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Liquid Phase Oxidation of C_6–C_8 Cycloolefins with Air Oxygen Catalyzed by Metal-Containing Microstructured Carbon Materials

Kh. M. Alimardanov and N. I. Garibov

Yu.G. Mamedaliev Institute of Oil Chemistry Processes, Azerbaijan National Academy of Sciences, ul. Khodzhaly 30, Baku, 1025 Azerbaijan
e-mail: hafiz-alimardanov@yahoo.com

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Abstract—Catalytic oxidation of cyclohexene and its methyl and vinyl derivatives with air oxygen in the presence of Co- and Mo-Co-modified microstructured carbon materials has been studied. Regardless of structure of the parent cycloalkene, cobalt-containing samples at 40–50°C are highly selective towards formation of corresponding hydroperoxides, whereas molybdenum-cobalt containing samples are selective towards cycloalkenes epoxidation. The ratio of epoxide to unsaturated alcohol strongly depends on the structure of the starting substrate.

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Presently, one of the preferred approaches to preparation of oxygen-containing compounds (alcohols, ketones, and epoxides) is one-stage liquid phase oxidation of cyclic saturated and unsaturated hydrocarbons in the presence of soluble salts or complex compounds of transition metals. Depending on the structure of starting substrates, nitric acid, ozone, molecular oxygen, organic peroxides and hydroperoxides, and hydrogen peroxide are used as oxidants [1–4].

Homogeneous catalysts, although highly selective, are known to easily react with the oxidation products, and their industrial applications are thus limited due to necessity their isolation and activation in specially developed units.

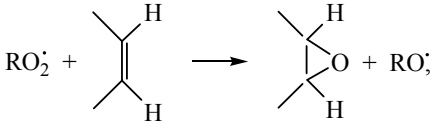
Recently, application of heterogeneous catalysts in the liquid phase oxidation with organic hydroperoxides and hydrogen peroxide has been reported [5]. Transition metal compounds immobilized on mesoporous and disordered silicates as well as on microstructured carbon materials has been found sufficiently reactive and selective [3–7].

The substrate oxidation pathway usually depends on both the oxidant nature and the catalyst structure [8–11]. For instance, upon oxidation with peroxyacids or peroxides with molybdenum or tungsten catalyst, the electrophilic addition of active oxygen to the substrate double bond occurs, and the primary product is the corresponding epoxide [9]. Oxidation of unsaturated hydrocarbons with molecular oxygen in the presence of cobalt compounds proceeds via allyl mechanism through interaction of the $[Co^{n+}\cdots O{=}O]$ activated complex with the substrate α-CH group. This evidently corresponds to the radical chain reaction, favorable due to high mobility of the α-hydrogen atoms [12] and steric possibility of the oxidant attack according to the following scheme.

$$RH + [Co^{n+}\cdots O_2] \rightarrow R^{\cdot} + HOO^{\cdot} + Co^{n+},$$

$$R^{\cdot} + O_2 \rightarrow ROO^{\cdot},$$

$$RO_2^{\cdot} + RH \rightarrow ROOH + R^{\cdot},$$



$$ROOH \rightarrow RO^{\cdot} + OH^{\cdot},$$

$$RO^{\cdot} + RH \rightarrow ROH + R^{\cdot},$$

$$2RO_2^{\cdot} \rightarrow R^{\cdot}{-}C{=}O + ROH + O_2.$$

The so obtained reaction mixtures, along with the primary oxidation products (hydroperoxides), contain the products of their secondary reactions with substrate (epoxides, unsaturated alcohols, and ketones) [13].

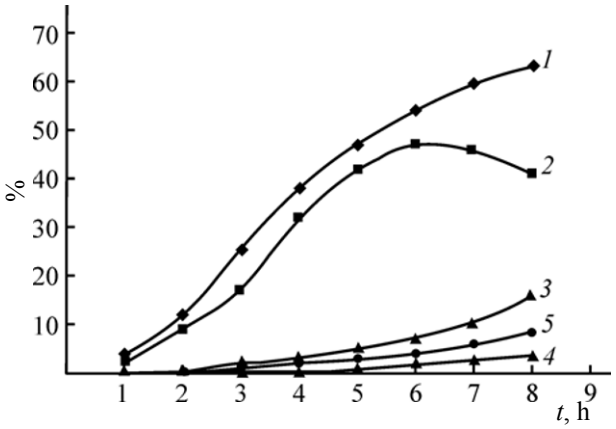


Fig. 1. Kinetics of cyclohexene conversion and the oxidation products accumulation. Catalyst: $CoBr_2$ (0.5×10^{-3} mol g^{-1} of Co^{2+}) on carbon, treated with H_3PO_4 and H_2O_2; 60°C, air flow rate 30 L h^{-1}. (*1*) Conversion of cyclohexene, (*2*) cyclohexenyl hydroperoxide, (*3*) cyclohexen-1-ol-3, (*4*) cyclohexen-1-one-3, and (*5*) epoxycyclohexane.

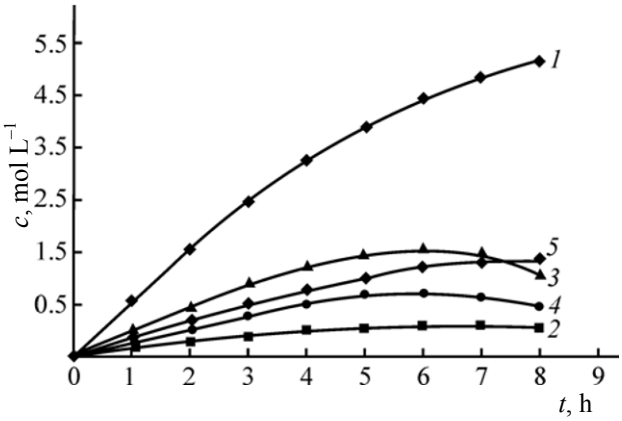


Fig. 2. Kinetics of cyclohexene conversion and the oxidation products accumulation. Catalyst: $CoBr_2$–$MoOBr_3$ on carbon, treated with H_3PO_4 and H_2O_2; 60°C, air flow rate 30 L h^{-1}. (*1*) Conversion of cyclohexene, (*2*) cyclohexenyl hydroperoxide, (*3*) cyclohexen-1-ol-3, (*4*) cyclohexen-1-one-3, and (*5*) epoxycyclohexane.

The aim of this work was to investigate the catalytic properties of superfine carbon materials modified with cobalt(II) bromide and molybdenum(V) oxobromide in oxidation of cyclohexene and its methyl and vinyl derivatives.

As seen from the data collected in Figs. 1–3 and in Tables 1–3, in the cases of the studied cycloalkene substrates the ratio of the oxidation products strongly depended on the nature of catalyst metal cation and its ligand surrounding. In particular, in the case of systems containing only Mo^{n+} catalysts, the activation of molecular oxygen and oxidation of substrates were slow. On the contrary, cobalt-containing catalysts were highly efficient in the substrates oxidation with air oxygen. The highest selectivity with respect to hydroperoxide was achieved in the case of $CoBr_2$-modified microstructured carbon material with Co^{n+} content of $(2–3)\times10^{-3}$ mol g^{-1}. The selectivity decreased in the series of substrates: 3-methylcyclohexene > cyclohexene > 1-methylcyclohexene > 4-vinylcyclohexene.

The hydroperoxides yield could be altered by changing the ligand surrounding of Co^{n+} and by modification of the complexes preparation procedure. The samples of cobalt-containing carbon materials obtained without preliminary treatment with the solution of phosphoric acid or of C_1–C_2 carboxylic acids were not catalytically active; cyclohexene conversion with such catalysts was not higher than 8–12%.

In the cases of the catalysts prepared with phosphoric acid (or C_1–C_2 carboxylic acids) treatment, the decomposition of hydroperoxides, primary products of oxidation of cycloalkenes, slowed down. That could be explained either by competing of the acids and the formed hydroperoxides for solvating the intermediate active complex, or by accumulation of inactive three-component intermediate $[Co^{n+}HA\cdot ROOH]$ at the catalyst surface. That intermediate further decomposed according to the following scheme.

$$[Co^{n+}\cdot HA\cdot ROOH] \rightarrow [Co^{n+}\cdots HA] + ROOH.$$

Subsequent conversion of hydroperoxide at 40–60°C proceeded with extended induction period, favoring

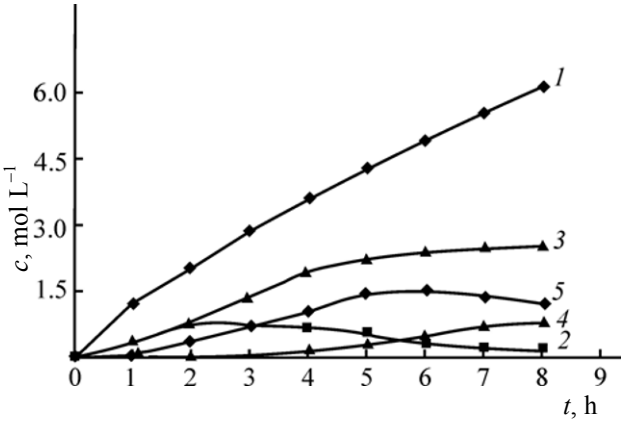


Fig. 3. Kinetics of 3-methylcyclohexene conversion and the oxidation products accumulation. Catalyst: $CoBr_2$ (0.5×10^{-3} mol g^{-1} of Co^{2+}) on carbon, treated with H_3PO_4 and H_2O_2; 70°C, air flow rate 30 L h^{-1}. (*1*) Conversion of 3-methylcyclohexene, (*2*) 3-methylcyclohexenyl hydroperoxide, (*3*) isomers of 3-methylcyclohexenol, (*4*) isomers of 3-methylcyclohexenone, and (*5*) 1,2-epoxy-3-methylcyclohexane.

Table 1. Liquid phase oxidation of cyclohexene with air oxygen in the presence of microstructured carbon material modified with Co(II), Mo(V,VI), H_3PO_4 and H_2O_2[a]

Modifier	Conversion of cyclohexene, %	Composition of oxidate, wt %					
		hydroperoxide	epoxide	unsatrurated alcohol	unsatrurated ketone	cyclohexene	nonidentidied compounds
AG-3 Carbon carrier							
$(CH_3COO)_2Co$	39.4	9.5	9.5	12.9	9.3	57.2	1.6
$CoCl_2$	47.6	16.5	5.8	13.4	15.0	46.5	2.8
$CoBr_2$ (**I**)	51.1	45.9	1.2	2.7	3.1	45.1	2.0
$Co(NO)_2$	58.4	12.1	9.1	15.6	23.4	36.5	3.3
$MoCl_5$	14.5	1.2	7.2	7.7	0.8	83.1	–
$MoOBr_3$	27.0	4.1	8.5	11.3	4.8	68.4	2.8
$(NH_4)_2MoO_4$	9.6	1.5	3.2	4.4	2.4	88.5	–
Na_2 MoO_4	9.2	1.4	3.2	4.3	2.1	89.0	–
$CoBr_2$ + $MoOBr_3$ (**II**)	52.7	5.1	16.8	18.1	12.5	41.8	5.8
AG-2 Carbon carrier							
$CoBr_2$ (**III**)	52.8	46.5	3.8	5.0	2.7	39.8	2.2
$CoBr_2$ + $MoOBr_3$ (**IV**)	47.1	4.0	17.8	19.9	7.7	47.8	2.8
Microstructured carbon material[b]							
$CoBr_2$ (**V**)	53.7	46.8	3.1	5.7	3.1	38.9	2.4
$CoBr_2$ + $MoOBr_3$ (**VI**)	55.3	6.9	16.3	20.1	12.5	39.5	4.7

[a] Me^{n+}:H_3PO_4:H_2O_2 = 4:1:4, (T = 50°C, τ = 6 h, air flow rate 20 L h^{-1}). [b] Catalyst was prepared according to [14].

the hydroperoxide accumulation in the mixture. However, at higher temperature (60–80°C) the hydroperoxides decomposition was accelerated; furthermore, the transformation was not selective: significant amount of non-identified oxygen-containing oligomers was accumulated along with the epoxide, unsaturated alcohols, and ketones.

With the two-component catalyst applied on carbon material, the metal complex participated in two simultaneous processes: the above-mentioned oxygen activation and the transfer of electrophilic oxygen from hydroperoxide to the more nucleophilic olefin double bond. Thus, the reaction proceeded via the mixed radical-ionic mechanism. The oxidation of cycloalkenes was highly selective with respect to the total of epoxide and unsaturated alcohol. In the described case, similarly to homogeneous catalysis, the components of catalytic system acted additively [12].

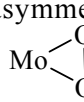
The structure of Mo-Co-containing carbon material was studied by means of IR spectroscopy in KBr pellet. In the IR spectrum of sample not treated with hydrogen peroxide solution (Fig. 4), the intense bands at 910, 940, and 990 cm^{-1} characteristic of MoO^{3+} and MoO^{4+} species were observed. Stretching of PO_4^{3-} group was assigned to the bands at 1090 and 1025 cm^{-1}. Following [15], the bands at 580 and 705–720 cm^{-1} were assigned to the products of oxidation and hydrolysis of $CoBr_2$, in particular, to $Co(OH)_2^+$ formed according to the scheme:

$$2CoBr_2 + O_2 + 2H_2O \rightarrow 2Co(OH)_2Br + Br_2.$$

After addition of hydrogen peroxide, IR spectrum contained intense bands at 920 and 955 cm^{-1} (MoO^{4+}), whereas the band at 990 cm^{-1} was weakened. A series of weaker bands appeared at 890, 680, 592, 562, 531, and 515 cm^{-1}. According to [16], they were assigned to

Table 2. Oxidation of 1-methylcyclohexene with air oxygen in the presence of modified microstructured carbon material (V_{air} = 20 L h^{-1})

T, °C	Time, h	Conversion, %	Composition of liquid catalyzate, wt %						Selectivity, %	
			hydro-peroxide	epoxide	alcohol	ketone	1-methylcyclo-hexene	nonidentidied compounds	hydroper-oxide	epoxide, alcohol
Catalyst **V**										
50	6	43.8	39.2	5.2	2.4	1.4	51.8	–	83.3	8.6
60	6	47.0	42.0	5.7	2.8	2.2	46.5	0.8	76.5	16.5
70	6	54.6	31.7	11.7	8.9	6.4	39.8	1.5	49.6	37.0
80	6	58.5	28.5	13.4	8.6	10.2	36.2	3.1	41.9	36.9
60	4	32.1	32.9	3.0	1.3	1.0	61.8	–	84.1	6.0
60	8	51.4	38.7	10.1	6.5	0.7	42.4	1.6	64.8	31.9
60	10	57.5	33.9	13.7	9.5	2.8	36.8	3.3	51.1	39.8
Catalyst **IV**										
60	6	44.2	3.6	20.9	14.5	4.5	50.9	5.6	6.6	75.3
70	6	49.4	3.2	22.9	16.5	5.1	45.7	6.6	5.4	75.6
80	6	53.0	3.7	24.4	16.8	4.4	41.9	8.8	5.9	74.6
Catalyst **VI**										
60	6	50.2	2.2	24.2	18.8	2.7	44.8	7.3	3.7	81.8
70	6	54.7	2.8	26.3	19.9	3.5	40.5	7.0	4.3	81.0
80	6	59.0	1.8	27.1	22.3	4.5	36.4	7.9	2.6	80.8

stretching vibrations of peroxide bond as well as to symmetric and asymmetric vibrations of the MoO_2 cyclic fragment.  . It was suggested that, similarly to the case of $H_3PW_{12}O_{40}$ heteropolyacids [16], the interacttion of $MoOBr_3 \cdot 2HBr$ with H_3PO_4 and excess of H_2O_2 led to formation of low-activity aquatic complex and the highly active molybdenyl peroxo-complex. The latter one participated in the transfer of cobalt-activated oxygen from the cyclohexene hydro-peroxide (or cyclohexenylperoxo radical) to the substrate double bond.

The composition and ratio of the oxidation products strongly depended on the parent cycloalkene structure, due to different electron density at the α-carbon atoms. In particular, oxidation of cyclohexene in the presence of catalysts **V** and **VI** gave approximately equal

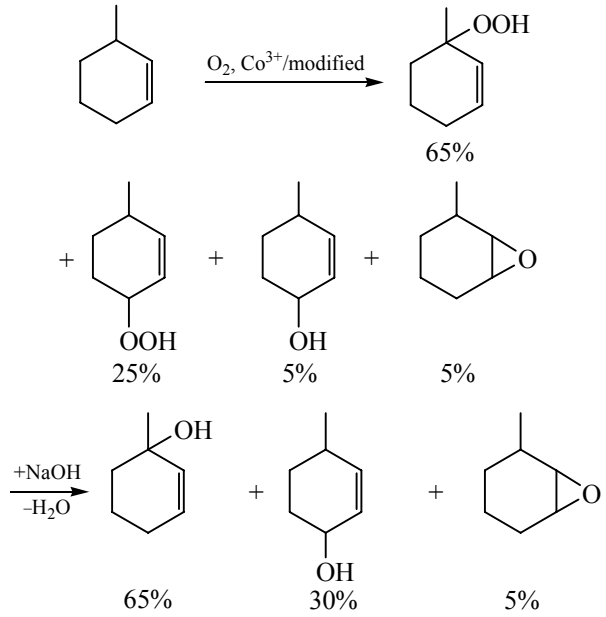
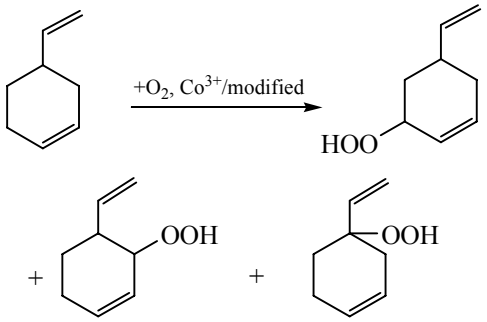


Table 3. Oxidation of 4-vinylcyclohexene with air oxygen in the presence of modified microstructured carbon material (V_{air} = 20 L h^{-1})

T, °C	Time, h	Conversion, %	Composition of liquid catalyzate, wt %						Selectivity, %	
			hydro-peroxide	epoxide	alcohol	ketone	4-vinyl-cyclohexene	nonidentidied compounds	hydro-peroxide	sum of epoxide and alcohol
Catalyst **V**										
50	6	28.4	23.0	5.4	4.8	–	66.8	–	66.8	33.2
60	6	31.2	25.5	5.8	4.9	–	63.8	–	68.0	32.0
70	6	35.0	27.6	6.1	6.5	–	59.8	–	66.1	33.9
80	6	44.5	21.6	11.2	8.0	3.0	49.9	6.3	41.5	41.7
90	6	51.0	21.2	12.4	9.1	4.4	44.3	8.6	36.3	41.6
70	4	29.7	24.6	5.5	4.5	–	65.4	–	68.5	31.5
70	8	41.4	24.4	8.6	7.5	1.9	53.1	4.5	50.4	37.6
70	10	44.7	22.5	9.5	8.8	2.0	49.3	7.9	43.5	39.8
Catalyst **IV**										
70	6	34.0	5.7	14.8	12.1	–	61.5	5.9	13.9	74.3
90	6	53.0	3.1	19.0	16.5	7.7	42.1	11.6	5.1	65.3
Catalyst **VI**										
70	6	38.2	3.4	18.9	14.9	2.0	57.7	3.1	7.3	82.3
90	6	55.6	2.7	21.9	18.1	6.7	39.7	10.9	4.1	70.8

amounts of epoxide and unsaturated alcohol. In the case of 3-methylcyclohexene, the hydroperoxide group formed at the tertiary carbon was more stable, the hydroperoxides were practically the only products (yield 18–22%) of oxidation catalyzed by **IV** at 40–50°C during 4 h.



After the alkaline reduction of 3-methylcyclohexene oxidate, the isomeric unsaturated alcohols were mainly identified, 3-methylcyclohexen-1-ol-3 being the major one.

The amount of 3-methylcyclohexen-1-ol-3 was determined according to the product of its dehydration at 180°C on Al_2O_3 promoted with 2 wt % NaOH–2-methylcyclohexadiene-1,3.

The oxidation of 4-vinylcyclohexene at 50°C catalyzed by **III** proceeded similarly. However, in that case the attack of hydroperoxide radical could occur via three pathways.

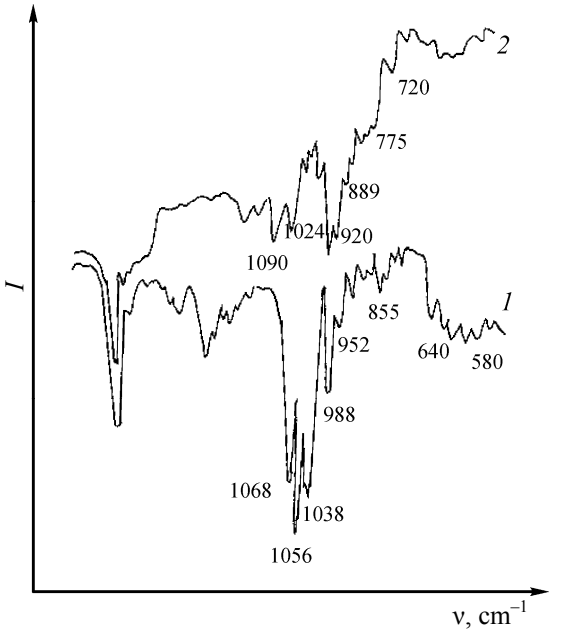


Fig. 4. IR spectra of solid mixture of $MoOBr_3 \cdot 2HBr$ with $CoBr_2$ (*1*) after treatment with a mixture of H_3PO_4 and H_2O_2 and (*2*) applied on microstructured carbon material, after four oxidation runs.

Reduction of the so obtained mixture with aqueous sodium hydroxide led to a complex mixture of unsaturated alcohols. When the oxidation was catalyzed by **V** or **VI**, the amount of 1,2-epoxy-4-vinylcyclohexane obtained was practically equal to the total of unsaturated alcohols.

In the case of 3-methylcyclohexene oxidation with the catalysts **V** and **VI**, the amount of unsaturated alcohol isomers was more than the corresponding epoxide. However, the oxidation of 1-methylcyclohexene revealed quite the opposite result. The presence of methyl group at the double bond accelerated the substrate epoxidation, and in presence of catalysts **V** and **VI** the epoxide is the major product of 1-methylcyclohexene oxidation.

EXPERIMENTAL

The parent cyclohexene and methylcyclohexenes were obtained by dehydration of corresponding alcohols on A-1 aluminum oxide containing 2.0 wt % of sodium hydroxide. butadiene-1,3 according to [17].

The microstructured carbon material was obtained by the reaction of metal aluminum with carbon tetrachloride according to [14]. To prepare the catalysts, the carbon material was doped with ethanol solutions of cobalt [$Co(CH_3COO)_2$, $Co(NO_3)_2$, $CoCl_2$, and $CoBr_2$] and molybdenum [$MoCl_5$, $MoOBr_3$, $(NH_4)_2MoO_4$, and Na_2MoO_4] salts during 24 h. Then, the catalyst was dried at 120–140°C and treated with 85 wt % phosphoric aci4-Vinylcyclohexene was prepared by dimerization of d and 30 wt % hydrogen peroxide. The fine dispersed AG-2 and AG-3 charcoals were used as a support. Concentration of metals in the so prepared individual cobalt, molybdenum, and mixed cobalt-molybdenum systems was of $(0.5–3.0)\times10^{-3}$ mol g^{-1}.

The oxidation experiments were performed in glass reactor of bubbling type equipped with the Schott filter, the thermocouple, the system of condensers and traps, without solvent. The purified oxygen flow rate was of 30 L h^{-1} per 100 g of the raw material. The formed hydroperoxide was determined by iodometric titration. The composition of oxidate was evaluated after reduction with sodium hydroxide solution, by GLC with Tsvet-500 chromatograph with flame ionization detector, 2000×2 mm column filled with 5 wt % of polyethyleneglycol succinate on Chromosorb, with helium as carrier gas, column temperature of 160°C, and evaporator temperature of 280°C.

The composition of catalysts was confirmed by IR, EPR, and UV spectroscopy. Fourier IR absorption spectra were registered with Perkin-Elmer FT-IR Spectrum BX spectrometer in KBr pellets at 450–4400 cm^{-1}. EPR spectra were recorded with JEOL YES-PE (9300 MHz) radiospectrometer at 77 and 300 K. Diphenylpicrylhydrazyl (g = 2.0036) was used as reference while evaluation of g-factor. Electron absorption spectra were registered with UV/Vis Specord M 40 spectrometer (Germany).

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