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# RING SIZE EFFECTS ON THE GAS PHASE PROTONATION OF CYCLIC KETONES

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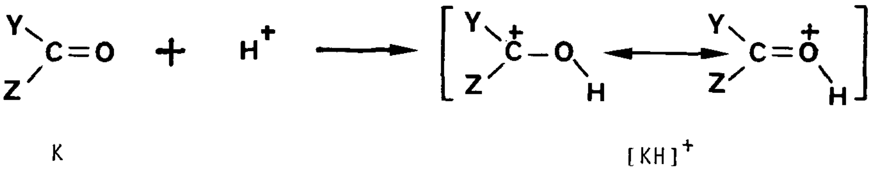
*Experimental proton affinities of cyclic ketones are determined showing evidence for a larger strain energy in protonated vs. neutral cyclic ketones .*

Ab-initio calculations [1,2] have shown that, in the gas phase, the protonation of ketones K occurs at the oxygen atom according to reaction [1] :



[1]

Moreover these theoretical results indicate that, in the protonated base $[KH]^+$, the carbon atom and its substituents Y and Z bear the largest part of the positive charge . As an important consequence, the repulsion between Y and Z increases when going from K to $[KH]^+$ . In the case of aliphatic ketones, these interactions induce an increase in the value of the YCZ angle during protonation [2] .

In the present work, we want to examine this effect in systems where the geometrical relaxation is hindered, specifically in the case of cyclic ketones where the YCZ angle has fixed values : on the basis of the arguments above, *one may expect lower proton affinities (PA) for strained cyclic ketones with respect to their acyclic counterparts* .

RESULTS : Table 1 reports the experimental gas phase basicity (GB) and the resulting proton affinity (PA) for cyclic ketones, together with values for some linear ketones used for comparison . These data were determined from equilibrium proton transfer reactions which were carried out in an ion cyclotron resonance (ICR) spectrometer operated in conditions similar to those already described [3] .

Table 1 - Free energy changes ($\Delta G_R$) in the equilibrium proton transfer reaction : $[KH]^+ + B \rightleftarrows K + [BH]^+$, gas phase basicities (GB), Proton affinities (PA) and heats of formation *(a)* .

| Ketone K | Reference Base B | GB(B) | $\Delta G_R$ *(b)* | GB(K) | PA(K) | $\Delta H_f^o(K)$ *(c)* | $\Delta H_f^o(KH^+)$ *(d)* |
|---|---|---|---|---|---|---|---|
| cyclobutanone | $(CH_3)_2O$ | 185.8 | 1.2 | 186.7 | 194.6 | - 24.2 | 146.4 |
|  | $C_2H_5CO_2H$ | 186.4 | 0.1 |  |  |  |  |
|  | $(CH_3)_3COH$ | 187.0 | - 0.4 |  |  |  |  |
| cyclopentanone | - | - | - | 192.5 *(4a)* | 200.4 | - 46.0 | 118.8 |
| cyclohexanone | $(nC_3H_7)_2O$ | 195.6 | 0.1 | 195.7 | 203.6 | - 55.0 | 106.6 |
|  | cycloheptanone | 196.6 | - 0.9 |  |  |  |  |
| cycloheptanone | $(nC_4H_9)_2O$ | 196.6 | 0.05 | 196.6 | 204.5 | - 59.1 | 101.6 |
| cyclooctanone | cycloheptanone | 196.6 | 0.9 | 197.5 | 205.4 | - 64.0 *(e)* | 95.8 |
| butanone | cyclopentanone | 192.5 | 0.2 | 192.7 | 200.6 | - 57.0 | 107.6 |
| 3-pentanone | cyclohexanone | 195.7 | - 0.9 | 194.8 | 202.7 | - 61.8 | 100.7 |
| 3-hexanone | cyclohexanone | 195.7 | 0.0 | 195.7 | 203.6 | - 66.9 | 94.7 |
|  | 4-methyl-cyclohexanone | 196.1 | - 0.4 |  |  |  |  |

*(a)* All values are expressed in $kcal.mol^{-1}$ . Reference value for the gas phase basicities is $GB(NH_3) = 196.4\ kcal.mol^{-1}$ ; PA are deduced from GB using a translational TΔS correction of $7.9\ kcal.mol^{-1}$ *(4a)* .

*(b)* Deviation on the experimental determination of $\Delta G_R$ was $0.1\ kcal.mol^{-1}$ ($\pm\ 0.2\ kcal.mol^{-1}$ for cyclobutanone) .

*(c)* Values taken from Ref. 5a .

*(d)* Calculated from $\Delta H_f^o(KH^+) = \Delta H_f^o(K) + \Delta H_f^o(H^+) - PA(K)$ ; $\Delta H_f^o(H^+) = 365.6$ kcal/mol [5b] .

*(e)* Estimated by group additivity methods [6] .

In the homologous serie going from cyclooctanone to cyclobutanone, it is seen (Table 1) that the decrease in proton affinity between consecutive homologues has values of

0.9, 0.9, 3.6 and 5.4 kcal/mol . The first two values of 0.9 kcal/mol merely account for the substituent effect of a methylene group in the cycloalkane ring : it has the same value than the effect of a methylene group in an alkyl chain, situated in γ-position with respect to the carbonyl (see 3-hexanone and 3-pentanone, Table 1) .An abrupt decrease in PA of 3.6 kcal/mol is observed between cyclohexanone and cyclopentanone . This reflects the inability of protonated cyclopentanone to reach the most stable geometry of protonated ketones because of the rigidity of the cycloalkane skeleton . The effect becomes even more pronounced (5.4 kcal/mol) in the case of cyclobutanone, in agreement with the expectations .

Another illustration of the incidence of ring constraints on the stability of protonated cyclanones $[KH]^+$ is given in Figure 1 in which the heat of formation of protonated ketones is plotted as a function of the logarithm of their number of carbon atoms, n .

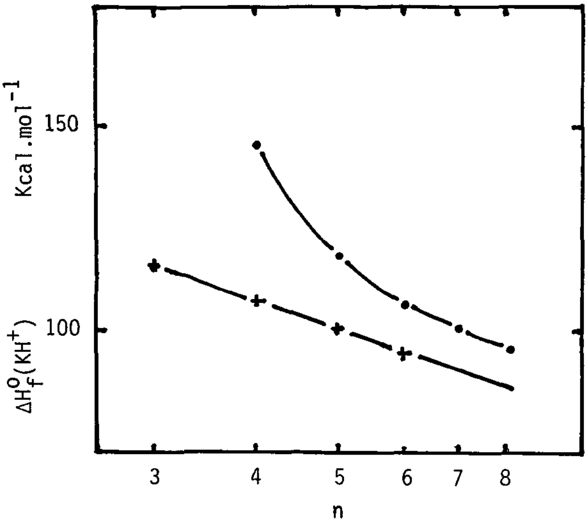


Figure 1 - Heats of formation of cyclic (.) and linear (+) protonated ketones versus the number, n, of carbon atoms .

A linear dependence of $\Delta H_f^o$ $(KH^+)$ with log n is observed for the protonated aliphatic ketones . Obviously, this is not the case for the cyclic compounds with n less than six . The difference $\Delta H_n^o = \Delta H_f^o\ (KH^+)_{cyclic} - \Delta H_f^o\ (KH^+)_{linear}$ can be considered as consisting of two terms, i. e. :

- firstly, a constant value of ≃ 10 kcal/mol which represents the difference in $\Delta H_f^o$ of the corresponding neutral ketones being due to the substitution of two methylene groups by two methyl groups
- secondly, a term which depends on the number of carbon atoms, n, with respective values of 29.8, 8 and 2 kcal/mol for n = 4, 5 and 6, and which becomes negligible for higher values of n . The repulsion energy developped between the substituents Y and Z upon

protonation of K is included in this second term . It has to be stressed however that it does not represent the major part of this latter . For the neutral ketones K, the ring strain energies has values of 22.3, 5.6 and 1.5 kcal/mol for n = 4, 5 and 6, respectively [6]. These values represent about 75 % of the second energy term determined above, thus, for the corresponding protonated species, only 25 % can be associated with the repulsion between the α-substituents of the carbonyl group .

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