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Chemiluminescence of the 9,10-anthrasemiquinone radical ion during autooxidation of 9,10-dibromoanthracene in the diphenylmethane—Bu^{t}OK—DMSO system

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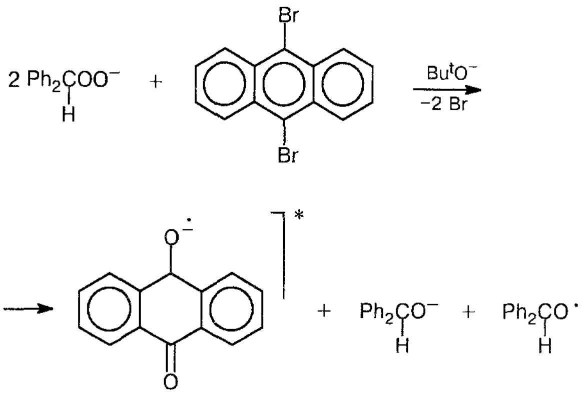
Chemiluminescent (CL) systems in which radicals are the photon emitters are known.[1,2] We found the CL-reaction of the oxidation of 9,10-dibromoanthracene (DBA) in the diphenylmethane (DPM)—Bu^{t}OK—DMSO system, in which the 9,10-anthrasemiquinone radical ion is the photon emitter. DBA is routinely used in CL investigations to obtain the photophysical parameters of the triplet excited state of molecule, *e.g.*, formed in the course of the disproportionation of $RO_2^{\cdot}$ radicals;[3] it is assumed that the activator is not involved in the reaction. We revealed that this is not true in all cases. Oxidation of DPM in DMSO in the presence of Bu^{t}OK is accompanied by CL, and the Ph_2CO^* triplet is an emitter, which is confirmed by the coincidence of the CL spectra and the phosphorescence spectra of the reaction medium and Ph_2CO. Addition of DBA causes an increase in light emission. The CL spectrum contain a component that we assigned to emission of the 9,10-anthrasemiquinone radical ion formed as the result of DBA oxidation in addition to the band of the radiative deactivation of singlet excited DBA. The CL spectrum of the radical ion with the maximum at 580 nm coincides with the photoluminescence spectrum of the reaction mixture excited with λ = 500 nm light. The formation of the radical ion is confirmed by the identity of the absorption spectrum of the reaction mixture with that of the radical ion generated from anthraquinone in a strong basic medium (Bu^{t}OK—DMSO): λ_{max} = 513 and 547 nm. The ESR spectrum of the reaction mixture (g = 2.0049±0.0002) is also identical to that of the radical ion.

The data obtained show that during the oxidation of DBA in the DPM—Bu^{t}OK—DMSO system the 9,10-anthrasemiquinone radical ion in the excited state is formed, whose deactivation causes the long-wave CL component. The role of DPM is to generate peroxyanions from the corresponding carbanions. Apparently, the latter are involved in the oxidation of DBA, which proceeds *via* the formation of an intermediate diperoxide that subsequently decomposes to the radical ion:



In the absence of DPM in the DMSO—Bu^{t}OK system saturated with oxygen, DBA does not form the 9,10-anthrasemiquinone radical ion.

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Reaction of PCl_5 with 1-hydroxy-10-anthrone

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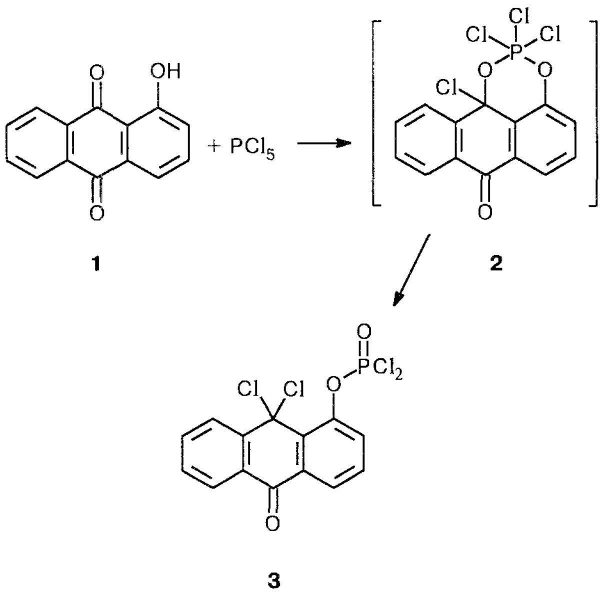
Previously,[1] it has been shown that the interaction between 1-hydroxy-9,10-anthraquinone (**1**) and PCl_5 (Scheme 1) affords 4-dichlorophosphoryloxy-10,10-dichloroanthrone (**3**). It was assumed that the reaction proceeds *via* cyclophosphorane **2** formation, however, the latter was not identified in the reaction mixture.

Scheme 1



We have studied the reaction of 1-hydroxy-10-anthrone (**1a**) with PCl_5 resulting in the products of the chlorination of the carbonyl group in the α-position, like in the case of compound **1**. In contrast to the reaction described previously, chlorination of the C atom in position 9 of the anthrone ring system also takes place. A study of the reaction by ^{31}P NMR and mass spectrometry demonstrated that 1-tetrachlorophosphoryloxy-10-anthrone (**4**) forms at the first stage, and subsequently undergoes intramolecular cyclization with the formation of trichlorocyclophosphorane **5** (Scheme 2).

Then phosphorane **5** either eliminates an HCl molecule and is transformed into cyclophosphorane **6**, or is oxidized by phosphorus pentachloride to form cyclophosphorane **8**. Compounds **6** and **8** subsequently isomerize into the corresponding dichlorophosphoryloxy-9-chloro-(9,10-dichloro)anthracenes (**7** and **9**). One cannot exclude the possibility of the chlorination of phosphoranes **6** and **7** by phosphorus pentachloride to afford compounds **8** and **9**, respectively. The combination of these data allows us to propose the reaction scheme (see Scheme 2).

PCl_5 (5.43 g, 0.013 mol) was added with stirring to a solution of 1-hydroxy-10-anthrone (2.74 g, 0.013 mol) in anhydrous benzene (50 mL) at *ca.* 20 °C. Five min after the beginning of the reaction a signal at −47 ppm corresponding to 1-tetrachlorophosphoryloxy-10-anthrone (**4**) was observed in the ^{31}P NMR spectrum of the reaction mixture. The mixture was heated at reflux for 1 h until HCl evolution ceased. In the ^{31}P NMR spectrum of the reaction mixture signals at 219.32 (PCl_3), 2.1 (1-dichlorophosphoryloxy-9-chloro-(9,10-dichloro)anthracene (**7** and **9**)), and −26.19 (compounds **5**, **6**, and **8** of the cyclophosphorane type) were observed. In the mass spectrum of the reaction mixture peaks at m/z 378 $[M]^+$, 380 $[M+2]^+$, 382 $[M+4]^+$, 384 $[M+6]^+$ (compounds **8** and **9**);

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