

RESEARCH ARTICLE

An Automated Tool for Predicting Ion-Molecule Reaction Rates in CI-MS: Application to PCDDs and PCDFs

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Correspondence: Manjeet Bhatia (manjeet.bhatia@quantumsimm.com)**Received:** 26 February 2026 | **Revised:** 25 August 2026 | **Accepted:** 1 September 2026**Keywords:** CI-MS | collision rates | DFT | polychlorinated dibenzo-p-dioxins | polychlorinated dibenzofurans

ABSTRACT

Polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are persistent environmental pollutants that bioaccumulate through the food chain, posing serious health risks to humans and animals. Dioxins and Furans are persistent, ultra-trace semi-volatile organic compounds (SVOCs) characterized by exceptionally low vapor pressures. Their quantification using chemical ionization mass spectrometry (CI-MS) and gas chromatography mass spectrometry (GC-MS) critically depends on their intrinsic physicochemical properties. In this work, density functional theory (DFT) calculations were employed to determine key molecular parameters of analytical relevance, including proton affinity, ionization energy, dipole moment, and polarizability of the 20 most important PCDDs and PCDFs. Furthermore, rate coefficients for ion-molecule reactions with the reagent ions H_3O^+ and NO^+ were evaluated via classical collision models. The thermodynamic feasibility of proton- and charge-transfer pathways was systematically examined under elevated temperature and energetic conditions typical of CI-MS. In particular, the enthalpy of reaction with NO^+ ions was computed to confirm the viability of charge transfer mechanisms. Additionally, we present a Python-based automated utility and database of over 200 VOCs with DFT-derived descriptors for rapid estimation of reaction rate coefficients, ion kinetic energies, effective temperatures, and center-of-mass energies in CI-MS processes. (Link: <https://github.com/Manjeetkb/rate-cal>)

1 | Introduction

Many major environmental pollutants include polychlorinated dibenzo-p-dioxins (PCDDs) and their chemically related compounds, polychlorinated dibenzofurans (PCDFs) [1, 2]. PCDDs and PCDFs are ultra-trace, persistent semi-volatile compounds characterized by exceptionally low vapor pressures. These substances are key examples of persistent organic pollutants that are known to cause toxicity in both humans and wildlife [3].

These molecules are polycyclic aromatic structures composed of two benzene rings linked by oxygen atoms (dibenzo-p-dioxin) or one oxygen and one carbon bridge forming a furan ring (dibenzofuran), with various numbers and positions of chlorine substituents [4]. There are 75 possible PCDD congeners and 135 PCDF congeners; a small subset (notably the 2378-substituted congeners such as 2378-TCDD) is especially toxic and used as toxicity benchmarks [5]. PCDD/PCDFs are not intentionally produced for general use; they are unintended byproducts of

Abbreviations: 1234678-HCDBD, 1,2,3,4,6,7,8-heptachlorodibenzo-p-dioxin; 1234678-HCDBF, 1,2,3,4,6,7,8-heptachlorodibenzofuran; 1234789-HCDBF, 1,2,3,4,7,8,9-heptachlorodibenzofuran; 123478-FCDBD, 1,2,3,4,7,8-hexachlorodibenzo-p-dioxin; 123478-HCDBF, 1,2,3,4,7,8-hexachlorodibenzofuran; 123678-HCDBD, 1,2,3,6,7,8-hexachlorodibenzo-p-dioxin; 123678-HCDBF, 1,2,3,6,7,8-hexachlorodibenzofuran; 123789-HCDBD, 1,2,3,7,8,9-hexachlorodibenzo-p-dioxin; 123789-HCDBF, 1,2,3,7,8,9-hexachlorodibenzofuran; 12378-PCDBD, 1,2,3,7,8-pentachlorodibenzo-p-dioxin; 12378-PCDBF, 1,2,3,7,8-pentachlorodibenzofuran; 14-D, 1,4-dioxin; 234678-HCDBF, 2,3,4,6,7,8-hexachlorodibenzofuran; 23478-PCDBF, 2,3,4,7,8-pentachlorodibenzofuran; 2378-TCDBD, 2,3,7,8-tetrachlorodibenzo-p-dioxin; 2378-TCDBF, 2,3,7,8-tetrachlorodibenzofuran; 2-CDBD, 2-chlorodibenzo-p-dioxin; DB-14-D, Dibenzo-1,4-dioxin; OCDBD, Octachlorodibenzo-p-dioxin; OCDBF, Octachlorodibenzofuran.

combustion, chlorine-based industrial processes (historically, paper bleaching), and chlorine-mediated chemical syntheses [6, 7]. PCDDs and PCDFs occur in environmental compartments (air, soil, sediments, biota, and foodstuffs) because they are highly persistent, hydrophobic, and lipophilic [8, 9]. Because of environmental persistence and bioaccumulation, human exposure is long-term and primarily via contaminated foodstuffs (animal fats, dairy, and certain fish) [10, 11]. The long biological half-life in humans raises concern about lifetime exposure even when environmental emissions are controlled. Monitoring and remediation strategies thus focus heavily on preventing formation and limiting food-chain entry [6]. PCDD/PCDF analysis is a mature but analytically demanding field because of: (1) very low environmental concentrations of toxic congeners (pg-ng levels), (2) the need for congener specificity, and (3) the chemically similar family members and matrix complexity. High-resolution gas chromatography coupled to high-resolution mass spectrometry (HRGC/HRMS) is the internationally accepted regulatory approach [12]. While advances in triple-quadrupole GC-MS/MS and high-resolution accurate-mass TOF systems have enabled the validation of alternative procedures for certain matrices, allowing for lower-cost or higher-throughput options where validated [13–16]. Chemical ionization mass spectrometry (CI-MS) techniques such as proton transfer reaction mass spectrometry (PTR-MS) and selected ion flow tube mass spectrometry (SIFT-MS) are optimized for volatile organic compounds (VOCs) [17, 18], quantification of semi-volatile organic compounds (SVOCs) is performed mainly via modified CI-MS methods [19–23]. Still, their application to PCDD/PCDFs is challenging due to their low volatility and tendency to associate with particles.

However, in recent years, the complementary use of PTR-MS with GC-MS (including TD-GC-MS), GC-MS/MS, or related techniques has benefited the quantification of SVOCs, as well as VOCs and intermediate-volatility compounds (IVOCs) [24, 25]. PTR-MS excels at real-time, high-sensitivity quantification of known (or previously identified) gas-phase species with soft ionization and minimal sample preparation. Still, it has limitations in isomer/isobar resolution, structural identification, and handling complex mixtures without chromatographic separation. GC-MS (or GC-MS/MS) provides chromatographic separation, robust compound identification (via retention times and fragmentation patterns or library matching), and reliable quantification, especially for SVOCs that require thermal desorption or specialized sampling [5, 14, 26, 27]. Combining them allows identification and method validation via GC-based methods, followed by accurate real-time or continuous quantification via PTR-MS, or cross-validation of concentrations and emission profiles.

H_3O^+ and NO^+ are commonly used reagent ions in CI-MS for VOC and SVOC analysis through proton transfer and charge transfer reactions, respectively. H_3O^+ proton transfer in PTR-MS is often ineffective for highly chlorinated congeners because proton affinities are reduced by chlorination relative to water. Published experimental product-ion studies for NO^+ with aromatics support NO^+ charge-transfer dominance and provide fragmentation expectations [28, 29]. Direct experimental proton affinity (PA) values for PCDD/PCDF congeners are

scarce; however, general thermochemical trends show chlorination lowers PA of aromatic systems, and many highly chlorinated congeners have PAs below that of water, explaining the poor performance of H_3O^+ protonation for these analytes. PTR-MS SOPs note the $\text{PA}(\text{H}_2\text{O})$ threshold as a principal limitation for H_3O^+ mode detection [30]. Physicochemical property data, such as PA and ionization energy (IE), have analytical relevance to CI-MS. Similarly, experimental REMPI and photoelectron spectroscopies and computational studies (e.g., Zimmermann et al. [31, 32]) provide IE values showing that most PCDD congeners have IE well below 9.26 eV ($\text{IE}[\text{NO}]$), enabling NO^+ charge transfer for many congeners. Knowledge of IE supports reagent-ion selection in CI-MS. Other molecular properties that are vital in understanding ion-molecule reactions and fundamental interactions between approaching ions and neutral analyte molecules are the dipole and polarizability of neutral molecules. DFT/QSAR studies show polarizability increases with chlorination and correlates with toxic potency metrics used in QSAR and receptor-binding models; dipole moments vary with substitution pattern and are often small for symmetric congeners [33]. These markers are also useful in modeling chromatographic behavior and interaction with sorbents.

In this study, these molecular properties that are of utmost importance in the analytic procedure of identification and quantification of PCDD and PCDFs are computed using B3LYP/6-311++G(d, p) DFT method. Ion-molecule interactions occur when reactants come closer to have collision reactions, and rate coefficients of such reactions are computed based on the dipole moment and polarizability of the neutral molecule. Classical trajectory models given by Su and Chesnavich are implemented at different temperatures and energetics to understand CI-MS reactions.

2 | Overview–Ion Chemistry

2.1 | H_3O^+ -CIMS

Hydronium ion (H_3O^+) is the most widely used reagent ion in CI-MS instruments such as PTR-MS and SIFT-MS because it is easy to generate in high concentrations (typically from ionizing humidified air/water vapor with a discharge) [29, 30]. It reacts predictably with VOCs whose PA is greater than that of water (~ 691 kJ/mol). The reaction is highly exothermic, leading mostly to protonated parent ions ($[\text{M}+\text{H}]^+$), minimizing fragmentation (soft ionization). The efficiency and selectivity of H_3O^+ chemistry depend on controlling the ion-molecule environment drift tube or flow tube pressure: PTR-MS operates at a few millibars, ensuring low-energy ion-molecule collisions and stable cluster formation [34]. Electric field (E/N ratio), a reduced electric field (E/N , where E is electric field strength and N is gas number density) between 80 and 120 Td (Td = Townsend = 10^{-21} V m²) is commonly used [34, 35].

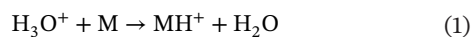
Lower E/N promotes more clustering of H_3O^+ with water ($\text{H}_3\text{O}^+ \cdot (\text{H}_2\text{O})_n$). Higher E/N generally leads to more declustering, higher ion energy, and possible fragmentation. Typically, nitrogen or air with controlled humidity is used as buffer gas. The

water vapor is essential both to generate H_3O^+ and to control cluster ion equilibria. The drift tube temperature (40°C–120°C) influences water clustering and ion-molecule kinetics [36].

2.1.1 | Types of Reactions of H_3O^+ With VOCs

In soft ionization mass spectrometry, the main pathways include:

- **Proton transfer (dominant mechanism)**



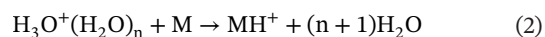
Occurs if $\text{PA}(\text{M}) > \text{PA}(\text{H}_2\text{O})$. This is the classic soft-ionization route, yielding protonated molecules $[\text{M}+\text{H}]^+$ with minimal fragmentation. For example, in the case of alcohols, ketones, aldehydes, amines, esters, ethers, and aromatics with sufficient PA.

- **No reaction (inefficient ionization)**

If $\text{PA}(\text{M}) < \text{PA}(\text{H}_2\text{O})$, proton transfer is endothermic or not favorable, so H_3O^+ cannot ionize the analyte effectively. Examples in this case include light alkanes, some halogenated compounds, CO_2 , N_2O , and O_2 [34]. These molecules pass through without ionization, giving PTR-MS inherent selectivity.

- **Cluster ion reactions**

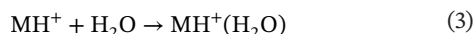
In humid conditions, H_3O^+ clusters with water:



Clustered hydronium can also protonate analytes, sometimes altering ionization efficiency or fragmentation patterns. Careful drift-tube tuning helps minimize cluster influence.

- **Hydration/dehydration reactions**

Some protonated VOCs form adducts or hydrated complexes:



This occurs especially with polar VOCs (alcohols, amines). These can complicate spectral interpretation but also provide structural clues.

- **Fragmentation pathways (at higher E/N)**

If the drift tube voltage is too high, excess internal energy leads to fragmentation. Protonated alcohols can lose water. Protonated esters may undergo rearrangement reactions.

Protonated aromatics may form fragment ions (benzyl cations, tropylium ions) [37]. Although fragmentation reduces quantification accuracy, it can be used for selective detection.

- **Secondary reactions (rare but possible)**

Protonated analyte (MH^+) can react with neutral water clusters or other VOCs. Charge transfer is usually not observed with H_3O^+ (unlike NO^+ or O_2^{+*}).

Selectivity in chemical ionization is enhanced for compounds with PA greater than that of water [$\text{PA}(\text{H}_2\text{O})$], as only these species undergo efficient proton transfer and are thus readily detected. This approach is well-suited for VOCs, but less effective for low-PA pollutants such as chlorinated dioxins and furans. Under soft ionization conditions, the resulting ions are predominantly intact protonated molecules $[\text{M}+\text{H}]^+$, facilitating accurate quantification. Reliable calibration, however, requires known reaction rate coefficients (k) for the $\text{H}_3\text{O}^+ + \text{M}$ reaction under specified instrumental conditions [28, 38]. For many VOCs, these rate coefficients have been experimentally determined using SIFT-MS or PTR-MS.

With many advantages, H_3O^+ -CIMS is not suitable for low-PA molecules, in case of clustering (clustering can complicate spectra), and cannot easily differentiate isomers. All the reaction types occurring with H_3O^+ ions to VOCs are summarized in Table 1.

H_3O^+ in CI-MS primarily drives proton transfer to VOCs with PA higher than water, yielding soft ionization and clean protonated molecular ions. Clustering, hydration, and occasional fragmentation occur depending on drift tube conditions (E/N, humidity, temperature). For low-PA compounds (like halogenated dioxins/furans), H_3O^+ is ineffective, requiring alternative reagent ions such as NO^+ or O_2^{+*} (charge transfer).

2.2 | NO^+ -CIMS

Nitric oxide cation (NO^+) is an important alternative to H_3O^+ in soft ionization mass spectrometry because it expands the range of detectable molecules: the IE of NO is 9.26 eV. This allows charge transfer to VOCs with IE < 9.26 eV (aromatics, alkenes, phenols, dioxins, furans). It can also undergo hydride abstraction (H^- transfer) and association reactions, depending on molecular structure. Compared to H_3O^+ , NO^+ is more suitable for low PA molecules that cannot be ionized by proton transfer

TABLE 1 | Summary table; possible reactions of H_3O^+ with VOCs.

Reaction type	Condition	Outcome	Example VOCs
Proton transfer	$\text{PA}(\text{M}) > \text{PA}(\text{H}_2\text{O})$	$[\text{M}+\text{H}]^+$ dominant	Alcohols, ketones, aromatics
No reaction	$\text{PA}(\text{M}) < \text{PA}(\text{H}_2\text{O})$	Undetected	Light alkanes, halogenated VOCs
Cluster ion transfer	Humid conditions	$[\text{M}+\text{H}]^+$ with water clusters	Polar VOCs
Hydration/dehydration	Polar VOCs, high humidity	$[\text{M}+\text{H}]^+ \cdot (\text{H}_2\text{O})_n$	Amines, alcohols
Fragmentation	High E/N	Fragments of MH^+	Esters, aromatics
Secondary reactions	Rare	Adducts or loss of selectivity	Mixed VOC environments

[28, 29]. Thus, NO⁺ chemistry complements H₃O⁺ chemistry, increasing chemical coverage.

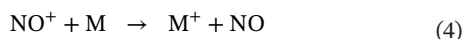
2.2.1 | Environmental Conditions for NO⁺ Ion Chemistry

To maintain predictable and selective ion-molecule reactions NO⁺ ions are generated from air or N₂/O₂ mixtures by discharge, producing NO⁺ among other ions [39]. Drift tube or flow tube pressures are typically 1-3 mbar in PTR-MS; ~ 1 Torr in SIFT-MS. The electric field (E/N ratio) is generally controlled in the range 80-120 Td. Lower E/N means fewer energetic collisions and reduced fragmentation. Higher E/N produces increased fragmentation or secondary ion-molecule reactions. Carrier gas is usually nitrogen, sometimes air, with low humidity to avoid competing hydration or H₃O⁺ formation. Tube temperatures (40-120°C) help control clustering and ion energetics.

2.2.2 | Types of Reactions of NO⁺ With VOCs

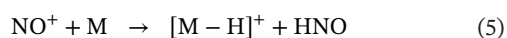
Unlike H₃O⁺, NO⁺ engages in multiple competing pathways depending on VOC properties:

- **Charge transfer (CT)**



Dominant if the ionization energy of the analyte (IE(M)) < 9.26 eV. The above reaction (4) may produce radical cations (M^{•+}), often without fragmentation (soft ionization). This type of reaction is particularly effective for aromatic VOCs (benzene, toluene, phenols, dioxins), alkenes, and polycyclic aromatics.

- **Hydride abstraction (H⁻ transfer)**



Hydride abstraction occurs for molecules with relatively weak C-H bonds and produces [M-H]⁺ ions (less common in H₃O⁺ chemistry). Type (5) is commonly reported in alkylbenzenes, aldehydes, and in some oxygenated VOCs. It can be useful for selectivity when charge transfer is inefficient.

- **Association (adduct formation)**



The association reaction (6) is favored with polar molecules or those with π -electrons that stabilize complexes. The

association type reaction yields strong diagnostic ions, e.g., aromatic-NO⁺ adducts. Commonly used for phenols, polycyclic aromatic hydrocarbons, and some oxygenates [40].

- **Fragmentation reactions**

At higher E/N values, radical cations (M^{•+}) from charge transfer may undergo fragmentation, for example, benzene → C₆H₆^{•+} → fragment cations and toluene → tropylium cation (C₇H₇⁺). Fragmentation reduces quantification accuracy, but sometimes improves compound identification.

- **No reaction (inefficient ionization)**

If IE(M) > 9.26 eV, charge transfer is not possible. Examples include methane, ethane, acetylene. Such molecules remain undetected with NO⁺ reagent ions. Other reagent ions, such as O₂⁺, can also be used for ionization; however, they may promote fragmentation.

Analytical implications include broader coverage, as NO⁺ detects many compounds missed by H₃O⁺ (low-PA, high-stability VOCs) [41, 42]. Improved selectivity results from different pathways (CT, H⁻ abstraction, adducts) that produce unique fingerprints. Soft ionization charge transfer often yields intact radical cations.

Still, many quantification challenges, such as competing channels (CT vs H⁻ abstraction vs association), complicate signal interpretation. Reaction rate constants (*k*) vary widely, requiring calibration or SIFT-MS kinetic data.

In CI-MS, NO⁺ reagent ions engage in charge transfer, hydride abstraction, association, and fragmentation reactions with VOCs [28]. All reactions under NO⁺-CI-MS are summarized in Table 2. Their reactivity depends on the ionization energy, the molecular structure, and the conditions inside the drift tube [34]. NO⁺ expands the detection to aromatic molecules and low-PA molecules that H₃O⁺ cannot ionize, but the interpretation can be more complex due to multiple competing channels.

3 | Computational Method

All molecular structures used in this study were obtained from reputable databases such as NIST and PubChem. These structures were then optimized using the B3LYP/6-311++G(d, p) DFT method, as implemented in the Gaussian 16 suite of programs [43]. The absence of negative vibrational frequencies confirms that all structures correspond to fully relaxed, minimum-energy geometries, making them suitable for further computational analysis.

TABLE 2 | Summary table; possible reactions of NO⁺ with VOCs.

Reaction type	Condition	Outcome	Example VOCs
Charge transfer (CT)	IE(M) < 9.26 eV	M ⁺ dominant	Aromatics, alkenes, phenols, dioxins
Hydride abstraction	Weak C-H bonds	[M-H] ⁺ + HNO	Aldehydes, alkylbenzenes
Association	Polar/ π -electron VOCs	[M.NO] ⁺	Phenols, PAHs
Fragmentation	High E/N	Product ions from M ^{•+}	Toluene → C ₇ H ₇ ⁺
No reaction	IE(M) > 9.26 eV	None	Methane, ethane

The rate coefficients were calculated using the parameterized trajectory method based on classical collision theory, as described by Su and Chesnavich [44–46]. The B3LYP/6-311++G(d,p) method offers an effective balance between computational cost and accuracy, making it well-suited for investigating both ground- and excited-state electronic properties of organic molecules [47]. Although no computational approach is entirely exact, the B3LYP functional [48] has demonstrated reliable performance across a broad range of molecular systems, including complex compounds such as dioxins and furans. When paired with the 6-311++G(d,p) basis set that incorporates diffuse and polarization functions, this method provides a robust framework for accurate calculations of molecular properties.

4 | Results and Discussion

The molecular geometries of dioxins and furans were fully optimized using the B3LYP/6-311++G(d,p) level of DFT method. Frequency analysis confirmed the absence of imaginary frequencies, indicating that all optimized structures correspond to true minima on the potential energy surface. The vibrational frequency calculations also provided dipole moments and polarizabilities for the neutral species, along with PA and IE, which are summarized in Table A1. Atomic coordinates and optimized structures are provided in Data S1.

Among the investigated compounds, DB-14-D, 14-D, 2378-TCDBD, 123678-HCDBD, and OCDBD exhibit vanishing dipole moments due to their high molecular symmetry. Other structurally similar derivatives, such as 1234678-HCDBD, 123478-FCDBD, 123478-HCDBF, 123678-HCDBF, 23478-PCDBF, 2378-TCDBF, 1234678-HCDBF, and OCDBF, show dipole moments close to zero. Dipole moment and polarizability are key parameters for estimating ion-molecule reaction rates, as they influence the interaction strength between reacting species.

The computed PA and IE values determine the preferred reaction pathway—proton transfer or charge transfer—in CI-MS. Proton transfer from H_3O^+ occurs only if the PA of the neutral molecule exceeds that of water (691 kJ/mol) [49]. Conversely, charge transfer from NO^+ is feasible when the IE of the neutral analyte is lower than that of NO (9.26 eV). The PA values of compounds such as 1234678-HCDBD, 12378-PCDBD, 123789-HCDBD, 123789-HCDBF, 123478-HCDBF, 123678-HCDBF, 12378-PCDBF, 1234678-HCDBF, OCDBF, and 1234789-HCDBF are significantly lower than that of water. Therefore, proton transfer from H_3O^+ is thermodynamically unfavorable, implying that these molecules would not yield detectable ion signals in H_3O^+ -CIMS. However, since their IE values are lower than that of NO , they can be efficiently ionized via charge transfer from NO^+ ions. The exothermic nature of the computed charge-transfer reaction enthalpies supports that such reactions occur readily upon collision.

4.1 | Rate Coefficients

Ion-molecule reactions lie at the heart of CI-MS, a soft ionization technique that allows the formation of molecular ions with minimal fragmentation. In such low-energy environments, the rate of reaction between reagent ions and neutral molecules depends

critically on long-range electrostatic interactions, such as ion-dipole and ion-induced dipole forces [50, 51]. At long range, before any chemical bond rearrangement occurs, the potential energy between an ion and a neutral molecule can be described by electrostatic interactions [44, 52]. The total potential energy $V(r, \theta)$ between an ion and a neutral molecule is typically expressed as:

$$V(r, \theta) = V_{\text{ion-dipole}}(r, \theta) + V_{\text{ion-induced dipole}}(r) \quad (7)$$

and

$$V(r, \theta) = -\frac{q\mu \cos \theta}{4\pi\epsilon_0 r^2} - \frac{1}{2} \frac{q^2 \alpha}{4\pi\epsilon_0 r^4} + V_{\text{dispersion}}(r) \quad (8)$$

where q is the charge of the ion, μ is the permanent dipole moment of the molecule, α is the isotropic polarizability, ϵ_0 is the permittivity of free space, r is the ion-molecule separation distance, and θ is the orientation angle between the ion field and the molecular dipole.

The first term represents the ion-dipole interaction, which depends on the alignment of the molecule's permanent dipole with the electric field of the ion (orientation-dependent). The second term represents the ion-induced dipole interaction, which is isotropic and always attractive. These interactions control the rate at which reactants approach each other, the stability of the intermediate complex, and ultimately the efficiency and selectivity of ion formation. The strength and nature of these interactions are determined primarily by two molecular parameters, the electric dipole moment and the polarizability of the neutral analyte.

The rate coefficients for H_3O^+ -CI-MS and NO^+ -CI-MS reactions were calculated at experimentally relevant reduced electric field values (E/N) of 100, 120, and 140 Td, and are summarized in Table A2. Generally, collision reaction rates in CI-MS tend to decrease as the reduced field E/N increases. Below, a comprehensive description is provided of the physical processes covering the kinetic and dynamical mechanisms (capture vs. energy control), the role of long-range forces and orientation, how ion energy and collision timescale change with E/N , how complex lifetime and stabilization change, and practical implications for CI-MS measurements.

4.1.1 | Collision at Low Ion Energy (E/N)

At low ion energy, long-range attractive potentials (ion-induced dipole $\propto -1/r^4$, ion-dipole $\propto -\cos \theta/r^2$) dominate. If a neutral enters the capture radius, it is very likely to form a transient complex that evolves to product, and the capture rate essentially determines the reaction rate. As a result, ion-molecule collisions are slow/soft, and high capture-based reaction rates are observed. Reaction capture for polar neutrals depends on the orientational alignment of the dipole with the ion's field. Alignment requires sufficient time for the torque from the ion field to reorient the molecule relative to its rotational inertia and thermal rotation. The rate at which ion-dipole interactions occur is orientation-dependent and strongly affected by rotational averaging and collision time. At low E/N , energy gained during the reaction complex formation can be transferred to internal rovibrational modes and then dissipated by buffer-gas collisions

(stabilization). At low ion energies, ion-molecule collisions allow sufficient interaction time for effective dipole orientation and energy redistribution, leading to stabilized product formation and higher reaction rates.

4.1.2 | Collision at High Ion Energy (E/N)

When E/N is higher, the collisions are too fast/energetic for long-range attraction to funnel neutral into a bound complex. When ions move faster (higher drift velocity/relative velocity), the collision or encounter time becomes short. If collision time is shorter than the reorientation time (or rotational period) of the neutral, the dipole cannot align effectively; hence the ion-dipole attractive well is less effective, and the capture cross section falls [37, 53]. After capture, a transient complex must live long enough to redistribute energy and proceed to product. Higher collision energies increase the probability that the complex will redissociate back to reactants (less stabilization) rather than evolve to a product. When the complex lifetime is shortened, the net effective rate to product drops even if capture occurs.

At higher E/N, the buffer gas collisions may be less effective at quickly removing energy from the complex (because the complex forms and dissociates faster), so stabilization probability is lower. Also, increased ion energy often raises internal excitation of products, increasing fragmentation likelihood rather than retention of intact parent ions. Because the ion-dipole interaction is orientation dependent, the effective enhancement of rate due to μ (dipole moment) drops with increasing effective temperature/ion energy. So, polar neutrals show a stronger decline in k with increasing E/N compared with nonpolar ones; see Figure 1a. The observed rates at varying E/N values for 123789-HCDBD ($\mu=1.89$ Debye) are shown in Figure 1b.

4.1.3 | Rates at Higher Temperature

The Langevin rate constants, which are temperature-independent, are generally lower than the experimentally or

theoretically determined rates that include dipolar interactions. For polar molecules, rate constants may decrease by up to an order of magnitude between 200 and 600 K. At lower temperatures, the “locked” dipole alignment occurs, leading to higher capture rates approaching the upper theoretical limit. At low temperatures (or in strong fields), molecular rotation is slow enough for the dipole to align with the ion’s field. The effective potential behaves as $\sim 1/r^2$, resulting in higher capture rates. At higher temperatures, rotational motion averages out the dipole orientation, effectively reducing the strength of the ion-dipole interaction. High temperatures favor faster rotation, weaker effective orientation (dipole averaging), and reduced rate coefficients; see Figure 2a,b. Temperature sets a neutral rotational population and affects orientational averaging. Higher neutral temperature similarly reduces ion-dipole enhancement. Under PTR-MS, in highly energetic collision conditions, the effective temperature becomes greater than 1000 K [46]. In a common working E/N = 200 Td maps to $T_{\text{eff}} \approx 2000$ K). Under SIFT-MS practical conditions (ions thermalize with the gas), where temperature varies from 80–600 K [54]. Computed rates at a temperature range of 50–600 K are shown in Table A3.

4.1.4 | Dipole Moment and Polarizability Dependence

As discussed earlier, the overall reaction rate depends strongly on the dipole moment and polarizability of the neutral analyte, and the observed rate coefficients clearly reflect these dependencies.

A permanent dipole moment arises from an asymmetric distribution of electronic charge within a molecule, producing partial positive and negative regions. When such a polar molecule encounters an ion, the ion’s electric field exerts a torque on the dipole, tending to align it so that the negative end faces the positively charged ion [55]. The potential energy of this ion-dipole interaction varies as $-1/r^2$ and depends on the orientation angle between the dipole axis and the electric field of the ion. For molecules possessing large dipole moments—such as water, alcohols, and alkylphenols—this interaction is

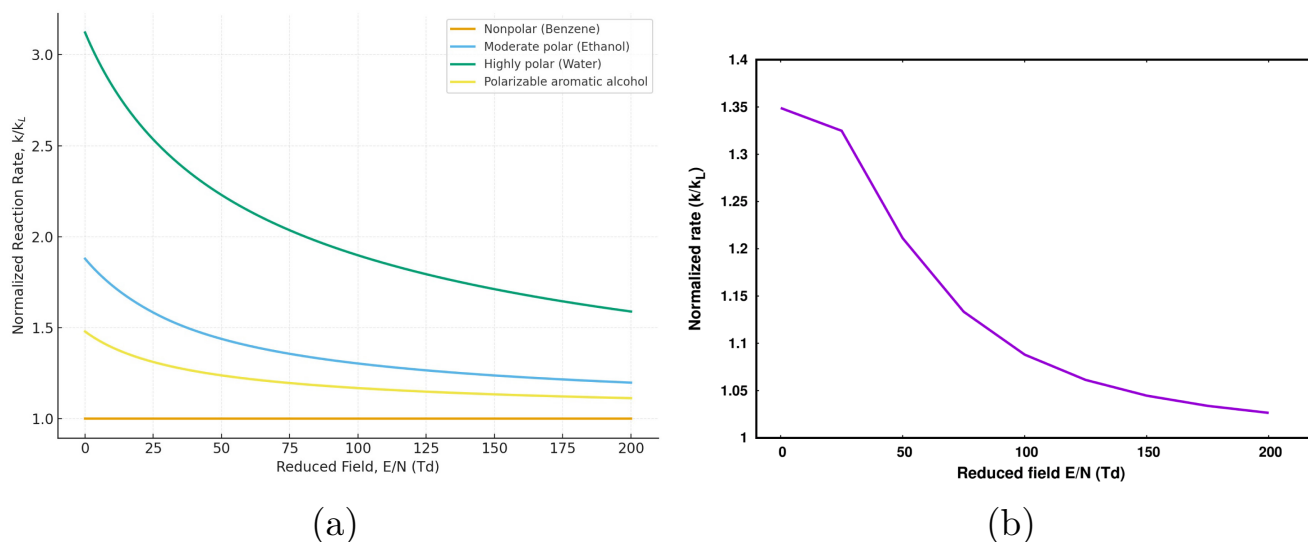


FIGURE 1 | Schematic representation of the variation of the rates with the applied electric field (E/N) (a) expected (b) reported for 123789-HCDBD.

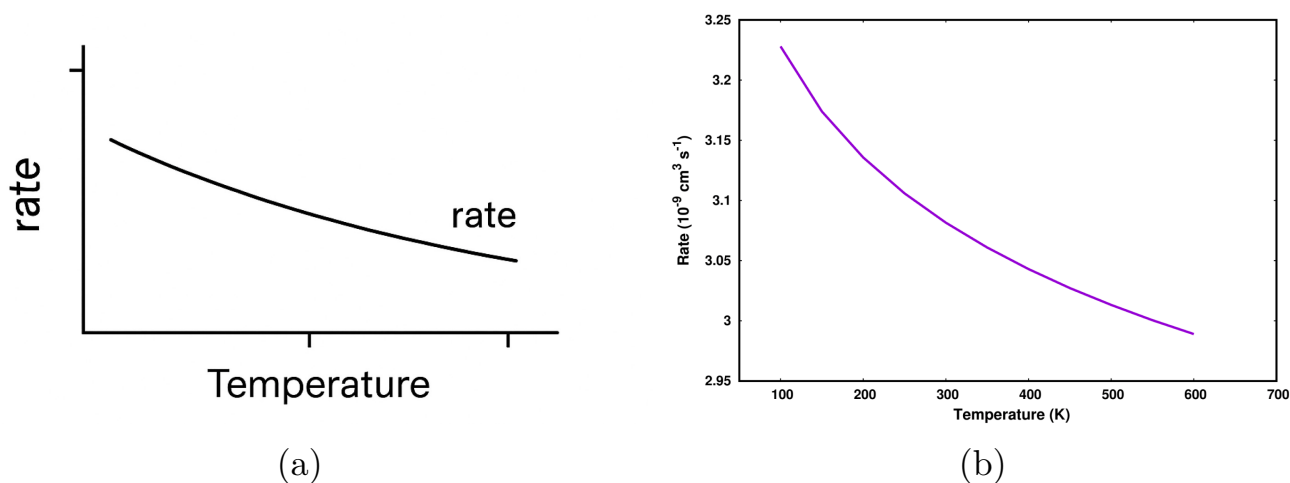


FIGURE 2 | Schematic representation of the variation of the rates with temperature (a) as per theory, (b) observed for 123789-HCDBF.

significant even at relatively large intermolecular separations, thereby increasing the capture cross-section and enhancing the rate coefficient.

In contrast, nonpolar analytes with zero permanent dipole moments lack the first term in the long-range potential (as given in Equation 8). For these molecules, the rate constant is governed solely by the Langevin (ion-induced dipole) contribution [50], which depends on the molecule's polarizability (α) and the ion charge. The polarizability represents the ease with which the electron cloud of a molecule can be distorted by an external electric field. A higher polarizability enhances the attractive interaction between the ion and the neutral, leading to greater collision efficiency and higher rates.

For large, flexible organic molecules (e.g., alkylphenols and terpenes), even a moderate dipole moment is complemented by substantial polarizability, both of which jointly contribute to the elevated ion-molecule reaction rates observed under soft ionization conditions. Conversely, molecules such as 14-D, which possess a negligible dipole moment and low polarizability, exhibit correspondingly low collision and reaction rate coefficients. This behavior directly reflects the weak long-range ion-molecule interaction potential governing their approach dynamics.

The interplay between ion-dipole and ion-induced dipole interactions is the cornerstone of ion-molecule reaction dynamics in soft CI-MS. While chemical reactivity at short range defines the ultimate product, long-range electrostatic forces dictate whether the reactants ever get close enough to react.

Dipole moment and polarizability govern the capture process, determining both the rate coefficient and the nature of the intermediate complex. Temperature and reduced electric field further modulate these effects by influencing rotational motion and collision energy.

In practical CI-MS applications, this means that analytes with high dipole moments and polarizabilities not only ionize more readily but also yield cleaner, softer spectra—allowing precise molecular identification. Hence, a deep understanding of these

fundamental electrostatic interactions bridges the gap between molecular physics and applied analytical chemistry.

4.2 | Enthalpy

When NO^+ collides with M, an electron jumps from M to NO^+ (if energetically favorable). The potential energy of the system suddenly changes; the products ($\text{M}^+ + \text{NO}$) are lower in energy by ΔH . The reaction enthalpy (ΔH) quantifies the net change in total internal energy between reactants and products at constant pressure. Experimentally, it determines fragmentation, ion intensity, and spectral appearance in mass spectrometry. For this charge transfer reaction:

$$\Delta H = H_{\text{products}} - H_{\text{reactants}} \quad (9)$$

ΔH , which varies from -138 to -239 kJ/mol as reported in Table A2, shows that charge transfer from NO^+ to M is energetically favorable, i.e., spontaneous once a collision occurs. Because $\Delta H < 0$, the system releases energy when NO^+ transfers its charge to M. But in a molecular collision, this released energy doesn't simply disappear; it gets redistributed among various forms of motion and excitation of the products; see Figure 3.

ΔH reflects how much energy is redistributed among internal and translational degrees of freedom after the collision. In soft ionization (CI-MS), such reactions occur without fragmentation because the total energy ($\sim 1\text{--}2$ eV) is not high enough to break bonds in most organic molecules. Thus, ΔH determines both the reaction feasibility and the stability of the product ion. The redistribution of ΔH directly determines whether M^+ remains intact or fragments (depends on internal energy). How fast products separate depends on translational energy. The ion kinetic energy distribution observed in CI-MS. The softness of ionization means gentle ionization, less fragmentation, and more selective spectra. ΔH marginally above -100 kJ/mol is mostly indicative of mild internal excitations, which lead to a stable parent ion. Enthalpy change, ΔH above -200 kJ/mol, excess energy may excite M^+ beyond the dissociation threshold and result in fragmentation. Among the investigated molecules DB-14-D, 14-D, 2-CDBD, and 2378-TCDBD, having Δ

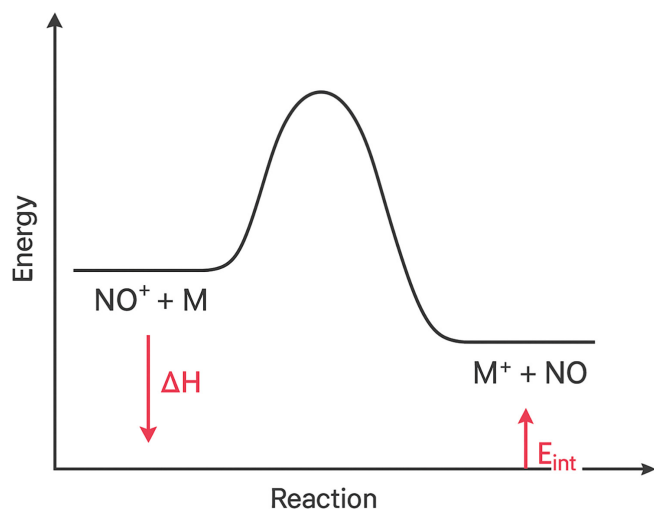


FIGURE 3 | Diagram showing the energy profile including internal energy redistribution.

H above -200 kJ/mol, are unlikely to proceed through charge transfer but could lead to fragmentation. From an experimental point of view, excessive ΔH , which is energy shared among vibrational, rotational, and translational modes after charge transfer, impacts fragmentation, ion intensity, and selectivity in CI-MS. Initial impression about the charge transfer from NO^+ to the analyte seems feasible because all the reactions are exothermic and occur on every collision; experimental verification (of possible fragmentation) is still awaited, especially for ΔH above -200 kJ/mol. Under ideal conditions, a reaction may occur following each effective collision; however, exceptions arise when competing reaction channels are available or when fragmentation pathways become significant. Therefore, the present study should be regarded as a kinetic and thermochemical screening tool that provides molecular-level information useful for designing and interpreting CI-MS experiments, rather than as a complete reaction-pathway or quantitative mass-spectral prediction model.

4.3 | Overview of Rate Cal Application

The “Rate Cal” application simplifies the calculation of rate coefficients under PTR-MS energetic conditions, utilizing the dipole moment and polarizability of the neutral molecule. An overview of the application is provided in Data S2. The link is provided to download the application on [GitHub](#).

4.3.1 | How It Works:

To use the application, simply:

- Enter the CAS number of the molecule.
- Select desired E/N values and temperature.
- Choose the relevant ions from the provided options.

After submitting your input, the application returns:

- Parameterized capture collision rate coefficients.

- Langevin rate coefficients.
- Ion energy.
- Center-of-mass energy.
- Effective collision temperature.

In addition, DFT-computed values of proton affinity and ionization energy can be included in the data, if available.

4.3.2 | Platform and Data Integration:

- The application is available for Windows and Linux users.
- A CSV file must be present in the same directory as the application.
- The default CSV file includes data for 200 molecules, each characterized through DFT calculations.

Users can extend the dataset by adding:

- Dipole moment and polarizability (required for rate calculations).
- Optional values such as proton affinity, ionization energy, etc.

4.3.3 | Additional Support for SIFT-MS:

While Rate Cal focuses on CI-MS reactions (which involve nonthermal energetic conditions), rate coefficient calculations under thermal conditions for SIFT-MS can be performed using a dedicated companion application.

For SIFT-MS users:

- Calculated rates compatible with SIFT-MS conditions are available.
- Table A3 provides rates at various thermal temperatures.

4.3.4 | Eliminating Calibration Challenges in CI-MS With Accurate Kinetic Modeling

In standard PTR-MS instruments, the concentration of neutral VOCs is typically determined by calibrating the instrument using gas standards of known concentration and the corresponding protonated ion signals. However, this calibration process is often laborious, time-consuming, and prone to experimental errors. Additionally, many alcohols and aldehydes are susceptible to fragmentation, further complicating accurate quantification.

To overcome these challenges, ion-molecule reaction kinetics, particularly the rate coefficient of the reaction, play a crucial role. With accurate kinetic data, it is possible to estimate volume mixing ratios (VMRs) and VOC concentrations without the need for external gas calibration, in line with the principles of ion-molecule chemistry. In other words, PTR-MS can enable absolute quantification of VOC concentrations without

compound-specific instrument calibration, provided that the reaction rate coefficients between the VOCs and reagent ions, along with the corresponding product-ion branching ratios, are known or reliably determined [56]. Therefore, independent determination of ion-molecule reaction rate coefficients is highly valuable for obtaining approximate VOC concentrations without compound-specific calibration. Experimental rate coefficients under PTR-MS operating conditions remain scarce and are often associated with substantial uncertainties. In CI-MS applications, these rate coefficients are essential for quantifying gas mixtures without traditional calibration procedures.

4.3.5 | Future Development and Expanded Capabilities

Upcoming versions of the application will feature an expanded database containing a greater number of molecules with associated molecular and kinetic data [57, 58]. A unified interface that provides rate coefficients for both PTR-MS and SIFT-MS under various models:

- Capture collision theory
- Average dipole orientation theory
- Parameterized collision models
- Support for negative ion chemistry
- Computation of reaction rates involving negative ions
- Inclusion of relevant reaction conditions for CI-MS workflows

5 | Conclusions and Perspectives

DFT calculations at the B3LYP/6-311++G(d,p) level were employed to determine the molecular and electronic properties of PCDDs and PCDFs. Key parameters of analytical significance—PA, IE, dipole moment, and polarizability—were evaluated to assess their relevance in CI-MS quantification of SVOCs linked to environmental and food contamination.

The computed proton affinities and ionization energies serve as effective indicators for selecting appropriate reagent ions in CI-MS. Several congeners, including 1234678-HCDBD, 12378-PCDBD, 123789-HCDBD, 123789-HCDBF, 123478-HCDBF, 123678-HCDBF, 12378-PCDBF, 1234678-HCDBF, OCDBF, and 1234789-HCDBF, possess proton affinities lower than that of water, rendering ionization via H_3O^+ energetically unfavorable. However, these species exhibit ionization energies below that of NO, indicating that charge transfer through NO^+ -CI-MS is thermodynamically feasible. When these energetic conditions are satisfied, the ion-molecule reactions proceed exothermically, indicating higher capture probability.

Rate coefficients were calculated using classical and parameterized trajectory models across a range of temperatures and field strengths compatible with PTR-MS and SIFT-MS instruments. The computed dipole moments and polarizabilities further elucidate ion-neutral interactions: ion-induced dipole forces dominate for nonpolar species, while both ion-dipole and ion-induced

dipole interactions govern the dynamics of polar molecules. Higher dipole moments enhance electrostatic attraction, leading to stronger interaction potentials. The temperature dependence of the computed rate coefficients aligns with theoretical expectations, while an increase in the reduced electric field results in a predictable decrease in reaction rates.

Enthalpy analyses confirm that charge transfer reactions with NO^+ are generally exothermic and proceed efficiently. A few molecules, such as DB-14-D, 14-D, 2-CDBD, and 2378-TCDBD, exhibit reaction enthalpies greater than -200 kJ mol^{-1} , suggesting limited charge transfer feasibility and a higher likelihood of fragmentation, which warrants further experimental validation.

This database offers a rapid and reliable computational framework for estimating reaction rates, significantly reducing the dependence on experimental calibration in the quantitative analysis of SVOCs in environmental, food, and industrial monitoring. These findings are expected to stimulate further experimental investigations into the detection and quantification of these persistent and toxic compounds.

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Ethics Statement

The author has nothing to report.

Conflicts of Interest

The author declares no conflicts of interest.

Data Availability Statement

Data is provided in the [Supporting Information](#).

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Supporting Information

Additional supporting information can be found online in the Supporting Information section. Supplementary Information.docx

TABLE A1 | DFT computed proton affinity, ionization energy, electric dipole moment, and polarizability of the investigated dioxin and furan using B3LYP/6-311++G** method.

Molecule	CAS number	Mass	PA	IE	Dipole Moment	Polarizability
		a u	KJ/mol	eV	Debye	Å ³
Dibenzo-1,4-dioxin (C ₁₂ H ₈ O ₂)	262-12-4	184.2	742.90	7.43	0	21.51
1,4-dioxin (C ₄ H ₄ O ₂)	290-67-5	84.1	721.81	7.85	0	7.29
2-chlorodibenzo-p-dioxin (C ₁₂ H ₇ ClO ₂)	39227-54-8	218.6	726.57	7.55	2.08	23.75
2,3,7,8-tetrachlorodibenzo-p-dioxin (C ₁₂ H ₄ Cl ₄ O ₂)	1746-01-6	322.0	691.84	7.80	0	30.52
1,2,3,6,7,8-hexachlorodibenzo-p-dioxin (C ₁₂ H ₂ Cl ₆ O ₂)	57653-85-7	390.9	694.50	7.96	0	34.50
1,2,3,4,6,7,8-heptachlorodibenzo-p-dioxin (C ₁₂ HCl ₇ O ₂)	35822-46-9	425.3	688.33	8.04	0.90	36.50
1,2,3,7,8-pentachlorodibenzo-p-dioxin (C ₁₂ H ₃ Cl ₅ O ₂)	40321-76-4	356.4	684.02	7.88	1.01	32.50
1,2,3,4,7,8-hexachlorodibenzo-p-dioxin (C ₁₂ H ₂ Cl ₆ O ₂)	39227-28-6	390.9	695.28	7.96	0.21	34.56
Octachlorodibenzo-p-dioxin (C ₁₂ Cl ₈ O ₂)	3268-87-9	459.7	696.93	8.11	0	38.50
1,2,3,7,8,9-hexachlorodibenzo-p-dioxin (C ₁₂ H ₂ Cl ₆ O ₂)	19408-74-3	390.9	676.89	7.96	1.89	34.41
1,2,3,7,8,9-hexachlorodibenzofuran (C ₁₂ H ₂ Cl ₆ O)	72918-21-9	374.9	669.96	8.48	2.19	34.55
1,2,3,4,7,8-hexachlorodibenzofuran (C ₁₂ H ₂ Cl ₆ O)	70648-26-9	374.9	684.72	8.37	0.38	34.78
1,2,3,6,7,8-hexachlorodibenzofuran (C ₁₂ H ₂ Cl ₆ O)	57117-44-9	374.9	684.46	8.42	0.74	34.72
1,2,3,7,8-pentachlorodibenzofuran (C ₁₂ H ₃ Cl ₅ O)	57117-41-6	340.4	682.79	8.32	1.49	32.64
2,3,4,7,8-pentachlorodibenzofuran (C ₁₂ H ₃ Cl ₅ O)	57117-31-6	340.4	693.37	8.35	0.67	32.88
2,3,7,8-tetrachlorodibenzofuran (C ₁₂ H ₄ Cl ₄ O)	51207-31-9	306.0	692.29	8.26	0.50	30.82
1,2,3,4,6,7,8-heptachlorodibenzofuran (C ₁₂ HCl ₇ O)	67562-39-4	409.3	685.55	8.45	0.69	36.79

(Continues)

TABLE A1 | (Continued)

Molecule	CAS number	Mass	PA	IE	Dipole Moment	Polarizability
		a u	KJ/mol	eV	Debye	Å ³
Octachlorodibenzofuran (C ₁₂ Cl ₈ O)	39001-02-0	443.7	677.46	8.47	0.13	38.75
1,2,3,4,7,8,9-heptachlorodibenzofuran (C ₁₂ HCl ₇ O)	55673-89-7	409.3	677.64	8.43	1.15	36.68
2,3,4,6,7,8-hexachlorodibenzofuran (C ₁₂ H ₂ Cl ₆ O)	60851-34-5	374.9	693.76	8.44	1.56	34.88

TABLE A2 | Computed rate coefficients Langevin rates (k_L), parametrized rates coefficients (k) at E/N values 100, 120, and 140 Td for H₃O⁺ and NO⁺ reagent ions under CI-MS (PTR-MS) conditions. Enthalpy change (ΔH) for NO⁺ is evaluated in the last column.

Molecule	k_L	H ₃ O ⁺			k_L	NO ⁺			ΔH kJ/mol
		100	120	140		100	120	140	
Dibenzo-1,4-dioxin (C ₁₂ H ₈ O ₂)	2.61	2.61	2.61	2.61	2.13	2.13	2.13	2.13	-239.57
1,4-dioxin (C ₄ H ₄ O ₂)	1.60	1.60	1.60	1.60	1.34	1.34	1.34	1.34	-207.53
2-chlorodibenzo-p-dioxin (C ₁₂ H ₇ ClO ₂)	2.72	3.20	3.08	3.00	2.22	2.56	2.47	2.41	-229.22
2,3,7,8-tetrachlorodibenzo-p-dioxin (C ₁₂ H ₄ Cl ₄ O ₂)	3.04	3.04	3.04	3.04	2.46	2.46	2.46	2.46	-205.73
1,2,3,6,7,8-hexachlorodibenzo-p-dioxin (C ₁₂ H ₂ Cl ₆ O ₂)	3.22	3.22	3.22	3.22	2.60	2.60	2.60	2.60	-189.53
1,2,3,4,6,7,8-heptachlorodibenzo-p-dioxin (C ₁₂ HCl ₇ O ₂)	—	—	—	—	2.66	2.70	2.69	2.68	-182.36
1,2,3,7,8-pentachlorodibenzo-p-dioxin (C ₁₂ H ₃ Cl ₅ O ₂)	—	—	—	—	2.53	2.58	2.56	2.56	-197.73
1,2,3,4,7,8-hexachlorodibenzo-p-dioxin (C ₁₂ H ₂ Cl ₆ O ₂)	3.22	3.22	3.22	3.22	2.60	2.60	2.60	2.60	-190.05
Octachlorodibenzo-p-dioxin (C ₁₂ Cl ₈ O ₂)	3.39	3.39	3.39	3.39	2.73	2.73	2.73	2.73	-175.17
1,2,3,7,8,9-hexachlorodibenzo-p-dioxin (C ₁₂ H ₂ Cl ₆ O ₂)	—	—	—	—	2.59	2.79	2.74	2.71	-190.06
1,2,3,7,8,9-hexachlorodibenzofuran (C ₁₂ H ₂ Cl ₆ O)	—	—	—	—	2.60	2.89	2.81	2.76	-148.53
1,2,3,4,7,8-hexachlorodibenzofuran (C ₁₂ H ₂ Cl ₆ O)	—	—	—	—	2.60	2.62	2.62	2.61	-151.69
1,2,3,6,7,8-hexachlorodibenzofuran (C ₁₂ H ₂ Cl ₆ O)	—	—	—	—	2.61	2.63	2.63	2.62	-147.67
1,2,3,7,8-pentachlorodibenzofuran	—	—	—	—	2.54	2.66	2.63	2.61	-157.28

(Continues)

TABLE A2 | (Continued)

Molecule	k_L	H ₃ O+			k_L	NO+			ΔH kJ/mol
		100	120	140		100	120	140	
(C ₁₂ H ₃ Cl ₅ O)									
2,3,4,7,8-pentachlorodibenzofuran	3.15	3.18	3.17	3.17	2.55	2.57	2.56	2.56	-153.97
(C ₁₂ H ₃ Cl ₅ O)									
2,3,7,8-tetrachlorodibenzofuran	3.06	3.08	3.07	3.07	2.48	2.49	2.49	2.48	-162.68
(C ₁₂ H ₄ Cl ₄ O)									
1,2,3,4,6,7,8-heptachlorodibenzofuran	—	—	—	—	2.68	2.70	2.69	2.69	-142.87
(C ₁₂ HCl ₇ O)									
Octachlorodibenzofuran	—	—	—	—	2.74	2.74	2.74	2.74	-138.69
(C ₁₂ Cl ₈ O)									
1,2,3,4,7,8,9-heptachlorodibenzofuran	—	—	—	—	2.67	2.73	2.72	2.71	-145.19
(C ₁₂ HCl ₇ O)									
2,3,4,6,7,8-hexachlorodibenzofuran	3.24	3.42	3.37	3.34	2.62	2.74	2.71	2.69	-145.44
(C ₁₂ H ₂ Cl ₆ O)									

TABLE A3 | Computed Langevin rates (k_L), and collision rates (k) for H₃O+ and NO+ reagent ions at thermal conditions (50-600K) for CI-MS (SIFT-MS) instruments.

Molecule	k_L	H ₃ O+					k_L	NO+				
		50	150	300	450	600		50	150	300	450	600
Dibenzo-1,4-dioxin	2.61	2.61	2.61	2.61	2.61	2.61	2.13	2.13	2.13	2.13	2.13	2.13
(C ₁₂ H ₈ O ₂)												
1,4-dioxin	1.60	1.60	1.60	1.60	1.60	1.60	1.34	1.34	1.34	1.34	1.34	1.34
(C ₄ H ₄ O ₂)												
2-chlorodibenzo-p-dioxin	2.72	6.57	4.23	3.68	3.42	3.28	2.22	5.35	3.45	2.99	2.78	2.76
(C ₁₂ H ₇ ClO ₂)												
2,3,7,8-tetrachlorodibenzo-p-dioxin	3.04	3.04	3.04	3.04	3.04	3.04	2.46	2.46	2.46	2.46	2.46	2.46
(C ₁₂ H ₄ Cl ₄ O ₂)												
1,2,3,6,7,8-hexachlorodibenzo-p-dioxin	3.22	3.22	3.22	3.22	3.22	3.22	2.60	2.60	2.60	2.60	2.60	2.60
(C ₁₂ H ₂ Cl ₆ O ₂)												
1,2,3,4,6,7,8-heptachlorodibenzo-p-dioxin	—	—	—	—	—	—	2.67	3.40	2.99	2.87	2.82	2.79
(C ₁₂ HCl ₇ O ₂)												
1,2,3,7,8-pentachlorodibenzo-p-dioxin	—	—	—	—	—	—	2.53	3.44	2.93	2.77	2.71	2.68
(C ₁₂ H ₃ Cl ₅ O ₂)												
1,2,3,4,7,8-hexachlorodibenzo-p-dioxin	3.22	3.35	3.29	3.27	3.26	3.25	2.60	2.70	2.65	2.64	2.63	2.62
(C ₁₂ H ₂ Cl ₆ O ₂)												
Octachlorodibenzo-p-dioxin	3.39	3.39	3.39	3.39	3.39	3.39	2.73	2.73	2.73	2.73	2.73	2.73
(C ₁₂ Cl ₈ O ₂)												
1,2,3,7,8,9-hexachlorodibenzo-p-dioxin	—	—	—	—	—	—	2.60	4.78	3.61	3.18	3.03	2.95
(C ₁₂ H ₂ Cl ₆ O ₂)												

(Continues)

TABLE A3 | (Continued)

Molecule	k_L	H_3O^+					k_L	NO^+				
		50	150	300	450	600		50	150	300	450	600
1,2,3,7,8,9-hexachlorodibenzofuran ($C_{12}H_2Cl_6O$)	—	—	—	—	—	—	2.60	5.59	3.89	3.34	3.15	3.04
1,2,3,4,7,8-hexachlorodibenzofuran ($C_{12}H_2Cl_6O$)	—	—	—	—	—	—	2.61	2.83	2.72	2.68	2.67	2.66
1,2,3,6,7,8-hexachlorodibenzofuran ($C_{12}H_2Cl_6O$)	—	—	—	—	—	—	2.61	3.16	2.86	2.77	2.73	2.71
1,2,3,7,8-pentachlorodibenzofuran ($C_{12}H_3Cl_5O$)	—	—	—	—	—	—	2.54	4.09	3.25	2.96	2.85	2.80
2,3,4,7,8-pentachlorodibenzofuran ($C_{12}H_3Cl_5O$)	3.15	3.75	3.43	3.33	3.29	3.27	2.55	3.03	2.77	2.69	2.66	2.64
2,3,7,8-tetrachlorodibenzofuran ($C_{12}H_4Cl_4O$)	3.06	3.46	3.25	3.19	3.16	3.14	2.48	2.80	2.63	2.58	2.56	2.54
1,2,3,4,6,7,8-heptachlorodibenzofuran ($C_{12}HCl_7O$)	—	—	—	—	—	—	2.68	3.17	2.90	2.82	2.79	2.77
Octachlorodibenzofuran ($C_{12}Cl_8O$)	—	—	—	—	—	—	2.74	2.80	2.77	2.76	2.76	2.76
1,2,3,4,7,8,9-heptachlorodibenzofuran ($C_{12}HCl_7O$)	—	—	—	—	—	—	2.68	3.75	3.14	2.96	2.89	2.85
2,3,4,6,7,8-hexachlorodibenzofuran ($C_{12}H_2Cl_6O$)	3.24	5.26	4.17	3.79	3.65	3.57	2.62	4.25	3.36	3.06	2.95	2.89