J. Braz. Chem. Soc., Vol. 19, No. 7, 1369-1373, 2008.
Printed in Brazil - ©2008 Sociedade Brasileira de Química
0103 - 5053 $6.00+0.00

Theoretical Study of the Gas-Phase Reaction between Formyl Cation and Aromatics

André A. S. T. Ribeiro and Claudio J. A. Mota*

Universidade Federal do Rio de Janeiro, Instituto de Química. Av. Athos da Silveira Ramos 149 CT,
Bloco A, Cidade Universitária 21941-909, Rio de Janeiro-RJ, Brazil

Cálculos teóricos da reação do cátion formila (CHO^+) com tolueno, cumeno e *p*-cresol mostraram que a transferência de próton é termodinamicamente preferida em relação a acilação. No caso do tolueneo, a acilação do anel aromático, para formação do complexo de Wheland, é 11,7 kcal mol^{-1} mais alta em energia (ΔH) que a protonação, em nível de cálculo MP4(SDTQ)/6-31++G(d,p)//MP2(full)/6-31G(d,p). Esta diferença diminui com a introdução de um grupo hidroxila no anel (*p*-cresol) ou substituindo o grupo metila por isopropila (cumeno). A protonação do tolueno pelo H_3^+ e pelo cátion isoformila é, respectivamente, 88,6 e 84,5 kcal mol^{-1} mais exotérmica que a acilação em nível MP4(SDTQ)/6-31++G(d,p)//MP2(full)/6-31G(d,p). A afinidade protônica do *p*-cresol foi calculada como sendo 195,4 kcal mol^{-1}.

Theoretical calculations of the reaction of formyl cation (CHO^+) with toluene, cumene and *p*-cresol showed that proton transfer is thermodynamically preferred over acylation. For toluene, acylation of the aromatic ring, to form the Wheland complex, is 11.7 kcal mol^{-1} higher in energy (ΔH) than protonation, at MP4(SDTQ)/6-31++G(d,p)//MP2(full)/6-31G(d,p) level of theory. This difference reduces upon introduction of a hydroxy group in the ring (*p*-cresol) or replacing the methyl group by an isopropyl group (cumene). Protonation of toluene by H_3^+ and isoformyl cation is 88.6 and 84.5 kcal mol^{-1}, respectively, more exothermic than acylation, at MP4(SDTQ)/6-31++G(d,p)//MP2(full)/6-31G(d,p). The proton affinity of *p*-cresol was calculated to be 195.4 kcal mol^{-1}.

Keywords: formyl cation, Friedel-Crafts acylation, gas phase ion reaction, proton transfer

Introduction

Friedel-Crafts acylation is an important reaction in organic and industrial chemistry.[1] Many important chemicals, like fragrances, pharmaceuticals and dyes are industrially produced through acylation steps. In addition, the Gatterman-Koch reaction[2] is a useful procedure to produce benzaldehydes, through the reaction of carbon monoxide and an aromatic compound, catalyzed by a strong Bronsted acid, like HF.

Acylation of aromatic compounds has long been studied in the gas phase.[3,4] Speranza and Sparapani showed that gas phase acetylation of alkylbenzenes does not follow the same reactivity trend found in solution,[5] suggesting that solvent, counter ion and catalyst play a major role in the reactivity of the CH_3CO^+ cation in condensed phase. Strong electrophilic acylium ions, such as CF_3CO^+, are able to acylate deactivated substrates, such as trifluorobenzene, in the gas phase.[6] Cerichelli *et al.*[7] reported that formyl cation behaves as a Bronsted acid in gas phase, exclusively transferring a proton to toluene, rather than producing formylated products. This behavior contrasts with the reactivity of $C_2H_5^+$ and i-$C_3H_7^+$ cations in gas phase, both capable of acting as Lewis (alkylation) and Bronsted (protonation) acids toward toluene. In the present study we carried out theoretical calculations on the thermochemistry of acylation (formation of the Wheland complex) and protonation (formation of arenium ions) for the reaction of the formyl cation with toluene, cumene and *p*-cresol, aiming to understand the thermodynamic gap between them and the role of formyl cation as Bronsted and Lewis acid.

Computational Methods

Geometry optimizations were done at Hartree-Fock, single reference second order Möller-Plesset perturbation theory (MP2/full), using the Gaussian 98 package of

---

*e-mail: cmota@iq.ufrj.br

molecular orbital program,[8] with 6-31G(d,p) basis set. To provide more accurate energy values, the optimized structures were subjected to a single point calculation at MP4(SDTQ)/6-31++G(d,p) level of theory and for study with cumene and *p*-cresol, at MP4(SDTQ)/6-31G(d,p) level. Minima were characterized by the absence of imaginary vibrational frequencies. The energy values were corrected for the zero point energy (ZPE) and 298.15 K with frequencies scaled[9] by 0.93 for all vibrational modes.

Results and Discussion

Geometry of the formyl cation and π-complex with toluene

Table 1 presents some selected geometric data for the formyl cation, toluene and the π-complex (**1**), at MP2(full)/6-31G(d,p) level of theory. The geometry of the formyl cation is linear. The values reported in Table 1 are close to reported[10-12] calculated data for the formyl cation, at similar and higher levels of calculation. Upon forming the π-complex **1**, the geometry is little affected. The C-H and C-O bond lengths decrease to 1.083 Å and 1.139 Å, respectively. The angle changes by only 0.1°. The same situation occurs for the toluene molecule. The calculated geometry is little affected by the interaction with the formyl cation. The most significant changes are in the C-C bond length of the aromatic ring, which showed a slight increase, relative to the isolated toluene molecule. The structure of complex **1** has the oxygen atom of the formyl cation pointing towards the aromatic ring at a distance of 2.427 Å. This arrangement has already been observed[13] for the interaction of formyl, acetyl and NO$^+$ cations with benzene, at DFT level of calculation.

Geometry of the Wheland intermediates for toluene

We were able to find three Wheland intermediates, correspondent to the attack at ortho, meta and para positions. The optimized structures are shown in Figure 1 and Table 2 shows some selected geometry values. The C-C bond between the aromatic ring and the formyl moiety varies slightly for each intermediate. In **2**, the Wheland intermediate formed upon acylation at ortho position, the C-C bond length is 1.628 Å, whereas in **3**, the intermediate formed upon acylation in meta position, this distance decreases to 1.585 Å. In **4**, the intermediate formed upon attack at para position, the C-C bond is 1.574 Å long. It is curious that the methyl hydrogen atom in **2** is eclipsed with respect to the aromatic carbon-formyl bond. All attempts to rotate the methyl group to place the hydrogen atom in staggered conformation failed. Stabilization of the eclipsed conformation by electrostatic interaction with the oxygen atom of the formyl moiety, might account for this behavior. The methyl hydrogen atom delocalizes the positive charge through hyperconjugation and thus, it is reasonable to believe that electrostatic interaction with the oxygen atom will better stabilize the structure.

Table 1. Selected geometric data for the formyl cation, toluene and π-complex (**1**), at MP2(full)/6-31G(d,p) level

Parameter	CHO$^+$	Toluene	π-complex (**1**)
d C-H/(Å)	1.092		1.083
d C-O/(Å)	1.154		1.139
∠ HCO/(degree)	180.0		179.9
d C-C$_{\text{ipso-ortho}}$/(Å)		1.397	1.403
d C-C$_{\text{ortho-meta}}$/(Å)		1.395	1.397
d C-C$_{\text{meta-para}}$/(Å)		1.393	1.398
d C-C$_{\text{ipso-metila}}$/(Å)		1.504	1.504
d C-H$_{\text{ortho}}$/(Å)		1.083	1.083
d C-H$_{\text{meta}}$/(Å)		1.082	1.082
d C-H$_{\text{para}}$/(Å)		1.081	1.081

Table 2. Selected geometric parameters of the Wheland intermediates, at MP2(full)/6-31G(d,p) level

Parameter	**2**	**3**	**4**
C$_{\text{ortho}}$-C$_{\text{ipso}}$^{a}/(Å)	1.463	1.382	1.417
C$_{\text{ortho}}$-C$_{\text{ipso}}$^{b}/(Å)	1.386	1.412	-
C$_{\text{ortho}}$-C$_{\text{meta}}$^{a}/(Å)	1.463	1.457	1.369
C$_{\text{ortho}}$-C$_{\text{meta}}$^{b}/(Å)	1.398	1.406	-
C$_{\text{meta}}$-C$_{\text{para}}$^{a}/(Å)	1.372	1.457	1.462
C$_{\text{meta}}$-C$_{\text{para}}$^{b}/(Å)	1.409	1.375	-
C$_{\text{ipso}}$-CH$_3$/(Å)	1.482	1.500	1.486
CHO angle/(degree)	125.3	124.7	124.1

^{a}Near the CHO moiety; ^{b}Opposed to the CHO moiety.

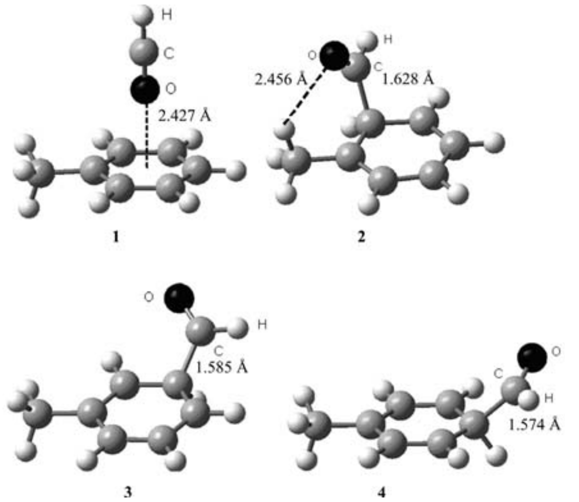


Figure 1. Optimized structures of the π-complex between formyl cation and toluene and of the Wheland intermediates, at MP2(full)/6-31G(d,p) level.

Thermochemical data for acylation and protonation of toluene by formyl cation

Calculations showed that the π-complex **1** is 10.8 kcal mol^{-1} lower in enthalpy than the free reactants, at MP2(full)/6-31G(d,p) and 10.9 kcal mol^{-1} at MP4(SDTQ)/6-31G++(d,p) level of theory. Table 3 shows the calculated enthalpy and Gibbs free energy at 298.15 K for acylation (formation of Wheland complex) and proton transfer (formation of arenium ions). Attack at the ortho and para position, to form the Wheland intermediates **2** and **4**, respectively, is preferred by 3.9 kcal mol^{-1} at MP2(full)/6-31G(d,p) and 4.3 kcal mol^{-1} at MP4(SDTQ)/6-31++G(d,p) level of theory, over attack at the meta position to form **3**. Nevertheless, the preferred thermodynamic pathway is protonation, lying 11.7 kcal mol^{-1} (ΔH) and 22.3 kcal mol^{-1} ($\Delta G_{298.15K}$) lower in energy with respect to acylation, at MP4(SDTQ)/6-31G++(d,p) level. Gas phase protonation of aromatic compounds has been widely studied in the literature, at experimental[14-18] and theoretical levels.[19-21] Thus, we did not include any structural and energetic discussion of arenium ion isomers in this work.

Ring and alkyl chain substitutions

To check the effect of electron releasing groups in the aromatic ring and alkyl chain substitution in the energetics of acylation, we performed calculations of formyl cation reactions with *p*-cresol (*p*-hydroxy-toluene) and cumene (isopropylbenzene), considering protonation and acylation. The thermochemical data are presented in Table 4. One can see that the thermodynamic gap between acylation and proton transfer is reduced to 9.3 kcal mol^{-1} (ΔH) and 19.9 kcal mol^{-1} ($\Delta G_{298.15K}$) in the case of *p*-cresol, and 11.4 kcal mol^{-1} (ΔH) and 21.9 kcal mol^{-1} ($\Delta G_{298.15K}$) in the reaction with cumene, both at MP4(SDTQ)/6-31G(d,p) level of theory.

These calculations can be validated by comparison with the experimental results, using published[22] proton affinity (PA) data for CO, toluene and cumene. Scheme 1 shows the gas phase reactions with the respective enthalpy variation. One can see that calculations are in good agreement with the experimental results. For toluene, the calculated ΔH is just 0.8 kcal mol^{-1} below experiment, at MP4(SDTQ)/6-31++G(d,p) level, whereas for cumene the difference between theory, computed at MP4(SDTQ)/6-31G(d,p) level, and experiment is just 0.2 kcal mol^{-1}. These small differences may validate the general trends taken from these calculations.

We did not find the experimental proton affinity of *p*-cresol in the literature. Thus, we decided to run calculations for all possible sites of protonation in the *p*-cresol molecule, especially to compare protonation at the ring and at the oxygen atom. Scheme 2 shows the

Table 3. Calculated thermochemical data for the reaction between formyl cation and toluene. All the energy values are computed in relation to the isolated reactants

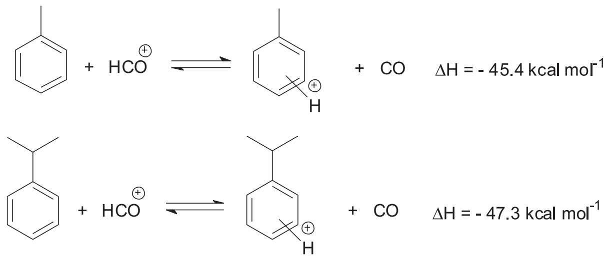
System	MP2/6-31G(d,p)		MP4/6-31++G(d,p)	
	ΔH/(kcal mol^{-1})	ΔG^{a}/(kcal mol^{-1})	ΔH/(kcal mol^{-1})	ΔG^{a}/(kcal mol^{-1})
π-complex (**1**)	–10.8	–9.8	–10.9	–9.9
Acylation				
(**2**)	–31.3	–28.5	–32.8	–30.0
(**3**)	–27.4	–25,3	–28.6	–26.4
(**4**)	–31.3	–29.1	–32.9	–30.7
Protonation				
toluene + CHO$^+$ → ^{b}toluene-H$^+$ + CO	–39.8	–48.2	–44.6	–53.0

[a] Calculated at 298.15 K; [b] Protonation in the para position.

Table 4. Thermochemical data for acylation and proton transfer of formyl cation with *p*-cresol and cumene

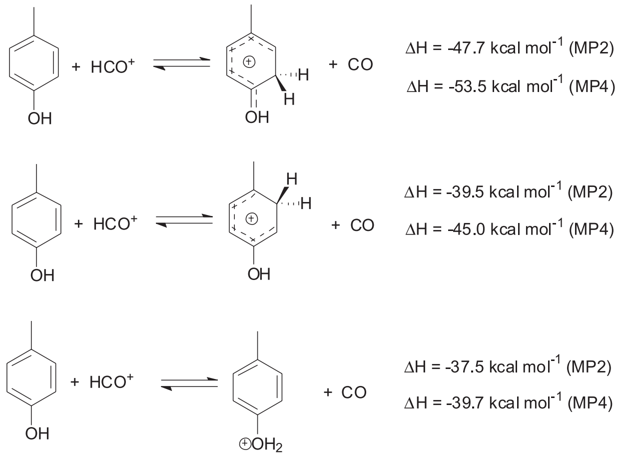
System	MP2/6-31G(d,p)		MP4/6-31G(d,p)	
	ΔH/(kcal mol^{-1})	ΔG^{a}/(kcal mol^{-1})	ΔH/(kcal mol^{-1})	ΔG^{a}/(kcal mol^{-1})
cumene + CHO$^+$	0	0	0	0
cumene + CHO$^+$ → ^{b}cumene-H$^+$ + CO	–41.8	–49.3	–47.5	–55.0
Wheland intermediate^b	–33.4	–30.4	–36.1	–33.1
p-cresol + CHO$^+$	0	0	0	0
p-cresol + CHO$^+$ → ^{c}*p*-cresol-H$^+$ + CO	–47.7	–54.3	–53.5	–60.0
Wheland intermediate^c	–41.5	–37,4	–44.2	–40.1

[a] Calculated at 298.15 K; [b] in the para position; [c] in the meta position relative to the methyl group.



Scheme 1. Thermochemistry of the gas phase proton transfer from the formyl cation to toluene and cumene. The ΔH was calculated using the experimental PA data.

thermochemical reactions between formyl cation and *p*-cresol, indicating preference for protonation in meta position relative to the methyl group. Protonation in the oxygen atom is the less favorable pathway. These results might be explained in terms of the stabilization of the ion formed. Protonation in the ring leads to delocalization of the charge in the substituent groups, whereas protonation in the oxygen atom do not permit delocalization of the charge in the π bonds. Using the experimental PA of CO (141.9 kcal mol^{-1}) and the calculated thermochemistry for proton transfer to the meta position (relative to the methyl group), we computed the PA of *p*-cresol as 195.4 kcal mol^{-1}.



Scheme 2. Calculated thermochemistry for proton transfer from formyl cation to *p*-cresol. MP2 accounts for results at MP2(full)/6-31G(d,p) level, whereas MP4 accounts for MP4(SDTQ)/6-31G(d,p).

Calculations showed that gas phase protonation of toluene by formyl cation is favored over acylation by 11.7 kcal mol^{-1} (ΔH) and 22.3 kcal mol^{-1} ($\Delta G_{298.15K}$), at MP4(SDTQ)/6-31G++(d,p) level. This gap is reduced when the size and number of substituents in the ring are increased. Hence, protonation is preferred over acylation by 11.4 kcal mol^{-1} (ΔH) and 21.9 kcal mol^{-1} ($\Delta G_{298.15K}$) in the reaction with cumene, whereas in the reaction with *p*-cresol protonation prevails over acylation by 9.3 kcal mol^{-1} (ΔH) and 19.9 kcal mol^{-1} ($\Delta G_{298.15K}$), both at MP4(SDTQ)/6-31G(d,p) level. It seems unlikely that such a thermodynamic gap, in the range of 9 to 12 kcal mol^{-1} (ΔH), would solely prevent acylation to occur in the gas phase reaction between formyl cation and toluene, as reported by Cerichelli, Crestoni and Fornarini.[7] In reactions of aromatic hydrocarbons with simple alkyl carbocations both, proton transfer and ring alkylation, do occur in gas phase, although the enthalpy difference in some cases[7] is over 30 kcal mol^{-1}. Protonation is usually preferred at higher temperatures and lower pressures, whereas ring alkylation prevails at lower temperatures and higher pressures.[23] It has also been reported[24] that formyl cation behaves as an electrophile, acylating the aromatic ring, and as a Bronsted acid, forming arenium ions, in superacid solution. The gas phase experiments of Cerichelli, Crestoni and Fornarini[7] were conducted at atmospheric pressure and 37 °C using radiolytic conditions. To produce the formyl cation, they irradiated a mixture of H_2 and CO with relative molar proportion of 34:1, respectively, together with typically 1.0 to 2.0 Torr of toluene. These conditions favors proton transfer, but it is surprising that no acylated product was observed, since acylation occurs in solution and for systems presenting a larger enthalpy gap, such as ethyl and propyl cations reacting with toluene.

It is well known that radiolysis of H_2 generates the H_3^+ ion,[25] which in turn, may react with CO to generate the formyl and isoformyl cations.[26] Since H_2 was present in large excess compared with CO and toluene in the experiments of Cerichelli, Crestoni and Fornarini,[7] we decided to check the thermodynamics of proton transfer to toluene using H_3^+ and isoformyl cation (COH^+) as reactant. Table 5 shows that both ions behave as strong Bronsted acid in gas phase, reacting exothermically with toluene. At MP4(SDTQ)/6-31G++(d,p) level, proton transfer from H_3^+ to toluene is exothermic by 88.6 kcal mol^{-1}, whereas from isoformyl cation the exothermicity is 84.5 kcal mol^{-1}. Both reactions are far more exothermic than acylation, lying about 50 to 60 kcal mol^{-1} below in enthalpy. Therefore, they are exceedingly more favorable and might provide an alternative explanation for the experimental results at high H_2 pressures.[7] On the other hand, we cannot completely rule out that reactivity may be governed by kinetics, as suggested by the authors. Apparently, there is no reported study of the reaction of formyl cation with toluene, cumene or *p*-cresol at low pressure, under gas phase ion molecule reaction conditions. Therefore, a conclusive scheme on the role of formyl cation as Bronsted (proton transfer) or Lewis acid (acylation) in the gas phase is still missing.

Conclusions

The gas phase reaction of formyl cation with toluene, *p*-cresol and cumene was investigated by means of

Table 5. Thermochemistry of proton transfer to toluene. Gas phase reaction with H_3^+ and isoformyl cation

System	MP2/6-31G(d,p)		MP4/6-31++G(d,p)	
	ΔH/(kcal mol^{-1})	ΔG/(kcal mol^{-1})	ΔH/(kcal mol^{-1})	ΔG/(kcal mol^{-1})
toluene + H_3^+ → [a]toluene-H^+ + H_2	–88.9	–89.1	–88.6	–88.9
toluene + [b]COH^+ → [a]toluene-H^+ + CO	–83.7	–87.9	–84.5	–88.8

[a]protonation in the para position; [b]isoformyl cation.

theoretical methods. It was found that, at MP4(SDTQ)/6-31++G(d,p)//MP2(full)/6-31G(d,p) level of theory, protonation is preferred over acylation by 9 to 12 kcal mol^{-1}. The energy gap reduces with introduction of a *p*-OH group (*p*-cresol) in the ring or alkyl chain substitution (cumene). The energy gap of 9 to 12 kcal mol^{-1} between proton transfer and acylation does not completely explain the experimental radiolytic gas phase results, where protonation is the only observed reaction. Alternative explanations might involve protonation by isoformyl cation or H_3^+, both lying 50 to 60 kcal mol^{-1} lower in energy than acylation. The role of the formyl cation as Bronsted and Lewis acid is still not completely understood.

Acknowledgements

Authors thank CNPq, FAPERJ and PRH-ANP for financial support.

Supplementary Information

Supplementary data are available free of charge at http://jbcs.sbq.org.br. They include three tables with absolute energies, ZPE and thermal corrections for all calculated structures.

References

1. Corma, A.; Garcia H.*; Chem. Rev.* **2003**, *103*, 4307.
2. Crounse, N. N. *Org. React.* **1949**, *5*, 290.
3. Olah, G. A; Kunh S. J. In *Friedel-Crafts and Related Reactions*, G. A. Olah, ed., Wiley: New York, 1964, vol. 3, p 1153.
4. Chatfield, D. A.; Bursey, M. M.; *J. Am. Chem. Soc.* **1975**, *97*, 3600.
5. Speranza, M.; Sparapani, C.; *J. Am. Chem. Soc.* **1980**, *102*, 3120.
6. Cacace, F.; Crestoni, M. E.; Fornarini, S.; *J. Phys. Chem.* **1994**, *98*, 1641.
7. Cerichelli, G.; Crestoni, M. E.; Fornarini, S.; *J. Am. Chem. Soc.* **1992**, *114*, 2002.
8. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, Jr., J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul,A. G. B.; Stefanov, B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A.; *Gaussian 98, Revision A.7*, Gaussian, Inc., Pittsburgh PA, 1998.
9. Hout Jr., R. F.; Levi, B. A.; Hehre, W. J.; *J. Comput. Chem.* **1982**, *2*, 234.
10. Hartz, N.; Rasul, G.; Olah, G. A.; *J. Am. Chem. Soc.* **1993**, *115*, 1277.
11. Yamaguchi, Y.; Richards Jr., C. A.; Schaefer III, H. F.; *J. Chem. Phys.* **1994**, *101*, 8945.
12. Raugei, S.; Klein, M. L.; *J. Phys. Chem. B* **2001**, *105*, 8212.
13. Esteves, P. M.; Carneiro, J. W.; Cardoso, S. P.; Barbosa, A G. H.; Laali, K. H.; Rasul, G.; Prakash, G. K. S.; Olah, G. A.; *J. Am. Chem. Soc.* **2003**, *125*, 4836.
14. Chiavarino B.; Crestoni, M. E.; Di Rienzo, B.; Fornarini, S.; *J. Am. Chem. Soc.* **1998**, *120*, 10856.
15. Fornarini, S.; Crestoni, M. E.; *Acc. Chem. Res.* **1998**, *31*, 827.
16. Solca, N.; Dopfer, O.; *Chem. Eur. J.* **2003**, *9*, 3154.
17. Jones, W.; Boissel, P.; Chiavarino, B.; Crestoni, M. E.; Fornarini, S.; Lemaire, J.; Maitre, P.*; Angew. Chem. Intern. Ed.* **2003**, *42*, 2057.
18. Schroder, D.; Loos, J.; Schwarz, H.; Thissen, R.; Dutuit, O.; *J. Phys. Chem. A* **2004**,*108*, 9931.
19. Sieber, S.; Schleyer, P. V R.; *J. Am. Chem. Soc.* **1993**, *115*, 6987.
20. Glukhovtsev, M. N.; Pross, A.; Nicolaides, A.; Radom, L.; *J. Chem. Soc., Chem. Commun.* **1995**, 2347.
21. Maksic, Z. B.; Eckert-Maksic, M.; Knezevic, A.; *J. Phys. Chem. A* **1998**, *102*, 2981.
22. Hunter, E. P.; Lias, S. G.; *J. Phys. Chem. Ref. Data* **1998**, *27*, 413.
23. Cacace, F.; *Acc. Chem. Res.* **1988**, *88*, 215.
24. Tanaka, M.; Fujiwara, M.; Ando, H.; *J. Org. Chem;* **1995**, *60*, 3846.
25. Auloos, P.; Lias, S. G.; *J. Chem. Phys.* **1964**, *40*, 3599.
26. McMahon,T. B.; Kebarle, P.; *J. Chem. Phys.* **1985**, *83*, 3919.

Received: August 20, 2007
Web Release Date: August 22, 2008

J. Braz. Chem. Soc., Vol. 19, No. 7, S1-S2, 2008.
Printed in Brazil - ©2008 Sociedade Brasileira de Química
0103 - 5053 $6.00+0.00

Theoretical Study of the Gas-Phase Reaction between Formyl Cation and Aromatics

André A. S. T. Ribeiro and Claudio J. A. Mota*

*Universidade Federal do Rio de Janeiro, Instituto de Química. Av. Athos da Silveira Ramos 149 CT,
Bloco A, Cidade Universitária 21941-909, Rio de Janeiro, Brazil*

Table S1. Zero Point Energies (ZPE), Enthalpy Changes ($H^0_{298} - H^0_0$), and Absolute Entropies (S^0_{298}). Calculated using MP2(full)/6-31G**, vibrational frequencies (scaled by 0.93)

Species	ZPE /(kcal mol^{-1})	$H^0_{298} - H^0_0$ /(kcal mol^{-1})	S^0_{298} /(cal mol^{-1} K^{-1})
1	86.06134	6.72931	90.78660
2	87.80534	5.98761	84.98712
3	87.31928	6.17586	87.08520
4	87.41027	6.12503	87.04056
toluene	75.69525	4.04738	69.43659
cumene	110.17996	6.03906	84.43749
p-cresol	78.13617	5.33249	78.93375
formyl cation	8.10615	2.41086	24.43389
m-formyl-*p*OH-toluene+	90.64024	6.67409	90.60804
p-formyl-cumene+	121.91025	7.70633	99.44490
*p*H-toluene+	82.17659	4.89011	75.97728
*p*H-cumene+	116.69757	6.44945	88.21236
*m*H-*p*OH-toluene+	85.44117	5.44921	79.80330
H_2	6.12488	2.07389	28.90905
H_3+	12.57128	2.36944	34.63506
CO	2.82531	2.07389	43.96947
COH+	7.56073	2.68821	37.41948
*o*H-*p*OH-toluene+	84.48525	5.60671	80.74167
*p*H-*p*OH-toluene+	84.67032	5.50882	80.18274
*p*OH$_2$-toluene+	91.67964	5.66946	81.3843

Table S2. Absolute Energies (-a.u.)

Species	MP2(full)/6-31G**//	/6-31++G**// MP2(full)/6-31G**			
	MP2(full)6-31G**	MP2(fc)	MP3(fc)	MP4SDQ(fc)	MP4SDTQ(fc)
1	384.02062	383.99763	384.02166	384.04331	384.10964
2	384.05511	384.027445	384.067798	384.084942	384.146419
3	384.04839	384.020385	384.061886	384.078198	384.139124
4	384.05454	384.026760	384.070074	384.086882	384.146041
toluene	270.72799	270.707750	270.746972	270.753216	270.800027
formyl cation	113.27109	113.266074	113.254276	113.287976	113.287976
*p*H-toluene+	271.03720	271.009871	271.059450	271.067225	271.110328
H_2	1.15766	1.157772	1.163277	1.164687	1.164687
H_3+	1.32428	1.325313	1.331356	1.332828	1.332828
CO	113.02818	113.02913	113.02470	113.03737	113.05161
COH+	113.20062	113.195509	113.201272	113.212009	113.223796

---

*e-mail: cmota@iq.ufrj.br

Table S3. Absolute Energies (-a.u.)

Species	MP2(full)/6-31G**//	/6-31G**// MP2(full)/6-31G**			
	MP2(full)6-31G**	MP2(fc)	MP3(fc)	MP4SDQ(fc)	MP4SDTQ(fc)
cumene	349.10659	349.060164	349.119223	349.128543	349.184505
p-cresol	345.76736	345.7285593	345.766037	345.7751123	345.826045
p-formyl-cumene+	462.43591	462.381728	462.444729	462.464384	462.532383
*p*H-cumene+	349.41839	349.372012	349.440460	349.451449	349.504388
*m*H-*p*OH-toluene+	346.08947	346.050681	346.096216	346.107612	346.156362
*o*H-*p*OH-toluene+	346.07492	346.036130	346.080935	346.091522	346.141408
*p*H-*p*OH-toluene+	346.05445	346.015906	346.063479	346.074217	346.122067
CO	113.02818	113.021213	113.017893	113.029870	113.043356
formyl cation	113.27109	113.26371	113.25215	113.26850	113.28526
m-formyl-*p*OH-toluene+	459.110361	459.0637228	459.1024277	459.1228471	459.1875355
*p*OH$_2$-toluene+	346.0732028	346.0344193	346.0758495	346.0844625	346.1344596