

DSM Science & Technology Awards 2006

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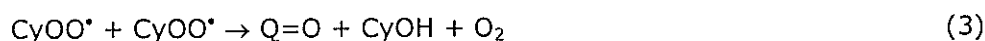
Mechanism of the cyclohexane autoxidation elucidated

1. Introduction

During the doctoral work of the candidate, the liquid-phase radical chain autoxidation of cyclohexane (CyH) was investigated in great detail. This important industrial process (1 MT/yr) accounts for the production of cyclohexanone (Q=O, Q = 1,1-cyclohexylene biradical), the most important intermediate in the production of polyamides like nylon-6 and nylon-6,6.¹ A major technological disadvantage is the low conversion of the alkane substrate to ensure a high selectivity and to minimize by-products. Chain-initiating radicals are thought to originate in the homolytic dissociation of CyOOH (reaction 1).



Up to now it was assumed that the chain propagation (reaction 2) and the chain termination (reaction 3) account for the production of hydroperoxide (CyOOH), and ketone plus alcohol (CyOH), respectively.¹



However, given the large chain-length (= rate of propagation / termination) of ≈ 50 , such a mechanism would produce predominantly CyOOH, and barely any CyOH and Q=O. This is at odds with the experimental observations. Figure 1 clearly identifies CyOOH as a primary reaction product, whereas CyOH and Q=O are secondary products which must however also originate from fast propagation reactions.

The precise chain mechanism, responsible for the production of the major products, as well as the by-products, was critically reinvestigated by means of complementary experimental and computational methods. Rate constants of the different reaction paths were calculated using Multi-Conformer Transition State Theory (MC-TST) based on quantum chemical energy- and vibrational/rotational data, and were fully confirmed by new experimental observations.

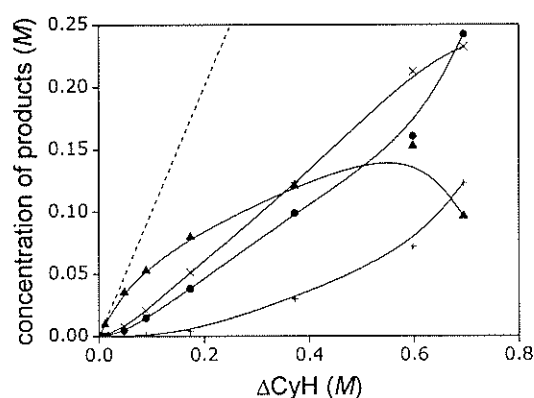


Figure 1. Evolution of the products as a function of the CyH conversion at 145 °C (▲: CyOOH, ×: CyOH, ●: Q=O, +: by-products, mainly adipic acid).

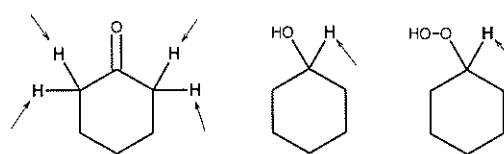
2. Main findings of the work

a) TST evaluation of the rate constant of the $\text{CyOO}^\bullet + \text{CyH}$ reaction

As this is the crucial propagation reaction in the overall mechanism, and several non-consistent rate expressions can be found in literature, we theoretically studied its kinetics in great detail. For both the reactants, and the Transition State (TS), several conformations (rotamers) exist; all of them need to be taken into account when calculating the thermally weighted partition functions. These partition functions are used as an input for the MC-TST calculation. The (hindered) internal rotations in the TS, were found to have a large positive impact on its partition, and thus on the rate constant. In our state-of-the-art approach,² we described appropriately those (hindered) internal rotations, included all thermally populated conformers, and took into account an asymmetric-barrier tunneling factor. The result is a rate constant which agrees within a factor of 2 with experimental values. The rate constant can be represented well by the Arrhenius equation $8.8 \times 10^{12} \text{ M}^{-1} \text{ s}^{-1} \times \exp(-17.8 \text{ kcal/mol} / RT)$, which can be used confidently in a wide T -range. Indeed, this expression agrees very well with the known rate expression for the analogous reaction $\text{CH}_3\text{OO}^\bullet + \text{C}_3\text{H}_8 \rightarrow \text{CH}_3\text{OOH} + i\text{-C}_3\text{H}_7^\bullet$: $2.0 \times 10^{12} \text{ M}^{-1} \text{ s}^{-1} \times \exp(-17.1 \text{ kcal/mol} / RT)$, considering the number of abstractable H-atoms. It is worth noting that the derivation of the rate constant of a reaction featuring hindered internal rotations in the TS is at the fore-front of first-principles kinetics, accomplished until recently only for much smaller systems such as $^\bullet\text{OH} + \text{CH}_4$.

b) Relative rate constants for the abstraction of αH -atoms

Next we determined, from first principles, the rate constants for αH -abstraction by CyOO^\bullet from the main products, CyOH , CyOOH and $\text{Q}=\text{O}$, relative to CyH . The αH -atoms are indicated in scheme 1.



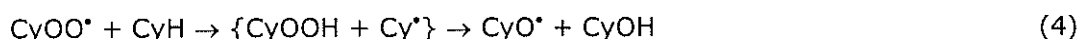
Scheme 1. αH -atoms in $\text{Q}=\text{O}$, CyOH and CyOOH .

It appears from our theoretical analysis that $\text{Q}=\text{O}$ reacts only 5 times faster than CyH , although it was assumed to be the predominant side-reaction and thought to produce all ring-opened by-products such as adipic acid (figure 1). CyOH is predicted to react 10 times faster than CyH . When monitoring the consumption of initially added model ketones (cyclopentanone and 3-pentanone) and alcohols (cyclopentanol and 3-pentanol), we reproduced those relative rate constants

experimentally,³ attesting the soundness of our approach. Exactly the same computational procedure predicts CyOOH to react 50 times as fast as CyH, and thus puts forward CyOOH as a very reactive intermediate that should yield much of the end-products. Striking enough, this fast α H-abstraction from CyOOH was hitherto entirely overlooked.

c) Products of the CyOO + CyH reaction*

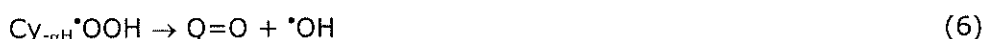
Before the initially formed Cy* radical is able to add O₂ to yield the main chain propagating radical, CyOO*, the {CyOOH + Cy*} products must first diffuse out of the solvent cage surrounding these products (fraction *p*). This is occurring at a rate of $\approx 8 \times 10^9 \text{ s}^{-1}$ at 145 °C. However, the caged products can also react *via* the hitherto overlooked cage-reaction (4), producing CyO* + CyOH, which is actually accounting for a small fraction of the reaction flux ($k \approx 2.5 \times 10^8 \text{ s}^{-1}$ at 145 °C) (fraction *q*).



This channel thus explains for the first time the previously observed direct formation of CyOH from CyH.

d) Products of the fast CyOO + CyOOH reaction*

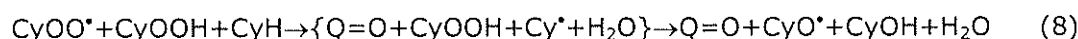
The primary product of reaction (5), Cy- α H*OOH, was shown by us to decompose immediately to Q=O and *OH, reaction (6).⁴



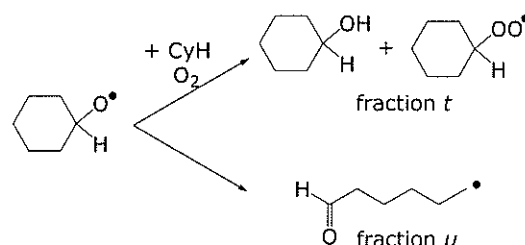
Given the rate constant of reaction (5), relative to the CyH propagation ($k^{\text{CyOOH}}/k^{\text{CyH}} = 50$), this reaction constitutes the most important ketone source. The *OH radical will rapidly abstract a H-atom from CyH.



Reactions (5) and (6) contribute to an exothermicity of more than 60 kcal/mol. This large amount of energy causes a nano-sized hot-spot, steering the fate of the primary cage products, {CyOOH + Q=O + H₂O + Cy*}. Indeed, they can either diffuse out of the solvent-cage and subsequently Cy* can add O₂ (fraction *r*), or a cage reaction analogous to reaction 4 can occur (reaction 8, fraction *s*). In sharp contrast to the unactivated, this activated cage-reaction accounts for 70 % of the reaction flux, a consequence of the hot-spot ($\sim 800 \text{ K}$).^{2,3}



Reaction (8) is identified as the major source of not only CyOH, but also of ring-opened by-products, as a large fraction of the CyO[•] radicals decompose *via* β C-C cleavage, forming ω-formyl radicals (fraction *u*, scheme 2); the other fraction reacts with CyH to yield CyOH (fraction *t*).



Scheme 2. Pathways for the CyO[•] radical.

This straightforward path relegates the currently assumed by-product formation from Q=O to a side-role, as we already showed Q=O to be significantly less reactive than previously assumed.³

e) The co-oxidation of CyOH

After the moderately fast αH-abstraction from CyOH, the [•]Cy_ωH radical will add O₂ and form a α-hydroxyalkylperoxyl radical, Q(OH)OO[•]. Hitherto it was assumed that this radical will abstract a H-atom from the CyH substrate. We demonstrated that Q(OH)OO[•] decomposes much faster to Q=O + HO₂[•], in an equilibrium reaction, strongly shifted towards the products.⁵ As HO₂[•] terminates very fast with ROO[•] radicals, CyOH co-oxidation slows down the overall oxidation rate.

f) Experimental verification

Scheme 3 summarizes the most important reactions proposed in our new mechanism.

Based on this mechanism, we derived eq. 1 from a detailed CyOOH balance at low conversions (up to ≈2%):

$$\frac{[CyOH]}{[CyOOH]} \approx \frac{q(1+t)}{p} + \frac{s(1+t')}{p} \times \frac{[Q=O]}{[CyOOH]} \quad [\text{Eq.1}]$$

In figure 3 the experimental [CyOH]/[CyOOH] ratio is plotted against the [Q=O]/[CyOOH] ratio; it is seen that Eq. 1 is obeyed for conversions even up till 3%, confirming the underlying mechanism, and providing an estimation for the values $p \approx 0.95$ and $q \approx 0.05$, $s \approx 0.7 \pm 0.2$ and r at $\approx 0.3 \pm 0.2$.

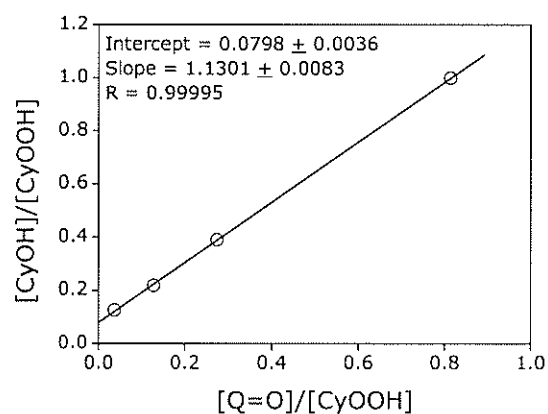


Figure 2. Plot of the [CyOH]/[CyOOH] ratio versus [Q=O]/[CyOOH]; validation of Eq. 1, derived from our new reaction mechanism.

g) The formation of by-products

One of the crucial questions yet to answer is which specie – either Q=O as thought in literature, or CyOOH as evidenced by our mechanism – is causing the majority of ring-opened by-products. Therefore we evaluated the amount of by-products that can effectively be formed from Q=O and CyOOH respectively.³ As can be seen from figure 4, Q=O can only explain some 20-30% of the observed by-products, whereas the majority of by-products originate from CyOOH.

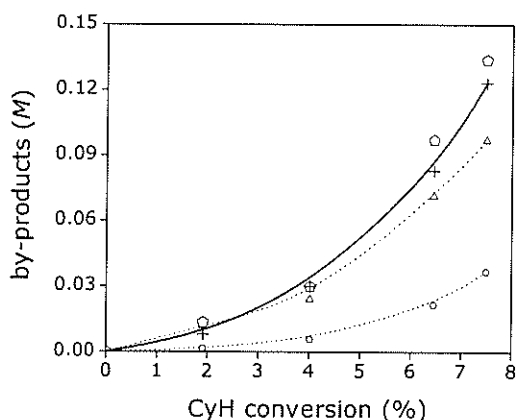


Figure 4. Modeled (Δ) and experimental (+) acid concentration: contribution of Q=O (o) and of CyOOH (Δ).

h) The intrinsic autocatalytic mechanism of the CyH autoxidation

More recently we also unraveled the intrinsic autocatalytic mechanism of the CyH autoxidation.⁶ Although it was known that "ketones light off the reaction", the reason remained rather enigmatic. From the shape of the initial O₂ consumption, we were able to measure for the first time the pronounced initiation enhancement by Q=O, as well as the pure initiation. The hypothesis of a labile perhemiketale molecule from CyOOH and Q=O was found to be many orders of magnitude too slow.

We found that the \cdot OH radical breaking away from a nearly dissociated CyO-OH molecule, can abstract a α H-atom from Q=O via a loose Transition State. The theoretically predicted rate (MC-TST) of this process agrees quantitatively with our experimental observations.⁶ This process is much more efficient in generating radicals than the homolytic dissociation reaction (1) as it quasi precludes in-cage-recombination of nascent radicals.

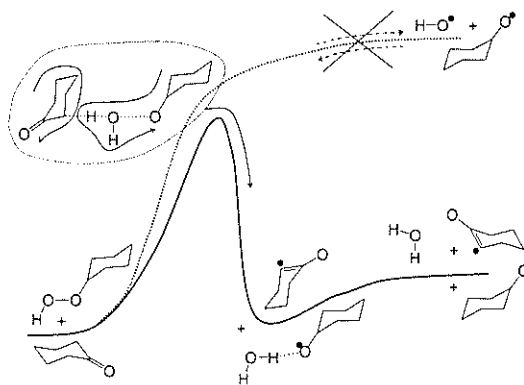


Figure 5. Comparison the newly proposed bimolecular initiation reaction (see text) and the homolytic dissociation of CyOOH.

In addition to this, we found strong evidence that even the "pure" CyOOH dissociation is in fact a bimolecular reaction involving one of the C-H bonds of CyH.

Briefly summarized, this studied revealed that Q=O and CyOH are not formed in the chain-termination reaction as assumed till now, but in the fast overlooked CyOOH propagation. A large fraction of the CyO* radicals, also formed from CyOOH, ring-open to ω -formyl radicals, and are identified as the precursors of by-products. We also unraveled the true nature of the autocatalytic mechanism as the ketone product was found to assist in the chain-initiation.

i) Preliminary achievements of the mechanism

Apart from the fact that the new insights in the CyH autoxidation will allow better process optimization, and understanding of catalysts action,⁷ they also allowed us to design new, environmentally friendly, catalytic systems.⁸ Here, inert H-bond acceptors, such as Teflon and perfluorodecaline (PFD), instead of soluble Co salts, catalyze not only the chain initiation reaction, but also the CyOOH-propagation. This results in a high Q=O/CyOOH ratio (see table 1) as sought in industry, eliminating the need for a separate deperoxidation step.

Table 1. Effect of PFD on the autoxidation selectivity of cyclohexane at 130/145 °C for various CyH conversions.

mL PFD	Conv. (%)	Q=O (%)	CyOH (%)	CyOOH (%)	By-products (%)
0.0 [a]	3	23.5	31.0	40.0	5.5
0.0 [a]	4	26.5	33.0	32.5	8.0
0.5 [a]	3	32.0	30.0	33.0	5.0
2.5 [a]	4	54.5	28.0	8.0	9.5
0.0 [b]	5	35.0	35.0	19.0	12.0
2.0 [b]	5	49.0	31.5	6.5	13.0

[a] 145 °C [b] 130 °C

3. References

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