Standard thermochemical characteristics of combustion and formation of 3,5-di-*tert*-butyl-*o*-benzoquinone and 3,6-di-*tert*-butyl-*o*-benzoquinone at T = 298.15 K

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ABSTRACT

Optimal conditions for investigations of thermodynamic properties have been determined experimentally by the method of combustion calorimetry for compounds of the *o*-benzoquinone series. In the present work, the energies of combustion in oxygen were measured at T = 298.15 K by static bomb combustion calorimetry for 3,5-di-*tert*-butyl-*o*-benzoquinone and 3,6-di-*tert*-butyl-*o*-benzoquinone. The experimental values have been used to calculate the standard ($p°$ = 0.1 MPa) molar enthalpy of combustion $\Delta_c H_m^o$ and formation $\Delta_f H_m^o$ for the examined compounds in the crystalline phase.

1. Introduction

In recent decades, the area of research concerned with the study of metal complexes based on redox-active ligands, in particular, sterically hindered *o*-benzoquinones, has been attracting more attention of researchers in the field of coordination chemistry [1–8]. The unique feature of *o*-quinone structures to be stabilized in three redox forms provides the basis for the complexes mentioned above. This property greatly expands the chemistry of transition [1–3] as well as non-transition [9,10] elements.

For example, the semiquinone complexes of transition metals are a very interesting object for studies of various intermolecular electronic and magnetic interactions due to the presence of an interconnected metal ion of variable valence and a ligand capable to reversibly change their redox state [1–3]. These systems are becoming increasingly important because they are the base for the construction of molecular magnets and other molecular devices [11,12]. Paramagnetic ligands have great potential as spin labels and provide an opportunity to study the structure and dynamics of the coordination sphere by EPR spectroscopy [13]. Furthermore, the study of transition metal complexes with ligands

of this kind has led to the discovery of the phenomenon of redox isomerism as well as photo- and thermomechanical effects [4,5].

The combination "redox-active ligand – non-transition element" allows simulation of reactivity of transition metals for non-transition elements [14–18]. The oxidative addition and reductive elimination reactions become possible for such compounds. Thus, it is possible to use the compounds of main group elements in catalysis [16]. Metal complexes based on *o*-benzoquinones may also be involved in a controlled polymerization process [19–21].

The compounds 3,5-di-*tert*-butyl-*o*-benzoquinone (3,5-DTBQ) and 3,6-di-*tert*-butyl-*o*-benzoquinone (3,6-DTBQ) studied in the current work are *o*-quinones, which are most frequently used for synthesis of coordination compounds with the aim of obtaining metal complexes having different important properties [1–3,9,10].

To optimize and find effective ways for the synthesis of substituted quinones and metal complexes based on them it is necessary to know their thermodynamic properties which are the key values and fundamental data.

It should be noted that the thermodynamic data for most compounds of the above class that show promise are scarce [22–24]. However, the experimental and computation thermodynamic values for *o*-, *m*-, and *p*-benzoquinone, and results on determination of enthalpies of formation of 3,5-di-*tert*-butyl-*o*-

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benzoquinone in the crystalline and gaseous phases were obtained earlier [25].

In this regard, the aim of the present research includes experimental determination of combustion energies of 3,5-di-*tert*-butyl-*o*-benzoquinone and 3,6-di-*tert*-butyl-*o*-benzoquinone in an isothermal calorimeter and calculation of standard thermochemical characteristics of their combustion and formation in the crystalline phase at $T = 298.15$ K.

2. Experimental

2.1. Samples

The compounds were prepared according to the procedures published earlier [26,27]. Both compounds were purified by repeated recrystallization from hexane and then dried under vacuum. The benzoquinones under study were characterized by X-ray analysis earlier [28,29]. To guarantee the purity of the samples, elemental analysis was performed, *viz.* Anal. elemental analysis method. The following results were obtained: calculated for 3,5-di-*tert*-butyl-*o*-benzoquinone and 3,6-di-*tert*-butyl-*o*-benzoquinone: C, 0.7636: H, 0. 0909; found for 3,5-di-*tert*-butyl-*o*-benzoquinone: C, 0.7661; H, 0.0921; found for 3,6-di-*tert*-butyl-*o*-benzoquinone: C, 0.7659; H, 0.0915. The masses of the samples were measured with accuracy to within 0.5×10^{-4} kg. The ^{1}H NMR spectrum yielded the following: for 3,5-di-*tert*-butyl-*o*-benzoquinone (CDCl$_3$), δ, 10^{-6} 1.21 *s* (9H, t-Bu), 1.25 *s* (9H, t-Bu), 6.20 *d* (1H, $J = 2.3$ Hz, C=CH), 6.92 *d* (1H, $J = 2.3$ Hz, C=CH); ^{1}H NMR spectrum for 3,6-di-*tert*-butyl-*o*-benzoquinone (CDCl$_3$), δ, 10^{-6}: 1.21 *s* (18H, t-Bu), 6,77 (2H, C=CH). The mass spectra (EIMS) of compounds were recorded on a mass spectrometer Polaris Q/Trace GC Ultra (Ion Trap analyser), 70 eV, ion source temperature 250 °C, the sample temperature (50 to 450) °C; EI-MS: *m*/z (3,5-DTBQ) = 220.21 (100%) [M$^+$], 221.28 (26.4%), 222.30 (4.8%); *m*/z (3,6-DTBQ) = 220.19 (100%) [M$^+$], 221.23 (20.0%), 222.24 (3.1%). The thermogravimetric analysis of compounds was done using the thermal microbalance TG209F1, Germany, Netzsch Gerätebau. The TG-analysis was carried over

the range from 300 K to 680 K in the argon atmosphere (figure 1). The thermal microbalance TG209F1 allows fixing the mass change in ±0.1 µg. The mean heating rate was 5 K · min^{-1}. The measuring technique of the TG-analysis was standard, according to Netzsch Software Proteus. The information for the studied *o*-benzoquinones is listed in table 1.

According to DSC (DSC204F1, Germany, Netzsch Gerätebau), the mole fraction of the main substances in 3,5-DTBQ and 3,6-DTBQ samples were: 0.996 and 0.994, respectively. The DSC curves for tested compounds are shown in figures 2 and 3. The temperatures and enthalpies of fusion of the crystalline compounds were derived from the DSC experiments and are presented in table 2, where the uncertainties are the standard deviations of the mean of three independent measurements. Also, the temperature and enthalpy of melting determined with DSC were reported by Fattahi *et al.* [25]. It should be noted that the corresponding values obtained in present work are in a good agreement with results of reference [25].

2.2. Apparatus

The energies of combustion of the compounds examined were measured in a modified isothermal combustion calorimeter B-08-MA with a static bomb. The design of the calorimeter was improved at the Research Institute of Chemistry of the Nizhny Novgorod State University. The improvements that resulted in a substantial increase in the measurement accuracy were described earlier [30,31].

The calibration of the calorimeter was performed by 10 combustion experiments of K-1 benzoic acid provided by the D.I. Mendeleev All-Russian Research Institute of Metrology with a certified energy of combustion, under bomb conditions, of $-(26454.4 \pm 2.2)$ J · g^{-1} (the uncertainty for combustion energy of benzoic acid correspond to expanded uncertainty of the mean (0.95 level of confidence). From ten calibration experiments, the energy equivalent (ε_{calor}) of the calorimeter was determined
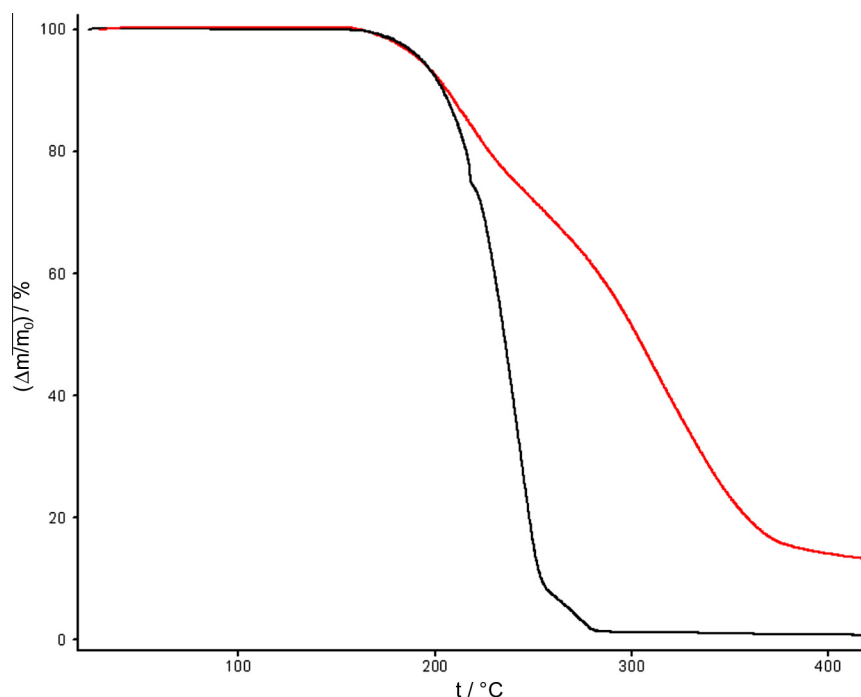

FIGURE 1. TG-curves for 3,5-di-*tert*-butyl-*o*-benzoquinone (red line) and 3,6-di-*tert*-butyl-*o*-benzoquinone (black line). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)