# Reactions of Cr, Mo, W, and Mn carbonyls with 3,6-di-*tert*-butyl-*o*-quinone under the action of elastic wave pulses

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Solid-state reactions of Cr, Mo, W, and Mn carbonyls with 3,6-di-*tert*-butyl-*o*-benzoquinone (Q) proceeding in molded powder-like mixtures (carbonyl—Q) treated with pulses of elastic waves were studied. The products of the reactions of Q with $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ are paramagnetic semiquinone complexes of Cr, Mo, and W. The formation of two semiquinone complexes with one or two manganese atoms was detected in the reaction of $Mn_2(CO)_{10}$ with Q.

**Key words:** solid-state reactions, carbonyls, quinones, elastic wave.

It has been shown previously[1] that the action of elastic waves on powder-like mixtures of organic compounds initiates chemical reactions involving electron and hydrogen transfer. This was convincingly demonstrated for different redox reactions of mixtures of $PbO_2$ with sterically hindered phenols (the corresponding phenoxyl radicals are formed); silicon di-*tert*-butylpyrocatechate with 3,6-di-*tert*-butyl-*o*-quinone (the corresponding silicon-containing biradicals are formed); and 3,6-di-*tert*-butylpyrocatechol with 3,6-di-*tert*-butyl-*o*-quinone, which give radical pairs consisting of 3,6-di-*tert*-butyl-2-hydroxyphenoxyl radicals.[1] Metal-containing mono-, bi-, and triradicals were synthesized by elastic wave action on metal (Zn, Cd, Al, Ga, In, Tl, Sn, Pb, Bi)—3,6-di-*tert*-butyl-*o*-quinone compositions, and it was shown that the degree of conversion of quinone to metal-containing compounds correlates with the redox potentials of the metals used and their ions.[2] Evidently, the study of redox processes that occur when a solid phase is treated with elastic wave is of scientific and practical interest.

We attempted to perform chemical reactions between W, Mo, Cr, and Mn carbonyls and 3,6-di-*tert*-butyl-*o*-quinone (Q) in the solid phase. Similar reactions of carbonyls of some of these metals and Q have previously been performed in a toluene solution only with photoirradiation.[3,4] The purpose of this work was to show that under the action of elastic waves chemical reactions proceed *via* new channels, because the nature and stability of paramagnetic species depend strongly on the conditions of the chemical reaction.

## Experimental

Experiments on the action of elastic wave (EW) pulses were carried out on the installation presented schematically in Fig. 1. An EW pulse appeared during uniaxial compression of a polypropylene (PP) plate subjected to high pressure (a rheologic explosion took place) and was introduced into a

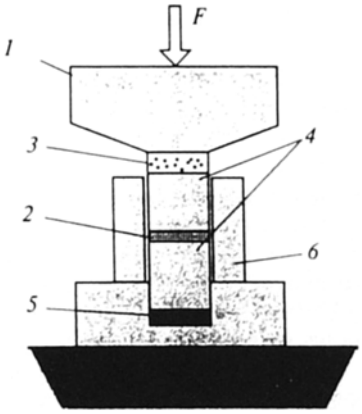

**Fig. 1.** Scheme of the device for pulse mechanical action: *1*, Bridgeman's anvil, *2*, sample, *3*, PP plate, *4*, waveguides, *5*, piezodetector, and *6*, holder.

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Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 11, pp. 2780—2784, November, 1996.

sample (a pellet of a metal carbonyl—Q mixture) through a steel waveguide. A steel holder prevented dispersion of the pellet substance. The pressure of the rheologic explosion ($P_{rh}$) detected by a piezodetector could be varied within wide limits: from 4 to 15 kbar depending on the width of the PP plate. ESR spectra were recorded on a Varian-E12-A spectrometer in the 3-cm range.

## Results and Discussion

The action of EW on a mixture of $Cr(CO)_6$ : Q = 1 : 1 (by weight) results in the appearance of a singlet ESR signal with a linewidth of $\Delta H$ = 1.5 mT and g = 1.9730.

Powder-like mixtures of $Mo(CO)_6$ (or $W(CO)_6$) : Q = 1 : 1 subjected to EW also gave singlet lines with $\Delta H$ = 1.2 mT and $\Delta H$ = 2.1 mT, at g = 2.0046 and g = 2.0036 ($g_{\perp}$ = 2.0124, $g_{\parallel}$ = 1.9992), respectively.

An additional signal with $\Delta H$ = 1.7 mT and g = 2.0025 was detected when a powder-like mixture of $Mn_2(CO)_{10}$ : Q = 1 : 1 underwent EW action ($P_{rh}$ = 4—5 kbar). The intensity of this broad signal decreased as the EW power increased to $P_{rh}$ = 9—10 kbar, and a six-component signal corresponding to HFC with the nucleus of one manganese atom appeared against the background of the broad signal. This is most likely associated with the fact that when the wave action is great the metal-metal bond in the binuclear manganese complex decomposes to form the $^{\cdot}Mn(CO)_5$ radical, which reacts with Q.

It has been established that all the paramagnetic centers to which the new singlet ESR signals are assigned appear at different threshold energies of EW action. The dependences of the relative yields of these particles ($G_{rel}$) on $P_{rh}$, which well illustrate this situation, are presented in Fig. 2. It can be seen that the maximum yields of radical products in different systems appear at different threshold pressures $P_{cr}$. For example, for chromium complexes, $P_{cr}$ = 4.0 kbar, and for molybdenum, tungsten, and manganese complexes, $P_{cr}$ = 4.6, 6.5, and 4.8 kbar, respectively. The energies that are introduced into the sample can be estimated from the formula $E = VP_{ew}^2/2M$, where $V$ is the volume of the steel waveguide between the PP plate and the sample; $M$ is Young's modulus of steel; and $P_{ew} = 0.4P_{cr}$.[2] Knowing the $E$ value and determining the number of paramagnetic complexes in a dry weighted sample $N$, one can estimate the mechanochemical yields (the number of paramagnetic species per 100 eV of energy introduced by EW) by the formula $G = (N/E) \cdot 100$. For chromium, molybdenum, tungsten, and manganese complexes, these values are equal to 0.72, 0.34, 0.09, and 0.29, respectively, for $P_{ew} = 0.4P_{cr}$ (the $P_{cr}$ are given above). It can be seen that the mechanochemical yields of the complexes obtained are fairly low, and in the series of chromium, molybdenum, and tungsten carbonyls they decrease as the number of the period in which the metal is found increases.

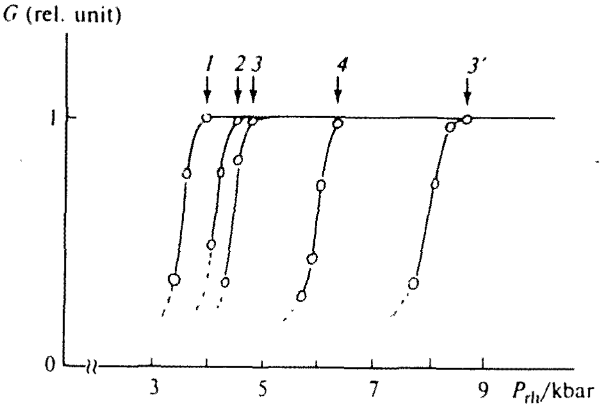


**Fig. 2.** Dependences of relative yields of paramagnetic products $G$ on the $P_{rh}$ value in mixtures: *1*, $Cr(CO)_6$ : Q = 1 : 1; *2*, $Mo(CO)_6$ : Q = 1 : 1; *3* and *3′*, $Mn_2(CO)_{10}$ : Q = 1 : 1 (*3*, for radical **4**; *3′*, for radical **7**); and *4*, $W(CO)_6$ : Q = 1 : 1.

Since it is impossible to resolve all the newly detected signals assigned to species that appear as a result of EW action, because of the strong exchange interaction in the solid phase, a solvent (toluene) was added to the ESR-tubes with the powders of the samples obtained. When the powder-like mixtures were dissolved in toluene, the ESR spectra of the solid phase contained signals with resolved HFS at the positions of the singlet signals. The ESR signal obtained after the $Cr(CO)_6$ : Q mixture was dissolved in toluene is presented in Fig. 3, *a*. This signal is similar to that described in Ref. 4 and belongs to the cation of the chromium tris-*o*-semiquinone complex. An unpaired electron interacts with six equivalent protons of three 3,6-di-*tert*-butyl-*o*-semiquinone ligands ($a_H$ = 0.085 mT) and the magnetic isotope $^{53}Cr$ ($a_{Cr}$ = 2.55 mT), g = 1.9690. The result obtained indicates that the following reaction occurs in the solid phase affected by elastic wave action in our experiments:

$$3\,Q + Cr(CO)_6 \xrightarrow[-6\,CO]{} [CrQ_3]^{\cdot +} A^- .$$

**1**

The structure of the radical cations (**1**) formed is considered in Ref. 1. Under our conditions, the $A^-$ anion is most likely $OH^-$.

According to the ESR spectrum (Fig. 3, *b*), when EW-treated powders of $Mo(CO)_6$ : Q = 1 : 1 are dissolved in toluene, species of two types, whose magnetic-resonance parameters differ insignificantly (for one of these species, g = 2.0035, $a_{H_1}$ = 0.55 mT, $a_{H_2}$ = 0.2 mT, $a_{Mo}$ = 0.15 mT; for the other species, g = 2.0032, $a_{H_1}$ = 0.56 mT, $a_{H_2}$ = 0.22 mT, $a_{Mo}$ = 0.15 mT), are formed. The hyperfine structure observed in the ESR spectra of these species attests to HFC of an unpaired electron with two nonequivalent protons of the *ortho*-semiquinone ligand and the magnetic isotope $^{95,97}Mo$. The ESR spectra presented in Fig. 3, *b* differ from the spectrum of the radical obtained in the photochemical

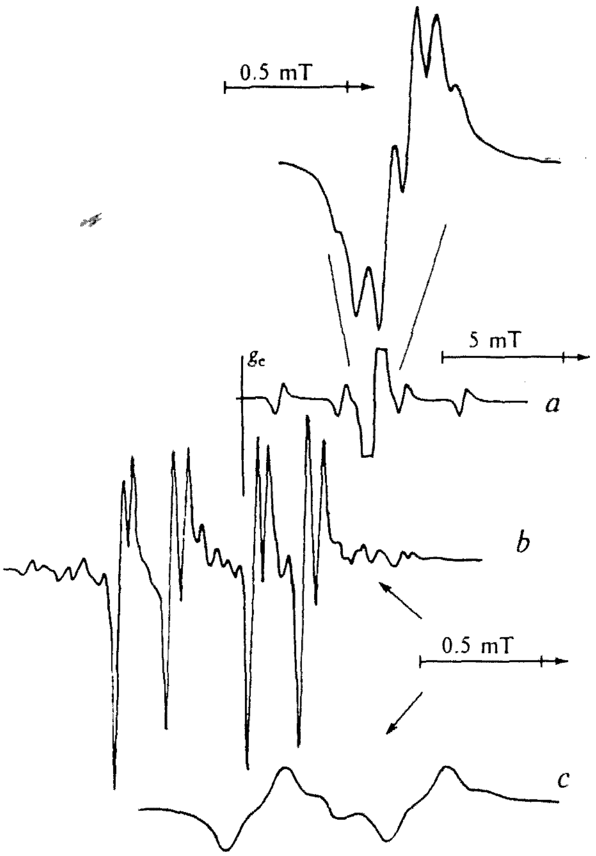
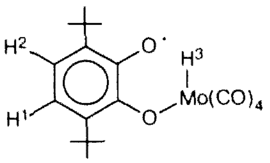


**Fig. 3.** ESR spectra of toluene solutions of powder mixtures treated with EW pulses: *a*, $Cr(CO)_6 : Q = 1 : 1$; *b*, $Mo(CO)_6 : Q = 1 : 1$; and *c*, $W(CO)_6 : Q = 1 : 1$.

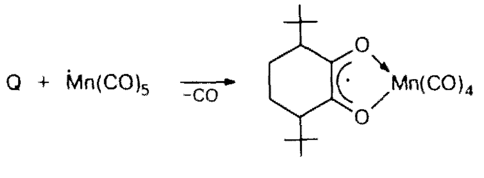
reaction,[3] which was detected in toluene at −60 °C ($a_{H1} = 0.38$ mT, $a_{H2} = 0.30$ mT, $a_{H3} = 0.016$ mT, and $a_{Mo} = 0.1937$ mT). The structure of compound **2** was assigned to the latter.



**2**

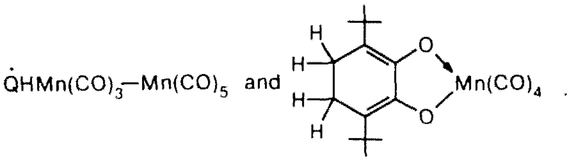
A comparison of the data of Ref. 3 with the results presented above makes it possible to conclude that the structures of the radicals are similar in both cases. The difference is apparently in the number of CO groups in the radicals obtained in our experiments and their possible replacement by other ligands (for example, due to the effect of traces of water in analytically pure toluene, which was used without special purification). In our case, HFC with the nucleus of the hydrogen atom linked to the molybdenum atom is probably observed, apparently because the corresponding HFC constant is small and the width of the line is somewhat greater. According to the spectrum (Fig. 3, *c*), the mechanochemical reaction between Q and $W(CO)_6$ probably results also in the formation of a phenoxyl type radical with g = 2.00, $a_{H1} = 0.65$ mT, and $a_{H2} = 0.13$ mT, whose structure resembles that of radical **2**.

The sharpest differences between the structures of paramagnetic species obtained by EW action and previously described particles generated under the conditions of liquid-phase photolysis were observed for the $Mn_2(CO)_{10}$—Q system. In fact, UV irradiation generates the $^{\cdot}Mn(CO)_5$ radical, which adds to *o*-quinone to give manganese-containing *ortho*-semiquinone complexes (**3**).



**3**

When the $Q—Mn_2(CO)_{10}$ system undergoes EW action, two types of species appear depending on the power of this action:



Thus, the signal presented in Fig. 4, *a* appears in the ESR spectra of the reaction products (after their dissolution in toluene) when the EW action is $P_{rh} = 4.8$ kbar. It probably corresponds to the interaction of an unpaired electron with two equivalent protons of the *ortho*-semiquinone ligand and two nonequivalent nuclei of $^{55}Mn$ ($a_H = 0.325$ mT, $a_{Mn1} = 0.5$ mT, $a_{Mn2} = 0.225$ mT). This spectrum can be assigned to the paramagnetic complex (**4**) formed in the reaction of the $^{\cdot}QH$ radical with $Mn_2(CO)_{10}$.

$$\dot{Q}H + Mn_2(CO)_{10} \longrightarrow \dot{Q}HMn(CO)_3{-}Mn(CO)_5$$

**4**

In fact, an insignificant amount of $QH_2$ always forms in the synthesis of Q, and the reaction[1] $Q + QH_2 \rightarrow 2\ ^{\cdot}QH$ occurs during mechanical action. In addition, the participation of the semiquinone $^{\cdot}QH$ radical in the reaction with $Mn_2(CO)_{10}$ also confirms the addition of $QH_2$ to the solid-phase system before the EW action, because this increases the yield of radical **4**.

Since only one example is known of the detection of splitting at the hydride hydrogen atom in a molybdenum-containing radical,[3] it can be assumed that weak interaction is very characteristic of hydride hydrogen atoms

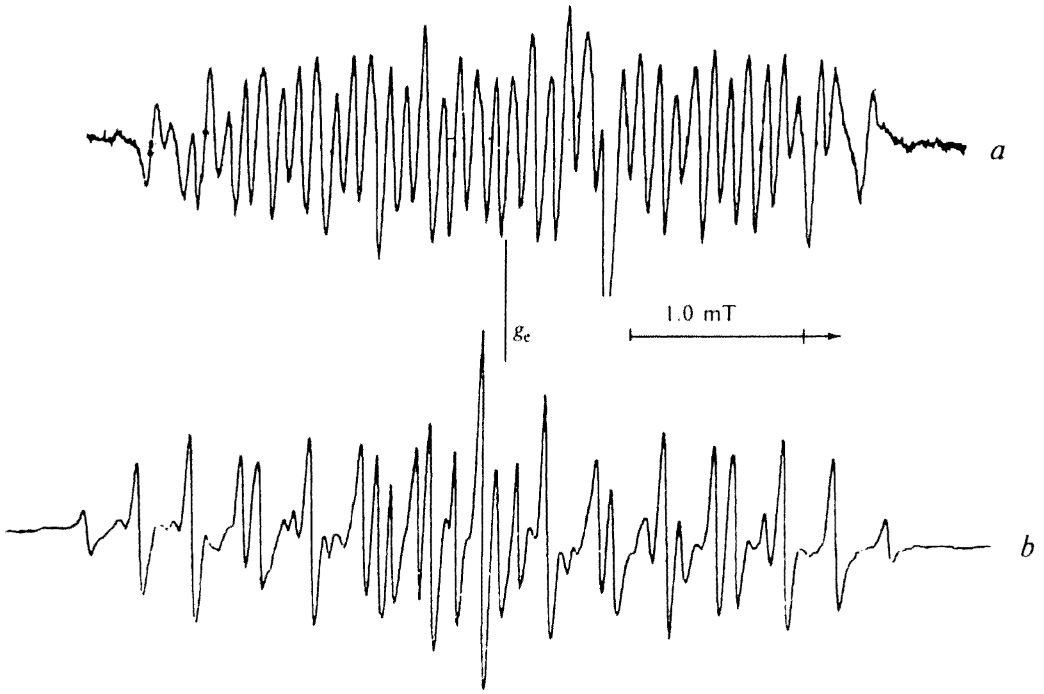
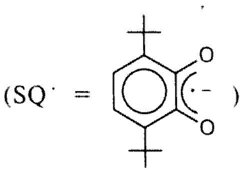
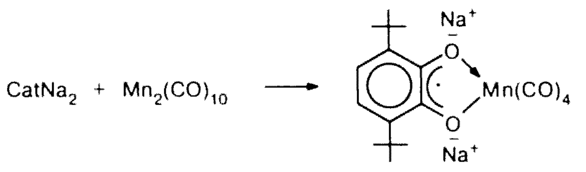


**Fig. 4.** ESR spectra of toluene solutions of a powdered $Mn_2(CO)_{10}$ : Q = 1 : 1 mixture treated with EW pulses at $P_{rh}$ = 4.8 (*a*) and 10 kbar (*b*).

in complexes with semiquinones. In fact, the reaction of SQ˙Tl and $Mn_2(CO)_{10}$ under photolysis conditions when the reaction resulted in the addition of two ˙$Mn(CO)_5$ radicals to a thallium ion has been described.[5] Small splitting (0.08 mT) from two manganese atoms was observed in the ESR spectrum along with a high HFC constant on the Tl nucleus (6 mT), and the proton constant $a_H$ = 0.33 mT, which is typical of SQ-complexes. The value of the constant $a_{Mn}$ = 0.5 mT attests to the coordination of the corresponding manganese atom with two oxygen atoms of SQ. When a similar reaction of $Mn_2(CO)_{10}$ with the dianion of the $CatNa_2$ salt occurs in THF or in a THF—toluene (1 : 1) mixture, the spectrum is characterized by the constants $a_{Mn}$ = 0.40 mT and $a_H$ = 0.33 mT (triplet of protons of the ring). We assigned this spectrum to the radical dianion complex (**5**).

(SQ˙ =  )



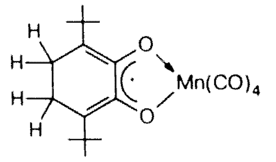
**5**

In addition, an ESR signal identical to that in the spectrum of complex **4** is observed simultaneously. It can be assumed that the reaction of SQ˙Na with $Mn_2(CO)_{10}$ occurs, resulting in the formation of radical **6**:

$$\dot{\mathrm{S}}\mathrm{QNa} + \mathrm{Mn_2(CO)_{10}} \longrightarrow \mathrm{NaS\dot{Q}Mn(CO)_3Mn(CO)_5}$$

**6**

The spectra of radicals **5** and **6** are identical, apparently due to the absence of HFC on the hydroxyl proton and the $Na^+$ cation in complexes **5** and **6**, respectively, which allows us to conclude that these fragements lie outside the sphere of the SQ-ligand. The ESR signal presented in Fig. 4, *b* is observed after the action of more powerful EW ($P_{rh}$ ≥ 9—10 kbar) on the reaction mixture (after dissolution in toluene). An unusual characteristic of this spectrum is that each line of the sextet from the manganese nucleus ($a_{Mn}$ = 0.6 mT) is split into five lines with a binomial distribution of intensities and with a splitting value of 0.325 mT. This splitting value is typical of SQ˙. Therefore, the formation of a bis-ligand complex can be excluded, as was observed for chromium complexes,[4] because in that case the splitting value would be halved. It can be assumed that the aromatic ring is hydrogenated and complex **7** forms.



**7**

(Alkyl groups in which the C—H bond are cleaved by EW action can be a source of hydrogen atoms.[1])

Proposed structure **7** agrees with the data of Ref. 6, in which the paramagnetic manganese-containing complexes formed in the photolysis of $Mn_2(CO)_{10}$ in the presence of cyclic α-diketones were studied in detail.

It should be emphasized that radicals **4** and **7** described above, which are products of mechanochemical reactions, form in fairly low yields, *i.e.*, the degree of the chemical transformation is small. Therefore, when these systems (after powders of the EW-treated mixtures are dissolved in toluene) are UV-irradiated, the known $SQ^{\cdot}Mn(CO)_4$ species begin to appear, and their concentration is considerably higher than that of the radical products of the mechanochemical reactions.

Thus, the greatest structural difference between the radicals obtained by EW action and radicals obtained by other methods was observed in the case of the reaction of Q with $Mn_2(CO)_{10}$. In this reaction, radical **5** was detected, and $Mn_2(CO)_{10}$ acted as a diamagnetic reagent, reacting with the $^{\cdot}QH$ radical similarly to $Mo(CO)_6$.[3] All radical reactions of $Mn_2(CO)_{10}$ studied before were accompanied by cleavage of the Mn—Mn bond.

The experimental results presented show that EW action makes it possible for chemical reactions to take place *via* new and unusual channels, and the yields of these reactions depend on the nature of the metal and its position in the periodic system.

This work was financially supported by the Russian Foundation for Basic Research (Projects Nos. 96-03-33619 and 96-03-32093a).

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*Received May 31, 1996*