

TABLE 2. Temperature variation of the solubility of the oxidation products of the spinel.

$t, ^\circ\text{C}$	Phase composition of the preparation	Percentage extraction of vanadate	
		by H_2O	by H_2SO_4
350	R_2O_3	0.49	15.8
550	$\text{R}_2\text{O}_3, \text{CrVO}_4$	2.22	4.56
800	$\text{R}_2\text{O}_3, \text{CrVO}_4$	2.03	0.9
900	$\text{R}_2\text{O}_3, \text{FeVO}_4$	—	51.2

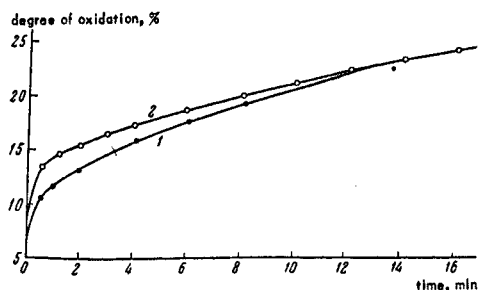


Fig. 6. Dependence of the degree of oxidation of the spinel on the duration of heat treatment at 400°:

1) without additive; 2) with 0.5% KCl.

of the iron-vanadium spinel. As a result of the formation of iron orthovanadate, the R_2O_3 becomes enriched in chromium but does not consist of pure Cr_2O_3 , as shown by the calculation of the lattice parameters.

The results of the treatment of the oxidation products of the spinel with hot water and 10% sulphuric acid are presented in Table 2. Their examination shows that samples containing the R_2O_3 phase and chromium orthovanadate are virtually insoluble in both solvents. This is also shown by experiments on the solubility of chromium orthovanadate: when CrVO_4 is treated with cold and boiling sulphuric acid for 40 min, not more than 1% of the substance dissolves. The presence of chromium in converter slags during their oxidative heat treatment favours the conversion of the vanadium into an insoluble form and chromium is therefore an undesirable constituent of the charge.

At heat-treatment temperatures in excess of 800° the degree of extraction of vanadium in the form of acid-soluble compounds increases sharply (Table 2). This is due to the formation (when the charge is cooled) of iron orthovanadate, whose solubility in boiling sulphuric acid is 50–60%.

The thermogram for the oxidation of the spinel in the presence of 0.5% of potassium chloride is identical with that for the oxidation of pure FeVCrO_4 . The phase composition of the oxidation products is also the same. Measurements of the rates of oxidation by continuous weighing at 400° showed (Fig. 6) that the presence of small amounts of potassium chloride in the spinel accelerates the rate of the process by a factor of 1.3–1.5 during the first few minutes.

SUMMARY

1. The oxidation of a spinel with the composition FeVCrO_4 has been investigated. The first effect on the thermogram corresponds to the formation of an R_2O_3 phase, the second to the formation of chromium orthovanadate, and the third to incongruent fusion of chromium orthovanadate.
2. The R_2O_3 phase consists of a solid solution of vanadium and chromium in hematite.
3. Slow crystallisation of the melt results in the formation of iron orthovanadate, the R_2O_3 phase becoming enriched in chromic oxide.
4. Addition of 0.5% of potassium chloride to the spinel accelerates the oxidation process.

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REDUCTION OF ORGANIC COMPOUNDS AT A GERMANIUM CATHODE

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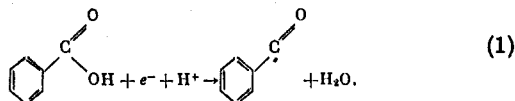
Organic compounds were reduced at 20° at a germanium electrode of n -type with $\rho = 3 \Omega \text{ cm}$ and p -type with $\rho = 15 \Omega \text{ cm}$ and also an electrode with a p - n junction^{1,2}. Preparative electrolysis was carried out for 100 h in a cell with a porous glass partition and germanium electrodes of

large area (up to 5 cm²). The compounds obtained were isolated and identified by the usual methods of organic analysis^{3,4}.

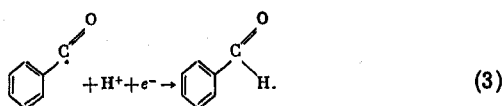
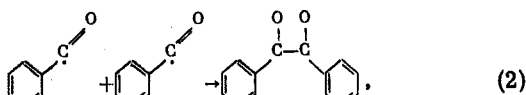
Reduction of Benzoic Acid

The reduction of benzoic acid was studied in 0.1 N H₂SO₄ solution containing 80% of ethanol. It took place over the entire current density range investigated, 10⁻⁵–10⁻² A × cm⁻², its rate depending on the concentration of benzoic acid and the conductivity type of the electrode (Fig. 1). When the concentration of benzoic acid was increased from 0.01 to 1 M, the potential shifted towards positive values by 50–60 mV. In this range the curves followed the Tafel equation with a slope $b = 0.13$ V.

The reduction of benzoic acid on *p*-type germanium took place with much greater difficulty, but under strong illumination the curves for *p*- and *n*-type germanium almost coincided. It may be supposed that, at potentials more positive than -0.1 V, the rate of the process is determined by the addition of a conductivity band electron to a benzoic acid molecule:



The radical thus formed becomes linked to the electrode surface, and can be subsequently removed in two ways:



Analysis of the catholyte showed that the main reduction product was benzil C₆H₅COCOC₆H₅ (m.p. 94–96°), accompanied by a very small amount of benzaldehyde.

At $i \gg 7 \times 10^{-3}$ A cm⁻² the reaction on both *p*- and *n*-type germanium is retarded, probably due to accumulation of the acid dimer on the electrode surface.

If the electrochemical reduction products are desorbed with difficulty, *i.e.* are fairly firmly bound to the electrode surface, the potential jump at the germanium–electrolyte boundary should be affected. Fig. 2 shows that, after the electrode has been maintained at potentials more negative than -0.2 V, the potential of the flat bands is displaced towards negative values as the concentration of benzoic acid in the electrolyte is increased (Figs. 2a and 2b), the phenomenon disappearing completely at potentials of about 0.1 V, *i.e.* when current is passed in the anodic direction. In the reduction of benzoic acid at a germanium electrode with a *p*-*n* junction (Fig. 1b) the proportion of hole current is zero up to $\phi \approx -0.6$, but after the electrode has been maintained at this potential for some time the hole current increases. The reverse current of the *p*-*n* junction can be restored to the previous value only after brief anodic treatment of the electrode. The reduction products accumulating on the electrode surface are bound to *via* negative atoms, which give rise to a positive space charge in

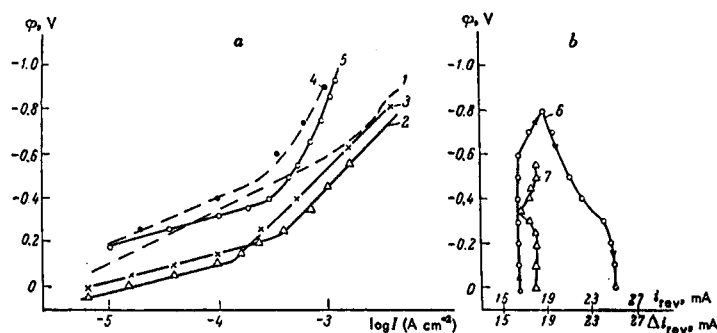


Fig. 1. Polarisation of *p*-type and *n*-type germanium cathodes (a) and an electrode with a *p*-*n* junction (b) in the reduction of benzoic acid in 0.1 N H₂SO₄:

- 1) *n*-type (80% ethanol);
- 2) *n*-type (80% ethanol + 0.01 M benzoic acid);
- 3) *n*-type (80% ethanol + 1 M benzoic acid);
- 4) *p*-type (80% ethanol);
- 5) *p*-type (80% ethanol + 1 M benzoic acid);
- 6) variation of $i_{\text{rev.dark}}$ of the *p*-*n* junction (80% ethanol + 1 M benzoic acid);
- 7) variation of $\Delta i_{\text{rev}} = i_{\text{rev.light}} - i_{\text{rev.dark}}$ (80% ethanol + 1 M benzoic acid).

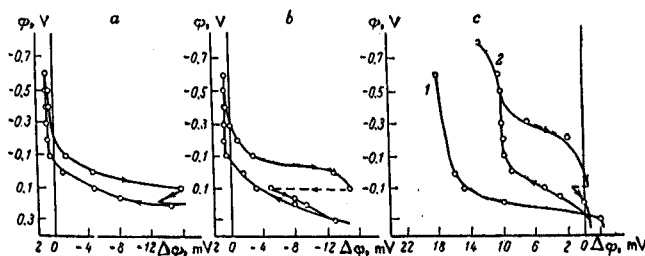


Fig. 2. Variation of the photopotential of *n*-type (a, b) and *p*-type (c) germanium electrodes with their potential in 0.1 N H₂SO₄ (80% ethanol):

- a) in the presence of 0.01 M benzoic acid;
- b) in the presence of 1 M benzoic acid;
- 1) without additive;
- 2) in the presence of 1 M benzoic acid.

the semiconductor. These may be oxygen atoms of keto-groups or carbon atoms with unpaired electrons. Anodic oxidation converts these products into benzoic acid and removes them from the electrode surface. When these compounds are adsorbed, the rate of surface recombination does not change markedly; atomic hydrogen is not appreciably adsorbed on the germanium surface. Otherwise there would have been an immediate decrease of $\Delta\phi_{\text{light}}$. At metallic electrodes benzoic acid is reduced to benzyl alcohol or hexahydrobenzoic acid⁵, and only a few investigators have found benzaldehyde⁶ and dimerisation products⁷ in the reduced material. Benzaldehyde is virtually not reduced at all at a germanium electrode. In alkaline solutions benzoic acid and benzaldehyde are not reduced at potentials lower than about -1.2 V.

Reduction of Benzoquinone

The limiting current shown in Fig. 3a is due to diffusional phenomena in the electrolyte, increasing from 5×10^{-4} to 2.5×10^{-3} A cm $^{-2}$ when the concentration of benzoquinone is raised from 0.01 to 0.05 M. At low current densities the kinetics of the electrochemical reaction obey the Tafel law and are virtually independent of the concentration of benzoquinone in the electrolyte. According to the literature^{8,9}, the reduction of benzoquinone at metallic electrodes in acid solutions takes place *via* the formation of the C₆H₅O₂⁺ ion (by the reaction of a benzoquinone molecule with a hydrogen ion) and its subsequent reduction. This mechanism is also valid for the germanium electrode.

The adsorption of the C₆H₅O₂⁺ ion on the surface of germanium leads to a downward bending of the bands (Fig. 4), particularly in the case of *p*-type germanium. The extent of the bending of the bands increases with the concentration of benzoquinone in solution in the potential range where the polarisation curves show a limiting diffusion current. This is easy to understand, since under these conditions the extent of adsorption of benzoquinone increases.

Fig. 3a shows that the reduction of benzoquinone on *p*-type germanium at positive potentials is somewhat more difficult than on *n*-type germanium. When the electrode is illuminated, the polarisation curve for *p*-type germanium completely coincides with that for *n*-type germanium, which shows that conductivity band electrons participate in the electrode reaction together with valence electrons.

The proportion of hole current varies with the concentration of benzoquinone and the electrode potential (Fig. 3b). When the germanium electrode is illuminated in solution containing 0.05 M benzoquinone, the steady-state potential of *p*-type germanium undergoes a positive shift of 30 mV and that of *n*-type germanium a negative shift of 70–80 mV, which indicates appreciable dissolution of germanium at positive potentials, its extent increasing with the concentration of benzoquinone. Since the rate of dissolution of germanium at a constant potential is also constant regardless of the concentration of benzoquinone in solution, the

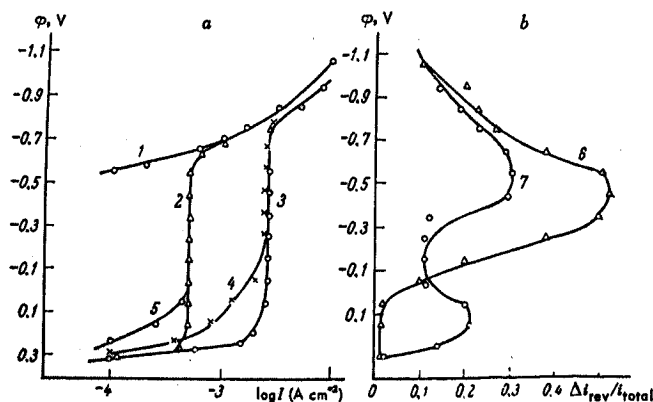


Fig. 3. Polarisation of *p*-type and *n*-type germanium in the reduction of benzoquinone:

- a): 1) *n*-type in 0.1 N H₂SO₄ without benzoquinone; 2) *n*-type, 0.01 M benzoquinone; 3) *n*-type, 0.05 M benzoquinone; 4) *p*-type, 0.05 M benzoquinone; 5) *p*-type, 0.01 M benzoquinone;
b): variation of the proportion of hole current with the potential of the electrode with a *p*-*n* junction: 6) 0.01 M benzoquinone; 7) 0.05 M benzoquinone.

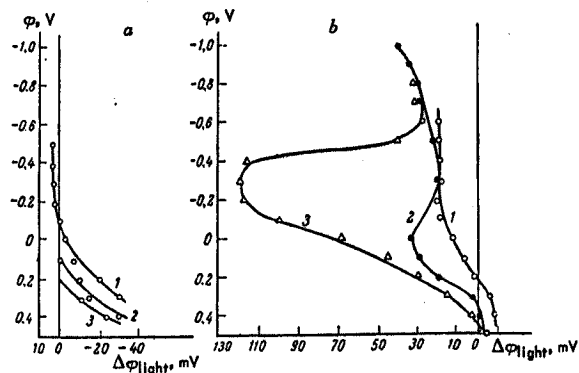


Fig. 4. Variation of the photopotential of *n*-type (a) and *p*-type (b) germanium electrodes with their potential:

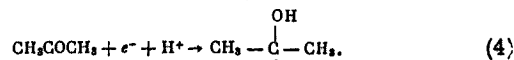
- 1) without benzoquinone in 0.1 N H₂SO₄;
2) 0.01 M benzoquinone;
3) 0.05 M benzoquinone.

overall fraction of hole current, measured with the aid of the electrode with a *p*-*n* junction, should be higher for solutions with a high benzoquinone content (Fig. 3b), which is actually the case at positive potentials, *i.e.* when the spontaneous dissolution of germanium takes place at an appreciable rate.

The increase of the hole component of the benzoquinone reduction current with polarisation for concentrations 0.01 and 0.05 M begins at potentials of 0.0 and -0.02 V respectively. At these potentials the rate of reaction is independent of the conductivity type of germanium and is determined by diffusional phenomena in the electrolyte. At potentials more negative than -0.6 V the reduction of benzoquinone is accompanied by evolution of hydrogen, *i.e.* by an increase in the rate of surface recombination. This leads to a decrease of the hole component of the overall cathodic current.

Reduction of Acetone

The reduction of acetone at the germanium electrode was investigated in 0.1 N solutions of H₂SO₄ and KOH (Fig. 5). It takes place on *p*-type and *n*-type germanium in both acid and alkaline media. In all cases the products are isopropanol, hydrogen, and a certain amount of resin which decomposes at 300°. Germanium enters into the composition of the resin, the germanium cathode after the electrolysis being corroded and pitted. In the reduction of acetone at lead and mercury cathodes¹⁰ organic compounds of lead and mercury are also formed. Probably, one of the first stages of the reaction is the formation of an active radical, which reacts with the electrode:



Since the electronegativity of germanium is lower than that of carbon¹¹, the electrons of outer germanium may approach so closely to the carbon radical that their bonds with the neighbouring germanium atoms are weakened and the compound formed passes into the electrolyte. This process

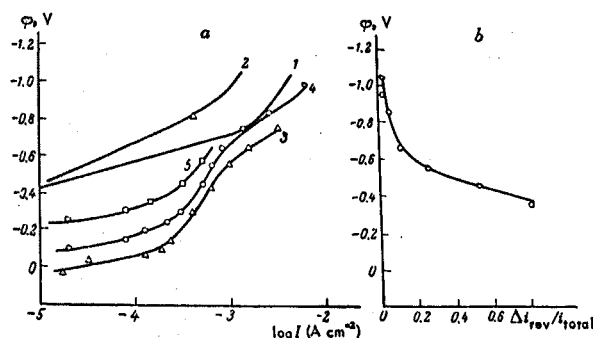


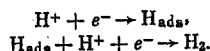
Fig. 5. a) Polarisation of *p*-type and *n*-type germanium in the reduction of acetone in 0.1 *N* H₂SO₄: 1) *n*-type, without acetone; 2) *p*-type, without acetone; 3) *p*-type, 1 M acetone; 4) *n*-type, 1 M acetone in the dark; 5) *n*-type, 1 M acetone in the light; b) variation of the proportion of hole current with the potential of the electrode with a *p-n* junction in 0.1 *N* H₂SO₄ + 1 M acetone.

is accelerated in the presence of holes on the surface (Fig. 5a).

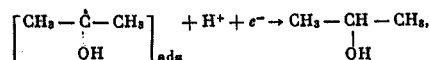
All the polarisation curves in Fig. 5a, characterising the reduction of acetone, consist of three sections: the region of low current densities where the curves follow the Tafel equation with a slope 0.11–0.14, a rising section, and a region of high current densities where the electrochemical reaction is appreciably accelerated.

Decrease of the concentration of acetone to 0.2 M has almost no effect on the polarisation curves, which indicates a high degree of surface coverage of the electrode by the organic compound. At fairly high current densities the rate of formation of this compound may be lower than the rate of discharge. The reaction is then retarded and the surface concentration of the organic substances increases. The rise observed on the polarisation curves may be explained similarly.

At negative potentials (more negative than -0.6 V) hydrogen is evolved:



There is then a possibility of the reaction of the adsorbed hydrogen with the radical or the occurrence of the electrochemical reaction



in which isopropanol is formed.

The reduction of acetone at the germanium electrode with a *p-n* junction takes place with participation of electrons from both the valence and conductivity bands (Fig. 5b). As the potential shifts in the negative direction, the proportion of hole current increases, in agreement with Dewald's findings¹². Measurements of the photopotential in solutions containing acetone showed that $\Delta\phi_{light}$ is small for both *p*-type and *n*-type germanium, decreasing appreciably when the concentration of acetone is increased.

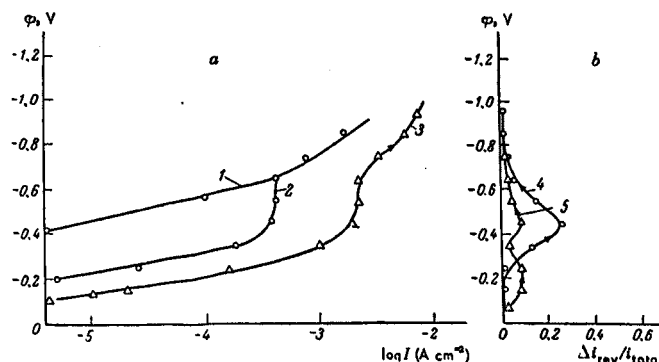


Fig. 6. a) Polarisation of *n*-type and *p*-type germanium in the reduction of nitrobenzene in 0.1 *N* H₂SO₄: 1) *n*-type, without nitrobenzene; 2) *n*-type and *p*-type, 0.01 M nitrobenzene; 3) *n*-type and *p*-type, 0.05 M nitrobenzene; b) variation of the proportion of hole current with the potential of the electrode with a *p-n* junction in 0.1 *N* H₂SO₄; 4) 0.01 M nitrobenzene; 5) 0.05 M nitrobenzene.

This phenomenon is associated with a sharp increase of the rate of surface recombination when acetone or its reduction products are adsorbed on the electrode.

Reduction of Nitrobenzene

The reduction of nitrobenzene on germanium in 0.1 *N* H₂SO₄ stops at the stage in which phenylhydroxylamine and azoxybenzene are formed. The polarisation curves (Fig. 6) for the reduction of nitrobenzene in 0.1 *N* H₂SO₄ on *p*-type and *n*-type germanium coincide and vary with the concentration of nitrobenzene in solution. The slopes b of the initial sections of the curves in Fig. 6a are about 0.06–0.07 V, i. e. are the same as the values obtained by Antropov and Vagramyan¹³ for a platinum electrode. At high current densities the polarisation curves show characteristic sections corresponding to the limiting current associated with the diffusion to the cathode of the substance undergoing reduction.

Experiments using the electrode with a *p-n* junction (Fig. 6b) showed that the reduction of nitrobenzene involves the participation of both free and valence electrons. The hole component of the overall cathodic current is small ($\gamma \leq 0.25$). As in the reduction of benzoquinone, it increases with decrease of the concentration of the test substance to a maximum in the region of the limiting current.

SUMMARY

1. The use of a semiconductor electrode in the investigation of the reduction of organic compounds provides more detailed information about the interaction of the initial compounds and electrolysis products with the electrode surface.
2. In its reducing properties the germanium cathode is close to metallic electrodes whose hydrogen overvoltages are not particularly high.

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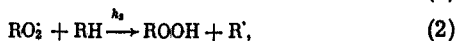
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CALCULATION OF THE PRE-EXPONENTIAL FACTORS FOR CERTAIN ELEMENTARY OXIDATION REACTIONS

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In liquid-phase chain oxidation of organic compounds the bimolecular radical reactions



play an important role. The absolute values of the constants k_1 , k_2 , and k_3 have been measured for a number of substances. Transition state theory¹ makes it possible to calculate the pre-exponential factors for elementary chemical reactions. Although such calculation is approximate for reacting species (particles) of complex configuration, even in this case it makes it possible to arrive at definite conclusions concerning the structure of the transition state. The possibility of calculating the pre-exponential factors for radical reactions has been demonstrated by Stepukhovich^{2,3}. The present paper deals with the calculation of the pre-exponential factors for reactions (1)–(3), using methane and cyclohexane as examples. The results of the calculation are compared with the experimental results.

According to the transition state theory, the pre-exponential factor k_0 for a bimolecular reaction is $k_0 = (kT/h)(f^*/f_A f_B)$, where k is the Boltzmann constant,

h the Planck constant, T the absolute temperature, f^* the partition function of the activated complex, and f_A and f_B are the partition functions of the initial substances; $f = f_{\text{transl}} \times f_{\text{rot}} \times f_{\text{vib}} g / \sigma$, where g is the degree of electronic degeneracy and σ the symmetry number of the particle. The partition function for translational motion depends only on temperature and the mass of the particle: $f_{\text{transl}} = (2\pi mkT)^{3/2} / h^3$. The present calculation has been made for only one temperature, $T = 400^\circ K$, when $(kT/h) \cdot (f^*/f_A f_B)_{\text{transl}} = 3.3 \times 10^9 (M^*/M_A M_B)^{3/2}$ litre mole⁻¹ s⁻¹, M being the molecular weight. The partition function for rotational motion depends on the product of the principal moments of inertia of the particle $I_1 I_2 I_3$ (on its configuration) and on temperature. For a polyatomic molecule (radical),

$$f_{\text{rot}} = \frac{8\pi^2 (8\pi^2 I_1 I_2 I_3)^{1/2} (kT)^{3/2}}{h^3} = 120 \sqrt{I_1 I_2 I_3},$$

when the moment of inertia I is expressed in mole Å². The partition function for free rotation of an atom or group of atoms about any axis is $f_{\text{free rot}} = (8\pi^2 I_D kT)^{1/2} / h$, where I_D is the moment of inertia (mole Å²) of a group of atoms rotating relative to the given axis, and $f_{\text{free rot}} = 7.2 \sqrt{I_D}$. At low temperatures the vibrational partition function may be taken as unity.

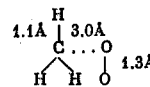
The Reaction $CH_3 + O_2 \rightarrow CH_3O_2$

The methyl radical has a planar configuration:



$$f_{\text{rot}} = 400, \sigma = 6, g = 2.$$

For oxygen, $\overset{1.2 \text{ Å}}{O}-O$, we have $f_{\text{rot}} = 192$, $\sigma = 2$, and $g = 3$, and for the transition state:



$$I_1 I_2 I_3 = 5.5 \times 10^4, f_{\text{rot}}^* = 2.8 \times 10^4, \sigma = 1, g = 2.$$

The partition function for free rotation of CH_3 about the C-O axis is $f_{\text{free rot}} = 13$. The C-O distance in the transition state was taken to be 3.0 Å on the basis of the following considerations: on recombination of two radicals (for example, methyl radicals) the distance between the reacting atoms is 4.5–4.8 Å.⁴ This large distance is due to the strong interaction between the spins of the unpaired electrons. It is to be expected that in the reaction of a radical with an oxygen molecule, which has a spin equal to unity, the spin interaction will also lead to a configuration of the transition state in which the C-O distance will be much greater than in the product radical in which $r_{C-O} = 1.35$ Å (as in the hydroperoxide molecule). On the other hand, this distance will be smaller than in the reaction between two radicals, and therefore we have taken the mean value:

$$r_{C-O} = \frac{4.65 + 1.35}{2} = 3.0 \text{ Å}.$$