J. Phys. Chem. A **2002,** *106,* 7078−7079

Reply to Comment on “Reactions of Phenyl Cations with Methanol and Methyl Fluoride”

Igor S. Ignatyev*

Department of Chemistry, Radiochemistry Laboratory, St. Petersburg State University, St. Petersburg, 199034, Russia

Tom Sundius

University of Helsinki, Department of Physical Sciences, P.O. Box 64, FIN-00014 Helsinki, Finland

Received: July 2, 2001; In Final Form: March 25, 2002

Phenylium ion automerization was revealed in the radiochromatographic study of reactions between nucleogenic cations and CH_3X (X = OH, F, Cl, Br).[1−3] However, the possibility of automerization was called in question by the results of theoretical studies[4−6] which predicted large barriers to 1,2-hydrogen shift. Nucleogenic cations formed by tritium decay may possess excess energy due to the fact that their nascent geometry is that of their neutral precursors.[7] Relaxation of their geometry to the equilibrium may release energy which makes the ion vibrationally excited. This excess energy (E_{def}) may allow the phenyl cation to overcome the 1,2-hydrogen shift barrier (E^*_{isomer}). Thus, the possibility of the phenylium ion automerization depends on the sign of the $E^*_{\text{isomer}} - E_{\text{def}}$ difference. All theoretical estimates predict this value positive. The state-of-the-art calculation of the 1980s by Schleyer, Kos, and Raghavachari[6] (MP2/6-31G(d,p)//3-21G) gave 52.2 kcal/mol for E^*_{isomer} and 32.3 kcal/mol for E_{def}. However, they predicted that at higher theory levels E^*_{isomer} should be 40 kcal/mol or more. This allowed researchers to claim that further improvement of the theory level may reduce or even invert the $E^*_{\text{isomer}} - E_{\text{def}}$ gap.[3,7]

In our previous study,[8] we estimated the phenylium automerization barrier height and deformation energy by the B3LYP/6−31(d,p) method. They were found to be 49.5 kcal/mol for E^*_{isomer} and 30.1 kcal/mol for E_{def}. This was the first estimate of these values (which included geometry optimization) with the help of the correlated methods. However, Speranza[9] argued that the B3LYP method is too inaccurate and repeated his previous statement that more refined calculations may reduce the $E^*_{\text{isomer}} - E_{\text{def}}$ difference to zero or negative values. Since B3LYP usually gives thermochemical parameters accurate within several kilocalories per mole,[10] it is difficult to believe that the 15 kcal/mol difference may disappear at higher levels of theory, especially if one takes into account the well-known propensity of B3LYP to underestimate the barrier heights.[11−13]

Nevertheless, although the overall accuracy of the B3LYP approach is satisfying, several cases of the comparative failure of this method are known.[10] Therefore, we estimated the $E^*_{\text{isomer}} - E_{\text{def}}$ difference with the B3LYP method with larger basis sets, as well as with more reliable correlated MO methods. The results of these calculations are presented in Table 1. All methods employed as well as our previous B3LYP calculations predict the nonplanar structure of protonated benzyne with C_s symmetry for the transition state.

Increasing the quality of the basis set within B3LYP employing correlation-consistent basis sets[14] leads to lower values of both the barrier height and deformation energy. The B3LYP method with the triple-ζ basis set (aug-cc-pVTZ) usually gives very satisfactory results.[15]

TABLE 1: Total Energy of the Phenylium Cation (E_e, Hartree), the Barrier Height for Automerization (E^*_{isomer}, kcal/mol), and the Deformation Energy of the Phenylium Cation (E_{def}, kcal/mol)

method/basis set	number of functions	E_e	E^*_{isomer}	E_{def}
B3LYP/6-31G(d,p)	115	−231.27126	49.5	30.1
B3LYP/cc-pVDZ	109	−231.27371	48.7	30.0
B3LYP/cc-pVTZ	250	−231.34094	49.1	30.7
MP2/6-31G(d,p)	115	−230.52989	42.8	34.0
MP2/6-311++G(d,p)	167	−230.59811	41.3	34.6
MP2/cc-pVDZ	109	−230.52495	41.2	33.8
MP2/aug-cc-pVDZ	183	−230.55230	40.1	34.0
MP2/cc-pVTZ	250	−230.73816	41.6	34.9
QCISD/cc-pVDZ	109	−230.56376	46.9	29.5
CCSD(T)/TZ2P//QCISD/cc-pVDZ	189	−230.73492	44.4	31.2
MP4/TZ2P	189	−230.68604	46.1	32.4

All MP2 calculations (with frozen core electrons) demonstrate lower barriers than those obtained by B3LYP, while the E_{def} values are nearly the same. With exclusion of the more truncated basis sets (aug-cc-pVDZ gives the low value, 40.1 kcal/mol, and 6-31G the highest value, 42.8 kcal/mol), all MP2 E^*_{isomer} values are in the narrow range 41.2−41.6 kcal/mol. However, there is a tendency of a small increase of the barrier height with the size of the basis set within the correlation-consistent basis set. Thus, one may expect the convergence of MP2 calculations at ca. 42 kcal/mol. However, it was noticed that the MP2 method “tends to favor bridged structures a bit too much”[6] and real values for the automerization barrier may be higher. Indeed, correlation beyond the MP2 level (QCISD, MP4) has the effect of a considerable increase of the barrier height with a small decrease of E_{def}. The increase in the quality of correlation by employing CCSD(T) gives a lower barrier height and higher “deformation” energy by the same amount of 2 kcal/mol. However, only single-point calculations are feasible with this method, and some uncertainty exists as to whether this narrowing of the gap is due to the better correlation procedure or the absence of optimization of the phenyl cation and the transition state. The best estimate achieved in this work is the one achieved by the MP4 method with the triple-ζ plus double polarization basis set (TZ2P) constructed from the triple-ζ set of ref 16, together with the polarization functions given in ref 17. With this method, the full geometry optimization was employed.

The automerization barrier height obtained with this method exceeds the upper limit of the excess energy which may be obtained by the nucleogenic phenyl cation by 14 kcal/mol (Table 1). All these high-end correlation methods predict the automerization barrier height to lie in the 44−47 kcal/mol range and E_{def} in the 30−32 kcal/mol range. Note that these values are the median ones between those obtained by the MP2 and B3LYP methods. The introduction of the ZPVE and thermal corrections (at 298 K) does not influence this result much: they do not lower the barrier by more than 2 kcal/mol (1.8 kcal/mol for ΔE_0 and 2.0 kcal/mol for ΔE_{298} at the best method employed, i.e., MP4/TZ2P).

Thus, all the state-of-the-art MO correlated calculations predict the $E^*_{\text{isomer}} - E_{\text{def}}$ gap in the 7−17 kcal/mol range, with more reliable estimates closer to the high end of the range. Therefore, it is highly improbable that the more sophisticated

10.1021/jp012506p CCC: $22.00

approaches, unachievable with the modern computational technique, may drastically change this relation. This makes the possibility of automerization in free phenylium cations dubious if we consider classical barriers and assume that the only source of the excess energy of the nucleogenic cation is the "deformation" energy. While quantum effects such as tunneling are not very probable due to experiment conditions (room temperature and the migration of the triton observed), there may exist other sources of excess energy in the experiments with nucleogenic cations, although they are usually not taken into account in the interpretation of experimental results.[7]

Acknowledgment. The Center for Scientific Computing in Espoo is thanked for the generous allotment of computer time.

References and Notes

(1) Speranza, M. *Tetrahedron Lett*. **1980**, *21*, 1983.

(2) Angelini, G. A.; Fornarini, S.; Speranza, M. *J. Am. Chem. Soc*. **1982**, *104*, 4773.

(3) Speranza, M.; Keheyan, Y.; Angelini, G. A. *J. Am. Chem. Soc*. **1983**, *105*, 6377.

(4) Dill, J. D.; Schleyer, P. v. R.; Binkley, J. S.; Seeger, R.; Pople, J. A.; Haselbach, E. *J. Am. Chem. Soc*. **1976**, *98*, 5428.

(5) Dewar, M. J. S.; Reynolds, C. H. *J. Am. Chem. Soc*. **1982**, *104*, 3244.

(6) Schleyer, P. v. R.; Kos, A. J.; Raghavachari, K. *J. Chem. Soc. Chem. Commun*. **1983**, 1296.

(7) Speranza, M. *Chem. Rev*. **1993**, *93*, 2933.

(8) Ignatyev, I. S.; Sundius, T. *Chem. Phys. Lett*. **2000**, *326*, 101.

(9) Speranza, M. *J. Phys. Chem. A* **2002**, *106*, 7076.

(10) Koch, W.; Holthausen, M. C. *A Chemist's Guide to Density Functional Theory*; Wiley-VCH: Weinheim, Germany, 2000.

(11) Durant, J. *Chem. Phys. Lett.* **1996**, *256*, 595.

(12) Glukhovtsev, M. N.; Bach, R. D.; Pross, A.; Radom L. *Chem. Phys. Lett.* **1996**, *260*, 558.

(13) Ignatyev, I. S.; Schaefer H. F. *J. Am. Chem. Soc*. **1997**, *119*, 12306.

(14) Dunning, T. H. *J. Chem. Phys*. **1989** *90*, 1007.

(15) Raymond, K. S.; Wheeler, R. A. *J. Comput. Chem*. **1999**, *20*, 207.

(16) Dunning, T. H. *J. Chem. Phys*. **1970**, *55*, 716.

(17) Szalay, P. G.; Stanton, J. F.; Bartlett, R. H. *Chem. Phys. Lett*. **1992**, *193*, 573.