The Reaction of 9,10-Phenanthrenesemiquinonato-bis(triphenylphosphine)copper(I) with Organic Peroxides

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Catecholate, *o*-semiquinone, and *o*-quinone complexes of transition metals have received considerable attention in recent years [1]. They serve as good models for studying intramolecular electron transport [2], and in the case of iron and copper compounds, studies of mimicking catechol 1,2-dioxygenase may be achieved [3–5]. Recently we prepared a series of triphenylphosphine copper(I) semiquinone complexes [6]. In these compounds the oxidation state one of the copper is stabilized by the phosphine ligands and the unpaired electron resides mainly on the semiquinone ligand [7]. Since copper(I) is known to react with peroxides and a great number of decompositions of disubstituted peroxides are catalyzed by them, it seemed to us of interest to study their reactions [8]. Since compound **1** possesses two redox active centers, e.g. the copper(I) and the semiquinone ligand, it was to be decided whether a radical–radical pairing reaction on the semiquinone ligand or an oxidative addition on the copper(I) would take place with the oxygen-centered radicals of the peroxides.

Results and Discussion

Three types of peroxides were used in this study. Di-t-butyl peroxide (**2**) and di-triphenylmethyl peroxide (**3**) supplying alkoxo radicals, bis[1-morpholino-cyclopentyl-(1)]peroxide (**4**), which delivers an alkoxo radical with the ability to act as an O,N-bidentate ligand, and dibenzoylperoxide (**5**) giving the radical $PhCO_2\cdot$.

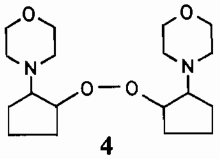
Di-t-butyl peroxide (**2**) and di-triphenylmethyl peroxide (**3**) did not react with 9,10-phenanthrenesemiquinonatobis(triphenylphosphine)copper(I) (**1**) in dichloromethane at room temperature for several days. No reaction could be observed even with bis[1-morpholino-cyclopentyl-(1)] peroxide (**4**) under similar conditions. Dibenzoyl peroxide (**5**) however, reacted relatively fast with the copper(I) semiquinone complex **1** in dichloromethane under ambient conditions.

$\underline{t}$–Bu–O–O–$\underline{t}$–Bu

2

$Ph_3C-O-O-CPh_3$

3



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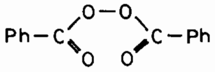
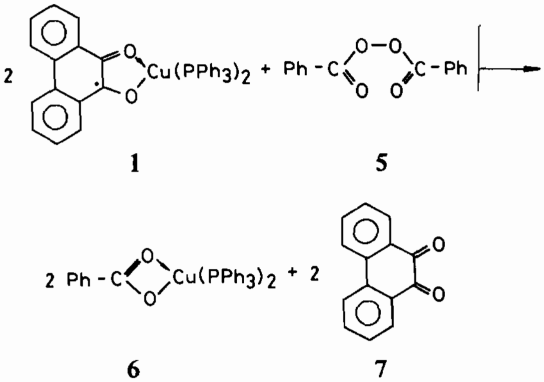


5

The purple colour of the solution of **1** turned to dark brown during the reaction. On working up the reaction mixture 9,10-phenanthrenequinone (**7**) and benzoatobis(triphenylphosphine)copper(I) (**6**) could be isolated in yields over 60%. The reaction proceeds according to eqn. (1).



(1)

The oxidation state of copper will be maintained due to the stabilizing effect of the phosphine ligand [9]. Dibenzoyl peroxide does not oxidize copper(I) to copper(II) in **1**. Only a few copper(II) complexes with phosphine ligands are known from the literature [10]. On the other hand no pairing reaction between the semiquinone ligand and $PhCO_2\cdot$ takes place. There is however a single electron transfer from the semiquinone ligand to the radical $PhCO_2\cdot$ resulting in 9,10-phenanthrenequinone (**7**) coordinated to the copper and the benzoate anion. The latter then displaces the quinone **1** in a fast reaction to give benzoatobis(triphenylphosphine)copper(I) (**6**). It is surprising that the peroxides **2–4** do not react with the semiquinone copper(I) complex **1**. In the copper(I) benzoate complex **6** the carboxylate ligand acts as a bidentate ligand and its geometry can be ascertained [11] as a distorted tetrahedral, as found recently for substituted benzoatobis(triphenylphosphine)copper(I) complexes.

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Experimental

The 9,10-phenanthrenesemiquinonatobis(triphenylphosphine)copper(I) was prepared as described previously [6]. Triphenylmethyl peroxide [12], bis[1-morpholino-cyclopentyl-(1)] peroxide [13] were prepared according to published methods. Dibenzoyl peroxide and di-t-butyl peroxide (Fluka) were used as purchased.

The Reaction of 9,10-Phenanthrenesemiquinonato-bis(triphenylphosphine)copper(I) (1) with Dibenzoyl Peroxide

9,10-Phenanthrenesemiquinonatobis(triphenylphosphine)copper(I) (1.20 g, 1.5 mmol), dibenzoyl peroxide (181.5 mg, 0.75 mmol), 15 ml dichloromethane were weighed in a Schlenck-tube under argon at −79 °C. The mixture was allowed to warm up to room temperature and kept here overnight. The colour of the solution turned to dark brown. Half of the solvent was stripped in vacuum and 25 ml ether was layered over the remaining solution. On standing yellow and red crystals separated out. They were filtered, washed with ether and dried in vacuum to give a mixture of 9,10-phenanthrenequinone (7) and benzoatobis(triphenylphosphine)copper(I) (**6**) 1.15 g. The yellow crystals of 7 showed melting point (m.p.) 208–212 °C. Literature m.p. 206–207.5 °C [14]; IR (Nujol): ν(CO) 1674 cm^{-1}. Lit. ν(CO) 1674 cm^{-1} [15]. They were separated from **6** by washing the mixture with CH_3CN until the washing liquid became colourless to give red crystals of **6** (0.711 g, 67%). m.p. 164–166 °C. *Anal.*: Calc. for $C_{43}H_{35}O_2P_2Cu$ (709.20): C, 72.8; H, 5.0. Found: C, 72.7; H, 5.0%. IR (Nujol): $\nu(CO_2)$ 1534 and 1394 cm^{-1}. The CH_3CN washing solution was stripped in vacuum to give 7 (0.20 g, 64%).

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