

## Mechanism of formation of *o*-semiquinone metal complexes under mechanical pulse action on metal oxide—quinone—pyrocatechol systems

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The possibility of the mechanochemical synthesis of metal-containing mono-, bi-, and triradicals under mechanical pulse action on mixtures of metal oxides (CuO, ZnO, CdO, PbO, Al<sub>2</sub>O<sub>3</sub>, Ga<sub>2</sub>O<sub>3</sub>, Sb<sub>2</sub>O<sub>3</sub>, Bi<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, GeO<sub>2</sub>, ZrO<sub>2</sub>, or SnO<sub>2</sub>) with quinone and pyrocatechol was examined. The reaction products are formed both on the surface of metal oxides and as individual solid phases. The mechanism of chemical processes that occur under the action of a single elastic wave pulse is proposed.

**Key words:** elastic wave pulse; ESR spectroscopy; metal oxides; solid-state reactions.

Previously,<sup>1</sup> it has been demonstrated that the solid-state mechanochemical synthesis of metal-containing mono-, bi-, and triradicals can be performed under the action of elastic wave pulses (EWP) on mixtures of metals and sterically hindered phenols. Under these conditions, the reaction proceeds readily on the "fresh" surface to give a product, which then forms exchange metal—quinone clusters.

In this work, we studied the mechanism of solid-state chemical reactions induced by the mechanical pulse using metal oxide—quinone—pyrocatechol mixtures as examples.

### Experimental

Mixtures of powdered metal oxides M<sub>x</sub>O<sub>y</sub> (ZnO, CdO, PbO, CuO, Al<sub>2</sub>O<sub>3</sub>, Ga<sub>2</sub>O<sub>3</sub>, Sb<sub>2</sub>O<sub>3</sub>, Bi<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, GeO<sub>2</sub>, ZrO<sub>2</sub>, or SnO<sub>2</sub>), 3,6-di-*tert*-butyl-*o*-quinone (Q), and 3,6-di-*tert*-butylpyrocatechol (QH<sub>2</sub>) taken in weight ratios M<sub>x</sub>O<sub>y</sub> : Q : QH<sub>2</sub> = 40 : 1 : 1 (system I), M<sub>x</sub>O<sub>y</sub> : QH<sub>2</sub> = 20 : 1 (system II), or M<sub>x</sub>O<sub>y</sub> : Q = 20 : 1 (system III) were carefully stirred with a glass stick in an agate mortar, pressed into 0.1-mm pellets, placed between steel wave guides of a unit (Fig. 1), and

subjected simultaneously to high pressure (180±10 kN cm<sup>-2</sup>) and EWP. Elastic wave pulses were generated by rheologic explosion of polypropylene (PP) plates (see Fig. 1). In all experiments, the geometric parameters of PP plates remained constant (the diameter was 15 mm and the height was 1.5 mm), which allowed us to rather closely reproduce the characteristics of EWP that acted on the sample under study. The Fourier analysis of the frequency parameters of EWP, which were recorded with the use of a piezodetector (see Fig. 1) attached to an S9-8 storage oscillograph and a PC computer, demonstrated that the fundamental frequency components of EWP are in the range of 100–900 kHz. The chemical reactions were initiated in the above-mentioned solid-phase systems only under the simultaneous action of static pressure and EWP.

The lower limits of the yields of the mechanochemical reactions under the EW action<sup>1</sup> were estimated by the following equation:

$$G = N/E, \quad (1)$$

where *N* is the number of newly formed paramagnetic particles in the sample (determined by ESR) and *E* is the energy introduced by EW. Its value was determined according to the following formula:

$$E = V p_c^2 / 2 E_{qu}, \quad (2)$$

<sup>†</sup> Deceased.

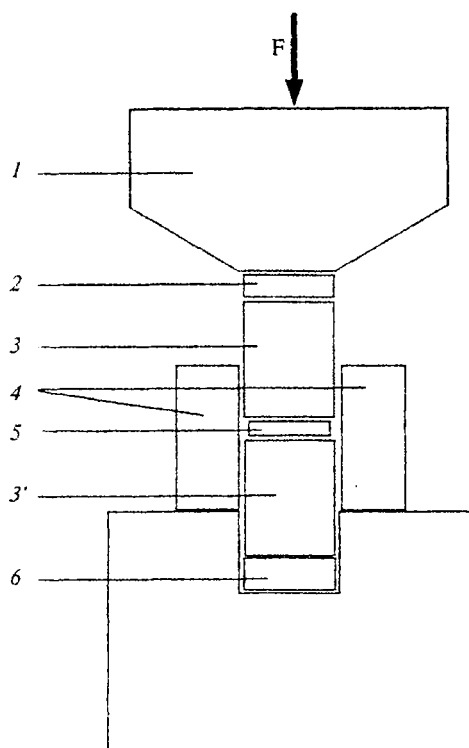


Fig. 1. Scheme of a unit for the EWP action: 1, Bridgeman's anvil; 2, polypropylene plate; 3 and 3', steel wave guides; 4, holder; 5, sample; 6, piezodetector.

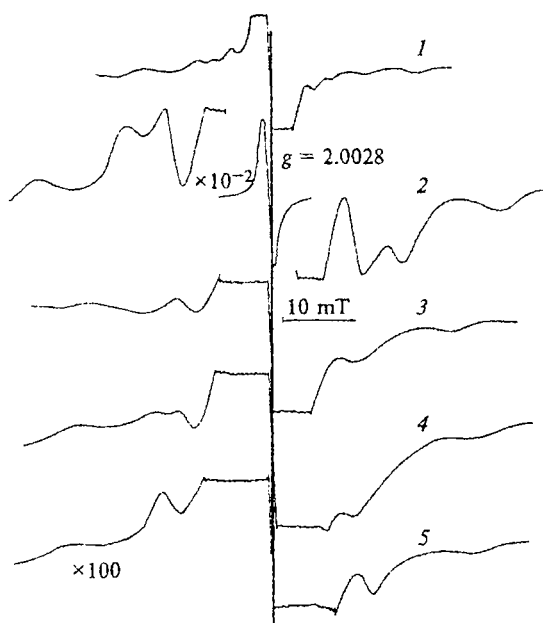


Fig. 2. ESR spectra of solid-state samples after the EWP action on system I with ZnO (1),  $\text{Al}_2\text{O}_3$  (2),  $\text{Ga}_2\text{O}_3$  (3),  $\text{GeO}_2$  (4), and  $\text{ZrO}_2$  (5).

where  $V$  is the volume of STV1 steel,  $p_c$  is the critical pressure of the explosion of a PP plate; and  $E_{Yu}$  is Young's modulus of STV1 steel.

The ESR spectra were recorded on a 3-cm-range Varian E-12 radiospectrometer at 77 and 300 K. The signal areas ( $A$ ), which have the Gaussian or Lorentz shapes, were calculated according to the following formula<sup>2</sup>:

$$A = K\Delta H_m^2 I_m, \quad (3)$$

where  $K$  is the numerical coefficient, which is equal to 0.52 and 1.81 for the Gaussian and Lorentz shapes of the line, respectively,  $I_m$  is the signal amplitude, and  $\Delta H_m$  is the line width between points of the maximum slope.

For broad multicomponent spectra of particles with  $S = 1$ , we used the following approximate relationship<sup>3</sup>:

$$A = K\Delta H_m^{3/2} (3/2D)^{1/2} I_m, \quad (4)$$

where  $D$  is the value of splitting between perpendicular components (the dipole-dipole interaction parameter) and  $K$  is equal to 1.2 and 2.0 for the Gaussian and Lorentz shapes of an individual line, respectively.

The number of paramagnetic sites in the sample ( $N_x$ ) is given by

$$N_x = N_e (A_x/A_e) \gamma, \quad (5)$$

where  $A_x$  and  $A_e$  are the integrated intensities of the signal in the sample and the standard, respectively, and  $N_e$  is the number of paramagnetic sites in the standard.

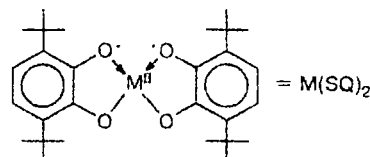
The multiplier  $\gamma = 1$  if a standard and a sample contain sites with the same spin  $S = 1/2$ . Since integrated intensities of ESR signals are determined not only by the number of sites but also by the total spin according to the formula

$$A_x = [N_x(g\beta)^2/4kT]S(S+1), \quad (6)$$

it is necessary to introduce a correction in Eq. (5) for samples with  $S > 1/2$ . Besides, in clusters of free-radical particles, each site with  $S > 1/2$  contains  $2S$  paramagnetic molecules, while in systems with odd  $S$  one of  $2S+1$  states is singlet, which leads to a decrease in the signal by a factor of  $1 + (2S)$  on condition that occupancies of levels are equal. Consideration of these factors leads to the following values for Eq. (5):  $\gamma = 1$  and  $\gamma = 3/5$  when  $S = 1$  and  $S = 3/2$ , respectively. On balance, the absolute concentrations were determined by ESR with an accuracy of no better than  $\pm 20\%$ .

## Results and Discussion

The ESR spectra of samples of system I ( $\text{M}_x\text{O}_y : \text{Q} : \text{QH}_2 = 40 : 1 : 1$ ) with CuO subjected to the EW action have a characteristic signal with  $a_{\perp} = 4$  mT and  $a_{\parallel} = 18$  mT and with an anisotropic superfine structure on  $^{63,65}\text{Cu}$  nuclei. The spectra of other oxides  $\text{M}^{\text{II}}\text{O}$  show either single lines with the  $g$  factor close to  $g_e$  or (for ZnO and CdO) a fine structure typical of biradicals<sup>4</sup> (Fig. 2, Table 1).

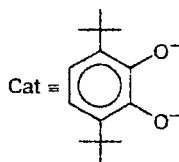


**Table 1.** Parameters of the ESR spectra of the solid-state systems  $M_xO_y+Q+QH_2$  (I),  $M_xO_y+QH_2$  (II), and  $M_xO_y+Q$  (III)

Oxide	System					
	I		II		III	
	$D$ (E)	$\Delta H$ ( $g_{av}$ )	$D$ (E)	$\Delta H$ ( $g_{av}$ )	$D$ (E)	$\Delta H$ ( $g_{av}$ )
ZnO	$D_1 = 23.7$ $D_2 = 13.6$ ( $E_2 = 0.7$ )	5.0			1.5 (1.9983)	
CdO	27.5	6.0	1.13 (2.0043)		1.38 (2.0043)	
PbO		2.25 (1.999)	1.75 (1.9983)		1.625 (2.0025)	
Al <sub>2</sub> O <sub>3</sub>	30.6 (1.7)	2.25	30 (1.83)	1.0 (2.0058)	30.4 (2.3)	1.0 (2.0058)
Cr <sub>2</sub> O <sub>3</sub>		1.6 (1.973)	1.25 (2.0035)		1.38 (2.0065)	
Ga <sub>2</sub> O <sub>3</sub>	25	2.5 (2.0043)	30.5 (1.83)	1.75 (2.0028)	24.3 (2.04)	3.0 (1.9998)
Sb <sub>2</sub> O <sub>3</sub>		0.875 (2.0043)			1.75 (2.0073)	
Bi <sub>2</sub> O <sub>3</sub>		1.75 (1.989) <sub>1</sub> 17.75 (1.978) <sub>2</sub>	1.5 (1.991) <sub>1</sub> 16 (1.995) <sub>2</sub>		0.75 (2.0073)	
TiO <sub>2</sub>			27.5		0.5 (2.0028)	
GeO <sub>2</sub>	27.5 (1)	1.88 (2.002)	2.5 (2.0058)		29.38 (3.13)	1.25 (2.0035)
ZrO <sub>2</sub>	30	0.8	2.0 (1.9988)		1.0 (2.0043)	
SnO <sub>2</sub>		2.25 (2.0028)	0.5 (2.0028)		1.0 (2.005)	

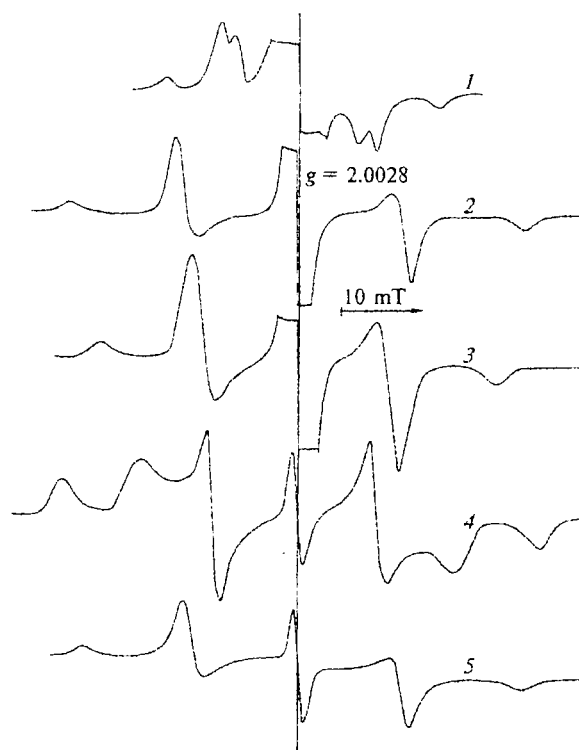
Notes. The values of  $D$  (E) and  $\Delta H$  are given as mT. For Bi<sub>2</sub>O<sub>3</sub>, the values  $\Delta H(g)$  for two types of particles are reported. For the systems with CuO, the identical ESR spectra were recorded;  $a_{\perp} = 4$  mT and  $a_{\parallel} = 18$  mT.

The ESR spectra of systems I and II with Al<sub>2</sub>O<sub>3</sub>, Ga<sub>2</sub>O<sub>3</sub>, QH<sub>2</sub>, or (Q + QH<sub>2</sub>) subjected to the EW action have single lines in the  $g_e$  region along with a fine structure typical of the (QH)M<sup>III</sup>(SQ)<sub>2</sub> biradical<sup>4</sup> (see Fig. 2, Table 1). The spectra of systems I and II with Bi<sub>2</sub>O<sub>3</sub> show two lines with  $\Delta H = 0.5$ –1.5 mT and  $\Delta H = 16$ –17 mT, which can be assigned to the Q<sup>•-</sup> and CatBiSQ particles, respectively, where



The spectra of systems I and II with TiO<sub>2</sub>, SnO<sub>2</sub>, and ZrO<sub>2</sub> and of systems I and III with GeO<sub>2</sub> also contain single lines in the  $g_e$  region and a fine structure typical of the CatM<sup>IV</sup>(SQ)<sub>2</sub> particles<sup>4</sup> (see Fig. 2, Table 1).

In the solid phase, attempts to resolve a superfine structure of an intense narrow signal with  $g = 2.00$  were unsuccessful. Moreover, stronger evidence is required in favor of the probable formation of triradicals under the

**Fig. 3.** ESR spectra of frozen (77 K) toluene solutions of products of the mechanochemical reactions in systems I and II with ZnO (1), Al<sub>2</sub>O<sub>3</sub> (2), Ga<sub>2</sub>O<sub>3</sub> (3), ZrO<sub>2</sub> (4), and TiO<sub>2</sub> (5).

EW action. For this purpose, we examined the ESR spectra of toluene extracts of solid-state samples at 300 and 77 K (frozen solutions), which allowed us to identify both monoradical (300 K) and biradical products (77 K) that formed under the EW action.<sup>4</sup> In addition, the ESR spectra of evacuated precipitates were recorded at 300 K after removal of toluene-soluble products of the mechanochemical reactions.

The spectra of systems I, II, and III with CuO, which were measured as described above, are similar to the spectra for the solid phase (Table 2). This indicates that CatCu<sup>II</sup> or (SQH)<sub>2</sub>Cu<sup>II</sup> particles, which are virtually indistinguishable by ESR, were formed under the EWP action. In toluene solutions of systems I and II with ZnO or CdO, SQ(Zn,Cd)SQH and (Zn,Cd)(SQ)<sub>2</sub> particles (Fig. 3) were detected at 300 and 77 K, respectively. Systems I and II with PbO were characterized by the formation of SQPbSQH and Pb(SQ)<sub>2</sub> particles at 300 K, which gave spectra with splitting on protons of the SQ ring and on the lead nucleus.<sup>4</sup> System III gave only a narrow singlet signal with  $g = 2.00$  (see Table 2).

The ESR spectra of precipitates of M<sup>II</sup>O oxides (except for the systems with CuO) have singlet lines, which are apparently due to SQ radicals, i.e., to particles of the —O—M<sup>II</sup>—SQ type (where the —O—M<sup>II</sup>— fragment belongs to the oxide), interacting with the surface.

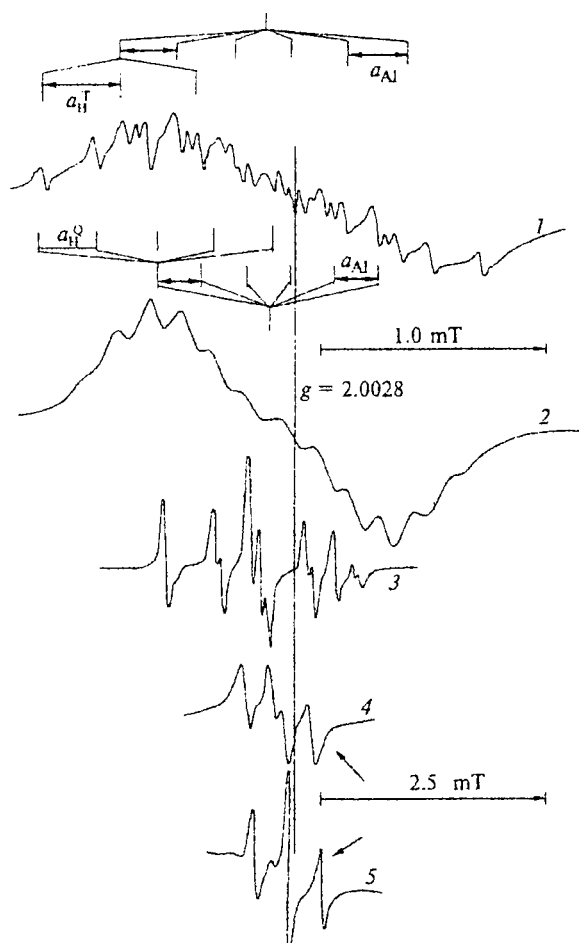


Fig. 4. ESR spectra of toluene solutions (300 K) of products of the mechanochemical reactions: 1,  $\text{Al}_2\text{O}_3$  (system I); 2,  $\text{Sb}_2\text{O}_3$  (I and III); 3,  $\text{GeO}_2$  (II); 4,  $\text{ZrO}_2$  (II); and 5,  $\text{ZrO}_2$  (I and III).

In the case of systems with  $\text{CuO}$ , the  $\text{CatCu}^{\text{II}}$  particles were formed on the oxide surface.

A solution of system I with  $\text{Al}_2\text{O}_3$  at 300 K contained two types of radical particles, namely,  $\text{CatAlSQ}$  (sextet of quintuplets) and  $\text{SQAl}(\text{SQH})_2$  (sextet of triplets) (Fig. 4, Table. 2). We failed to resolve singlet lines for systems II and III with  $\text{Al}_2\text{O}_3$ . Systems I and II at 77 K gave the ESR spectra of the  $\text{Al}(\text{SQ})_3$  triradical (see Fig. 3, Table 2). In the case of systems I and II, biradical particles with identical ESR parameters were detected in precipitates on  $\text{Al}_2\text{O}_3$  both at 77 K and 300 K. Solutions of systems I and II with  $\text{Ga}_2\text{O}_3$  at 77 K gave the spectra only from  $\text{Ga}(\text{SQ})_3$ , while precipitates of these systems gave the spectra only from the biradical (systems I and II at 77 K and 300 K). Hence it follows that the  $(-\text{O}-\text{M}^{\text{III}}(\text{SQ})-\text{SQ})$  particles were fixed on the surface of oxides  $\text{Al}_2\text{O}_3$  and  $\text{Ga}_2\text{O}_3$  at 300 K.

At 300 K, the  $[\text{CrQ}_3]^+\text{X}^-$  particles ( $\text{X}^-$  is, for example,  $\text{OH}^-$ ) were detected in systems I and II with  $\text{Cr}_2\text{O}_3$ .<sup>5</sup> Solutions of systems I and II with  $\text{Bi}_2\text{O}_3$  at 300

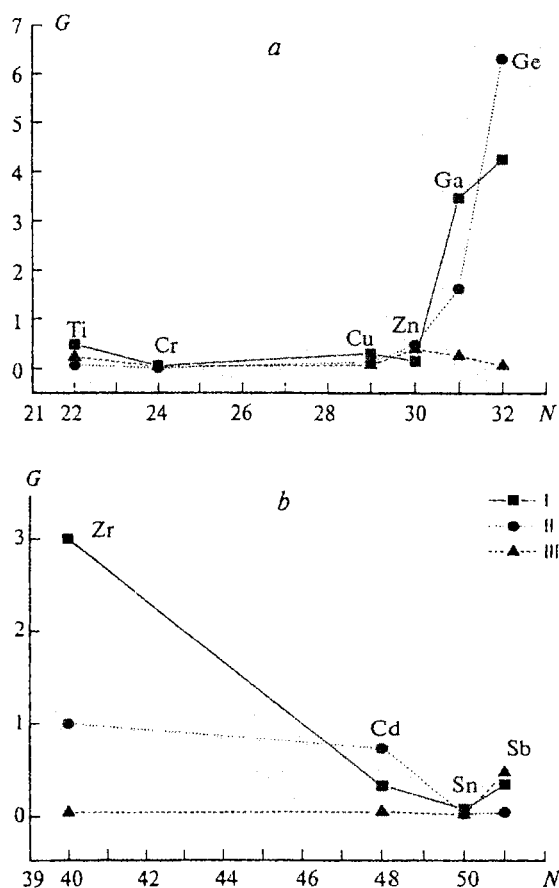


Fig. 5. Changes in the yields of the semiquinone metal complexes in systems I, II, and III depending on the atomic number of Period IV (a) and V (b) metal atoms, respectively.

K gave the 10-line spectrum (the unpaired electron interacts with the Bi nucleus with  $J = 9/2$ ) typical of the  $\text{CatBi}^{\text{III}}\text{SQ}$  particle. The spectrum of system II with  $\text{Sb}_2\text{O}_3$  contains a multiplet due to interaction between the unpaired electron and antimony isotopes  $^{121}\text{Sb}$  ( $J = 5/2$ ) and  $^{123}\text{Sb}$  ( $J = 7/2$ ), which is associated with the formation of the  $\text{CatSb}^{\text{III}}\text{SQ}$  complex. In systems I and III with  $\text{Sb}_2\text{O}_3$ , the complex  $(\text{Cat})_2\text{Sb}^{\text{V}}\text{SQ}^4$  was formed. This complex gave a multiplet in the ESR spectrum (see Fig. 4). Precipitates on  $\text{Cr}_2\text{O}_3$ ,  $\text{Sb}_2\text{O}_3$ , and  $\text{Bi}_2\text{O}_3$  gave only singlet lines, i.e., monoradicals were formed on the surface of these oxides.

In extracts of systems I and II with  $\text{TiO}_2$  at 300 K, the  $\text{SQTiCatSQH}$  radicals were detected (doublet of doublets from nonequivalent protons of SQ and a super-fine structure from titanium isotopes  $^{47}\text{Ti}$  ( $J = 5/2$ , 7.28%) and  $^{49}\text{Ti}$  ( $J = 7/2$ , 5.51%),  $\mu(^{47}\text{Ti}) = \mu(^{49}\text{Ti})$ ), while these systems at 77 K contained the  $(\text{SQ})_2\text{TiCat}$  biradicals (see Fig. 4, Table. 2). On the surface of oxides  $\text{M}^{\text{IV}}\text{O}_2$  ( $\text{TiO}_2$ ,  $\text{GeO}_2$ ,  $\text{ZrO}_2$ , or  $\text{SnO}_2$ ) at 300 and 77 K,

**Table 2.** Parameters of the ESR spectra of toluene solutions (t.s.) at 300 K and 77 K and precipitates (p) at 300 K for the systems  $M_xO_y + Q + QH_2$  (I),  $M_xO_y + QH_2$  (II), and  $M_xO_y + Q$  (III)

Oxide	System						
	I (t.s.)		II (t.s.)		II (p)		III (t.s.),
	$a/mT$ (300 K)	$D(E)/mT$ (77 K)	$a/mT$ (300 K)	$D(E)/mT$ (77 K)	$D(E)/mT$ (300 K)	$\Delta H$ (300 K)	$a/mT$ (300 K)
ZnO	$a^T_H = 0.375$	—	—	13 (0.67) <sup>a</sup>	14 (0.83) <sup>a</sup>	—	—
CdO	—	—	—	—	—	1.5	—
PbO	$a_H = 0.3$	—	$a_H = 0.35$	—	—	2.5	—
	$a^{PB}_H = 4.8$		$a^{PB}_H = 7.35$				
Al <sub>2</sub> O <sub>3</sub>	$a^T_H = 0.33$	15 <sup>b</sup>	—	15 <sup>b</sup>	30.1 (2.3) <sup>a</sup>	—	—
	$a_{Al} = 0.25$						
	$a^Q_H = 0.25$						
	$a_{Al} = 0.19$						
Cr <sub>2</sub> O <sub>3</sub>	$a_{Cr} = 2.5$	—	—	—	—	1.25	—
Ga <sub>2</sub> O <sub>3</sub>	—	13.75 <sup>b</sup>	—	13.75 <sup>b</sup>	26.8 (2.27) <sup>a</sup>	—	—
Sb <sub>2</sub> O <sub>3</sub>	$a_H = 0.15$	—	$a_{121Sb} = 4.7$	—	—	—	$a_H = 0.15$
	$a_{121Sb} = 0.3$		$a_{123Sb} = 2.4$				$a_{121Sb} = 0.3$
	$a_{123Sb} = 0.167$						$a_{123Sb} = 0.167$
Bi <sub>2</sub> O <sub>3</sub>	$a_{Bi} = 3.5$	—	$a_{Bi} = 3.5$	—	—	—	—
TiO <sub>2</sub>	$a_{H1} = 0.41$	29 <sup>a</sup>	$a_{H1} = 0.41$	27.5 <sup>a</sup>	—	1.13	—
	$a_{H2} = 0.33$		$a_{H2} = 0.33$				
	$a^T_H = 0.375$		$a^Q_H = 0.22$				
GeO <sub>2</sub>	$a^Q_H = 0.22$	30 (3.33) <sup>a</sup>	$a^{OH}_H = 0.03$	28.75 (2.92) <sup>a</sup>	—	1.25	—
ZrO <sub>2</sub>	$a_{H1} = 0.45$	29.35 (3.1) <sup>a</sup>	—	29.35 (3.1) <sup>a</sup>	—	1.5	—
	$a_{H2} = 0.30$		$a^T_H = 0.375$				
SnO <sub>2</sub>	$a^T_H = 0.375$	34.5 (1.66) <sup>a</sup>	$a^T_H = 0.375$	29 <sup>a</sup>	—	—	$a^T_H = 0.375$
	$a_{Sn} = 0.42$					1	

Notes.  $a^T_H$  is a triplet from two protons;  $a^Q_H$  is a quintuplet from four protons. For the systems with CuO, the identical ESR spectra were recorded:  $a_{\perp} = 4$  mT and  $a_{\parallel} = 18$  mT. The dash indicates that data are unavailable.  
<sup>a</sup> Biradicals. <sup>b</sup> Triradicals.

the  $—O—\overset{|}{Ti}—SQ$  species exists (see Table 2). A solution of system II with GeO<sub>2</sub> at 300 K gave the spectra from two species, namely, SQGeOHCat (quintuplet of doublets from four protons of the ring and from the proton of the OH group due to the intramolecular exchange between the free valence and the bond between two pyrocatechol ligands) and SQGeSQHCat (triplet from two protons of SQ) (see Fig. 4). System I with GeO<sub>2</sub> contained only the SQGeOHCat species. This is apparently associated with the fact that GeO<sub>2</sub> is sensitive to redox properties of a medium. The spectrum of a solution of system II with ZrO<sub>2</sub> has a triplet from, apparently, the SQZrOHCat species. In the case of system I with ZrO<sub>2</sub>, the spectrum has doublet of doublets from the SQZrSQHCat species in which protons of the SQ ring are nonequivalent (see Fig. 4). At 77 K, solutions of systems I and II with GeO<sub>2</sub> and ZrO<sub>2</sub> contained biradicals (see Fig. 3). The SQSnSQHCat species was detected in a solution of system I with SnO<sub>2</sub> at 300 K (triplet from equivalent protons of SQ with the splitting on <sup>117,119</sup>Sn nuclei). At 77 K, a weak signal from biradicals was observed. These biradicals, as in the

**Table 3.** The mechanical yields (*G*) and the degrees of chemical conversions of Q and QH<sub>2</sub> ( $\alpha$ ) in the  $M_xO_y : Q : QH_2$ ,  $M_xO_y : QH_2$ , and  $M_xO_y : Q$  systems

Oxide	System						U/eV
	I		II		III		
	G	$\alpha$	G	$\alpha$	G	$\alpha$	
Al <sub>2</sub> O <sub>3</sub>	3.59	0.48	0.62	0.16	2.1	0.36	7.3
TiO <sub>2</sub>	0.48	0.06	0.07	0.0126	0.23	0.0124	3.1
Cr <sub>2</sub> O <sub>3</sub>	0.047	0.005	0.004	$1.65 \cdot 10^{-3}$	0.034	0.08	1.9
CuO	0.29	0.092	0.12	0.038	0.06	0.019	5.3
ZnO	0.135	0.007	0.46	0.063	0.38	0.053	3.3
Ga <sub>2</sub> O <sub>3</sub>	3.45	0.6	1.59	0.12	0.24	0.04	4.6
GeO <sub>2</sub>	4.24	0.68	6.3	0.54	0.044	0.01	6.0
ZrO <sub>2</sub>	3.0	0.2	1.0	0.05	0.043	0.0135	2.3
CdO	0.33	0.017	0.73	0.022	0.048	0.014	2.5
SnO <sub>2</sub>	0.076	0.014	0.023	$4.26 \cdot 10^{-3}$	0.014	0.0032	3.8
Sb <sub>2</sub> O <sub>3</sub>	0.34	0.133	0.042	0.024	0.47	0.122	4.2
PbO	0.24	0.03	0.1	0.035	0.039	0.014	3.2
Bi <sub>2</sub> O <sub>3</sub>	1.6	0.087	0.54	0.33	0.006	0.0024	2.9

cases of Sn, Zn, Ti, and Ge oxides, are particles of the (SQ)<sub>2</sub>M<sup>IV</sup>Cat type. After extraction of the products, the

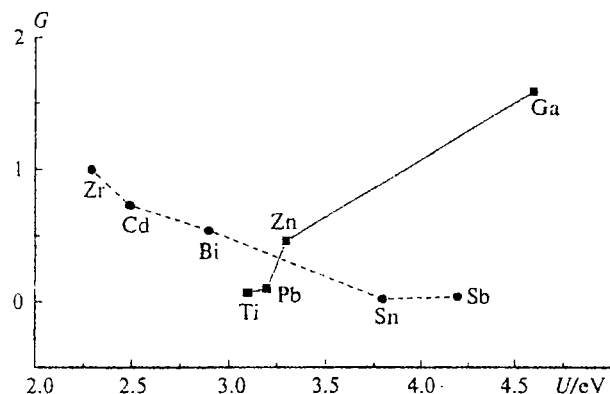


Fig. 6. Changes in the yields ( $G$ ) of the semiquinone metal complexes (system II) depending on the width of the forbidden zone ( $U$ ) for oxide of the corresponding metal.

ESR spectra of system III with  $\text{TiO}_2$ ,  $\text{GeO}_2$ , or  $\text{ZrO}_2$  at 300 K had only low-intensity singlet lines corresponding, apparently, to biradicals containing metal atoms with a coordinate number of six. Under these experimental conditions, such biradicals were characterized by averaged spin-spin interactions at elevated temperatures and by the appearance of the ESR spectrum as a single singlet line.<sup>4</sup> The ratio between concentrations of surface sites and products extracted was  $10^{-2}$ – $10^{-3}$ , i.e., the amount of surface sites formed under the EWP action was from two to three orders of magnitude smaller than the amount of the remaining products.

Therefore, mono-, bi-, and triradicals were formed in solid-state samples subjected to the EW action. Such surface complexes (mono- and biradicals) and a new solid phase can form from the reaction products depending on the oxide type ( $\text{M}^{\text{II}}\text{O}$ ,  $\text{M}^{\text{III}}_2\text{O}_3$ , or  $\text{M}^{\text{IV}}\text{O}_2$ ). In the solid phase, molecular products are linked in exchange clusters and dissociate into individual mono-, bi-, and triradicals only in toluene solutions (this is true for monoradicals of all the oxides under consideration and for the  $\text{Cu}^{\text{II}}(\text{SQH})_2$  particle as well as for biradicals of oxides  $\text{ZnO}$ ,  $\text{CdO}$ ,  $\text{TiO}_2$ ,  $\text{GeO}_2$ ,  $\text{ZrO}_2$ , and  $\text{SnO}_2$  and triradicals of oxides  $\text{Al}_2\text{O}_3$  and  $\text{Ga}_2\text{O}_3$ ). An analogous situation has been observed previously<sup>1</sup> under the action of EW pulses on  $\text{M}-\text{Q}$  systems.

In toluene solutions, these radical products die in a period of a few days in the presence of atmospheric oxygen, while in solid-state mixtures these radicals are stable for months after the EW synthesis.

With the aim of elucidating the mechanism of solid-state processes yielding the above-considered organometallic compounds under the action of EW on systems I, II, and III, we calculated the yields ( $G$ ) for all particles formed in the solid phase as well as the degrees of chemical conversions ( $\alpha$ ) of the initial  $\text{Q}$  and  $\text{QH}_2$  particles (Table 3, Fig. 5). The value  $G$  changes monotonically as the order number of the metal atom in the

solid-phase products increases. For the series  $\text{ZnO}-\text{Ga}_2\text{O}_3-\text{GeO}_2$ ,  $\text{SnO}_2-\text{CdO}-\text{ZrO}_2$ , and  $\text{PbO}-\text{Bi}_2\text{O}_3$ , a pronounced tendency is observed for an increase in the yield of products by 1–2 orders of magnitude in going from system III to system II (see Table 3 and Fig. 5).

In heterogeneous catalysis,<sup>6</sup> these dependences are attributed to Lewis acid sites, which are coordinatively unsaturated metal ions on the oxide surface. Such sites readily react with electron donors. A large number of acid sites are formed on the oxide surface under the EW action, which agrees well with the published data.<sup>6,7</sup> It is known<sup>6</sup> that the efficiency of solid-phase catalysts changes as the width of the forbidden zone  $U$  increases (the values of this parameter<sup>6</sup> are given in Table 3). Actually, the value of  $G$  increases as  $U$  increases for the series of oxides  $\text{TiO}_2$ ,  $\text{PbO}$ ,  $\text{ZnO}$ , and  $\text{Ga}_2\text{O}_3$ , while for the series of oxides  $\text{ZrO}_2$ ,  $\text{CdO}$ ,  $\text{Bi}_2\text{O}_3$ ,  $\text{SnO}_2$ , and  $\text{Sb}_2\text{O}_3$ , the inverse dependence is observed (Fig. 6). Besides, the catalytic activity of the oxide surface increases due to the fact that dislocations that appear under the mechanical action reach the surface.<sup>8</sup> In this case, chemical bonds are rearranged and charge relaxation processes occur on the surface of the initial oxide. According to the theory of dislocations,<sup>7</sup> ~70% of surface atoms can be transformed into the active state because they are located in the zone of action of elastic distortions about dislocations that reach the surface. Previously,<sup>8,9</sup> it has also been demonstrated that treatment of a  $\text{Q} + \text{QH}_2$  mixture with EWP afforded monoradicals  $\text{QH}^\cdot$ , biradicals  $2\text{QH}^\cdot$  (radical pairs), free electrons  $e^-$ , and protons  $\text{H}^+$ .

Therefore, coordinatively unsaturated metal ions that appear when dislocations reach the oxide surface can interact with  $e^-$ ,  $\text{H}^+$ ,  $\text{QH}^\cdot$ ,  $\text{Q}$ , and  $\text{QH}_2$  to form particles located on the surface. However, such particles are few in number. Consequently, it can be assumed that metal ions on the surface are reduced to the multivalent state through reduction reactions at the broken metal–oxygen bonds (breakage occurs when dislocations reach the surface). These reactions proceed with the participation of  $e^-$  and  $\text{H}^+$ . Free electrons can reduce metal ions according to the reactions  $\text{M}(n) + e^- \rightarrow \text{M}(n-1)$  and protons react with  $\text{O}^-$  ions, which are located on the oxide surface and formed under the EWP action, to yield surface-bound  $\text{OH}$  groups. Then these metal atoms or fragments of the  $\text{MOH}$  lattice that are weakly bound with the oxide surface are mechanically removed and react with  $\text{QH}^\cdot$  radicals and  $\text{Q}$  and  $\text{QH}_2$  molecules. The removal of particles from the surface occurs under the action of EWP and surface elastic waves appearing when dislocations reach the oxide surface,<sup>8</sup> which agrees well with our results.

Therefore, the convection model proposed previously<sup>1</sup> adequately describes the solid-state reactions under the EWP action.

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