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Competitive Hydrogenation of Benzene and Toluene: Theoretical Study of Their Adsorption on Ruthenium, Rhodium, and Palladium

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Benzene and toluene adsorption on hexagonally close packed Pd, Rh, and Ru surfaces has been studied by semiempirical method. Simple MO arguments, supported by extended Hückel calculations, are used to show that toluene is more strongly adsorbed than benzene (the energy gap between the frontier orbitals is smaller and the bending of the methyl group removes the steric repulsion). The differences in the ease of adsorption on the different metals induce differences in the competitive hydrogenation reactions. These differences are increased by the presence of acceptor coadsorbates which induce a shift of the surface work function to large values. © 1990 Academic Press, Inc.

INTRODUCTION

Physical techniques such as XPS or X-ray absorption spectroscopy are often not sensitive enough to probe unambiguously the subtle changes in the electronic structure of noble metals induced by environment effects (support, additives, adsorbates). In contrast, chemical probes can be sensitive tools to monitor these effects. Thus, the ratio $K_{T/B}$ of the adsorption coefficients of toluene and benzene, determined from a kinetic analysis of the competitive hydrogenation of these hydrocarbons (*1*, *2*), was used to follow the changes in the electronic structure of platinum clusters supported in Y zeolite. Toluene is found to be more strongly adsorbed on the metallic surfaces than benzene. $K_{T/B}$ is very large on ruthenium, about 9–10 on rhodium, and about 1 for palladium. A large decrease in the work function, $\Delta\Phi$, follows the adsorption of toluene (*3*). This is interpreted as a large electron transfer from the toluene molecule to the metal. Large $K_{T/B}$ ratios have been associated with electron-deficient character of the metal (*1*). Depending upon the acidity of the support or upon the presence of electron acceptor adsorbates, $K_{T/B}$ increases, whereas it decreases in the presence of electron donor adsorbates (*1*) or supports (*4*). This was attributed to the substituent effect of the methyl group which makes toluene more an electron donor than benzene. The $K_{T/B}$ probe was also used to monitor the effect of alloying platinum with molybdenum (*5*), zirconium (*2*), and iron (*4*). More recently (*6*) competitive hydrogenation experiments carried out on different Group VIII metals have shown that $K_{T/B}$ increases in the series Pd < Pt < Rh < Ir $\ll$ Os(Ru). This order was correlated with the inverse of the electronic heat capacity of these metals.

In view of the potential usefulness of this technique to probe the electronic structure of metals, especially the modifications due to environment effects, we thought that these results should be rationalized on more reliable theoretical bases. Since $K_{T/B}$ measures the relative probability for toluene and benzene to be adsorbed on a metal surface, its value should depend both on the energy barrier that these hydrocarbons have to overcome before being associatively bonded to the surface and on how

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strongly they are bonded. Indeed, since the two hydrocarbons are in competition for the same sites, the relative probability of being hydrogenated depends upon how easily they are adsorbed and the difficulty with which they desorb before reaction with adsorbed hydrogen. Therefore a theoretical investigation has been undertaken in the present paper to compare the height of the adsorption energy barrier and the depth of the potential energy well for benzene and toluene on ruthenium, rhodium, and palladium.

Recently (*7*), the chemisorption of benzene on hexagonally close packed surfaces was studied within the framework of extended Hückel theory (EHT). The stable configuration for adsorbed benzene was determined and compared with experimental findings (*8*) based on HREELS and LEED analyses. Benzene adsorbs oriented parallel to the surface, over a threefold hollow site. When the adsorbate is strongly adsorbed on the surface, it is very distorted and undergoes a Kekulé distortion. The C–H bonds bend away from the surface. Distortions and binding energies depend on the back donation to the adsorbate and increase with the metal electropositivity (ruthenium vs palladium). The adsorption process must overcome a barrier which also depends on the metal electropositivity through the height of the Fermi level. Indeed, the transition state is associated with an electron transfer from a metal–adsorbate antibonding orbital to the Fermi level. Small barriers correspond to poorly electropositive metals (palladium vs ruthenium). In this paper, we extend these previous investigations by varying the adsorbate since toluene adsorption is compared to that of benzene.

METHOD

Calculation Method

We present here results of EHT calculations on arene–M_6 clusters. In a previous study (*7*), it has been shown that tight binding calculations on infinite slabs agree with the cluster results with no major correction for $n = 6$ or over. Despite the limitation of the method, these calculations are sensitive to a change in electronegativity of the metal. Ruthenium, rhodium, and palladium have been chosen to study the displacement along a row of the Periodic Table. Their parameters are listed in Table 1. They have been optimized for bulk band structure and for coordination chemistry. The H_{ii} integrals have been shifted to prevent excessive charge transfer from the adsorbate to the metal. They reproduce the change in electronegativity of the metal. H_{ij} off-diagonal terms are derived from the diagonal terms by the use of the weighted H_{ij} formula (*9*). No repulsive potential had been added to the calculations.

TABLE 1

Extended Hückel Parameters Used in Calculations

Orbital		H_{ii}(eV)	ξ_1	ξ_2	c_1	c_2
Pd	5*s*	−11.3	2.09			
	5*p*	−6.25	2.09			
	4*d*	−13.3	5.80	2.185	0.6072	0.6072
Rh	5*s*	−0.7	2.07			
	5*p*	−6.00	2.07			
	4*d*	−12.30	5.59	2.06	0.6107	0.6107
Ru	5*s*	−9.85	2.03			
	5*p*	−5.75	2.03			
	4*d*	−10.30	5.38	2.01	0.6085	0.6085
C	2*s*	−21.4	1.625			
	2*p*	−11.4	1.625			
H	1*s*	−13.6	1.3			

Metal–metal bond lengths of the clusters have been kept fixed all along the study at their bulk values (2.65 Å for ruthenium, 2.69 Å for rhodium, and 2.75 Å for palladium). For benzene and toluene, the reference energies (with no interaction with the surface) are computed at 1.46 and 1.08 Å for the C–C and C–H distances, respectively, and with 1.54 and 1.09 Å for the methyl group of toluene.

RESULTS AND DISCUSSION

Comparison between Toluene and Benzene Adsorption

Toluene adsorption is similar to that of benzene (*10*); it adsorbs oriented parallel to the surface, over a threefold hollow site. The C–H bonds and the C–CH_3 bond bend away from the surface. Toluene undergoes a Kekulé distortion.

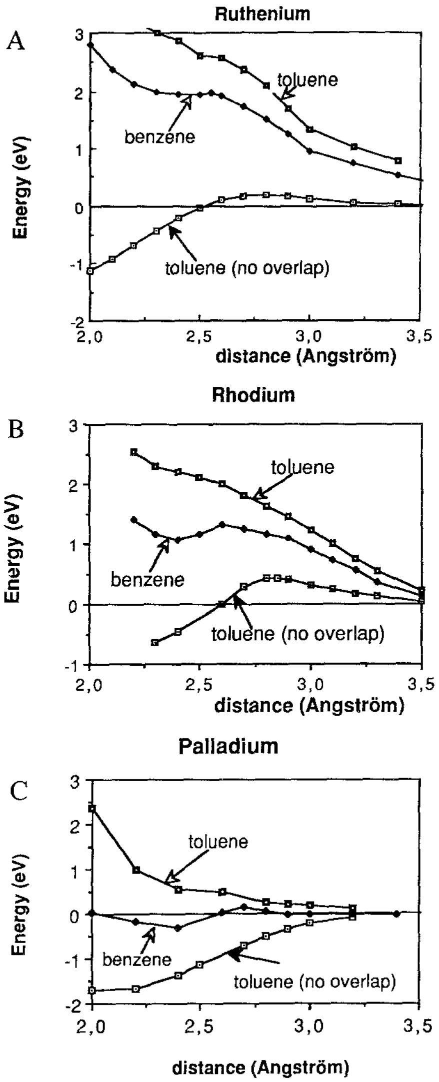

FIG. 1. Binding energy curves of toluene on (A) Ru_6, (B) Rh_6, and (C) Pd_6. In the lowest curves the overlap between the methyl group and the surface has been set to zero. Negative energies correspond to a stabilization with respect to desorption.

To compare toluene and benzene adsorption, two major effects are to be considered, namely, the electronic effects and the steric effects. Considering the electronic effects only, one would expect an increase in the adsorption values going from benzene to toluene: the frontier energy gap of toluene is smaller than that of benzene. Thus, the HOMO is higher and the antibonding metal–adsorbate level is expected to cross more easily the Fermi level. Indeed, in the conjugation of the π_{CH_3} level with the benzene π orbitals, the methyl group acts as a donor and raises one component of the E_{1g} level of the aromatic ring. The electron transfer from the antibonding metal–adsorbate level to the Fermi level costs less energy. The barrier to the adsorption should therefore be lower for toluene than for benzene. This energy difference between benzene and toluene remains at shorter distances from the surface than the transition state and the binding energy of toluene should also be larger than that of benzene for the stable adsorbed configuration. Orbitals of the methyl group also conjugate with one component of the E_{1u} orbital of the aromatic ring. In the isolated molecule, a destabilization due to the occupied π_{CH_3} level slightly prevails over the conjugation of the vacant $\pi^*_{CH_3}$ level (the methyl is donor). However, this second conjugation becomes more important as soon as the E_{1u} level is raised in energy by the back donation from the metal during the adsorption. Hence, toluene is more distorted than benzene and its binding energy is larger. From both electron transfers, easier donation to the Fermi level, and easier back-donation to the π^* level, toluene adsorption should be easier. This is true from both a kinetic and a thermodynamic point of view.

Figure 1 shows the energy diagram for the parallel approach of the adsorbate by assuming no distortion of the adsorbate. The toluene system is found to be more repulsive than the benzene system on the three metals. The reason is the steric repulsion which dominates over the electronic effects. Repulsion at large distances gives a decreasing exponential law with distance. Toluene possesses a methyl group, and for the same distances of the ring from the surface, one has to consider in addition the repulsion of the methyl hydrogens. As for the adsorption on graphite (*11*), the best methyl orientation has one H atom away from the surface, and the other two are then equally spaced to the surface. At distances above the surface corresponding to the transition state in benzene adsorption, there are slight changes in the slopes of the curves but this does not lead to a stabilization at shorter distances.

If the overlap between the methyl group and the metal atoms of the surface is artificially cancelled, the through-space interaction disappears and the electronic effect may be seen. In Fig. 1 (lower curves), the binding energy curves of toluene with cancellation of the through-space interaction are shifted down, below those of benzene. The adsorption barriers are reduced relative to those of benzene. The magnitude of this depends on the nature of the metal; it increases with the metal electropositivity. It is weak for toluene–Pd_6 since the reference value is already small, 0.17 eV. The barrier for the toluene–Rh_6 cluster is reduced from 1.3 to 0.48 eV. For the toluene–Ru_6 cluster the reduction is more pronounced, from 1.96 to 0.19 eV. These results can be explained from the electronic shift of the metallic energy levels. In toluene, the E_{1g} degeneracy is lifted and one of the levels is raised to -12.55 eV, which is so close to the LUMO level of the metal cluster (-12.44 eV on Pd_6) that the adsorption barriers are strongly reduced and on palladium the barrier vanishes. The reduction of the barrier with the metal electropositivity is due to an increased mixing with one of the E_{2u} levels. On Ru_6, the metallic levels are high in energy and provide a significant back-donation which is also favored by the diffuseness of the ruthenium orbital and by the short distance at which the TS (transition state) occurs (2.55 Å for benzene–Ru_6, 2.6 Å for benzene–Rh_6, 2.70 Å for benzene–Pd_6). For toluene–M_6 (see Fig. 1, lower curves), all the geometries of the TS are shifted to larger distances (2.7 and 2.82 Å for M = Ru and Rh, respectively). This corresponds to an "early" transition state, reached sooner on the reaction path and consistent with better electronic effects. However, the TS geometry for the toluene–Ru_6 takes place at the shortest distance to the surface.

As long as we do not consider the distortions, toluene is more difficult to adsorb than the benzene molecule because of the steric repulsion between the methyl group and the surface. If the methyl group is bent away from the surface, the steric repulsion decreases. On the ruthenium surface, we have seen that the mixing with the E_{2u} orbitals was important; large distortions follow. Thus, calculations on Ru_6 clusters have been performed for toluene adsorption allowing two degrees of freedom in addition to ρ and θ, the C–CH_3 bond length l, and the C–CH_3 bending away from the surface, θ_C. A transition state for adsorption is found for the same ρ and θ values as for the benzene adsorption and for $l = 1.79$ Å and $\theta_C = 36°$. The toluene adsorption barrier is lower than that for benzene by 0.19 eV (Fig. 2a). With respect to benzene, the electron donation to an empty metallic orbital at the Fermi level occurs sooner at larger distances from the surface. The large adsorption ability of toluene on Ru_6 is therefore related to favorable electronic effects and to large distortions. The bending away from the surface allows a relief of the steric repulsion. This possibility does not exist on palladium surfaces. The large adsorption energy of toluene on the ruthenium surface after distortion also corresponds to a large ring expansion and to an easier cleavage of the C–C ring. The C–C bonds adjacent to the methyl group are weaker than those of the benzene molecule (4.57 vs 4.88 eV for $\rho = 1.46$ Å calculated by reference to the energies of C–H and ethylidyne radicals). As for hydrocarbon fragments, the introduction of a repulsive potential for the Ru–C bonds is necessary to avoid unrealistic short distances from the surface. Otherwise no energy well is calculated. These results are in very good agreement with the experimental data showing that $K_{T/B}$ on Ru/SiO_2 is very large (*6*). The hydrogenation of ben-

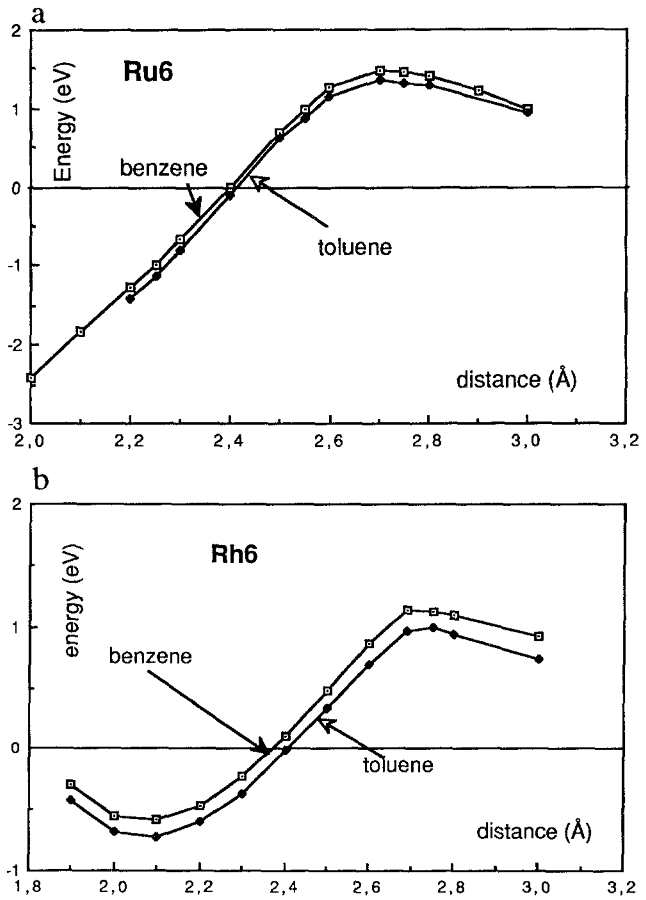

FIG. 2. Binding energy curves of benzene and toluene on Ru_6 (a) and Rh_6 (b) allowing for distortions.

zene was stopped as soon as a small amount of toluene was introduced in the reaction mixture. The toluene molecule might be dissociatively adsorbed under the operating conditions as can be inferred from the theoretical results.

On rhodium surfaces distortions are less important but allow enough relief of the repulsive effects to favor toluene adsorption. The transition state is found for $l = 1.74$ Å and $\theta_C = 17°$. The toluene adsorption barrier is lower than that for benzene by 0.14 eV (Fig. 2b). Distortions on Rh_6 clusters do not lead to fragmentation of the arene molecule and the geometry of an adsorption optimum can be calculated without the introduction of any repulsive potential. It is found when the molecule is at 2.1 Å above the surface. This distance is imposed by the repulsion of the σ_{CC} orbitals of the ring and is similar for the two systems since the C–CH_3 bond is bent away from the surface. Toluene is slightly more distorted than benzene. The ring expansion is slightly larger ($\rho = 1.573$ Å vs 1.565 Å), the C–H bonds are bent further away from the surface (24° vs 22.5°), the C–CH_3 bond is increased in length up to $l = 1.757$ Å and bent ($\theta_C = 29°$). The binding energy, 0.726 eV, is larger than that of benzene, 0.592 eV. The energy difference is the same as that calculated at the transition state in spite of the slight increase of the distortions. If benzene less easily adsorbs on the rhodium surface, it also less easily desorbs.

On Pd surfaces, the distortions are negligible at the transition state and the binding energy curve should remain close to that given in Fig. 1. Toluene does not differ by much from benzene. The transition state is low in energy, but higher than that of benzene (0.38 vs 0.17 eV). Allowing distortions leads to the following parameters for the adsorbed toluene: $\rho = 1.56$ Å, $\theta = 20°$; the C–CH_3 is elongated to $l = 1.75$ Å and bent by $\theta_C = 20°$. Toluene is at 2.17 Å above the Pd(111) surface; the binding energy is slightly smaller than that of benzene (1.10 vs 1.24 eV). The selectivity should be small since the barrier is weak but the $K_{T/B}$ ratio should be slightly smaller than 1.

The binding energy profile of the toluene molecule depends on the three metal surfaces. On ruthenium surfaces (more electropositive) toluene has to overcome the largest barrier; the adsorption energy is large, leading either to dissociation or to irreversibility. On palladium surfaces (less electropositive) toluene adsorbs reversibly, after passing over a small barrier. The adsorption on rhodium surfaces represents the intermediate situation.

These theoretical forecasts on rhodium and palladium are again in agreement with the $K_{T/B}$ ratios measured from the competitive hydrogenation. Indeed, $K_{T/B}$ is close to one on Pd/SiO_2 and toluene is much more strongly adsorbed than benzene on Rh/SiO_2 ($K_{T/B} = 10$); however, unlike on ruthenium, it does not block the metal surface.

Coadsorbate and Support Effects

The relative heights of the activation barrier for the adsorption of benzene and toluene on ruthenium are related to the energy shift of their π levels. The energy difference of the E_{1g} levels, 0.18 eV, must be considered relative to the energy difference between them and the value for which the antibonding metal–adsorbate orbital becomes empty. This value varies with $-\Delta\Phi$ and thus a modification of the work function will change the selectivity (see Fig. 3). In the presence of donors (such as NH_3), the work function decreases, the crossing of the levels occurs at a higher energy, the adsorption barrier increases and the selectivity drops. Accordingly, a decrease in $K_{T/B}$ has been observed upon ammonia adsorption or when the metal is interacting with electron-donating species such as alkali (*1*) or easily oxidizable metals like molybdenum (*5, 12*) or iron (*4*). In the presence of electron-acceptor coadsorbates like sulfur (*1*) or when the surface metal atoms are interacting with the acidic sites of supports (*1, 13*), the reverse happens, namely the $K_{T/B}$ ratio increases.

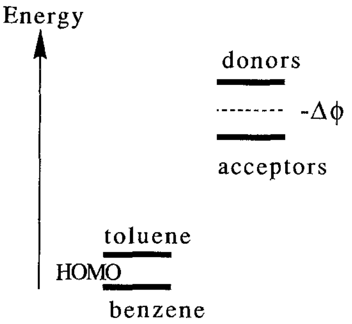

FIG. 3. MO diagram for the arene–metal interaction. The difference between the E_{1g} levels in the benzene and the toluene is constant while the $-\Delta\Phi$ value varies in the presence of additives. The changes in the relative values induce modification of the selectivity. The geometries of benzene and toluene are those from the transition-state structure.

For an increase in the work function due to the presence of an electron-accepting coadsorbate, the energy gain at the transition state which results from an electron transfer to a lower pure metal–coadsorbate level is still present at the potential energy well. Indeed, the stabilization of these electrons transferred at the transition state remains unaffected during all the adsorption process if the electron-accepting level has zero amplitude on the adsorbate. For a similar reason, the difference in energy between the binding energy curves of toluene–Rh_6 and benzene–Rh_6 is similar for the TS, the energy well, or any other point of the adsorption process (see Fig. 2b). However, the electron-accepting coadsorbate should induce a general shift down of the metallic levels, which also reduces the magnitude of the back-donation and consequently of the distortions of the adsorbates at short distances, close to the energy well. This principally decreases the toluene adsorption energy because of the larger steric repulsion with the methyl group. The differences at the transition state are larger than those at the optimum of geometry. Thus, the difference in energy of the adsorbed species is reduced at the energy well with respect to that of the transition states and the increase in selectivity is expected to be larger when the adsorption is irreversible (kinetic control) instead of involving an equilibrium (thermodynamic control). According to this model, coadsorbate effects can be considered as inducing a modification of the metal electropositivity. Adsorptions on rhodium surfaces in the presence of electron-accepting coadsorbates are modified to become Pd-like adsorptions (small barriers and reversibility) whereas the presence of electron-donating coadsorbates induces a Ru-like behavior (high barrier and irreversibility).

CONCLUSION

Previous studies have shown that the ratio $K_{T/B}$ of the adsorption coefficients of toluene and benzene is a sensitive probe of the electronic structure of metal surfaces. However, the interpretation of these experimental findings awaited theoretical support. Thanks to the present study, a number of results can be rationalized:

(1) Toluene is found to be more easily adsorbed than benzene when the distortions allow the methyl substituent to stand away from the surface. The adsorption energy barrier is lower and the adsorption well is deeper. The selectivity for toluene adsorption is forecast to be the largest on ruthenium, in agreement with the very large $K_{T/B}$ ratio observed on Ru/SiO_2 catalyst (*6*). Moreover, the forecast that rhodium and palladium are selective and nonselective, respectively, corroborates the experimental results on Rh/SiO_2 and Pd/SiO_2 catalysts (*6*).

(2) The selectivity to toluene adsorption depends also on the electron-donating or electron-accepting species interacting with the metal surface since they change the work function and thus the energy barrier and the potential well depth. It becomes possible to account at least qualitatively for the experimental change of $K_{T/B}$ observed experimentally as a function of the nature of coadsorbates and supports.

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