



Structure and photochemistry of the methanol complexes with methylglyoxal and diacetyl: FTIR matrix isolation and theoretical study

Małgorzata Mucha, Zofia Mielke*

Faculty of Chemistry, University of Wrocław, F. Joliot-Curie 14, 50-383 Wrocław, Poland

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ABSTRACT

The FTIR spectra of the argon matrices doped with methanol and methylglyoxal or diacetyl have been studied. The matrices were irradiated with the output of medium pressure mercury lamp. The spectra analysis indicate the presence of hydrogen bonded complexes between methanol and α -dicarbonyl in solid argon. The structures of the complexes are established by the ab initio MP2/6-311++G(2d,2p) calculations. Methylglyoxal in solid argon subjected to $\lambda \geq 395$ nm radiation photodissociates mostly into carbon monoxide and methane but when it is exposed to the full output of mercury lamp acetaldehyde and carbon monoxide are the main photodissociation products. Irradiation of the methylglyoxal–methanol complex leads to its photo-conversion into the methylhydroxyketene–methanol complex.

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1. Introduction

The simple α -dicarbonyls: glyoxal (G), methylglyoxal (MG) and diacetyl (Dac) are important compounds in atmospheric and combustion chemistry. They are formed in the atmosphere during the oxidation of hydrocarbons emitted by biogenic and anthropogenic sources [1,2]. Various carbonyl compounds are found in relatively high concentrations in polluted water droplets [3,4]. Moreover, methylglyoxal plays an important role in biological systems. It is formed in vivo in numerous enzymatic and non-enzymatic reactions and it reacts with biological macromolecules, like proteins and DNA, changing their chemical and biochemical properties [5]. Diacetyl is an important flavour compound in products generating the typical butter-aroma [6].

Although α -dicarbonyls are important atmospheric species and their complexes may play a role in atmospheric chemistry, there is little information in the literature on interaction of simple α -dicarbonyls with other molecules [7,8]. We have recently studied the interaction of the three α -dicarbonyls, G, MG and Dac, with water [9] and the interaction of G with methanol [10] by help of FTIR matrix isolation technique. The photochemical behaviour of the complexes has been also studied [10,11]. All the complexes between α -dicarbonyls and water that are trapped in argon matrices are stabilized by the O–H \cdots O(=C) hydrogen bond between water

and the carbonyl oxygen. In contrast with water, methanol forms with glyoxal a non-hydrogen bonded complex in solid argon. The calculations show that the larger stability of the non-hydrogen bonded complex relative to the hydrogen bonded one is determined by the larger contribution of the dispersion energy in a more stable complex.

The photochemical behaviour of the glyoxal–methanol complex was found to be particularly interesting [10]. The irradiation of the complex with $\lambda > 370$ nm leads to its photo-conversion into hydroxyketene–methanol complex. The isotopic studies evidence that hydroxyketene is formed in a photo-induced hydrogen exchange reaction between glyoxal and methanol. This can be contrasted with G–H₂O complex where water has no effect on the photochemical behaviour of glyoxal [11].

The goal of the reported studies was twofold. First, we wanted to identify and characterize the complexes formed by the two α -dicarbonyls, MG and Dac, with methanol by help of FTIR matrix isolation and ab initio MP2 studies. In particular we wanted to obtain information whether the hydrogen bonded complexes or non-hydrogen bonded ones are present in the matrices. Our second goal was to study the photochemical behaviour of the methylglyoxal–methanol complex. One may expect that the MG–CH₃OH complex undergoes similar photochemical conversion like the G–CH₃OH one; the hydrogen exchange reaction between methylglyoxal and methanol shall lead to the formation of methylhydroxyketene–methanol complex. Methylhydroxyketene has not been identified so far. The results of the studies are presented in this paper.

* Corresponding author. Tel.: +48 71 3757475.

E-mail address: zm@wchuwr.pl (Z. Mielke).

2. Experimental

2.1. Infrared matrix isolation studies

Monomeric methylglyoxal was prepared in the following way: from the 40% aqueous solution of methylglyoxal, CH_3COCHO (Al-

drich), the major amount of water was distilled off in a vacuum line. The residue was depolymerized at about 363 K, the product was passed through P_4O_{10} and was trapped at 77 K. The sample was stored at liquid nitrogen temperature. Diacetyl, $\text{CH}_3\text{COCOCH}_3$ (97%, Aldrich), was carefully outgassed and vacuum distilled, discarding the most volatile and the least volatile impurities. The

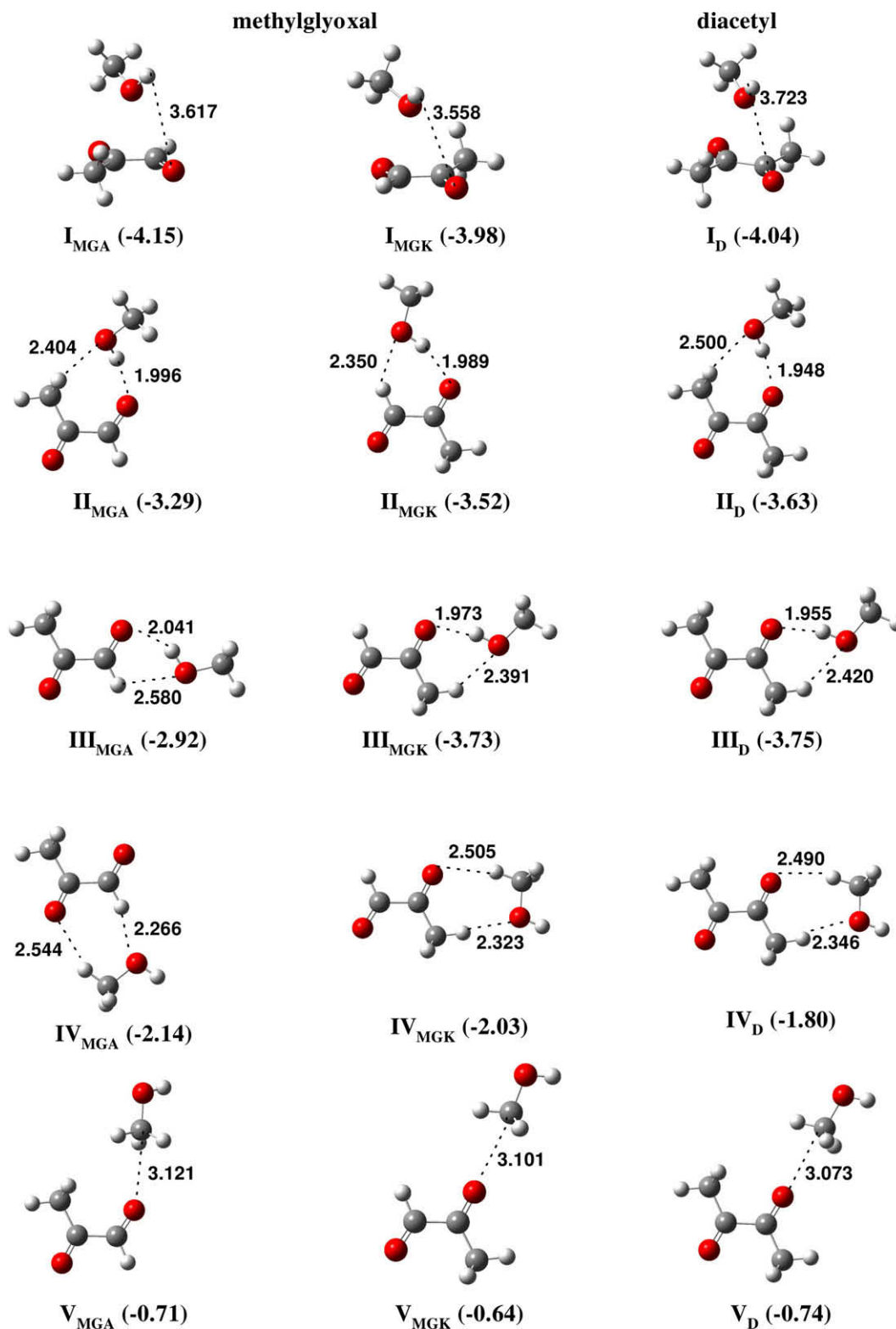


Fig. 1. The optimized structures of the MG- CH_3OH and DAC- CH_3OH complexes. The $\Delta E^{\text{CP}}(\text{ZPE})$ binding energies (kcal/mol) are given in parentheses.

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