydrophobic anionic activated complex and a hydrophobic cationic macroion would be stronger than that between a neutral ester and a cationic macroion in the reactant state. This is because there exist both electrostatic and hydrophobic interactions for the former combination, whereas there are only hydrophobic forces for the latter. The underlying ideas are that (1) the stronger the hydrophobicities of reactants and macroions, the larger the iceberg structure, and (2) the stabilization of the iceberg structure contributes toward a decrease in the partial molar volume and the entropy.<sup>10</sup> In the presence of NaPSS, the attraction of the anionic macroions toward neutral or cationic ester is much stronger than that toward the activated ester, because the neutral esters in reaction 1 are more strongly attracted by

the anionic macroions than the anionic activated complexes and because the cationic esters of reaction 2 are also more strongly attracted by the anionic macroions than the neutral activated complex through the intermediary of electrostatic and hydrophobic interactions (see Table I and Figure 4). We should note here that the explanations stated above are completely consistent with those on the alkaline fading reactions of dyes with macroions.<sup>10</sup>

The changes in the  $\Delta H^*$  term on addition of the macroions seem to demonstrate also the important role of the hydrophobic hydration. Tables II and III show that the polyelectrolyte influence is enthalpy controlled; namely, the rate acceleration or deceleration with macroions is caused by the decrease or increase in the enthalpy of activation. These observations are the same as those reported previously for the alkaline hydrolyses of hydrophobic triphenylmethane dyes,<sup>10</sup> but are in contrast to the entropy-controlled reaction systems, for which only electrostatic interactions are important.<sup>7,8</sup> These dependences of  $\Delta H^*$  are believed to be accounted for as follows with the assumption that  $\Delta H^* = \Delta H_{int}^* + \Delta H_e^* + \Delta H_h^*$ . In the presence of PMVA, the iceberg formation is enhanced in the course of activation as is seen in Figure 4, and the enthalpy level of the activated complex is lower than that of the reactant. Thus, the  $\Delta H^*$  would be smaller than that in the absence of polymer. On the contrary, the addition of NaPSS stabilizes the iceberg structure more strongly for the reactant than the activated complex. Thus, the  $\Delta H_h^*$  would increase. The intrinsic quantity  $\Delta H_{int}^*$  is indifferent to the polymer addition. Furthermore, the  $\Delta H_e^*$  term is assumed to be unimportant for the reactions under consideration. The  $\Delta H^*$  should therefore decrease or increase with PMVA or NaPSS addition.

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## Chemisorption of Cyclohexene on Nickel. A Volumetric and Neutron Inelastic Spectroscopy Study

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Absorption of cyclohexene on Raney nickel was studied at different surface coverages by using neutron inelastic spectroscopy and volumetric methods. At high coverage, hydrogen, benzene, and cyclohexane are detected on the surface. At low coverage, only hydrogen and benzene are present on the nickel.

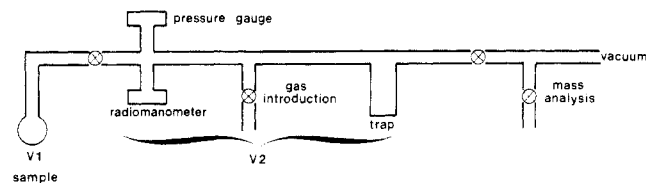
Hydrogenation of aromatic molecules on transition metals is a well-studied reaction. The detailed mechanism and the limiting steps are now rather clear<sup>1</sup> and the spectroscopic studies concerning the structure of adsorbed

benzene<sup>2,3</sup> have explained why the reaction rate is comparatively low.

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- (2) H. Jobic and A. Renouprez, *Surf. Sci.*, **111**, 53 (1981).
- (3) A. Renouprez, G. Clugnet, and H. Jobic, *J. Catal.*, **74**, 296 (1982).

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**Figure 1.** Principle of the equipment used for volumetry, analysis of labeled molecules, and mass spectroscopy measurements.

Now, if one considers cyclohexene hydrogenation, it is known that its rate is increased by 3 orders of magnitude<sup>4</sup> compared to benzene hydrogenation. It was thus tempting to investigate in detail the chemisorption of cyclohexene on nickel.

The stoichiometry of adsorption is followed by using volumetry. The gas-phase analysis is performed by mass spectroscopy. Exchange experiments between the gas and surface complex are performed with <sup>14</sup>C-labeled hydrocarbons.

Finally, the adsorbed species are studied with neutron inelastic spectroscopy. We have shown that this method can be a very helpful tool to identify a given molecule.<sup>2</sup> Its limitations are known: relatively poor resolution and consequently difficulty for identifying weak vibrations. Moreover, as all vibrational modes are active, when several species contribute to the spectrum, the peak assignment may be very difficult, without complementary information. In the present case, valuable information was derived from the three techniques mentioned above and helped in the identification of the surface complex.

### Experimental Section

**Samples.** Raney nickel is prepared from Ni–Al alloy following a procedure already described.<sup>5</sup> One obtains a porous material containing less than 2% unattached Al. Outgassing 40 g of nickel for neutron experiments is performed in a special quartz reactor<sup>6</sup> where the catalyst is disposed on 15 platelets. The temperature is kept at 200 °C for 24 h and, finally, the temperature is raised to 320 °C for 1 h. At the end of the treatment the vacuum produced by cryopumping is better than 10<sup>-6</sup> torr and the area of the material has decreased to 15 m<sup>2</sup> g<sup>-1</sup>. The flat background measured on the bare metal with neutron spectroscopy shows that the coverage with residual hydrogen or water is negligible.

**Volumetry and Radio Tracer Experiments.** Figure 1 shows the equipment used for volumetry, mass analysis, and radiotracer studies. The sample is contained in the cell V<sub>1</sub> connected by a valve to the measuring section of volume V<sub>2</sub>. The total pressure in V<sub>2</sub> is measured by a Texas gauge. The pressure of labeled molecules is determined by the radiomanometer composed of a scintillator and a photomultiplier.

Hydrocarbons are first introduced into V<sub>2</sub>, where their volume is measured, allowed to expand into V<sub>1</sub>, and equilibrated with the sample. One can further condense the gas phase contained in V<sub>1</sub> + V<sub>2</sub> and measure its amount and composition in V<sub>2</sub> after closing the valve connecting V<sub>1</sub> and V<sub>2</sub>.

**Neutron Inelastic Spectroscopy Experiments.** All neutron experiments were performed at the high-flux reactor at the ILL. We have already described in previous publications<sup>2,3</sup> the application of this spectroscopy to the

**TABLE I**

	1	2	3
adsorbed vol of C <sub>6</sub> H <sub>10</sub> , mmol g <sup>-1</sup>	0.12, 0.053 <sup>a</sup>	0.077	0.043
vol of <sup>14</sup> C molecules introduced, mmol g <sup>-1</sup>	0.095	0.077	0.200
ratio between labeled and total introduced molecules	0.64	0.5	0.82
ratio between the partial pressure of C <sup>14</sup> molecules and total pressure, after exchange	0.66	0.49	0.80
α <sup>b</sup>			
β <sup>c</sup>			

<sup>a</sup> After condensation in V<sub>2</sub> of 0.067 mmol g<sup>-1</sup>. <sup>b</sup> α is measured in the gas phase in V<sub>1</sub> + V<sub>2</sub>. <sup>c</sup> β is measured after condensation of gas phase in V<sub>2</sub>.

structure determination of adsorbed molecules. The instrument IN1 is installed on the hot source of the reactor which delivers fast neutrons.

It allows the determination of vibrational modes between 300 and 3000 cm<sup>-1</sup> with an energy resolution of ca. 5%.

The bare material is placed in an aluminum container cooled to 77 K and a first spectrum is recorded step by step by rotating the monochromator. The sample is warmed at 300 K, cyclohexene is introduced, and after equilibrium, the sample is cooled down. A second spectrum is measured. The corrected spectrum corresponding to the adsorbed phase is obtained by subtracting the two spectra.

### Results

**Volumetry, Mass Spectroscopy, and Exchange Experiments.** Preliminary volumetric experiments have allowed the determinations of the pressure range corresponding to different surface coverages. Following the procedure described in the Experimental Section, we were able to determine the composition of the gas phase with mass spectroscopy and to obtain information on the chemisorbed species with exchange experiments. Three different equilibrium pressures were selected.

**High Surface Coverage.** Cyclohexene is adsorbed at 300 K; the equilibrium pressure measured in V<sub>1</sub> + V<sub>2</sub> is 0.6 torr. Upon evacuation and condensation of the gas phase in V<sub>2</sub>, 60% of the adsorbed amount is eliminated. The composition of this phase measured with the mass spectrometer is 1 C<sub>6</sub>H<sub>6</sub>, 3 C<sub>6</sub>H<sub>10</sub>, 4 C<sub>6</sub>H<sub>12</sub>; no hydrogen is detected.

The 40% molecules remaining on the nickel are then exchanged with a known excess of <sup>14</sup>C-labeled benzene. The mass analysis shows that only benzene is present in the gas phase, at the end of the reaction. Its radioactivity corresponds exactly to the ratio between labeled and total benzene in the system. The exchange is therefore complete and all the molecules of the surface are in the form of benzene. Table I reports the figures corresponding to this experiment.

**Medium Surface Coverage.** The second set of measurements is performed at lower coverage. The equilibrium pressure at 300 K is only 0.2 torr. Only 75% of the previous amount is fixed by the nickel. Upon the introduction of a quantity of labeled C<sub>6</sub>H<sub>6</sub> equal to that already fixed by the metal, one only detects benzene in the gas phase and this time again the decrease of activity shows that all the surface molecules can be exchanged.

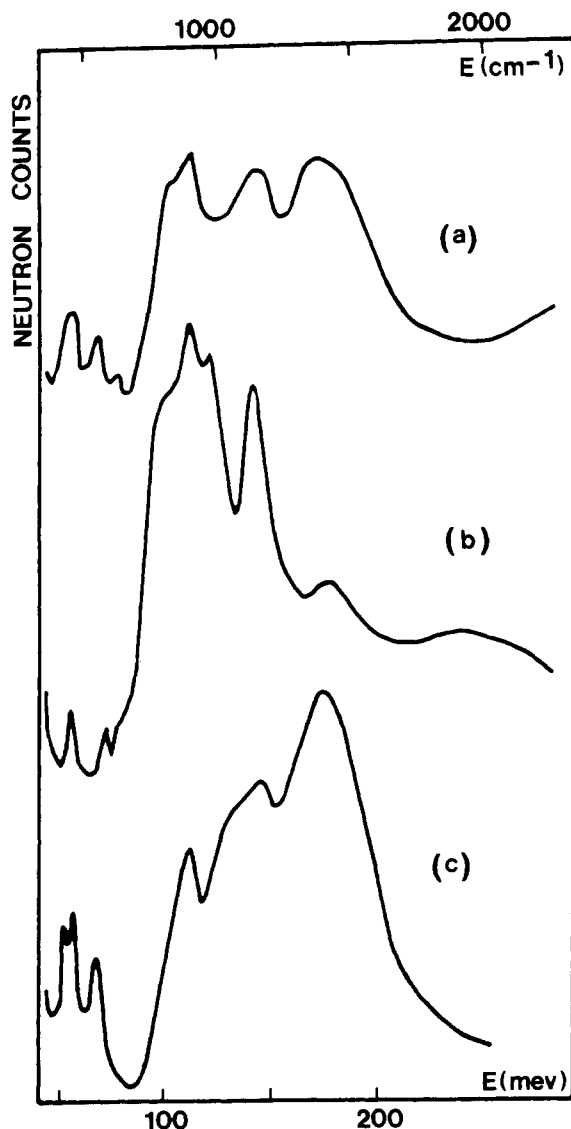
Finally, at very low coverage (30% of the former value) for an equilibrium pressure of 10<sup>-6</sup> torr, the exchange with labeled benzene leads to the same conclusions as in case 2.

**Neutron Experiments.** The neutron spectrum corresponding to a high surface coverage is shown in Figure 2a.

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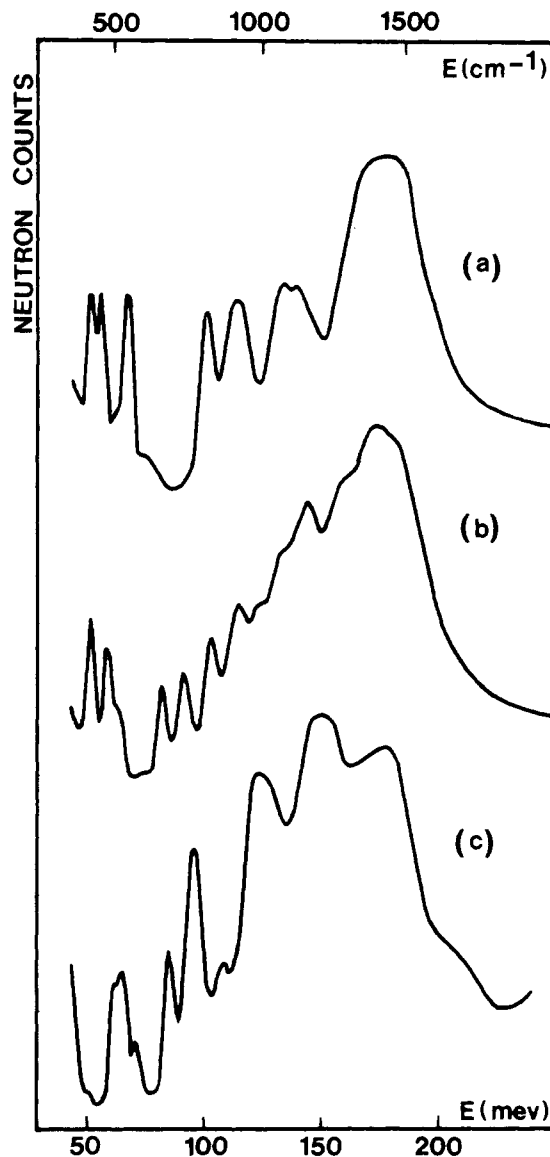
**Figure 2.** (a) Neutron spectrum after adsorption of cyclohexene on nickel at 1 torr, 300 K, and cooling to 77 K. (b) Neutron spectrum of cyclohexene adsorbed at pressure lower than  $10^{-5}$  torr. (c) Neutron spectrum of cyclohexene adsorbed on a nickel surface precovered with hydrogen.

The comparison with the spectrum of free cyclohexene shown in Figure 3b indicates that deep modifications have occurred on the surface.

Benzene is identified by the peak at 112 meV with a shoulder at 102 meV;<sup>2</sup> the band at 140–145 meV is also assigned to this molecule with a contribution of atomic hydrogen; hydrogen also scatters at 120 meV.<sup>5</sup>

The presence of cyclohexane is evidenced by the peak at 68 meV due to C–C–C and C–C–H angle deformation which is at the same frequency as for the free molecule (Figure 3a); the intense peak at 157 meV is also assigned to the CH<sub>2</sub> deformation and wagging of cyclohexane. The proportion of cyclohexane on the surface as can be judged from its characteristic frequencies (for example, the mode at 78 meV) is on the order of 30%.

When the pressure is lowered to  $10^{-6}$  torr (as in the second step of the first volumetric experiment), the situation is clarified; the corresponding spectrum is shown Figure 2b. All the cyclohexane molecules are evacuated from the surface. The peak at 68 meV has disappeared and the intensity around 170–175 meV (due to CH<sub>2</sub> groups) has strongly decreased. The situation appears to be intermediate between the case of benzene adsorbed on the



**Figure 3.** (a) Neutron inelastic spectrum of solid cyclohexane at 77 K. (b) Neutron inelastic spectrum of solid cyclohexane at 77 K. (c) Neutron spectrum of solid cyclohexadiene.

bare surface and benzene adsorbed on a hydrogen-precovered nickel where  $\theta_H \sim 0.5$ .<sup>3</sup>

We have shown that, on bare nickel, some hydrogen (contributing 15% of the total intensity around 120 meV) was found on the surface upon benzene chemisorption. In the present case the intensity at 120 and 140 meV corresponding to adsorbed hydrogen is appreciably higher.

Furthermore, the frequencies of the CH bending modes are slightly shifted to higher frequencies but less than in the case of the hydrogen-precovered nickel where  $\theta_H \sim 0.5$ .

The NIS spectrum obtained with cyclohexene adsorbed on a hydrogen-precovered nickel is shown in Figure 2c. The similarity with the spectrum of Figure 3a proves that all the molecules have been converted to cyclohexane.

#### Discussion and Conclusion

At low adsorption pressure or if the weakly adsorbed molecules are evacuated at 300 K, only benzene and hydrogen are detected on the surface; as shown by neutron spectroscopy, the perturbation of the ring is intermediate between that obtained upon benzene adsorption on a bare surface and on a surface covered with H<sub>2</sub> for  $\theta_H \sim 0.5$ .

Similar indications were derived from magnetic measurements elsewhere;<sup>7,8</sup> the decrease of saturation

magnetization upon the adsorption of one benzene molecule  $\mu_B$  on the bare surface,  $2 \mu_B$  on the surface covered with hydrogen, and  $2.7 \mu_B$  in the case of cyclohexene.

Finally, the exchange experiments corroborate these findings: in the present case all the molecules present on the nickel surface can be exchanged for  $^{14}\text{C}$ -labeled benzene while, if benzene is directly chemisorbed on bare nickel, only 80–90% of the benzene can be exchanged.<sup>9</sup>

At higher cyclohexene pressure, neutron measurements show that cyclohexene is present in the adsorbed phase with benzene and hydrogen. However, cyclohexene is only slightly perturbed: the characteristic frequencies are very close to their values in the solid state; cyclohexene is thus probably physisorbed at the surface; therefore, it is not surprising that pumping off at 300 K leads to a condensed phase containing cyclohexene, benzene, and cyclohexene.

These results on polycrystalline samples can be interestingly compared with those reported by Tsai, Friend, and Muettterties,<sup>10</sup> on Ni flat or stepped single crystal faces.

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(9) J. P. Candy and P. Fouilloux, *J. Catal.*, **38**, 110 (1975).

(10) M. C. Tsai, C. M. Friend, and E. L. Muettterties, *J. Am. Chem. Soc.*, **104**, 2539 (1982).

Operating under ultrahigh-vacuum conditions, i.e., equilibrium pressures not greater than  $10^{-9}$  torr, they have found that, for temperatures of 300–400 K, cyclohexene is converted to benzene and hydrogen and they did not detect any cyclohexene. This is quite similar to what we have observed in the second and third parts of our experiment. Indeed, when cyclohexene is formed, its sticking coefficient on an already covered surface is so low that one should increase the pressure to 1 torr to observe a physisorbed layer containing this molecule.

Now the question remains of the existence of cyclohexadiene as an intermediate in the formation of benzene from cyclohexene. No direct proof of the existence of this molecule has been afforded by the above authors. A separate neutron measurement on Raney nickel where cyclohexadiene was directly adsorbed on the bare surface gave a spectrum very similar to that observed upon adsorption of cyclohexene at low pressure. It is thus not conclusive, insofar as cyclohexadiene might be a transient state but with a very short lifetime.

Finally, at low pressure, cyclohexene (or cyclohexadiene) forms directly chemisorbed benzene and hydrogen. If now the cyclohexene pressure is augmented, this molecule reacts with adsorbed hydrogen in a bimolecular process which is probably rate limiting.

Registry No. Nickel, 7440-02-0; cyclohexene, 110-83-8.

## Hydroxide Complex of the Magnesium Octaethylporphyrin Cation: Spectrum and Formation Constant in Alcohol–Water Solvents

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The formation of the complex between photogenerated magnesium octaethylporphyrin cation and hydroxide has been studied in mixed alcohol/water solvents. This complex has been postulated as a participant in the transport of hydroxide and/or hydrogen ion across bilayer lipid membranes. The absorption spectrum of the complex ( $\lambda_{\text{max}} = 665 \text{ nm}$ ) is red shifted from that of the cation ( $\lambda_{\text{max}} = 680 \text{ nm}$ ) in both methanol/water (M/W) and ethanol/water (E/W) solvents. The formation constants for the complex in the two solvent systems are 16 (in M/W) and  $190 \text{ M}^{-1}$  (in E/W). The difference in the two constants is too great to be explained entirely by the Born equation (with correction for ion screening) in which the dielectric constant of the solvent system is the pertinent variable. Differential solvation effects appear to be involved. The rate constants,  $k_2$ , for the reaction of the cation with the *p*-dinitrobenzene anion, *p*-DNB<sup>-</sup> (*p*-DNB is the electron acceptor for the photogeneration of the magnesium octaethylporphyrin cation), and  $k_4$ , for the reaction of the complex with *p*-DNB<sup>-</sup>, are  $1.1 \times 10^9$  and  $2.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  in M/W and  $1.3 \times 10^9$  and  $1.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  in E/W. Although the rate constants are within an order of magnitude of being diffusion controlled, the fact that  $k_4 \geq k_2$  is indicative of some degree of activation control.

### Introduction

Recent work<sup>1</sup> has suggested that the photogenerated cation of magnesium octaethylporphyrin in a lipid bilayer membrane can mediate the transport of OH<sup>-</sup> and/or H<sup>+</sup> across the membrane. There is much evidence to support the contention<sup>1</sup> that under these conditions a water molecule is probably tightly bound to the Mg in both the oxidized (cationic) and unoxidized (neutral) magnesium octaethylporphyrin (e.g., electrochemical evidence for an-

ionic complexation of cations of magnesium porphyrins,<sup>2</sup> of magnesium chlorin,<sup>3</sup> and of chlorophyll *a*,<sup>3</sup> X-ray crystallographic data for  $\text{MgTPP}^+\text{ClO}_4^-$  (TPP = tetraphenylporphyrin) indicating that the Mg is penta-coordinate ligating  $\text{ClO}_4^-$  through the oxygen,<sup>4</sup> and X-ray

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