Iron(III) hydroxocomplex - methyl viologen dication system as a prospective tool for determination of hydroxyl radical reaction rate constants with environmental pollutants

Yuliya E. Tyutereva\textsuperscript{a,b}, Vyacheslav P. Grivin\textsuperscript{a,b}, Jing Xu\textsuperscript{c}, Feng Wu\textsuperscript{d}, Victor F. Plyusnin\textsuperscript{a,b} and Ivan P. Pozdnyakov\textsuperscript{a,b,*}

\textsuperscript{a}V.V. Voevodsky Institute of Chemical Kinetics and Combustion, 3 Institutskaya str., 630090 Novosibirsk, Russian Federation

\textsuperscript{b}Novosibirsk State University, 2 Pirogova St., 630090 Novosibirsk, Russian Federation

\textsuperscript{c}State Key Laboratory of Water Resources and Hydropower Engineering Science, Wuhan University, 430072 Wuhan, P.R. China

\textsuperscript{d}Hubei Key Lab of Biomass Resource Chemistry and Environmental Biotechnology, School of Resources and Environmental Science, Wuhan University, 430079, P. R. China

*Corresponding author:
Ivan P. Pozdnyakov, Ph.D., Voevodsky Institute of Chemical Kinetics and Combustion, SB RAS, Institutskaya str. 3, 630090 Novosibirsk, Russian Federation, E-mail: ipozdnyak@kinetics.nsc.ru
ABSTRACT

Reactivity of oxidative species with target pollutants is one of the crucial parameters for application of any system based on advanced oxidation processes (AOPs). This work presents new useful approach how to determine the hydroxyl radical reaction rate constants ($k_{OH}$) using UVA laser flash photolysis technique. Fe(III) hydroxocomplex at pH 3 was applied as a standard source of hydroxyl radicals and methyl viologen dication (MV$^{2+}$) was used as selective probe for *OH radical. Application of MV$^{2+}$ allows to determine $k_{OH}$ values even for compounds which do not generate themselves optically detectable transient species in reaction with hydroxyl radicals. Validity of this approach was tested on a wide range of different persistent pesticides and its main advantages and drawbacks in comparison with existing steady-state and time-resolved techniques were discussed.

KEYWORDS: AOPs, hydroxyl radical, laser flash photolysis, iron hydroxocomplex, methyl viologen dication, reaction rate constants

DECLARATIONS

Ethics approval and consent to participate – "Not applicable"

Consent for publication -“Not applicable”

Availability of data and materials -“Not applicable”

Competing interests - "The authors declare that they have no competing interests"

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Advanced oxidation processes based on generation of highly oxidative hydroxyl (\(^{\bullet}\)OH) radicals are very popular nowadays due to increasing contamination of natural waters and necessity to develop effective and low cost water treatment procedures (Deng and Zhao, 2015; Shen et al., 2019). As the absorption band of \(^{\bullet}\)OH radical lies in the deep UV (Buxton et al., 1988) the direct observation of its reactions with target pollutants is complicated. Usually, unknown hydroxyl radical reaction rate constant \((k_{OH}^X)\) is determined by competitive method using a substance (S) with known \(k_{OH}^S\) value as a standard (Haag and Yao, 1992, Orellana-García et al., 2015, Sánchez-Polo et al., 2013). The main advantage of aforesaid approach is the possibility to use steady-state (photo)chemical methods of generation of \(^{\bullet}\)OH radical and widespread and convenient HPLC technique for calculation of \(k_{OH}^X\) value. However, this approach has some serious drawbacks as follows:

1) This is relative method giving \(k_{OH}^X/k_{OH}^S\) ratio in result, so standard with very well determined \(k_{OH}^S\) value has to be used.
2) If photochemical excitation is used for \(^{\bullet}\)OH radical generation, neither \(X\) nor \(S\) should exhibit good absorption and/or own photochemical activity under excitation light.
3) If there are reactions between secondary organic radicals and initial compounds \(X\) and \(S\), the determination of \(k_{OH}^X\) using this method will give an incorrect result.

Less popular, but more straightforward approach is based on using a time-resolved method (laser flash photolysis (LFP) or pulse radiolysis (PR), namely), which allows direct optical registration of \(^{\bullet}\)OH radical reaction with target compound (Peller et al., 2005; Rafqah et al., 2004; Terzian et al., 1995; Zona et al., 2012). The main advantage of this approach that it is absolute method which allows direct calculation of \(k_{OH}^X\) values. However, it also has some drawbacks as follows:

1) Both LFP and PR techniques are less common and more sophisticated methods in comparison with ordinary HPLC.
2) In LFP method a photochemical system with high quantum yield of hydroxyl radical generation is needed and X should not exhibit good absorption and/or own photochemical activity under excitation light.

3) If \( \cdot \text{OH} \) adduct with X molecule exhibits low absorption in registration range of LFP or PR setup or its absorption is borrowed by intensive absorption of initial compounds, the calculation of \( k_{\text{OH}X} \) will be very complicated or even impossible.

Last two drawbacks could be overcome by addition of another hydroxyl radical probe which do not absorb at excitation wavelength, reacts readily with hydroxyl radical and produce an intermediate with good absorption in convenient optical range (Catastini et al., 2004). In this work we developing this approach using Fe(III) hydroxocomplex as well-recommended photolytic source of hydroxyl radical and methyl viologen dication as a selective probe for this active species.

**EXPERIMENTAL**

All chemicals used in the study were of analytical reagent grade or higher purity and were used without further purification. Milli-Q water was used in all photochemical experiments. The initial pH of solutions was adjusted to \(~3\) by chemically pure perchloric acid and was controlled by the Anion-4100 ionometer (Infraspak-Analit, Russia). Optical spectra were recorded using Agilent 8453 spectrophotometer (Agilent Technologies, USA).

Time-resolved experiments were performed using a laser flash photolysis (LFP) setup described in details elsewhere (Pozdnyakov et al., 2006). Briefly, a tunable LS-2137U laser (Lotis, Belarus) with an excitation wavelength of 355 nm was used as excitation source with pulse duration of about 6 ns, and pulse energy from 1 to 15 mJ. Quartz cells with an optical path length of 1 cm and a total volume of 3 ml at normal oxygen content in solutions were applied.

**RESULTS AND DISCUSSION**
The set of organic pesticides used in this study as typical environmental contaminants is presented in Fig 1. It worth to note, that all of these compounds exhibit no absorption at 355 nm, are stable in the presence of Fe(III) ions and do not complex with them. It was demonstrated by coincidence of sum of absorption spectra of individual species with spectrum of the mixture and stability of the latter during characteristic times of LFP experiments. It is also assumed that X-•OH adducts exhibit negligible absorption at wavelengths higher than 400 nm. Such situation is typical for X-•OH adducts formed upon hydroxyl radical attack to benzene ring (Buxton et al., 1988; Terzian et al., 1995, Zona et al., 2002) and coincide with known literature data for target compounds (Table 1). 

**Figure 1.** The structural formulae of organic pesticides used in this study

The elementary reactions of •OH radicals with target pollutants were studied with efficient sensitizer of these radicals, Fe(OH)$_2^+$ hydroxocomplex (Benkelberg et al., 1995; Lee and Yoon, 2004; Pozdnyakov et al., 2000). In our LFP experiments the concentration of Fe(III) perchlorate was fixed as 600 µM at pH 2.9. In these conditions the FeOH$_2^+$ hydroxocomplex was a main form of Fe(III) in solution (about 80%) and a sole photoactive species with absorption of about 50% of UV light quanta.

\[
\text{FeOH}_2^{2+} \xrightarrow{hv} \text{Fe(II)} + \text{OH}^* \tag{1}
\]
As a selective probe for •OH radical MV$^{2+}$ was proposed which has several advantages as follows:

1) Has no own absorption at wavelength higher than 310 nm and does not interact or oxidized by Fe(III) ions in acid media.

2) Reacts readily with hydroxyl radical with rate constant $(2.5 \pm 0.2) \times 10^8$ M$^{-1}$s$^{-1}$ (Solar et all., 1985; Zhang et al., 2008)

3) Produce MV(•OH)$^{2+}$ intermediate with good absorption in convenient optical range ($\lambda_{\text{max}} = 470$ nm, $\varepsilon_{\text{max}} = 16000 \pm 700$ M$^{-1}$cm$^{-1}$, Solar et all., 1985; Zhang et al., 2008) where does not absorb nor Fe(III) hydroxocomplex, not adducts of •OH radical with target compounds.

In condition of our LFP experiments typical •OH radical concentration is about 1 µM which is much less than concentration of both MV$^{2+}$ (240 µM) and target compounds (25 – 500 µM) used in this study. It allows taking into account only reactions of •OH radical with aforesaid compounds and use psevdo first order approximation in solving of the following kinetic scheme:

\[
\begin{align*}
&\text{OH}^* + X \overset{k^\text{OH}}{\rightarrow} X(\text{OH}^*) \quad (2) \\
&\text{OH}^* + \text{MV}^{2+} \overset{k^\text{MV}}{\rightarrow} \text{MV}(\text{OH}^*)^{2+} \quad (3) \\
&MV(\text{OH}^*)^{2+} \overset{k_d}{\rightarrow} \quad (4) \\
&\frac{d[\text{OH}^*]}{dt} = -(k^X_{\text{OH}}[X]_0 + k^\text{MV}_{\text{OH}}[\text{MV}^{2+}]_0)[\text{OH}^*] \quad (5) \\
&\frac{d[\text{MV}(\text{OH}^*)^{2+}]}{dt} = k^\text{MV}_{\text{OH}}[\text{MV}^{2+}][\text{OH}^*] - k_d[\text{MV}(\text{OH}^*)^{2+}] \quad (6)
\end{align*}
\]

Where $k_d$ is the observed rate constant of MV(•OH)$^{2+}$ adduct decay. It worth to note that according to Solar et al., the main pathway of MV(•OH)$^{2+}$ disappearance in aqueous solutions is disproportionation with the rate constant, $2k_{\text{dis}} = (1.3 \pm 0.2) \times 10^8$ M$^{-1}$s$^{-1}$. However, due to very low concentration of MV(•OH)$^{2+}$ adduct we can successfully use first-order reaction (4) to
describe the decay of this species in our time window (Fig. 2). Solution of kinetic scheme (5-6) gives the dependence of MV(•OH)\(^{2+}\) adduct concentration on time:

\[
[MV(OH^•)^{2+}] = \frac{k_{OH}^{MV}[MV^{2+}]_0[OH^•]_0}{(k_{obs}-k_d)} \left[ e^{(-k_d t)} - e^{(-k_{obs} t)} \right] 
\]

(7)

Where

\[
k_{obs} = k_{OH}^{MV}[MV^{2+}]_0 + k_{OH}^{X}[X]_0
\]

(8)

Taking into account that only MV(•OH)\(^{2+}\) adduct exhibits transient absorption at 470 nm (\(\Delta A_{470\text{nm}}(t)\)) one can obtain the following equation for changing of this parameter with time:

\[
\Delta A_{470\text{nm}}(t) = c_{\text{max}} \frac{k_{OH}^{MV}[MV^{2+}]_0[OH^•]_0}{(k_{obs}-k_d)} \left[ e^{(-k_d t)} - e^{(-k_{obs} t)} \right] = A \left[ e^{(-k_d t)} - e^{(-k_{obs} t)} \right] 
\]

(9)

\[\text{Figure 2.} \text{ Kinetic curves of transient absorption of MV(•OH)\(^{2+}\) adduct at 470 nm in presence of 0 (1), 25 (2), 50 (3), 75 (4) and 100 (5) µM of 2,4-DB. Each curve was obtained by averaging of 20-30 independent laser flashes, excitation energy was 5.6 mJ/pulse. Smooth curves are the best fits by eq. 9.}\]
Evolution of transient absorption of MV\((\cdot\text{OH})^{2+}\) adduct at 470 nm in the presence of different concentration of 2,4-DB herbicide is shown at Figure 2. Similar results were obtained for all other target compounds used in the study. It worth to note that amplitude of the signal at 470 nm is gradually decrease with increasing of 2,4-DB concentration due to competition between the herbicide and MV\(^{2+}\) for \(\cdot\text{OH}\) radicals (eq. 9). However in all cases signal to noise ratio is high enough to determine \(k_{\text{obs}}\) value with about 10-15% precision. Very good fit was obtained for all concentration of 2,4-DB as well as for other compounds (Fig. 3) which proves validity of simplified kinetic scheme (5-6) and allows to calculate \(k_{\text{OH}X}\) values for studied pesticides (Table 1).

![Figure 3](image)

**Figure 3.** The dependence of \(k_{\text{obs}}\) calculated by eq. 9 from initial concentration of 2,4-DB (1), MSM (2), TCP (3) and AMT (4). Straight lines are the best fits by eq. 8.

Analysis of data presenting in Table 1 allows to conclude that our approach gives the \(k_{\text{OH}X}\) values which are well coincides with result obtaining by both steady-state (stationary photolysis, ozonation) and time-resolved (LPF, PR) methods. It worth to note that \(k_{\text{OH}X}\) values are practically independent on pH for the studied compounds. It could be explained by the fact that studied herbicides (for exception of AMT, ATR and DIC) do not contain an acid/base substituent...
directly attached to aromatic π-system. For this reason deprotonation of an aliphatic substituent
does not change greatly red-ox properties of a target molecule and its reactivity towards
hydroxyl radical. This is clearly seen in comparison of $k_{OH}^X$ values for 2,4-DB, 2,4,5-T and TCP
which are practically the same for both neutral and anionic form of the herbicide. In a case of
ATR at all pH higher than 2.5 these compound exists mainly in neutral form ($pK_a = 1.6$), so $k_{OH}^X$
values for this compound is not affected by pH (Table 1). Similar situation is expected for DIC
($pK_a = 1.9$) which exist as monoanion in environmentally relevant pH range.

For AMT which contains protonated amino group directly attached to the triazole π-system $k_{OH}^X$
increase about 1.6 times for neutral form in comparison with cationic one (Table 1). So we can
conclude that for aromatic amines, phenols and similar compounds with $pK_a$ values higher than 3
$k_{OH}^X$ values obtained by our approach could be used only as tentative estimates of the reactivity
of the compounds towards hydroxyl radical at higher pH. However, our approach allows to
measure $k_{OH}^X$ values for a set of target compounds (from two to four) for a day due to high
analytical signal of MV(•OH)$^{2+}$ adduct at selected registration wavelength (470 nm). It is not a
case of general approach using LFP or PR techniques where one first needs to find the
absorption maximum of unknown adduct of •OH radical with studied contaminant and this is
limiting time-consuming step. In a case of application of steady-state techniques one need to
spend a time for finding a proper competing standard and for time-consuming HPLC
measurements.
Table 1. $k_{\text{OH}}$ values and optical properties of X-•OH adducts for studied organic pesticides

| Compound (pK$_a$) | pH  | $k_{\text{OH}}$ $\times 10^{-9}$ M$^{-1}$s$^{-1}$ | $\lambda_{\text{max}}$(X-•OH) nm | Method$^a$ | reference |
|-----------------|-----|--------------------------------------------|--------------------------------|-----------|-----------|
| AMT (4.14)      | 3.4 | 1.5                                       | < 300                           | LFP       | Catalstini et al., 2004 |
|                 | 3.0 | 0.36 ± 0.02                               | -                               | SSP       | Orellana-García et al., 2015 |
|                 | 7.0 | 0.59 ± 0.03                               | -                               | SSP       | Orellana-García et al., 2015 |
|                 | 2.9 | 0.47 ± 0.04                               | -                               | LFP       | This work |
| ATR (1.6)       | 3.0 | 2.9                                       | -                               | SSP       | Orellana-García et al., 2015 |
|                 | 7.0 | 2.7                                       | -                               | SSP       | Orellana-García et al., 2015 |
|                 | 3.6 | 2.6 ± 0.4                                 | -                               | SSP       | Haag and Yao, 1992 |
|                 | 2.9 | 3.5 ± 0.6                                 | -                               | LFP       | This work |
| 2,4-DB (2.6)    | 2.5 | 5.2                                       | 310                             | PR        | Peller et al., 2005$^b$ |
|                 | 9.0 | 6.6                                       | 310                             | PR        | Zona et al., 2002$^b$ |
|                 | 3.0 | ~7.0                                      | 315                             | LFP       | Pozdnyakov et al., 2016 |
|                 | 2.9 | 5.0 ± 0.3                                 | -                               | LFP       | This work |
| DIC (1.9)       | 2.9 | 3.2 ± 0.3                                 | -                               | LFP       | This work |
| MSM (3.75)      | 3.4 | 3.5                                       | 355                             | LFP       | Rafqah et al., 2004 |
|                 | 2.9 | 2.5 ± 0.2                                 | -                               | LFP       | This work |
| 2,4,5-T (2.7)   | 8.5 | 6.4                                       | 320                             | PR        | Zona et al., 2012 |
|                 | 2.9 | 6.3 ± 0.5                                 | -                               | LFP       | This work |
| TCP (2.7)       | 7.0 | 1.7                                       | -                               | Ozonation | Solís 2014 |
|                 | 2.9 | 1.4 ± 0.3                                 | -                               | LFP       | This work |

$^a$SSP, LFP and PR stands for steady-state photolysis, laser flash photolysis and pulse radiolysis, accordingly; $^b$data for 2,4-D (2,4-dichlorophenoxyacetic acid) a close analogue of 2,4-DB was taken.
CONCLUSIONS

LPF of Fe(III) hydroxocomplex - MV$^{2+}$ system at pH 3 could be successfully used to determine $k_{OH}$ values for a wide range of different persistent pesticides. Validity of this approach was proven on by comparison of obtained $k_{OH}$ values with literature ones found by another approaches. The main advantages of proposed system in comparison with existing popular competitive steady state approaches or direct LFP with target molecule are as follows:

1) Absolute method allowing direct measurement of $k_{OH}$ value in opposite to competitive steady state approaches.

2) MV($^\cdot$OH)$^{2+}$ adduct absorption spectrum does not overlap with spectra of $^\cdot$OH adducts with typical environmental contaminants.

3) “One-wavelength registration” method, allowing to avoid time-consuming determination of transient absorption spectrum of $^\cdot$OH adduct with a studied environmental contaminant.

4) $k_{OH}$ values could be obtained with good experimental precision (c.a. 10-15%) due to high absorption of MV($^\cdot$OH)$^{2+}$ adduct in convenient optical range ($\lambda_{\text{max}} = 470$ nm, $\varepsilon_{\text{max}} = 16000 \pm 700$ M$^{-1}$cm$^{-1}$).

5) The method could be applied for compounds which do not generate themselves optically detectable transient species in reaction with hydroxyl radicals.

However, some limitations of aforesaid approach also should be stressed:

1) The method should not be applied for compounds which generate X($^\cdot$OH)$^{2+}$ adducts with good absorption at 470 nm. In this case direct measurement of observed rate constant of formation of transient absorption of X-$^\cdot$OH adduct in the maximum of its absorption is recommended.
2) For aromatic amines, phenols and similar compounds with $\text{pK}_a$ values higher than three $k_{OH}^X$ values obtained by our approach could be used only as tentative estimates of the reactivity of the compounds towards hydroxyl radical at higher pH.

We believed that current approach will be successfully used in the studies devoted to application of AOPs based on hydroxyl radical generation for determination of $k_{OH}$ values for target environmental contaminants.

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