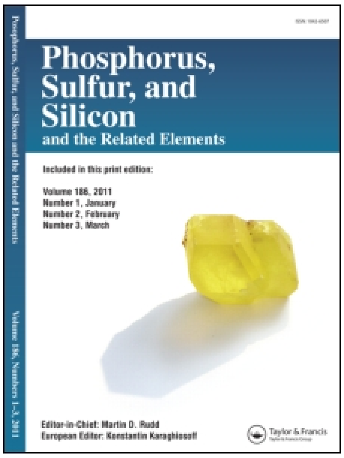
This article was downloaded by:
On: *28 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Fluorescence Quenching of Rhodamine Through Single-Electron Transfer from Trivalent Phosphorus Compounds

Shinro Yasui; Munekazu Tsujimoto; Kenji Itoh; Atsuyoshi Ohno

To cite this Article Yasui, Shinro , Tsujimoto, Munekazu , Itoh, Kenji and Ohno, Atsuyoshi(1999) 'Fluorescence Quenching of Rhodamine Through Single-Electron Transfer from Trivalent Phosphorus Compounds', Phosphorus, Sulfur, and Silicon and the Related Elements, 144: 1, 497 — 500

To link to this Article: DOI: 10.1080/10426509908546290

URL: http://dx.doi.org/10.1080/10426509908546290

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Phosphorus, Sulfur and Silicon, 1999, Vol. 144-146, pp. 497-500
Reprints available directly from the publisher
Photocopying permitted by license only

Fluorescence Quenching of Rhodamine Through Single-Electron Transfer from Trivalent Phosphorus Compounds

SHINRO YASUI[a], MUNEKAZU TSUJIMOTO[a], KENJI ITOH[b] and ATSUYOSHI OHNO[b]

[a]*Tezukayama College, Gakuen-Minami, Nara 631–8585, Japan and* [b]*Institute for Chemical Research, Kyoto University, Uji, Kyoto 611–0011, Japan*

Fluorescence from rhodamine 6G in the photoexcited state (Rh^{+*}) was quenched by single-electron transfer (SET) from various types of trivalent phosphorus compounds Z_3P in aqueous acetonitrile. Dependence of the quenching rate on the oxidation potential of Z_3P suggests that the SET from Z_3P to Rh^{+*} is followed by a rapid reaction of the resulting radical cation $Z_3P^{\bullet +}$ with water in the solvent.

Keywords: trivalent phosphorus compounds; single-electron transfer; fluorescence quenching; rhodamine

INTRODUCTION

Single-electron transfer (SET) is a fundamental process in chemical reactions. Many kinetic studies have been performed on the SET reactions of various types of compounds to find relationship between kinetics and thermodynamics of the SET process. However, SET processes occurring from trivalent phosphorus compounds (Z_3P) have never been investigated kinetically, although Z_3P undergoes SET easily to an electrondeficient compound.[1]

Rhodamine 6G (**Rh**$^+$) is photoexcited to its singlet excited state **Rh**$^{+*}$ upon irradiation at 525 nm, fluorescence from which is quenched by SET from an electron donor. We tried the photoreaction of **Rh**$^+$ with Z_3P and found that SET from various types of Z_3P to **Rh**$^{+*}$ takes place to quench the fluorescence from the latter. The reaction system is convenient to elucidate how the rate of SET from Z_3P is regulated by an electronic and geometric structure of the compound; the rate is evaluated by the quenching rate constant, which can be easily obtained based on the Stern-Volmer analysis. We herein present preliminary results concerning the fluorescence quenching of **Rh**$^{+*}$ by SET from Z_3P, showing the dependence of rate of the SET on the oxidation potential of Z_3P.

RESULTS AND DISCUSSION

Rhodamine 6G (**Rh**$^+$) was photolyzed at 525 nm in the presence or absence of Z_3P in aqueous acetonitrile under argon atmosphere at 20°C. It was found that the fluorescence from **Rh**$^+$ in the photoexcited state (**Rh**$^{+*}$) occurring at 545 nm is quenched by Z_3P, and the Stern-Volmer analysis gave a constant $k_q\tau_0$ for each compound, where k_q is a quenching rate constant and τ_0 is a fluorescence lifetime of **Rh**$^{+*}$ in this solvent. Rhodamine B, a dye structurally very close to **Rh**$^+$ used here, has a fluorescence lifetime of 2.38 ns in methanol.[2] Taking this value also for **Rh**$^{+*}$ in aqueous acetonitrile, we can evaluate k_q values. The logarithm of k_q thus evaluated is plotted against E_p, the oxidation potential of Z_3P determined by cyclic voltammetry,[3] in Figure 1. As E_p decreases, $\log k_q$ increases to reach a plateau; k_q in the plateau region is about 10^{10} $M^{-1}s^{-1}$, which is nearly equal to a diffusion-limited rate constant for SET in solutions.

Most likely, the quenching results from SET from Z_3P to **Rh**$^{+*}$ (Eq.(1)). That is, Z_3P and **Rh**$^{+*}$ form an encounter complex (k_{12}), within which the SET occurs to quench the fluorescence from **Rh**$^{+*}$ (k_{23}), and the radical cation $Z_3P^{\bullet +}$ generated reacts with water in the solvent (k_{30}). The conversion of the resulting phosphoranyl radical $Z_3P^{\bullet}$-OH to $Z_3P{=}O$ is a highly exothermic process (Eq.(2)).[1] In support for this mechanism, when the methanol solution of **Rh**$^+$ and triphenylphosphine Ph_3P in equimolar amounts (5×10^{-3} M) was irradiated with the light of >450 nm, triphenylphosphine oxide $Ph_3P{=}O$ was given as a sole product. Thus, SET from Ph_3P to $\mathbf{Rh^{+*}}$ gives the radical cation $Ph_3P^{\bullet +}$, which reacts with methanol to eventually give the observed product, $Ph_3P{=}O$.

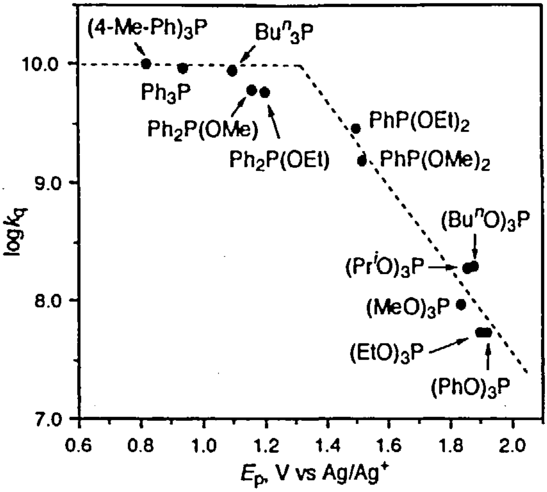


Figure 1. Dependence of $\log k_q$ on E_p of Z_3P.

$$Z_3P + Rh^{+*} \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} [\,Z_3P \cdots Rh^{+*}\,] \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} [\,Z_3P^{\bullet +} \cdots Rh^{\bullet}\,] \xrightarrow[+H_2O\,/\,-H^+]{k_{30}} Z_3P^{\bullet}\text{-}OH + Rh^{\bullet} \qquad (1)$$

$$Z_3P^{\bullet}\text{-}OH \xrightarrow{Rh^{+*} \curvearrowright Rh^{\bullet}} Z_3P^{+}\text{-}OH \xrightarrow{-H^+} Z_3P{=}O \qquad (2)$$

SET reactions taking place via the sequence shown by Eq.(1) gives different kinetic behaviors depending on thermodynamics of each step.[4] Thus, when SET step (k_{23}) is exothermic ($\Delta G_{23} < 0$),

$$k_q = k_{12} \qquad (3)$$

is given, indicating that the quenching rate is diffusion-limited in this case. Meanwhile, when SET step is endothermic ($\Delta G_{23} > 0$) and an irreversible chemical reaction takes place as k_{30} step (*i.e.*, $k_{32} << k_{30}$),

$$k_q = K_{12}k_i\exp(-\alpha\Delta G_{23}/RT) = K_{12}k_i\exp(-\alpha F\Delta E^0/RT)\ (0 < \alpha < 1) \tag{4}$$

is eventually obtained with the aid of the Horiuchi-Polanyi equation. Here, $K_{12} = k_{12}/k_{21}$ and $\exp(-\Delta G_{23}/RT) = K_{23} = k_{23}/k_{32}$, and k_i is the quenching rate constant when $\Delta G_{23} = 0$. Eq.(4) predicts a linear correlation between $\log k_q$ and ΔE^0 with a slope of $-\alpha F/(2.3RT)$ in this case. On the other hand, if k_{30} step represents any mode of reactions resulting in disappearance of the radical pair (not only an irreversible chemical reaction), k_q is expressed by Eq.(5), instead of Eq.(4), when $G_{23} > 0$.[5]

$$k_q = k_{30}K_{12}\exp(-F\Delta E^0/RT). \tag{5}$$

Eq.(5) predicts the slope in the plot of $\log k_q$ vs ΔE^0 to be $-F/(2.3RT)$ (= −17 at 20°C). In fact, many types of electron donors undergo SET whose kinetics follows this prediction.

Figure 1 shows that k_q is diffusion-limited when $E_p(Z_3P) < 1.3$ V vs Ag/Ag^+ in the present reaction. More importantly, when $E_p > 1.3$ V, a linear correlation is seen between $\log k_q$ and E_p^{ox} with the slope of −3.7. Clearly, the observed kinetics follows the predictions by Eqs.(3) and (4) (not the prediction by Eq.(5)), since $\Delta E^0 = E_0(Z_3P) - E_0(\mathbf{Rh}^{+*}) \approx E_p(Z_3P) - E_p(\mathbf{Rh}^{+*})$. That is, k_{30} step in Eq.(1) is highly exothermic, thus providing the condition $k_{32} \ll k_{30}$. In addition, we have determined $E_0(\mathbf{Rh}^{+*}) \approx 1.2$ V vs Ag/Ag^+. Therefore, the point at which the kinetic behavior is changed is quite reasonable.

In conclusion, this study has shown that Z_3P undergoes SET to $\mathbf{Rh}^{+*}$ to quench the fluorescence from the latter; the SET step is followed by a rapid reaction of the resulting radical cation $Ph_3P^{\bullet+}$ with nucleophile in the solvent.

References

[1] a) S. Yasui, *Rev. Heteroatom Chem.*, 12, 145 (1995) and references cited therein; b) S. Yasui, K. Shioji, M. Tsujimoto, and A. Ohno, *Chem. Lett.*, 1995, 783; c) S. Yasui, M. Tsujimoto, K. Shioji, and A. Ohno, *Chem. Ber./Recueil*, 130, 1699 (1997).

[2] K. Itoh, Y. Chiyokawa, M. Nakao, and K. Honda, *J. Am. Chem. Soc.*, 106, 1620 (1984).

[3] S. Yasui, M. Tsujimoto, M. Okamura, and A. Ohno, *Bull. Chem. Soc. Jpn.*, 71, 927 (1998).

[4] G. B. Schuster, *J. Am. Chem. Soc.*, 101, 5851 (1979).

[5] D. Rehm and A. Weller, *Israel J. Chem.*, 8, 259 (1970).