

PHOTOXYGENATION OF SATURATED AND ALKYLAROMATIC HYDROCARBONS, CATALYZED BY PLATINUM METAL HALIDES*†

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(Received 25 February 1991)

Earlier we found that, during light irradiation, a PtCl_6^{2-} ion in solutions of organic solvents reacts with arenes to form σ -aryl complexes of Pt(IV) [2–4], with acetone to form a σ -acetonyl derivative of Pt(IV) [5], with olefins to form π -olefin complexes of Pt(II) [6,7] and with alkanes [8–10]. In the latter case, the chlorination of *n*-hexane and the dehydrogenation of the saturated hydrocarbon occur in a CH_3COOH solution with the formation of a π -hexene complex of Pt(II). It is assumed [9,10] that in this case a photoexcited particle containing Pt(IV) separates a hydrogen atom from the alkane (evidently by means of the chloride ligand, which during photolysis of the Pt–Cl bond generates a chlorine radical) and is itself reduced to Pt(III). Then the recombination of Pt(III) and R^\cdot can occur with the formation of a σ -alkyl derivative of Pt(IV), or the oxidation of the alkyl radical to a carbocation with detachment of a proton. The olefin arising in this case is coordinated with the Pt(II) formed. The R^\cdot radical can separate a chlorine atom from the platinum complex, while the R^+ carbocation is capable of adding a Cl^- anion. In both cases, RCl is produced. During irradiation, a PtCl_6^{2-} ion [11–13] (and also similar derivatives of Pd and Ir [13]) oxidizes alcohols, and here, with the addition of CuCl_2 , the system becomes a photosensitizer for the oxidation of alcohols by molecular oxygen [14,15]. At the same time it is known that, during light irradiation of alkane solutions in air in the presence of chloride complexes of gold(II) with large concentrations of the complex, it is almost exclusively products of alkane chlorination that are formed [16], but with relatively low concentrations of the complex, instead of alkyl chloride, alcohol and ketone are found in the reaction products in roughly equal quantities [17,18]. It is important to stress that the yield of products of alkane oxygenation reaches several hundreds of moles per 1 mole of the gold complex. Iron (III) [19–21] and copper(II) [22,23] chlorides also proved to be effective photocatalysts for the oxygenation of alkanes. It was important to investigate the possibility of using alkanes and alkylaromatic compounds of halide complexes of platinum and other platinum metals as photocatalysts for the oxygenation of alkanes and alkylaromatic compounds.

* *Neftekhimiya* 31, No. 6, 822–828, 1991.

† Report XXIII from series "Photoinitiated reactions of organic compounds with transition metal complexes"; see [1] for report XXII.

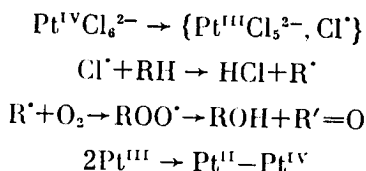
EXPERIMENTAL

Oxygenation reactions were carried out in a cylindrical glass vessel of 20 mm diameter, enclosed in a sleeve cooled by running water (10°C), during vigorous stirring by means of a magnetic stirrer and irradiation with the full light of a DRL-250 luminescent lamp (250 W). The volume of the reaction solutions was 10 ml. The concentration of the catalysts was 5×10^{-4} mole/l, and the concentration of the organic substrates 0.46 mole/l. The concentrations of oxygenation products were determined by means of GLC (LKHM-80-6 chromatograph, column 2 m, sorbent INERTON AW-HMDS with 5% Carbowax 1500, carrier gas argon, temperature programming regime 50–170°C at 4 deg/min).

The quantum yield of the photochemical reaction of cyclohexane in the presence of Na_2PtCl_6 was determined at 25°C in an oxygen atmosphere using the full and monochromatic light ($\lambda = 365$ and 436 nm) of an NVO lamp (200 W). The light flux intensities were $I_{365} = 1.1 \times 10^{17}$ and $I_{436} = 1.58 \times 10^{17}$ quant/sec. Absorption spectra were obtained on a Philips PU8700 spectrophotometer.

RESULTS AND DISCUSSION

Irradiation in air of a solution of cyclohexane and H_2PtCl_6 (concentration 5×10^{-4} mole/l) in acetonitrile leads to the formation, in roughly equal quantities, of cyclohexanol and cyclohexanone. To determine the quantum yield of products [24], irradiation was also carried out in an atmosphere of pure oxygen with monoaromatic light of two different wavelengths. The quantum yield values obtained with allowance for absorption of light of the given wavelength by the solutions are presented in Table 1. As can be seen, the accumulation of oxygenation products has no induction period. In the first hour of irradiation, in the absorption spectrum of the reaction solution there is a rapid drop in intensity of the 313 nm band characteristic of a Pt(IV) compound. After 2 hr, there is practically no Pt(IV) complex in the reaction solution. At the same time, oxygenation products continue to accumulate. It is therefore possible to assume that, in the initial period of the reaction, reduction of Pt(IV) occurs, accompanied by the formation of platinum in a low state of oxidation and products of oxygenation of cyclohexane by the scheme



The generation of chlorine radicals during irradiation of a solution of PtCl_6^{2-} in CH_3CN was recorded in [25,26]. The mechanism of oxygenation of cyclohexane seems to change as Pt(IV) disappears and a low-valency platinum derivative is formed. It can be assumed that the low-valency platinum complex oxidatively adds an oxygen molecule with the formation of a peroxide derivative capable of oxygenation of an alkane with the participation of light. The participation of complexes of this kind was assumed in the thermal oxidation of cyclohexene in the presence of phosphine complexes of Pt(0) [27] and in the photochemical oxygenation of cyclohexane, catalyzed by $\text{Mo}(\text{CO})_6$ [28]. To confirm the hypothesis concerning the participa-

TABLE 1. CONCENTRATION c ($\times 10^4$, mole/l) OF PRODUCTS FORMED DURING IRRADIATION IN O_2 ATMOSPHERE OF SOLUTION OF CYCLOHEXANE (0.46 mole/l) AND H_2PtCl_6 (5×10^{-4} mole/l) IN CH_3CN , AND CALCULATED QUANTUM YIELDS Φ FOR LIGHT WITH WAVELENGTH $\lambda = 365$ AND 436 nm

λ , nm	Product	Reaction time, hr					
		1		2		3	
		c	Φ	c	Φ	c	Φ
365	Cyclohexanol	28	0,018	51	0,017	88	0,019
	Cyclohexanone	29	0,019	56	0,018	91	0,020
436	Cyclohexanol	8	0,011	17	0,011	30	0,014
	Cyclohexanone	11	0,015	18	0,012	33	0,015

tion of low-valency complexes capable of coordinating dioxygen in a process catalyzed by a platinum compound, an additional investigation is required. Note, however, that some results obtained in the present work can be regarded as evidence of a change in the mechanism during the reaction. Thus the competing oxygenation of cyclohexane and ethyl benzene indicates that, when $(Bu_4N)_2PtCl_6$ is used as the catalyst, in the initial period of the reaction (15 min) the ratio of the reactivities of a single C–H bond in methylene groups of ethyl benzene and cyclohexane Ψ amounts to 36, but then (after 1 hr or more; here the rate is determined from the slope of the tangent to the curve of accumulation) it is appreciably lower – about 13. 1-Phenylethanol and acetophenone are obtained from ethyl benzene in this case. The reactivity of the methyl group in *p*-xylene in relation to that in toluene (photocatalyst Na_2PtCl_6) also changes: in the initial period, *p*-toluyl aldehyde accumulates 6 times more rapidly than benzaldehyde, but after only 1 hr the relative rate falls to 4, and after 2 hr to 3. Note that no *p*-toluyl or benzyl alcohols were found in the oxidation products. If it is assumed that there exists some correlation between the logarithms of the relative oxygenation rates and the Hammett–Brown constants σ^+ , values of parameter ρ^+ can be estimated nominally for a reaction time of 0.25, 1 and 2 hr at -1.9 , -1.1 and -0.8 respectively.

Note that other compounds are also oxidized in the presence of $PtCl_6^{2-}$ during irradiation. Thus, the following quantities of *p*-toluyl aldehyde are obtained from *p*-toluyl alcohol (4.6×10^{-2} mole/l):

Irradiation time, hr	0.5	1	2	3
[<i>p</i> -Toluyl aldehyde] $\times 10^4$, mole/l	4.6	8.7	10.1	13.2

Triphenylphosphine (0.02 mole/l) is readily oxidized to triphenylphosphinoyl:

Irradiation time, hr	0.25	0.5	1	2	3
[$Ph_3P=O$] $\times 10^2$, mole/l	1.26	1.32	1.77	1.92	2.00

Triphenylphosphine readily reduces Pt(IV) to Pt(II), and it is obvious that, when it is present in excess, low-valency platinum complexes should catalyze the oxidation of phosphine. Further evidence of the participation of such complexes in the process is the fact that the oxidation of cyclohexane during irradiation is catalyzed by a chloride derivative of Pt(II)

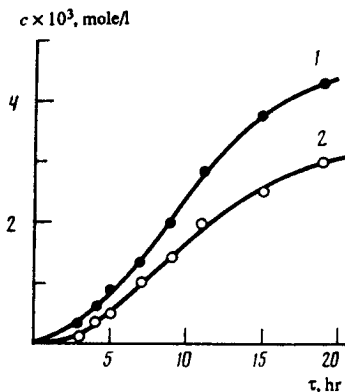


FIG. 1. Kinetic curves of accumulation of cyclohexanol (1) and cyclohexanone (2) during photooxidation of solution of cyclohexane (0.46 mole/l) in acetonitrile in presence of 5×10^{-4} mole/l $\text{Na}_2\text{PtCl}_4 \cdot 4\text{H}_2\text{O}$.

(Fig. 1). The long induction period in this reaction is worthy of note. This is possibly connected with the fact that, during photoexcitation of a PtCl_4^{2-} ion, no homolysis of the Pt-Cl bond occurs, and consequently chlorine radicals are unable to attack the cyclohexane molecules. Nevertheless, photoreduction of the complex can occur during the induction period, after which oxygenation begins. There may be other explanations for the induction period in this case.

A very considerable induction period (up to 7 hr) is observed during the photooxygenation of cyclohexane in the presence of Na_2PtBr_6 (Fig. 2). As in the case of bromide complexes of iron [21] and copper [23], when hydroquinone is added the induction period is virtually removed. During combined oxidation of ethyl benzene and cyclohexane, the products of

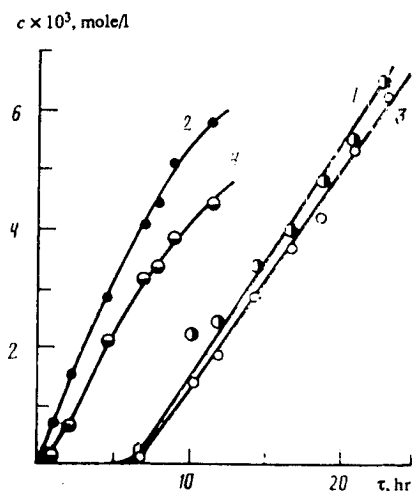


FIG. 2. Kinetic curves of accumulation of cyclohexanol (1, 2) and cyclohexanone (3, 4) during photooxidation of cyclohexane (0.46 mole/l) in acetonitrile in presence of 5×10^{-4} mole/l $\text{Na}_2\text{PtBr}_6 \cdot 6\text{H}_2\text{O}$. 1-3 - without hydroquinone; 2-4 - with hydroquinone (5×10^{-4} mole/l).

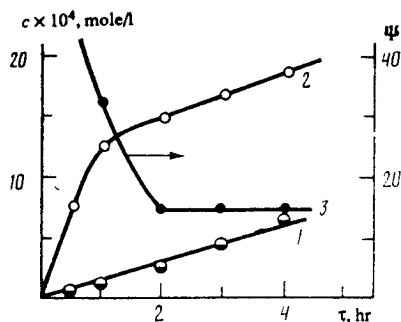


FIG. 3. Kinetic curves of accumulation of products of oxygenation of cyclohexane (total concentration of cyclohexanol and cyclohexanone (1)) and ethyl benzene (total concentration of 1-phenylethanol and acetophenone (2)), and also reactivity of single C-H bond in methylene group of ethyl benzene in relation to reactivity of C-H bond in cyclohexane Ψ (3) during photooxygenation of mixture of cyclohexane (0.46 mole/l) and ethyl benzene (0.46 mole/l) in acetonitrile in presence of 5×10^{-4} mole/l $\text{Na}_2\text{PtBr}_6 \cdot 6\text{H}_2\text{O}$.

oxygenation of the two hydrocarbons accumulate by different mechanisms (Fig. 3). In the initial period, products of the oxygenation of ethyl benzene accumulate very rapidly, after which the rate of their formation decreases. Products of the oxygenation of cyclohexane accumulate almost linearly; the addition of ethyl benzene (like hydroquinone) removes the induction period in the oxidation of cyclohexane. The relative reactivity Ψ changes with time: from 32 for the initial section to 14 at 4 hr, after which the decrease in Ψ with time becomes negligible (Fig. 3). With combined oxidation of *p*-xylene and toluene (0.46 mole/l) in the presence of Na_2PtBr_6 , the accumulation rate of *p*-toluyl aldehyde exceeds the benzaldehyde formation rate only in the first 0.5 hr of irradiation (as in the case of ethyl benzene, the reaction proceeds without an induction period), but within 4 hr irradiation, when products practically stop accumulating, 2.6×10^{-5} mole/l *p*-toluyl aldehyde and 3.7×10^{-5} mole/l benzaldehyde are formed. The value of ρ^+ for the initial period of the reaction is estimated at -0.8 . The data obtained can be interpreted in the following way. During photohomolysis of the Pt-Br bond, bromine radicals are formed, and these readily separate the hydrogen atom from the weaker α -CH bond in ethyl benzene, but are incapable of doing this in the case of cyclohexane. Therefore, during oxidation of cyclohexane, a greater induction period is observed. However, as the reduction of Pt(IV) progresses, the second mechanism comes into play, with the participation of low-valency platinum complexes, and cyclohexane begins to be oxidized at roughly the same rate as ethyl benzene.

Chlorides of other platinum group metals differ sharply in their ability to photocatalyze the oxygenation of cyclohexane in a CH_3CN solution. An Li_2PdCl_4 complex is almost inactive: within 15 hr irradiation, 1.7×10^{-4} mole/l of cyclohexanol and 3.7×10^{-4} mole/l of cyclohexanone are formed. An Na_2OsCl_6 complex is slightly more active: 4.8×10^{-4} mole/l of cyclohexanol and 7.8×10^{-4} mole/l of cyclohexanone are formed within 19 hr irradiation. Note that, without a metal complex, 1.9×10^{-4} mole/l of cyclohexanol and 1.8×10^{-4} mole/l of cyclohexanone are formed within 20 hr under the same conditions. The kinetic curves of photooxidation of cyclohexane in the presence of RhCl_3 and RuCl_3 are given in Fig. 4. As can be seen, the second complex is slightly more active. Both reactions have an induction period.

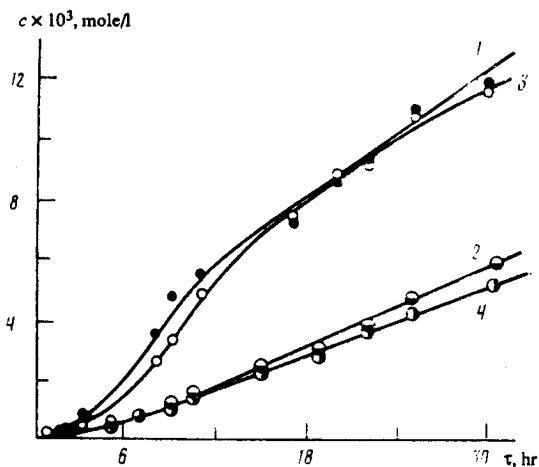


FIG. 4. Kinetic curves of accumulation of cyclohexanol (1) and cyclohexanone (2) during photooxidation of solution of cyclohexane (0.46 mole/l) in acetonitrile in presence of 5×10^{-4} mole/l $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ (1, 3) and $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ (2, 4).

The combined oxidation of ethyl benzene and cyclohexane, catalyzed by RuCl_3 , indicates that, in the initial period of the reaction (1 hr), the C-H bond in the methylene group of the alkylaromatic hydrocarbon is 30 times more active than the C-H bond in cycloalkanes. However, as the reaction progresses, the oxygenation rate of cyclohexane increases, and therefore the relative activity Ψ , determined from the slopes of the tangents to the curves of accumulation, becomes equal to 13 after only 3 hr, and then remains constant. The relative accumulation rate of aldehydes in reactions of competing oxygenation of *p*-xylene and toluene also changes with time. Whereas 1.5 hr after the start of the reaction the ratio of the yields of *p*-toluyl aldehyde and benzaldehyde, which can be taken as the ratio of the initial oxidation rates, amounts to 1.45, after only 2 hr the relative accumulation rate, determined from the ratio of the slopes of the tangents, changes to 0.65 and then remains constant. Assuming the existence of correlation between the logarithm of the ratios of rates and the Hammett-Brown constant σ^+ , it is possible to estimate the value of ρ^+ at +0.5 for a reaction time of less than 1.5 hr, and at +1.9 for a time of more than 4 hr. All these data can evidently indicate that, in the course of the reaction, complete or partial change in the mechanism of the reaction occurs.

SUMMARY

During light irradiation in air, alkanes and arylalkanes in a CH_3CN solution in the presence of catalytic amounts of PtCl_6^{2-} , PtCl_4^{2-} , RhCl_3 and RuCl_3 complexes are oxygenated with the formation of alcohols and ketones. The accumulation of products of cyclohexane oxidation occurs with an induction period, which is particularly great in the case of photocatalyst PtBr_6^{2-} , but is removed almost entirely when hydroquinone is added. It has been suggested that, in the developed period of the reaction, photooxygenation is catalyzed by complexes of metals in a low state of oxidation.

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