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Density Functional Theory Study of The Reaction Mechanism of the Elimination of n-butyrophenone

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Abstract
The reaction mechanism of elimination of n-butyrophenone has been investigated by theoretical approaches using density functional theory B3LYP/6-31+g(d) level of theory in the gas phase . The mechanism for elimination reaction is Norrish type II. The proposed mechanism of elimination reaction of n-butyrophenone takes place via a six-membered cyclic transition state to give a mixture of (1-phenylethenol, which tautomerizes to acetophenone) and ethene. Analysis of the progress along the reaction coordinate, in terms of geometrical parameters suggest these reactions are dominated by the abstraction of a hydrogen atom from the g-carbon by the carbonyl oxygen to give the diradical, and together with an important cleavage of Ca-Cb bond in the transition state through a single-step reaction mechanism. The results indicate that the transition state has an intermediate character between reactants and products. According to the results obtained in the energy profile for the elimination of n-butyrophenone and in the Intrinsic Reaction Coordinate (IRC) analysis, the reaction is endothermic. The energy barriers of n-butyrophenone to form six-membered ring transition state (TS) was found to be 54.75 kcal mol-1 and the energy barriers to form products (1-phenylethenol and ethene) was found to be 20.25 kcal mol-1. The calculated kinetic and thermodynamic parameters are in reasonable agreement with the reported experimental values.

Keywords: n-butyrophenone, Six-membered ring transition state, Density Functional Theory.

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1. INTRODUCTION

Ketones are a major class of organic chemicals and are widely used as solvents. They are important in the chemistry of the atmosphere and in combustion systems from direct emissions and as intermediates[1,2]. Their photodissociation in the lower atmosphere results in formation of free radicals and may influence the atmospheric oxidation capacity. Ketones are also used as fuel tracers for monitoring fuel properties, such as, temperature, concentration, density, pressure, velocity, and distribution, using laser-induced fluorescence [1,2] and as fuel additives in reducing soot emissions [3,4] .

Chemical kinetics and dynamics of unimolecular reactions of isolated molecules in the gas phase are well understood [5,6]. The framework of a unimolecular process is often applied, at least as an idealization, to condensed phase processes although the effects of the environment on the process can be profound [7,8].

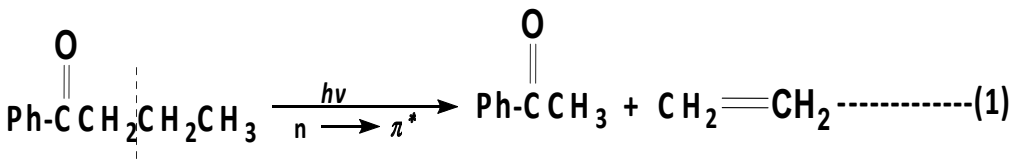
Photochemical reactions of ketones are initiated when a photon promotes an electron from a non-bonding (n) orbital to a π* antibonding orbital in the carbonyl group, forming an excited state. This excited state can then undergo one of several characteristic reactions: Norrish Type I (α-cleavage), which breaks a carbon-carbon bond adjacent to the carbonyl; Norrish Type II (intramolecular hydrogen abstraction), where a hydrogen atom is transferred to the carbonyl oxygen; or photoreduction, where the excited ketone abstracts a hydrogen atom from a solvent molecule. Other reactions include Paterno-Büchi cycloaddition to form oxetanes and rearrangement reactions like lumiketone and di-π-methane rearrangements. Photo induced hydrogen abstraction reaction, which is better known as the Norrish type II reaction, has been a highlight in the development of a general picture of how photochemical reactions occurs [9]. The rate constant for internal hydrogen abstraction depends on electronic configuration, on C-H bond strength or inductive substituent effects, and on conformational factors [9]. These factors will determine the observed product ratios of photoreactions where more than one product is possible [9].

Carbonyl compounds are widespread in the atmosphere. Certain carbonyls are directly emitted by various sources, but the vast majority of them are produced in the atmosphere by oxidation of hydrocarbons [10]. Photolysis is an important removal pathway for atmospheric carbonyls. In the lower atmosphere, where the availability of radiation is limited to a wavelength of above 290 nm, the photolysis of carbonyls is driven by their weak absorption band in the wavelength range 240–360 nm as a result of a dipole forbidden n →π* transition [10,11].

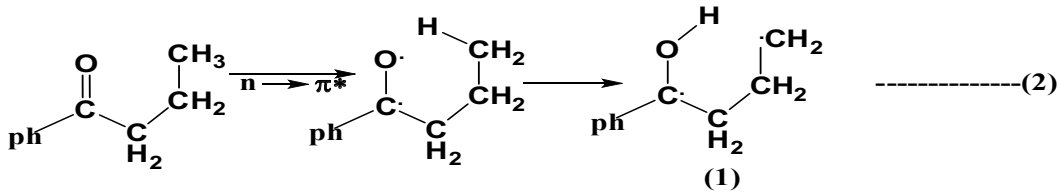
The initial photo excitation processes available to molecules with labile leaving groups, may directly populate a so-called $^1n\sigma^*$ or $^1\pi\sigma^*$ state, i.e., a state formed by promoting an electron from a non-bonding (n) or bonding π valence orbital to an antibonding σ* orbital [12, 13 ,14,15,16,17 and 18]. In many other cases, the primary photo excitation may involve a strongly absorbing π*←π transition; light-driven bond fission in such cases only occurs after non-adiabatic coupling between the ππ* state and an (n/π)σ* continuum.

The activation energies for singlet and triplet states of saturated ketones are about 80–85 and 75–80 kcal/mol, respectively, whereas of unsaturated ketones, these are in the range of 45–75 kcal/mol. For this reason, the photoreactions of saturated ketones occur in the UV region, 270–290 nm, and of unsaturated ketones in the UV region, 310–330 nm[19]. The excited carbonyl compounds have radical characters at both carbon and oxygen atoms of the carbonyl group, and hence most of their photoreactions proceed through radical intermediates. The important photoreactions of carbonyl compounds are the reduction of carbonyl compounds by hydrogen abstraction, fragmentation including the Norrish types I and II[19].

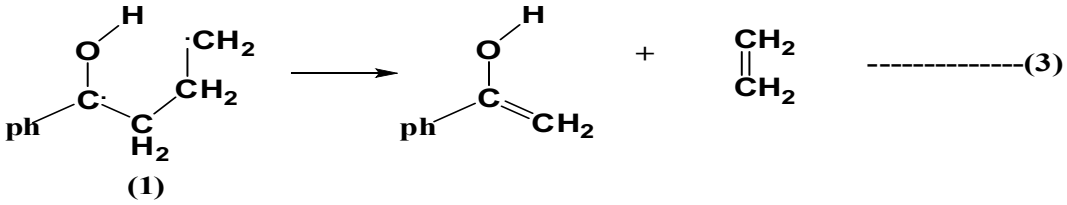
Photolysis of Ketones, that have at least one γ-hydrogen atoms on a chain connected to the carbonyl group such as *n*-butyrophenone in this pathway, undergoes the Norrish type II process (intramolecular elimination), as shown in equation (1) [20,21,22], the cleavage occurs at the Cα-Cβ bond to give, as the major product, phenyl ketone of shorter chain length and an alkene. Thus for *n*-butyrophenone is known to occur through the following pathways in equation (1):



This reaction occurs in an interesting way. Whatever the nature of the n →л* excited state, S1 or T1, the primary photochemical reaction is the abstraction of a hydrogen atom from the γ-carbon by the carbonyl oxygen to give the diradical (1), as in equation (2):



The subsequent dark reactions readily are understood as typical of diradicals, cleavage of diradicals (1) at Cα-Cβ gives ethene and 1-phenylethenol, as in equation (3), 1-phenylethenol which tautomerizes to acetophenone.



Although the reaction occurs from both the singlet and the triplet states of n, л* transition, the quantum yield from the singlet state is generally lower than that form the triplet state. In the our case which involve aryl-alkyl ketones, the reaction occurs only with the triplet state because aromatic ketones can undergo rapid intersystem crossing.

A large number of gas-phase unimolecular reaction, which have been studied, appeared to take place by way of 4-centre and 6-centre cyclic activated complexes [23].

Serinyel et al [24]. for example, have published on the combustion kinetics of 3-pentanone and used thermochemistry and kinetic parameters corresponding to studies on acetone in their model development. Several studies on the fundamental thermochemistry of the intermediate radicals on ketones or their elementary oxidation kinetics have recently appeared. Sebbar et al.[25]. published on the thermochemistry of 2-butanone and show that although the primary C−H bond on butanone adjacent to the carbonyl is similar to acetone, the secondary C−H bond energy is more than 5 kcal mol^{-1} weaker. Hudzik and Bozzelli [26] have also reported on thermochemical parameters of ketones series as a function of temperature and reveal problems with matching entropy and experimental data of heat capacity with vibration analysis using only frequencies from DFT and ab initio methods.

In this work, the mechanism of unimolecular elimination reaction of *n*-butyrophenone to give ethene and 1-phenylethenol which tautomerizes to acetophenone, will be discussed theoretically using density functional theory B3LYP/6-31+g(d) level of theory in the gas phase by means of the description of the energy, the geometry, and the stability of transition state structures involved in such reaction. This information provides a detailed energy profile for *n*-butyrophenone elimination, that supports results which have been obtained experimentally.

2. METHOD OF CALCULATIONS

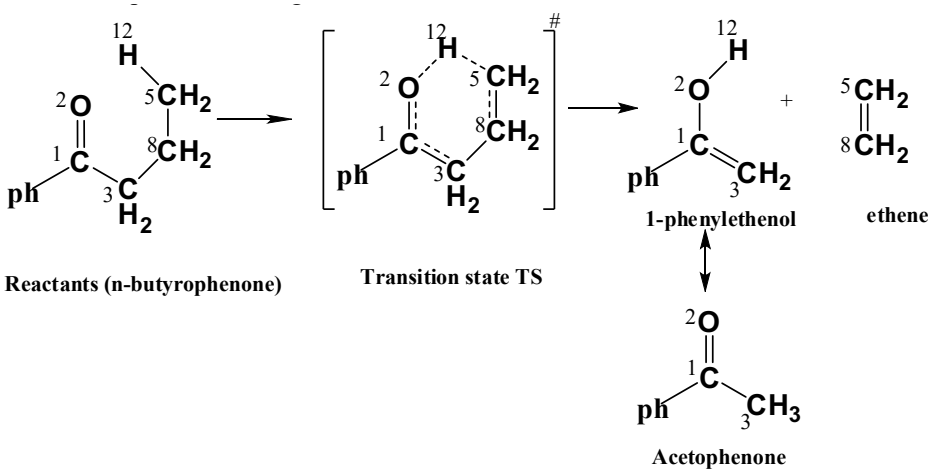
n-butyrophenone was chosen as model molecule to investigate the mechanism of intramolecular elimination reaction. The calculations were done with the Gaussian09 [27] software packages, at B3LYP/6-31+g(d) level. All structures were fully optimized in gas phase at the same mentioned method . The B3LYP/6-31+g(d) level of theory is widely used, efficient DFT approach for investigating hydrogen abstraction mechanisms and locating transition states (TS)[28,29]. It offers a good balance between computational cost and accuracy for characterizing structural and energetic parameters, including the inclusion of diffuse functions that are often necessary to describe radical species involved in hydrogen transfer.

The geometries of the reactants, intermediates, transition and products, involved in the reactions were all fully optimized by using the methods B3LYP/6-31+g(d). The structures thus obtained were subjected to vibrational analysis calculations toward their characterization as local minima (all positive force constants) or transition states (one imaginary force constant only). The Intrinsic Reaction Coordinate IRC[30] calculations for the later structures, were performed along the transition vector defined by the vibration mode of this imaginary frequency should be assess that the saddle point structure connected downhill the corresponding forward and backward minima. This methodology allowed the identification of the reaction intermediates and transition state structures along the reaction path. The standard state is 1 atm and 298.15 K, which are default in Gaussian calculations.

3. RESULTS AND DISCUSSION

The elimination reaction of ketones is a Norrish type II reaction, which generally is the photochemical intramolecular abstraction of a γ-hydrogen by the carbonyl group to produce a 1,4-biradical as a primary photoproduct through cyclic transition state.

The mechanism of intramolecular elimination reaction of *n*-butyrophenone to give ethene and 1-phenylethenol which tautomerizes to acetophenone as can be explained above in equations (1-3), scheme 1 shows the atoms directly involved in the reaction and the overall process. Figure 1 explains the energy profiles for the process in the gas phase with B3LYP/6-31+g(d). Tables 1 and 3 show the relative energies, ΔH°, ΔG° and ΔS° data for the structures involved, and table 2 shows the bond length for each steps of the structures of the reaction path from reactants to products in Angstrom.



Scheme 1: Proposed mechanism of Intramolecular elimination Reaction of *n*-butyrophenone

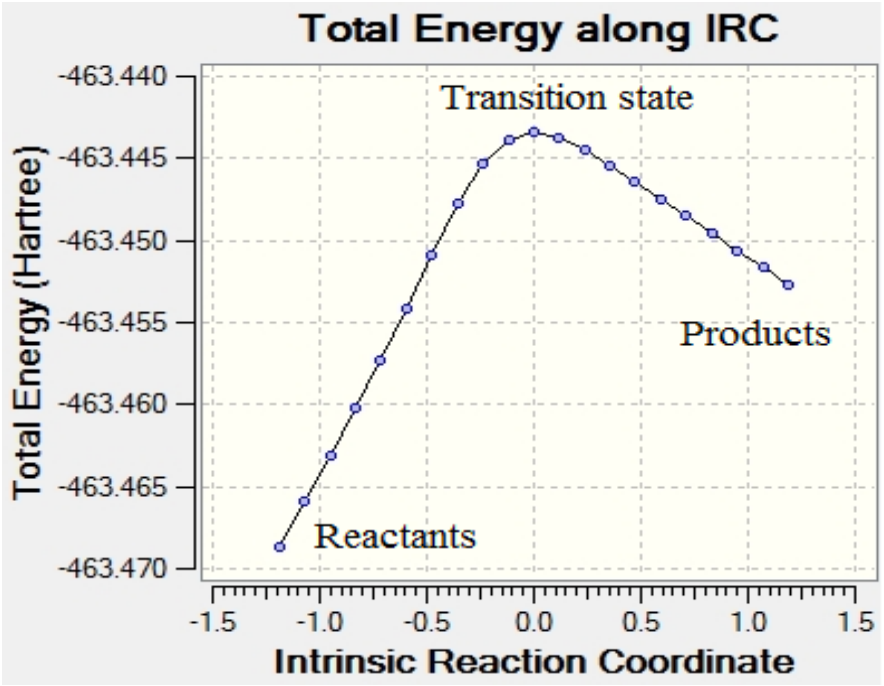


Figure 1. Intrinsic Reaction Coordinate (IRC) analysis of six-membered ring transition state using B3LYP/6-31+g(d) methods, Explained the energy profile for the elimination of *n*-butyrophenone, Energy for each of the structures in a.u.

Table 1. Energies (B3LYP) for each of the structures of the reaction path from the standard thermochemistry output of a frequency calculation [a]

Structure	ENERGY E(B3LYP)
Reactants[b]	-463.469
Transition state	-463.443
Products	-463.453

[a] The standard thermochemistry output calculations are available as supplementary material (see Table S2). Energy in a.u.
[b] Reactants, cyclic transition state-TS, and product respectively (refer to Scheme 1).

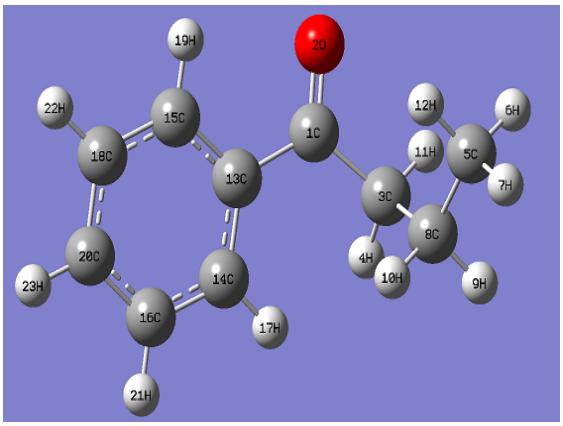
3.1 Six-membered ring Transition state Formation:

The starting point for this step process is structure 1(scheme1) where the incoming carbonyl oxygen (O2) of *n*-butyrophenone is the site of the intramolecular γ-hydrogen abstraction, where the hydrogen atom (H12) abstracted from the γ -carbon by the carbonyl oxygen (O2). The distance H12-O2 is 2.939 Å at the start in the reactant molecule (table 2 and scheme 1), which shortened to 1.165 Å in transition state molecule, simultaneously the bond H12…C5 (1.095 Å) in the reactant, stretched to 1.454 Å in the transition state, the bond C8…C5,which distance is 1.533 Å is shortened to 1.402 Å, partial formation of double bond between C8…C5 (Figure 2, table 2 and table S1), the carbonyl bond C1…O2 distance is 1.225 Å, which stretched to 1.314 Å i.e bond weakening and rehybridization in the transition state between C1…O2 (figure 2), simultaneously there is a partial formation of the double between C1…C3, from 1.523 Å to 1.388 Å. The bond between C3…C8, starts to break from 1.548 Å to 2.213 Å in the transition state (Figure 2, table 2 and table S1). The γ -hydrogen transfer to the oxygen atom has been shown to be intramolecular. This mechanism occurs via six-membered ring transition state TS as can be shown in figure 2. The calculated result of the vibrational analysis shows that there is only one strong imaginary frequency in the transition states, and the imaginary frequency of TS is −1235.525 cm^{-1}. The imaginary mode corresponds to γ -hydrogen transfer and C3…C8 bond cleavage, and the six membered ring cyclic transition state contraction. The transition state are verified by the intrinsic reaction coordinate (IRC) analysis, that is, TS connects directly the reactant and product in the reaction path as can be shown in figure 1. The reaction pathway includes only a one-step elementary reaction process, see figure 1.

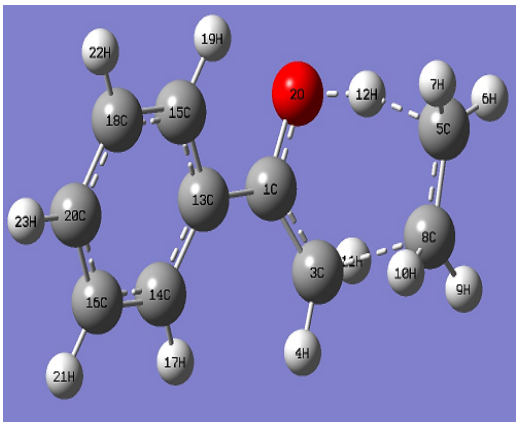
The energy barriers for the elimination reaction of *n*-butyrophenone to form six-membered ring transition state (TS) is 54.75 kcal mol^{-1} (table 3), downhill from these transition state structure, the system evolves to form products (scheme1) via the formation of an C5-C8 double bond and complete transfer of the (H12) to oxygen (O2), and complete breaking of C3-C8 bond to form ethene and 1-phenylethenol which tautomerizes to acetophenone. The energy barriers for the these products is equal 20.25 kcal mol^{-1} (table 3), scheme 1 and figure 2.

Table 2. Bond length for the structures of the reaction path from reactants to products for the bonds involved in six-membered transition state in Angstrom

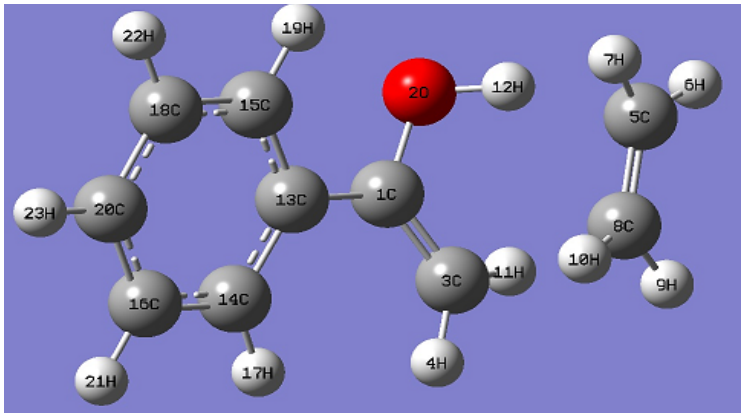
Bond length in Å	Reactants	Transition state TS	Products
O2…H12,	2.939	1.165	1.007 (in 1-phenylethenol)
H12…C5,	1.095	1.454	**1.757 (no bonding)**
C5…C8,	1.533	1.402	1.355 (in ethene)
C8…C3,	1.548	2.213	**2.376 (no bonding)**
C3…C1,	1.523	1.388	1.344(in 1-phenylethenol)
C1…O2,	1.225	1.314	1.354(in 1-phenylethenol)



Reactants



Transition state -TS



Products

Figure 2. Optimized structures of reactants, six-membered ring transition state-TS, and products calculated by B3LYP/6-31+g(d).

According to the results obtained above in the energy profile for the elimination of *n*-butyrophenone, figure 1, and Intrinsic Reaction Coordinate (IRC) analysis, and Table 3, the reaction is endothermic.

Table 3:Calculated energies of reactants, six-membered ring transition states, and products using B3LYP/6-31+g(d) in kcal mol^{-1} [a,b] of elimination of *n*-butyrophenone

Compound	ΔE kcal mol^{-1}	ΔG kcal mol^{-1}	ΔH kcal mol^{-1}	ΔS Cal mol^{-1}K^{-1}
Reactants[c]	0	0	0	0
Transition state	54.75	55.92	54.75	-3.93
Products	20.25	32.62	19.65	-43.49

[a] All structures were fully optimized. Cartesian coordinates of all structures are available as supplementary material(see Table S1).

[b] Energies reported relative to the sum of energies of separated reactants(see Table S2 in supplementary material).

[c] Reactants, cyclic transition state and product refer to Scheme 1.

If we consider the energy values (table 3) calculations (B3LYP) show that the initial elimination has energy barrier of 54.75 kcal mol^{-1}, less than that of 2-pentanone in our previous work (56.13 kcal mol^{-1} [31], whereas the potential energy barrier to form the product is 20.25 kcal mol^{-1}. This suggests that the elimination reaction of *n*-butyrophenone is endothermic and a single-step process. Similar conclusions for this type of reaction have been drawn from the theoretical and experimental results for other simple ketones [32] and theoretical results for 2-pentanone [31].

If Gibbs energy is considered, B3LYP calculations show barriers of 55.92 kcal $mol^{-1}$for elimination of *n*-butyrophenone to form six-membered ring transition state and 32.62 kcal mol^{-1} to form the ethene and 1-phenylethenol which tautomerizes to acetophenone.

4. CONCLUSIONS

On the bases of our elimination model of *n*-butyrophenone to form six-membered ring transition state, carbonyl oxygen(O2) is main role to which hydrogen transfer (H12) from γ -carbon to form biradical through six-membered ring transition state, which can be investigated by theoretical approaches using density functional theory B3LYP/6-31+g(d) level of theory in the gas phase.

Intramolecular elimination of *n*-butyrophenone take place by Norrish type II elimination reaction by a single-step reaction mechanism. According to thermodynamic point of view the reaction is endothermic reaction. Similar results for this type of reaction have been drawn from the theoretical results for 2-pentanone [31].

The energy barriers for the elimination reaction of *n*-butyrophenone to form six-membered ring transition state (TS) was found to be 54.75 kcal mol^{-1}, and the energy to form products ethene and 1-phenylethenol which tautomerizes to acetophenone was found to be 20.25 kcal mol^{-1}. From this work, we can conclude that theoretical investigations of mechanisms of the elimination reaction of *n*-butyrophenone improve the understanding of photoinduced hydrogen abstraction reaction, would be helpful to validate the proposed mechanisms in the literature and model mechanism of more complicated ketones.

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Conflict of Interest

The authors declare that there is no conflict of interests regarding the publication of this article.

SUPPLEMENTARY INFORMATIONS

Supplementary information (output results of B3LYP calculations) are available free of charge, on request.

5. REFERENCES

Schulz, C.; Sick, V. Tracer-LIF Diagnostics: Quantitative Measurement of Fuel Concentration, Temperature and Fuel/Air Ratio in Practical Combustion Systems. Prog. Energy Combust. Sci.2005, 31, 75−121.

Hanson, R. K.; Seitzman, J. M.; Paul, P. H. Planar Laser-Fluorescence Imaging of Combustion Gases. Appl. Phys. B: Laser Opt.1990, 50, 441−454.

Pepiot-Desjardins, P.; Pitsch, H.; Malhotra, R.; Kirby, S. R.;Boehman, A. L. Structural Group Analysis for Soot Reduction Tendency of Oxygenated Fuels. Combust. Flame 2008, 154, 191−205.

Hong, Z.; Davidson, D. F.; Vasu, S. S.; Hanson, R. K. The Effect of Oxygenates on Soot Formation in Rich Heptane Mixtures: A Shock Tube Study. Fuel 2009, 88, 1901−1906.

P. J. Robinson and K. A. Holbrook, Unimolecular Reactions, Wiley, New York, 1973.

R. G. Gilbert and S. C. Smith, Theory of Unimolecular and Recombination Reactions, Blackwell, Oxford, 1990.

N. J. Turro, V. Ramamurthy and J. C. Scaiano, Modern Molecular Photochemistry of Organic Molecules, University Science Books, Sausalito, CA, 2010.

Adam Campbell, Nikolas R. Dos Santos and Igor Alabugin, Photochemical Uncaging of Aldehydes and Ketones via Photocyclization/ Fragmentation Cascades of Enyne Alcohols:An Unusual Application for a Cycloaromatization Process, Molecules 2023, 28, 570,https://doi.org/10.3390/molecules28155704

Wagner, P. J.; Park, B. S. Org. Photochem. 1991, 11,227.

B. J. Finlayson-Pitts and J. N. J. Pitts, Chemistry of the Upper and Lower Atmosphere, Academic Press, 2000.

E. K. C. Lee and R. S. Lewis, Adv. Photochem., 1980, 12, 1.

Cronin, B., Nix, M. G. D., Qadiri, R. H., and Ashfold, M. N. (2004). High resolution photofragment translational spectroscopy studies of the near ultraviolet photolysis of pyrrole. Phys. Chem. Chem. Phys. 6, 5031–5041.doi: 10.1039/b411589

Ashfold, M. N. R., Cronin, B., Devine, A. L., and Dixon, R. (2006). The role of πσ∗ excited states in the photodissociation of heteroaromatic molecules. Science 312, 1637–1640. doi: 10.1126/science.1125436

Ashfold, M. N. R., King, G. A., Murdock, D., and Nix, M. G. (2010). πσ∗ excited states in molecular photochemistry. Phys. Chem. Chem. Phys. 12, 1218–1238. doi: 10.1039/B92170.

Devine, A. L., Cronin, B., and Nix, M. G. D. (2006). High resolution photofragment translational spectroscopy studies of the near ultraviolet photolysis of imidazole. J. Chem. Phys. 125:184302. doi: 10.1063/1.2364504

Nix, M. G. D., Devine, A. L., Cronin, B., and Ashfold, M. N. (2007). Ultraviolet photolysis of adenine: dissociation via the 1πσ∗ state. J. Chem. Phys.126:124312. doi: 10.1063/1.27128

Roberts, G. M., and Stavros, V. G. (2014). The role of πσ ∗ states in the photochemistry of heteroaromatic biomolecules and their subunits: insights from gas-phase femtosecond spectroscopy. Chem. Sci. 5, 1698–1722. doi: 10.1039/c3sc53175.

Marchetti, B., Karsili, T. N. V., and Ashfold, M. N. R. (2016). A 'bottom up', ab initio computational approach to understanding fundamental photophysical processes in nitrogen containing heterocycles, DNA bases and base pairs. Phys. Chem. Chem. Phys. 18, 20007–20027. doi: 10.1039/C6CP001.

Biswanath Dinda, Essentials of Pericyclic and Photochemical Reactions,2017, Springer

Photochemistry of Carbonyl Compounds,pp.241-275.

H. Nishiguchi, K. Yukawa, H. Yamashita, M. Anpo, J. Photochem. Photobiol. A 99 (1995) 1.

F.S. Wettack, W. Albert Noyes Jr., J. Am. Chem. Soc. 90 (1968) 3901.

H.E. O'Neal, R.G. Miller, F. Gunderson, J. Am. Chem. Soc. 96 (1974) 3351.

O'Neal HE, Benson SW (1967). A Method for Estimating the Arrhenius A factors for Four- and Six-centre Unimolecular Reactions, J. Phys. Chem. 71(9): 2903 - 2921.

Serinyel, Z.; Chaumeix, N.; Black, G.; Simmie, J. M.; Curran, H. J.Experimental and Chemical Kinetic Modeling Study of 3-Pentanone Oxidation. J. Phys. Chem. A 2010, 114, 12176−12186.

Sebbar, N.; Bozzelli, J. W.; Bockhorn, H. Thermochemistry and Kinetics for 2-Butanone-3yl Radical (CH3C(=O)CH·CH3) Reactions with O2. Z. Phys. Chem. 2011, 225, 993−1018.

Hudzik, J. M.; Joseph, W.; Bozzelli, J. W. Thermochemistry and Bond Dissociation Energies of Ketones. J. Phys. Chem. A 2012, 116, 5707−5722.

Gaussian 09 (2009) MJ Frisch; GW Trucks; HB Schlegel; GE Scuseria; MA Robb; JR Cheeseman; G Scalmani;V Barone; B Mennucci; GA Petersson; H Nakatsuji; M Caricato; X Li; HP Hratchian; AF Izmaylov; J Bloino; G Zheng; JL Sonnenberg; M Hada; M Ehara; K Toyota; R Fukuda; J Hasegawa; M Ishida; T Nakajima; Y Honda; O Kitao; H Nakai; T Vreven; JA Montgomery Jr; JE Peralta; F Ogliaro; M Bearpark; JJ Heyd; E Brothers; KN Kudin; VN Staroverov; R Kobayashi; J Normand; K Raghavachari; A Rendell; JC Burant; SS Iyengar; J Tomasi; M Cossi; N Rega; NJ Millam; M Klene; JE Knox; JB Cross; V Bakken; C Adamo; J Jaramillo; R Gomperts; RE Stratmann; O Yazyev; AJ Austin; R Cammi; C Pomelli; JW Ochterski; RL Martin; K Morokuma; VG Zakrzewski; GA Voth; P Salvador; JJ Dannenberg; S Dapprich; AD Daniels; Ö Farkas; JB Foresman; JV Ortiz; J Cioslowski; DJ Fox; Gaussian, Inc., Wallingford CT.

Pierre L. Bhoorasingh and Richard H. West, Transition state geometry prediction using molecular group contributions, Phys. Chem. Chem. Phys., 2015, 17, 32173-32182.

DOI: 10.1039/C5CP04706D.

Møller, K H, Otkjaer, R V, Hyttinen, N, Kurten, T C & Kjaergaard, H G, 'Cost-Effective

Implementation of Multiconformer Transition State Theory for Peroxy Radical Hydrogen Shift Reactions', Journal of Physical Chemistry A, 2016, vol. 120, no. 51, pp. 10072-10087. http://dx.doi.org/10.1021/acs.jpca.6b09370.

Fukui, K., "The path of chemical-reactions-The IRC approach," Acc. Chem. Res., 1981,14,363-68.

Musa E. Mohamed, Computational Reaction Mechanism Study of the Elimination of 2-pentanone, Journal of Computational Methods in Molecular Design, 2015, 5 (3):63-68

Eric W.-G. Diau, Carsten Kötting, and Ahmed H. Zewail, CHEMPHYSCHEM, 2001, 2, 273 -293.

Supplementary data

Density Functional Theory Study of The Reaction Mechanism of the Elimination of n-butyrophenone

Table S1: Bond length of reactants (n-butyrophenone), transition state and products (1-phenylethenol and ethene) using B3LYP/6-31+g(d) methods

n-butyrophenone		Transition state		1-phenylethenol		ethene	
Bond length		Bond length		Bond length		Bond length	
C(1)-O(2)	1.225	C(1)-O(2)	1.314	C(1)-O(2)	1.354	C(5)-H(6)	1.088
C(1)-C(3)	1.523	C(1)-C(3)	1.388	C(1)-C(3)	1.344	C(5)-H(7)	1.088
C(1)-C(13)	1.503	C(1)-C(13)	1.484	C(1)-C(13)	1.481	C(5)-C(8)	1.355
C(3)-H(4)	1.096	O(2)-H(12)	1.165	O(2)-H(12)	1.007	C(8)-H(9)	1.085
C(3)-C(8)	1.548	C(3)-H(4)	1.085	C(3)-H(4)	1.082	C(8)-H(10)	1.085
C(3)-H(11)	1.095	C(3)-C(8)	2.213	C(3)-H(11)	1.087		
C(5)-H(6)	1.096	C(3)-H(11)	1.084	C(13)-C(14)	1.406		
C(5)-H(7)	1.096	C(5)-H(6)	1.090	C(13)-C(15)	1.405		
C(5)-C(8)	1.533	C(5)-H(7)	1.089	C(14)-C(16)	1.393		
C(5)-H(12)	1.095	C(5)-C(8)	1.402	C(14)-H(17)	1.085		
C(8)-H(9)	1.098	C(5)-H(12)	1.454	C(15)-C(18)	1.396		
C(8)-H(10)	1.097	C(8)-H(9)	1.085	C(15)-H(19)	1.084		
C(13)-C(14)	1.405	C(8)-H(10)	1.086	C(16)-C(14)	1.399		
C(13)-C(15)	1.406	C(13)-C(14)	1.407	C(16)-H(21)	1.087		
C(14)-C(16)	1.396	C(13)-C(15)	1.406	C(18)-C(20)	1.396		
C(14)-H(17)	1.085	C(14)-C(16)	1.394	C(18)-H(22)	1.087		
C(15)-C(18)	1.393	C(14)-H(17)	1.086	C(20)-H(23)	1.087		
C(15)-H(19)	1.085	C(15)-C(18)	1.395				
C(16)-C(20)	1.397	C(15)-H(19)	1.085				
C(16)-H(21)	1086	C(16)-C(20)	1.398				
C(18)-C(20)	1.399	C(16)-H(21)	1.087				
C(18)-H(22)	1.087	C(18)-C(20)	1.398				
C(20)-H(123)	1.087	C(18)-H(22)	1.087				
		C(20)-H(123)	1.087				

Table S2: Standard thermochemistry output results of a frequency calculations using B3LYP/6-31+g(d) methods

output results of frequency calculation of reactants (n-butyrophenone)

	(Hartree/Particle)
Zero-point correction=	0.195646
Thermal correction to Energy=	0.206079
Thermal correction to Enthalpy=	0.207023
Thermal correction to Gibbs Free Energy=	0.158448
Sum of electronic and zero-point Energies=	-463.342934
Sum of electronic and thermal Energies=	-463.332501
Sum of electronic and thermal Enthalpies=	-463.331557
Sum of electronic and thermal Free Energies=	-463.380132

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	129.316	39.099	102.235

output results of frequency calculation of transition state

	(Hartree/Particle)
Zero-point correction=	0.188177)
Thermal correction to Energy=	0.198113
Thermal correction to Enthalpy=	0.199058
Thermal correction to Gibbs Free Energy=	0.152353
Sum of electronic and zero-point Energies=	-463.255186
Sum of electronic and thermal Energies=	-463.245249
Sum of electronic and thermal Enthalpies=	-463.244305
Sum of electronic and thermal Free Energies=	-463.291009

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	124.318	39.427	98.297

output results of frequency calculation of 1-phenylethenol

	(Hartree/Particle)
Zero-point correction=	0.138033)
Thermal correction to Energy=	0.145690
Thermal correction to Enthalpy=	0.146634
Thermal correction to Gibbs Free Energy=	0.105437
Sum of electronic and zero-point Energies=	-384.746058
Sum of electronic and thermal Energies=	-384.738402
Sum of electronic and thermal Enthalpies=	-384.737458
Sum of electronic and thermal Free Energies=	-384.778655

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	91.422	30.171	86.70

output results of frequency calculation of ethene

	(Hartree/Particle)
Zero-point correction=	0.051103
Thermal correction to Energy=	0.054146
Thermal correction to Enthalpy=	0.055090
Thermal correction to Gibbs Free Energy=	0.028914
Sum of electronic and zero-point Energies=	-78.542166
Sum of electronic and thermal Energies=	-78.539123
Sum of electronic and thermal Enthalpies=	-78.538179
Sum of electronic and thermal Free Energies=	-78.564355

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	33.977	8.101	55.092