The Role of Intermediate Complexes in Benzofuran Protonations

By **Estanislao Silla,**† **Juan Bertrán, Enric Canadell,** and **J. I. Fernández-Alonso,*** Departamento de Química Física y Química Cuántica and C.S.I.C., Facultad de Ciencias, Universidad Autónoma, Cantoblanco, Madrid 34, Spain

The relative stabilities of σ- and π-complexes in aromatic benzofuran protonation have been studied by various methods. The results of CNDO/2 and INDO calculations on the one hand and STO-3G computations on the other support different explanations of the experimental facts. Our results give a theoretical foundation to Olah's suggestion with regard to a two-step mechanism for some electrophilic substitutions.

It is generally assumed[1] that σ-complexes represent satisfactory models for the transition states of electrophilic aromatic substitutions. A considerable amount of direct experimental evidence indicates that σ-complexes do exist as stable intermediates.[2] However it seems that, in some reactions, π-complexes are formed initially, and only when the temperature is raised does σ-complex formation take place.[3] Olah[4] concluded that in some exothermic reactions the transition state of highest energy is of a π-complex nature. It was Dewar[5] who originally suggested that π-complexes might play an important role in electrophilic aromatic substitutions.

A systematic experimental study of benzofuran electrophilic substitutions[6] established the positional reactivity order $2 > 3 \geqslant 6 > 4 > 5 > 7$. The experimental facts were initially interpreted in terms of a

---

† This work was performed in part during a stay of E. S. at the Laboratorio di Chimica Quantistica ed Energetica Molecolare del C.N.R., Pisa, Italy; *present address:* Colegio Universitario, Castellón, Spain.

[1] C. K. Ingold, 'Structure and Mechanism in Organic Chemistry,' 2nd edn., Cornell University Press, Ithaca, New York, 1964.

[2] G. A. Olah, S. J. Kuhn, and A. Paulath, *J. Amer. Chem. Soc.*, 1958, **80**, 6535, 6541.

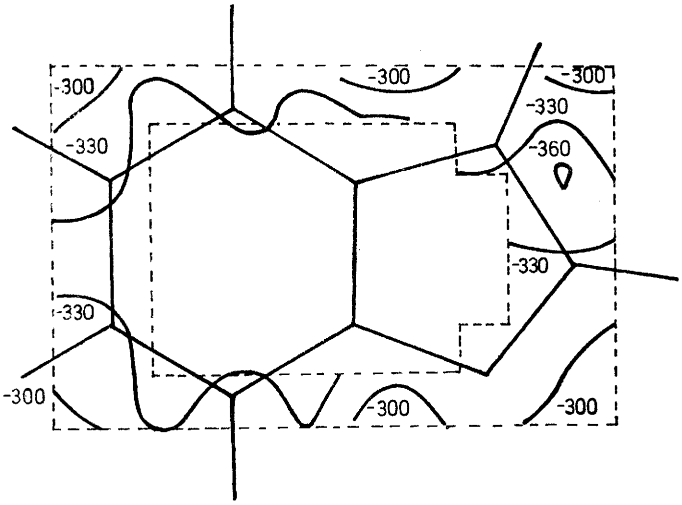
[3] G. A. Olah, *J. Amer. Chem. Soc.*, 1965, **87**, 1103.

[4] G. A. Olah, *Accounts Chem. Res.*, 1971, **4**, 240.

[5] M. J. S. Dewar, *J. Chem. Soc.*, 1946, 406, 407; 'The Electronic Theory of Organic Chemistry,' Clarendon Press, Oxford, 1949.

[6] R. Royer and L. René, *Bull. Soc. chim. France*, 1969, 1029, 1037; P. Demmerseman, L. René, N. Platzer, and R. Royer, *ibid.*, 1973, 2349.

delocalized model of the transition state.[7] It must be emphasized that the delocalized model[8] assumes a transition state not far from the π-complex intermediate. More recently Silla *et al.*[9] have interpreted these facts on the basis of a σ-complex model. It is surprising that both models, which assume such differing transition states, work well in this case. We hoped that a study of the relative energies of σ- and π-complexes would clarify the reasons for this.



Isoenergetic lines (kcal mol^{-1}) for protonated benzofuran in a parallel plane 1 Å from the molecule. The energies were obtained by the CNDO/2 method. Calculations were restricted to the zone between the dashed lines

We carried out an initial exploration of the protonation energy of benzofuran by the CNDO/2 method with the original parametrization,[10] in a parallel plane located 1 Å from benzofuran. The Figure shows the isoenergetic lines with the minimum between positions 2 and 3 outside the molecule. We have analysed this region in more detail. A direct method of minimization[11] locates the proton 1.282 Å from C(2), 1.290 Å from C(3), and 1.077 Å above the molecular plane, with the benzofuran structure retained. This corresponds to a π-complex. The energetics and the geometry remain practically unchanged when relaxation of the hydrogen bonded to C(2) is allowed. A σ-complex at position 2 appears as a secondary minimum, 19.7 kcal mol^{-1} less stable than the π-complex.

STO-3G Energies of σ-complexes of benzofuran

Position	Energy (a.u.)
2	−376.916 2
3	−376.912 7
4	−376.916 1
5	−376.915 5
6	−376.917 0
7	−376.910 2

Calculations by the INDO method[10] give similar results. The geometries of the σ- and π-complexes are practically identical, and the π-complex is found to be 17.7 kcal mol^{-1} more stable than the σ-complex.

For comparison with the results obtained by semiempirical methods, we have evaluated the energy of some points by an *ab initio* method using an STO-3G basis.[12] The Table gives the energies of σ-complexes at different positions, with the same geometry as in the previous CNDO/2 calculations.[8] The order of positional reactivity is $6 > 2 > 4 > 5 > 3 > 7$. Two aspects are worthy of mention. First, position 6 appears only 0.5 kcal mol^{-1} more favoured than position 2. Secondly, the geometries employed are those optimized in the CNDO/2 method but not necessarily the best for the *ab initio* calculations. This may be the reason for the shifting in the reactivities of the five-membered ring centres with respect to those in the six-membered ring. Three positions corresponding to a π-complex have been evaluated. The first corresponds to the geometry of the minimum in the Figure, the second to the minimum obtained by Pople *et al.*[13] for the π-complex in protonated benzene, and the third to the same geometry of the CNDO/2 complex. The compared energies show that these π-complexes are, respectively, 29, 24, and 25 kcal mol^{-1} less stable than the σ-complex at position 2.

Thus the calculated relative stabilities of the σ- and π-complexes depend markedly on the method employed. In a related study on protonated benzene, Heidrich and Grimmer[14] also found the π-complex to be more stable than the σ-complex when using CNDO/2 with original parametrization. On the other hand the contrary was observed when the *ab initio* STO-3G basis was used, also in accord with our results. These authors remark that the difference in energies diminishes when the more refined STO-431G basis is used; in this case the energies of the σ- and π-complexes are not very different. Given that our results on benzofuran protonation are similar to Heidrich and Grimmer's results on protonated benzene, we would expect that the energies of σ- and π-complexes in benzofuran protonation also would not be very different.

With these results in mind we can try to interpret the benzofuran protonation process. If both intermediates are on the reaction path, to establish the order of reactivity the highest energy complex must be taken into account. The CNDO/2 and INDO methods support the use of σ-complexes whereas *ab initio* STO-3G calculations support the use of the π-complex. Olah suggests a two-step mechanism for some electrophilic substitutions. Our results may provide some theoretical foundation for this, in that benzofuran protonation

---

[7] O. Chalvet, J. Royer, and P. Demmerseman, *Bull. Soc. chim. France*, 1970, 1483.

[8] J. Bertrán, O. Chalvet, R. Daudel, T. W. McKillop, and G. H. Schmid, *Tetrahedron*, 1970, **26**, 339.

[9] E. Silla, J. Bertrán, and J. I. Fernández-Alonso, *J.C.S. Perkin II*, 1975, 366.

[10] J. A. Pople and D. L. Beveridge, 'Approximate Molecular Orbital Theory,' McGraw-Hill, New York, 1970.

[11] D. Rinaldi and J. L. Rivail, *Compt. rend.*, 1972, **274(C)**, 1664; D. Rinaldi, These, Nancy, 1975.

[12] W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, 1969, **51**, 2657; N. D. Newton, W. A. Lathan, W. J. Hehre, and J. A. Pople, *ibid.*, 1970, **52**, 4064.

[13] W. J. Hehre and J. A. Pople, *J. Amer. Chem. Soc.*, 1972, **94**, 6901.

[14] D. Heidrich and M. Grimmer, *Internat. J. Quantum Chem.*, 1975, **9**, 923.

may be a two-step reaction, the first step leading to a π-complex which determines the region of attack, and the second to a σ-complex, determining the positional order.

E. S. thanks Drs. G. Alagona, C. Ghio, and J. M. Riera for discussions. This work was supported in part by Fomento Investigación Universidad (Madrid).

[5/2256 *Received, 18th November, 1975*]