ISSN 0036-0244, Russian Journal of Physical Chemistry A, 2013, Vol. 87, No. 3, pp. 393–396. © Pleiades Publishing, Ltd., 2013.
Original Russian Text © L.S. Shul'pina, Yu.N. Kozlov, T.V. Strelkova, G.B. Shul'pin, 2013, published in Zhurnal Fizicheskoi Khimii, 2013, Vol. 87, No. 3, pp. 414–417.

CHEMICAL KINETICS AND CATALYSIS

Kinetics and Mechanism of Benzene Oxidation by Peroxymonosulfate Catalyzed with a Binuclear Manganese(IV) Complex in the Presence of Oxalic Acid

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Received February 21, 2012

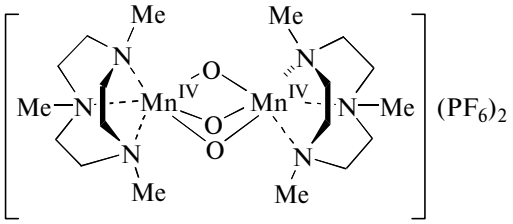
Abstract—It is established that Oxone (peroxymonosulfate, $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$) oxidizes benzene to *p*-quinone very efficiently and selectively in a homogeneous solution in aqueous acetonitrile in the presence of a catalyst, i.e., dimeric manganese(IV) complex $[LMn(O)_3MnL](PF_6)_2$ where L is 1,4,7-trimethyl-1,4,7-triazacyclononane, and a cocatalyst, i.e., oxalic acid. The dependences of the maximum rate of quinone accumulation on the initial concentrations of reagents are studied. It is proposed that benzene is oxidized by the manganyl particle containing the Mn(V)=O fragment that forms upon the reaction of the reduced form of the starting dimeric manganese complex with Oxone.

Keywords: benzene oxidation, kinetics and mechanism, catalysis, manganyl particle, Oxone.

DOI: 10.1134/S003602441303028X

INTRODUCTION

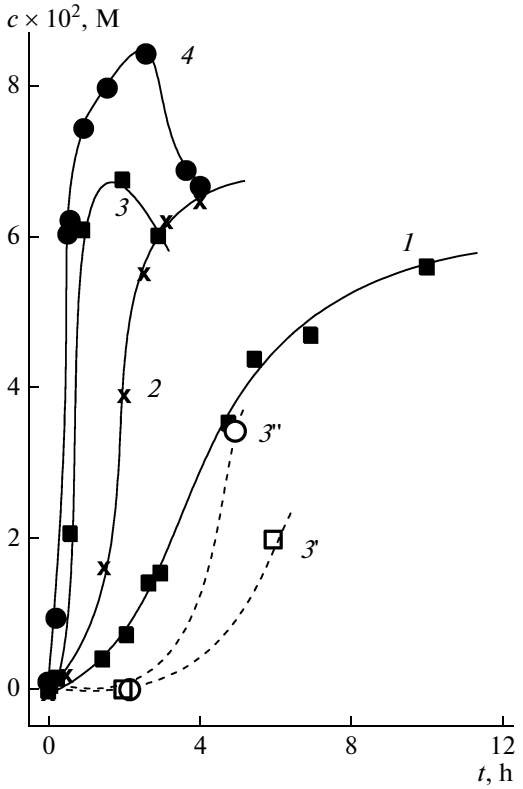
The oxidation of benzene to phenol and quinone (as well as other arenes to phenols and quinones), which is of great importance from a practical point of view, can be performed selectively via reactions with peroxy compounds catalyzed using transition metal complexes [1–5]. We found earlier that binuclear manganese(IV) complex with the macrocyclic nitrogen-containing ligand 1,4,7-trimethyl-1,4,7-triazacyclononane (L) $[LMn(O)_3MnL](PF_6)_2$ (compound **1**) in the presence of an organic acid such as oxalic acid (compound **2**) catalyzes the efficient oxidation of saturated hydrocarbons, olefins, sulfides, and secondary alcohols by hydrogen peroxide in acetonitrile at room temperature [6–13]. Unfortunately, this catalytic system using hydrogen peroxide as the oxidizing agent allowed no high-yield oxidation of aromatic compounds. In this work, we studied the possibility of using Oxone (peroxymonosulfate, $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$) instead of hydrogen peroxide to oxidize benzene. This oxidizing agent was found to transform benzene to *p*-quinone efficiently. Our study of the process allowed us propose the following mechanism for it:



(1)

EXPERIMENTAL

Our experiments were performed in air in thermostated glass vessels at 50°C. The volume of the reaction solution was 5 mL. The substrate (benzene), catalyst **1**, and cocatalyst **2** were added as definite volumes of the starting compound (benzene) or preprepared starting solutions of **1** and **2** in acetonitrile. The reaction was initiated after the addition of solid Oxone, which dissolves quickly in our chosen solvent. (Note: Mixing peroxy compounds with organic substances, especially at elevated temperatures, can result in an explosion!) The solvent was aqueous acetonitrile. (Oxone is insoluble in dry acetonitrile.) For NMR control of the reaction, D_2O was used (MeCN : D_2O ratio, 2 : 1 (v/v). Samples (0.3 mL) of the reaction solution were taken at intervals and definite amounts of a solution of the internal standard (1,4,-dinitroben-



Accumulation of *p*-quinone upon oxidation of benzene (initial concentration, 0.1 M) with Oxone (initial concentration, 0.032 M) catalyzed by complex **1** in the presence of oxalic acid (0.05 M) at different concentrations of **1**: 0.5×10^{-5} (*1*), 1.0×10^{-5} (*2*), 1.0×10^{-4} (*3*), and 2.0×10^{-4} (*4*); *3'* is the experiment of curve *3*, but performed in the absence of oxalic acid; *3"* is the experiment of curve *3*, but acetic acid (0.1 M) was used instead of oxalic acid. The maximum initial reaction rate W_0 was determined from the slope of the tangent to this kinetic curve at the point of the maximum rate.

zene) in acetone were added immediately after cooling to room temperature. All salts, including the unreacted Oxone, were precipitated; as was shown in special experiments, the concentration of the product in the sample remained unchanged over time. The concentration of *p*-quinone was determined by ^{1}H NMR spectroscopy (Bruker AV-300, 300 MHz).

RESULTS AND DISCUSSION

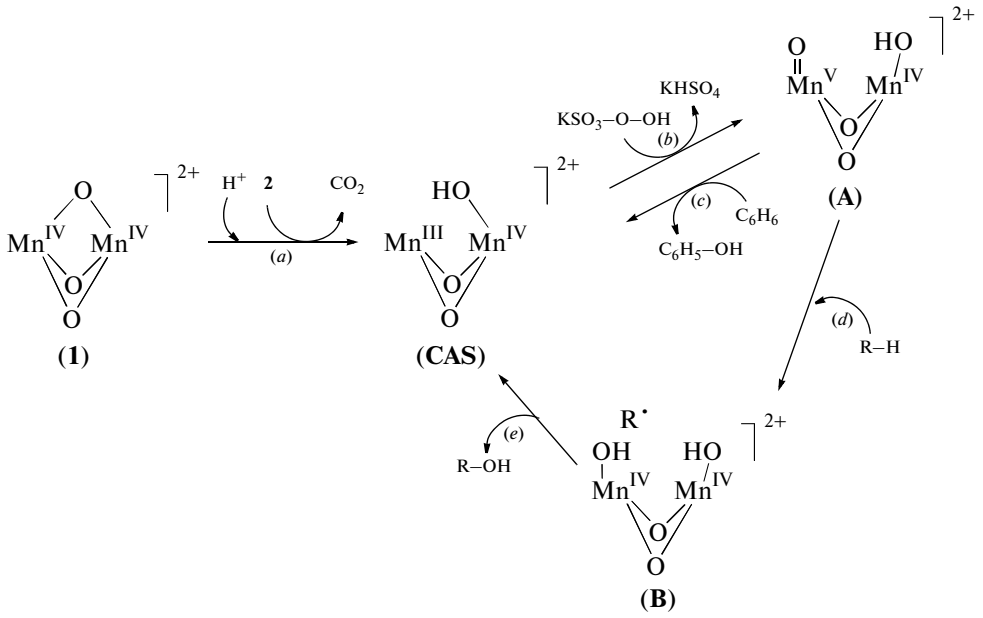
We found that the catalyst **1**–oxalic acid (**2**)–Oxone (**3**) system oxidizes benzene to quinone efficiently in a homogeneous solution of aqueous acetonitrile. The highest yield of quinone under our experimental conditions was 0.25 mol/mol of Oxone. The turnover number per catalyst **1** reached 1150. The figure shows examples of the kinetic time curves of quinone formation at different concentrations of catalyst **1**. As can be seen, the reaction proceeds with self-excited acceleration, the reaction delay period diminishing as the initial concentration of the catalyst increases. This period can be reduced considerably via the addition of hydroquinone. We showed in special experiments that hydroquinone is also oxidized rapidly to quinone using the described system.

Phenol (0.03 M) transforms almost quantitatively to quinone under the action of catalyst **1** (3.0×10^{-5} M), oxalic acid (0.05 M), and Oxone (0.032 M). In our experiment, the yield of quinone was 0.027 M and, in addition, catechol was obtained in small amounts (0.003 M). Such high selectivity of oxidation of phenol to *p*-benzoquinone, which is atypical of hydroxyl radicals, was observed earlier upon the oxidation of phenol with xenon difluoride in aqueous solutions [14]. According to [14], phenol transformation is in this case induced by xenon monoxide (XeO) formed upon the hydrolysis of xenon difluoride.

Our preliminary kinetic data show that the maximum oxidation rate of phenol in the narrow range of variation in reagent concentration is proportional to the concentrations of the substrate, catalyst **1**, and Oxone; this corresponds to the concept of the complex formation between oxalic acid and catalyst **1**.

To obtain additional data allowing conclusions on the nature of the oxidizing particle in the investigated system, we also studied oxidation of saturated hydrocarbons by the catalyst **1**–oxalic acid–Oxone system. It was found that the selectivity parameters (regioselectivity, bonding selectivity, and stereoselectivity) in the oxidation of *n*-heptane, methycyclohexane, and *cis*- and *trans*-1,2-dimethylcyclohexanes was considerably higher than those found for systems that oxidize by involving hydroxyl radicals (e.g., systems based on vanadium complexes [15–18]). In addition, these parameters are close to those obtained for the oxidation with the catalyst **1**–oxalic acid–hydrogen peroxide system [6–13]. It should be noted that there are differences in the behavior of systems containing Oxone or hydrogen peroxide. For example, the chromatography of the reaction products before and after reduction with triphenylphosphine (we developed this procedure in [7, 8, 10, 19, 20]) show that the oxidation of cyclohexane with Oxone yields only slight amounts of cyclohexylhydroperoxide, while alkylhydroperoxide is the main intermediate product in the reaction with hydrogen peroxide at the initial moment [6–13].

The features found for oxidation of benzene with Oxone allow us to propose the mechanism shown in Scheme 1. In the first step (*a*), the catalyst **1** precursor transforms to catalytically active species (CAS), i.e., partially reduced dimeric Mn(III)Mn(IV) derivatives. Complexes of this type were suggested and recorded as intermediates in catalytic reactions, and some of them were isolated and characterized [21–23]. The reduction of one of the Mn(IV) ions to Mn(III) proceeds during the induction period under the action of oxalic acid, the reductive properties of which are known. Indeed, upon replacement of oxalic acid for acetic



Scheme 1.

acid possessing no reductive properties, the induction period increases drastically (curve *3*" in figure). Virtually the same induction period was noted for the reaction in the absence of cocatalyst (**2**) (curve *3*' in figure). In the case of reactions depicted by curves *3*' and *3*", a very slow reduction of one of the Mn(IV) ions of the dimeric complex appears to occur under the action of hydrogen peroxide formed upon hydrolysis of Oxone during the induction period. We showed in [6–13] that hydrogen peroxide can reduce Mn(IV) to Mn(III). In contrast to hydrogen peroxide, Oxone itself has no reductive properties. The formation of a catalytically active complex containing Mn(III) is also possible due to the slow disproportionation of the Mn(IV) ions in the initial dimeric Mn(IV)–Mn(IV) complex to the Mn(III)–Mn(V) complex.

CAS reacts with Oxone at step (*b*) to form the binuclear complex $[Mn(V)=OMn(IV)–OH]^{2+}$ (**A**). Compounds containing the Mn(V)=O and Mn(IV)=O fragments are well known [24–27]. Their reactivities are probably similar to that of xenon monoxide. High-valent manganese oxo derivative **A** reacts with benzene (step *c*) to from phenol [28], which is further oxidized to hydroquinone or quinone. Particle **A** can react also with alkane R–H by abstracting the hydrogen atom (step *d*) to form radical R$^{\bullet}$ (structure **B**). This radical in turn abstracts the hydroxyl ligand [29–31] from one of the Mn(IV) ions to form alcohol R–OH (step *e*).

CONCLUSIONS

The difference between the primary products of alkane oxidation by hydrogen peroxide and Oxone is likely due to different reactivities of the dimeric manganese oxoperoxide complex formed in the case of hydrogen peroxide and the dimeric manganese oxohydroxide complex formed in the case of Oxone (complex **A** in the scheme).

ACKNOWLEDGMENTS

This work was financially supported by the Russian Foundation for Basic Research, project nos. 06-03-32344-a and 12-03-00084-a.

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