



# A Theoretical Study of the Enol Contents of Cyclohexanone, Cyclopentanone and Acetone

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## Authors' contributions

This work was carried out in collaboration between all authors. All authors read and approved the final manuscript.

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## ABSTRACT

PM3 and DFT calculations have been performed with complete optimization of geometries on cyclohexanone, cyclopentanone, and acetone. The enol content trend determined in this work was cyclohexanone > cyclopentanone > acetone, which was found to agree with published experimental and theoretical works. Equilibrium constants, strain energies of enols, and electron distributions are reported.

**Keywords:** Keto – Enol tautomerism; PM3; DFT; cyclokanones and acetone.

## 1. INTRODUCTION

The equilibrium enol content of simple ketones is known to be very low, both in pure substances and in aqueous solution. Apart from their structural interest, the equilibrium proportions of enol are needed in interpreting the rates of halogenations of ketones at very low halogen

concentrations, where the reaction between enol and halogen becomes rate-determining step [1,2].

Schwarzenbach and Wittwer determine the enol content of cyclopentanone, cyclohexanone and acetone to be 0.0048, 0.02, and 0.00025% respectively by using bromine titration [3].

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Gero improved the bromine titration by the use of the iodine monochloride instead of bromine, because the rate of addition reaction is essential in order to obtain accurate information on the enol content. His values for cyclopentanone, cyclohexanone and acetone were 0.088, 1.2, and 0.00015% respectively [4].

A careful work by Bell and Smith on the bromine titration [5] shows what large errors the method can lead to when the proper precautions are not taken. They found that the enol contents for cyclopentanone and cyclohexanone are, respectively, 0.0013 and 0.00041%, of which the latter is 3000 times as small as that reported by Gero.

Ultraviolet [6] and infrared [7] spectroscopy were also used as tools for studying the keto-enol equilibria. Ebraheem showed that five-membered rings prefer exocyclic double bonds rather than endocyclic double bond as cyclohexanone derivatives using NMR spectroscopy [8]. Likewise, Sloop et al. [9] show by X-ray crystallography the preference for the five membered ring system to exhibit exocyclic double bonds as well.

Hine and Arata [10] determined the enol content of cyclohexanone, cyclopentanone and acetone by calorimetric measurements. The relative order of enol content was cyclohexanone > cyclopentanone > acetone, which was the same as that reported by Gero and by Schwarzenbach, but different from Bell's observed order (cyclopentanone > cyclohexanone > acetone).

Dubois et al. [11] proposed an approach based on the kinetic study of halogenation at low concentrations of ketones and found their results are in agreement with Hine and Arata [10] that cyclohexanone solutions must contain more enol than cyclopentanone, and also with ab initio calculations [12].

Experimental data show that the keto form of acetone is thermodynamically more stable than its enolic form [13,14]. The experimental energy difference between the two forms varies from 12 to 13.9 kcal mole [13,15], both for the gas phase and in solution, which is in agreement with recent ab initio molecular dynamics calculation (11.8 kcal/mol) [16]. Thus, the problem of determining the enol content has proven to be difficult and intractable.

This paper aims to address the dispute with regard to the enol content of cyclohexanone, cyclopentanone, and acetone by utilizing quantum thermodynamic calculations to provide predictions of the equilibrium constants, electron density distributions, and strain energies using PM3 [17] and DFT/ B3LYP (G 03, Revision B.03) [18,19] methods.

## 2. RESULTS AND DISCUSSION

The calculated equilibrium constants of cyclohexanone, cyclopentanone, and acetone, in gas phase and aqueous solution are given in Table 1, together with the results by other works for comparison.

**Table 1. Calculated equilibrium constants (K) of the enolization of ketones in the gas phase ( $\epsilon = 1$ ) and aqueous solution ( $\epsilon = 78.4$ ) by PM3 method at 25°C**

	K					
	this work	Hine <i>et al.</i> <sup>c)</sup>	Guthrie <sup>d)</sup>	Dubois <i>et al.</i> <sup>e)</sup>	Kresge <sup>f)</sup>	
Cyclohexanone	$1.4 \times 10^{-6}$ <sup>a)</sup> , $1.0 \times 10^{-8}$ <sup>b)</sup>	$3.3 \times 10^{-8}$	$1.6 \times 10^{-7}$	$2.3 \times 10^{-7}$	$4.1 \times 10^{-7}$	
Cyclopentanone	$6.9 \times 10^{-10}$ <sup>a)</sup> , $7.2 \times 10^{-10}$ <sup>b)</sup>	$2.5 \times 10^{-9}$	————	$1.0 \times 10^{-8}$	————	
Acetone	$5.3 \times 10^{-11}$ <sup>a)</sup> , $3.0 \times 10^{-12}$ <sup>b)</sup>	$2.4 \times 10^{-9}$	$7.9 \times 10^{-9}$	$3.5 \times 10^{-9}$	$4.6 \times 10^{-9}$	

a) In gas phase b) In aqueous solution c) From Ref [10] in gas phase, d) From Ref [20] in aqueous solution e) From Ref [11] in aqueous solution, f) From Ref [21] in aqueous solution

It can be seen from Table 1 that all K values by this work, Hine et al. [10], Guthrie, Dubois et al. [11] and Kresge show a decrease in going from cyclohexanone to cyclopentanone and acetone, suggesting a decrease in the enol forms of the ketones.

Enol contents of cyclohexanone, cyclopentanone and acetone are assembled in Table 2, together by other workers for comparison.

It can be seen from Table 2, that the enol content of cyclohexanone in aqueous solution of Dubois et al. [11] is  $2 \times 10^{-5}$ , while the enol content reported by Kresge [21] is  $4.1 \times 10^{-7}$ , which is less than that of Dubois et al. [11].

The present result by PM3 shows that enol content of cyclohexanone in aqueous solution ( $1.0 \times 10^{-6}$ ) is less than that of Dubois et al. [11] ( $2.3 \times 10^{-5}$ ) but higher than that of Kresge [21] ( $4.1 \times 10^{-7}$ ). Also, the enol content of cyclopentanone in aqueous solution ( $7.2 \times 10^{-8}$ ) is less than that of Dubois et al. [11] ( $1.0 \times 10^{-6}$ ),

but unfortunately no value is given by Kresge for comparison. The enol content of acetone in aqueous solution ( $3 \times 10^{-10}$ ) is less than that of Kresge [21] ( $4.6 \times 10^{-9}$ ). There is no recent work on the enol content of the ketones in the gas phase for comparison apart from the work of Hine et al. [10].

Enol contents of ketones calculated by DFT in the gas phase show low values as compared to those acquired through PM3 calculations. These DFT results may become more accurate in the near future when newly developed experimental equipment becomes available.

The most interesting finding (Table 2) is the relative ordering of enol contents of cyclohexanone > cyclopentanone > acetone in data by Schwarzenbach, Gero, Hine, Dubois, Kresge, and this work, which is the opposite tendency to that found by Bell, who reported that cyclopentanone exhibits a higher enol content than cyclohexanone.

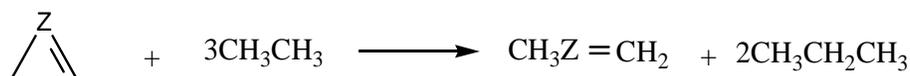
**Table 2. Enol contents of ketones at 25°C by PM3 and DFT methods**

Investigator	Compound Enol content, %		
	Cyclohexanone	Cyclopentanone	Acetone
G. Schwarzenbach <sup>[3]</sup>	$2.0 \times 10^{-2}$ a)	$4.8 \times 10^{-3}$ a)	$2.5 \times 10^{-4}$ a)
A. Gero <sup>[4]</sup>	$1.2$ b)	$8.8 \times 10^{-2}$ b)	$1.5 \times 10^{-4}$ b)
R. B. Bell <sup>[5]</sup>	$4.1 \times 10^{-4}$ a)	$1.3 \times 10^{-3}$ a)	$<10^{-4}$ a)
J. Hine <sup>[9]</sup>	$3.3 \times 10^{-6}$ c)	$2.5 \times 10^{-7}$ c)	$2.4 \times 10^{-7}$ c)
this work	$1.4 \times 10^{-4}$ c*)	$6.9 \times 10^{-8}$ c*)	$5.3 \times 10^{-9}$ c*)
	$1.0 \times 10^{-6}$ a*)	$7.2 \times 10^{-8}$ a*)	$3.0 \times 10^{-10}$ a*)
	$1.0 \times 10^{-9}$ c**)	$2.0 \times 10^{-10}$ c**)	$3.5 \times 10^{-11}$ c**)
S. Sunner <sup>[21]</sup>	—	—	$1.6 \times 10^{-4}$ d)
J. Osugi <sup>[7]</sup>	$2.0$ e)	—	$4.0 \times 10^{-2}$ e)
Calculated value <sup>[22]</sup>	$4.9 \times 10^{-4}$ f)	—	$2.8 \times 10^{-6}$ f)
J. Dubois <sup>[10]</sup>	$2.3 \times 10^{-5}$ a)	$1.0 \times 10^{-6}$ a)	$3.5 \times 10^{-7}$ a)
A. Kresge <sup>[20]</sup>	$4.1 \times 10^{-7}$ a)	—	$4.6 \times 10^{-9}$ a)

a) In aqueous solution. a\*) PM3 in aqueous solution b) In 75% methanol-water. c) Idealized gas state. c\*) PM3 in gas phase. c\*\*) DFT in gas phase d) In 60% by, volume ethanol-water. e) In toluene solution. f) Values calculated by assumption, of Lienhard and Wang [23]

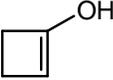
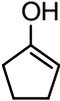
Schechter and his coworkers have found that the rate for enolization of cycloalkanones is a function of ring size and interpreted the rate order for acid-catalyzed enolization of cycloalkanones primarily on the basis of different steric requirements in the conversion of ketones to transition states having endocyclic unsaturated character [24]. If the rates of acid-catalyzed enolization of cycloalkanones are related to the enol contents at equilibrium, cyclohexanone is considered to contain more enol content than cyclopentanone.

The strain energy of cyclic compounds can be estimated by comparing the strain energy with its free components using a group separation reaction. For example, the strain energy of cyclopropenol may be calculated from the following equation, where Z is COH:



In the above equation, one strained methylene, one strained acetylene and a strained Z group are in the reactant, while the same groups, free from strain, are in the product. The exothermicity of this reaction, then, is a measure of the strain energy of cyclopropenol [25]. The strain energies of cyclopropenol, cyclobutenol, cyclopentenol and cyclohexenol are given in Table 3.

**Table 3. Strain energy calculations (kcalmol<sup>-1</sup>) in the gas phase ( $\epsilon = 1$ ) by PM3 and DFT methods**

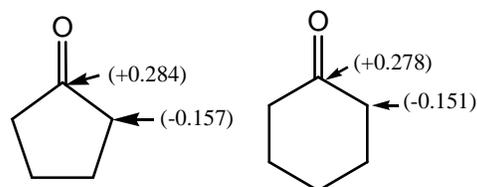
enol structure				
strain energy	-57.770 <sup>a)</sup> -58.234 <sup>b)</sup>	-32.093 <sup>a)</sup> -36.152 <sup>b)</sup>	-4.768 <sup>a)</sup> -8.329 <sup>b)</sup>	-3.115 <sup>a)</sup> -5.231 <sup>b)</sup>

a) PM3 b) DFT

It can be seen from this table that the strain energy as a function of the ring size is  $3 > 4 > 5 > 6$ , suggesting that the enol contents should increase from 3-membered ring to the 6-membered ring. i.e. enol content of cyclohexanone > cyclopentanone. This agrees with our previous work [26] and Schechter's work [25], where  $\Delta G$  decreases in going from 3-membered ring to the 5-membered ring.

Brown et al. [27] reported that a 5-membered ring cycloalkanone was stabilized relative to that of a 6-membered ring cycloalkanone. This agrees with our present PM3 calculations on the charge (electron) distribution, where the electrostatic attraction between the carbonyl carbon and the  $\alpha$ -carbons decreases when going from 5-membered ring to 6-membered ring, suggesting an increase in the destabilization

of the ketone tautomer in going from the 5-membered to 6-membered ring. See Fig. 1.



**Fig. 1. Cycloalkanone calculated charge distributions**

This agrees with our previous work on cyclopropanone [28], cyclobutanone [26] and cyclopentanone [29], where the electrostatic attraction between the carbonyl carbon and the  $\alpha$ -carbons decreases when going from

3-membered ring to 4-membered ring and 5-membered ring by using MINDO – Forces method [30].

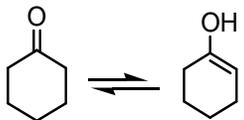
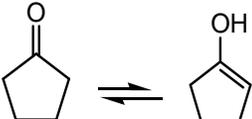
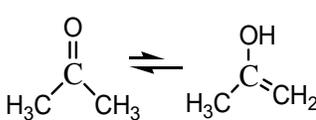
The proposal that an exocyclic double bond in 5-membered systems is more stable toward changes involving loss of the exocyclic double bond than the corresponding exocyclic double bond in 6-membered ring systems was supported by higher heat of hydrogenation of cyclohexanone ( $\Delta H = -15.42$  kcal/mol) as compared to cyclopentanone ( $\Delta H = -12.50$  kcal/mol) [31].

Finally, it may be reasonable to state that cyclohexanone contains greater enol content than cyclopentanone. Heats of formation of the three ketones and their enol forms in the gas phase at 25°C were calculated by use of Benson and co-workers' second order approximation based on the law of additivity of group properties [32]. They were -53.10 kcal/mol for cyclohexanone, -54.50 for cyclopentanone, and -

51.70 for acetone, and the values of their enol forms were -37.01, -27.56 and -31.40 kcal/mol, respectively. The differences for reactions of enolization  $\Delta \Delta H_f^\circ$ , were 16.09 kcal/mol for cyclohexanone, 17.94 for cyclopentanone and 20.30 for acetone, while our calculated values, were 9.062, 12.719 and 14.536 kcal/mol, respectively. The present results are tabulated in Table 4 together with the results of Hine and Arata [10] and Benson et al. [32] for comparison.

Therefore, it can be seen from Table 4 that the value of the difference for the reaction of enolization ( $\Delta \Delta H_f^\circ$ ) of acetone in the gas phase ( $13.416$  kcalmol<sup>-1</sup>) is in better agreement with the recent experimental value ( $13.9$  kcalmol<sup>-1</sup>) [12,14] than with ab initio molecular dynamics calculation ( $11.8$  kcalmol<sup>-1</sup>) [16]. Also, the present work shows that the enol content of cyclohexanone > cyclopentanone > acetone, agrees with the works of Hine et al. [10] and Benson et al. [31] to a greater degree than the HF calculations performed by Noak [12].

**Table 4. Reactions of enolization ( $\Delta \Delta H_f^\circ$  in kcal/mol) in gas phase and aqueous solution by PM3 method**

Keto - Enol Tautomerism	$\Delta \Delta H_f^\circ$ in kcal/mol gas phase				$\Delta \Delta H_f^\circ$ in kcal/mol aqueous solution
	9.062 <sup>a)</sup>	10.13 <sup>b)</sup>	16.09 <sup>c)</sup>	15.6 <sup>d)</sup>	12.113 <sup>a)</sup>
	12.719 <sup>a)</sup>	11.66 <sup>b)</sup>	17.94 <sup>c)</sup>	20.7 <sup>d)</sup>	14.753 <sup>a)</sup>
	13.416 <sup>a)</sup>	11.98 <sup>b)</sup>	20.30 <sup>c)</sup>	18.8 <sup>d)</sup>	16.970 <sup>a)</sup>

a) this work b) Ref [10] c) Ref [31] d) Ref [12]

### 3. CONCLUSION

It can be concluded that the enol contents of the investigated compounds follow the order cyclohexanone > cyclopentanone > acetone. Our efforts agree with the works of Hine and Arata, Gero and Schwarzenbach, but differ from Bell's observed order cyclopentanone > cyclohexanone > acetone. Dubois et al. [11] have shown that cyclohexanone exhibits greater enol content than cyclopentanone.

Experimental data show that the keto form of acetone is thermodynamically more stable than its enolic form. Ultraviolet, Infrared, NMR and X-ray spectroscopy show the preference of five-membered rings to exhibit exocyclic double bonds rather than an endocyclic double bond as does cyclohexanone. The present results were supported by calculations of equilibrium constants (K) for the enolization of ketones in the gas phase and aqueous solution using the PM3 method. Equilibrium constant (K) values were found to decrease from cyclohexanone to cyclopentanone and acetone, indicating a decrease in the enol forms of ketones. This agrees with the works of Hine et al. [10], Guthrie, Dubois et al. [11] and Kresge. The enol content of cyclohexanone in aqueous solution (Dubois et al. [11]) is  $2 \times 10^{-5}$  whereas Kresge reported a lesser value ( $4.1 \times 10^{-7}$ ). Our PM3 calculations in aqueous solution of the enol content of cyclohexanone shows a value of  $1.0 \times 10^{-6}$ . In general, DFT derived enol contents of ketones in the gas phase show lower values than PM3 calculations.

Calculations have also shown that the degree of enolization for cycloalkanes is a function of ring size. Likewise and in agreement with our previous work, the enol content trend we determined is supported by strain energy calculations (PM3 and DFT), where enol content becomes more favorable with increasing ring size. Furthermore, the electrostatic attraction between the carbonyl carbon and the  $\alpha$ -carbon decreases when going from 5-membered ring to 6-membered ring, suggesting an increase in destabilization of the ketone tautomer in going from the 5-membered ring to 6-membered ring. This agrees with our previous work on cyclopropanone, cyclobutanone and cyclopentanone where the electrostatic attraction decreases from going from 3-membered ring to 4-membered ring and 5-membered ring.

Since equilibrium [enol] are needed to permit interpretation of the rates of ketone halogenations at a very low [halogen], where the reaction between enol and halogen becomes rate-determining, theoretical calculations are needed to give more insight into keto-enol tautomeric behavior of this class of cycloalkanes.

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### COMPETING INTERESTS

Authors have declared that no competing interests exist.

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