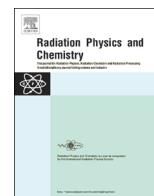




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Review

Rate coefficients of hydroxyl radical reactions with pesticide molecules and related compounds: A review



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HIGHLIGHTS

- The $\cdot\text{OH}$ rate coefficients with aromatic pesticides are $(2\text{--}10) \times 10^9 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$.
- For triazine type pesticides the values are around $2.5 \times 10^9 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$.
- For non-aromatics with double bond or several C–H they are $\sim 1 \times 10^9 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$.
- For aromatics k_{OH} 's are determined by diffusion; for triazines by chemical activation.
- They are activation controlled when molecule does not have double or C–H bonds.

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ABSTRACT

Rate coefficients published in the literature on hydroxyl radical reactions with pesticides and related compounds are discussed together with the experimental methods and the basic reaction mechanisms. Recommendations are made for the most probable values. Most of the molecules whose rate coefficients are discussed have aromatic ring: their rate coefficients are in the range of $2 \times 10^9\text{--}1 \times 10^{10} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$. The rate coefficients show some variation with the electron withdrawing–donating nature of the substituent on the ring. The rate coefficients for triazine pesticides (simazine, atrazine, prometon) are all around $2.5 \times 10^9 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$. The values do not show variation with the substituent on the s-triazine ring. The rate coefficients for the non-aromatic molecules which have C=C double bonds or several C–H bonds may also be above $1 \times 10^9 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$. However, the values for molecules without C=C double bonds or several C–H bonds are in the $1 \times 10^7\text{--}1 \times 10^9 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ range.

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1. Introduction

Hydroxyl radicals ($\cdot\text{OH}$) play a very important role in advanced oxidation processes (AOP) and also in the degradation of persistent organic pollutants (POP) in surface waters (Ikehata and El-Din, 2006; Sievers, 2011). Large number of rate coefficients of the $\cdot\text{OH}$ + organic molecule reactions was measured by a large variety of techniques. For several molecules also the place of attack was determined, the first degradation products were identified and degradation mechanisms were suggested.

In this manuscript we survey the rate coefficients (k_{OH}) published on $\cdot\text{OH}$ reactions with pesticides and related compounds. For some of the molecules (actually for the most frequently used ones) several published k_{OH} 's are available, for example 2,4-D, MCPA, fenuron, diuron, linuron, atrazine, simazine, molinate. Sometimes there are considerable differences between the published values: the lowest and highest value may differ by one order of magnitude. We intend to help those, who may use these k_{OH} 's, e.g. for modelling degradation mechanisms or for investigating the fate of pollutants in the environment. By analysing the methods of k_{OH} determination and the k_{OH} 's obtained we select the most probable value by disclosing the unrealistic values and making averaging for the seemingly reliable rate coefficients.

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2. Limitations of the rate coefficients and the basic reaction types of organic molecules with hydroxyl radical

2.1. Limitations, the diffusion controlled rate coefficient

In liquid phase a chemical reaction may take place when the reactants approach each-other by diffusion (Noyes, 1961). For the estimation of the “theoretical maximum”, the fully diffusion controlled rate coefficient (encounter rate coefficient, k_{diff} , $\text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$), the Smoluchowski relation is used (Elliot et al., 1990; Ashton et al., 1995):

$$k_{\text{diff}} = 4\pi(D_{\text{O}} + D_{\text{OH}})(r_{\text{O}} + r_{\text{OH}})N \times 10^3 \quad (1)$$

In (1) D_{O} and D_{OH} are the diffusion coefficients of the target molecule and the hydroxyl radical, respectively, r_{O} and r_{OH} are the reaction radii of the corresponding species. N is the Avogadro's number. Ashton et al. (1995) in their studies on the temperature dependence of the $\cdot\text{OH} + \text{aromatic molecule}$ reaction used $0.22 \times 10^{-9} \text{ m}$ and $2.31 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ as r_{OH} and D_{OH} , respectively. The D_{O} 's of simple aromatic molecules are much smaller. In many molecules discussed here an important target of $\cdot\text{OH}$ attack is the aromatic ring, which has the same size in benzene derivatives, so r_{O} is assumed to be more-or-less structure independent. Therefore, k_{diff} probably has also little structure dependence. Based on pulse radiolysis experiments with aromatic molecules, which readily react with $\cdot\text{OH}$ (e.g. toluene), k_{diff} is suggested to be in the 8×10^9 – $1.1 \times 10^{10} \text{ mol}^{-1} \text{dm}^3 \text{s}^{-1}$ range (Elliot et al., 1990; Ashton et al., 1995; Schuler and Albarran, 2002; Wojnárovits and Takács, 2013). Using $D_{\text{O}} = 0.5 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ and $r_{\text{O}} = 0.32 \times 10^{-9} \text{ m}$, and the same values for D_{OH} and r_{OH} as used by Ashton et al. (1995), $k_{\text{diff}} = 1.1 \times 10^{10} \text{ mol}^{-1} \text{dm}^3 \text{s}^{-1}$ is obtained. We accept the latter value as the diffusion controlled rate coefficient and consider all published k_{OH} 's which are well above this limit as unrealistic.

When $\cdot\text{OH}$ and the target molecule are in contact the rate of the chemical step is basically determined by the chemical structure. The rate coefficient of the chemically activated reaction (k_{chem}), i.e. the rate coefficient that would be measured if diffusion were not rate influencing (Elliot et al., 1990), is expected to be correlated e.g. with the Hammett substituent constant (Hansch et al., 1991; Wojnárovits and Takács, 2013). According to the Noyes equation:

$$1/k_{\text{OH}} = 1/k_{\text{diff}} + 1/k_{\text{chem}} \quad (2)$$

When k_{chem} is much higher than k_{diff} the reaction may be called diffusion controlled reaction, in the opposite case when $k_{\text{chem}} \ll k_{\text{diff}}$ it may be called chemically controlled reaction.

2.2. Reaction types

$\cdot\text{OH}$ may react with dissolved organic molecules in direct electron transfer, addition to double bond or in H-abstraction from a C–H bond. $\cdot\text{OH}$ is strongly oxidizing with a standard reduction potential vs. normal hydrogen electrode (NHE) of $E(\cdot\text{OH}/\text{OH}^-) = 1.9 \text{ V}$. In spite of this very high reduction potential direct electron transfer is rarely observable, and when it is observed intermediate complexes are likely to be involved (von Sonntag, 2006), e.g. $\text{Fe}^{2+} + \cdot\text{OH} \rightarrow (\text{FeOH}^{2+}) \rightarrow \text{OH}^- + \text{Fe}^{3+}$. Electron transfer requires rearrangement of water molecules around the charged reaction centre, this rearrangement disfavors the reaction (entropy factor).

Due to the electrophilic character, $\cdot\text{OH}$ readily reacts with C=C and C=N double bonds but not with C=O which is electron deficient at the carbon atom, the position where the $\cdot\text{OH}$ would prefer to add (von Sonntag, 2006). $\cdot\text{OH}$ reacts with C=C double bonds at close to diffusion controlled rates, however, the reaction is highly regioselective mainly due to the electrophilic nature. The rate coefficient of $\cdot\text{OH}$ addition to the benzene, $7.8 \times 10^9 \text{ mol}^{-1} \text{dm}^3 \text{s}^{-1}$ (Schuler and Albarran, 2002), is close to k_{diff} . The k_{OH} 's for simple aromatic molecules with electron donating substituent, like $-\text{CH}_3$, $-\text{CH}_2\text{CH}_3$, $-\text{CH}(\text{CH}_3)_2$ or $-\text{CH}_2\text{CO}_2^-$, are practically the same as for benzene. Stronger electron releasing substituent, like $-\text{OH}$, $-\text{NH}_2$ slightly increases k_{OH} . The strongly electron withdrawing substituent attached to the benzene ring, $-\text{CHO}$ in benzaldehyde, $-\text{CO}_2\text{H}$ in benzoic acid, $-\text{CN}$ in benzonitrile or $-\text{NO}_2$ in nitrobenzene decreases k_{OH} (Wojnárovits and Takács, 2013). For simple aromatic molecules k_{OH} 's are in a narrow range: 2×10^9 – $1 \times 10^{10} \text{ mol}^{-1} \text{dm}^3 \text{s}^{-1}$.

The HO–H bond dissociation energy is 499 kJ mol^{-1} ; in saturated hydrocarbons the energies of primary, secondary and tertiary C–H bonds are 423, 412 and 403 kJ mol^{-1} , respectively. When there is a double bond in the molecule and the H-atom in α -position is abstracted (e.g. $\text{CH}_2=\text{CH}-\text{CH}_2-\text{H}$, or $\text{C}_6\text{H}_5\text{CH}_2-\text{H}$) the energy is 360 – 370 kJ mol^{-1} . Despite the considerable driving force, there is some remarkable selectivity. Primary hydrogen is less likely to be abstracted than secondary and tertiary hydrogen (von Sonntag, 2006).

3. Methods of rate coefficient determination

3.1. Generation of hydroxyl radicals

The methods used for rate coefficient determination may differ in the way of $\cdot\text{OH}$ generation or in the way of obtaining k_{OH} . In radiolysis and VUV-photolysis the water molecules serve as the source of hydroxyl radicals. The cleanest source of $\cdot\text{OH}$ is probably the radiolysis of water (Buxton et al., 1988; Spinks and Woods, 1990). During water radiolysis hydroxyl radical, hydrated electron (e_{aq}^-) and hydrogen atom (H^\cdot) transient products form according to Eq. (3) (the values in brackets are the yields in $\mu\text{mol J}^{-1}$ units):



The experiments with $\cdot\text{OH}$ are generally carried out in N_2O saturated solutions. In such solutions, due to transformation (4), the reacting radicals and their yields are: $\cdot\text{OH}$ $0.55 \mu\text{mol J}^{-1}$ and H^\cdot $0.06 \mu\text{mol J}^{-1}$. H^\cdot gives $\sim 10\%$ contribution to reacting radicals. H^\cdot generally reacts with organic molecules in reactions similar to that of $\cdot\text{OH}$, albeit the k_{H} 's are usually one order of magnitude smaller than the k_{OH} 's. Due to the slow reaction, H^\cdot reactions do not influence significantly k_{OH} in pulse radiolysis; their influence in steady-state experiments is also small.

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