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A New Specific Mechanism for the Acid Catalysis of the Addition Step in the Baeyer–Villiger Rearrangement

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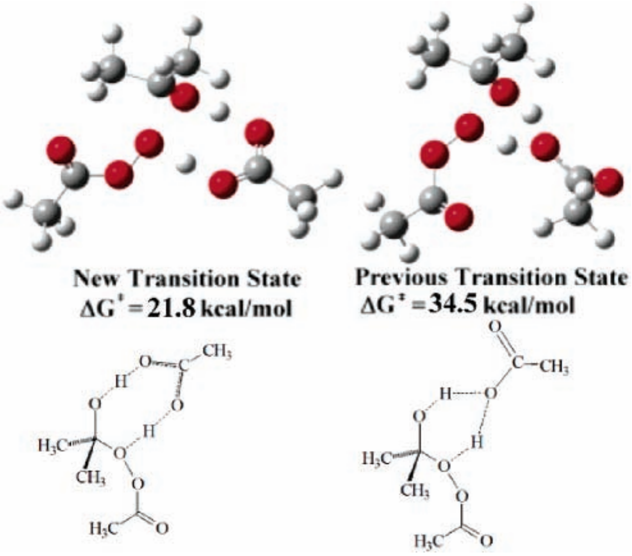
ABSTRACT

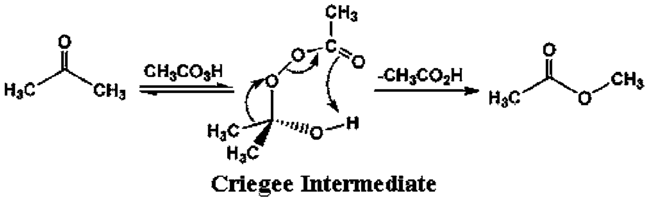


A new transition state of the addition step in the Baeyer–Villiger reaction was found. The role of proton acceptor is played by the carbonyl oxygen atom, and the free energy barrier is 12.7 kcal/mol lower than that previously reported. This finding changes the mechanism for the acid catalysis and could be of interest for similar reactions in which it is known that such catalysis occurs, especially in nonpolar solvents.

The Baeyer−Villiger (BV) reaction, a process by which ketones are converted into esters or lactones,[1] is of great significance in organic synthesis. As a result, it has been extensively studied experimentally for about 100 years, and it is still the subject of many publications.[2−4]

The basic mechanism of the Baeyer−Villiger reaction has been well-known since 1948.[5] The reaction occurs in a two-stage mechanism (Scheme 1). In the first step, the carbonyl addition of a peroxyacid to ketones produces a tetrahedral

Scheme 1. Baeyer−Villiger Reaction



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adduct called the Criegee intermediate. The second step is the migration of the alkyl or aryl group from the ketone moiety to the nearest peroxide oxygen in the intermediate.

The latter step is accepted to be the rate-determining one, involving a concerted mechanism; namely, the migration is simultaneous with the departure of the acid group.[6]However, some kinetic results for the reaction have demonstrated ambiguity in the rate-determining step depending on the substrate, catalyst, and so forth.[7−12]

Several theoretical attempts have been made to explain the mechanism in more detail.[13−19] To the best of our knowledge, the complete reaction, including addition, migration steps, and Brønsted acid catalysis, has only been studied in 1997 by Okuno[16] and very recently by Grein et al.[19] From ref 16, despite quite large ΔG barriers, it seems that the mechanism was adequately described from a qualitative point of view.

Unexpectedly, the work of Grein et al., after a considerable improvement in the level of calculations for different substrates, but modeling essentially the same stationary points as in Okuno's work, shows results that in our opinion seem to be in contradiction with experimental evidence. The most important contradiction is that the authors obtained ΔG barriers as large as 45 kcal/mol for the catalyzed addition step. These ΔG values are too high to expect appreciable rate coefficients at common reaction temperatures.

They also obtained a very large difference between the barriers of the first and second steps and concluded that the first step is the rate-determining one, at least for the substrates modeled. However, a difference of more than 15 or 25 kcal/mol (depending on the reference energy for the second step: reactants or Criegee intermediate) between both barriers seems to be conclusive for any substrate, and this conclusion, not done by the authors, would be in contradiction with previous evidence.[7−12]

These facts point to a possible overestimation of the ΔG barrier in the first reaction step. In an attempt to clarify these discrepancies, we have explored the potential energy surface of the reaction of acetone with peracetic acid catalyzed by acetic acid, looking for an additional transition state with lower energy that will therefore ensure more reliable ΔG reaction barriers for the first step. For comparison, the uncatalyzed reaction, as well as the reaction catalyzed in a previously proposed way,[16,19] were modeled. To perform these calculations in a fast and qualitatively reliable way that would allow the comparison with previous results, the B3LYP functional was chosen. We have performed the geometry optimizations with the 6-311G(d,p) basis set in the gas phase. The energy results were improved by single-point calculations with the same functional and the 6-311++G(d,p) basis set, including the solvent effects (on electronic energies) by the SCI-PCM continuum model, using dichloroethane as solvent. All the calculations were performed with the Gaussian 03[20] program. To propose results that can be compared with other theoretical works and with possible experiments, we have reported three different values of ΔG. The first one is, apparently, similar to that reported in ref 19, which was obtained by adding thermodynamic corrections in gas phase to the electronic energy + SCI-PCM solvent correction, but using 1 atm as standard state, which is the correct standard state for gas phase. The second one is similar to the approach used in ref 17 (i.e., we used 1 M as the most appropriate reference state for solution). To do that, it is necessary to multiply the partition functions at 1 atm for the molar volume at the reference temperature. As a consequence, the ΔG values decrease in 1.89 and 3.78 kcal/mol for bimolecular (uncatalyzed) and termolecular (catalyzed) reaction, respectively, at 300 K.

In addition, we also used the approach proposed by Benson,[21] according to which the ratio between the reactions in solution and in gas phase, in nonpolar solvents, is:

$$R \cong \frac{n\,10^{2n-2}}{e^{n-1}} \tag{1}$$

but the author previously assumed that:

$$R \cong \frac{K_x(\mathrm{sol})}{K_x(\mathrm{gas})} \equiv \frac{\exp\left(\dfrac{-\Delta G_{\mathrm{sol}}}{RT}\right)}{\exp\left(\dfrac{-\Delta G_{\mathrm{gas}}}{RT}\right)} \tag{2}$$

Combining expressions 1 and 2, it is evident that:

$$\Delta G_{\mathrm{sol}} \cong \Delta G_{\mathrm{gas}} - RT[\ln(n\,10^{2n-2}) - (n-1)] \tag{3}$$

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Table 1. Enthalpies and Free Energies Including SCI-PCM Correction (in kcal/mol) of the Different Transition States (TS) and Criegee Intermediate, Relative to Reactants

	1 atm[a]		1 M[b]	
system	ΔH	ΔG	ΔG_{1M}	ΔG_{1MFV}[c]
TS uncatalyzed	33.5	45.8	43.9	41.3
TS catalyzed (previous)	18.9	43.2	39.4	34.5
TS catalyzed (new)	5.8	30.5	26.7	21.8
Criegee	−0.1	13.7	11.8	9.2

[a] Using standard state of 1 atm as calculated by Gaussian program. [b] Using standard state for solution of 1 M. [c] Using, additionally, the method of free volume corrections to liquid phase proposed by Benson.[21]

Accordingly, ΔG_{sol} at 300 K decreases in 2.56 and 4.95 kcal/mol for a bimolecular ($n = 2$) at 300 K and for termolecular ($n = 3$), respectively, with respect to ΔG_{gas}. This approach was previously used in ref 16, but apparently the authors used the standard state of 1 atm instead of 1 M. In Table 1, we have tabulated all ΔG values relative to the reactants.

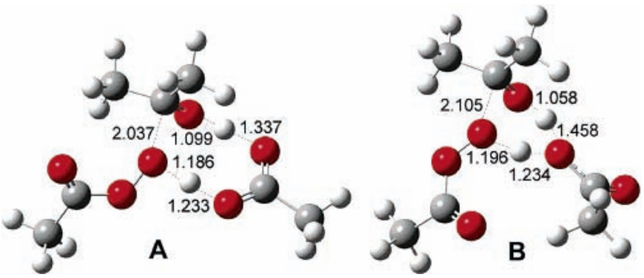

Figure 1. Molecular graphics and main geometrical parameters of the new (A) and previous (B) transition states.

Figure 1A shows an alternative transition state (TS) for the addition step of the reaction under study. The main difference with the previously proposed transition state, shown in Figure 1B, is that in the new one the proton acceptor is the carbonyl oxygen. This structural difference leads to a change in ΔG of 12.7 kcal/mol (Table 1 and Figure 2). This energy drop is, in our opinion, large enough to exclude the previously proposed transition state and the conclusions derived from it. Obviously, the TS for step 2 including the catalyst should be modeled assuming the newly proposed mechanism. These calculations are in progress.

The obtained ΔG barrier of 30.5 kcal/mol is 12.7 kcal/mol lower than the one previously reported for a similar system. The previous value seems to be quite large even after the inclusion of the thermodynamic corrections for the liquid phase. As shown in Figure 2, we obtained a ΔG barrier of 21.8 kcal/mol that which seems to be reliable for a reaction catalyzed with acetic acid, which is a very weak acid catalyst not used in practice. The calculations using trifluoroacetic acid are in progress.

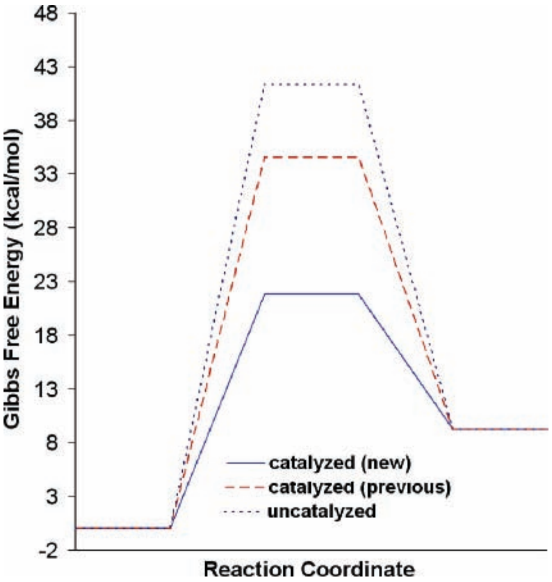

Figure 2. Relative free energies for the first step of the Baeyer−Villiger reaction including solvation electronic energies according to the SCI-PCM model 1 M standard state and thermodynamic corrections to liquid phase.

In our opinion, a detailed mechanism for the concerted general acid catalysis has not yet been clearly established. Thus the previous attempts to find a reasonable TS have failed. We have been successful in finding a TS for which more reasonable energy barriers are obtained. Our study could be of interest for similar addition reactions for which it is known that a general acid catalysis occurs, especially in nonpolar solvents.

The results of ΔG reported here, to the best of our knowledge, are lower than any other previously reported. We are not aware of any experimental data on the kinetics of the reaction of propanone with peracetic acid catalyzed by acetic acid that could be compared with our results. Moreover, we have modeled here the first step of a complex mechanism; any comparison with kinetics of the full reaction could lead to wrong conclusions. We are currently modeling the second step, catalyzed by acetic acid, and also the full mechanism using trifluoroacetic acid as a catalyst. The upcoming results, which hopefully will be comparable with available experimental data, are intended to be reported in a further article.

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