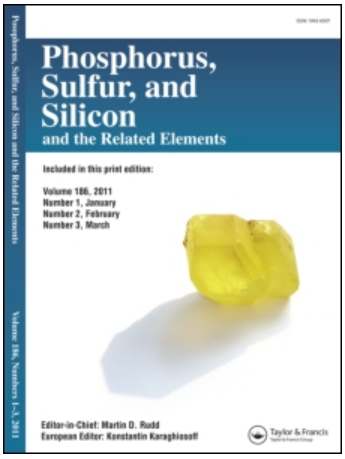

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Chemiluminescent Autoxidation of Phosphonate Carbanions

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CHEMILUMINESCENT AUTOXIDATION OF PHOSPHONATE CARBANIONS

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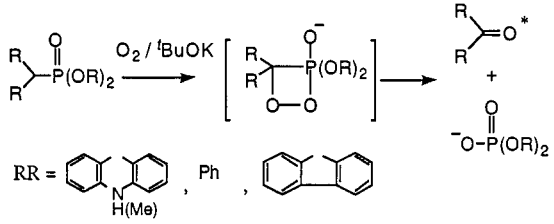
Chemiluminescence (CL) is a phenomenon where chemically generated excited states release energy as light instead of heat. Previously, we have reported that CL was observed in autoxidation of the suitable phosphonate carbanions, and phospha-1,2-dioxetanes generated by the Wittig type reaction were suggested 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 phospha-1,2-



SCHEME 1

dioxetane formation. The -NH- derivatives provided more efficient CL ($\Phi_{CL} \sim 10^{-6}$) than the -NMe- derivatives ($\Phi_{CL} \sim 10^{-7}$). These results support the formation of phospha-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

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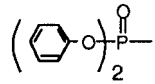
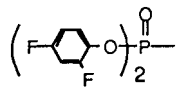
TABLE I Relative Emission Efficiency of Acridanyl Phosphonates (X=Me)

$(RO)_2P$—	Relative Φ_{CL}
$(EtO)_2P$—	1.0
$(CF_3CH_2O)_2P$—	15.1
	4.6
	6.6
	6.5
	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).

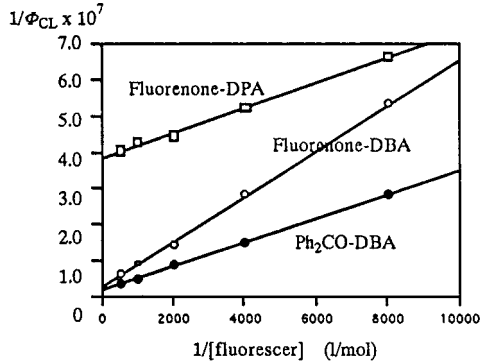


FIGURE 1 Linear relationship in double-reciprocal plot of 1/[fluorescer] vs. $1/\Phi_{CL}$.

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