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Chemiluminescent Oxidation of Phosphonates : Phospha-1,2-dioxetanes as Possible Intermediates

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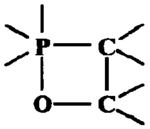
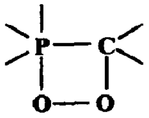
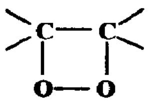
Abstract : Chemiluminescence was observed in autooxidation of the phosphonate carbanions and the related reaction, which gave a strong proof of phospha-1,2-dioxetanes as the intermediates in these reactions.

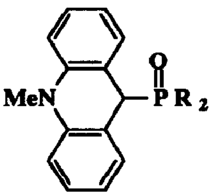
Numbers of experimental and theoretical studies on the mechanism of the Wittig and the related reactions support that the four-membered oxaphosphetanes are the crucial intermediates.[1] Similarly, four-membered cyclic peroxides, phospha-1,2-dioxetanes, were postulated [2] as the most likely common intermediates in autooxidation of phosphonium ylids or phosphonate carbanions. Synthetically this oxidation affords carbonyl compounds.[3] Recently, phospha-1,2-dioxetanes were proposed as the chemiluminescent intermediates in thermal decomposition of 3-phospha-1,2-dioxa-4,5-diazines.[4] As a phospha-1,2-dioxetane should lead to a formation of a carbonyl compound in an excited state as established in thermal decomposition of dioxetanes,[5] observation of chemiluminescence should be a strong proof of the four-membered peroxides. Ando et. al. observed, in fact, the signals in the ^{31}P NMR ascribed to the chemiluminescent phospha-1,2-dioxetanes generated by photooxygenation of the phosphonium ylid as well as by decomposition of the diazine.[6] We report here on chemiluminescent oxygenation of phosphonate carbanions and the related reaction.


oxaphosphetane

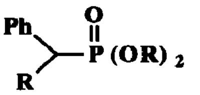

phospha-1,2-dioxetane


dioxetane

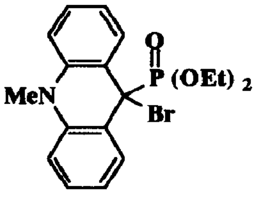
Autooxidation of the phosphorus compounds (**1a-e**) in the presence of excess potassium *tert*-butoxide and oxygen in dimethylformamide (DMF) or tetrahydrofuran (THF) gave pale-blue light emission in the dark, which lasted during several minutes at room temperature. The emission became stronger by heating. The thorough oxygenation of the carbanions from **1a** or **2a** in THF gave *N*-methylacridone or benzophenone in 79% or 69% yield, respectively. Because phosphonate **1a** has no absorption in a visible region, the emitter should be the excited *N*-methylacridone in the light emission of **1a**. Very weak light emission was also observed in the similar reaction of the carbanions derived from **2a** or **2b** in the presence of 9,10-dibromoanthracene or 9,10-diphenylanthracene as the fluorescent additives. The excited states of benzophenone generated from **2a** was shown to be triplet because 9,10-dibromoanthracene was more effective than the other in indirect chemiluminescence.[7]



1a : R = OEt
b : R = OMe
c : R = OPr-*i*
d : R = OCH(Me)CH(Me)O
e : R = Ph



2a : R = Ph
b : R = COOEt



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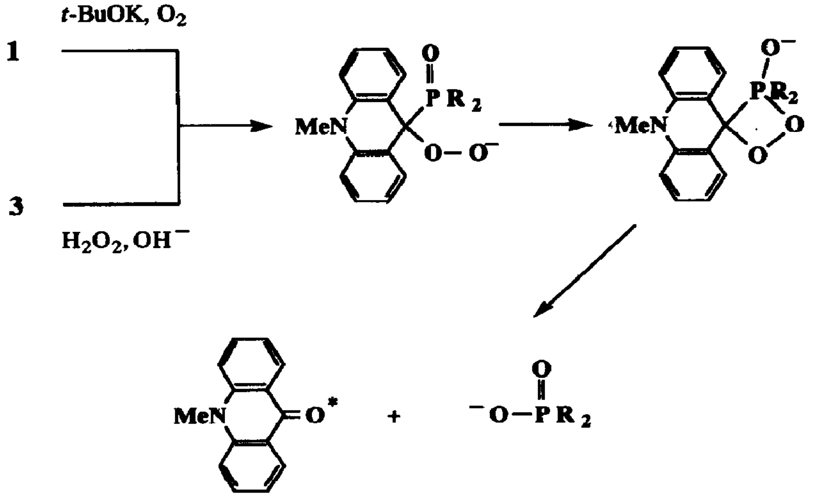
On the other hand, a similar treatment of triethyl phosphonoacetate bearing no radical stabilizing aryl group showed neither reaction progress or chemiluminescence. Addition of radical trapping agents such as sulfur or *p*-benzoquinone quenched the emission of **1** at once. These results suggest that the oxidation goes on through a radical reaction step. As can be seen in oxygenation of *N*-methyl-9-cyanoacridanide anion,[8] the present autooxidation might involve a single electron transfer from the carbanions to oxygen in the formation of carbon-oxygen bond.

Next, we attempted to generate a phospha-1,2-dioxetane by another path. When brominated phosphonate **3**, prepared by the bromination of **1a** with 1,3-dibromo-5,5-dimethylhydantoin in refluxing CCl_4 , was treated with alkaline hydrogen peroxide in THF and H_2O, light emission at 450 nm was observed as expected, which agreed with a fluorescence spectrum of *N*-methylacridone measured in the same solvents. Thus, the emission is due to the fluorescence from *N*-methylacridone excited in the singlet state. This reaction is an ionic process because light emission was not interrupted by the addition of the radical trapping agents. In this reaction *N*-methylacridone was also generated, so that the high energy intermediate should be the phospha-1,2-dioxetane.[9]

The detection of light emission in the reactions described above gave the strong evidence of phospha-1,2-dioxetanes as illustrated in **Scheme 1**.

Further, the comparison of the reaction rates of the autooxidation of phosphonates **1a-d** and phosphine oxide **1e** was made to explore the effect of substituents on the phosphorus atoms by monitoring increase of *N*-methylacridone with a UV-visible spectrum at 40° C. Assuming that the amount of dissolved oxygen is enough

Scheme 1



excess against the reactants (**1a-e** : 4 x 10^{-4} M in DMF, *t*-BuOK: 4 x 10^{-3} M in DMF) at the initial stage, the rates could be conveniently followed under pseudo 1. order reaction conditions. All the rates observed were estimated approximately as 2~7 x 10^{-3} s^{-1}. No remarkable deference in the rates of **1a-d** was found,[10] whereas the substituents on phosphorus atoms affect the rates in the Horner-Wittig reaction due to the nature of the pentacoordinate phosphorus atoms. Larsen et. al. have proposed [11] the oxaphosphetane intermediates in the Horner-Wittig reaction by comparing the rates, where the cyclic phosphonate reacted about 20 times faster than the acyclic ones and the phosphonates did much faster than the phosphine oxides. However, it is impossible to mention the four-membered intermediates from the oxidation rates obtained in the present study.

Although the kinetic study could give no support for the cyclic intermediates, chemiluminescence observed in above reactions gave a strong proof of phospha-1,2-dioxetanes as the intermediates in the oxidation of phosphonate carbanions. The present oxidation containing phosphorus chemistry can provide new examples in the field of chemiluminescence.

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