ЖУРНАЛ СТРУКТУРНОЙ ХИМИИ

2011. Том 52, № 4 *Июль – август* *С. 735 – 739*

UDC 538.1:547.24

^{31}P NMR AND COMPUTER SIMULATIONS OF THE STRUCTURE OF TRICHLORFON AND ITS DERIVATIVES

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Received June, 29, 2009

Trichlorfon or O,O-dimethyl-(2,2,2-trichloro-1-hydroxyethyl) phosphonate is an organophosphorus insecticide with cholinesterase inhibitor activity that has been widely used in protection of field and fruit crops. Trichlorfon rearranges to other more toxic organophosphate insecticides (such as dichlorvos at pH 6—8) in aqueous media. Trichlorfon is a thermally labile compound that cannot be easily determined by gas chromatography coupled with mass spectrometry (GC-MS) and has no functional group for sensitive detection by high performance liquid chromatography (HPLC). In this study, ^{31}P dynamic nuclear magnetic resonance is used to elucidate the stability of trichlorfon and derivatives. These spectrums are compared with the theoretical studies with the Gaussian software to determine the stability and identify the structure. Two derivatives are identified by this method.

K e y w o r d s: trichlorfon derivatives, dichlorvos, phosphorus-31 nuclear magnetic resonance (^{31}P NMR), theoretical study.

INTRODUCTION

Trichlorfon or O,O-dimethyl-(2,2,2-trichloro-1-hydroxyethyl) phosphonate is an organophosphorus (OP) insecticide with acetylcholinesterase (AChE) inhibitor activity, which has been widely used in protection of field and fruit crops [1].

AChE is responsible for terminating the transmission of nerve impulses. AChE inhibition causes accumulation of acetylcholine (Ach) at the nerve synapse and disruption of the nerve function [2].

The intensive use of insecticides in agricultural areas adjacent to shrimp farming zones has been observed. Trichlorfon is one of the most used compounds, which is known as an OP pesticide of high solubility (14 %) and moderate toxicity. It is very quickly hydrolyzed to other OP such as dichlorvos (2,2-dichlorovinyl dimethyl phosphate) that is much more toxic [3].

There are some techniques for the identification and determination of OP such as gas and liquid chromatography with different detectors [4—6], electrochemical biosensor [7], and high performance thin-layer chromatography [8], however, these techniques require several extraction and clean-up steps before the analysis.

A new approach to the study of OP pesticide and degradation products is phosphore-31 nuclear magnetic resonance (^{31}P NMR) [9, 10]. This technique enables a direct study of complex media and avoids problems encountered in extraction recovery and chemical derivatization.

The aim of this work is the identification of some degraded products of trichlorfon by ^{31}P NMR and a theoretical study with the Gaussian-98 software [11]. The ^{31}P NMR data, previously produced

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by Z. Talebpour et al. [10], was used to study the thermodynamics of degradation product reactions of trichlorfon.

COMPUTATIONAL METHODS

Calculations were performed using the Gaussian 98 system of codes [11]. The geometric structure, infrared (IR) frequency, and chemical shifts of ^{31}P NMR of isolated compounds were calculated at HF and B3LYP using the 6-311+G basis set.

RESULTS AND DISCUSSION

Identification of trichlorfon degradation products. A decomposition diagram of trichlorfon under different conditions and the proposed pathway for the degradation of this compound are illustrated in Fig. 1 [3]. The results from ^{31}P NMR at 18.9654, –2.0843, and 1.7316 ppm are related to trichlorfon, dichlorvos and methyl dihydrogen phosphate respectively [10, 12]. The structural models proposed for trichlorfon, dichlorvos, 2,2-dichlorovinyl methyl hydrogen phosphate, dimethyl hydrogen phosphate, methyl dihydrogen phosphate, and methyl hydrogen 2,2,2-trichloro-1-hydroxyethyl phosphonate were optimized first, then the IR frequencies and ^{31}P NMR of these compounds were calculated at the HF/6-311+G and B3LYP/6-311+G level.

A comparison between the experimental data and B3LYP/6-311+G and HF/6-311+G calculations demonstrate that the HF/6-311+G results are much closer to the experimental data (Table 1). So, this method was chosen to use through this work. For all calculations, phosphoric acid was used as the reference compound. From a comparison of the theoretical and experimental ^{31}P NMR, equation (1) was derived

$$y = 1.1762x - 1.8352 \qquad R^2 = 0.995. \tag{1}$$

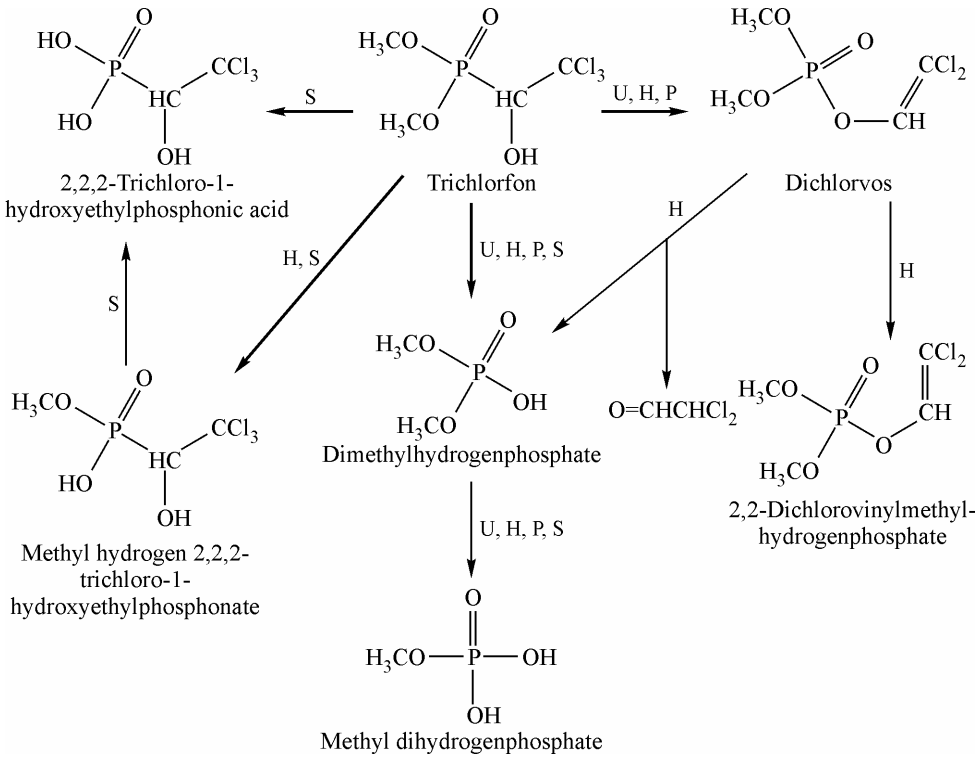

Fig. 1. Proposed degradation pathways for trichlorfon in the environment. Photolysis (U); hydrolysis (H); solid and microorganisms (S); plants (P)

T a b l e 1

^{31}P NMR *experimental and theoretical data for trichlorfon, dichlorvos, and methyl dihydrogen phosphate*

Compounds	Chemical shift (HF) (ppm)	Chemical shift (B3LYP) (ppm)	Chemical shift (Experimental) (ppm)
Trichlorfon	17.4995	14.6669	18.9654
Methyl dihydrogen phosphate	3.7769	7.5442	1.7316
Dichlorvos	–0.7709	1.4781	–2.0843

T a b l e 2

Calculated ^{31}P NMR *chemical shifts deduced from Eq.*1 *for unknown compounds*

Compounds	Chemical shift (ppm)
2,2-dichlorovinyl methyl hydrogen phosphate	–2.72
Methyl hydrogen 2,2,2-trichloro-1-hydroxyethyl phosphonate	17.86

T a b l e 3

Difference in the Gibbs free energy (ΔG) *of the proposed reactions of trichlorfon degradation products*

Compounds	ΔG_t (kcal/mol)
Dichlorvos (a)	–19.36182
2,2-dichlorovinyl methyl hydrogen phosphate (b)	–16.12575
Dimethyl hydrogen phosphate (c)	–15.88793
Methyl hydrogen 2,2,2-trichloro-1-hydroxyethyl phosphonate (d)	–3.29756
Methyl dihydrogen phosphate (e)	–12.89094

In this equation, X is theoretical and Y is the experimental data of ^{31}P NMR; the regression of 0.995 is quietly promising for this equation (Fig. 2).

Also ^{31}P NMR of 2,2-dichlorvinyl methyl hydrogen phosphate and methyl hydrogen 2,2,2,-trichloro-1-hydroxyethyl phosphonate were calculated. These data were used as X in equation (1), and the experimental data were predicted (Table 2) which were consistent with the chemical shift in the experimental spectra referent to (d) and (e) in Fig. 3 [10].

Thermodynamic calculation. The Gibbs free energy like other thermodynamic functions is a state function. It means that ΔG is dependent on the initial and final states of a system. When a reaction occurs spontaneously, the Gibbs free energy of the reaction decreases.

It has been found that with increasing temperature and time the trichlorfon concentration decreases, and it degrades into other compounds [10]. The identification of the degradation product of trichlorfon is important because some degradation products such as dichlorvos are toxic.

The proposed models for the most probable reactions of the degradation product from trichlorfon are shown in Fig. 4. The geometries were optimized at the Hartree—Fock level. The harmonic vibrational frequencies were calculated after the geometry optimization was obtained. The calculated vibrational frequencies are relatively consistent with the nature of located stationary points at the same level as the optimization. Zero-point vibrational energy corrections (ZPVE) were applied to calculate different Gibbs free energies (ΔG).

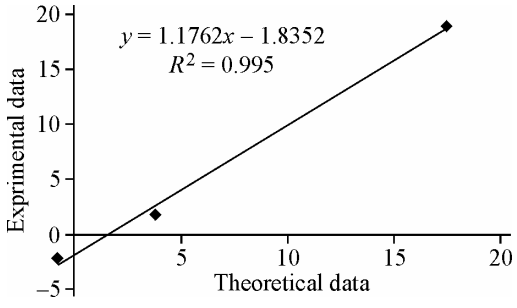

Fig. 2. Correlation of the theoretical and experimental ^{31}P NMR chemical shifts (ppm) of trichlorfon, dichlorvos and methyl dihydrogen phosphate

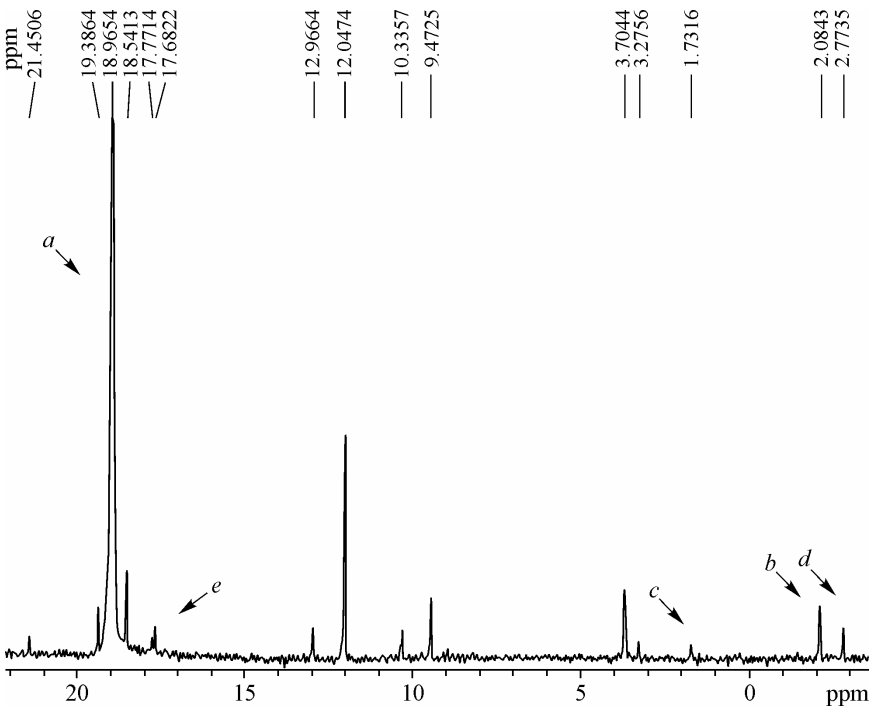

Fig. 3. ^{31}P NMR: (*a*) trichlorfon, (*b*) dichlorvos, (*c*) methyl dihydrogen phosphate, (*d*) 2,2-dichlorovinyl methyl hydrogen phosphate, (*e*) methyl hydrogen 2,2,2-trichloro-1-hydroxyethyl phosphonate

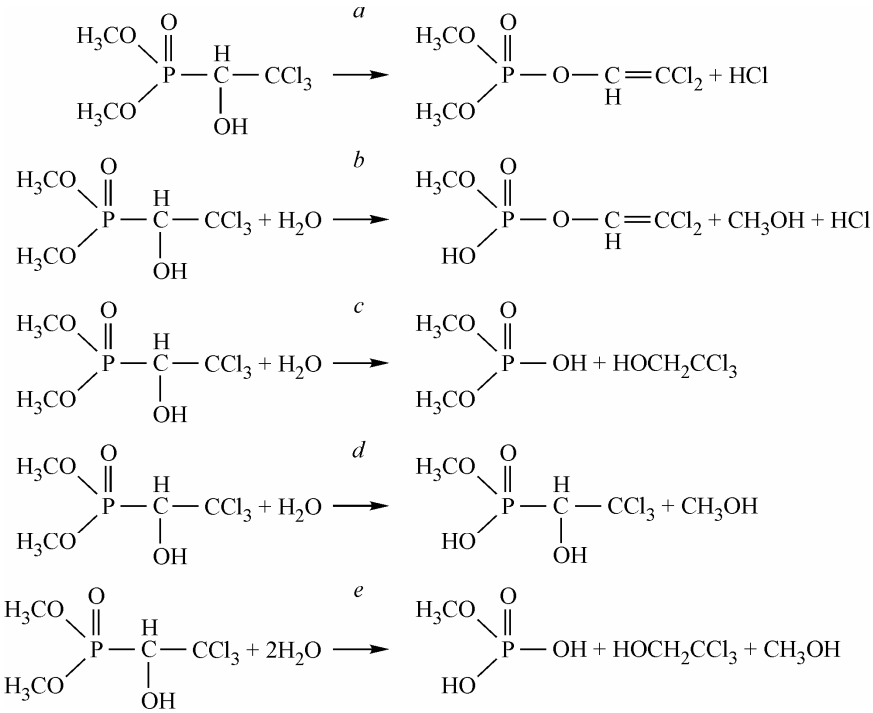

Fig. 4. Proposed reactions of trichlorfon: (*a*) dichlorvos, (*b*) 2,2-dichlorovinyl methyl hydrogen phosphate, (*c*) dimethyl hydrogen phosphate, (*d*) methyl hydrogen 2,2,2-trichloro-1-hydroxyethyl phosphonate, (*e*) methyl dihydrogen phosphate

The difference in the Gibbs free energy (ΔG) was calculated for all reactions using Eq. 2

$$\Delta G_t = \Delta G_{\text{products}} - \Delta G_{\text{initialcompounds}}. \quad (2)$$

The calculated ΔG (in kcal/mol) for all reactions are shown in Table 3. The negative sign of ΔG for all formation reactions proposed spontaneous reactions for the illustrated pathway (Fig. 4). Also an energy gap is found between dichlorvos and other compounds. It shows that this compound can be the main product of trichlorfon degradation. The reported experimental data also confirm these theoretical data [10].

Acknowledgements. The authors gratefully acknowledge the Research Council of Shahid Beheshti University for financial support.

REFERENCES

1. *Dust J.M., Warren C.S.* // Water Qual. Res. J. Can. – 2001. – **36**. – P. 589 – 604.
2. *Chang C.C., Lee P.P., Hsu J.P. et al.* // Aquaculture. – 2006. – **253**. – P. 653 – 666.
3. http: // www.inchem.org/documents/ehc/ehc/ehc132.htm
4. *Frenich A.G., Gonzaler-Rodriguez M.J., Arrebola F.J. et al.* // Anal. Chem. – 2005. – **77**. – P. 4640 – 4648.
5. *Chen Y.I., Su Y.S., Jen J.F.* // J. Chromatogr. A. – 2002. – **976**. – P. 349 – 355.
6. *Blasco C., Font G., Pco Y.* // J. Chromatogr. A. – 2002. – **970**. – P. 201 – 212.
7. *Longobordi F., Solfrizzo M., Compagnone D. et al.* // J. Agric. Food. Chem. – 2005. – **53**(24). – P. 9389 – 9394.
8. *Futagami K., Narazaki C., Kataoka Y. et al.* // J. Chromatogr. B. Biomed. Sci. Appl. – 1997. – **704**. – P. 369 – 373.
9. *Segev O., Columbus I., Ashani Y. et al.* // J. Org. Chem. – 2005. – **70**. – P. 309 – 314.
10. *Talebpour Z., Ghassempour A.R., Zendehzaban M. et al.* // Analytica Chem. Acta. – 2006. – **576**. – P. 290 – 296.
11. *Frisch M.J., Trucks G.W., Schlegel H.B. et al.* // Gaussian-98, Revision A. 6. – Gaussian, Inc.: Pittsburgh, PA, 1998.
12. *Boroit-Marqui F., Demontety C., Gilard V. et al.* // Environ. Chem. Lett. – 2004. – **2**. – P. 93 – 97.