THERMAL DECOMPOSITION OF DICYCLOHEXYLPEROXYDICARBONATE IN DIFFERENT TYPES OF SOLVENTS

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We have obtained data on the rates of homolysis and induced decomposition of dicyclohexylperoxydicarbonate (PC) in different types of solvents: n-decane, cyclohexane, chlorobenzene, acetonitrile. The rate of induced decomposition is determined by the activity of the radicals formed from the solvent. We have established that benzene and chlorobenzene participate in radical reactions of induced decomposition of PC, which leads to formation of a number of isomeric aryl-containing compounds.

The effect of the medium on a chemical reaction can be due to various factors: solvation of the reacting particles, formation of complexes with hydrogen bonds, viscosity, etc. In chain reactions, as a result of reaction with free radicals, the solvent can act as a component of a chemical transformation, for example, in the decomposition of peroxide initiators: acylperoxides, peroxydicarbonates, etc. In [1], it is shown that decomposition of dicyclohexylperoxydicarbonate (PC) in alkylaromatic hydrocarbons occurs only as a result of homolysis of the peroxide bond; and in benzene, the peroxide reacts with the radicals formed [2]. In this paper, we have investigated the thermal decomposition of PC in different types of solvents and we have analyzed the effect of the medium on the chain stages of decomposition of the peroxide.

EXPERIMENTAL

Decomposition of PC was carried out under an N_2 or O_2 atmosphere at 45-75°C. The solvents chlorobenzene, n-decane, and cyclohexane were purified according to the technique in [3]; acetonitrile was purified according to the technique in [4]. The PC concentration was determined colorimetrically [5]. This method, in the case of PC and also some acylperoxides, allows us to selectively analyze them in a mixture with hydroperoxides. As the free-radical acceptor, we used 4-(spiro-tetrahydrofurano-2')-2-spirocyclohexyl-1,2,3,4-tetrahydroquinoline-N-oxyl ($>NO_I^{\cdot}$) [6, 7], whose concentration and also the concentration of its conversion product quinonenitrone were determined from the absorption spectrum respectively at 289 nm [$\varepsilon = 1.39 \cdot 10^4$ liters/(moles·cm)] and 371 nm [$\varepsilon = 1.9 \cdot 10^4$ liters/(moles·cm)]. Analysis of the PC conversion products in aromatic solvents in the absence of O_2 after complete consumption of the peroxide was done on the Ribermag R 10-10C chromatograph–mass spectrometer, capillary column SE-30. The mass spectra were obtained for electron energy 70 eV, ionization chamber temperature 150°C.

RESULTS AND DISCUSSION

Decomposition of PC in all the investigated solvents is described by first-order kinetics; the linearity of the semilogarithmic anamorphism is retained all the way to large degrees of conversion (Fig. 1). However, in a number of solvents, we observe an increase in the effective rate constant k_{eff} with an increase in the initial PC concentration (Fig. 2). The effective rate constant varies according to Eq. (1), characteristic for induced decomposition of peroxide (Fig. 2, curves 1-4) [2, 8]:

$$k_{eff} = k_M + a\,[PC]_0^{0.5}, \tag{1}$$

where k_M is the rate constant for monomolecular decomposition of PC, a is a kinetic parameter characterizing the rate of induced decomposition.

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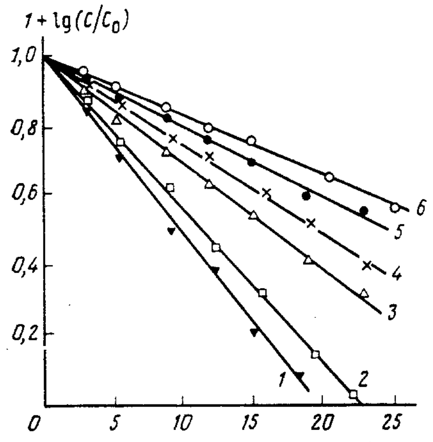
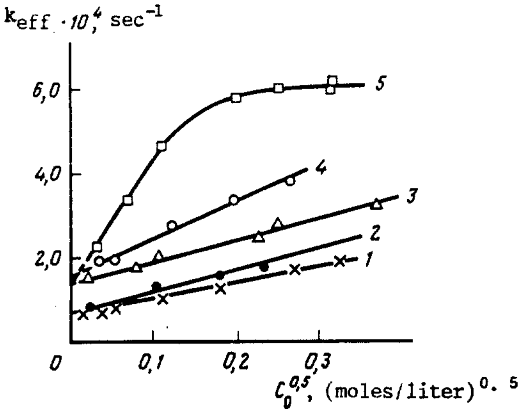


Fig. 1



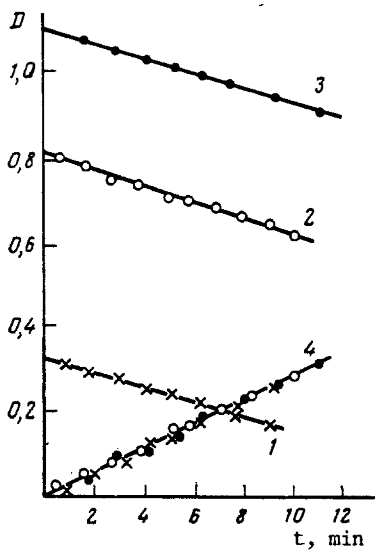


Fig. 2

Fig. 3

Fig. 1. Semilogarithmic anamorphism of the kinetic curves for consumption of PC in chlorobenzene (1, 2) and n-decane (3-6) under an inert atmosphere at 75°C; $[PC]_0 \cdot 10^2$, moles/liter: 10.0 (1); 4.4 (2); 10.4 (3); 6.25 (4); 1.2 (5); 0.1 (6).

Fig. 2. Dependence of the rate constant for decomposition of PC, k_{eff}, on its initial concentration at 60°C in the solvents: 1) n-decane; 2) cyclohexane; 3) benzene; 4) chlorobenzene; 5) acetonitrile.

Fig. 3. Kinetics of consumption of $>NO^{\cdot}_{I}$ (1-3) and accumulation of quinonenitrone (4) upon decomposition of PC in n-decane at 60°C in O_2; $[PC]_0 = 2.0 \cdot 10^{-4}$ moles/liter; $\left[>NO_I^{\cdot}\right]_0 \cdot 10^5$, moles/liter: 2.5 (1), 6.0 (2), 8.0 (3).

In ethylbenzene, isopropylbenzene, and m-xylene for differential initial PC concentrations $k_{eff} = k_M$ (Table 1) [1], i.e., induced decomposition is not observed.

The dependence of k_{eff} on $[PC]_0^{0.5}$ in acetonitrile, in contrast to other solvents, deviates from linearity when $[PC]_0 > 1 \cdot 10^{-2}$ moles/liter (Fig. 2, curve 5). The value of k_M in acetonitrile, determined by the extrapolation $[PC]_0 \to 0$ of the linear section of curve 5 (Fig. 2), is virtually the same as in aromatic solvents (60°C).

TABLE 1. Kinetic Parameters of Monomolecular and Induced Decomposition of PC in Different Solvents under an Inert Atmosphere [k_M, sec^{-1}; a, (liters/mole)$^{0.5}$·sec^{-1}; $k_C = a/\sqrt{2ek_M}$, (liters/(mole·sec))$^{0.5}$]

Solvent	$\lg k_0$	E, kJ/mole	$k_M \cdot 10^4$ (60°)	$\lg a_0$	E, kJ/mole	$a \cdot 10^4$ (60°)	E, kJ/mole	$k_C \cdot 10^2$ (60°)
Chlorobenzene	17,4	135,6	1,6	11,7	94,6	9,2	26,8	6,2
n-Decane	15,4	124,3	0,7	13,0	105,1	3,6	42,1	3,6
Cyclohexane			0,7			4,8		4,8
Acetonitrile			1,5			30,0		20,7
Benzene	14,9	120,1	1,4	13,2	105,1	4,7	44,8	3,4
Alkylbenzenes			1,3					

In Table 1, we present the kinetic parameters for the stage of homolysis and induced decomposition of PC in different solvents under an inert atmosphere. The first-order reaction rate constant for decomposition of PC in the presence of oxygen does not depend on $[PC]_0$, and is equal to the value of k_M determined under an inert atmosphere. These data are evidence for the suppression of induced decomposition of peroxide in O_2.

The values of k_{eff} and k_M in aromatic solvents and acetonitrile are higher than in paraffinic hydrocarbons over the entire peroxide concentration interval (Table 1). Thus, aromatic solvents promote homolysis of the peroxide bond of PC. However, the rate constant for homolysis changes insignificantly for a strong difference in polarity of the aromatic solvents and acetonitrile. This fact, and also the absence of chain decomposition in alkylaromatic hydrocarbons and its complete suppression in O_2 in all solvents allow us to conclude that the rate of induced decomposition of PC is determined more by the nature of the free radicals of PC and the solvent than by the physical properties of the solvent.

One important characteristic of the efficiency of the initiator is the yield coefficient, describing the yield of radicals from the solvent cage. In order to determine it, we used the stable radical $\rangle NO_I^{\cdot}$ [6, 7], from which upon reaction with peroxyl radicals quinonenitrone is formed (X) with an intense absorption band at $\lambda_{max} = 371$ nm; this nitroxyl also reacts with alkyl and alkoxyl radicals, but in this case other products are formed which do not have an absorption band in the visible region of the spectrum, which allows us in a number of cases to use $\rangle NO_I^{\cdot}$ for selective identification and quantitative determination of the peroxy radicals. In order to eliminate catalytic decomposition of PC in the presence of $\rangle NO_I^{\cdot}$, we used low concentrations of nitroxyl, for which the rate of catalytic decomposition of peroxide is negligibly small:

$$k_M[\mathrm{PC}] \gg k_x[\rangle NO_I^{\cdot}][\mathrm{PC}] \text{ and } [\rangle NO_I^{\cdot}] \ll k_M/k_x, \tag{2}$$

where k_x is the effective rate constant for catalytic decomposition of PC [9, 10].

In decomposition of PC in chlorobenzene [10] and n-decane (Fig. 3), the consumption rates of $\rangle NO_I^{\cdot}$ are identical in N_2 and O_2, and are equal to the rate of accumulation of quinonenitrone (in O_2); in this case, they are 1.5 times higher than the rate of homolysis of PC, i.e., the following relations hold:

$$-d[\rangle NO_I^{\cdot}]/dt_{N_2} = -d[\rangle NO_I^{\cdot}]/dt_{O_2} = d[X]/dt_{O_2} = 1.5k_M[\mathrm{PC}]_0. \tag{3}$$

This means that all the radicals leaving the solvent cage are converted in the presence of oxygen to peroxyl radicals, and the yield coefficient describing the yield of radicals from the case is 2e = 1.5.

Close values of 1.45 (60°C) and 1.35 (50°C) are determined for the decomposition of PC in ethylbenzene and m-xylene [1] using 2,2,6,6-tetramethylpiperidine-1-oxyl ($\rangle NO_{II}^{\cdot}$) as the acceptor for the alkyl radicals. From data on accumulation of phenoxyl radicals in decomposition of PC in benzene in the presence of 2,4,6-tri-tert-butylphenol [11], it follows that 2e = 1.5; i.e., the yield coefficients for the yield of radicals from the cage in this and other aromatic solvents are about the same. We should especially consider experimental data on consumption of $\rangle NO_{II}^{\cdot}$ in the decomposition of PC in benzene. Its consumption rate is very low and formally corresponds to 2e = 0.3, which reflects the complex mechanism for conversion of this nitroxyl. Some reasons why $\rangle NO_{II}^{\cdot}$ cannot be used as a radical counter in decomposition of PC in benzene are considered in [1, 9].

Above it has been noted that the kinetic characteristics of decomposition of PC (Table 1) are determined by the nature of the radicals $R^{\cdot}$ of the solvent S, formed when it reacts with the primary radicals of the initiator $r_i^{\cdot}$. Let us consider the kinetic equations for consumption of PC, which are obtained from analysis of the usual scheme for decomposition of the initiator, taking into account the participation of the solvent in the radical reactions:

$$\begin{array}{l}
1)\ \mathrm{PC} \xrightarrow{k_M} 2r_i^{\cdot},\\
2)\ r_i^{\cdot} + \mathrm{PC} \xrightarrow{k_2} r_i^{\cdot} + \text{Products},\\
3)\ r_i^{\cdot} + S \xrightarrow{k_3} R^{\cdot},\\
4)\ R^{\cdot} + \mathrm{PC} \xrightarrow{k_4} r_i^{\cdot} + \text{Products},
\end{array}$$

$$\left.\begin{array}{l}
5)\ r_i^{\cdot} + r_i^{\cdot} \xrightarrow{k_5}\\
6)\ R^{\cdot} + R^{\cdot} \xrightarrow{k_6}\\
7)\ R^{\cdot} + r_i^{\cdot} \xrightarrow{k_7}
\end{array}\right\} + \text{Products.}$$

As a result of rupture of the peroxide bond of PC, alkoxycarboxyl radicals $C_6H_{11}OCOO^{\cdot}$ are formed, which are decarboxylated, converted to alkoxyl radicals $C_6H_{11}O^{\cdot}$; isomerization of the alkoxy radicals leads to formation of alkyl radicals [12, 13]. At the present time, it does not seem possible to say anything about the specific nature of the primary radicals $r_i^{\cdot}$, then reacting with the peroxide [reaction (2)]. There is no doubt that a reaction occurs between the radicals from the PC $r_i^{\cdot}$ and solvents containing reactive C—H bonds.

Depending on which free radicals preferentially participate in the stages of chain propagation and chain termination, different kinetic equations hold for decomposition of the peroxide. If induced decomposition is driven only by radicals of one kind ($r_i^{\cdot}$ or $R^{\cdot}$) and the same radicals are consumed in the quadratic termination stages [respectively reactions (5) and (6)], then k_{eff} depends as follows on [PC]:

$$k_{eff} = k_M + a\,[\mathrm{PC}]^{0.5}, \tag{4}$$

where $a = (k_2/\sqrt{k_5})\cdot\sqrt{2ek_M}$ (for $r_i^{\cdot}$) or $a = (k_4/\sqrt{k_6})\cdot\sqrt{2ek_M}$ (for $R^{\cdot}$). Expression (4) coincides with the experimentally determined dependence (1) for k_{eff}.

If only solvent radicals participate in induced decomposition of PC [reaction (4)] and the radicals disappear by means of cross disproportionation [reaction (7)], then the kinetic equation for consumption of PC has the form

$$-d\,[\mathrm{PC}]/dt = (k_M + b)[\mathrm{PC}],$$

where $b = 0.5e\{k_7^{-0.5}[ek_M(ek_Mk_7 + k_3k_4)]^{0.5} - k_M\}$.

Apparently, it is just this case which is realized when using acetonitrile with high initial PC concentrations, when k_{eff} does not depend on $[\mathrm{PC}]_0$ (Fig. 2, curve 5). For low concentrations $[\mathrm{PC}]_0$, k_{eff} follows the dependence in (1); under these conditions, chain termination should occur with participation of only the radicals formed from acetonitrile [reaction (6)].

We should note that stages (1)-(7) taken all together satisfactorily describe the experimental dependences of k_{eff} on [PC] only the initial stages of decomposition of PC. From Fig. 1, it is obvious that the experimental curves for decomposition of PC are described by first-order equations all the way up to high degrees of conversion, while according to the scheme, consumption of PC should be described by a power-law dependence such as $d[\mathrm{PC}]/dt = k_M[\mathrm{PC}] + a[\mathrm{PC}]^{3/2}$, and the semilogarithmic anamorphisms should deviate from a straight line. One reason for discrepancy between experiment and theory may be the participation of decomposition products of PC (cyclohexanol, cyclohexanone) in the induced decomposition (not

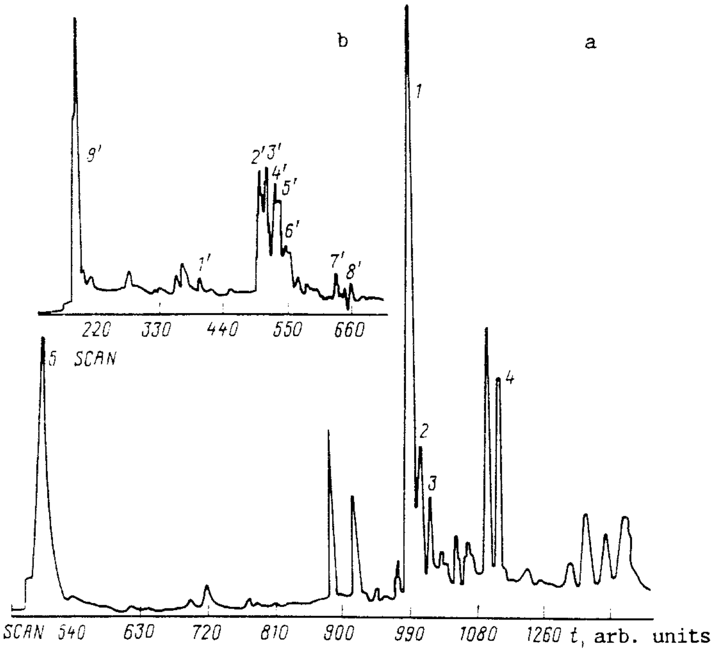


Fig. 4. Chromatograms of the decomposition products of PC in benzene (a) and chlorobenzene (b) at 60°C.

taken into account in the scheme), which leads to a change in the composition of the radicals and accordingly to a change in the rates of reactions in which they take part.

The following question is of interest: How does decomposition of PC occur upon reaction with free radicals? In the literature, a mechanism has been proposed for decomposition of PC in benzene, according to which the chain stage is connected with abstraction of the α-hydrogen atom of the cyclohexanone ring by alkoxycarboxyl radicals with subsequent decomposition of the unstable radical formed [14]. It is also suggested that the radicals driving the chain may be cyclohexoxyl radicals [15]; abstraction of a hydrogen atom in the β, γ, or δ position of the cyclohexanone fragment of the PC molecule cannot lead to rupture of the O—O bond, and most likely abstraction of an α-hydrogen atom leads to it [16].

The values of the kinetic parameters k_c obtained in the given work (Table 1) do not contradict the mechanism discussed in the literature for induced decomposition of PC by abstraction of a hydrogen atom. In fact, the rate constants for abstraction of a hydrogen atom by alkyl radicals are characterized by the value $k_H \sim 10^2\text{-}10^3$ liters/(moles·sec), constants for quadratic disappearance of alkyl radicals $k_t \sim 10^8\text{-}10^9$ liters/(moles·sec), and consequently, $k_H/\sqrt{k_t} \sim 10^{-2}$ [liters/(moles·sec)]$^{0.5}$, i.e., close to k_c in order of magnitude. The absence of chain decomposition of PC in alkylaromatic hydrocarbons and in all the investigated solvents in O_2 is connected with the fact that the chain propagation constants k_c for alkylaromatic and peroxyl radicals are not large.

In aromatic solvents not containing mobile C—H bonds (benzene, chlorobenzene), formation of cyclohexadienyl radicals $r_iArH^\cdot$ is possible, which display reducing properties and are not capable of abstracting an H atom from the PC molecule. In this case, the reaction of chain propagation can be represented as transfer of a hydrogen atom from the cyclohexadienyl radical to the peroxide bond, analogously to the decomposition of benzoyl peroxide induced by $C_6H_5—C_6H_6^\cdot$ radicals [17]:

$$8)\ r_iArH^\cdot + \mathrm{PC} \rightarrow r_iAr + \text{cyclo-}\ C_6H_{11}OH + r_i^\cdot + CO_2.$$

Cyclohexoxyl ($rO^\cdot$) and alkyl ($r'^\cdot$) radicals, formed from $rO^\cdot$ as a result of isomerization, can also participate in induced decomposition of PC in benzene and chlorobenzene. Their reaction with PC can occur in two directions: abstraction of a hydrogen atom from the peroxide molecule and reduction of the peroxide bond. Decomposition of PC induced by $rO^\cdot$ and $r'^\cdot$ radicals leads to formation of cyclohexanone and cyclohexanol, and when cyclohexadienyl radicals along with cyclohexanol radicals participate, we should obtain products whose molecules contain the fragments C_6H_5 or C_6H_4Cl.

TABLE 2. Mass Spectra of Products r_iAr Obtained in Decomposition of PC in Benzene (1-4) and Chlorobenzene (1'-8')

Number of peak	Mass spectrum (fragmentation)
1	M^+ 176(77), 158(10), 143(16), 133(100), 130(63), 117(59), 105(60), 104(64), 91(97), 77(32), 55(45)
2	M^+ 176(46), 158(7), 143(10), 130(46), 117(42), 104(51), 91(100), 77(11)
3	M^+ 176(57), 158(79), 143(85), 129(65), 104(100), 91(69), 77(25)
4	M^+ 176(<1), 94(100), 83(68), 77(18), 67(13), 55(94)
1'	M^+ 212(<1), 210(3), 183(5), 181(15), 156(5), 154(13), 141(6), 139(18), 127(31), 125(100)
2' and 4'	M^+ 212(10), 210(33), 169(35), 167(100), 156(10), 154(30), 141(15), 139(38)
3'	M^+ 212(17), 210(50), 194(4), 192(15), 179(4), 177(10), 175(14), 140(12), 138(35), 127(37), 125(100)
5'	M^+ 212(15), 210(48), 194(7), 192(9), 131(37), 129(66), 127(31), 125(59), 91(100)
6'	M^+ 212(81), 210(40), 166(12), 164(21), 153(18), 151(35), 140(7), 138(28), 127(19), 125(100)
7' and 8'	M^+ 212(<1), 210(<1), 130(30), 218(100), 113(10), 111(3), 83(80), 55(53)

The chromatograms of the reaction mixture upon decomposition of PC in benzene and chlorobenzene after consumption of the PC along with cyclohexanol and cyclohexanone (unresolved peaks 5 and 9', Fig. 4) include a series of isomeric products of the type r_iAr with molecular mass 176 in benzene (peaks 1-4) and 210 (212) in chlorobenzene (peaks 1'-8'). The fragment $r_i^{\cdot}$ represents a cyclohexoxyl radical (peaks 4, 7', and 8') or isomeric alkyl radicals $r'^{\cdot}$, including those with an open chain. A characteristic indicator of such compounds is the presence in the mass spectrum of a base ion with m/z 91 in benzene and 125 (127) in chlorobenzene (Table 2).

The presence of esters rO—Ar in the decomposition products of PC (rO—C_6H_5 in benzene and rO—C_6H_4Cl in chlorobenzene) is evidence that the cyclohexoxyl radicals $rO^{\cdot}$ are added to the aromatic ring and form cyclohexadienyl radicals.

Adducts of the type $-\overset{|}{\underset{|}{C}}-Ar$ are obtained when alkyl radicals participate, which in turn are formed as a result of isomerization of cyclohexoxyl radicals [12, 13], and also in exchange reactions of free radicals with cyclohexanol and cyclohexanone. Apparently a large number of such compounds are connected with involvement of cyclohexanol and cyclohexanone in the free-radical process.

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ELECTROCHEMICAL REDUCTION OF THE COMPLEX OF Zn(II) WITH 4-(2'-OXOPROPYLIDENE)-2,2,5,5-TETRAMETHYL-3-IMIDAZOLIDINE-1-OXYL

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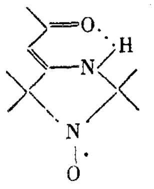
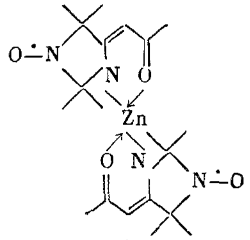
Polarography and electrolysis/EPR were used to study the electrochemical reduction of the complex of Zn(II) with 4-(2'-oxopropylidene)-2,2,5,5-tetramethyl-3-imidazolidine-1-oxyl in acetonitrile. The reaction center in the electron transfer to the protonated ligand $\dot{L}H$ is the nitroxyl radical. It has been found that $E_{1/2}$ of the reduction is highly sensitive toward the presence of proton donors. A stepwise reduction of the radical centers of the ligands in stages has been established in the ZnL_2 complex. It has been concluded that exchange reactions take place between the products of two- and three-electron reduction and the initial molecule.

The electrochemical conversions of metal complexes are frequently accompanied by a change in the degree of oxidation of the metal ion. The conversions of complexes, containing electrochemically active and paramagnetic ligands are of great interest from a theoretical standpoint.

The objective of the present work was to study the mechanism of the electrochemical reduction of the complex ZnL_2, in which unprotonated 4-(2'-oxopropylidene)-2,2,5,5-tetramethyl-3-imidazolidine-1-oxyl ($\dot{L}H$) acts as the ligand L



$\dot{L}H$



ZnL_2

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