ORIGINAL PAPER

Viscosity and Temperature Effects on the Rate of Oxygen Quenching of Tris-(2,2′-bipyridine)ruthenium(II)

Evan W. Reynolds · J. N. Demas · B. A. DeGraff

Abstract We compare the bimolecular quenching rate constant (k_2) of luminescent tris(2,2′-bipyridine)ruthenium(II) by oxygen in water, ethylene glycol and glycerol as a function of temperature and viscosity to several theoretical models. The Smoluchowski equation with experimentally determined diffusion coefficients produced calculated values that were in the best agreement with experiment. For the less viscous solvent, water, this equation produced a value that was approximately an order of magnitude larger than the experimental value. With an increase in solvent viscosity, the Smoluchowski value approached the experimental value. Using the Smoluchowski equation with calculated diffusion coefficients based on the known radii of the reacting species produced deviations an order of magnitude larger in water and a factor of two or three lower in ethylene glycol and glycerol. If an assumption is made that the radii of both molecules are equal, we have the Stokes Einstein equation, and the only parameters become temperature and viscosity. Using this relationship, the calculated values for water are about a factor of two larger and with ethylene glycol and glycerol about a factor of 6 smaller than experimental data. These results show that bimolecular quenching is a more complex process affected by many parameters such as solvent cage effects in addition to viscosity and temperature.

Keywords Oxygen quenching · Viscosity · Diffusion limited rate constant · Smoluchowski equation · Tris(2,2′-bipyridine)ruthenium(II)

E. W. Reynolds · J. N. Demas (✉)
Department of Chemistry, University of Virginia,
Charlottesville, VA 22904-4319, USA
e-mail: demas@virginia.edu

B. A. DeGraff
Department of Chemistry, James Madison University,
Harrisonburg, VA 22807, USA

Introduction

There is considerable fundamental and experimental interest in the diffusion limited rate constant for chemical and photophysical processes. Oxygen quenching of excited states is of great interest because of the wide use of luminescence quenching in sensor technology and bimolecular quenching in energy conversion. Diffusion limited reactions proceed at a rate that is dependent on solvent conditions such as viscosity (η) and temperature (T) that affect the rate of diffusion of chemical species. The Smoluchowski [1] equation gives the diffusion limited bimolecular rate constant (k_d)

$$k_d = 4000\pi N \sigma_{AB}(D_A + D_B) \tag{1}$$

where σ_{AB} is the encounter distance of the reactants A and B (taken to be the sum of the two radii), D is the diffusion coefficient for the reaction partners, and N is Avogadro's number. Assuming spherical molecules diffusing through a continuous media the Stokes-Einstein [1] equation describes the viscosity and temperature effects on D

$$D = \frac{kT}{6\pi r\eta} \tag{2}$$

where r is the molecular radius of A and B, and k is Boltzmann's constant. Assuming that the two radii are the same, these equations yield [2]

$$D = \frac{8RT}{3000\eta} \tag{3}$$

where the solvent viscosity is in Poise and k_d is in M^{-1}-s^{-1}. Because of the difficulties of directly measuring Ds, this is the most common form of the diffusion equation for estimating diffusion limited rate constants since it only requires the temperature and the viscosity. Equation 3 works well for a variety of systems, but oxygen quenching frequently presents problems. For example, Eftink and Ghiron [3]

examined the viscosity effects on oxygen quenching of short-lived organic dyes in solution, and showed that the rate of quenching due to changing solvent viscosity does not strictly follow this $1/\eta$ proportionality. Further, the value of the predicted rate constants is frequently in poor agreement with experiment, especially for viscous media. The explanation is that the Stokes-Einstein relationship is based on comparable sizes between the donor and the quenchers and on the solvents being continuous. Oxygen, being a very small molecule, appears to negate the size and continuous media assumptions.

The k_d versus T/η plots are frequently not perfectly linear, thus a modified version of Eq. 3 is sometimes used [4].

$$D = \frac{AT}{3000\eta^{\alpha}} \qquad (4)$$

where A and α are adjustable parameters. α has no physical significance. Equation 4 generally fits quenching data well.

In spite of enormous interest in metal complex based oxygen sensors, there has been no quantitative analysis of temperature/viscosity effects on the bimolecular quenching rate constants, k_2s, for these long-lived complexes. Here we study the bimolecular quenching of a luminescent ruthenium(II) complex by oxygen in water, ethylene glycol and glycerol. This permits us to compare various theoretical models and their dependence on temperature and viscosity.

Calculations

Data for the pressure-based bimolecular quenching rate constant as a function of temperature in the three solvents was obtained from Morris et al. [5]. All data compiled for oxygen quenching of the metal complex tris-(2,2′-bipyridine)ruthenium(II) dichloride, [Ru(bpy)$_3$]Cl$_2$. The model used by Morris was used to calculate rate constants as a function of temperature and pressure using the Stern-Volmer equation

$$\frac{\tau_0}{\tau} = 1 + K_{SVP}P_{O_2} \qquad (5a)$$

$$K_{SVP} = k_{2P}\tau \qquad (5b)$$

where k_{2P} (atm^{-1} s^{-1}) is a pseudo bimolecular quenching constant in terms of oxygen pressure. To convert k_{2p} to a true bimolecular rate constant k_2 (M^{-1} sec^{-1}), the oxygen solubility as a function of temperature is required. k_2 was determined using Henry's law

$$k_2 = k_{2P}K_H \qquad (6)$$

where K_H (atm^{-1}M^{-1}) is the Henry's law constant.

The solubility of oxygen in water as a function of temperature is available [6]. However, we could find no temperature dependence of solubility for ethylene glycol and glycerol. A reasonable estimate of the solubility versus temperature was obtained by observing the solubility in the similar solvents ethanol, methanol, isopropanol and n-butanol [7]. The solubility is reasonably linear with temperature and the temperature coefficient is rather insensitive to solvent. The average percent change for these solvents was -0.251 ± 0.016 % over an increase of 1 °C. We assumed that ethylene glycol and glycerol exhibited similar changes in oxygen solubility. Assuming -0.251 %/°C and using the literature values [8] for oxygen solubility at 293 K we estimated the solubility over the required range of temperatures.

D is known for water at room temperature, but for glycerol D is only known for glycerol water mixtures up to 92.5 % glycerol [9]. To estimate D at 100 % glycerol, we made a log(D) versus log(η) plot and extrapolated the last two points to 100 % glycerol. We estimate that the error could be a factor as large as 5 to 10.

Since the complex is roughly spherical, the radii of the Rubpy$_3^{2+}$ (6.5 A) was estimated from the Ru to 5-hydrogen distance plus half the C-H distance in the x-ray structure of the complex. The radii of oxygen was taken as the internuclear bond distance (1.21 A).

Viscosity data as a function of temperature for each of the solvents was available in the literature [10-12]. With this, all the information required for the analysis of viscosity effects on the quenching of luminescent metal complexes was in hand.

Results and Discussion

Table 1 shows the quenching viscosity data. Figure 1 shows plots of the quenching rate versus T/η for the three solvents, which have widely differing viscosities. For comparison we include the rate constants predicted by Eq. 1 using experimental Ds and rs, Eq. 1 using the Stoke-Einstein approximation of Eq. 3, and the empirical Eq. 4. For water and glycerol at room temperature we have D values and estimates of the molecular radii, but we have no D for glycol so that curve is omitted.

There are small deviations from linearity for the k_2 versus T/η plots, and the empirical Eq. 4 fits the data well with αs near 1. However, a linear plot fits the data reasonably well, and there is no physical basis for α's different from 1. We would consider the linear fit adequate for most purposes. The important point is that while all solvents give reasonably linear k_2 versus T/η plots as predicted, theory gives a poor match to the absolute rate constants.

For a quantitative comparison of the different estimates of k_d we calculated k_d at 293 K by all three methods and compared them with the measured k_d. Table 2 summarizes the results.

Table 1 Viscosity and k_2 values for the quenching of [Ru(bpy)$_3$]Cl$_2$ by oxygen versus temperature

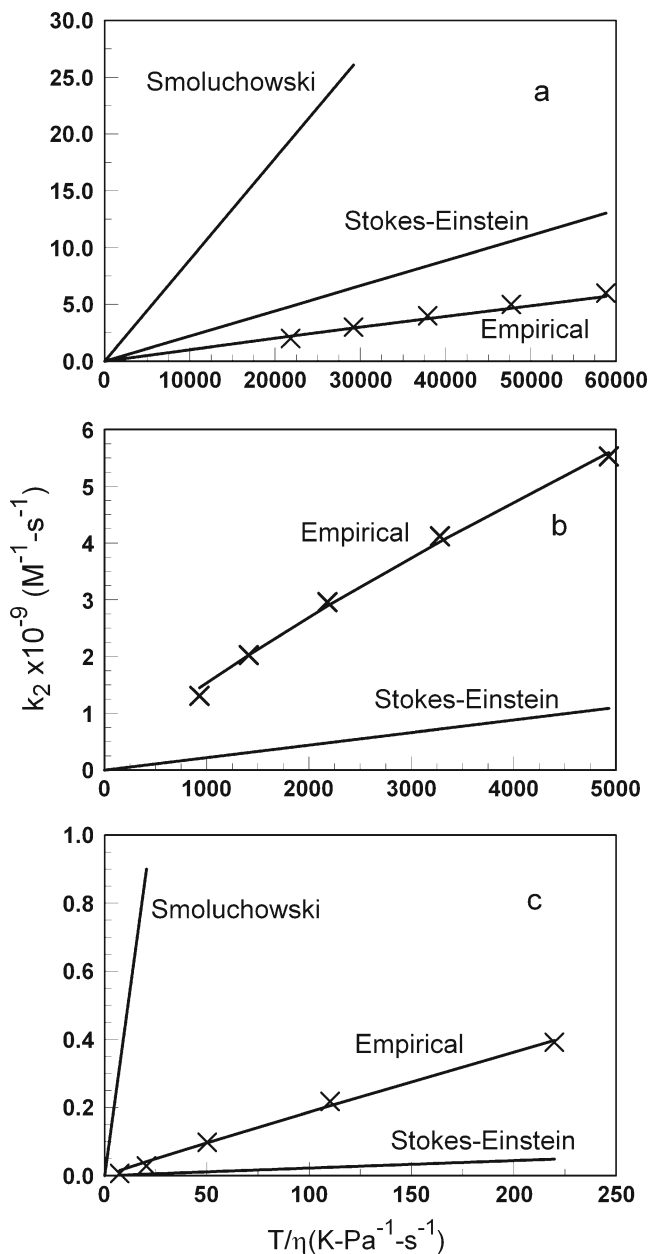| Temperature (K)	Water		Ethylene glycol		Glycerol	
	η (cP)	$k_2 \times 10^{-9}$ (M^{-1}s^{-1})	η (cP)	$k_2 \times 10^{-9}$ (M^{-1}s^{-1})	η (cP)	$k_2 \times 10^{-9}$ (M^{-1}s^{-1})
283	1.300	2.154	30.51	1.306	3878	0.006694
293	1.002	2.978	20.81	2.027	1434	0.0288
303	0.7991	3.858	13.87	2.961	604.4	0.09787
313	0.6557	4.734	9.535	4.122	284.6	0.2175
323	0.5491	5.545	6.554	5.526	147.3	0.3915

Fig. 1 k_2 plotted vs. T/η for the quenching of [Ru(bpy)$_3$]Cl$_2$ by oxygen in the solvents water (**a**), ethylene glycol (**b**), and glycerol (**c**). Xs represents actual data; *solid line* are calculated behavior from Eqs. 1 and 3 as well as best fit from Eq. 4

We consider the Smoluchowski equation with experimentally determined Ds as the best method for generating the true diffusion limited rate constants, although this is rarely possible given the lack of available Ds. For water, the Smoluchowski prediction is roughly an order of magnitude too large. In glycerol, the results are probably within experimental error given the uncertainties of the extrapolation.

Using Eq. 2 for estimating the D of oxygen in water gave good agreement with the experimental D, 1.8×10^{-5} M^{-1}-s^{-1} versus 2.2×10^{-5} M^{-1}-s^{-1}. Consequently, this resulted in a k_d that is much above the experimental value, as is the calculation with known Ds. However, for glycol and glycerol it is a factor of 3 too low. The Stoke-Einstein equation, by ignoring the dissimilarities in radii, is about a factor of 2 lower still for each solvent. It appears that the more viscous the media, the more closely the k_ds approach the measured values.

Even for energetically very favorable processes measured k_2s that are lower than the theoretical limit are not uncommon or hard to explain. If every encounter does not produce a quenching event, the experimental value will be too low. We will return to this later. A k_d below the experimental value requires an alternate explanation. For viscous media quenching is frequently too fast relative to Eq. 1 with Ds calculated from Eq. 2, as we also observe here. The interpretation is that the Smoluchowski equation fails because the assumptions of a spherical molecule in a continuous media for Eq. 2 are incorrect, especially for the small non-spherical oxygen. This is not completely surprising. The increasing viscosity of glycol and glycerol is a consequence of the complex entangled hydrogen bonded network of the polyalcohols. It seems reasonable that small linear oxygen could more easily penetrate these networks than large spherical molecules on which Eq. 2 is based.

Despite the fact that the plots are nearly linear, the predicted values by the relationship of Eq. 3 still vary widely from the actual data. So this model is not very good at predicting the values for the rate of quenching of metal complexes by oxygen based solely on temperature and viscosity. Also interesting is how the predicted values for water are higher than the experimental values, while for the other two solvents the predicted values are lower.
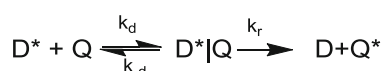
Table 2 Diffusion limited rate constant k_d (M^{-1}·s^{-1}) calculated from different equations compared with experimental values at 293 K

^aBased on a long extrapolation from 92.5 % to 100 % glycerol on a log(D) vs log(η) plot

Solvent	Experimental	Eq. 1 with known Ds	Eq. 1 with D calculated from Eq. 2	Stokes Einstein Eq. 3 assuming equal radii
Water	3.0×10^9	1.5×10^{10}	1.2×10^{10}	6.5×10^9
Ethylene Glycol	2.0×10^9	No available D	5.9×10^8	3.1×10^8
Glycerol	2.9×10^7	1.7×10^{8a}	0.9×10^7	4.5×10^6

The empirical Eq. 4 is just that, empirical. It is useful for predicting trends with known data, but not for predicting diffusion limited rate constants for new systems.

We turn now to a more detailed look at the quenching process and its possible ramifications. The common model for the diffusion controlled reactions, adopted for bimolecular quenching is given below.

$$D^* + Q \underset{k_{-d}}{\overset{k_d}{\rightleftharpoons}} D^*|Q \overset{k_r}{\longrightarrow} D+Q^*$$

where the diffusion limited rate constant k_d represents the encounter rate for formation of the encounter complex D|Q*, k_{-d} is the dissociate rate constant for the encounter pair to reform D* and Q, and k_r is the rate for energy transfer and dissociation of the encounter pair resulting in quenching. The bimolecular quenching constant is then given by

$$k_2 = \frac{k_r k_d}{k_r + k_{-d}} \qquad (7)$$

If $k_r \gg k_{-d}$, the quenching rate is k_d, the upper limit. If $k_{-d} \gg k_r$, then a pseudo equilibrium is established and $k_2 = k_r (k_d/k_{-d})$. The maximum rate is k_d and the minimum zero.

The fact that the observed quenching constant is less than the theoretical limit for low viscosity water and comparable to the theoretical value for more viscous glycol and glycerol can be accounted for on the basis of the above model. In low viscosity water, there is little hindrance to dissociation and k_{-d} can compete effectively with k_r, which produces a quenching constant well below the theoretical limit. For viscous glycol and glycerol, there is a substantial cage trapping of the quencher in the encounter pair; k_r can now compete more effectively, and the quenching constant is nearer the diffusion-controlled limit. Thus, higher viscosity solvents enhance quenching efficiency per encounter over a lower viscosity solvent. This effect has been observed in triplet state quenching [13]. This, of course, doesn't solve the issue of the experimental k_2s being above the calculated k_d, but it does reduce the magnitude of the deviation from Eqs. 1 and 2. Since oxygen is small and non-spherical, larger than theoretical values calculated from Eq. 1 and 2 are not unexpected.

An alternative explanation of the low k_2 in water has to do with spin statistics in the excited state. Oxygen quenching of a pure triplet excited state will result in quenching only 1/9 of the time [14], a factor that closely matches the

discrepancy for Rubpy$_3$$^{2+}$. However, as the excited state of the complex is a strongly mixed spin orbit state containing both singlet and triplet character, it is unclear whether the 1/9 factor would apply. Arguing for it is the fact that analogous Os(II) complexes where spin orbit coupling is much stronger have somewhat higher quenching constants than the Ru(II) complexes but still not at the diffusion controlled limit. On the other hand similar Ir(III) complexes with spin orbit coupling equally as large as osmium show an order of magnitude lower quenching constant than the Ru(II) complexes [15]. Clearly, the quenching process is complex and subject to many factors.

Conclusions

From the data compiled it is shown that the quenching of luminescent transition metal complexes by oxygen is a complex process dependent on more parameters than simply the temperature and viscosity of the solvent. In the absence of known diffusion coefficients for the solvent, the Smoluchowski equation with calculated diffusion coefficients based on the radii of the reacting species seems to give the most reasonable estimates.

Reference

1. Lakowicz, JR (2006) Principles of fluorescence spectroscopy, Third Edition Springer Science+Business Media LL
2. Bowen EJ (1954) Fluorescence quenching in solution and in the vapor state. Trans Faraday Soc 50:97–102
3. Eftink MR, Ghiron CA (1987) Temperature and viscosity dependence of fluorescence quenching by oxygen in model systems. Photochem Photobiol 45(6):745–748
4. Hirayama S, Yasuda H, Scully AD, Okamoto M (1994) Study of the fractional power dependence on solvent viscosity of the rate constant for bimolecular diffusion-influenced quenching reactions between oxygen and the singlet and triplet states of anthracene derivatives. J Phys Chem 98(17):4609–4616
5. Morris KJ, Roach MS, Xu W, Demas JN, DeGraff BA (2007) Luminescence lifetime standards for the nanosecond to

microsecond range and oxygen quenching of Ruthenium(II) complexes. Anal Chem 79:9310–9314

6. Tromans D (2000) Modeling oxygen solubility in water and electrolyte solutions. Ind Eng Chem Res 39:805–812

7. Kretschmer CB, Nowakowska J, Wiebe R (1946) Solubility of oxygen and nitrogen in organic solvents from −25° to 50°. Ind Eng Chem 38(5):506–509

8. Tian H, Chen K (1994) Solvent effect on the triplet lifetime of some rhodamine dyes. Dyes and Pigments 26:167–174

9. Jordan J, Ackerman E, Berger RL (1956) Polarographic diffusion coefficients of oxygen, defined by activity gradients in viscous media. J Am Chem Soc 78:2979–2983

10. Kampmeyer PM (1952) The temperature dependence of viscosity for water and mercury. J Appl Phys 23(1):99–102

11. Chen YM, Pearlstein AJ (1987) Viscosity-temperature correlation for glycerol-water solutions. Ind Eng Chem Res 26 (8):1670–1672

12. Tsierkezos N, Molinou I (1998) Thermodynamic properties of water + ethylene glycol at 283.15, 293.15, 303.15, and 313.15 K. Chem Eng Data 43(6):989–993

13. Gijzeman OLJ, Kaufman F, Porter G (1973) Quenching of aromatic triplet states in solution by nitric oxide and other free radicals. J Chem Soc, Faraday Trans 2: Mol Chem Phys 69(Pt 5):727–737

14. Gijzeman OLJ, Kaufman F, Porter G (1973) Oxygen quenching of aromatic triplet states in solution. J Chem Soc, Faraday Trans 2: Mol Chem Phys 69(Pt 5):708–720

15. Demas JN, Harris EW, McBride RP (1977) Energy transfer from metal complexes to oxygen. J Am Chem Soc 99:3547–3551