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S.P. Mezyk, T.D. Cullen, K.A. Rickman
(California State University at Long Beach)

B.J. Mincher
(Idaho National Laboratory)

February 2017

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Prepared for the U.S. Department of Energy
Office of Nuclear Energy
Under DOE Idaho Operations Office
Contract DE-AC07-05ID14517

The reactivity of the nitrate radical ($\cdot\text{NO}_3$) in aqueous and organic solutions

Stephen P. Mezyk¹*, Thomas D. Cullen¹, Kimberly A. Rickman¹, Bruce J. Mincher²

1. Department of Chemistry and Biochemistry, California State University at Long Beach, Long Beach, California, 90840, United States
2. Idaho National Laboratory, P.O. Box 1625, Idaho Falls, Idaho 83415, United States

Corresponding author information:

* Stephen Mezyk

Email: Stephen.Mezyk@csulb.edu

ph: 562-985-4649

FAX: 562-985-8557

Keywords: nitrate radical kinetics, organic solvents, Tho

ABSTRACT

Rate constants for the nitrate ($\cdot\text{NO}_3$) radical reaction with alcohols, alkanes, alkenes and several aromatic compounds were measured in aqueous and *tert*-butanol solution for comparison to aqueous and acetonitrile values from the literature. The measured trends provide insight into the reactions of the $\cdot\text{NO}_3$ radical in various media. The reaction with alcohols primarily consists of hydrogen-atom abstraction from the α -hydroxy position, and is faster in solvents of lower polarity where the diffusivity of the radical is greater. Alkenes react faster than alkanes, and their rate constants are also faster in non-polar solution. The situation is reversed for nitrate radical reaction with the aromatic compounds, where the rate constants in *tert*-butanol are slower. This is attributed to the need to solvate the NO_3^- anion and corresponding tropylium cation produced by the $\cdot\text{NO}_3$ radical electron transfer reaction. A linear correlation was found between measured rate constants in water and acetonitrile, which can be used to estimate aqueous nitrate radical rate constants for compounds having low water solubility.

INTRODUCTION

The nitrate ($\bullet\text{NO}_3$) radical is an important reactive species in environmental chemistry, ranging from atmospheric gas-phase chemistry to multiple condensed phase aerosols. The nitrate radical is the major reactive species in the troposphere at night [1], being formed by the reaction of ozone with the nitrite radical [1.2]. As such, the reactions of NO_3^\bullet in the gas phase have been extensively investigated over many decades [2-4]. However, considerably less information is available for the reactions of NO_3^\bullet in the condensed phase [5]. There are only a few reports concerning $\bullet\text{NO}_3$ kinetics in the aqueous solution [6-16]. Considerably more kinetic data is available for reactions in acetonitrile [8,9,17-22] where the $\bullet\text{NO}_3$ radical is generated by the laser photolysis of dissolved $\text{Ce}^{\text{IV}}(\text{NO}_3)_6^{2-}$. Most reaction rate constants for this radical have been reported in acetonitrile due to the ease of the experimental set-up using laser flash photolysis. However, it has been demonstrated that for hydrogen abstraction reactions the rate constants for the aqueous and gas phases are similar, but slower than for acetonitrile [5]. In contrast, electron transfer reactions were found to be slower in acetonitrile for this radical.

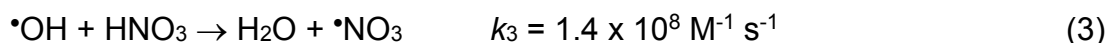
Nitrate radicals can be formed, and react, in highly acidic environments, such as in atmospheric aerosols [23] or in concentrated nitric acid solutions. The latter conditions are utilized in strategies for the recovery of actinides from dissolved nuclear fuel, typically depending on liquid-liquid solvent-extraction. This chemistry uses selective ligands in an organic diluent to complex and partition the desired metal ions. The fuel dissolution is aqueous nitric acid and is radioactive due to fission product and actinide decay. The $\bullet\text{NO}_3$ radical is produced during the high-energy irradiation of HNO_3 [24], and this radical may

also act as an oxidizing agent for the organic ligands resulting in deleterious effects on solvent extraction performance in this condensed phase system.

The radiolysis of aqueous nitric acid has included investigations of $\bullet\text{NO}_3$ radical formation mechanisms [6,17,25-31] and yields [6,29,30]. Two major pathways have been identified. Equations 1 and 2 show the direct action of radiation on nitrate anions and nitric acid:



The reaction of hydroxyl radicals ($\bullet\text{OH}$) with nitric acid also produces $\bullet\text{NO}_3$ and is shown in Equation 3 [6]:



The reaction of nitrate anions with ionized water (H_2O^+) can also produce $\bullet\text{NO}_3$ [30]:



Although produced in the aqueous phase, the neutral $\bullet\text{NO}_3$ radical will react with organic species at the solvent extraction interface or could diffuse into the organic phase and react there. Thus, an understanding of the reactivity of the radiolytically-produced $\bullet\text{NO}_3$ radical toward solvent extraction ligands in various media is important to evaluating the radiation stability of proposed solvent formulations.

The purposes of this study were to develop techniques to measure $\bullet\text{NO}_3$ radical reaction kinetics with solvent extraction ligands in aqueous and organic solutions by electron pulse radiolysis, and to compare these rate constants to those for model compounds. Data collected here in 6 M HNO_3 and *tert*-butanol are compared to literature

data for acetonitrile, and are used to elucidate the reactivity/structure relationships in an actual compound used in radioactive solvent extraction applications. These comparisons illustrate the need measure radical kinetics under conditions as near as possible to the real solvent extraction process, and to also provide insight into reaction mechanisms for the $\cdot\text{NO}_3$ radical in organic and aqueous solutions. Further, a correlation is presented between the commonly available acetonitrile rate constants and the experimentally harder to obtain aqueous rate constants, which may be useful for extrapolating $\cdot\text{NO}_3$ rate constants for atmospheric organic containing aerosols, or estimating rate constants for sparingly aqueous soluble solvent extraction ligands.

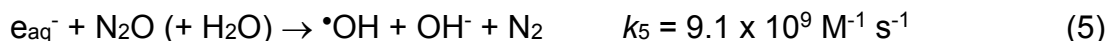
EXPERIMENTAL

All chemicals were purchased from the Sigma-Aldrich chemical company or VWR International at high purity (at least ACS grade) and used as received. Aqueous solutions were made using Milli-Q purity water.

Hydroxyl radical rate constants were measured using the linear accelerator (LINAC) electron pulse radiolysis system at the Radiation Laboratory, University of Notre Dame. This irradiation and transient absorption detection system has been described in detail previously [32]. During all irradiation experiments, solutions were saturated with N_2O to prevent air ingress. Dosimetry was performed using N_2O -saturated solutions of 1.00×10^{-2} M KSCN at $\lambda = 475$ nm, ($G_{\epsilon} = 5.2 \times 10^{-4} \text{ m}^2 \text{ J}^{-1}$) with average doses of 3–5 Gy per 2–3 ns pulse [33].

Aqueous measurements

For the aqueous measurements, the $\bullet\text{NO}_3$ radical was generated in pulse irradiated 6 M HNO_3 . To improve our initial $\bullet\text{NO}_3$ radical yield the nitric acid was pre-saturated with N_2O gas, which converted any hydrated electrons that were not scavenged by acidity or nitrate anion into $\bullet\text{OH}$ radicals, via the reaction:

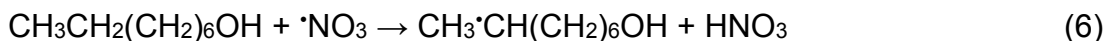


The electron pulse radiolysis of a 6.0 M HNO_3 solution gives an absorption spectrum with characteristic fingerprint bands between 550 and 700 nm identified it as being due to the $\bullet\text{NO}_3$ radical [31]. Its reaction kinetics were determined by monitoring the absorbance change at 640 nm. The lifetime of the $\bullet\text{NO}_3$ radical in the ligand-free acidic solution is long, $> 50 \mu\text{s}$, and the decay follows first-order kinetics (assumed to be reaction with trace amounts of impurities). Upon addition of a solute, the decay becomes faster (Figure 1a), and by plotting the fitted exponential decay kinetic parameters against the solute concentration, the true second-order rate constant can be determined. This is shown for the reactions with *o*-, *m*-, and *p*-xylene in Figure 1b.

Solvent extraction ligands are designed to have low water solubility. Due to the limited solubility of CMPO (octylphenyldiisobutylcarbamoyle-methylphosphine oxide), and DMDOHEMA (dimethyl dioctyl hexylethoxymalonamide) in aqueous solution, 20% acetone was used as a co-solvent, resulting in a final nitric acid concentration of 4.8 M for those measurements.

tert-butanol measurements

An organic-soluble source of nitrate ion was necessary to generate $\cdot\text{NO}_3$ radical in the organic phase. Tetrabutyl ammonium nitrate (TBANO_3) was found to have a solubility of ~ 1.4 M in both *n*-octanol and *tert*-butanol. However, when an *n*-octanol solution of TBANO_3 was pulse-irradiated, no $\cdot\text{NO}_3$ radical was measurable. This may be because of a very fast reaction between the radical and the alcohol itself (discussed in more detail below), which would react with alkane CH_2 groups by $\cdot\text{H}$ -atom abstraction:



Electron pulse radiolysis of TBANO_3 in *tert*-butanol, which lacks methylene groups, was more successful. The absorbance spectrum of the $\cdot\text{NO}_3$ radical in this organic solution is shown in Figure 2. The spectrum is similar to that in nitric acid above, although slightly blue shifted. The absorbance maximum at 630 nm was used to measure the kinetics in *tert*-butanol solution, in the same way as was discussed above for aqueous solution.

RESULTS AND DISCUSSION

The values measured here for $\cdot\text{NO}_3$ reaction rate constants for various ligands and model compounds in aqueous and *tert*-butanol solution are shown in bold in Table 1. Data collected from the literature for aqueous solution, and for acetonitrile are also shown for comparison.

It can be seen in Table 1 that the rates constants for many solutes increase across the series: *tert*-butanol > acetonitrile > water. This is attributed to the increased mobility of the $\cdot\text{NO}_3$ radical in solutions of decreasing dielectric strength [8], resulting in the fastest rate constants for *tert*-butanol. The alcohols react with the $\cdot\text{NO}_3$ radical in all three

solvents, with increasing rate constants with carbon chain length. The increase is especially dramatic for *tert*-butanol solution where the rate constant is faster by more than two orders of magnitude for octanol versus methanol. This trend suggests that the mechanism is one of H-atom abstraction by the $\cdot\text{NO}_3$ radical, with the hydrogen atoms at the alpha position being most susceptible. Only ethanol does not fit this trend, exhibiting higher than expected rate constants in all three solvents. Ethanol has methylene ($-\text{CH}_2-$) H-atoms available only at the alpha position, explaining its faster than expected reaction rate.

Based on the discussion above, diluents with activated methylene groups should scavenge $\cdot\text{NO}_3$ radical resulting in protection of the ligands. For example, the rate constants for the ligand DMDOHEMA (Figure 3) and its commonly-used diluent octanol are nearly identical at $\sim 4.3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ in *tert*-butanol, but DMDOHEMA is used at a concentration of 0.65 M while octanol is present at 5 % of the diluent (0.32 M). Therefore, 33% of $\cdot\text{NO}_3$ radical would be scavenged by this concentration of octanol rather than reacting with the ligand. This also explains why no $\cdot\text{NO}_3$ radical was detected in neat irradiated octanol solutions of TBANO₃ (see Experimental Section) since the high concentration of neat octanol (6.3 M) quickly scavenges any produced $\cdot\text{NO}_3$ radical. The radical is detected in irradiated *tert*-butanol solutions of TBANO₃, however; because there are no susceptible $-\text{CH}_2-$ groups.

The rate constant for dodecane (Table 1) is much slower than for the alcohols, apparently because there is no $-\text{OH}$ group to activate alpha- CH_2 H-atoms. Dodecane is the diluent for many ligands, and its reaction rate constant with $\cdot\text{NO}_3$ radicals measured in *tert*-butanol is only $6.4 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$. Unfortunately, no comparative data for other alkane

reactions with $\cdot\text{NO}_3$ radical were found in the literature. This value is almost two orders of magnitude lower than that of DMDOHEMA, or CMPO (Figure 3) at $3.24 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$. Even at its high concentration of approximately 4.4 M dodecane will not scavenge a significant amount of $\cdot\text{NO}_3$. For example, in the 0.65 M DMDOHEMA formulation containing 5 % octanol/dodecane, it may be calculated that only 6 % of the $\cdot\text{NO}_3$ radicals reacts with the dodecane. Solvent formulations based on dodecane-only as the diluent are not effective at protecting ligands by scavenging this radical. For comparison to dodecane, the presence of a double bond in 1-dodecene increases the rate constant to $3.7 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ for reaction with $\cdot\text{NO}_3$ radical, more than a factor of 50 faster. This suggests that the addition reaction is fast, the product of which would be a nitro-alkane.

It is shown in Table 1 that the aromatic species all have very fast reactions with $\cdot\text{NO}_3$ radical ($\sim 10^9 \text{ M}^{-1} \text{ s}^{-1}$). Fast reactions with aromatic compounds were attributed by Neta and Huie to electron transfer reactions when in aqueous solution [10]. Unlike the other solutes in Table 1, rate constants were slightly lower for the aromatic compounds when in organic solution, the series increasing in the order: *tert*-butanol < water < acetonitrile. Presumably the electron transfer reaction occurs in all three solvents, and the rate constant is slower in *tert*-butanol based upon the difficulty of solvating the produced NO_3^- anion and corresponding tropylium cation [36] in that non-polar solvent. The faster rate constant in acetonitrile may be a combination of the ability to solvate the ions and $\cdot\text{NO}_3$ radical diffusivity.

The correlation of $\cdot\text{NO}_3$ radical reactivity with chemical structure has been investigated previously, with plots of $\log(k)$ vs C-H bond strength [9,13], Hammett sigma parameters [18,20], ionization energies [9,19], and indirect correlations with Marcus and

Rehm-Weller theories [20,22]. However, for a more direct comparison, we followed the method of Ito *et al.* [9] in plotting the logarithm of the absolute rate constant in acetonitrile against the same parameter in 6.0 M HNO₃. These data are shown in Figure 4, with a very good linear correlation observed.

However, three outliers to this general agreement were seen; for ethylene glycol when using literature values, and toluene and nitrotoluene. Our value for ethylene glycol, $(5.35 \pm 0.36) \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ is lower than the two previous measurements ranging from $7.6\text{--}16 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ [9,29], and far more consistent with the linear correlation plot. However, no such improvement was found for the toluene and 3-nitrotoluene rate constant values. The $\cdot\text{NO}_3$ reaction with toluene has been shown to have a significant deuterium isotope effect in acetonitrile [19] suggesting that $\cdot\text{H}$ -atom abstractions dominate in this solvent. In water, however, it's possible that the electron abstraction reaction is the major mechanism, resulting in a faster rate constant. It is assumed that similar reactions could occur for the mono-nitrated toluene. Neglecting these two latter data points, a good linear fit to the data is observed, giving the correlation equation as:

$$\log_{10} k_{\text{CH}_3\text{CN}} = (0.772 \pm 0.060) \cdot \log_{10} k_{\text{H}_2\text{O}} + (2.19 \pm 0.42) \quad (7)$$

The very good ($R^2 = 0.95$) correlation obtained suggests that the aqueous rate constants for water-insoluble organic ligands could be extrapolated to acidic water conditions from acetonitrile data. This could prove useful, as many of the molecules proposed for use as metal complexing agents in nuclear solvent extraction have been purposefully designed to be insoluble in water, making measurement of their rate constants challenging. Insight into the structure/activity relationships of nitrate radical reactions may also be obtained by this approach.

For example, the compound 1-(2,2,3,3,-tetrafluoropropoxy)-3-(4-sec-butylphenoxy)-2-propanol, also called Cs-7SB (Fig. 4), is used as a solvent modifier in formulations containing calixarene and crown ether ligands for cesium and/or strontium extraction from nuclear waste solutions [37]. It is not expected that the reaction of the nitrate radical is with the Cs-7SB aromatic ring ($\leq 10^6 \text{ M}^{-1} \text{ s}^{-1}$ for benzene in Table 1). There are only three methylene groups available for $\cdot\text{H}$ -atom abstraction, suggesting a rate constant of $\sim 2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ in aqueous solution based on the reactivity of the compounds listed in Table 1. Discounting both these unreactive portions of the molecule it might be expected that Cs-7SB could be modeled as an isopropylanisole analog for nitrate radical reactions. No rate constant has been reported for the $\cdot\text{NO}_3$ reaction with isopropylanisole in acetonitrile; however, the measured value for isopropylbenzene is $3.0 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ in this solvent [21]. Based on Equation 7 the equivalent reaction with the isopropyl group for this molecule in acidic water would also have a slow rate constant of $\sim 3.1 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$.

This calculated value for isopropylbenzene is much slower than that measured for anisole itself, which has been determined in acetonitrile as $5.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (average of 3 reported values [18,19,21]), and can be calculated using Equation 7 to be $(4.8 \pm 0.8) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ in acidic water; in very good agreement with the aqueous measured value of $(4.42 \pm 0.27) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ [34]. Thus, it can be assumed that the predominant nitrate radical reaction is due to the electron-donating $-\text{OCH}_3$ moiety in anisole, and correspondingly at the $-\text{OCH}_2-$ bridging group next to the aromatic ring in Cs-7SB. As there are only 2 C-H bonds in this modifier group, we correct our calculated value of $(4.8 \pm 0.8) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ by multiplying by 0.67, to give an overall predicted nitrate radical rate

constant with Cs7SB of $(3.2 \pm 0.6) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. While it is recognized that no consideration of inductive or steric effects has been made in this simple analysis, the predicted value is in very good agreement with the measured value of this rate constant of $2.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ [37].

Also of interest in solvent extraction studies are the effects of metal complexation on the rate constants for reaction of the ligands with the $\cdot\text{NO}_3$ radical. Formation of the metal complex typically involves multiple ligands and sufficient anions, in this case NO_3^- , to create a neutral species that is soluble in the organic phase. It can be seen from Table 1 that the reaction of the $\cdot\text{NO}_3$ radical with the lanthanide complexes of CMPO are an order of magnitude faster than the corresponding reaction with free CMPO in the same diluent. Even accounting for the three CMPO molecules coordinated around each lanthanide ion, this rate constant increase is still much larger than expected; indicating either a change in reaction mechanism, from H-atom abstraction for the free ligand to electron transfer for the complex, or significantly greater stabilization of the radical complex species. Additional experiments on analogous metal-ligand complexes are presently being undertaken.

CONCLUSIONS

New data for the rate constants for $\cdot\text{NO}_3$ radical reactions in *tert*-butanol and aqueous solution were measured and compared to literature values for water and acetonitrile. The trends in reactivity were used to shed light on the reaction mechanisms occurring. For nitrate radical reaction with alcohols, the mechanism probably proceeds by

H[•] atom abstraction, for which the rate increases with the chain length of the alcohol. By comparison, the dodecane rate is slow, indicating that the alcohol -OH group activates the alpha hydrogen atoms assisting H[•]-atom abstraction. Further evidence for this is provided by the especially high rate constants for ethanol, which has only the alpha-position H[•]-atoms available for reaction. The rate of alcohol reactions with the [•]NO₃ radical are fastest in non-polar *tert*-butanol, and decrease with increasing solvent polarity. The aqueous rates are slowest, indicating that the [•]NO₃ radical has higher diffusivity in less polar solvents. For alkenes, the rate increases, probably indicating addition to the double bond. Alkene rate constants are again faster in *tert*-butanol than in water.

Nitrate radical reactions with aromatic compounds did not follow this trend. For all the compounds investigated the rate constants were slightly slower in *tert*-butanol, suggesting that the electron transfer reaction is inhibited by the need to solvate the produced NO₃⁻ anion. The fastest rate constants are found in acetonitrile, due to the ability to both solvate the NO₃⁻ anion and tropylium cation, and increased [•]NO₃ radical mobility in that solvent. Finally, a correlation was shown between acetonitrile and aqueous rate constants that can be used to estimate aqueous rate constants for sparingly soluble species.

ACKNOWLEDGMENTS

The kinetic radiolysis experiments were performed using the LINAC accelerator facility at the Radiation Laboratory, University of Notre Dame, which is supported by the Office of Basic Energy Sciences, U.S. Department of Energy. This project was performed

under the auspices of the USDOE Assistant Secretary for NE, under the FCR&D Radiation Chemistry program; DOE-Idaho Operations Office Contract DE-AC07-05ID14517 and the Nuclear Energy Universities Program DE-NE0008406.

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Table 1. Comparison of $\cdot\text{NO}_3$ reaction rate constants ($\text{M}^{-1} \text{s}^{-1}$) for aqueous, *tert*-butanol, and acetonitrile solution. **Values measured in this study shown in bold.**

SOLUTE	aqueous	<i>tert</i> -butanol	acetonitrile
methanol	$(2.07 \pm 0.15) \times 10^5$ $(5.8 \pm 4.3) \times 10^5$ [9-11,13,15,29]	$(2.37 \pm 0.44) \times 10^6$	$(2.3 \pm 0.3) \times 10^6$ [8,9,19,25]
ethanol	1.4×10^6 [6,9-11,13,15]	$(1.63 \pm 0.05) \times 10^7$	6.7×10^6 [8,9]
1-propanol	$(2.2 \pm 1.5) \times 10^5$ [13,15]	$(1.03 \pm 0.21) \times 10^7$	5.1×10^6 [8]
2-propanol	2.5×10^6 [6]	$(1.50 \pm 0.13) \times 10^7$	
1-butanol	1.9×10^6 [15]	$(1.74 \pm 0.44) \times 10^7$	6.9×10^6 [8]
<i>tert</i> -butanol	$(5.7 \pm 1.3) \times 10^4$ [9,13]		2.3×10^5 [9]
1-pentanol	2.4×10^6 [15]		6.7×10^6 [8]
1-hexanol	3.3×10^6 [15]		6.1×10^6 [8]
1-heptanol	3.6×10^6 [15]		8.0×10^6 [8]
1-octanol	5.8×10^6 [15]	$(4.33 \pm 0.43) \times 10^8$	8.5×10^6 [8]
dodecane		$(6.45 \pm 0.33) \times 10^6$	
1-dodecene		$(3.70 \pm 0.50) \times 10^8$	
1-octene	$(8.34 \pm 1.1) \times 10^6$	$(2.88 \pm 0.17) \times 10^9$	
2-methyl-1-butene	$(2.45 \pm 0.34) \times 10^5$	$(1.81 \pm 0.11) \times 10^9$	
propene-3-ol	$(2.2 \pm 0.2) \times 10^8$ [9]		1.9×10^8 [8]
ethylene glycol	$(5.35 \pm 0.36) \times 10^5$ $(1.2 \pm 0.6) \times 10^6$ [9,29]		6.6×10^6 [9]
acetone	4.4×10^3 [13]		2.4×10^5 [18]
acetaldehyde	4.9×10^5 [18]		2.3×10^7 [18]
benzene	$\leq 1.0 \times 10^6$		1.0×10^6 [18]
toluene	$(1.71 \pm 0.15) \times 10^9$	$(9.51 \pm 1.15) \times 10^8$	1.3×10^8 [19]
<i>o</i> -xylene	$(2.47 \pm 0.15) \times 10^9$	$(1.93 \pm 0.18) \times 10^9$	3.4×10^9 [21]
<i>m</i> -xylene	$(1.30 \pm 0.11) \times 10^9$	$(9.72 \pm 0.51) \times 10^8$	1.7×10^9 [21]

<i>p</i> -xylene	$(1.07 \pm 0.09) \times 10^9$	$(9.19 \pm 1.40) \times 10^8$	5.4×10^9 [21]
anisole	$(3.85 \pm 0.15) \times 10^9$ [34]	$(7.12 \pm 0.93) \times 10^8$	5.1×10^9 [18,19,21]
	3.2×10^9 [10]		
4-methyl-anisole	$(4.92 \pm 0.29) \times 10^9$ [32]		1.3×10^{10} [21]
3-nitrotoluene	$(2.80 \pm 0.19) \times 10^7$		6×10^5 [19]
tributylphosphate	$(4.3 \pm 0.7) \times 10^6$ [35]	$(1.42 \pm 0.09) \times 10^7$	
DMDOHEMA*	$(2.22 \pm 0.10) \times 10^8$	$(4.27 \pm 0.46) \times 10^8$	
CMPO*	$(1.28 \pm 0.13) \times 10^{8*}$	$(3.24 \pm 0.17) \times 10^8$	
Nd(CMPO) ₃ (NO ₃) ₃		$(3.37 \pm 0.05) \times 10^9$	
Eu(CMPO) ₃ (NO ₃) ₃		$(2.52 \pm 0.05) \times 10^9$	

*20% acetone/4.8 M HNO₃