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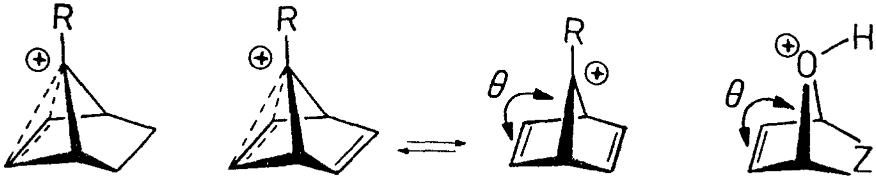
EXPERIMENTAL AND THEORETICAL STUDIES ON THE HOMOCONJUGATION IN BICYCLIC CARBENIUM AND OXONIUM IONS IN THE GAS PHASE.

Raymond Houriet* and Thierry Schwitzguebel,
Institute of Physical Chemistry, EPFL, CH-1015 Lausanne, Switzerland

Pierre-Alain Carrupt and Pierre Vogel*
Institute of Organic Chemistry, University of Lausanne, CH-1005 Lausanne, Switzerland.

Summary. Gas phase basicities and ab initio MO calculations show that non-vertical stabilization by the double bond in substituted 7-norborn-2-enyl and 7-noborna-2-dienyl cations remarkably decreases compared to the unsubstituted compounds.

The 7-norborn-2-enyl (1)[1] and 7-norborna-2,5-dienyl (2)[2] cations are relatively stable species because of their bishomoaromatic character.[3] The latter is enhanced through bending of the C-7 bridge towards the olefinic moiety (non-vertical stabilization[4]). This phenomenon was evidenced by the NMR spectra of 2 in HSO_3F solution[5] which showed a relatively high energy barrier for the C-7 bridge flipping $2 \rightleftharpoons 2'$ (E_a > 19.6 kcal/mol).[5b] We report gas phase basicity measurements which confirm that the bishomoaromaticity (π-participation) in 1 and 2 can be suppressed on substituting C-7 with an hydroxy group (4,5). These experimental results are supported by ab initio MO calculations. Furthermore, we show that homoconjugative interaction is not possible in allylic oxonium ions like the protonated 7-oxanoborn-2-ene 3.



R = H 1
R = OH 4

2 (C_s)
5'

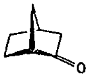
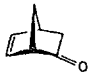
2' (C_{2v})
5

Z : CH_2-CH_2 3
Z = CH=CH 6

The gas phase basicities for compounds M = 7-13 are summarized in Table 1. They were derived from the measurement of the equilibrium constants for reaction (1)(where B are reference bases[6]) in an ion cyclotron resonance spectrometer.[8]

$$MH^+ + B \rightleftharpoons BH^+ + M \qquad (1)$$

Table 1. Gas phase basicities (GB) in kcal/mol[a)]

								
M :	7	8	9	10	11	12	13	14
GB(M)[b)] :	192.5	191.5	195.6	195.1	196.0	193.0	193.2	196.8
ΔE[c)] :	252.7	250.8	255.0	254.5	258.7	256.6	246.0[e)]	267.3[e)]
ΔE[d)] :	204.3	202.6	207.7	207.0 192.1[e)]	215.4	212.8 195.5[e)]	208.1[e)]	215.6[e)]
B :	THF	THF	nPr_2O	9	nPr_2O	Et_2O	Me_2S	cyclohexanone[g)]
ΔG_r [f)] :	0.2	-0.8	0.0	-0.8	0.4	0.0	-0.2	0.5
B :	Et_2O		nBu_2O	nPr_2O	nBu_2O	THP	Et_2O	cycloheptanone[g)] (cyclooctanone)[g)]
ΔG_r [f)] :	-0.7		-0.95	-0.6	-0.7	0.1	0.1	0.6 (-0.5)

a) They refer to $GB(NH_3)$ = 196.4 kcal/mol[6].

b) Measured at 323 K, ±0.2 kcal/mol (deviation on experimental $\Delta G_r(1)$).

c) Calculated energy difference between MH^+ and M; ab initio STO 3G with complete geometry minimization on M and MH^+[7]; MH^+ protonated on the O atom.

d) Single point calculation, with 4-31G on STO 3G geometry; MH^+ protonated on the oxygen atom.

e) For MH^+ protonated on an olefinic carbon atom.

f) $\Delta G_r(1) = -RT\ell nK(1) = GB(M) - GB(B)$, at 323 K, under conditions described previously[8]. At least three independent measurements, pressure ratio of the bases varying in fivefold range.

g) GB values from reference 10.

Thermodynamic favoured protonation of compounds 7, 9 and 11 occurs on the oxygen atom. Their GB values correspond with those for aliphatic ketones, respectively ethers of comparable size.[6] The difference between GB(7) and GB(9) c.a. 3 kcal/mol can be interpreted in terms of difference in bond angle deformations. The more strained ketone 7 is found less basic than 9.[10] Interestingly, the strain in 7-oxanorbornane does not significantly affect its basicity as shown by the difference GB(7-oxanorbornane, 11) - GB (tetrahydrofuran) = 3.7 kcal/mol wich is found similar to $GB(iPr_2O) - GB(nPr_2O)$ = 3.1 kcal/mol[6].

The introduction of a double bond (8, 10 and 12) causes a decrease in GB relative to saturated analogs (7, 9 and 11). It is known that the double bonds at α,β or γ positions of amines lowers their GB.[6] This is attributed to the inductive effect of sp^2 vs sp^3 hybridized carbon atoms which destabilizes the corresponding ammonium ions. Our results show a similar effect for ketone pairs 7/8 and 9/10 and for the ether pair 11/12. In contrast to the secondary ion 1, the hydroxy substituted derivative 4 is not stabilized by the homoallylic double bond.

This is also the case with 2-hydroxy-2-norborn-5-enyl cation (10-H$^+$). Because the hydroxycarbenium ions are intrinsically more stable than the corresponding unsubstituted ions, the need for vertical and non-vertical participation of the double bond is much smaller in the former than in the latter species. From the comparison of the proton chemical shifts of the OH groups in 4 and 7-hydroxy-7-norbornyl cations in FSO_3H solution, Winstein et al.[11] concluded that 4 was stabilized by bishomoaromaticity. Our results contradict this statement.

In the case of 3, the octet electronic structure of the oxonium ion forbids the neighbouring group participation by the double bond. The substituant effects on alkoxide and oxoniums are well interpreted by the classical electrostatic theory.[12] The comparison of GB(12) and GB(11) shows that the polarizability of the olefinic moiety at C-2,3 is not greater than that of the ethano bridge at C-5,6 in 3. Upon bending of the HOC$^+$(7) bridge in 4 and of the H-O$^+$(7) bridge in 3 towards the double bond, no stability can be gained as suggested by our ab initio calculations which are summarized in Table 2.

Table 2. Relative ab initio energies E(kcal/mol) for 1-6 as a function of the bending angle θ of the C(7) or HO$^+$(7) bridge towards C-2,3.

1	θ = 84.0° : E = 0;	92.0° : 2.1;	100.4° : 7.2;	109.0° : 14.3;	118.0° : 21.9
2	θ = 80.8° : E = 0;	88.5° : 2.5;	96.8° : 8.7;	108.0° : 21.1;	119.6° : 26.6
3	θ = 122.9° : E = 0;	112.2° : 7.3;	102.1° : 28.1;	93.4° : 58.0;	85.1° : 103.2
4	θ = 119.8° : E = 0;	110.8° : -0.2;	101.8° : 2.5;	93.0° : 7.2;	84.0° : 13.0
5	θ = 120.5° : E = 0;	105.3° : 0.5;	96.6° : 2.7;	88.7° : 6.0;	81.5° : 10.3
6	θ = 119.1° : E = 0;	110.0° : 13.7;	99.0° : 26.7;	91.4° : 53.5;	84.4° : 89.3

a) Angle θ fixed, all other geometrical parameters are completely optimized with the STO 3G basis set.

Two remarks can be made concerning the protonation of 13 and 14. Norbornene (GB = 193.2 kcal/mol) is found more basic than cyclohexene (GB = 180.0 kcal/mol) and also than branched olefins forming tertiary carbocations upon protonation, e.g. GB(1-methylcyclopentene) = 190.4 kcal/mol.[6] This indicates that 13H$^+$ is a stabilized carbocation (non-classical norbornyl structure), in accordance with previous conclusions.[6] Similarly, norbornadiene 14 (GB = 196.8 kcal/mol) is more basic than cyclohexadiene (GB = 192.5 kcal/mol).[14]

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