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J. of Supercritical Fluids 36 (2005) 154–159

THE JOURNAL OF Supercritical Fluids

www.elsevier.com/locate/supflu

Specific interactions between phosphorus compounds and carbon dioxide: Ab initio approach

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Received 11 October 2004; received in revised form 23 March 2005; accepted 31 March 2005

Abstract

The optimized structures of several complexes of phosphorus containing compounds and CO_2 in the gas phase were determined theoretically. The Gaussian 03 computer software package was used to perform the ab initio computations, including Hartree–Fock (HF/6-31+G(d)) and density functional theory (B3LYP/6-31+G(d)). At the same level of calculation, the binding energy between CO_2 and phosphorus containing compounds was calculated. The binding energies for CO_2–trialkyl phosphate complexes increased with the number of alkyl groups attached to the phosphorus. Harmonic infrared frequencies were calculated for the CO_2 bending mode (ν_2) in the various complexes. The appearance of a second peak in the CO_2 bending mode (ν_2) at lower wavenumber verified the strong interaction between CO_2 and phosphorus containing compounds. The results of the ab initio computations were in good agreement with data previously reported.

Keywords: Carbon dioxide; Ab initio calculation; Lewis acid and base; Binding energy

1. Introduction

Phosphorus (symbol P, atomic number 15) has three unpaired electrons in the outer 3p orbitals that are available for chemical bonding. By 1970, some 100,000 organophosphorus compounds were known, and many thousands more have been synthesized since that time [1]. Phosphorus compounds have been widely used in many areas, including agriculture (fertilizer), food technology, fire retardants, medicine, detergents, metal surface treatments, and high performance glass products. They have also been applied in the dental and medical area [2].

As a result of society's new emphasis on green engineering and chemistry and the wide range of conditions in which they could be applied, the use of supercritical solvents such as carbon dioxide in applications involving phosphorus compounds would be attractive. As an example, Pearce et al. [3] utilized CO_2 as a solvent to remove organophosphorus pesticide residue on soft fruit using supercritical fluid extraction (SFE) techniques. CO_2 has also been considered as an alternative to hexane in extracting phospholipid gums from oilseed [4]. Furthermore, the characteristics of CO_2 itself have attracted a lot of attention from researchers interested in investigating the fundamental mechanism of how CO_2 molecules interact with other compounds, known as CO_2-philic compounds, at the molecular level. It is an intriguing fact that CO_2 has two potential sites with which to interact with other compounds: the carbon in CO_2 can act as a Lewis acid to interact with unshared electron containing compounds, such as carbonyl compounds and one or both of the oxygens can interact with acidic protons.

Researchers have investigated the interaction between carbon dioxide and a wide range of CO_2-philes, such as perfluoro-*n*-hexane [5,6], formic acid [7], trifluoroacetic acid [8], fluorocarbons [9], amine bases [10], peracetylated sugars [11], and carbonyl oxygen on certain polymers [12]. These approaches can be simply categorized into two groups: experimental and theoretical studies. Meredith et al. [10] determined the equilibrium constants between CO_2 and Lewis bases quantitatively by using FTIR spectroscopy. Of the three Lewis bases studied, namely triethylamine (TEA), pyridine

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doi:10.1016/j.supflu.2005.03.010

(PYR), and tributyl phosphate (TBP), TBP showed the highest equilibrium constant of 1.29 [L/mol] with CO_2, suggesting that the carbon atom in CO_2 interacts with the unshared electrons of the oxygen in the TBP compound. This interaction appears to be much stronger than that with the unshared electrons in the nitrogen atoms in TEA and PYR. However, when comparing phosphorus to nitrogen, some basic differences must be remembered. Phosphorus is much less electronegative than nitrogen, and its greater size causes bond lengths to be considerably longer in phosphines (P–C, 1.84 Å) than in amines (N–C, 1.70 Å). In part because of the size of the molecules involved, little progress has been made with theoretical calculations in organophosphorus chemistry.

Owing to the substantial progress in both computational techniques and capacity in recent years, not only has the number of theoretical studies increased significantly, but their accuracy has also dramatically improved. Most recently, Raveendran and Wallen [11] demonstrated theoretically that CO_2 has the potential to undergo a strong interaction with the carbonyl groups of an acetate functionality, almost half as strong as that of the hydrogen bonding in a water dimer. Specifically, these interactions occur between the carbon in CO_2 and the oxygen of the carbonyl functional group.

Given recent efforts to determine the possible (or most economically feasible) hydrocarbon based CO_2-philic molecules have proved to be successful in terms of both experimental and theoretical results, we hope to extend our understanding of the interaction between the unshared electrons and CO_2. In particular, we have selected alkyl phosphate (i.e. the oxygen in P=O) and the unshared electrons in trialkyl phosphite (i.e. P alone) for theoretical studies designed to investigate the difference between P=O and P in the presence of CO_2. In this study, assuming a 1:1 complex between the phosphorus compound and CO_2, the optimized structure, stabilization energies of the CO_2 complexes, and their vibrational spectra are calculated using the commercially available computer package Gaussian 03 [18].

2. Computational methods

We performed an ab initio calculation with a Pentium IV desktop computer (2.8 GHz and 1.5 GB memory). The Gaussian 03 program suite was used to perform the ab initio computations. The geometries of the CO_2–phosphorus containing compound complexes were optimized for both Hartree–Fock (HF/6-31+G(d)) and density functional theory (DFT) (B3LYP/6-31+G(d)). However, density functional theory at this level may not be accurate. The Moller–Plesset (MP) approach [13] is computationally expensive and often cannot be applied to large molecular systems such as the one in this study. Hence, in this study, both HF and DFT level (B3LYP) calculations were applied to obtain the optimum geometries and calculate the frequency of the complex. At the same level of calculations, the binding energies between phosphorus containing compounds (**1**–**10**; shown in Fig. 1) and CO_2 were calculated (see Table 1). Binding energies were calculated by evaluating the energy of the complexes, and then subtracting the energies of the individual molecules. These energies were corrected for basis set superposition error (BSSE) using the counterpoise correction method [14]. The binding energies are reported both with and without the BSSE corrections.

3. Results and discussion

3.1. Optimum geometries and binding energies

The optimized structure of the CO_2–phosphorus containing compounds (phosphoric acid, **1**; alkyl phosphate, **2** and **5**; dialkyl phosphate, **3** and **6**; trialkyl phosphate, **4**, **7**, and **8** in Fig. 1) are shown in Fig. 2. As the figure shows, the electron donor O atom of phosphorus containing compounds donates an electron to the C atom in CO_2 to establish a complex. Also, one of the O atoms in CO_2 can form a complex with the H atom in phosphorus containing compounds. Upon formation of a complex between CO_2–phosphorus containing compounds (**1**–**8**), the binding energy was esti-

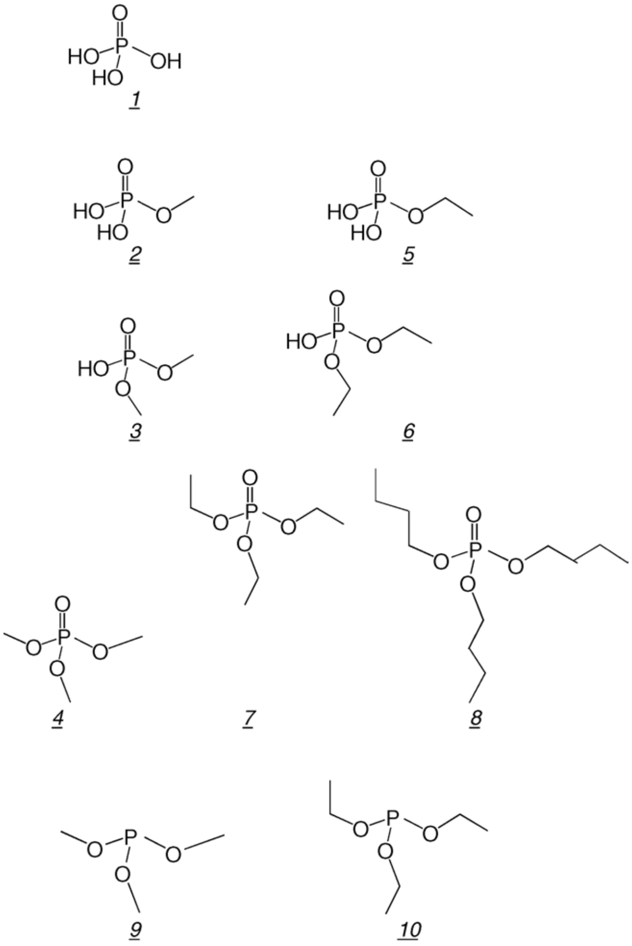

Fig. 1. Chemical structure of the phosphorus compounds.