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PHOTO-OXIDATION OF ALKANES BY ATMOSPHERIC OXYGEN, CATALYSED BY A VANADATE–ANTHRAQUINONE SYSTEM*†

G. V. NIZOVA and G. B. SHUL'PIN

N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences, Moscow

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The oxidation of alkanes in air in an acetonitrile solution during irradiation with visible light in the presence of an anthraquinone–oxometallate system (where the oxometallate is $(\text{Bu}_4\text{N})\text{VO}_3$, $(\text{Bu}_4\text{N})_2\text{WO}_4$ or $(\text{Bu}_4\text{N})_2\text{Mo}_2\text{O}_7$), leading to the formation of alkylperoxides, ketones and alcohols, occurs at different rates and selectivities by comparison with photo-oxidation sensitized only by anthraquinone.

Earlier we showed that, in the presence of certain transition metal complexes such as FeCl_3 , CuCl_2 , AuCl_4^- [2], VO_3^- [3], polyoxometallates [3–5] etc, alkanes in an acetonitrile [2, 4, 5] or methylene chloride [3] solution are readily oxidized during irradiation in air, with the formation of alkylperoxides, ketones and alcohols. On the other hand it has long been known that anthraquinone is an effective sensitizer for the photo-oxidation of alkanes [6]. It was of interest to investigate the combined photocatalytic action of anthraquinone and certain complexes.

EXPERIMENTAL

The reactions were carried out in air in cylindrical, 20 mm diameter glass vessels equipped with water-cooled (20°C) jackets. A magnetic stirrer was used to stir the reaction solution. The total volume of the solution was 5 ml. Irradiation was carried out with the full light of a halogen lamp (150 W). The process was followed by taking samples after certain time intervals for GLC analysis after the addition of a portion of triphenylphosphine, which reduces the alkylhydroperoxides to the corresponding alcohols. The procedure is described in detail in [2]. A Perkin–Elmer 8500 chromatograph equipped with steel columns of 2 m length was used; the sorbent was Chromosorb W80/100 with 5% Carbowax and an NR 3390A integrator, and the carrier gas was helium.

The formation of a cyclohexylperoxide radical was recorded from EPR spectra of the spin adduct of a benzylidene-*tert*-butylamine-*N*-oxide trap on a Varian Eg spectrometer after the addition of this reagent to 0.4 ml of the reaction solution after irradiation for 0.5 hr. The experimental conditions were as follows: modulation frequency 100 kHz, modulation amplitude 0.5 Oe, microwave power 80 MW, microwave frequency 9.5 Hz.

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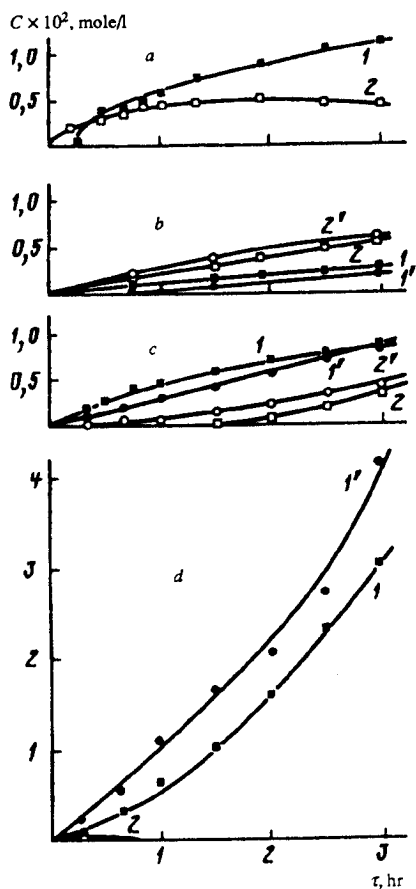


Fig. 1. Kinetic curves of the accumulation of total cyclohexanol and cyclohexanone (*1*) and cyclohexylhydroperoxide (*2*) during the oxidation of cyclohexane (0.46 mole/l) in air in a CH_3CN solution (20°C) during irradiation with the full light of a halogen lamp (150 W) in the presence of anthraquinone (5×10^{-4} mole/l) (*a*) and also with the addition (1×10^{-4} mole/l) of $(\text{Bu}_4\text{N})_2\text{WO}_4$ (*b*), $(\text{Bu}_4\text{N})_2\text{Mo}_2\text{O}_7$ (*c*) and $(\text{Bu}_4\text{N})\text{VO}_3$ (*d*). *1'* and *2'* — corresponding curves of accumulation after pre-irradiation of solutions in the presence of cyclohexane for 0.5 hr.

RESULTS AND DISCUSSION

In the present work we investigated the oxidation of cyclohexane and also *n*-hexane, 3-methylhexane and ethylbenzene by atmospheric oxygen during irradiation with visible light in the presence of catalytic amounts of anthraquinone and transition metal oxo complexes $(\text{Bu}_4\text{N})\text{VO}_3$, $(\text{Bu}_4\text{N})_2\text{WO}_4$ and $(\text{Bu}_4\text{N})_2\text{Mo}_2\text{O}_7$. Figure 1*a* gives kinetic curves of the accumulation of cyclohexylhydroperoxide and total cyclohexanol and cyclohexanone during the oxidation of cyclohexane, photosensitized by anthraquinone alone. As can be seen from Fig. 1*a*, after 2 hr the reaction is virtually complete, and the overall concentration of products does not exceed 1.5×10^{-2} mole/l. The addition of catalytic amounts of $(\text{Bu}_2\text{N})_2\text{WO}_4$ or $(\text{Bu}_4\text{N})_2\text{Mo}_2\text{O}_7$ does not lead to any appreciable change in the oxidation rate (Fig. 1*b* and *c* respectively). The synergism during combined photocatalysis by anthraquinone and $(\text{Bu}_4\text{N})\text{VO}_3$ is much more

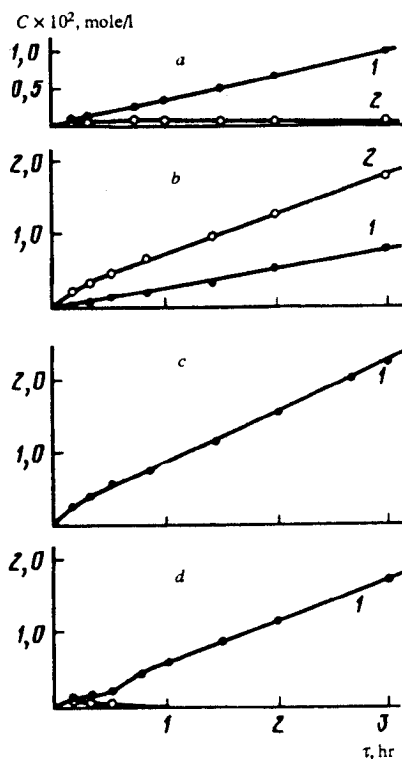


Fig. 2. Kinetic curves of the accumulation of total 1-phenylethanol and acetophenone (1) and 1-phenylethylhydroperoxide (2) during the oxidation of ethylbenzene (0.46 mole/l) in air in a CH_3CN solution (20°C) during irradiation in the presence of anthraquinone (5×10^{-4} mole/l) (a) and also with the addition (1×10^{-4} mole/l) of $(\text{Bu}_4\text{N})_2\text{WO}_4$ (b), $(\text{Bu}_4\text{N})_2\text{Mo}_2\text{O}_7$ (c) and $(\text{Bu}_4\text{N})\text{VO}_3$ (2).

pronounced (Fig. 1d). In the presence of $(\text{Bu}_4\text{N})\text{VO}_3$ alone, no oxidation products of cyclohexane are found even after irradiation for 3 hr. It must be pointed out that in [3] a vanadate ion photocatalysed the oxidation of cyclohexane under different conditions: in a CH_2Cl_2 solution during irradiation with the light of a luminescent lamp. A characteristic feature of the reaction in this case is that, over the entire irradiation time, the peroxide is found only in small concentration. It is interesting that, after preliminary irradiation of the anthraquinone and oxometallate solution for 0.5 hr before the addition of cyclohexane, the shape of the kinetic curves (Fig. 1, curves 1' and 2') changes sharply. Here there is no induction period, and the ratio of the concentrations of peroxide and total ketone and alcohol changes. In the case of $(\text{Bu}_4\text{N})\text{VO}_3$, preliminary irradiation of the solution has no strong effect on oxidation, although the rate of the reaction increases slightly.

The photo-oxidation of cyclohexane in the temperature range 0–40°C for anthraquinone and anthraquinone–oxometallate systems showed that the rate of the reaction hardly depends on temperature.

Figure 2 gives kinetic curves of ethylbenzene oxidation catalysed by anthraquinone both in pure form and in the presence of oxo complexes. As can be seen from Fig. 2, the effect of the latter is less pronounced than during the oxidation of cyclohexane.

Table 1. Selectivities in the photochemical oxidation of *n*-hexane and 3-methylhexane*

System	<i>n</i> -Hexane			3-Methylhexane		
	C(1)	C(2)	C(3)	1°	2°	3°
Anthraquinone	1	55	57	1	43	550
Anthraquinone-(Bu ₄ N) ₂ WO ₄	1	24	24	1	17	183
Anthraquinone-(Bu ₄ N) ₂ Mo ₂ O ₇	1	30	30	1	9	89
Anthraquinone-(Bu ₄ N)VO ₃	1	26	26	1	3	49

* Normalized values of the reactivity of C-H bonds at different carbon atoms are given, i.e. the number of hydrogen atoms bound with the given carbon is taken into account.

It was of interest to compare the selectivities of photo-oxidation of different alkanes by the systems studied. From data in Table 1 it follows that, both for regioselectivity during the oxidation of C-H bonds in positions 1, 2, and 3 of hexane and for selectivity during the oxidation of primary, secondary and tertiary 1°, 2°, 3° bonds in 3-methylhexane, when an oxometallate is added the reactivity of a catalytically active particle increases, which leads to a reduction in process selectivity. However, in this case the values of selectivity are slightly higher than those observed earlier for the oxidation of *n*-hexane and 3-methylhexane by H₂O₂-VO₃⁻-pyrasine-2-carboxylic acid systems (C(1)/C(2)/C(3) = 1:8:7 and 1°/2°/3° = 1:14:64) [7] and H₂O₂ in CH₃CN (C(1)/C(2)/C(3) = 1:10:7 and 1°/2°/3° = 1:6:30) [7].

As is known, during the anthraquinone-photosensitized oxidation of alkanes, a key reaction is the detachment of the hydrogen atom from the RH alkane by the excited anthraquinone [8], as a result of which an alkyl radical R· is formed, reacting rapidly with an oxygen molecule. The arising alkylperoxide radical ROO· is then converted to intermediate (alkylperoxidases) and final (ketones and alcohols) products. It can be assumed that, in the presence of vanadate, a complex of a polyoxovanadate particle with anthraquinone is formed, and the reactivity of this photo-excited complex in the detachment of hydrogen from an alkane is higher than in the case of free anthraquinone. The intermediate formation of ROO· radicals was recorded by EPR with the use of a free radical trap — *N*-*tert*-butyl- α -phenylnitron. The EPR spectrum of the adduct of a cyclohexylperoxide radical and nitron consists of a triplet signal with the following parameters: $g = 2.0058 \pm 0.0002$, $A_N = 13.78 \pm 0.02$, $A_H^{\beta} = 2.55 \pm 0.05$.

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