Research paper

Photoisomerization of a small cyclic ketone in the vapor phase

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ABSTRACT

Photoisomerization channels in the vapor phase photochemistry of cyclohexanone (CH) are studied by performing photolysis with 311 nm UV light, and analyzing the photoproducts by means of FTIR spectroscopy. In addition to 5-hexenal, identified previously as a photoisomerization product, we observe an efficient parallel isomerization channel producing butylketene as a primary photoproduct, but it remained unidentified in earlier studies. Calculation at DFT/B3LYP/6-311++G** level predicts formation of this ketene to be favorable both with respect to thermodynamic and kinetic factors.

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1. Introduction

Photoisomerization is an important chemical process associated with light-induced change in physical as well as chemical properties of numerous organic and biological substances [1]. Photochromism is such a common phenomenon displayed by many substances; the underlying process is photoisomerization [2]. The simplest possible change in molecular geometry that can occur in a photoisomerization process is the rotation about a chemical bond, and the key step of photochemistry of vision involves such a rotation across a double bond of the retinal protein Rhodopsin in the excited state [3,4]. On the other hand, isomerization reactions occurring via complex mechanism involving breaking and formation of multiple covalent bonds are also common among organic substances. In present paper we report the finding of such a reaction channel for a six member cyclic ketone, cyclohexanone (CH), occurring in vapor phase under the exposure of UV light of wavelength 311 nm.

The basic vapor phase photochemistry of small cyclic ketones and related compounds has been extensively investigated over the past couple of decades and numerous reports of such studies are available in the literature [5–21]. Three probable primary photochemical reaction channels of CH are depicted in Scheme 1. Experimental reports on the first two channels, which involve dissociation of the molecule to carbon monoxide, cyclopentane and 1-pentene and isomerization to 5-hexenal are available in the literature [5–9]. Channel-3 is a parallel second isomerization reaction and the product is butylketene. However, in the available literature, occurrence of this reaction in the vapor phase photochemistry of CH was never discussed. Likewise, in the case of the five-member cyclic ketone, cyclopentanone (CP), two parallel photoisomerization could produce the unsaturated aldehyde, 4-pentenal and propylketene. In the previous vapor phase photochemistry study of CP, isomerization to 4-pentenal formation was reported [20,21], but to our knowledge, no report for identification of propylketene is available in the literature. In the present paper we report experimental identification and mechanism for production of butylketene from the photolysis of cyclohexanone. Studies of dynamics for photodissociation of carbonyl and related compounds have attracted much attention in recent years [22–28], and to that respect we also discuss here the dynamics of α-cleavage of CH, and specifically the electronic state where this initial step of the reaction could occur.

It has been suggested recently that CH could be used as a second generation fuel. A number of reports show that CH blended synthetic Fischer-Tropsch fuel generates less amount of soot on combustion [29,30]. Therefore, from the perspective of atmospheric significance, photochemistry of CH is also very important. Although the global averaged atmospheric concentration of CH is not known, but some local studies suggest that its abundance is similar to that of acetone, the most abundant linear ketone in earth's troposphere [31,32]. Thermal dissociation pathway of CH has been investigated extensively by various research groups. Recently Porterfield et al. performed such study in a set of flash-pyrolysis microreactors [33], and occurrence of isomerization of the molecule to cyclohexene-1-ol was suggested in addition to identification of various smaller decomposition fragments. A computational study for the unimolecular thermal decomposition kinetics of the compound is also reported [34], where six different decomposition pathways are identified and the corresponding rate
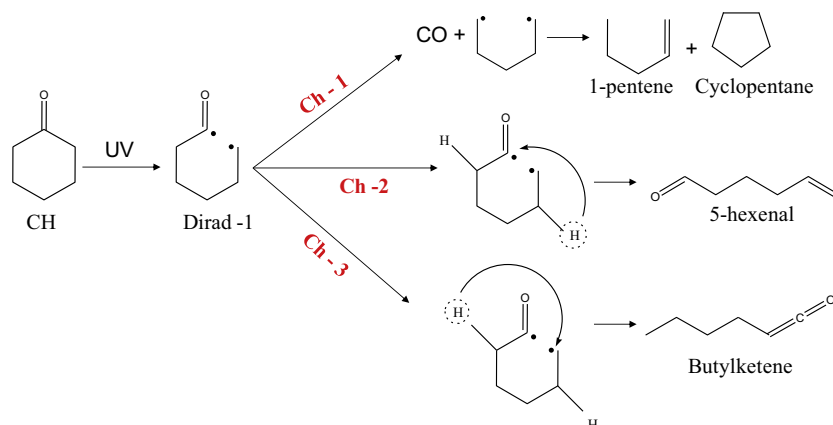
Scheme 1. Probable photochemical channels of cyclohexanone.

constants were computed using the quantum composite G3B3 method coupled with RRKM theory. Kinetics of thermal oxidation of CH has been studied by Serinyel et al. in a fused silica jet-stirred reactor in the temperature range of 530–1220 K and at ∼10 atm pressure [35]. The goal of the present paper is to give conclusive experimental evidence for occurrence of alkylketene formation from CH upon photolysis of the compound in the vapor phase. We also argue here as why their identifications were missed in earlier studies. A brief discussion is also presented explaining the photodissociation mechanism of CH.

2. Experimental and computational methods

Details of the experimental arrangement made to perform the photochemical experiments have been described elsewhere [36,37]. Briefly, the photolysis reactor is a cylindrical quartz cell of length 18 cm and inner diameter 3 cm, and the two open ends of the tube are closed by two circular KBr windows of thickness 3 mm. Photolysis was carried out using three similar UV-B lamps that have emission maximum at 311 nm (Philips TL 01, 20 W) and the temperature of the reactor was maintained at 310 ± 1 K. The spectral bandwidth of the emitted wavelength of the lamp is shown in Supplementary data (Fig. A). The products were analyzed by means of mid-infrared spectroscopy, and for this purpose the reactor cell was placed directly in the sample compartment of a FTIR spectrometer (Bruker IFS 66S). Additionally, the IR spectra of the reaction mixture were measured at a regular interval of time by transferring it into a multi-pass gas absorption cell that has a maximum path length of 8 m. The spectra were recorded with an instrument resolution of 0.5 cm^{-1}. For further confirmation of the identified products, the ro-vibrational band contours of their IR bands were simulated theoretically using PGOPHER programme [38]. The initial guess of the rotational constants required for this purpose were obtained from electronic structure calculation. Spectroscopic grade CH was obtained from Sigma Aldrich, and before every experimental run the compound was degassed by means of several freeze–pump–thaw cycles. Nitrogen and oxygen gases used were of purity 99.99%. Quantum chemical calculations were performed using Gaussian 09 program package [39].

3. Results and discussions

3.1. Photolysis and identification of butylketene

Photolysis of CH under exposure of 311 nm UV light was performed at different low vapor pressures of the sample within the reactor cell, and also upon dilution of the sample vapor in dry nitrogen at different total pressures. For infrared spectral analysis of the end products, the photolyzed gas mixture from the reactor was transferred into a multi-pass infrared gas absorption cell. Probable major photo-reaction channels have already been shown in Scheme 1, and as stated before, 5-hexenal, carbon monoxide, cyclopentane and 1-pentene were identified in previous studies as major photoproducts. Fig. 1a presents the infrared spectral features of different photodissociation products appeared after 60 minutes UV irradiation of 5 mbar of CH diluted in N$_2$.The main finding of the present study is butylketene as a major photoisomerization product in addition to 5-hexenal and other photodissociation products. Theoretically calculated IR spectra of butylketene and 5-hexenal are presented as the two lowermost traces.

Depicted in Fig. 1b are the spectral traces in a narrow range (2030–2240 cm^{-1}) of the mid-IR spectra. Trace-1 indicates that the parent molecule CH does not have any absorption band within given spectral segment, but some of the photoproducts absorb as seen in trace-2. Two types of bands are apparent here, a long train of sharp features, which can be attributed easily as the ro-vibrational bands for the stretching fundamental of carbon monoxide, and a broad profile over which the former sharp features develop. The maximum of the broad profile appears at 2132 cm^{-1}, and we have attributed the band to $\nu_{C=O}$ of butylketene. The experimental spectrum after UV photolysis has been deconvoluted to $\nu_{C=O}$ bands of butylketene and CO as seen in traces 3 and 4, respectively. It is worth mentioning that the vapor phase IR spectrum of butylkene is not available in the literature to make a comparison with the observed band. However, the frequency for $\nu_{C=O}$ of butylketene predicted by electronic structure calculation at DFT/B3LYP/6–311++G** level, 2135 cm^{-1} with a scaling factor of 0.97 (Table 1), agrees satisfactorily with the band maximum of the observed broad feature (trace 2). For furthermore corroboration of the assignment, the ro-vibrational contour of this vibrational band has been simulated employing the PGOPHER fitting method, and it is shown as trace-5. To perform this simulation the rotational constant values of butylketene used were calculated by the same electronic structure theory method. All the unscaled frequencies and corresponding infrared intensities of butylketene predicted by calculation at DFT/B3LYP/6-311G** level of theory are given in Supplementary data (Table A). It is notable that the predicted intensities of other infrared bands of butylketene are more than an order of magnitude smaller compared to the C=O stretching band. In consequence, other bands did not show up with significant intensity in the measured spectrum. A weak band at 3017 cm^{-1} of the photolyzed gas mixture could be attributed to C—H stretching band of butylketene. A further experimental confir-