

## Hydrogen Hydroperoxide Oxidation of Ethane and Other Alkanes Catalyzed by Chromium Compounds

G. Süß-Fink\* and G. B. Shul'pin\*\*

\* *Institut de Chimie, Université de Neuchâtel, avenue de Bellevaux 51, CH-2000 Neuchâtel, Switzerland*

\*\* *Semenov Institute of Chemical Physics, Russian Academy of Sciences, ul. Kosygina 4, Moscow, 117977 Russia*

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**Abstract**—Chromium oxo derivatives ( $\text{H}_2\text{CrO}_4$ ) catalyze the effective oxidation of ethane and other saturated hydrocarbons with hydrogen peroxide or *tert*-butyl hydroperoxide in an acetonitrile solution at 60°C. Alkyl hydroperoxides, ketones (aldehydes), and alcohols are formed as main products. The oxidation of ethane gives ethyl hydroperoxide, acetaldehyde, ethanol, and acetic acid. The turnover frequency reaches 620  $\text{h}^{-1}$  in this case, and the product yield in terms of  $\text{H}_2\text{O}_2$  consumed is 21%.

### INTRODUCTION

Selective oxidative functionalization of very inert lower saturated hydrocarbons (ethane and methane) under mild conditions (i.e., at temperatures below 100°C) remains an important task of metal complex catalysis [1–4]. In principle, soluble chromium complexes [5, 6] are suitable catalysts [7–9] for alkane oxidation processes, although these processes have been developed basically for hydrocarbons with relatively reactive C–H bonds (namely, containing benzyl groups [10–13] or tertiary C–H bonds [14]) and alkylbenzenes [15, 16]. Earlier, we showed that relatively inert cyclohexane could be oxidized with iodosobenzene [17], air [18–27], or hydrogen peroxide [28, 29] at room temperature in the presence of some chromium complexes as a catalyst. However, the yields of products were low.

In this paper, we report the oxidation of saturated hydrocarbons, including particularly unreactive ethane, with hydrogen peroxide at a temperature of 60°C.

### EXPERIMENTAL

The oxidation reactions of lower alkanes were carried out in a steel autoclave (of 100 ml capacity with a reaction solution volume of 5 ml), and those of higher alkanes were carried out in a cylindrical glass vessel with a jacket through which water from a thermostat was circulated (the solution volume was 10 ml). The reaction mixture sampled (in 0.5 ml portions) at certain time intervals was analyzed by gas–liquid chromatography both before and after the 10–20-min treatment of a sample with an excess of solid triphenylphosphine. The comparison of the chromatograms of samples before and after reducing the reaction solution with

triphenylphosphine (the method developed previously as reported in [30–34]) allowed the actual concentrations of ketones or aldehydes, alcohols, and alkyl hydroperoxides present in the reaction medium to be determined. The GLC analyses were performed with a DANI-86.10 chromatograph on a 0.25 m  $\times$  0.32 mm  $\times$  0.25  $\mu\text{m}$  PLOT column with the CP-WAX52CB packing, an SP-4400 integrator, and helium as a carrier gas, and with an LKhM-80-6 chromatograph on 2-m columns packed with 5% Carbowax 1500-coated Inerton AW-HMDS (0.25–0.315 mm) with argon as a carrier gas. Chromatograms were preliminarily calibrated with authentic compounds, the alkane oxidation products. Acetonitrile used as a solvent was distilled over phosphorus pentoxide prior to the experiment.

### RESULTS AND DISCUSSION

This work is the first study of the  $\text{CrO}_3$ -catalyzed oxidation of higher and lower saturated hydrocarbons with hydrogen peroxide and *tert*-butyl hydroperoxide at elevated temperatures (up to 60°C). The hydrogen peroxide oxidation of cyclooctane catalyzed by  $\text{H}_2\text{CrO}_4$  is exemplified in Fig. 1. The principal reaction product is the alkyl hydroperoxide, which gradually decomposes during the oxidation reaction yielding primarily cyclooctanone. When pyridine is added, the reaction is accelerated, although insignificantly; the reaction rate is nearly 15% lower in the absence of the base. After 8 h, the turnover frequency becomes as high as 280. The dependence of product concentrations on the concentrations of  $\text{CrO}_3$  and  $\text{H}_2\text{O}_2$  is presented in Tables 1 and 2, respectively.

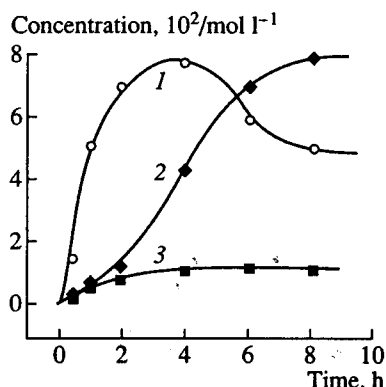


Fig. 1. Buildup curves for the formation of (1) cyclooctyl hydroperoxide, (2) cyclooctanone, and (3) cyclooctanol in the oxidation of cyclooctane ( $0.6 \text{ mol l}^{-1}$ ) with hydrogen peroxide ( $0.6 \text{ mol l}^{-1}$ ) in the presence of pyridine ( $0.06 \text{ mol l}^{-1}$ ) catalyzed by  $\text{H}_2\text{CrO}_4$  ( $5 \times 10^{-4} \text{ mol l}^{-1}$ ) at  $60^\circ\text{C}$ .

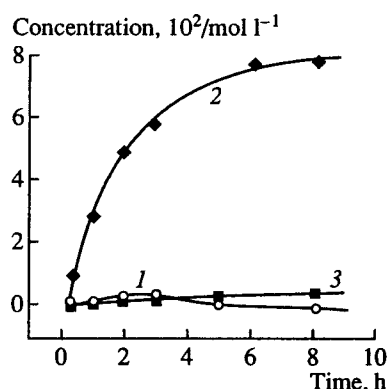


Fig. 2. Buildup curves for the formation of (1) cyclooctyl hydroperoxide, (2) cyclooctanone, and (3) cyclooctanol in the  $\text{H}_2\text{CrO}_4$ -catalyzed ( $5 \times 10^{-4} \text{ mol l}^{-1}$ ) oxidation of cyclooctane ( $0.6 \text{ mol l}^{-1}$ ) with *tert*-butyl hydroperoxide ( $0.35 \text{ mol l}^{-1}$ ) at  $60^\circ\text{C}$ .

In the oxidation by *tert*-butyl hydroperoxide (Fig. 2), the current concentration of cyclooctyl hydroperoxide is retained at a low level, and the reaction mixture contains primarily cyclooctanone. It is interesting that the addition of pyridine leads to some decrease in the reaction rate and product yield in this case. The oxidation with hydrogen peroxide in acetic acid is much less effective. For example, the 7-h reaction at  $60^\circ\text{C}$  yields cyclooctanone and cyclooctanol only in concentrations of  $0.011$  and  $0.024 \text{ mol l}^{-1}$ , respectively, after triphenylphosphine treatment.

The oxidation of *n*-octane in acetonitrile with hydrogen peroxide produced a mixture of possible positional isomers (Table 3). From the concentrations of the formed alcohols alone, the unnormalized ratio C(1) : C(2) : C(3) : C(4), i.e. the relative reactivity of hydrogen atoms in the 1-, 2-, 3-, and 4-positions of the hydrocarbon chain, can be calculated as  $1.0 : 4.0 : 3.6 : 3.3$ . This selectivity parameter is somewhat higher than

in the case of oxidation with the  $\text{H}_2\text{O}_2$ - $h\nu$  system ( $1.0 : 2.8 : 2.9 : 2.7$ ). The product buildup in the *n*-octane oxidation with *tert*-butyl hydroperoxide is illustrated in Table 4.

The selectivity parameters for the oxidation of *cis*- and *trans*-decalin isomers and adamantane are summarized in Table 5. The data presented in Table 5 indicate that the selectivity parameters for chromium-containing systems with both peroxide oxidants (entries 1 and 2) differ from the corresponding values obtained for systems that generate hydroxyl radicals (entries 3 and 5) and the system producing both hydroxyl and *tert*-butoxyl radicals (entry 4). Note that the systems based on chromium complexes do not display stereoselectivity. Based on the data obtained, it may be assumed that both reactions catalyzed by chromium complexes proceed without the formation of free hydroxyl radicals (at least via one of the routes of the process) and, probably, involve the attack of peroxy derivatives at C-H bonds.

Table 1. Initial oxidation rate (cyclooctanone and cyclooctanol concentrations,  $\text{mol l}^{-1}$ ) depending on the  $\text{CrO}_3$  concentration in the cyclooctane oxidation with hydrogen peroxide in MeCN

$[\text{CrO}_3]$	Cyclooctanone, $\text{mol l}^{-1}$	Cyclooctanol, $\text{mol l}^{-1}$
$10 \times 10^{-4}$	0.0057	0.073
$5 \times 10^{-4}$	0.0013	0.037
$2.5 \times 10^{-4}$	0.0010	0.023
$1.25 \times 10^{-4}$	0.0005	0.019

Conditions:  $[\text{cyclooctane}]_0 = 0.62 \text{ mol l}^{-1}$ ,  $[\text{H}_2\text{O}_2]_0 = 0.5 \text{ mol l}^{-1}$ ,  $60^\circ\text{C}$ , 50 min. The concentrations were measured after reduction with triphenylphosphine.

Table 2. Initial oxidation rate (cyclooctanone and cyclooctanol concentrations,  $\text{mol l}^{-1}$ ) depending on the  $\text{H}_2\text{O}_2$  concentration in the cyclooctane oxidation with hydrogen peroxide in MeCN

$[\text{H}_2\text{O}_2]_0$	Cyclooctanone, $\text{mol l}^{-1}$	Cyclooctanol, $\text{mol l}^{-1}$
0.06	0.00065	0.0055
0.12	0.0009	0.011
0.24	0.0015	0.024
0.36	0.0015	0.023
0.60	0.0013	0.037

Conditions:  $[\text{cyclooctane}]_0 = 0.62 \text{ mol l}^{-1}$ ,  $[\text{CrO}_3]_0 = 0.5 \times 10^{-3} \text{ mol l}^{-1}$ ,  $60^\circ\text{C}$ , 50 min. The concentrations were measured after reduction with triphenylphosphine.

**Table 3.**  $\text{H}_2\text{CrO}_4$ -catalyzed oxidation of *n*-octane with hydrogen peroxide in MeCN (shown is the product concentration,  $\text{mol l}^{-1}$ ; ONE is ketone, AL is aldehyde, and OL is alcohol; the number specifies the position of the functional group in the alkane chain)

Reaction time, h	Carbonyl compounds				Alcohols			
	AL	ONE-4	ONE-3	ONE-2	OL-4	OL-3	OL-2	OL-1
20	0.00013	0.0003	0.0004	0.0004	0.0047	0.0051	0.0050	0.00017
60	0.00065	0.0010	0.0012	0.0010	0.0123	0.0134	0.0141	0.0040
120	0.00071	0.0022	0.0025	0.0019	0.0165	0.0182	0.0195	0.0053
180	0.0017	0.0039	0.0044	0.0036	0.0165	0.0181	0.020	0.0050
300	0.0018	0.0052	0.0058	0.0048	0.0135	0.0152	0.017	0.0050
480	0.0015	0.0068	0.0083	0.0083	0.0100	0.0110	0.013	0.0055

Conditions:  $[\textit{n}\text{-octane}]_0 = 0.62 \text{ mol l}^{-1}$ ,  $[\text{H}_2\text{O}_2]_0 = 0.5 \text{ mol l}^{-1}$ ,  $[\text{CrO}_3] = 0.5 \times 10^{-3} \text{ mol l}^{-1}$ ,  $60^\circ\text{C}$ . The concentrations were measured after reduction with triphenylphosphine.

**Table 4.**  $\text{H}_2\text{CrO}_4$ -catalyzed oxidation of *n*-octane with *tert*-butyl hydroperoxide in MeCN (shown is the product concentration,  $\text{mol l}^{-1}$ ; ONE is ketone and OL is alcohol; the number indicates the functional-group position in the alkane chain; the aldehyde was not found in a detectable concentration)

Reaction time, h	Ketones			Alcohols			
	ONE-4	ONE-3	ONE-2	OL-4	OL-3	OL-2	OL-1
20	0.0004	0.00043	0.00041	0.00043	0.00043	0.00078	0.00017
60	0.0012	0.0013	0.0015	0.00043	0.0005	0.0010	0.0003
120	0.0021	0.0022	0.0028	0.00047	0.00043	0.00093	0.00026
180	0.0029	0.0031	0.0038	0.00058	0.00061	0.0010	0.0002
360	0.0047	0.0049	0.0063	0.0004	0.00045	0.0009	0.00021
600	0.0059	0.0062	0.0081	0.00023	0.00062	0.00053	0.00021

Conditions:  $[\textit{n}\text{-octane}]_0 = 0.62 \text{ mol l}^{-1}$ ,  $[\textit{t}\text{-BuOOH}]_0 = 0.35 \text{ mol l}^{-1}$ ,  $[\text{CrO}_3] = 0.5 \times 10^{-3} \text{ mol l}^{-1}$ ,  $60^\circ\text{C}$ . The concentrations were measured after reduction with triphenylphosphine.

**Table 5.** Selectivity of alkane oxidation with  $\text{ROOH-H}_2\text{CrO}_4$  and some other systems in MeCN<sup>a</sup>

Run no.	Oxidant system	Oxidation substrate (selectivity parameter) <sup>b</sup>		
		<i>cis</i> -Decalin ( <i>cis/trans</i> )	<i>trans</i> -Decalin ( <i>trans/cis</i> )	Adamantane ( $3^\circ : 2^\circ$ )
1	$\text{H}_2\text{O}_2\text{-H}_2\text{CrO}_4$ ( $60^\circ\text{C}$ )	3.9	4.3	1.4
2	<i>t</i> -BuOOH- $\text{H}_2\text{CrO}_4$ ( $50^\circ\text{C}$ )	4.3	6.1	4.0
3	$\text{H}_2\text{O}_2\text{-hv}$ ( $20^\circ\text{C}$ )	1.3	2.7	0.9
4	<i>t</i> -BuOOH- $\text{hv}$ ( $20^\circ\text{C}$ )	5.1	4.4	1.1
5	$\text{H}_2\text{O}_2\text{-VO}_3^-\text{-PCA}^c$	2.1	2.4	0.7
6	$\text{H}_2\text{O}_2\text{-Mn(IV)}^d\text{-CH}_3\text{COOH}$	0.12	33.4	2.0

<sup>a</sup> Product concentrations were measured after reduction with  $\text{PPh}_3$ .

<sup>b</sup> The parameter *trans/cis* =  $[\textit{trans}\text{-decalol-9}]/[\textit{cis}\text{-decalol-9}]$  is the concentration ratio of *trans*-decalol-9 to *cis*-decalol-9 formed in the oxidation of isomeric decalins. The  $3^\circ : 2^\circ$  parameter represents the normalized (with reference to the number of hydrogen atoms in each position) relative reactivity of hydrogen atoms at the tertiary and secondary carbon atoms.

<sup>c</sup> PCA is 2-pyrazinecarboxylic acid.

<sup>d</sup> The complex  $[\text{LMn}^{\text{IV}}(\text{O}_3)\text{Mn}^{\text{IV}}\text{L}]^{2+}$ , where L = 1,4,7-trimethyl-1,4,7-triazacyclononane.

**Table 6.** H<sub>2</sub>CrO<sub>4</sub>-catalyzed oxidation of ethane with hydrogen peroxide in acetonitrile<sup>a</sup>

Run no.	[H <sub>2</sub> O <sub>2</sub> ] <sub>0</sub> , mol l <sup>-1</sup>	Products, mol l <sup>-1</sup>				TOF <sup>b</sup>
		CH <sub>3</sub> CH <sub>2</sub> OOH	CH <sub>3</sub> CHO	CH <sub>3</sub> CH <sub>2</sub> OH	CH <sub>3</sub> COOH	
1	0.6	0.09	0.003	0.01	0	206
2	1.2	0.08	0.09	0.06	0.02	500
3	2.4	0.07	0.16	0.06	0.02	620

<sup>a</sup> Reaction conditions: ethane, 30 bar; H<sub>2</sub>CrO<sub>4</sub>, 5 × 10<sup>-4</sup> mol l<sup>-1</sup>; 1 h at 60°C. The product concentrations were measured before and after reduction with triphenylphosphine.

<sup>b</sup> Turnover frequency.

It turns out that inert ethane can be effectively oxidized with hydrogen peroxide in the H<sub>2</sub>CrO<sub>4</sub>-catalyzed reaction. As main products, ethyl hydroperoxide, acetaldehyde, ethanol, and acetic acid are formed. The turnover frequency attained in this case was 620 h<sup>-1</sup>, and the maximum total product yield was 21% in terms of H<sub>2</sub>O<sub>2</sub> reacted (Table 6, entry 3). As follows from Table 6, the relative product composition depends on the initial concentration of hydrogen peroxide. At a high initial concentration of the oxidant, the major product is acetaldehyde. Note that some amount of acetic acid that appears under the specified conditions is due to the hydrolysis of acetonitrile; however, this amount is small: only 0.002 mol l<sup>-1</sup> was found. We revealed that other lower alkanes, propane and *n*-butane, were also effectively oxidized by hydrogen peroxide under H<sub>2</sub>CrO<sub>4</sub>-catalyzed conditions (the turnover fre-

quency could be as high as 190 and 38, respectively, as shown by the results summarized in Table 7).

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**Table 7.** Oxidation of propane and *n*-butane with hydrogen peroxide in acetonitrile

Substrate	Pressure, bar	Products (concentration mol l <sup>-1</sup> )
Propane	5	CH <sub>3</sub> CH <sub>2</sub> CHO (0.009)
		CH <sub>3</sub> COCH <sub>3</sub> (0.026),
		CH <sub>3</sub> CH(OH)CH <sub>3</sub> (0.031),
		CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> OH (0.02),
		CH <sub>3</sub> CH <sub>2</sub> COOH (0.009)
Butane	1	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> CHO (0.0003),
		CH <sub>3</sub> COCH <sub>2</sub> CH <sub>3</sub> (0.0052),
		CH <sub>3</sub> CH(OH)CH <sub>2</sub> CH <sub>3</sub> (0.012),
		CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> CH <sub>2</sub> OH (0.0011)
		CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> COOH (0.00037)

Reaction conditions: H<sub>2</sub>CrO<sub>4</sub>, 5 × 10<sup>-4</sup> mol l<sup>-1</sup>; 1 h at 60°C.

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