

PHOTOOXIDATION OF CYCLOHEXANE WITH DIOXYGEN IN ACETONITRILE IN THE PRESENCE OF TRANSITION METAL CHLORIDES*

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Irradiation of cyclohexane solution in acetonitrile ($\lambda = 300, 365, \text{ or } 436 \text{ nm}$) in the presence of dioxygen and catalytic amounts of FeCl_3 , CuCl_2 , $\text{Na}[\text{AuCl}_4]$ or $\text{H}_2[\text{PtCl}_6]$ gives rise to cyclohexanol and cyclohexanone (after GLC). The quantum yields with respect to the products lie within the range of 0.01 to 0.05. The most efficient of the catalysts used is FeCl_3 , and the most efficient radiation wavelength is $\lambda = 365 \text{ nm}$. A reaction pathway is suggested; it is assumed that the first step is photoexcitation of $\text{M}-\text{Cl}$ followed by electron transfer from the ligand to the metal associated with the formation of the Cl^\cdot radical, which reacts (probably after solvation by the solvent) with RH giving R^\cdot . The Fe(II) species is oxidized by ROO^\cdot , and the photocatalytically active complex is restored. Complexes with metals in low oxidation states (particularly in the case of Cu , Au and Pt), however, can react with molecular oxygen to give peroxo or oxo complexes, which can directly hydroxylate alkanes.

Oxidation of aliphatic hydrocarbons with molecular oxygen in gentle conditions is a demanding and important task. Selective introduction of functional groups into alkane molecules under the catalytic effect of transition metal complexes is of interest from the preparative aspect as well as from the point of view of investigation into the mechanism of the processes¹⁻⁴. A number of systems where alkanes are photooxidized by dioxygen in the presence of transition metal complexes have been studied recently. Such oxidation reactions are of interest because they proceed at room temperature and solar energy can be employed. Salts such as FeCl_3 (refs⁵⁻⁷), CuCl_2 (ref.⁸), $\text{Na}[\text{AuCl}_4]$ (refs^{9,10}), $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ (ref.¹¹), $\{\text{Pt}[\text{NC}_6\text{H}_5\text{NC}(\text{S})\text{SCH}_3]_2\}$ (ref.¹²), oxo complexes such as CrO_3 (ref.¹³), $\text{Cr}_2\text{O}_7^{2-}$, Cr_4O_{13} (ref.¹⁴), VO_3^- , $\text{H}_7\text{Mo}_6\text{V}_5\text{O}_{39}^{5-}$ (ref.¹⁵), $\text{PW}_{12}\text{O}_{40}^{3-}$ (refs^{15,16}), $\text{W}_{10}\text{O}_{32}^{4-}$ (refs^{17,18,19}) and UO_2^{2-} (ref.²⁰) have been used as photocatalysts for the oxidation of alkanes and arylalkanes. Acetic acid, methylene chloride or acetonitrile served mostly as the solvents. The

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entire spectrum of the medium-pressure Hg discharge tube or solar radiation was usually employed for the photochemical initiation. The quantum yields mostly failed to be determined.

The aim of this work was to present the first results concerning (i) the quantum yields for the systems described, (ii) the associated changes in the UV-VIS spectra, and (iii) the use of a new photocatalyst, viz. $[\text{PtCl}_6]^{2-}$.

EXPERIMENTAL

The oxidation of cyclohexane (20 ml of 0.46 mol l^{-1} solution in acetonitrile) was carried out in a thermostatted cylindrical quartz vessel interfaced to a volumetric burette. The reaction mixture was shaken vigorously under dioxygen at 25°C while irradiated with filtered ($\lambda = 300, 365$ or 436 nm) light of a high-pressure HBO 200W (Osram) mercury lamp. Monochromatization of the radiation was achieved by means of KSIF 300, 365, and 436 filters (Zeiss, Jena). The light intensity for the arrangement used was $I_{300} = 2.54 \cdot 10^{16}$, $I_{365} = 1 \cdot 10^{18}$, and $I_{436} = 1.58 \cdot 10^{18}$ quanta s^{-1} , as determined by ferrioxalate actinometry.

All chemicals used were of reagent grade purity.

The concentrations of cyclohexanol and cyclohexanone were determined in 1, 2 and 3 h of irradiation by gas chromatography on a Chrom 5 instrument (Laboratorní přístroje, Prague) using a column 1.2 m long packed with 15% Carbowax 20M on GAS CHROM R. The UV-VIS spectra were measured on a Philips PU 8 700 spectrophotometer.

RESULTS AND DISCUSSION

The quantum yields were calculated taking into account absorbances of the photocatalyst solutions (solutions of FeCl_3 , CuCl_2 , $\text{Na}[\text{AuCl}_4]$ and $\text{H}_2[\text{PtCl}_6]$ absorb, for instance, 100%, 48%, 50% and 47%, respectively, of radiation 365 nm wavelength). The product concentrations and quantum yields are given in Table I. It must be stressed that cyclohexylhydroperoxide, which also forms during the photochemical reaction, decomposes to approximately identical amounts of cyclohexanol and cyclohexanone. It is noteworthy that in 3 h of irradiation in the absence of a photocatalyst, the concentration of cyclohexanol or cyclohexanone, as determined by GLC, does not exceed 0.05 mol l^{-1} .

Table I demonstrates that (i) FeCl_3 is the most active of the catalysts tested; (ii) cyclohexanol and cyclohexanone are formed in approximately identical quantities; (iii) the dependence of the product concentrations on time are nearly linear; and (iv) the highest quantum yields, using any of the catalysts, were achieved with radiation 365 nm wavelength.

The reaction course was also monitored spectrophotometrically. In the case of the FeCl_3 catalyst, no spectral changes seem to occur in the 300–400 nm range (where two bands are present at 312 and 362 nm) during the 3 h exposure (for all three wavelengths of radiation). This suggests that the photocatalytically active complex forming in the starting stage of the reaction remains unaltered for at least three hours.

Significant changes, however, were observed in the absorption spectra of the remaining photocatalysts during the oxidation reactions. In the spectrum of the reaction solution containing CuCl_2 , the intensity of the absorption band at 460 nm decreased within 1 h of exposure and a new band appeared at 256 nm (Fig. 1). It should be noted that, as our preliminary results²¹ indicate, the EPR signal of the Cu(II) complex in the reaction solution vanishes within several hours of irradiation.

Exposure of the reaction solution containing $\text{Na[AuCl}_4]$ is accompanied by a decrease in the absorption bands at 350 and 470 nm (Figs 2 and 3). It is interesting that a difference appears between the spectra obtained when using initiating radiation of 365 and 436 nm wavelength. In the former case, the spectral change appears soon and within 3 h the photocatalyst is completely transformed into some other complex.

During the irradiation of cyclohexane in the presence of $\text{H}_2[\text{PtCl}_6]$ with radiation 365 nm wavelength, the spectrum undergoes appreciable changes (Fig. 4). Noteworthy is the increase in the intensity of the band at 463 nm and vanishing of the intense absorption in the ultraviolet region. In two hours, the complex has de-

TABLE I
Concentrations (c , mmol l^{-1}) and quantum yields (Φ) of cyclohexanol (*I*) and cyclohexanone (*II*) in catalyzed photooxidation of cyclohexane with dioxygen

Photo-catalyst		$\lambda = 300 \text{ nm}^a$			$\lambda = 365 \text{ nm}^a$			$\lambda = 436 \text{ nm}^a$		
		1 h	2 h	3 h	1 h	2 h	3 h	1 h	2 h	3 h
FeCl_3	<i>I</i> c	15	21	34	100	259	386	25	49	63
	Φ	0.020	0.014	0.015	0.030	0.039	0.039	0.022	0.022	0.01
	<i>II</i> c	10	18	28	110	255	540	23	56	85
	Φ	0.013	0.012	0.013	0.033	0.039	0.055	0.020	0.025	0.02
CuCl_2	<i>I</i> c	16	37	49	37	67	108	30	44	61
	Φ	0.022	0.013	0.022	0.023	0.021	0.023	0.009	0.007	0.00
	<i>II</i> c	9	27	36	33	62	106	26	42	60
	Φ	0.012	0.018	0.016	0.021	0.019	0.023	0.008	0.006	0.00
NaAuCl_4	<i>I</i> c	—	—	—	39	69	88	12	25	42
	Φ	—	—	—	0.024	0.020	0.018	0.008	0.008	0.00
	<i>II</i> c	—	—	—	46	82	115	15	32	48
	Φ	—	—	—	0.028	0.024	0.024	0.010	0.011	0.01
H_2PtCl_6	<i>I</i> c	—	—	—	28	51	88	8	17	30
	Φ	—	—	—	0.018	0.018	0.019	0.011	0.011	0.14
	<i>II</i> c	—	—	—	29	56	91	11	18	33
	Φ	—	—	—	0.019	0.018	0.020	0.015	0.012	0.01

^a For light intensity see Experimental.

composed. The spectral changes are considerably slower if radiation with $\lambda = 436$ nm is employed.

Based on the results obtained, the following reaction mechanism is suggested. If FeCl_3 is used as the photocatalyst, excitation of FeCl_3 occurs in the first stage, followed by electron transfer from the ligand to the central atom giving rise to FeCl_2 . The chlorine radical, which emerges from the photochemical cleavage of the $\text{Fe}-\text{Cl}$ bond, reacts further with an $\text{R}-\text{H}$ bond of a next molecule of cyclohexane giving the R^\bullet radical. The latter enters into a rapid reaction with a molecule of dioxygen, and the peroxy radical ROO^\bullet arises. This can be reduced with Fe(II) , whose formation is assumed in the first reaction stage. The hydroperoxide decomposes due to the action of the metal catalyst (and presumably also of the radiation) to give alcohol and ketone in approximately identical amounts²². This mechanism can be written as

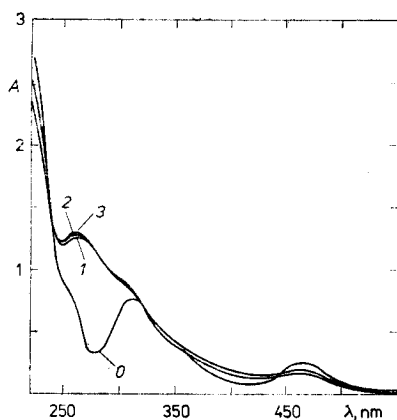
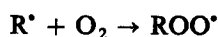
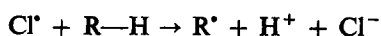
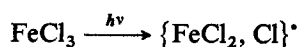


FIG. 1

Changes in the UV-VIS spectra in dependence on the time of irradiation of cyclohexane in CH_3CN in the presence of CuCl_2 ; $c(\text{cyclohexane}) = 0.46 \text{ mol l}^{-1}$, $c(\text{CuCl}_2) = 0.0005 \text{ mol l}^{-1}$, $\lambda = 365 \text{ nm}$. Exposure (min): 0 0, 1 60, 2 120, 3 180

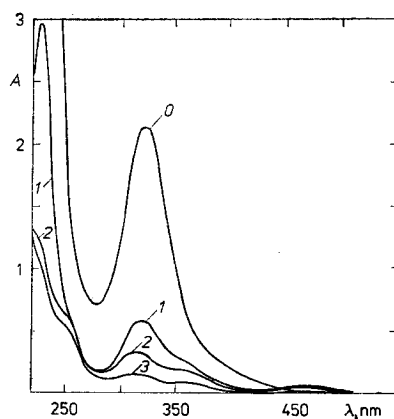
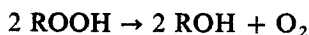
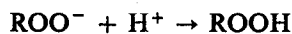
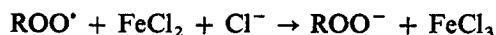


FIG. 2

Changes in the UV-VIS spectra in dependence on the time of irradiation of cyclohexane in CH_3CN in the presence of $\text{Na}[\text{AuCl}_4]$; $c(\text{cyclohexane}) = 0.46 \text{ mol l}^{-1}$, $c(\text{Na}[\text{AuCl}_4]) = 0.0005 \text{ mol l}^{-1}$, $\lambda = 365 \text{ nm}$. Exposure (min): 0 0, 1 60, 2 120, 3 180



This mechanism is assumed to pertain to the first 3 h of irradiation. The mechanism of oxidation in the presence of the remaining three catalysts is less clear. In these reactions the first reaction stage may be photochemical cleavage of the metal-chloride ionic bond; the spectral changes point to a fast reduction of the metal ions on the action of radiation, and the catalyst loses in efficiency. In 1 to 2 h, however, the photochemical oxidation of cyclohexane proceeds at a high rate although complexes with the metal in the higher oxidation state are absent. Presumably, in this period of time a complex with the metal in a lower oxidation state forms following a mechanism similar to that suggested for the oxidation catalyzed by FeCl_3 , this complex giving with dioxygen the peroxo or oxo complex which oxidizes cyclohexane under the effect of radiation. Compounds of Cu(I) and Pt(I) are known to easily coordinate

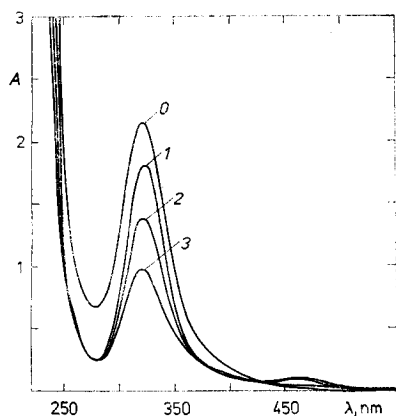


FIG. 3

Changes in the UV-VIS spectra in dependence on the time of irradiation of cyclohexane in CH_3CN in the presence of $\text{Na}[\text{AuCl}_4]$; $c(\text{cyclohexane}) = 0.46 \text{ mol l}^{-1}$, $c(\text{Na}[\text{AuCl}_4]) = 0.0005 \text{ mol l}^{-1}$, $\lambda = 436 \text{ nm}$. Exposure (min): 0 0, 1 60, 2 120, 3 180

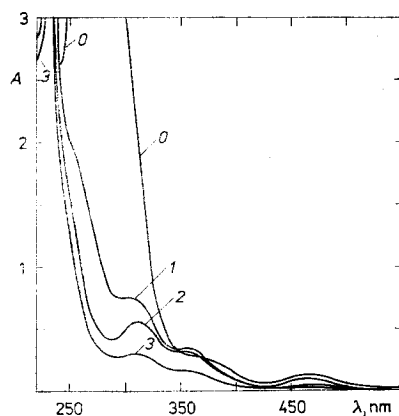


FIG. 4

Changes in the UV-VIS spectra in dependence on the time of irradiation of cyclohexane in CH_3CN in the presence of $\text{H}_2[\text{PtCl}_6]$; $c(\text{cyclohexane}) = 0.46 \text{ mol l}^{-1}$, $c(\text{H}_2[\text{PtCl}_6]) = 0.0005 \text{ mol l}^{-1}$, $\lambda = 365 \text{ nm}$. Exposure (min): 0 0, 1 60, 2 120, 3 180

dioxygen. Interactions of Cu(I) compounds with dioxygen have also been observed to result in the formation of OH[•] radicals^{3,21}, which in our system may hydroxylate alkanes. Additional research would be necessary to confirm or refuse this hypothesis.

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