the use of a polar organic phase [e.g., 4-methyl-2-pentanone] results in very low conversions.

The carbonylation process is applicable to a variety of iodoarenes, affording acids in fair to very good yields. Chloro, methoxy, and hydroxymethyl substituents are unaffected, as well as the thiophene ring. The reaction times and product yields are listed in Table I. Bromobenzene does not react under the described conditions.

The carbonylation process may proceed by reaction of the in situ generated cyanotricarbonylnickelate ion[13] with the aryl iodide to give $ArNi(CO)_2CN$. The latter may arise by single electron transfer with intermediate formation of a radical pair within a solvent cage. Carbonylation of (σ-aryl)nickel (to the acylmetal complex), followed by carbon–nickel bond cleavage by base, would give the acid.

In conclusion, phase-transfer catalysis can be used, under nonphotolytic conditions, to carbonylate iodoarenes to carboxylic acids when nickel cyanide is employed as the metal catalyst. This method, which also avoids the use of nickel tetracarbonyl, is exceptionally simple in execution and workup of the reaction.

Experimental Section

General Data. See the same section in ref 13 for information on the use of instrumentation. The iodoarenes, hydrated nickel cyanide, and cetyltrimethylammonium bromide were commercial products and were used as received. Solvents were distilled prior to use.

General Procedure for the Phase-Transfer-Catalyzed Carbonylation of Aryl Iodides by Nickel Cyanide. A mixture of 5 N sodium hydroxide [20 mL], nickel cyanide [0.183 g, 1.0 mmol], aryl iodide [10 mmol], and cetyltrimethylammonium bromide [0.060 g, 0.16 mmol] in toluene (20 mL) was stirred under carbon monoxide at 90 °C [±5 °C, oil bath temperature]. After the reaction time indicated in Table I (reaction followed by gas chromatography), the layers were separated and crushed ice was added to the aqueous phase. The latter was then acidified with 10% HCl and extracted with ether or ethyl acetate (4 × 25 mL). The combined extracts were washed with water (25 mL), dried ($MgSO_4$), and evaporated, affording the acid. Characterization of the acid was made in comparison with properties (infrared, nuclear magnetic resonance, mass spectrometry) of authentic materials.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council and to British Petroleum for support of this research.

Registry No. $Ni(CN)_2$, 557-19-7; C_6H_5I, 591-50-4; 4-$CH_3C_6H_4I$, 624-31-7; 3-$CH_3C_6H_4I$, 625-95-6; 2-$CH_3C_6H_4I$, 615-37-2; 4-ClC_6H_4I, 637-87-6; 4-$CH_3OC_6H_4I$, 696-62-8; 2-$HOCH_2C_6H_4I$, 5159-41-1; 1-$C_{10}H_7I$, 90-14-2; 2-C_4H_3SI, 3437-95-4; C_6H_5COOH, 65-85-0; 4-$CH_3C_6H_4COOH$, 99-94-5; 3-$CH_3C_6H_4COOH$, 99-04-7; 2-$CH_3C_6H_4COOH$, 118-90-1; 4-ClC_6H_4COOH, 74-11-3; 4-$CH_3OC_6H_4COOH$, 100-09-4; 2-$HOCH_2C_6H_4COOH$, 612-20-4; 1-$C_{10}H_7COOH$, 86-55-5; 2-C_4H_3SCOOH, 527-72-0.

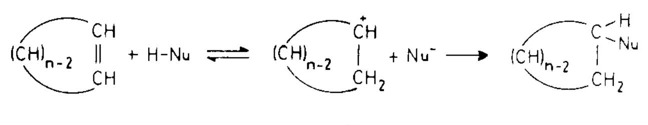
Kinetic Interpretation of Aromaticity: A Theoretical Study

Josep M. Bofill,[1a] Josep Castells,*[,1a] Santiago Olivella,*[,1a] and Albert Solé[1b]

Departaments de Química Orgànica i Química Física, Universitat de Barcelona, Martí i Franquès 1, 08028-Barcelona, Catalunya, Spain

Received April 1, 1988

Scheme I

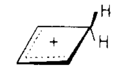


1 1H+

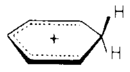
In spite of having been of great utility in the understanding of carbocyclic and heterocyclic chemistry, *aromaticity*, in our opinion, remains an ill-defined and unquantified concept with an unsatisfactory theoretical support. Definitions of aromaticity based on a purported thermodynamic "extra stability" are questionable; moreover, the quantum-mechanics foundations of this "extra stability" are unclear. In particular, recent theoretical studies of the electronic structure of benzene[2] have raised serious doubts about the current molecular-orbital interpretation of the benzene "extra stability" based on the π-electron delocalization.

Tendency to react with "reversion to type", that is, regeneration of the aromatic ring, appears to be the most, if not the only, distincitive attribute of the peculiar chemical behavior of benzene and benzene-like (i.e., aromatic) species. Consider, for the sake of simplicity, the stepwise reaction between a cyclic conjugated polyene (1) and the conjugate acid (H–Nu) of a nucleophile (Nu) (Scheme I). It is well-known that after the first step, namely, the formation of the conjugate acid of the cyclic polyene ($1H^+$), two alternative reaction pathways are possible: (a) addition of Nu to $1H^+$ (nonaromatic behavior) and (b) abstraction of a proton from $1H^+$ by Nu ("reversion to type", aromatic behavior). Herein lies the difference between alkene addition and aromatic substitution.

Tendency to "revert to type" can be rationalized, in principle, on either a thermodynamic[3] or a kinetic basis.[4] Here we present a theoretical study of two possible pathways (i.e., the Nu addition to the *vicinal* position and the H^+ abstraction) for the model reaction of water, as a representative nucleophile, with the conjugate acid of two archetypal cyclic conjugated polyenes: cyclobutenylium ion ($2H^+$) and cyclohexadienylium ion ($3H^+$). The results lend computational support to a kinetic interpretation of the tendency to "revert to type" (aromatic behavior) shown by benzene after an electrophilic attack.



2H+



3H+

Computational Details

Due to the molecular size of the systems considered, the geometries of the transition structures for both the H_2O addition and H^+ abstraction reactions of $2H^+$ and $3H^+$ were calculated by using the MNDO SCF-MO model[5] as implemented in the MOPAC[6] program package. This model has proved effective in theoretical studies of the transition-state structures of numerous organic reactions, giving

---

[1] (a) Departament de Química Orgànica. (b) Departament de Química Física.

[2] Shaik, S. S.; Hiberty, P. C.; Lefour, J. M.; Ohanessian, G. *J. Am. Chem. Soc.* 1987, *109*, 363. Cooper, D. L.; Gerrat, J.; Raimondi, M. *Nature (London)* 1986, *323*, 699. Hiberty, P. C.; Shaik, S. S.; Lefour, J. M.; Ohanessian, G. *J. Org. Chem.* 1985, *50*, 4659. Shaik, S. S.; Hiberty, P. C. *J. Am. Chem. Soc.* 1985, *107*, 3089.

[3] See, e.g.: Roberts, J. D.; Caserio, M. C. *Basic Principles of Organic Chemistry*; W. A. Benjamin: New York, 1965; pp 783–784.

[4] Dixon, W. T. *J. Chem. Soc., Chem. Commun.* 1969, 559.

[5] Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* 1977, *99*, 4899.

[6] Stewart, J. J. P. *QCPE Bull.* 1983, *3*, 101. Olivella, S. *QCPE Bull.* 1984, *4*, 109.

0022-3263/88/1953-5148$01.50/0

Table I. Calculated[a] Total Energies (hartrees) and Relative Energies[b] (kcal/mol) for the Transition Structures of the H_2O Addition to the Vicinal Position and the H^+ Abstraction Reactions of Cyclobutenylium ($2H^+$) and Cyclohexadienylium ($3H^+$) Ions

ion	rctn	SCF/6-31G	SCF/6-31G*	MP2/6-31G	MP2/6-31G*[c]
$2H^+$	H_2O addn	−229.973 75 (0.0)	−230.060 94 (0.0)	−230.437 13 (0.0)	(0.0)
	H^+ abstn	−229.883 67 (56.5)	−229.966 04 (40.7)	−230.354 80 (51.7)	(35.9)
$3H^+$	H_2O addn	−306.905 35 (0.0)	−307.008 21 (0.0)	−307.548 11 (0.0)	(0.0)
	H^+ abstn	−306.912 53 (−4.5)	−307.008 22 (0.0)	−307.567 42 (−12.1)	(−7.6)

[a] At the MNDO-optimized geometries. [b] In parentheses. [c] Estimated by assuming additivity of the d-polarization functions and electron correlation effects.

results comparable with those from good ab initio calculations.[7] Transition structures were located by the usual reaction coordinate method, refined by minimizing the norm of the gradient,[8] and characterized by calculating and diagonalizing the Cartesian force constant matrix.[8]

Since it is well-known that MNDO grossly overestimates the energy of the transition structures involved in hydrogen abstraction processes,[9] to obtain more reliable energies, we performed single-point ab initio calculations[10] with the large split-valence 6-31G basis set[12] (denoted SCF/6-31G), with the split-valence plud d-polarization 6-31G* basis set[13] (denoted SCF/6-31G*), and with incorporation of valence-electron correlation using second-order Moller–Plesset perturbation theory[14] with the 6-31G basis set (denoted MP2/6-31G). The best relative energies (denoted MP2/6-31G*) were estimated by assuming additivity of the d-polarization functions and correlation energy effects.[15]

Results and Discussion

The total and relative energies, calculated at the various levels of theory, of the four aforementioned transition structures are collected in Table I. It is readily seen that at the present highest level of theory, namely, from the estimated MP2/6-31G* relative energies, the transition structure for the H^+ abstraction from $2H^+$ is found to lie 35.9 kcal/mol above the transition structure for the H_2O addition to this ion. In sharp contrast, the transition structure for the H^+ abstraction from $3H^+$ lies 7.6 kcal/mol below the transition structure for the H_2O addition. Inclusion of the zero-point vibrational energy corrections (calculated from the MNDO harmonic vibrational frequencies) leads to a potential energy difference between the transition structures for H^+ abstraction and H_2O addition of 33.1 kcal/mol, in the case of $2H^+$, and −11.3 kcal/mol, in the case of $3H^+$. From these potential energy differences and the differences between the absolute entropies of the transition structures (computed by standard methods using the MNDO harmonic frequencies and the principal moments of inertia), the activated-complex theory predicts a rate constant ratio for H^+ abstraction vs H_2O addition of 2.123×10^{-24} and 1.212×10^{9} for the ions $2H^+$ and $3H^+$, respectively, at 25 °C. Thus, in contrast to the normal (nonaromatic) chemical behavior predicted for cyclobutadiene, benzene is predicted to show an aromatic chemical behavior (tendency to "revert to type") when it reacts with hydroxonium ion (H_3O^+). The latter is essentially due to the higher potential energy barrier involved in the H_2O addition to the intermediate ion $3H^+$, formed in the first step of the reaction, as compared to its deprotonation by H_2O. This conclusion clearly illustrates the kinetic basis of the benzene *aromaticity*.

Finally, it should be noted that the reliability of the present quantitative results rests on the assumption that the structure of the transition states at the MP2/6-31G* level of theory will be very similar in geometry to those obtained by MNDO. Admittedly, the MP2/6-31G* calculated energies of the transition structures located at this level of theory may differ somewhat from those calculated for the MNDO-optimized ones. Nevertheless, it seems unlikely that the former energies may reverse the relative energy ordering found for the above transition states using the latter approach.

Acknowledgment. The calculations were carried out by using the IBM 3083 and IBM 4341 computers at the Centre d'Informàtica de la Universitat de Barcelona.

Registry No. $2H^+$, 12316-90-4; $3H^+$, 26812-57-7.

Supplementary Material Available: Cartesian coordinates of the MNDO-optimized transition structures for the H_2O addition and the proton loss reactions of $2H^+$ and $3H^+$ (3 pages). Ordering information is given on any current masthead page.

---

[7] Schröder, S.; Thiel, W. *J. Am. Chem. Soc.* **1985**, *107*, 4422.

[8] McIver, J. W.; Komornicki, A. *J. Am. Chem. Soc.* **1972**, *94*, 2625.

[9] Dewar, M. J. S.; Ford, G. P. *J. Am. Chem. Soc.* **1979**, *101*, 5558.

[10] All ab initio calculations were carried out by using a locally modified version of the GAUSSIAN 80 system of programs.[11]

[11] Binkley, J. S.; Whiteside, R. A.; Krishnan, R.; Seeger, R.; DeFress, D. J.; Schlegel, H. B.; Topiol, S.; Kahn, L. R.; Pople, J. A. *QCPE* **1981**, *13*, 406.

[12] Hehre, W.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 257.

[13] Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.

[14] Moller, C.; Plesset, M. *Phys. Rev.* **1934**, *46*, 618. Pople, J. A.; Binkley, J. S.; Seeger, R. *Int. J. Quantum Chem., Symp.* **1976**, *10*, 1.

[15] McKee, M. L.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1981**, *103*, 4673. Nobes, R. H.; Bouma, W. J.; Radom, L. *Chem. Phys. Lett.* **1982**, *89*, 497.

Tandem [2,3]-Sigmatropic Rearrangement of Sulfonium Ylides and Bromine Allylic Rearrangement on a 4-Methoxy-2-pyrone Derivative

Pedro de March,* Marcial Moreno-Mañas,* and J. L. Roca

Departamento de Quimica, Universidad Autónoma de Barcelona, 08193 Bellaterra, Barcelona, Spain

Received February 16, 1988

Sulfur ylides are being used increasingly in synthetic chemistry by means of their [2,3]-sigmatropic rearrangements. Ando and co-workers[1] have throughly investigated the formation and rearrangement of these ylides which

---

[1] (a) Ando, W. *Acc. Chem. Res.* **1977**, *10*, 179. (b) Ando, W. *The Chemistry of Diazonium and Diazo Groups*;, Patai, S., Ed.; Wiley: New York, 1978; Chapter 9, p 341.

0022-3263/88/1953-5149$01.50/0 © 1988 American Chemical Society