Electronic Supplementary Material (ESI) for RSC Advances

RSC Advances RSCPublishing

PAPER

View Article Online
View Journal | View Issue

Oxidation reactions catalyzed by osmium compounds. Part 4.☆ Highly efficient oxidation of hydrocarbons and alcohols including glycerol by the $H_2O_2/Os_3(CO)_{12}$/pyridine reagent

Georgiy B. Shul'pin,[a,]* Yuriy N. Kozlov,[a] Lidia S. Shul'pina,[b]
Wagner A. Carvalho [c] and Dalmo Mandelli [c]

[a] *Semenov Institute of Chemical Physics, Russian Academy of Sciences, ulitsa Kosygina, dom 4, Moscow 119991, Russia*
[b] *Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, ulitsa Vavilova, dom 28, Moscow 119991, Russia*
[c] *Center of Natural and Human Sciences, Federal University of ABC (UFABC), Santa Adélia Street, 166, Bangu, Santo André, SP, 09210-170, Brazil*

* Corresponding author. Tel.: +7 495 9397317; fax: +7499 1376130; +7495 6512191; *e-mail addresses:* Shulpin@chph.ras.ru and gbsh@mail.ru (G.B. Shul'pin)

Supplementary information

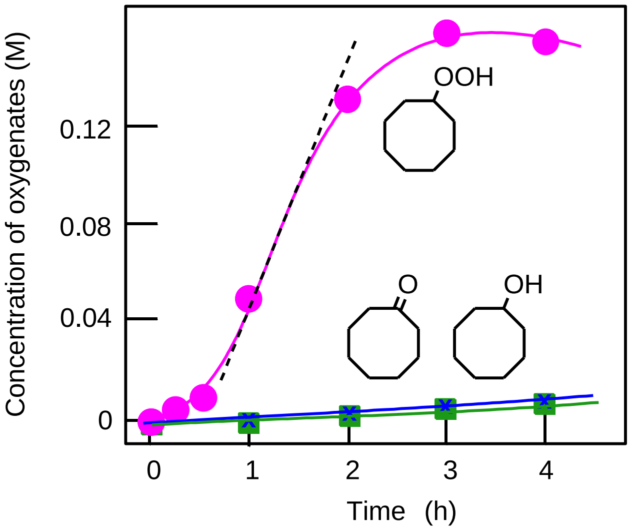

Fig. S1. Oxidation of cyclooctane with H_2O_2 catalyzed by **1** in the absence of pyridine. Accumulation of cyclooctyl hydroperoxide, cyclooctanone, and cyclooctanol with time is shown. Conditions: [cyclooctane]$_0$ = 0.5 M, [**1**]$_0$ = 1 × 10^{-4} M, [H_2O_2]$_0$ = 1.5 M (70% aqueous). Solvent MeCN, 60 °C. Concentrations of the three products (cyclooctyl hydroperoxide, cyclooctanol and cyclooctanone) were calculated by the comparison of the concentrations of cyclooctanol and cyclooctanone measured before and after reduction with PPh_3 (for this method, see Refs. 7b,8f,9). A dotted line corresponds to the maximum initial rate.

Table S1. Oxidation of cyclooctane with H_2O_2 catalyzed by **1** in the presence of different amines [a]

Entry	Amine	Yield (% based on cyclooctane) after		
		2 h	8 h	24 h
1	Pyridine	2	5	11
2	4-Picoline	2	3	8
3	Pyrazine	0	0	0.2
4	2,2′-Bipyridine	0	0.4	2
5	Imidazole	1	1.1	1.3

[a] Conditions: [cyclooctane]$_0$ = 0.5 M, [**1**]$_0$ = 1 × 10^{-5} M, [H_2O_2]$_0$ = 0.25 M (70% aqueous), [amine] = 0.02 M. Solvent MeCN, 60 °C.

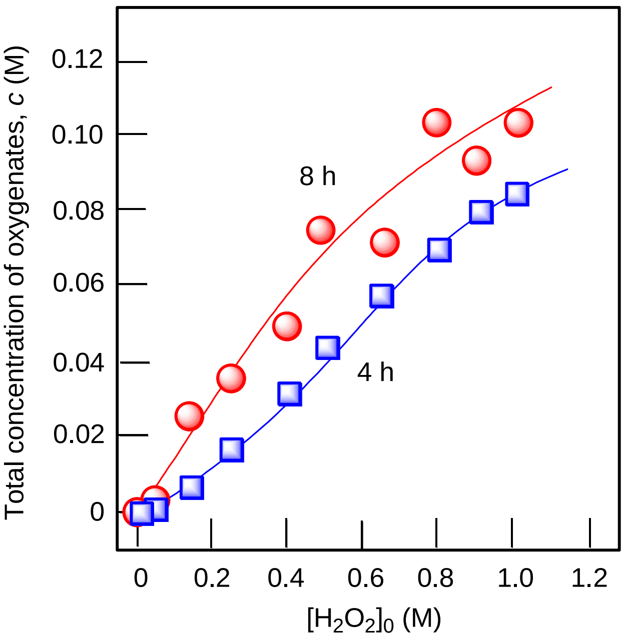

Fig. S2. Dependence of yield of oxygenates after 4 and 8 h on initial concentration of hydrogen peroxide in the cyclooctane oxidation. Conditions: [cyclooctane]$_0$ = 0.5 M, [py] = 0.1 M, [**1**]$_0$ = 1 × 10^{-5} M, H_2O_2, 70% aqueous, solvent MeCN, 60 °C. Concentration of water in the reaction was maintained constant [H_2O] = *const* by adding necessary amounts of H_2O.

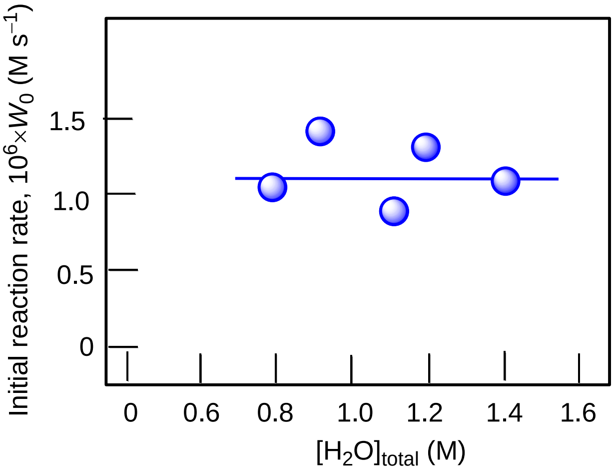

Fig. S3. Dependence of initial reaction rate W_0 on totall concentration of water in the cyclooctane oxidation. Conditions were the same as in the experiment shown in Fig. S2.

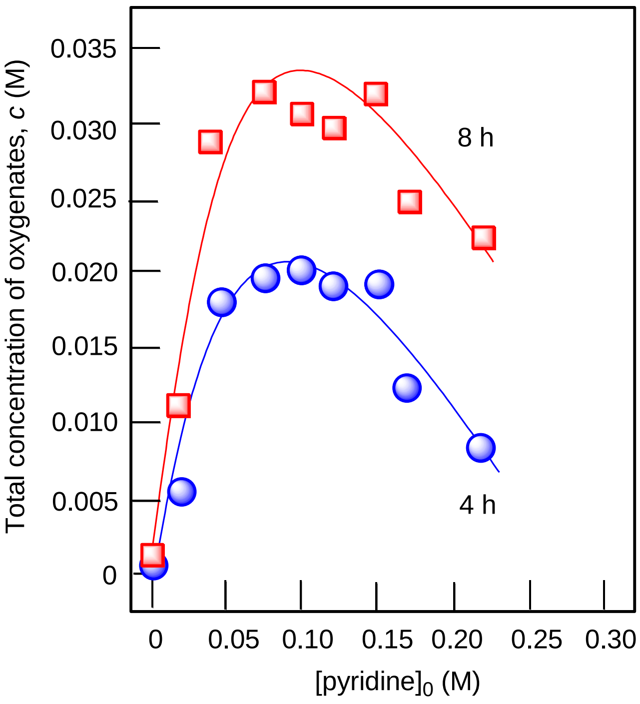

Fig. S4. Dependence of yield of oxygenates after 4 and 8 h on initial concentration of pyridine in the cyclooctane oxidation. Conditions were the same as in the experiment shown in Fig. 3.

Table S2 Cyclohexane oxidation with H_2O_2 in acetonitrile catalyzed by various metal complexes [a]

Entry	Catalyst	Concentration (M)	Cocatalyst	Time (h)	TON	TON (per one ion)	Initial TOF (h^{-1})	Initial TOF (per one ion)(h^{-1})	Yield (%) [b]	Ref.
1	**1** [b]	5×10^{-6}	pyridine	13	60 000	20 000	24 000	8000	56	This work
2	Cp*$_2$Os [c]	1×10^{-6}	pyridine	24	51 000	51 000	6000	6000	6	7c
3	(*n*-Bu$_4$N)[VO$_3$] [d]	$1 \cdot\times 10^{-5}$	PCA	6	5000	5000	700	700	12	9a,13–15
4	(*n*-Bu$_4$N)[VO$_3$] [d]	$1 \cdot\times 10^{-6}$	PCA	17	20 000	20 000	2100	2100	5	9a,13–15
5	"**Cu$_4$**" [e]	5×10^{-5}	HCl	2	200	50	600	150		16a
6	"**Cu-1**" [f]	5×10^{-5}	None	5	2200	2200			14	16b
7	[Mn$_2$L$_2$O$_3$][PF$_6$] [g]	3×10^{-5}	MeCOOH	2	3300	1650	2700	1350	46	16c
8	[Co$_4$Fe$_2$OSae$_8$] [b,h]	5×10^{-5}	HNO$_3$	6	2280	380			46	16d
9	[Co$_4$Fe$_2$OSae$_8$] [h]	11×10^{-5}	HNO$_3$	5	720	120	11 200	1870	21	16d
10	[Co$_4$Fe$_2$OSae$_8$] [h]	4.4×10^{-5}	HNO$_3$	5	3570	600			26	16d
11	Cp$_2$Fe [i]	1×10^{-4}	PCA	1.5	1200	1200	75	75	32	16e

[a] Yield was based on cyclohexane in cases when its amount was lower than the oxidant amount.
[b] Cyclooctane was used instead of cyclohexane.
[c] Decamethylosmocene, Cp* is pentamethylcyclopentadienyl.
[d] The efficient oxidizing reagent (*n*-Bu$_4$N)[VO$_3$]/PCA/H_2O_2 (PCA is pyrazine-2-carboxylic acid) was initially described by one of us in Refs. 9a,13b–d. Mechanistic studies demonstrated [14,15] that this system operates with the participation of hydroxyl radicals.
[e] "**Cu$_4$**" is tetracopper(II) triethanolaminate complex [O<Cu$_4${N(CH$_2$CH$_2$O)$_3$}$_4$(BOH)$_4$][BF$_4$]$_2$.
[f] "**Cu-1**" is complex Cu(MeCN)$_4$BF$_4$; *t*-BuOOH was used instead of H_2O_2.
[g] L = 1,4,7-trimethyl-1,4,7-triazacyclononane.
[h] [Co$_4$Fe$_2$OSae$_8$] is complex [Co$_4$Fe$_2$OSae$_8$]·4DMF·H_2O, where H$_2$Sae = salicylidene-2-ethanolamine.
[i] Ferrocene, Cp is cyclopentadienyl ligand.

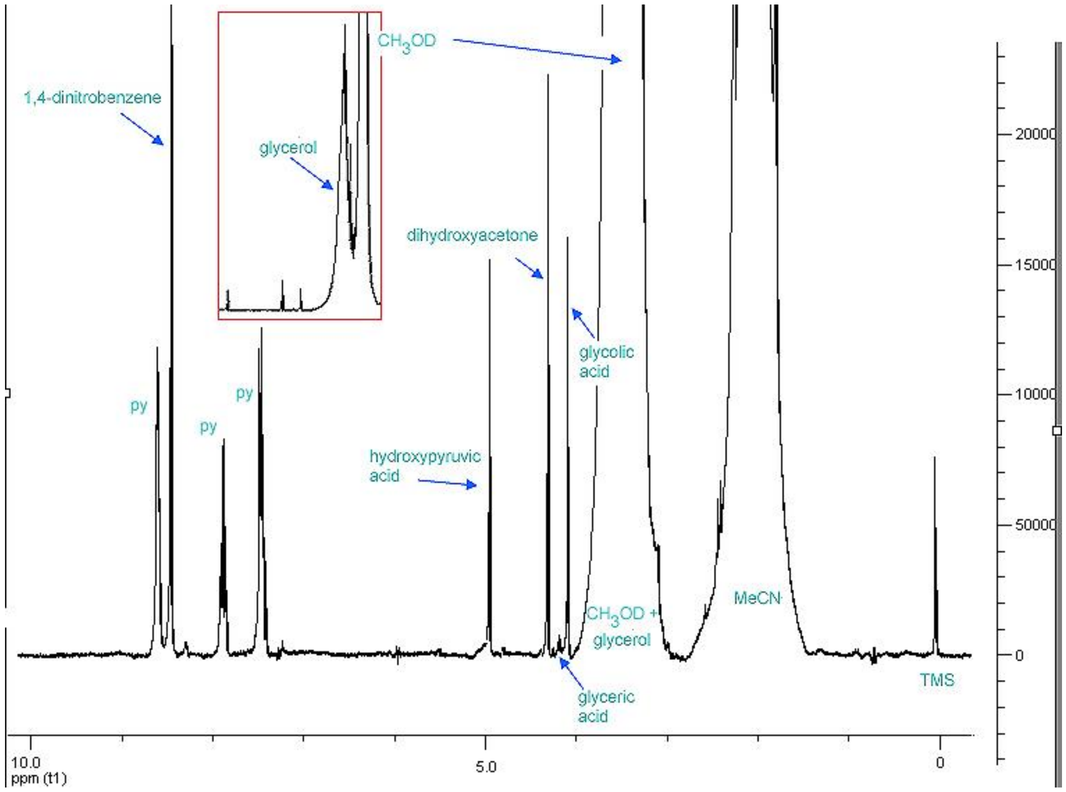

Fig. S5. An example of the ^{1}H NMR spectrum of the reaction mixture obtained in the glycerol oxidation with H_2O_2 catalyzed by $Os_3(CO)_{12}$ and pyridine.

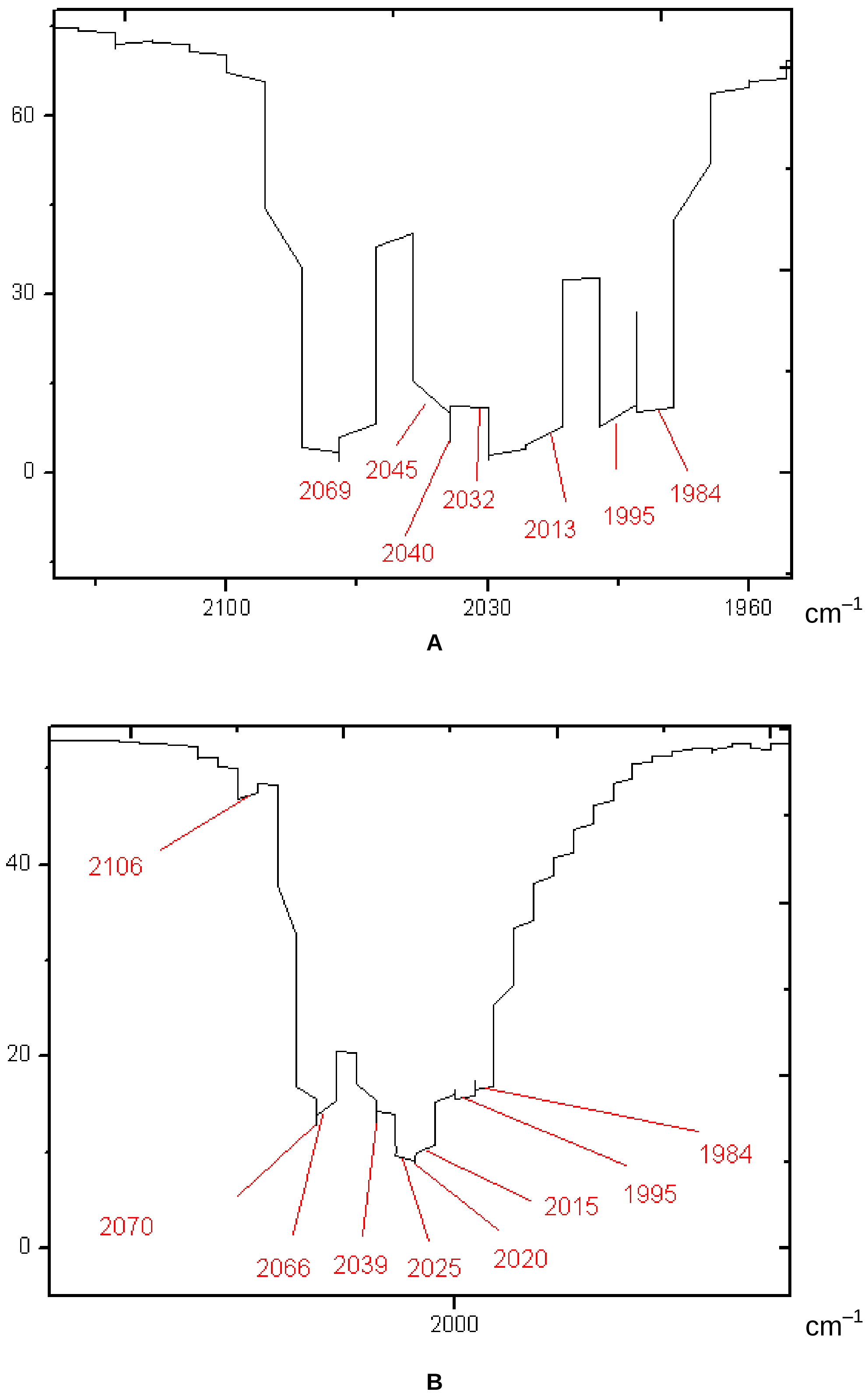

Fig. S6. The IR spectra of $Os_3(CO)_{12}$ (precatalyst **1**) (graph A) and evaporated stock solution of **1** in MeCN. Both spectra were recorded for the KBr tablet.

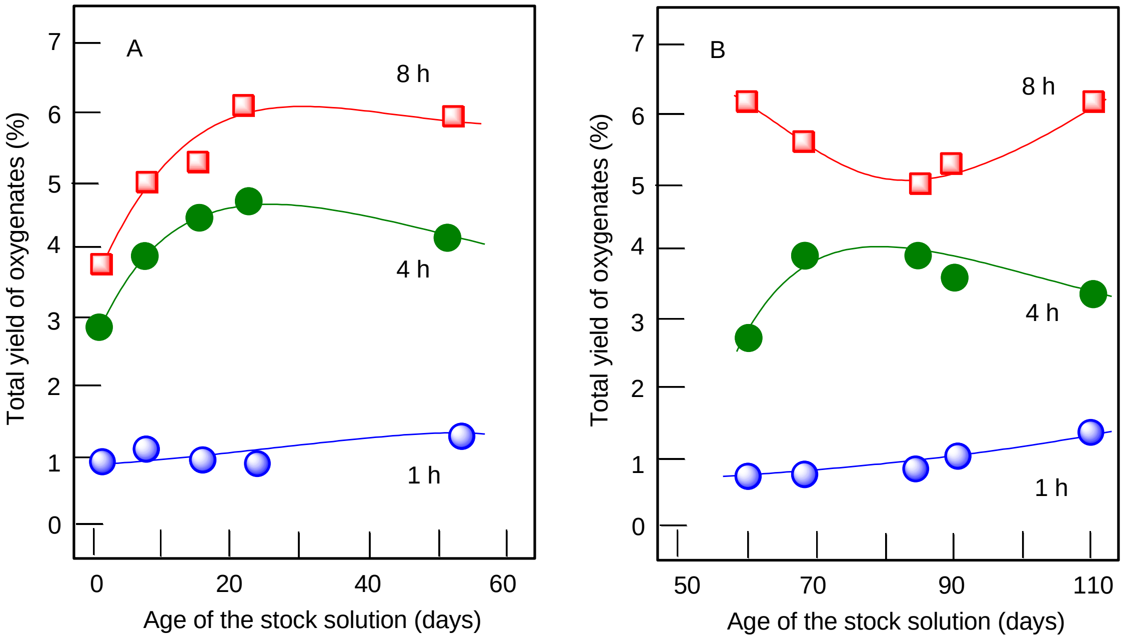

Fig. S7. Oxidation of cyclooctane with the $H_2O_2/Os_3(CO)_{12}$ (compound **1**)/pyridine system using the stock solutions stored previously at room temperature (Graph A) and in the refrigerator (Graph B). Yields of sum of products after 1, 4, and 8 h are shown. Other conditions: $[Os_3(CO)_{12}]_0 = 1 \times 10^{-5}$ M; $[H_2O_2]_0 = 0.25$ M; $[\text{pyridine}]_0 = 0.1$ M; $[\text{cyclooctane}]_0 = 0.5$ M; 60 °C.

Estimation of alkyl hydroperoxide concentration by comparison of chromatograms obtained *before* and *after* reduction of the reaction solution with PPh_3

The quantification of alkyl hydroperoxides and ketones (aldehydes) and alcohols present in the reaction solution was performed using developed previously by Shul'pin [7b,8f,9] simple GC method with reduction of the reaction samples with tryphenylphosphine. Alkyl hydroperoxides formed in the oxidation of alkanes decompose in the chromatograph to afford corresponding alcohols and ketones (aldehydes) as main products:

$$R'CH(OOH)R'' \rightarrow R'CH(OH)R'' + R'C(=O)R'' + \ldots$$

The alcohol/ketone (aldehyde) ratio is usually around 1:1. It should be noted that under mild conditions the alkyl hydroperoxide, ROOH, can be easily transformed into the corresponding ketone (or aldehyde), R′COR″, *via* dehydratation without formation of the alcohol, ROH. However, at elevated temperature ROOH decomposes *via* a multistep radical-chain mechanism. Some stages of this process afford both products, the ketone and alcohol in the 1:1 ratio (ROOH = RO• + HO•; 2ROOH = RO• + ROO• + H_2O; ROO• + ROO• = ROH + R′COR″ + O_2; see Ref. 1*e*, pp. 41, 47). If an excess of solid PPh_3 is added to a sample of the reaction solution *ca*. 10 min before GC analysis the alkyl hydroperoxide, ROOH, present in the reaction mixture is completely reduced to the corresponding alcohol:

$$\text{R'CH(OOH)R''} + PPh_3 \rightarrow \text{R'CH(OH)R''} + O{=}PPh_3$$

In this case, the chromatogram differs from that of a sample not subjected to the reduction (the alcohol peak rises, while the intensity of the ketone peak decreases). Measuring a sum of concentrations alcohols+ketone (aldehyde) *after* reduction with PPh_3 gives us precise value of *total* concentration of all primary products (that is of alkyl hydroperoxide, alcohol and ketone). The comparison of this value with concentrations of the alcohol and ketone (aldehyde) *before* reduction with PPh_3 allows us to estimate the *real* concentrations of the alkyl hydroperoxide, alcohol, and ketone (aldehyde) in the reaction solution.

The oxidation of alkane occurs in accord with the following equation

$$\text{RH} \rightarrow \underset{x_{\text{real}}}{\text{ROOH}} + \underset{y_{\text{real}}}{\text{ROH}} + \underset{z_{\text{real}}}{\text{R'C(=O)R''}}$$

where [ROOH] = x_{real}, [ROH] = y_{real}, and [R'C(=O)R"] = z_{real} are real concentrations of the three products in the reaction sample. Injecting the sample directly into chromatograph leads to decomposition of really present in the solution alkyl hydroperoxide to give detectable by GC additional concentrations y_{add} and z_{add} of ROH and R'C(=O)R":

$$\underset{x_{\text{real}}}{\text{ROOH}} \rightarrow \underset{y_{\text{add}}}{\text{ROH}} + \underset{z_{\text{add}}}{\text{R'C(=O)R''}}$$

Assuming that alkyl hydroperoxide decomposes in the GC to produce the corresponding alcohol and ketone in the ≈1:1 ratio we can calculate the real concnetrations of the three products of alkane oxidation using the following equations:

$$[\text{ROOH}] = x_{\text{real}} \approx (z_{\text{before}} - z_{\text{after}}) + (y_{\text{after}} - y_{\text{before}})$$
$$[\text{ROH}] = y_{\text{real}} \approx y_{\text{before}} - (z_{\text{before}} - z_{\text{after}})$$
$$[\text{R'C(=O)R''}] = z_{\text{real}} = z_{\text{after}}$$

where y_{before} and z_{before} are the amounts of alcohol and ketone (aldehyde) measured by GC before reduction with PPh_3; y_{after} and z_{after} the amounts of alcohol and ketone (aldehyde) measured by GC after reduction with PPh_3, respectively. A more detailed description has been published.[7b]