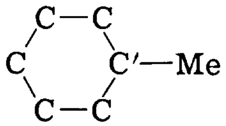
Stability of Surface Complexes and Activation Energy of Hydrogenation of Methyl-Substituted Benzenes

The great advances in the study of organometallic complex compounds and their utilization in homogeneous catalysis led to the idea of the formation of surface π complexes in the explanation of the mechanism of some heterogeneous catalytic reactions (*1*). The present paper discusses the possibility of correlation of the activation energy of hydrogenation of certain methyl-substituted benzenes with the stability of the surface π complexes estimated from the standpoint of the electron structure of the molecule (characterized by MO–LCAO method).

More recent experimental data on the activation energy of hydrogenation of methyl-substituted benzenes in gaseous (*2*) and liquid (*3*) phases were used. The molecular orbitals of ten methyl-substituted benzenes were calculated after the MO–LCAO method, Hückel's approximation (*4*). The methyl–benzene interaction was taken into account by an induction model with a Coulomb integral (*5*)

$$\alpha_{C'} = \alpha_C - 0.5\beta_0$$



Völter (*2*) has found that the activation energy of hydrogenation of certain benzene derivatives changes symbatically with the stability of the corresponding complexes with hydrochloric, perchloric, and picric acids. He related this to the change in the donor properties of the benzene ring on substitution.

If we accept that initial state of the rate-controlling step of the hydrogenation reaction is a hydrocarbon adsorbed as a π complex and that the energy curves of the reaction for the separate hydrocarbon do not cross each other up to the transition state (Fig. 1), the energy of activation of hydrogenation of the separate hydrocarbon should be proportional to the energy of bonding of the hydrocarbon to the surface.

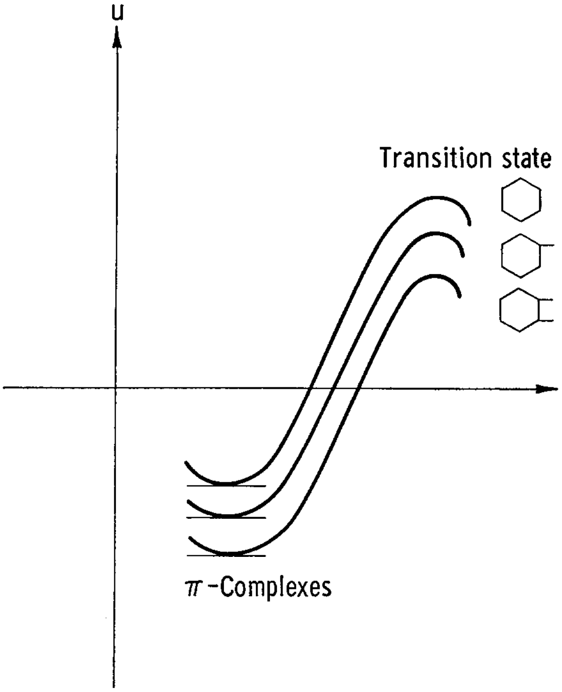


FIG. 1. Energy curves of the hydrogenation reactions.

In order to evaluate the relative stability of the surface π complexes, it is assumed that they possess properties similar to those of the aromatic "sandwich" compounds. In the case of one and the same metal atom, the stability of the "sandwich" compounds formed by different aromatic ligands depends on the disposition of the ligands' MO, more precisely on the reacting orbits of the metal and the ligands. As indicated by the calculation results of the MO of dibenzene-chromium (*6*), the energy of the complex is determined by the donor–acceptor bonds (participation of the bonding orbital of the ligand) as well as by the dative bonds (participation of the first antibonding orbital of the ligand).

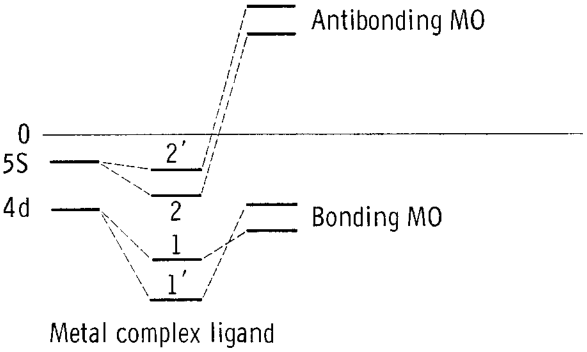


FIG. 2. π-Energy levels of MO of methyl-substituted benzenes.

The results of the calculations showed that in the presence of methyl substituents a displacement of the levels of the bonding and antibonding orbits towards higher values takes place (Fig. 3). Figure 2, which gives an idea of the relative position of the reacting levels, shows that the above displacement leads to the strengthening of the donor–acceptor bonds (1–1′) due to the closer disposition of the interacting levels and to the weakening of the dative bonds (2–2′) of the complex as a result of the separation of the antibonding levels of the ligand. A relation of this kind is observed in the MO of dibenzene-chromium and chromocene (*7*). The experimental stability of dibenzene-chromium and dimesitylene-chromium is in accordance with above considerations.

In order to characterize the influence of the substituents on the stability of the complex, we introduce the value S, as

$$S = \Sigma\epsilon_b - \epsilon_{ab}$$

where ϵ_b is the sum of the π-electron energy of the bonding orbits of the ligand, and ϵ_{ab} is the π-electron energy of the first antibonding orbital of the ligand.

Only the first antibonding orbital is taken

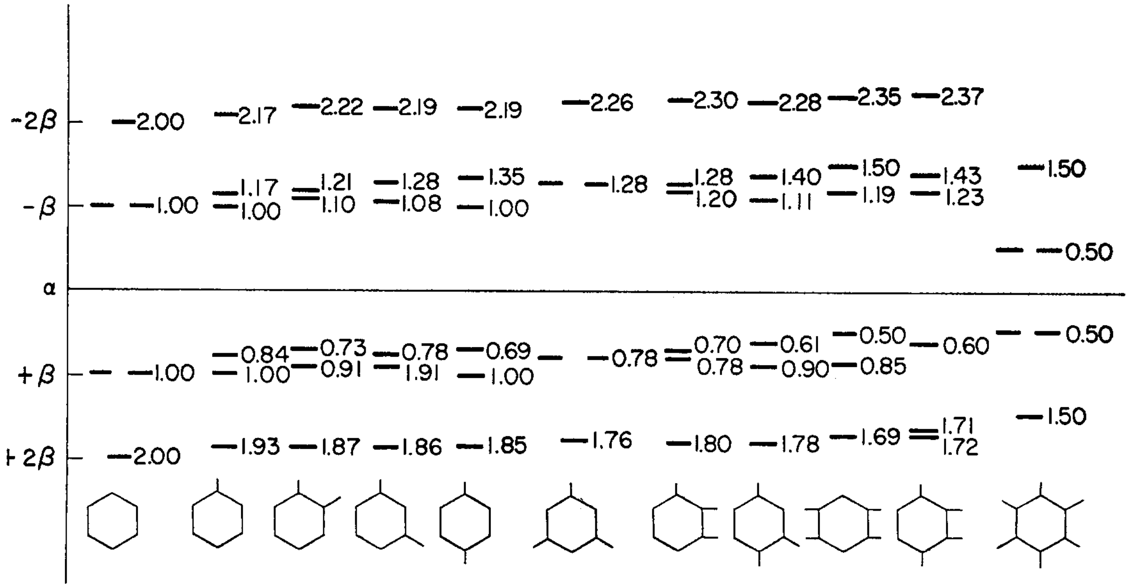


FIG. 3. Donor–acceptor (1) and dative (2) bonds in the π complex; (1′) and (2′)—after introduction of the methyl substituent.

into consideration since only this orbital is of significance in the formation of the complex (*6*). The minus sign expresses the different directions of change of the donor–acceptor and dative bonds in the presence of methyl substituent.

The above considerations show that the change of S should depend on the changes in the stability of the complex, since the MO levels of complexes with the same metal depend on the bonding and antibonding orbits of the ligand.

Figure 4 presents the relation of S to the activation energy (E) of gaseous-phase hydrogenation of benzene, toluene, p-xylene, and mesitylene on a nickel catalyst (*2*). Figure 5 presents the same dependence for the hydrogenation of ten aromatic hydrocarbons in the liquid phase on rhodium catalyst under pressure (*3*). In both cases a proportionality between S and E is observed, the proportionality in the second case being less strictly observed.

The value S determined in a similar manner for the methyl-substituted ethylenes, butadienes, and benzenes correlates with the equilibrium constants of formation of the respective silver complexes (*9*).

It is evident that similar experimental results in heterogeneous catalysis can be qualitatively correlated with the electronic structure of the organic molecule from the viewpoint of the π-complex conception. When velocity constants are considered it is necessary to take into consideration the influence of the steric factor which becomes more important with the increase of the number of substituents. Actually, in the cases discussed here, the preexponential factor of the velocity constant changes symbatically with the number of methyl substituents in the benzene ring.

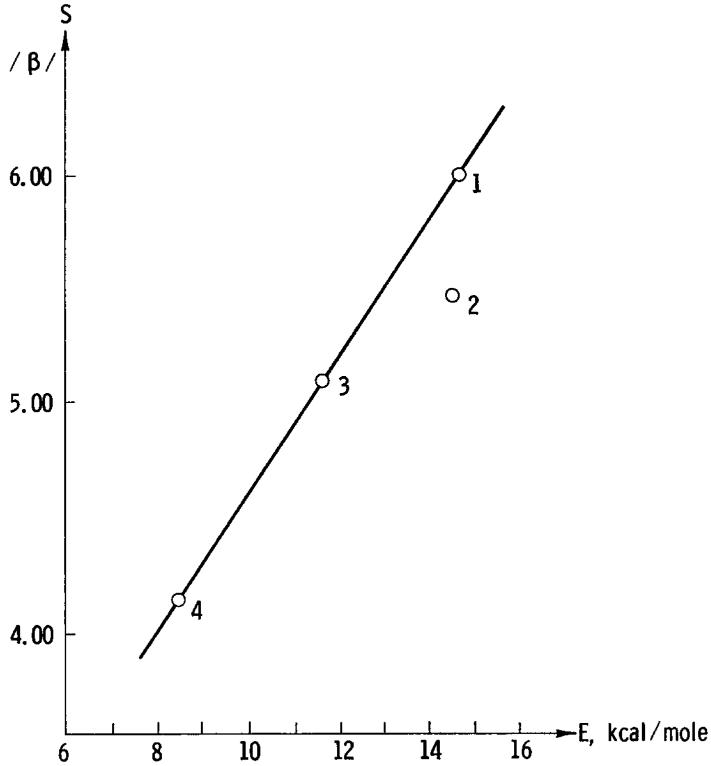


FIG. 4. Correlation between the activation energy of hydrogenation (E) and S (*2*): 1, benzene; 2, toluene; 3, o-xylene; 4, mesitylene.

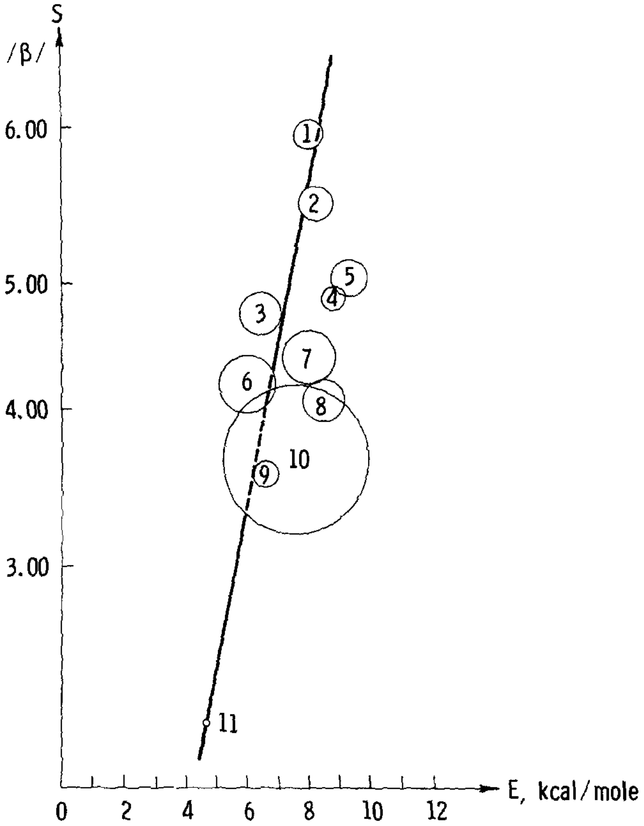


Fig. 5. Correlation between the activation energy of hydrogenation (E) and S (S): 1, benzene; 2, toluene; 3, *o*-xylene; 4, *m*-xylene; 5, *p*-xylene; 6, mesitylene; 7, pseudocumene; 8, durene; 9, prehnitene; 10, hemimellitene; 11, hexamethylbenzene. The radius indicates the error of the activation energy determination.

References

1. Rooney, J. J., and Webb, G., *J. Catalysis* **3**, 488 (1964).
2. Völter, J., *J. Catalysis* **3**, 297 (1964).
3. Smith, H. A., and Campbell, W. E., *Proc. Intern. Congr. Catalysis, 3rd, Amsterdam, 1964* **2**, 1373 (North-Holland Publ. Co., Amsterdam 1965).
4. Hückel, E., *Z. Physik.* **70**, 204 (1931); *ibid.* **72**, 310 (1931); *ibid.* **76**, 628 (1932).
5. Streitwieser, A., *in* "Molecular Orbital Theory," p. 135. Wiley, New York, 1962.
6. Shustorovich, E. M., and Dyatkina, M. E., *Dokl. Akad. Nauk SSSR* **128**, 1234 (1959).
7. Shustorovich, E. M., and Dyatkina, M. E., *Dokl. Akad. Nauk SSSR* **131**, 113 (1960).
8. Fischer, E. O., *Angew. Chem.* **69**, 715 (1957).
9. Shopov, D., and Andreev, A., *Compt. Rend. Acad. Bulgare Sci.* **19**, No. 6 (1966).

D. Shopov
A. Andreev

Bulgarian Academy of Sciences
Sofia, Bulgaria
Received April 5, 1966