

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>

Chemiluminescent Autoxidation of Phosphonate Carbanions

Jiro Motoyoshiya^a; Yutaka Takaguchi^a; Hiromu Aoyama^a

^a Shinshu University, Japan

Online publication date: 27 October 2010

To cite this Article Motoyoshiya, Jiro , Takaguchi, Yutaka and Aoyama, Hiromu(2002) 'Chemiluminescent Autoxidation of Phosphonate Carbanions', *Phosphorus, Sulfur, and Silicon and the Related Elements*, 177: 8, 1977 — 1979

To link to this Article: DOI: 10.1080/10426500213411

URL: <http://dx.doi.org/10.1080/10426500213411>

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.

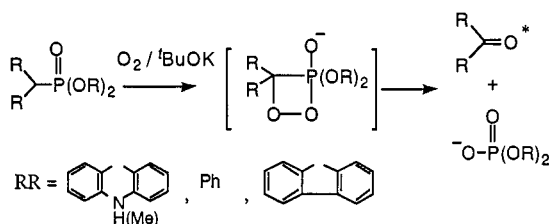
CHEMILUMINESCENT AUTOXIDATION OF PHOSPHONATE CARBANIONS

Jiro Motoyoshiya, Yutaka Takaguchi, and Hiromu Aoyama
 Shinshu University, Japan

(Received July 29, 2001; accepted December 25, 2001)

Chemiluminescence (CL) is a phenomenon where chemically generated excited states release energy as light instead of heat. Previously, we have reported that CL was observed in autoxidation of the suitable phosphonate carbanions, and phospho-1,2-dioxetanes generated by the Wittig type reaction were suggested as the possible high energy species.^{1,2} We now report the detail of this CL system involving the phosphorus chemistry.

In autoxidation of acridanyl phosphonate carbanions, a weak light emission was observed in a dark, which was identified as the fluorescence of the excited acridones. The electronic effect of the phosphonate substituents on the CL quantum yield was observed (Table I); namely, the electronegative substituents and the cyclic structure increased the emission efficiencies probably due to acceleration of phospho-1,2-



SCHEME 1

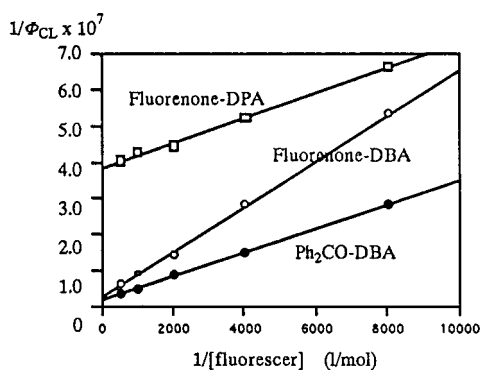
dioxetane formation. The -NH- derivatives provided more efficient CL ($\Phi_{\text{CL}} \sim 10^{-6}$) than the -NMe- derivatives ($\Phi_{\text{CL}} \sim 10^{-7}$). These results support the formation of phospho-1,2-dioxetanes as well as the intramolecular CIEEL (chemically induced electron exchange luminescence) mechanism in this CL. On the other hand, the energy transfer CL

Address correspondence to Jiro Motoyoshiya, Department of Chemistry, Faculty of Textile Science and Technology, Shinshu University, Ueda, Nagano 386-8567, Japan. E-mail: jmotoyo@giptc.shinshu-u.ac.jp

TABLE I Relative Emission Efficiency of Acridanyl Phosphonates (X=Me)

$(\text{RO})_2\text{P}(=\text{O})-$	Relative Φ_{CL}
$(\text{EtO})_2\text{P}(=\text{O})-$	1.0
$(\text{CF}_3\text{CH}_2\text{O})_2\text{P}(=\text{O})-$	15.1
	4.6
	6.6
$(\text{C}_6\text{H}_5\text{O})_2\text{P}(=\text{O})-$	6.5
$(\text{F-C}_6\text{H}_4\text{O})_2\text{P}(=\text{O})-$	5.4

was detected in autoxidation of benzhydryl and fluorenyl phosphonates in the presence of fluorescers such as 9,10-dibromoanthracene (DBA) and 9,10-diphenylanthracene (DPA), in which a bimolecular process in the energy transfer to the fluorescers was established (Figure 1).

**FIGURE 1** Linear relationship in double-reciprocal plot of $1/[\text{fluorescer}]$ vs. $1/\Phi_{\text{CL}}$.

REFERENCES

- [1] J. Motoyoshiya, Y. Isono, S. Hayashi, Y. Kanzaki, and S. Hayashi, *Tetrahedron Lett.*, **32**, 5875 (1994).
- [2] J. Motoyoshiya, S. Tsuboi, K. Kokin, Y. Takaguchi, S. Hayashi, and H. Aoyama, *Heterocyclic Commun.*, **4**, 25 (1998).