

Supporting Information

Photochemical Reactions of Cyclohexanone: Mechanisms and Dynamics

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Table S1: relevant experimental studies of gas-phase photochemistry of cyclohexanone. The reaction channels and quoted yields refer to Figure 1.

Reference	Radiation source	Observations and/or quantum yields (Φ)
Bamford and Norrish (1938)	Broadband radiation from a high-pressure Hg lamp	CO + [cyclopentane or 1-pentene] (channels b and c) identified as major products (87%); channel d yielding C ₂ H ₄ +C ₃ H ₆ +CO found to be less important (13%)
Benson and Kistiakowsky (1942)	Broadband radiation from a high-pressure Hg lamp	Channels (b) and (c) dominate (98%) with 3:1 ratio of the cyclopentane:1-pentene; the C ₂ H ₄ +C ₃ H ₆ +CO channel d shown to be minor (2%)
Blacet and Miller (1957)	253.7 nm, 265.4 nm, 313 nm	Channels (b) and (c) dominate; yield of 1-pentene higher than that of cyclopentane; minor yield of C ₂ H ₄ +C ₃ H ₆ +CO (channel d). The quantum yields increase at higher temperature and lower wavelengths.
Srinivasan (1959)	313 nm	5-hexenal (channel e) identified for the first time as a significant product with the yield exceeding the yield of CO; remains a major product in liquid phase photolysis
Srinivasan and	313 nm	2-methyl-cyclopentanone (channel f) identified in the

Cremer (1965)		liquid phase photolysis of cyclohexanone
Scala and Ballan (1972)	106.7 nm, 123.6 nm, 147 nm	A number of additional products found in addition to the ones shown in Figure 1; the ratio C ₂ H ₄ /CO and H ₂ /CO increasing and 1-pentene/CO and cyclopentane/CO decreasing at lower wavelengths.
Shortridge and Lee (1970)	Photosensitization by triplet benzene and 248-313 nm photolysis	Cyclopentane and 1-pentene (channels b and c) form on a singlet potential energy surface, while 5-hexenal (channel e) has a triplet precursor.
Shortridge and Lee (1973)	174.5 and 193.1 nm	Evidence found for the occurrence of C _α -C _β bond cleavage at low pressures.
Baulch et al. (1981)	Photosensitization by He(6 ³ P ₁) and 253.7 nm photolysis	Same products observed in photosensitization as in direct photolysis implying that photolysis is occurring on the triplet surface.
Hoops et al. (2009)	Irradiation with λ>200 nm of products of reaction between cyclohexene and ozone	1-hexen-1-one ketene product detected, believed to result from photolysis of cyclohexanone.

Table S2: ADC(2) vertical excitation energies for the twist-boat conformer of cyclohexanone. The percentage in the third column refers to the fractional weight of the dominant excited state wavefunction in this transition.

State	Energy (in eV)	Orbital transition	Description	Oscillator strength	Dipole moment (Debye)
1	4.17	HOMO → LUMO 62 %	n(oxygen) → π*(C=O)	0.0000	0.95
2	7.42	HOMO → LUMO + 1 62 %		0.0090	4.84
3	8.28	HOMO → LUMO + 2 66 %		0.0038	4.82

Table S3: OM2/MRCI vertical excitation energies for the twist-boat conformer of cyclohexanone.

State	Energy (in eV)	Orbital transition	Description	Oscillator strength	Dipole moment (Debye)
1	3.91	HOMO → LUMO 92 %	n(oxygen) → $\pi^*(C=O)$	0.0007	3.44
2	6.37	HOMO → LUMO + 1 90 %		0.2880	1.64
3	7.31	HOMO - 2 → LUMO 98 %		0.0205	11.26

Table S2 summarizes the ADC(2) vertical excitation energy of the twist-boat conformer. Table S3 shows for comparison the OM2/MRCI vertical excitation energy. The vertical excitation energies reported here are very similar to those of the global minimum conformer (chair conformer). The identity of the first excited state predicted by ADC(2) and OM/MRCI is a $n \rightarrow \pi^*$ transition. This transition is localized on the carbonyl group, therefore it does not change much due to geometric changes. The higher transitions can be described by orbital description that are different from those from the chair conformer and seem to be more conformer dependent.

The comparison here has been done for validation purposes of the OM2/MRCI method. The overall agreement between properties predicted by ADC(2) and OM2/MRCI is very well. We therefore believe that the semiempirical potential energy surface is of sufficient accuracy for the photochemical dynamics simulation.

Table S4: Statistics of different reaction channels observed in the dynamics following excitation to the S_1 state

Reaction Channel	Number of trajectories (out of 76 total)	Percentage (%)
Ring opening	38	50
H transfer or H detachment reactions	13	17
Ring opening and CO detachment	11	15
Unreactive trajectories	6	8
Ring opening and recombination	4	5
Other different rare events	4	5