On the Hydrophobicity of Nitrogen Dioxide: Could there be a "lens" effect for NO$_2$ reaction kinetics?

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Abstract

Solvent "lens" effects for the reaction kinetics of NO$_2$ can be evaluated on the basis of published Henry's law constants for nitrogen dioxide in various solvents. Water-to-organic solvent partition coefficients were derived from Henry's law constants and used to assess the tendencies of NO$_2$ toward fleeing the aqueous environments and concentrating in biological hydrophobic media. It is concluded, based only on the estimated aqueous medium-to-cell membrane partition coefficient for NO$_2$, that such tendencies will be relatively small, and that they may account for an acceleration of chemical reactions in biological hydrophobic media with reaction kinetics that are first order on NO$_2$ by a factor of approximately 3 ± 1. Thus, kinetic effects due to mass action will be relatively small but it is also important to recognize that because NO$_2$ will tend to dissolve in cell membranes, reactions with cell membrane components will not be hindered by lack of physical solubility at these loci. In comparison to other gases, nitrogen dioxide is less hydrophobic than NO, O$_2$ and N$_2$.

Keywords

Nitrogen dioxide; partition coefficient; Henry's law constant; solubility; kinetics; reactivity; compartmentation

Introduction

Exposures to nitrogen dioxide (NO$_2$) can occur in industrial and occupational settings, and during war and acts of terror involving the use of explosives. Moreover, NO$_2$ is present in polluted air [1–4] and also can be formed endogenously [5–11]. The reaction of peroxynitrite with carbon dioxide, reactions catalyzed by myeloperoxidase using nitrite as the electron donor, and acidification of nitrite followed by oxidation of the resulting nitric oxide (NO) are among the biological processes that can result in the endogenous formation of NO$_2$ [5;7–9;12]. Nitrogen dioxide is involved in biological oxidations, including the nitration of protein tyrosine residues and possibly also the nitration of membrane lipids, reactions with low molecular weight antioxidants, and the oxidation of thiol residues. Cell signaling and covalent modifications mediated by NO$_2$ will depend in part on its physicochemical properties relevant to passive transport, such as its ability to diffuse and penetrate into membranes, its relative solubility in membranes and aqueous solutions, and its ability to chemically react within the membranous or aqueous milieu. Despite the biological importance of NO$_2$, it has been recently pointed out that the relative solubility of NO$_2$ in membranes and aqueous medium is unknown [13–15], revealing the lack of even the most essential parameter necessary to interpret the reactivity of

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NO_2 across different cellular and biological compartments. In contrast, the solubility of NO in several solvents has been studied in detail and this has led to the proposal for the existence of an acceleration or "lens" effect [13;14] whereby the hydrophobicity of NO helps focus some of the chemical reactivity of NO, such as its autoxidation, in cell membranes and lipid particles. This brief exercise presented here represents an attempt to estimate the relative solubility of NO_2 in biological membranes and any possible ensuing acceleration or "lens" effects in NO_2 reaction kinetics.

Methods

Solvent "lens" effects [13;14] for the reaction kinetics of NO_2 are evaluated herein on the basis water-to-organic solvent partition coefficients (K_w^s) as these coefficients may result in high, compartmentalized concentrations of NO_2, that thereby increase the rates of reaction of NO_2 in these compartments. Values of K_w^s were derived from Henry's law constants for NO_2 (K_H^s) calculated from published solubility studies of gaseous NO_2 in various solvents [16;17] (see equations 5,6 and 8 below, for operations applied in this process). When necessary, data were corrected for temperature to 37 °C using equation 7 and published enthalpies of solution ($\Delta_{sol} H$) for NO_2 in various solvents [17;18].

Results

On Solvent "Lens" Effects in Reaction Kinetics

Moller *et al*. studied the acceleration of the autoxidation of NO when NO is allowed to partition between water and organic media [13]. Since under a wide range of experimental conditions the rate law for the autoxidation of NO was found to be

$$-\frac{d[NO]}{dt} = 4k[NO]^2[O_2]$$

(1)

and diffusion across compartments is not rate-limiting, these authors interpreted the acceleration they observed as arising from the larger concentration of NO in the organic media resulting from the hydrophobicities of NO and O_2 [13]. It is important to recognize that solvent effects on the rate constant *k* could either amplify or dampen effects due to reactants' hydrophobicities since the rate constant is subject to solvent effects. However, it is probable that hydropobicity is the dominant factor in the "lens" effect since the rate constant in equation (1) in the solvent carbon tetrachloride has been found to be close to that in aqueous solution [14;19].

On Estimating the Solvent "Lens" effect for NO_2

Studies on the solubility of NO_2 are experimentally challenging and it is not surprising that related literature is rather scarce. The solubility studies for NO_2 are complicated by the reactivity of NO_2 and N_2O_4 with many solvents. [*Caution:* The authors are aware of one explosion with fire that occurred in a research laboratory while using NO_2 in tetrahydrofuran.] It is also important to consider that NO_2 dimerizes to form N_2O_4 and the latter can react with traces of water present in solvents (Equations 2–4).

$$2NO_2 \rightleftharpoons N_2O_4$$

(2)

$$NO_2/N_2O_4 + \text{Solvents} \rightarrow \text{Products} \tag{3}$$

$$N_2O_4 + H_2O \rightarrow NO_2^- + NO_3^- + 2H^+ \tag{4}$$

Despite the complications arising from the hydrolysis reaction (Equation 4), water is perhaps the most studied solvent, owing to the environmental importance of NO$_2$, and a number of reactive uptake studies have been conducted in water from which Henry's law constants for NO$_2$ in water can be derived [18;20]. In contrast, few gaseous NO$_2$-organic solvent partitions [16;17] had been measured and apparently, no organic solvent-to-water partition coefficients for NO$_2$ had been reported to date.

The solubility of a gas in a solvent can be described in different ways, but usually, the Henry's law constant K_H^s is used to this effect. Thus, for NO$_2$, we can write equation (5):

$$K_H^s = \frac{[NO_2]_s}{p_{NO_2}} \tag{5}$$

where $[NO_2]_s$ is the molar concentration of NO$_2$ in organic solvent s and p_{NO_2} is the partial pressure of NO$_2$ in the gas phase in units of atmospheres. When the solvent s is water (w), we write K_H^w. Water-to-organic solvent partition coefficients (K_w^s) can then be calculated by dividing the Henry's law constant for organic solvent (K_H^s) by the equivalent for water (K_H^w) using equation (6):

$$K_w^s = K_H^s / K_H^w = \frac{[NO_2]_s}{p_{NO_2}} / \frac{[NO_2]_w}{p_{NO_2}} = [NO_2]_s / [NO_2]_w \tag{6}$$

Cheung *et al.*[18] compared literature values for K_H^w for NO$_2$ with values they obtained and recommend $K_H^w = 1.4 \pm 0.2 \times 10^{-2}$ M atm^{-1} for 20 °C and $K_H^w = 2.3(+0.3 - 0.9) \times 10^{-2}$ M atm^{-1} for 3 °C. From these two values, using equation (7), one can calculate an approximate enthalpy of solution ($\Delta_{sol} H$) for NO$_2$ in water of -20 kJ mol^{-1} and extrapolate $K_H^w = 9.1 \times 10^{-3}$ M atm^{-1} for 37 °C.

$$K_H^w(T_2) = K_H^w(T_1) \cdot \exp\left(\frac{-\Delta_{sol}H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right) \tag{7}$$

We identified two published solubility studies for gaseous NO$_2$ in organic solvents[16;17] and the data published in these articles are summarized in Table 1. Mendiara *et al.* published Henry's law constants in terms of molar fractions and in units of atm ($k_{NO_2}^H$) [16] and these were converted to K_H^s (units of M atm^{-1}) using equation 8, which is valid for dilute solutions, where MW^s and ρ^s represent the molecular weight and the density of solvent s, respectively.

$$K_H^s = (k_{NO2}^H \cdot MW^s / \rho^s)^{-1}$$

(8)

Values of K_H^s were extrapolated to 37 °C using $\Delta_{sol} H = -12$ kJ mol^{-1} for 1,1,2,2-tetrachloroethane [17], chloroform and carbon tetrachloride. $\Delta_{sol} H = -11$ kJ mol^{-1} was used for n-decane [17]; $\Delta_{sol} H = -9$ kJ mol^{-1} was used for nitrate esters[17] and $\Delta_{sol} H = -20$ kJ mol^{-1}, which was derived from data recommended by Cheung *et al.* [18], was used for water. Nitrate esters refer to 1,4- and 2-3-butylene glycol dinitrate, 1,2-propylene glycol dinitrate, and glyceryl trinitrate, all of which exhibited similar solubility properties [17]. Although not specified by Lur'e *et al.* [17], it is assumed here that these authors used pure chemicals (and not mixtures of isomers) in their study and that they refer to the linear isomer of decane (i.e. n-decane) and to the 1,1,2,2-tetrachloroethane isomer of tetrachloroethane that is produced at an industrial scale and is unreactive towards NO$_2$.

Henry's law constants for NO$_2$, K_H^s, shown in Table 1, are 1.2 to 6.7 times larger for organic solvents compared to water. The relative insensitivity of K_w^s to changes in solvent suggests the NO$_2$-solvent interactions are of a very general type, as has been previously interpreted for NO [21]. This slight preference that NO$_2$ has for dissolving in organic solvents relative to water has implications, for example, on reactive uptake of gas phase NO$_2$ by the lung epithelial lining fluid layer (ELF) that is covered by a thin film composed primarily of phospholipids and surfactant proteins and must be taken into account when modeling the local dose of NO$_2$ in the respiratory tract. Thus, for example, it becomes important to compare Henry's law constants for NO$_2$ in water to those in organic solvents since a higher solubility of NO$_2$ in the lipids near the air/lung ELF interface will tend to enhance NO$_2$ reactive uptake [18] by providing a subphase where NO$_2$ can dissolve that is vicinal to biological reactive targets (if all other experimental parameters remained unchanged).

Henry's law constants and water-to-organic solvent partition coefficients for N$_2$, O$_2$, NO, and NO$_2$ are shown on Table 2 [22–24]. In order to simplify comparisons, only the same or similar solvents for which these constants are known for NO$_2$ are shown. It is interesting to note that NO$_2$ is more soluble in all solvents, including water, than the other gases. However, since the most marked difference occurs when the solvent is water, this results in a lower hydrophobicity for NO$_2$.

In order to compare NO$_2$ to NO (since biological "lens" effects have been reported for the latter [13;14]) we begin by selecting a K_H^w value for NO at 37 °C. The most recent K_H^w values for NO compiled by Sander [20] as well as a recent determination by Zacharia *et al.* [25] average 1.9×10^{-3} M atm^{-1} at 25 °C. Then, to correct this value to 37 °C, we employ the enthalpy of solution $\Delta_{sol} H$ for NO in water, taken as -13 kJ mol^{-1}, which is the average of values compiled by Sander [20] and the heat of solution derived from solubility data at various temperatures given in Perry and Green [26]. Then, using equation (6), one arrives at $K_H^w = 1.6 \times 10^{-3}$ M atm^{-1} for NO at 37 °C.

Henry's law constants and water-to-organic solvent partition coefficients K_w^s for NO and NO$_2$ at 37 °C are shown in Table 3. Henry's law constants for NO at 25 °C and enthalpies of solvation in several solvents, which were used here for temperature corrections to 37 °C, were reported by Shaw *et al.* [27]. In addition, the solvation equation of Abraham [21;28] was used as predictor for the partition coefficients for NO in chloroform and n-decane since experimental data for NO in these solvents are not available but are available for NO$_2$. Since the enthalpies of solvation are unknown for chloroform and n-decane, the values for carbon tetrachloride and n-hexane, respectively, were used as surrogate values to calculate K_w^s. We are now in a position

to compare K_w^s values for NO with NO_2 at 37 °C (Table 3). In order to facilitate comparisons, when experimental data are not available for the same solvent for NO and NO_2, experimental values for related solvents are shown in Table 3.

Discussion

One can notice that all K_w^s values are higher than one, indicating that both NO and NO_2 are more soluble in organic solvents than they are in water, more so NO than is NO_2. However, even for NO, the water-to-organic solvent relative solubilities are not very pronounced. Nevertheless, there will be some thermodynamic tendency for NO and NO_2 to flee the aqueous environment where they will most likely be produced. Thus, NO is 7.7–11 times more soluble in hydrocarbons, 8.3 times more soluble in carbon tetrachloride, 10 times more soluble in chloroform, and 4.8 times more soluble in nitrobenzene than it is in water. Indeed, the "lens" effect or acceleration of the autoxidation of NO in liposomes by a factor of ~ 30 relative to aqueous solution has been explained using water-to-liposome partition coefficients of 3.6 and 3.2 for NO and O_2, respectively [13;14;29]. Thus, when one considers the form of the rate expression in equation (1), a theoretical acceleration factor of $(3.6)^2(3.2) = 41$, which is not very different from the observed value of ~30, can be calculated. It is important to recognize that it is because the rate expression is second order in NO and first order in O_2 and that because both NO and O_2 are relatively hydrophobic it is that the overall effect results in a large acceleration factor.

In comparison to NO, the relative solubilities of NO_2 for organic solvents are less pronounced. NO_2 is 5.5 times more soluble in the hydrocarbon n-decane, 1.2 times more soluble in carbon tetrachloride, 1.9 times more in chloroform, and 6.7 times more soluble in 1,1,2,2-tetrachloroethane than it is in water. Going towards more polar solvents, NO_2 is 4.2 times more soluble in the nitrate esters, 1,4- and 2-3-butylene glycol dinitrate, 1,2-propylene glycol dinitrate, and glyceryl trinitrate than it is in water. Thus, for NO_2 in these solvents, the water-to-organic solvent partition coefficients vary from 1.2 to 6.7, suggesting that NO_2 is slightly hydrophobic but less so than is NO.

Averaging across the hydrocarbons, the K_w^s for NO is 9.9 while the K_w^s for NO_2 in n-decane is 5.5; across the chlorocarbons, the average K_w^s for NO is 9.2 while the average K_w^s for NO_2 is 3.3. The K_w^s for NO in nitrobenzene (4.8) is 14% larger than the K_w^s for NO_2 in nitrate esters (4.2).

Water-to-solvent partition coefficients, in particular those for 1-octanol and chloroform, are often used in predicting solubilities and derived properties for various chemical species in and across cell membranes [30]. The paucity of solubility data for NO_2 does not allow for the estimation of $K_w^{1-octanol}$ or K_w^{CH3Cl} using, for example, the solvation equations of Abraham as has been done for NO (5.5 and 8.3, respectively[21]; however, since, on the average, water-to-solvent partition coefficients for NO_2 are about 40% of those for NO and are bracketed between 1.2 and 6.7, and the solvent the NO_2-solvent interactions are of a very general type and do not appear to change much across solvents of various types, it is reasonable to expect the partition coefficient for water to the fatty acyl chains region of the cell membrane to be 3 ± 1.

Salting Out Effects

The biological aqueous medium ionic strength will result in a small salting out effect for the uncharged NO_2 radical. Salting out effects for uncharged species like NO_2 usually are small and obey a simple model for ionic strengths up to 5 M (equation 9) [31].

$$\ln\gamma=bI \tag{9}$$

where γ is the activity coefficient for the uncharged species, b is a constant that is typically between 0 and 0.3 for small dissolved gases, and I is the ionic strength, usually less than 0.25 M for biological fluids [32]. Thus, $0 \le \gamma \le 1.19$ for NO_2 and since this effect will occur only in the aqueous phase, the net effect will be an increase in K_w^s for NO_2 of as much as 19 %.

Rate Laws for Reactions of NO_2 with Biological Target Molecules

Rate laws for chemical reactions of NO_2 (and its dimer N_2O_4 with which it trends to exist in equilibrium) with substrate molecules generally have the form qiven in equation (10)

$$-\frac{d[S]}{dt}=k_1[NO_2][S]+k_2[NO_2]^2[S]=k_1[NO_2][S]+k_2K_{11}[N_2O_4][S] \tag{10}$$

where S represents the biological target molecule, and k_1 and k_2 are observed rate constants for the first and second order terms, respectively[33]. The second order term occurs not because the reaction has a termolecular component but instead because the reaction involves N_2O_4. This relationship occurs because $[NO_2]^2$ and $[N_2O_4]$ are linearly related through the equilibrium constant for reaction 2 (equation 11).

$$K_{10}=\frac{[NO_2]^2}{[N_2O_4]} \tag{11}$$

On The Formation of N_2O_4

Because of equation (11), the $[NO_2]$ is one of the parameters that determine whether or not N_2O_4 will participate in these reactions. The equilibrium constant K_{11} for the dissociation of N_2O_4 is relatively insensitive to solvent effects and values obtained in various solvents range from 0.25×10^{-4} to 4.6×10^{-4} M at 37 °C [16;34–36]. The solution equilibria favor the formation of the dimer relative to the gas phase where K_{11} is 1.46×10^{-2} M [37] so it is important to evaluate whether or not N_2O_4 may play a role in the biological reactions of NO_2. If one assumes $[NO_2]$ does not surpass 0.1 μM (a rather high concentration for biological systems, even for the less reactive NO [9]), then, one can calculate $[NO_2]/[N_2O_4]= K_{11}/[NO_2]$ will be between 250 and 4600. Thus, the equilibrium mixture will contain between 0.02 and 0.4% N_2O_4 on a molar basis. There is no doubt that there will be little N_2O_4 formed at equilibrium. However, it is unlikely that equilibrium will be reached, and consequently, that there will be even less N_2O_4 formed compared to equilibrium conditions. This is because the relatively high reactivity of NO_2 for biological molecules will outcompete dimerization to form N_2O_4 since biological molecules can react with NO_2 with rate constants [38] that although they can be smaller than the rate constant for the dimerization of NO_2 ($k_{N2O4} = 9\times10^8$ $M^{-1}s^{-1}$ in water [39]), the biological molecules can be present in concentrations that are much larger than NO_2 can achieve in tissues and more than compensate for the difference in rate constants. The rates of disappearance of NO_2 due to its dimerization (R_{12}) and due to reaction with a biological substrate S (R_{13}) can be expressed as depicted in equations 12 and 13, respectively.

$$R_{12} = -\frac{d[NO_2]}{dt} = 2k_{N2O4}[NO_2]^2 \tag{12}$$

$$R_{13} = -\frac{d[NO_2]}{dt} = k_s[NO_2][S] \tag{13}$$

As an example, one can evaluate $R_{13}/R_{12} = 0.5(k_S/k_{N2O4})([S]/[NO_2])$ when $[NO_2] = 0.1 \times 10^{-6}$ M, a high $[NO_2]$ that represents a favorable biological scenario for dimerization to N_2O_4. Now, let us consider that the substrate that will react with NO_2 is intracellular glutathione (GSH) ($[GSH]_{intracellular} \approx 2$ mM; $k_{GSH} = 2 \times 10^7$ M^{-1}s^{-1} [38]). Evaluation of R_{13}/R_{12} for these values of rate constants and concentrations yields 200 revealing that it is very unlikely that any significant N_2O_4 will be formed even under conditions where high $[NO_2]$ is produced that favor formation of N_2O_4. Hence, it would be safe to assume that formation of N_2O_4 in biological systems will be very inefficient, that reaction products resulting from reactions of biological molecules with N_2O_4 will be negligible, and that N_2O_4 will not function as a substantial reservoir for NO_2.

On The Formation of N_2O_3

NO_2 can react with NO to form dinitrogen trioxide (N_2O_3) in a reversible reaction as depicted in reaction 14

$$N_2O_3 \rightleftharpoons NO + NO_2$$
$$K_{14} = \frac{[NO][NO_2]}{[N_2O_3]} \tag{14}$$

This equilibrium has been studied by Shaw *et. al.* [27] and using their data one can calculate $K_{14} = 0.34 \times 10^{-4}$ M in carbon tetrachloride, and 2.2×10^{-4} in acetonitrile, at 37 °C. In water, $K_{14} = 7.3 \times 10^{-5}$ M at 25 °C [40] and assuming $\Delta_{14}H = 62$ kJmol^{-1} (as in acetonitrile [24]), one can calculate $K_{14} = 1.9 \times 10^{-4}$ M at 37 °C. As we observed with K_{11}, K_{14} is also relatively insensitive to solvent effects. Moreover, $K_{11} \approx K_{14}$. The relative amount of NO_2 that will react with NO to form N_2O_3 at equilibrium will depend on the concentrations of both of these reactants. For $[NO] = 0.1$ μM, one can calculate $[NO_2]/[N_2O_3] = K_{14}/[NO]$ will be between 340 and 2200. Thus, only 0.05 to 0.3% of NO_2 will form N_2O_3 at equilibrium when $[NO] = 0.1$ μM. The rate constant for the reaction of NO_2 with NO ($k_{N2O3} = 1.1 \times 10^9$ M^{-1}s^{-1} in water [40]) to form N_2O_3 is also similar to the rate constant for the dimerization of NO_2 ($k_{N2O4} = 9 \times 10^8$ M^{-1}s^{-1} [39]) to form N_2O_4. The rate laws for these processes are given in equations 15 and 16, respectively.

$$\frac{d[N_2O_3]}{dt} = k_{N2O3}[NO][NO_2] \tag{15}$$

$$\frac{d[N_2O_4]}{dt} = k_{N2O4}[NO_2]^2 \tag{16}$$

The overall case for N_2O_3 formation is thus similar to the case for N_2O_4, however, it is likely that $[NO_2] < [NO]$ and that $R_{15} > R_{16}$, because of the higher reactivity of NO_2 for biological molecules as compared to NO. Consequently, although conditions will not favor formation of either N_2O_3 or N_2O_4, N_2O_3 will generally be more likely to form than will be N_2O_4.

On the Reactions of NO_2 with Target Molecules in Cell Membranes

As seen above, the reactions of NO_2 with biological molecules follow rate laws that are first order in NO_2 and first order in the biological molecule for environmentally and biologically relevant concentrations of NO_2. Any gain in mass action due to gains in $[NO_2]$ in the hydrophobic region of the cell membrane will be modest because we estimate a water to the hydrophobic region of the cell membrane partition coefficient of 3 ± 1 (Figure 2). Reactions of NO_2 in cell membranes will proceed with rates that are consistent with rate constants, concentrations for biological molecules in the cell membrane, and an estimated three-fold increase in $[NO_2]$.

Conclusions

NO_2 has a slight preference to dissolve in organic solvents compared to water and this may have some implications, for example, during reactive uptake of NO_2 by the lung epithelial lining fluid. NO_2 is 1.2 times more soluble in CCl_4, 1.9 times in $CHCl_3$, 4.2 times more soluble in the nitrate esters, 1,4- and 2-3-butylene glycol dinitrate, 1,2-propylene glycol dinitrate, and glyceryl trinitrate, 5.5 times in *n*-decane, and 6.7 times more soluble in 1,1,2,2-tetrachloroethane than it is in water, and the preference for solvent increases by approximately 19% when the ionic strength of the aqueous medium is taken into account. Henry's law constants indicate NO_2 is more soluble than NO in all solvents studied here with the most marked difference in water, resulting in a lower hydrophobicity for NO_2, as compared to NO. The available data on the solubility of NO_2 leads us to conclude that "lens" effects due to the slight hydrophobicity of NO_2 will be small, probably around a factor of approximately 3 ± 1. Thus, only a small acceleration of NO_2 reactions is expected to occur in hydrophobic cellular compartments (if all other experimental parameters remained unchanged). Nitrogen dioxide is less hydrophobic than NO, O_2 and N_2. Due to the low concentrations of NO_2 that can be achieved in biological systems and in relation to the dissociation constant of N_2O_4, it is unlikely that N_2O_4, at any time, represents any significant reservoir of NO_2, or significantly contributes to the reactivity of NO_2. Finally, although biological conditions do not favor formation of either N_2O_3 or N_2O_4, it is estimated that N_2O_3 will generally be more likely to form than will be N_2O_4.

Acknowledgments

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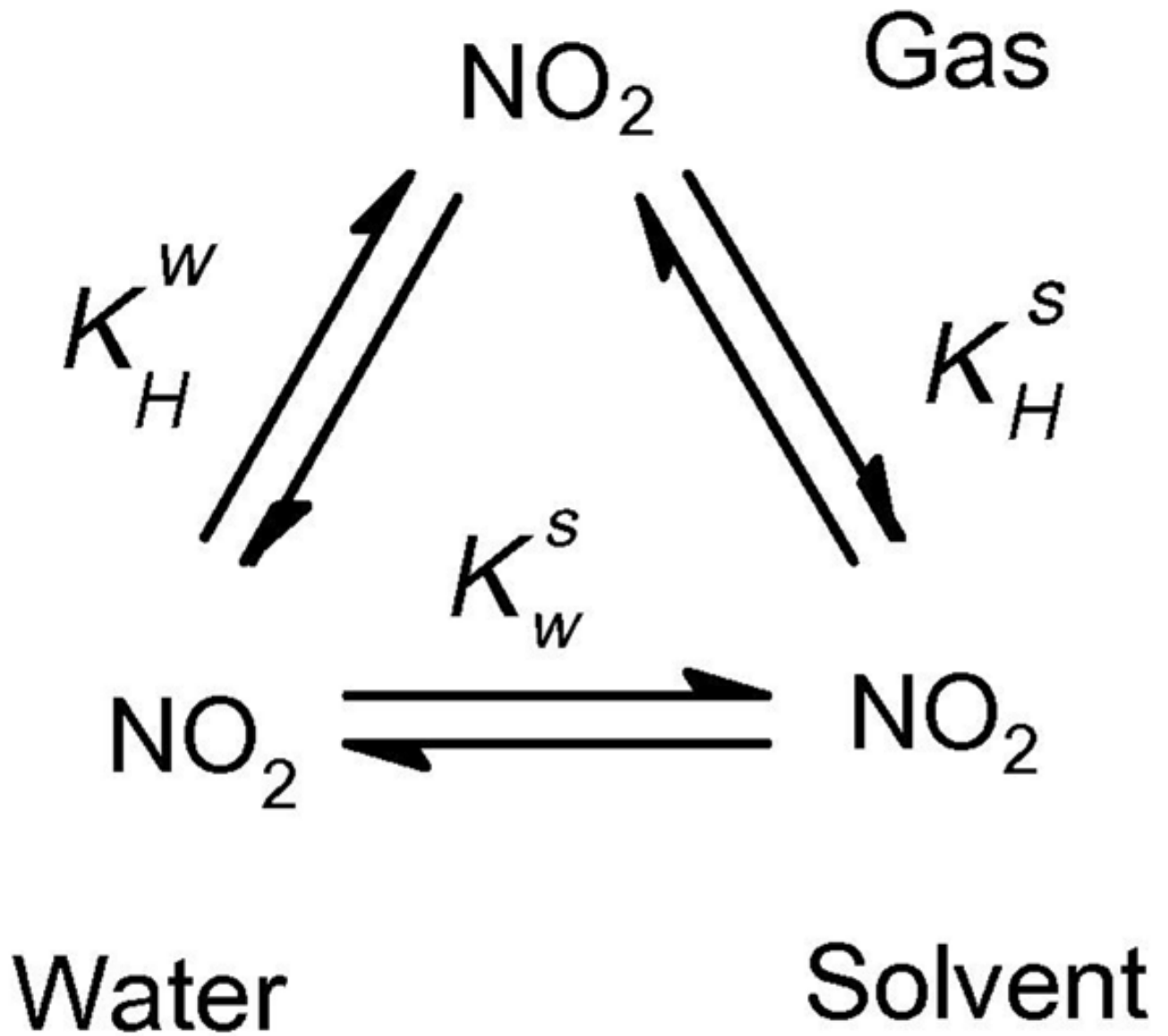
$$NO_2 \quad Gas$$
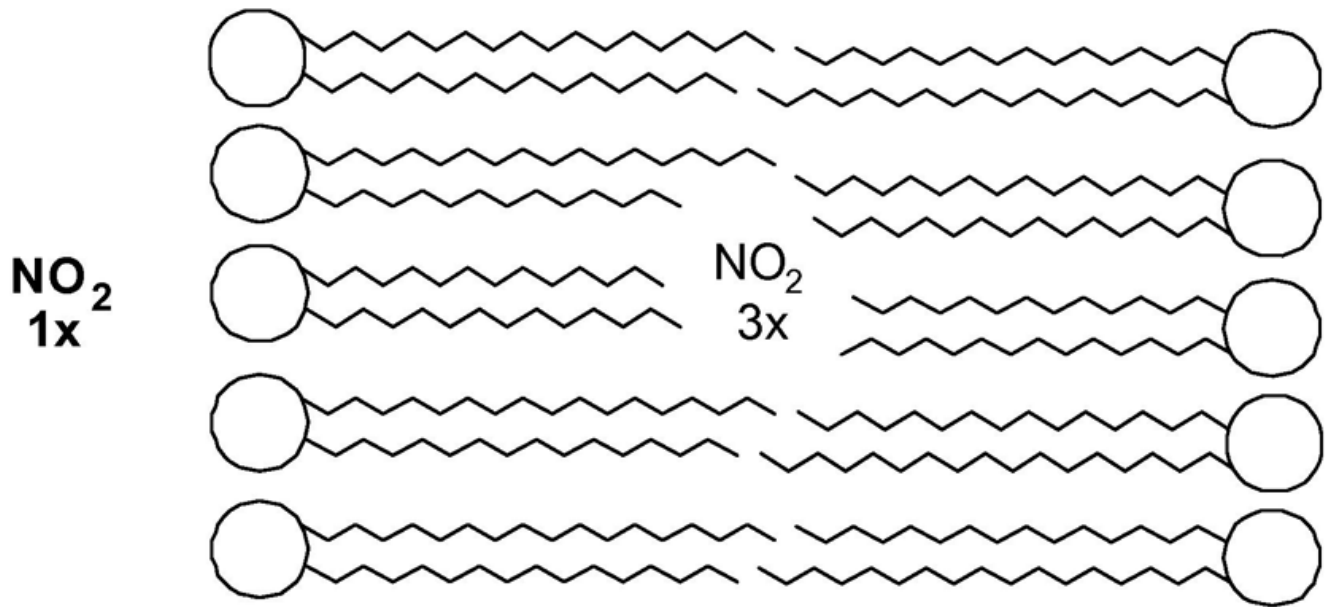
$$K_H^W \qquad K_H^S$$

$$K_W^S$$

$$NO_2 \rightleftharpoons NO_2$$

$$Water \qquad Solvent$$

Figure 1.

Figure 2.

Table 1

Henry's law constants for nitrogen dioxide in various solvents and water-to-organic solvent partition coefficients at 37 °C. From left to right, second column: Henry's law constants K_H^s (M atm^{-1}) at temperatures specified in the corresponding reference; third column: Henry's law constants K_H^s for 37 °C calculated using Eq. (7) as indicated in the text; fourth column, water-to-organic solvent partition coefficients K_w^s calculated using Eq. (6) with values for K_H^s and K_H^w for 37 °C.

Solvent	$10^2 \times K_H^s$	$10^3 \times K_H^s$, 37 °C	K_w^s 37 °C	Ref.
CCl$_4$	1.69; 20 °C	11	1.2	[16]
CHCl$_3$	2.15; 20 °C	17	1.9	[16]
n-Decane	5.96; 25 °C	50	5.5	[17]
1,1,2,2-Tetrachloroethane	7.34; 25 °C	61	6.7	[17]
Nitrate esters	4.33; 25 °C	38	4.2	[17]
Water	1.4; 20 °C	9.1 (K_H^w)	1.0	[18]

Table 2

Henry's law constants K_H^s (M atm^{-1}) and water-to-organic solvent partition coefficients K_w^s for N_2, O_2, NO, and NO_2 at 25 °C [16,[17],[21]_[24]].

Solvent	N_2		O_2		NO		NO_2	
	$10^2 \times K_H^s$	K_w^s	$10^2 \times K_H^s$	K_w^s	$10^2 \times K_H^s$	K_w^s	$10^2 \times K_H^s$	K_w^s
CCl$_4$	0.663	10.1	1.24	9.90	1.43	7.35	1.49	1.21
CHCl$_3$	0.552	8.40	1.16	9.26	1.62[a]	8.3[a]	1.99	1.62
1,1,2,2-Tetrachloroethane	—	—	—	—	—	—	7.34	5.95
n-Decane	0.623	9.52	1.13	9.01	1.27[a]	6.49[a]	5.96	4.85
n-Hexane	1.06	16.2	1.53	12.2	1.80	9.26	—	—
Nitrate esters	—	—	—	—	—	—	4.33	3.52
1-Propyl nitrate ester	0.589	9.00[b]	0.832[b]	6.62	—	—	—	—
Nitrobenzene	—	—	—	—	0.786	4.03	—	—
Water[c]	0.0656	1	0.125	1	0.195	1	1.23	1

[a] Calculated using Abraham's solvation equations.

[b] At 20 °C.

[c] $K_H^s = K_H^w$.

Table 3

Henry's law constants K_H^s (M atm^{-1}) for NO and water-to-organic solvent partition coefficients K_w^s for NO and NO$_2$ in various solvents at 37 °C.

Solvent	NO		NO$_2$
	$10^2 \times K_H^s$; 37 °C	K_w^s	K_w^s
CCl$_4$	1.38	8.3	1.2
CHCl$_3$	1.58	10	1.9
1,1,2,2-Tetrachloroethane	—	—	6.7
Cyclohexane	1.77	11	—
n-Hexane	1.74	11	—
n-Decane	1.23	7.7	5.5
Nitrate esters	—	—	4.2
Nitrobenzene	0.76	4.8	—
Water	0.16	1.0	1.0