

# Computational Insights into Phthalate Ester-Linked VOCs: A DFT-Based Approach for CI-MS Analysis

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## Abstract

### Rationale

The presence of VOCs, notably diethyl phthalate, dimethyl phthalate, di-n-butyl phthalate, di(2-ethylhexyl) phthalate, and similar compounds in soft drinks, raises significant concerns due to their known or potential adverse health effects. Monitoring these compounds is imperative to comprehend their implications on human health and the overall quality of soft drinks. CI-MS techniques emerge as powerful tools for VOC quantification in soft drinks, offering fast analysis times, high detection sensitivity, real-time analysis capabilities, and versatility across various scientific fields.

### Methods

Achieving absolute quantification of VOCs through PTR-MS presents challenges, with individual VOC calibration proving labor-intensive. Theoretical approaches pioneered by Su and colleagues, including DFT, offer avenues for approximating VOC concentrations and understanding ion-molecule reactions. Specifically, DFT method B<sub>3</sub>LYP/6-311++G(d, p) computes molecular parameters like dipole moment, polarizability, proton affinity and ionization energy for large phthalate esters. Rate constants of ion-molecule reactions are determined using the parametrized trajectory method under varying E/N and temperature conditions.

### Results

The analysis of computed parameters across seven complex molecules reveals notable findings. Bis(2-methoxyethyl) phthalate, for instance, exhibits a superior dipole moment, suggesting intensified electrostatic interactions with ions and heightened rate constants. The increased proton affinity observed in certain molecules renders them suitable for specific ionization methods. Furthermore, enthalpy change and free energy computations affirm the reactivity of ions with phthalate esters, with distinct variations noted in rate constants according to dipole moment and polarizability.

## Conclusions

In conclusion, the parametrized trajectory method, coupled with computational analysis of molecular parameters, offers a means to compute rate constants for ion-molecule reactions, enabling determination of VOC concentrations in soft drinks without external calibration standards in PTR-MS analyses. The observed variations in rate constants with temperature and reagent ions align with collision theory principles and existing literature findings, underscoring the utility of these approaches in VOC identification and quantification using PTR-MS.

## I. Introduction

Soft drinks, commonly consumed worldwide, have garnered attention in recent years due to concerns about the presence of volatile organic compounds (VOCs) related to phthalate esters [1, 2]. Phthalate esters, frequently used as plasticisers in packaging materials, can leach into beverages, introducing various VOCs into the liquid [3, 4]. Understanding the diverse range of VOCs associated with phthalate esters in soft drinks is crucial for evaluating potential health risks and implementing measures to ensure product safety. Some notable VOCs related to phthalate esters in soft drinks include: diethyl phthalate, dimethyl phthalate, di-n-butyl phthalate, di(2-ethylhexyl) phthalate. Prominently, diethyl phthalate commonly identified VOC in soft drinks, known for its use in packaging materials and its potential migration into beverages [5, 6, 7]. It has been a focus of research due to its widespread presence and potential health implications. Dimethyl phthalate, another phthalate ester derivative has been detected in soft drinks. This VOC is of concern due to its potential links to adverse health effects and its ability to migrate from packaging into the liquid contents. Di-n-butyl phthalate and di(2-ethylhexyl) have also been identified in soft drinks and pose health risks with known endocrine-disrupting properties [6].

Understanding and monitoring these compounds is crucial for assessing their implications on human health and the overall quality of soft drinks. The investigation of VOCs in soft drinks involves advanced analytical techniques, with a particular focus on methods such as gas chromatography-mass spectrometry (GC-MS) and chemical sensors [8, 9, 10]. These methodologies enable the identification and quantification of specific VOCs, shedding light on the composition of soft drinks and the extent of phthalate ester migration. Direct-injection mass spectrometry (DIMS) techniques, such as proton transfer reaction mass spectrometry (PTR-MS) and selected ion flow mass spectrometry (SIFT-MS) have been powerful tools in the VOC quantification [11, 12]. In particular, PTR-MS has been extensively used for the characterisation of VOCs in various fields including food aroma analysis [13, 14]. PTR-MS is mostly used in sensory predictions and aroma release or quality control in food science, specifically in the analysis of fermented food products [15, 16]. PTR-MS is an ideal technique for VOCs analysis since it eliminates time-consuming and artefact-prone sample preparation. Moreover, PTR-MS provides fast analysis time, high detection sensitivity, and real-time analysis of trace-level compounds over traditional GC-MS, thus a preferred technique in environmental, food science, medical, and biological science [17, 18, 19, 20].

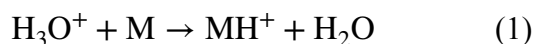
An absolute quantification of the VOCs can be obtained more accurately when the PTR-MS instrument is calibrated for each single VOC. Generally, instrument calibration is a laborious process, and it is not always feasible to develop accurate standards for every VOC detected by PTR-MS [21, 22, 23]. In order to get an approximate estimation of the VOC concentrations without

calibration, an independent determination of the ion-neutral reaction rate constants is extremely vital. Su and co-workers provided several theoretical or numerical approaches aiming at ion-molecule collision reactions taking place in drift tube chamber [24, 25, 26]. These approaches take molecular parameters, such as electric dipole moment and polarizability of the neutral molecule to evaluate collision rates. In particular, the parameterized trajectory model estimates collision rates as a function of centre-of-mass kinetic energy and temperature under PTR-MS drift tube conditions [26].

In parallel, the theoretical computation of rate coefficients has also been carried out by many authors in the literature [27, 28, 29]. Furthermore, the ionization mechanism through different reagent ions namely  $\text{H}_3\text{O}^+$ ,  $\text{NH}_4^+$ ,  $\text{NO}^+$ ,  $\text{O}_2^+$  and ion-molecule reaction kinetics relies on the chemical and physical properties of neutral VOCs. Computational approaches, such as density functional theory (DFT), play a crucial role in understanding the molecular interactions and properties of these VOCs [30]. DFT investigations contribute valuable insights into the electronic structure, stability, and reactivity of the compounds, aiding in the assessment of potential risks associated with their presence in soft drinks.

## II. Overview

VOCs related to phthalate esters in soft drinks have become a subject of growing concern due to their potential impact on food safety and quality [31]. The presence of VOCs related to phthalate esters in soft drinks raises concerns about potential health risks, as certain phthalates have been associated with adverse effects on human health, including endocrine disruption [6, 32]. Therefore, researchers and regulatory bodies are actively engaged in assessing the levels of these compounds in various beverages. Research efforts and analytical techniques, such as GC-MS and nuclear magnetic resonance (NMR), are employed to identify and quantify these VOCs in soft drinks [2, 3, 7, 8, 33]. PTR-MS on the other hand could be in the forefront for quantification of VOCs in soft-drinks due to its advantages over traditional mass spectrometry-based analytic techniques. Conventional PTR-MS instrument uses  $\text{H}_3\text{O}^+$  reagent ion as a primary proton donor to ionize many types of volatile compounds. In PTR-MS, the reaction between  $\text{H}_3\text{O}^+$  and an analyte sampled species M,

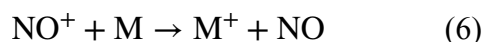
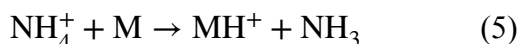
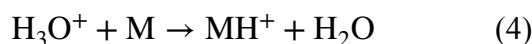


$$\frac{[\text{MH}^+]}{[\text{H}_3\text{O}^+]} = \frac{i(\text{MH}^+)}{i(\text{H}_3\text{O}^+)} = k[\text{M}]t \quad (2)$$

$$[\text{M}] = \frac{1}{kt} \frac{[\text{MH}^+]}{[\text{H}_3\text{O}^+]} \quad (3)$$

Here  $k$  is the reaction-rate constant and  $t$  represents the reaction time, usually 100 ms in a typical PTR-MS instrument. The concentration  $[\text{M}]$  in principle can be determined without calibration simply by recording the ratio of the  $\text{MH}^+$  ion counts to those of the  $\text{H}_3\text{O}^+$ , provided reaction rate constant  $k$  is known already. It is worthwhile to mention that dissociation and fragmentation may occur upon reaction between compounds, especially alcohols and  $\text{H}_3\text{O}^+$  ions. Thereby, the product ion counts could differ from as assumed in the above equations.

However, modern chemical ionization mass spectrometry (CI-MS) instruments allow the operator to switch between different reagent ions, being capable of exploiting reagent ions other than  $\text{H}_3\text{O}^+$ , simply by passing a different reagent gas through the ion source. Frequently used ions in such CI-MS include  $\text{NH}_4^+$ ,  $\text{NO}^+$ , and  $\text{O}_2^{+\bullet}$  which have been applied efficiently for the ionization of the VOCs [34, 35, 36, 37]. These chemical-ionization methods are more or less selective to a certain class of VOCs or have functional-group-dependent ionization mechanisms. The VOC quantification from different CI-MS ions generally proceed through proton transfer or charge transfer to the neutral molecule as given in the equations below.



The mentioned reactions, especially 6 and 7 are influenced by the thermodynamics and the ionization energy (IE) of NO and  $\text{O}_2$  molecules. If the IE of the analyte is lower than that of NO, simple charge transfer is likely the primary ionization pathway. Concurrently, reactions other than charge transfer, such as hydride ion transfer  $(\text{M} - \text{H})^+$ , hydroxide ion transfer  $(\text{M} - \text{OH})^+$ , and alkoxide  $(\text{M} - \text{OR})^+$  ion transfer often occur alongside adduct  $(\text{NO}^+\text{M})$  ion formation [38]. Similarly, if the IE of the analyte is lower than that of  $\text{O}_2$ , the reaction proceeds through charge transfer. However, the charge transfer process in equation 7 frequently leads to partial fragmentations of the resulting product cation [39].

Gas-phase molecular properties, such as proton affinity (PA) and IE of the neutral VOCs are of utmost importance in the selection of appropriate reactant gas (ions) to be utilized in CI-MS. Similarly, collision models take molecular polarizability and the electric dipole moment of the VOCs as input parameters to compute rate constants. Here's how PA, IE, electric dipole moment and polarizability of the neutral molecules provide insights into the analysis via PTR-MS:

- Proton Affinity: In PTR-MS, the sample molecules (VOCs) are ionized through a proton transfer reaction. The primary ion source in PTR-MS is typically  $\text{H}_3\text{O}^+$  (hydrated proton). PA is crucial in determining which VOCs will undergo proton transfer and form ions in the presence of  $\text{H}_3\text{O}^+$ . Molecules with higher PA will more readily accept a proton, resulting in the formation of protonated ions. The ability of a VOC to undergo proton transfer and the efficiency of ion formation are influenced by the PA of the VOC relative to that of  $\text{H}_3\text{O}^+$ .

$$\text{PA} = -\Delta E_{\text{elec}} - \Delta \text{ZPE} - \Delta E_{\text{vib}} + \frac{5}{2}RT \quad (8)$$

Where  $\Delta E_{\text{elec}}$ ,  $\Delta \text{ZPE}$ ,  $\Delta E_{\text{vib}}$  are the difference in the electric energy, zero-point energy, vibrational energy of the protonated and neutral molecules. The translational energy contribution is represented as the last term of equation 8.

- Ionization Energy: IE is still relevant in PTR-MS, as it plays a role in the formation of the primary ions, particularly  $\text{NO}^+$  and  $\text{O}_2^{+\bullet}$ . The energy required to ionize the reagent gas to

produce ions influences the overall efficiency and sensitivity of the charge transfer process. Lower IE of the reagent gas is generally favorable, as it allows for efficient ionization of the sample molecules at lower energies. The equation below represents IE of an N-electron system.

$$IE = E_0(N - 1) - E_0(N) \quad (9)$$

- **Electric Dipole Moment:** The electric dipole moment is a measure of the separation of positive and negative charges within a molecule. It quantifies the overall polarity of a molecule. In the context of CI-MS, the electric dipole moment is relevant because the ionization process often involves the interaction between charged species, such as ions and neutral molecules. The presence of an electric dipole moment can influence the strength of these interactions. A molecule with a significant electric dipole moment may experience stronger interactions with charged species, potentially affecting the rate of chemical ionization reactions.
- **Polarizability:** Polarizability is a measure of how easily the electron cloud of a molecule can be distorted by an external electric field. It is related to the molecule's ability to respond to an applied electric field by inducing temporary dipoles. In CI-MS, polarizability is relevant because it affects the way molecules interact with each other during ionization. Molecules with higher polarizability may undergo more pronounced changes in electron distribution when subjected to an external electric field. The polarizability of a molecule can influence the efficiency and rate of chemical ionization reactions, as it affects the strength and nature of the interactions between the neutral molecules and ions in the ionization source.

Summarily, the efficiency and selectivity of ionization depend on the PA of the analyte molecules and the IE of the reagent gas. Experimental conditions in PTR-MS are optimized to achieve sensitive and selective detection of a wide range of VOCs in real-time applications. It's important to note that the specific values of PA and IE can vary depending on the molecules involved and the experimental conditions. The choice of reagent gas in CI-MS is often influenced by its ability to efficiently ionize a wide range of analyte molecules while minimizing unwanted fragmentation.

### III. Computational Method

DFT analysis of VOCs relevant to phthalate esters in soft drinks is conducted using the B<sub>3</sub>LYP/6-311++G(d, p) method implemented in the Gaussian suite of codes [40]. Molecular structures are obtained from popular databases such as NIST and PubChem. These structures are fully optimized to ensure a true stationary point is obtained. Subsequently, relevant molecular properties are evaluated on the fully optimized structures. The choice of the B<sub>3</sub>LYP/6-311++G(d, p) level of theory for computing molecular properties of organic molecules is based on its balance between computational accuracy and efficiency. This hybrid functional and basis set combination has demonstrated its effectiveness in capturing the electronic structure and properties of a wide range of organic compounds. B<sub>3</sub>LYP combines the benefits of Becke's three-parameter exchange functional (B3) and the Lee-Yang-Parr correlation functional (LYP), providing a well-balanced description of both electronic structure and correlation effects [41]. The 6-311++G(d, p) basis set is a versatile choice for organic molecules. It includes multiple polarization functions (d and p) for each atom, allowing for the representation of electron correlation effects and accurately describing the shape and flexibility of molecular orbitals. This basis set strikes a balance between accuracy and computational expense, making it suitable for studying larger organic systems. B<sub>3</sub>LYP/6-311++G(d, p) is preferred over the previously used B<sub>3</sub>LYP/6-31+G(d, p) [30], which has been extensively

validated for various organic compounds and shown good performance in predicting molecular geometries, vibrational frequencies, electronic properties, and reaction energetics [28, 42, 43, 44].

## IV. Results

The molecular properties such as electric dipole moment, polarizability, PA, IE and electron affinity (EA) of phthalate esters are determined through computational analysis using B<sub>3</sub>LYP/6-311++G(d, p) DFT method. The structures are meticulously optimized to ensure absence of negative frequencies, presenting minimum energy configurations. The optimized geometries of seven phthalate esters are illustrated in the first column of Table 1, while Table 2 showcases the computed molecular parameters.

These parameters, including electric dipole moment, polarizability, PA, and IE play crucial roles in characterising reaction kinetics and guiding the selection of CI-MS reagent ions for VOC quantification via PTR-MS. Molecules with significant electric dipole moments prone to stronger interactions with charged species, potentially influencing chemical ionization reaction rates. Notably, bis(2-methoxyethyl) phthalate exhibits the highest dipole moment of 4.90 Debye, while benzyl benzoate displays the lowest at 2.34 Debye, suggesting weaker interactions with ions. The measured dipole moment value for dimethyl phthalate, 3.34 Debye, matches closely with the computed value of 3.38 Debye [45].

Polarizability, on the other hand, impacts the efficiency and rate of chemical ionization reactions by affecting the nature and strength of interactions between neutral molecules and ions in the ionization source. For instance, diethoxyethyl phthalate exhibits the highest polarizability at 31.98 Å<sup>3</sup>, whereas dimethyl phthalate has a smaller polarizability of 19.42 Å<sup>3</sup>. This increase in polarizability with the rise of carbon atoms is attributed to the greater the number of electrons, leading to reduced control of the nuclear charge on charge distribution. Electric dipole moment and polarizability values serve as crucial parameters in calculating rate constants in CI-MS reactions using collision models such as Langevin and parametrised trajectory methods, as elaborated in the preceding sections.

Similarly, PA and IE are the fundamental concepts in chemistry, particularly in the realm of CI-MS techniques for studying chemical reactions and molecular behavior. PA quantifies the energy change associated with the addition of a proton (H<sup>+</sup>) to a neutral atom or molecule to form a positive ion, reflecting the propensity of a species to accept a proton. Higher PA values indicate a greater likelihood of proton acceptance and positive ion formation. The computed PA values reveal that bis(2-methoxyethyl) phthalate, with the highest PA at 923.20 KJ/mol, exhibits a strong tendency to accept a proton, especially from specific ions such as from H<sub>3</sub>O<sup>+</sup> or NH<sub>4</sub><sup>+</sup> ions. Conversely, dimethyl phthalate displays caution in proton acceptance, notably from NH<sub>4</sub><sup>+</sup>, due to its lower PA of 833.24 KJ/mol. However, H<sub>3</sub>O<sup>+</sup> ion is anticipated to donate a proton to all the molecules, given that the respective molecule's PA surpasses that of the H<sub>2</sub>O molecule i.e. 691 KJ/mol. Similarly, NH<sub>4</sub><sup>+</sup> effectively transfer a proton to the molecules with PA higher than that of NH<sub>3</sub> (853.6 KJ/mol) in a proton transfer reaction. In CI-MS, the preference for NH<sub>4</sub><sup>+</sup>-CI-MS over H<sub>3</sub>O<sup>+</sup>-CI-MS arises when the disparity in PA between the neutral molecule and H<sub>2</sub>O molecule widens, leading to increased fragmentations. Moreover, NH<sub>4</sub><sup>+</sup> ions offer enhanced benefits such as higher VOC selectivity and improved separation of isobaric compounds [34, 35]. With the exception of dimethyl phthalate and diethyl phthalate, all molecules readily accept a proton from NH<sub>4</sub><sup>+</sup> in an exothermic proton transfer reaction.

Enthalpy change and free energy further provide insights on the exothermicity of  $\text{NH}_4^+$  reactions with phthalates esters which is outlined below. The investigated molecules contain multiple protonation sites due to the presence of highly electronegative oxygen atoms in the molecular structures. PA values are computed at the atom with the highest negative electrostatic potential, indicating potential protonation sites, see third column of Table 1. The highest negative charge on the oxygen atom rationalise the potential protonation sites. Additionally, natural bond order (NBO) charges provide insights into electron charges and electrostatic potential within a molecule [46].

IE on the other hand determines the energy required to remove an electron from a neutral atom to form a positive ion of higher charge. It is the reverse process of EA, which measures the energy change associated with gaining an electron. IE is an important property in understanding the stability of ions and the likelihood of an atom or ion losing an electron. In the context of CI-MS, it refers to the tendency of a neutral molecule to accept an electron and form a negative ion during the ionization process. Lower ionization energy of the reagent gas is generally preferred in CI-MS because it facilitates the ionization of analyte molecules at lower energy levels. Commonly used reagent ions, including  $\text{NO}^+$  and  $\text{O}_2^+$ , induce exothermic electron transfer reactions with phthalate esters, as their computed IE values fall below those of  $\text{NO}$  and  $\text{O}_2$  molecules. The electron transfer from  $\text{NO}^+$  is exothermic and reactions proceed at collision rates if the IE of the analyte is less than the IE of  $\text{NO}$  molecule i.e. 9.26 eV [47]. Lacko et al. [48] reported that, in addition to simple charge transfer, there's a large possibility for hydride abstraction and association reactions in the case of selected phthalates, as observed with SIFT-MS. High branching ratios are predominantly observed in association and adduct formation reactions. Similarly, electron transfer via  $\text{O}_2^+$  is exothermic if the IE of the analyte is less than 12.06 eV. It is worthwhile to note that  $\text{O}_2^+$ , a radical cation produces fragmentation with the analyte molecule due to the excessive energy stored in the product side. Ionization through  $\text{NO}^+$  or  $\text{O}_2^+$  ions leads to advantage in the separation of isobaric VOCs [36, 37]. In the case of energetic  $\text{O}_2^+$  ions, Lacko et al. observed a higher incidence of charge transfer followed by fragmentation. It's important to highlight that SIFT-MS and PTR-MS operate under distinct temperature and energy conditions. Therefore, ion-molecule reactions tend to be more energetic in PTR-MS compared to the milder temperature conditions in SIFT-MS.

Nonetheless, the true validation of these theoretical values necessitates rigorous experimentation, providing tangible evidence to corroborate and refine the theoretical understanding. By integrating theoretical insights with empirical data, a comprehensive understanding of the system can be attained, enhancing the reliability and applicability of scientific interpretations. The present calculations lay the groundwork for supporting empirical findings, offering insight into the underlying principles governing the complex ion-molecule reactions.

### **Enthalpy and Free Energy**

Table 3 presents the computed enthalpy change and free energy change of reactions involving phthalates and reagent ions commonly utilized in PTR-MS instruments. The negative change in enthalpy ( $\Delta H$ ) signifies the exothermic nature of a reaction and provides insights into the bond energies of reactants and the products. The reported enthalpy change shows that the proton transfer reaction of  $\text{H}_3\text{O}^+$  and phthalates is exothermic. The reaction of  $\text{NH}_4^+$  to the VOCs is also exothermic with the exception for dimethyl phthalate and diethyl phthalate. The PA of dimethyl phthalate and diethyl phthalate is significantly lower than the value required for the molecule to accept a proton from  $\text{NH}_4^+$  ions therefore the endothermic reactions were expected. Similarly, the

$\Delta H$  for other reactions of  $\text{NH}_4^+$  is relatively lower than  $\text{H}_3\text{O}^+$  during the reaction. This means protonation via  $\text{H}_3\text{O}^+$  is more exothermic than the protonation from  $\text{NH}_4^+$  ions. The charge transfer relations from  $\text{NO}^+$  and  $\text{O}_2^{+\bullet}$  ions are highly exothermic, especially  $\text{O}_2^{+\bullet}$  draws a large amount of energy. The elevated enthalpy values signify the energy required to initiate bond breaking for fragmentations to occur.  $\text{O}_2^{+\bullet}$  exhibits notably high enthalpy values, as do some other cations, as demonstrated in Table 3. This observation potentially justifies why reactions of  $\text{O}_2^{+\bullet}$  with phthalates predominantly result in fragmentations.

Similarly, Gibbs free energy change ( $\Delta G$ ) indicates the feasibility and spontaneity of the proton transfer and electron transfer reactions. The reactions that proceed without an energy input have negative  $\Delta G$  values, while a positive  $\Delta G$  indicates that input energy is needed for the reaction to take place. All studied reactions, encompassing protonation and electron transfer, demonstrate feasibility and exothermic spontaneity. The reactions of  $\text{NH}_4^+$  with dimethyl phthalate and diethyl phthalate shows otherwise different trend due to their lower PA values. It is important to note that the present computational calculations are conducted under standard temperature (298.150 K) and pressure (1 atm) conditions. Understanding the enthalpy change and free energy of any reaction is vital for comprehending its energy requirements, directionality, spontaneity, rate, and stability.

## Rate Constants

In standard PTR-MS setups, determining the concentration of a neutral VOC involves calibrating the instrument with a known concentration standard and measuring protonated ion signals, as indicated in equation 3. However, calibration procedures are often labor-intensive, time-consuming, and prone to experimental errors, particularly for alcohols and aldehydes which are susceptible to fragmentation. To overcome these challenges, ion-molecule reaction kinetic data, including reaction rate constants, are essential for accurately estimating volume mixing ratios (VMRs) and VOC concentrations without relying on external gas standard for calibration [49].

Collision-based theoretical models, such as those developed by Su et al., are employed to calculate rate of ion-molecule reactions driven by the experimental conditions within PTR-MS drift tubes [24, 25, 26]. The theoretical approach is well-documented in the literature and provides a refined procedure for obtaining parametrized trajectory rates, as briefly outlined below.

$$\frac{k}{k_L} = K_c(\tau, \epsilon) \quad (10)$$

$$k_L = \sqrt{\frac{\pi \alpha q^2}{\mu \epsilon_0}} \quad (11)$$

$$\tau = \frac{\mu_D}{\sqrt{\alpha T}} \quad (12)$$

$$\epsilon = \frac{\mu_D}{\sqrt{\alpha K E_{\text{cm}}}} \quad (13)$$

$$K(\tau, \epsilon) = 1 + c1\tau^{0.4}\epsilon^2S + C2(1 - S) * \sin[c3\{c4 + \ln(\tau)\}]\tau^{0.6}(\epsilon - 0.5)^{1/2}$$



$$c1 = 0.7271143, c2 = 3.71823, c3 = 0.586920, c4 = 4.97894$$

$$S = \begin{cases} \exp[-2(\epsilon - 1.5)]; & \epsilon > 1.5 \\ 1; & \epsilon \leq 1.5 \end{cases}$$

where,  $\alpha$ ,  $\mu$ , and  $\mu_D$  are polarizability, reduce mass of the reactants, and electric dipole moment of the neutral molecule, respectively.  $k_L$  is the Langevin rate constant [50].  $KE_{cm}$  represents the collisional kinetic energy of the ion and the molecule. Table 4 presents rate constants obtained at 300 K using both the Langevin and parametrized trajectory methods. The Langevin rates  $k_L$  are notably lower and remain temperature-independent. This arises from the consideration of solely long-range ion-induced dipole interactions, adjusted based on the polarizability and the reduced mass of the reactants. However, within the PTR-MS drift tube, the collisions occur under conditions where the applied field renders room temperature less relevant. The parametrized trajectory method offers rates at appropriate center-of-mass kinetic energy and higher effective temperatures. The applied electric field or reduced electric field (E/N) predominantly governs ion-molecule chemistry inside the PTR-MS instrument and consequently, collision dynamics [23, 50]. Due to varying E/N values, collisions inside the drift tube are highly energetic ( $\sim 0.5$  eV) compared to typical room temperature collision energies ( $\sim 0.023$  eV). The selected working value of E/N balances sensitivity, fragmentation, and the presence of water clusters. Higher E/N values often chosen to prevent ion cluster formation, albeit intensifying collisions. This heightened collision energy significantly influences rate constants and product-ion distributions in PTR-MS drift tube reactions [51]. The parametrized trajectory method reliably predicts rates consistent with PTR-MS drift-tube energetics, yielding larger reaction rates compared to Langevin rates. The molecules with small dipole moments primarily rely on charge-induced dipole interactions, whereas those with higher dipole moments also involve ion-permanent dipole interactions, leading to increased rates. Consequently, compounds like bis(2-methoxyethyl) phthalate (4.90 Debye) and dibutyl phthalate (3.96 Debye) exhibit higher rates due to their elevated dipole moment and polarizability values. Also, the rate constants decrease with increase in temperature, aligning with literature findings and collision theory expectations. The rate coefficients for major ions like  $H_3O^+$ ,  $NH_4^+$ ,  $NO^+$ , and  $O_2^+$  at 120 Td are detailed in Table 4. Figure 1 visually represents how rates vary for different ions. Ion mass is another influential factor affecting rates, illustrated in Figure 2 alongside the variation of rates with temperature. The reaction rates, derived from the parametrized trajectory method, are instrumental in identifying and quantifying relevant VOCs in soft drinks. Moreover, the parametrised trajectory rates can be obtained at any temperature and E/N values using the provided Python-Tkinter code [52], which currently supports over 135 molecules with computed molecular parameters, but can be customised as needed.

Current experimental data regarding rate coefficients at effective temperature and collisional energy are somewhat scarce. Moreover, the existing data on the temperature dependency of these rates typically align reasonably well with the expectations of collision theory, notably in predicting a gradual decrease in rates as temperature rises [53, 54]. However, there remains a notable gap in experimental data at higher energy levels and under conditions of elevated temperatures. To comprehensively validate the parametrised trajectory model, particularly under these more extreme conditions, a greater wealth of experimental data is imperative. Such data would not only bolster the quantitative accuracy of the model but also provide invaluable insights into the intricacies of reaction kinetics at higher energy regimes and elevated temperatures. Therefore, efforts to gather

additional experimental data are crucial for refining and enhancing the predictive capabilities of the model in scenarios characterized by heightened energy and temperature conditions.

## V. Conclusions

The DFT method B<sub>3</sub>LYP/6-311++G(d, p) is employed to compute molecular parameters of phthalate esters commonly found in soft drinks. This method, a hybrid functional combined with a versatile basis set, is a well-established and reliable computational tool known for providing reasonably accurate results in molecular property calculations while remaining computationally feasible for a broad spectrum of organic systems. Various molecular properties such as electric dipole moment, polarizability, PA, and IE of VOCs, responsible for undesirable flavor in soft drinks, are determined using the DFT method. These properties are particularly valuable for VOC identification and quantification using PTR-MS. PA and IE of a molecule aid in determining the appropriate reagent ion for CI-MS ionization. The investigated phthalate esters can be ionised from H<sub>3</sub>O<sup>+</sup> as their PA values are well above the PA of H<sub>2</sub>O molecule. Similarly, PA determines that NH<sub>4</sub><sup>+</sup> could be used as a proton donor to all the molecules barring dimethyl phthalate and diethyl phthalate. IE of a molecule assists in selecting reagent ions, for example NO<sup>+</sup> and O<sub>2</sub><sup>+</sup> for charge transfer reactions. The computed enthalpy change and free energy of the reaction between respective ions and the molecule supports the aforementioned statement. Notably, the reactions involving NH<sub>4</sub><sup>+</sup> with dimethyl phthalate and diethyl phthalate are found to be endothermic, with positive enthalpy change and free energy. Such reactions, characterized by their rapid and exothermic nature, occur at collision rates predicted by collision models.

The rate constants for ion-molecule reactions involving various reagent ions such as H<sub>3</sub>O<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, NO<sup>+</sup>, and O<sub>2</sub><sup>+</sup>, and phthalate esters are computed using the parametrised trajectory method. The electric dipole moment and polarizability of neutral molecule serves as key parameters in determining rate constants in CI-MS reactions. Higher dipole moment indicates stronger interactions with charged ions, leading to higher reaction rates. A higher dipole moment contributes with both ion-induced dipole interactions and ion-permanent dipole interactions. For the reason, bis(2-Methoxyethyl) phthalate found to have higher rates. The parametrised trajectory method-derived rates, incorporating centre-of-mass and temperature dependence, best describe PTR-MS drift-tube reactions.

In summary, the enthalpy changes, free energies, and rates of the ion-molecule reactions for different ions are helpful in determining VMRs and VOC concentrations without the need for prior calibration using external gas standards. However, it must be noted that, due to the varying energetics of ions like NO<sup>+</sup>, and O<sub>2</sub><sup>+</sup> and the complexity of the analyte molecule, accurately predicting product ions, which is essential for determining VOC concentrations, is challenging.

## Declarations

Ethical Approval

Not applicable

## Competing interests

Not applicable

## Authors' contributions

Not applicable

## Funding

Not applicable

## Availability of data and materials

Data is available on request from the author.

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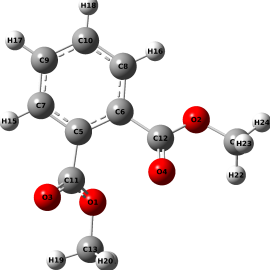
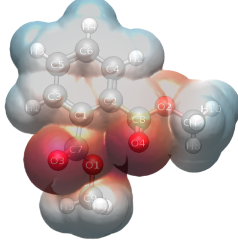
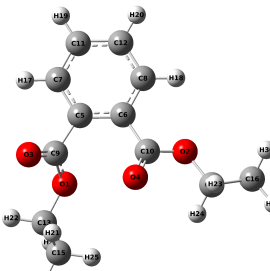
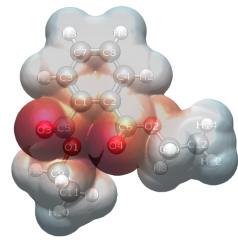
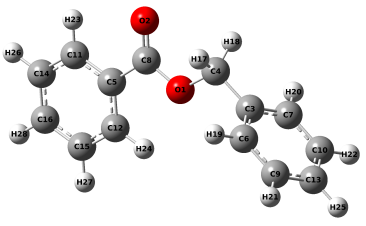
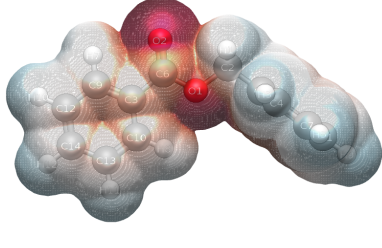
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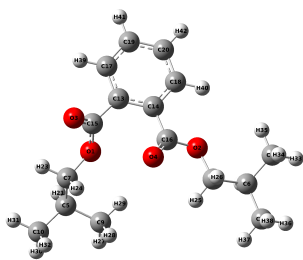
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Table 1. Optimized structures of phthalate esters using B<sub>3</sub>LYP/6-311++G(d, p) DFT and protonation sites in terms of NBO charges (a u).

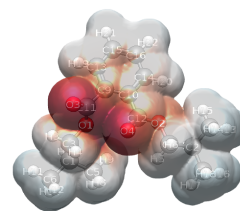
Optimized Geometry	NBO Charge	Electrostatic potential
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<p data-bbox="391 799 486 833">84-66-2</p> 	<p data-bbox="742 799 885 911">O1=-0.55787 O2=-0.56561 O3=-0.58738 O4=-0.59035</p>	
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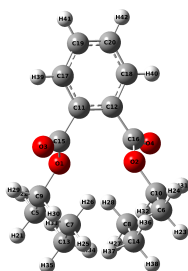
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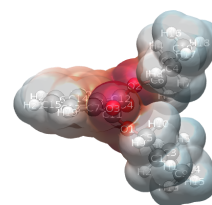
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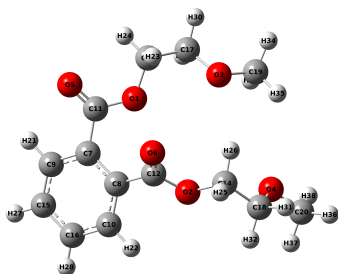
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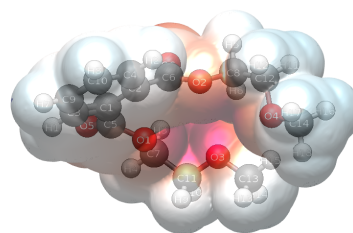
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O4=-0.59400



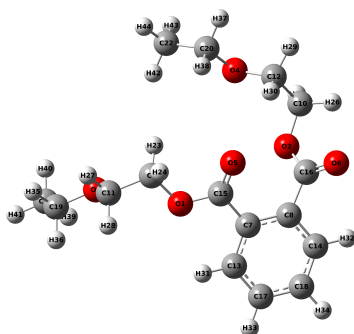
117-82-8



O1=-0.55644  
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O3=-0.59388  
O4=-0.59016  
O5=-0.58980  
O6=-0.58813



605-54-9



O1=-0.55530  
O2=-0.54867  
O3=-0.60272  
O4=-0.60709  
O5=-0.59695  
O6=-0.59149

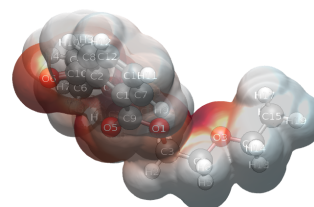


Table 2. Computed molecular parameters of seven phthalate esters using B<sub>3</sub>LYP/6-311++G(d, p) level of DFT theory.

Molecule	CAS no.	Molar Mass a u	Dipole Moment Debye	Polarizability (Å <sup>3</sup> )	Proton Affinity KJ/mol	IE (eV)	EA (eV)
Dimethyl Phthalate (C <sub>10</sub> H <sub>10</sub> O <sub>4</sub> )	131-11-3	194.18	3.38	19.42	833.24	9.16	0.14
Diethyl Phthalate (C <sub>12</sub> H <sub>12</sub> O <sub>4</sub> )	84-66-2	222.24	3.67	23.16	847.51	9.05	0.11
Benzyl Benzoate (C <sub>14</sub> H <sub>12</sub> O <sub>2</sub> )	120-51-4	212.24	2.34	25.05	861.65	8.87	0.02
Diisobutyl Phthalate (C <sub>14</sub> H <sub>22</sub> O <sub>4</sub> )	84-69-5	278.34	3.82	30.49	856.79	8.99	0.15
Dibutyl Phthalate (C <sub>16</sub> H <sub>22</sub> O <sub>4</sub> )	84-74-2	278.34	3.96	30.17	856.09	9.03	0.13
Bis(2-Methoxyethyl) Phthalate (C <sub>14</sub> H <sub>18</sub> O <sub>6</sub> )	117-82-8	282.29	4.90	28.19	923.20	8.68	0.04
Diethoxyethyl Phthalate (C <sub>16</sub> H <sub>22</sub> O <sub>6</sub> )	605-54-9	310.34	3.85	31.98	876.51	8.56	0.10

Table 3. Computed enthalpy change and free energy change of the reactions of phthalate esters with CI-MS reagent ions. All energy values are in KJ/mol.

Molecule	Enthalpy ( $\Delta H$ )				Free Energy ( $\Delta G$ )			
	H <sub>3</sub> O <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	NO <sup>+</sup>	O <sub>2</sub> <sup>+</sup>	H <sub>3</sub> O <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	NO <sup>+</sup>	O <sub>2</sub> <sup>+</sup>
Dimethyl Phthalate (C <sub>10</sub> H <sub>10</sub> O <sub>4</sub> )	-144.84	+20.22	-97.34	-213.49	-145.92	+17.8	-102.30	-215.05
Diethyl Phthalate (C <sub>12</sub> H <sub>12</sub> O <sub>4</sub> )	-158.96	+6.09	-110.53	-226.68	-160.43	+3.29	-115.55	-228.30
Benzyl Benzoate (C <sub>14</sub> H <sub>12</sub> O <sub>2</sub> )	-175.20	-10.14	-107.99	-224.14	-175.60	-11.88	-104.48	-217.23
Diisobutyl Phthalate (C <sub>14</sub> H <sub>22</sub> O <sub>4</sub> )	-168.32	-3.26	-116.06	-217.23	-168.67	-4.95	-113.29	-233.92
Dibutyl Phthalate (C <sub>16</sub> H <sub>22</sub> O <sub>4</sub> )	-165.50	-0.44	-101.93	-218.08	-166.85	-3.13	-104.52	-225.14
Bis(2-Methoxyethyl) Phthalate (C <sub>14</sub> H <sub>18</sub> O <sub>6</sub> )	-237.22	-72.16	-128.04	-244.19	-228.85	-65.13	-138.54	-251.26
Diethoxyethyl Phthalate (C <sub>16</sub> H <sub>22</sub> O <sub>6</sub> )	-189.71	-24.65	-139.89	-256.04	-178.25	-14.53	-139.63	-260.25

Table 4. Rate constants from parametrised trajectory method of the reactions of common CI-MS reagent ions with phthalate esters at various temperatures. Computed rates are in the units of  $10^{-9}\text{cm}^3\text{s}^{-1}$  at E/N is equals to 120 Td. Where Td= $10^{-21}\text{V} \cdot \text{m}^2$ .

Molecule	T K	$k_L$				$k$			
		$\text{H}_3\text{O}^+$	$\text{NH}_4^+$	$\text{NO}^+$	$\text{O}_2^{+\bullet}$	$\text{H}_3\text{O}^+$	$\text{NH}_4^+$	$\text{NO}^+$	$\text{O}_2^{+\bullet}$
Dimethyl Phthalate ( $\text{C}_{10}\text{H}_{10}\text{O}_4$ )	300	2.47	2.53	2.02	1.96	3.82	3.93	2.99	2.88
	350					3.74	3.84	2.93	2.84
	380					3.70	3.80	2.90	2.81
Diethyl Phthalate ( $\text{C}_{12}\text{H}_{12}\text{O}_4$ )	300	2.68	2.75	2.19	2.13	4.12	4.24	3.20	3.09
	350					4.03	4.15	3.15	3.04
	380					3.99	4.10	3.12	3.01
Benzyl Benzoate ( $\text{C}_{14}\text{H}_{12}\text{O}_2$ )	300	2.80	2.87	2.28	2.22	3.36	3.35	2.61	2.53
	350					3.27	3.32	2.59	2.51
	380					3.22	3.30	2.58	2.50
Diisobutyl Phthalate ( $\text{C}_{14}\text{H}_{22}\text{O}_4$ )	300	3.06	3.13	2.48	2.41	4.33	4.46	3.37	3.26
	350					4.26	4.38	3.32	3.21
	380					4.22	4.34	3.30	3.19
Dibutyl Phthalate ( $\text{C}_{16}\text{H}_{22}\text{O}_4$ )	300	3.04	3.12	2.46	2.39	4.44	4.57	3.45	3.33
	350					4.36	4.49	3.39	3.28
	380					4.32	4.44	3.37	3.25
Bis(2- Methoxyethyl) Phthalate ( $\text{C}_{14}\text{H}_{18}\text{O}_6$ )	300	2.94	3.01	2.38	2.31	5.18	5.33	4.05	3.91
	350					5.04	5.19	3.95	3.82
	380					4.97	5.11	3.90	3.77
Diethoxyethyl Phthalate ( $\text{C}_{16}\text{H}_{22}\text{O}_6$ )	300	3.12	3.20	2.52	2.45	4.36	4.49	3.39	3.28
	350					4.29	4.42	3.35	3.23
	380					4.26	4.38	3.32	3.21

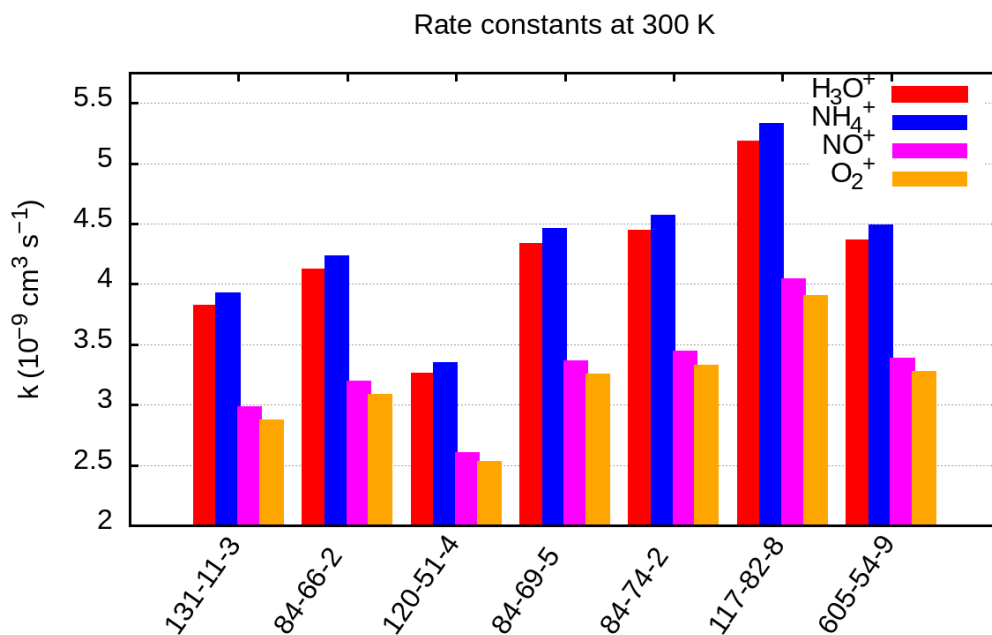


Figure 1. Rate constant fluctuations of phthalates with popular reagent ions at 300 K and 120 Td.

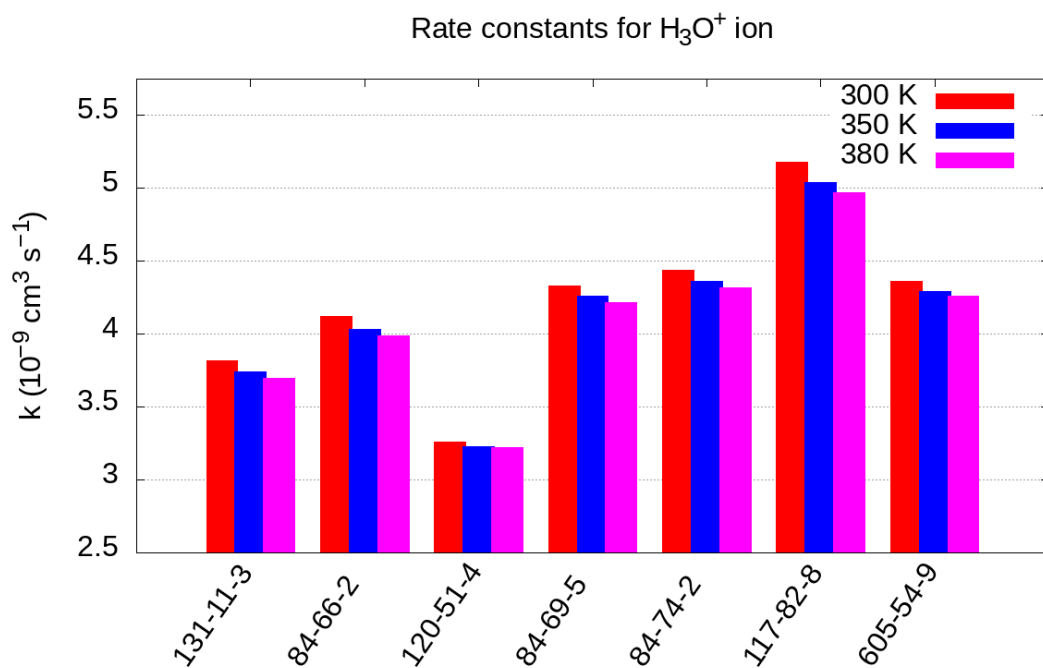


Figure 2. Computed rates of the reactions of phthalates and H<sub>3</sub>O<sup>+</sup> ions at different temperatures at 120 Td.