KINETICS, PRODUCTS, AND MECHANISM OF THE PHOTOCHEMICAL OXIDATION OF CYCLOHEXANE

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The photochemical oxidation of saturated hydrocarbons makes it possible to obtain valuable oxygen-containing products under mild conditions [1-3]. The kinetics of the formation of these products and the mechanism of the photolysis of solutions of O_2 in organic substrates have not been adequately studied. In the present work the kinetic laws and mechanism of the photooxidation were studied in the example of cyclohexane (RH) at 22°C.

EXPERIMENTAL

The procedure for the purification of RH was described in [4]. The photolysis of RH was carried out in a quartz cuvette with an optical path $l = 5$ cm, which was covered with a self-sealing membrane made from vacuum-tight rubber, and the irradiation was carried out with the unfiltered light of a DRSh-250 lamp.

Known instrumentation [4] was used for the flash photolysis and the high-speed recording of the free radicals. The photolytic source was an IFP 5000-2 lamp, and the energy in a flash was 400 J with $U = 5$ kV and $C = 32$ μF. About 90% of the radiant energy was emitted within 50 μsec. The reactor was an 18 × 1 cm thermostated quartz cell. In order to accumulate the products in an amount sufficient for analysis, the reaction mixture was subjected to the action of 10-40 light flashes.

Cyclohexanol (ROH) and cyclohexanone (R'O) were analyzed by GLC (90°C, 15% polyethylene glycol adipate on Chromaton N-AWD MCS).

Special experiments revealed that cyclohexyl hydroperoxide (ROOH) completely decomposes in the column under the conditions of the chromatographic analysis when $[\mathrm{ROOH}] \leqslant 2 \cdot 10^{-4}$ mole/liter to form ROH and R'O, whose ratio varies from 1.1 to 1.5.

The active peroxides were analyzed iodometrically, I_2 being detected spectrophotometrically [5]. For the purposes of identification the peroxides were reduced by triphenylphosphine, ROH being formed quantitatively [1]. In control experiments it was shown that cyclohexyl hydroperoxide is completely reduced to ROH within 15 min when $[\mathrm{ROOH}] \leqslant 2 \cdot 10^{-4}$ mole/liter. The amount of ROH formed in the photochemical reaction was calculated from the difference between the concentration of cyclohexanol after reduction and the concentration of ROOH. The H_2O_2 was determined by a method involving the polarographic separation of H_2O_2 and the organic peroxides, which permits the detection of $[H_2O_2] \geqslant 10^{-4}$ mole/liter [6]. The O_2 content in the liquid phase was determined by a spectrophotometric method based on the ability of the radical anion of semianthraquinone to be rapidly oxidized by molecular O_2 to anthraquinone when an alkaline solution of anthraquinone in methanol is irradiated by UV light [4].

DISCUSSION

Photolysis of RH saturated with air ($[O_2] = 1.9 \cdot 10^{-3}$ mole/liter) under the conditions of continuous irradiation results in the formation of ROH, R'O, and ROOH in a 1:0.6:0.9 ratio. No H_2O_2 was detected in the oxidation products. The reaction products are formed in parallel (Fig. 1) in contrast to the data in [1], where the only product of the photooxidation of RH in the initial moment in time was ROOH. The yield of the sum of the oxygen-containing products as calculated for the O_2 consumed, $\Delta[O_2]$, was ∿50%. About half of the O_2 is utilized for the formation of unidentified oxidation products of RH.

In individual experiments with additions of R'O it was shown that in the range from $[\mathrm{R'O}] = 10^{-4}$ to 10^{-3} mole/liter cyclohexanone does not have an appreciable influence on the kinetics of the accumulation of the products.

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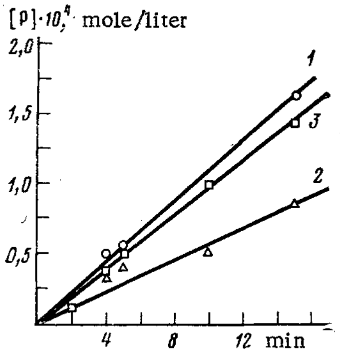

Fig. 1

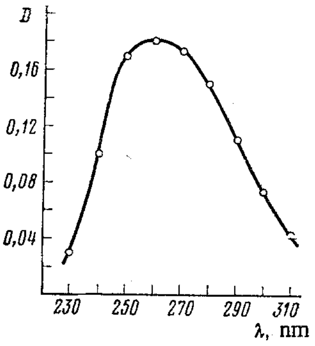

Fig. 2

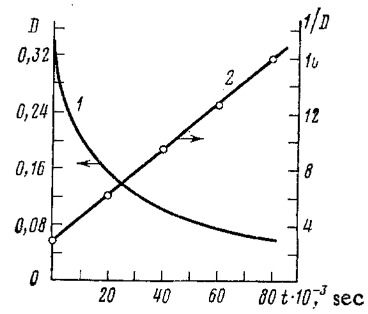

Fig. 3

Fig. 1. Kinetic plots of the accumulation of ROH (1), R'O (2), and ROOH (3) during the continuous irradiation of solutions of O_2 in RH (22°C).

Fig. 2. Optical absorption spectrum of peroxide radicals.

Fig. 3. Typical kinetic plot of the consumption of peroxide radicals (1) and corresponding linearized plot (2).

The flash photolysis of an RH—O_2 mixture results in the formation of the same products which form under the conditions of continuous irradiation with a total yield relative to the O_2 consumed of ∿30%; however, the [ROH]/R'O ratio increases to 2.0 ± 0.5 (Table 1). For comparison we note that in the case of initiation by tert-butyl hypochlorite, the flash photolysis of RH saturated with O_2 results in the formation of ROH and R'O in almost equal concentrations, their total yield relative to the O_2 consumed being close to quantitative, while ROOH and H_2O_2 are not present among the oxidation products [4, 6].

The flash photolysis of an RH—O_2 mixture results in the formation of particles which have a broad absorption spectrum with λ_{max} at 260-265 nm (Fig. 2) and a lifetime equal to 10-30 msec. When a UFS-5 filter was used, the formation of these particles was not observed. A comparison with the literature data (Table 2) makes it possible to identify these particles as peroxide radicals. From Table 2 it follows that different peroxide radicals have almost identical absorption spectra and that λ_{max} at 240 to 270 nm is only weakly dependent on the position of the functional groups and on the length of the carbon chain. Therefore, the identification of the peroxide radicals from the UV spectra is impossible.

The kinetics of the consumption of the peroxide radicals $r\dot{O}_2$ in the RH—O_2 system are described well by a second-order equation: $-d[r\dot{O}_2]/dt = 2k_t[RO_2]^2$. Making the transition to the values of the optical density, we have $-D/dt = (2k_t/\varepsilon_{r\dot{O}_2}\cdot l)D^2$ (Fig. 3), where $2k_t$ is the effective rate constant of the destruction of rO_2 radicals in reactions with one another, and $\varepsilon_{r\dot{O}_2}$ is the extinction coefficient of $r\dot{O}_2$.

The results of the measurements of the kinetic parameter $K' = 2k_t/\varepsilon_{r\dot{O}_2}$ at various temperatures are as follows:

T., °C	10	30	40	60
$K'\cdot10^{-3}$	2,9	4,8	5,4	6,0

From Table 1 it follows that in the case of the flash photooxidation of RH, ∿70% of the O_2 is utilized for the formation of unidentified oxidation products. The significant difference between $\Delta[O_2]$ and the total content of ROH, R'O, and ROOH is apparently due to the formation of several species of peroxide radicals in the RH—O_2 system. The overall extinction coefficient of these perioxide radicals was determined from the consumption of O_2 [4]: ε =

TABLE 1. Composition of Flash-Photolysis Products of Solutions of O_2 in Cyclohexane (C, mole/liter, 22°C)

$[ROH]\cdot10^4$	$[R'O]\cdot10^4$	$[ROOH]\cdot10^4$	$\Delta[O_2]\cdot10^4$	$[ROH]\cdot10^4$	$[R'O]\cdot10^4$	$[ROOH]\cdot10^4$	$\Delta[O_2]\cdot10^4$
0,58	0,30	0,54	—	1,12	0,5	0,63	3,10
0,77	0,51	0,88	2,85	1,27	0,51	0,71	3,7

TABLE 2. Extinction Coefficients and Recombination Rate Constants of Peroxide Radicals

Radical*	Medium	λ_{max}, nm	ε, liters/mole · cm	$2k_t$ (22°C), liter/mole · sec	E, kJ/mole	lg A	Lit. cited
$CH_3\dot{O}_2$	Gaseous phase	235	870	$2{,}3 \cdot 10^8$			[7]
$CH_3\dot{O}_2$	Same	240	1150	$2{,}6 \cdot 10^8$			[8]
$C_3H_7\dot{O}_2$	" "	240		$6{,}9 \cdot 10^5$	18,65±0,50	9,15±0,03	[9]
$R\dot{O}_2$	RH *	260	650±100†	$1{,}6 \cdot 10^6$	8,4±1,3	7,7±1,15	[4]
cyclo-$C_6H_{11}\dot{O}_2$	cyclo-C_6H_{12}	265	800±120†	$2{,}2 \cdot 10^6$	5,4±0,8	7,3±1,1	[6]
cyclo-$C_6H_{11}\dot{O}_2$	cyclo-C_6H_{12}	275	2000	$1{,}6 \cdot 10^6$			[10]
cyclo-$C_6H_{11}\dot{O}_2$	cyclo-C_6H_{12}	255	1900	$2{,}3 \cdot 10^6$			[11]
$r\dot{O}_2$ ‡	cyclo-C_6H_{12}	260	650±100	$2{,}5 \cdot 10^6$	11,6±1,7	8,4±1,3	—
cyclo-$C_6H_{10}(OH)\dot{O}_2$	cyclo-$C_6H_{11}OH$	246	1600	$1{,}2 \cdot 10^7$			[11]
$(CH_3)_2C(OH)\dot{O}_2$	H_2O	248	1100	$1{,}1 \cdot 10^7$			[12]
$\dot{O}_2CH_2COOH$	H_2O	290	900	$2{,}8 \cdot 10^9$			[13]

*Here $R\dot{O}_2$ denotes $C_6H_{13}\dot{O}_2$, $C_7H_{15}\dot{O}_2$, $C_8H_{17}\dot{O}_2$, $C_9H_{19}\dot{O}_2$, $C_{10}H_{21}\dot{O}_2$, $C_{12}H_{25}\dot{O}_2$, $C_{13}H_{27}\dot{O}_2$, and $C_{16}H_{33}\dot{O}_2$, and RH denotes the corresponding n-paraffins.

†Calculated from the data in [4, 6] with consideration of the influence of the probing radiation on the system under investigation.

‡Here $r\dot{O}_2$ denotes peroxide radicals formed as a result of the isomerization of the cyclohexoxy radical.

650 ± 100 liters/mole·cm. The effective rate constant for the destruction of rO_2 radicals in reactions with one another calculated with the aid of the values of ε and k', i.e., $2k_t = 2.8 \cdot 10^8 \exp(-11.6 \pm 1.7\ \text{kJ/mole}/RT)$ liters/mole·sec, is consistent with the results of the measurements of the rate constants for the disproportionation of secondary peroxyalkyl radicals both by flash photolysis (see Table 2) and by other methods [14].

The experimental results obtained (see Table 1) show that the contribution of the disproportionation of peroxycyclohexyl radicals to the overall process of the destruction of the peroxide radicals is 30%. Apparently, one of the main paths for the formation of peroxide radicals other than peroxycyclohexyl radicals is the isomerization of the cyclohexoxy radicals $R\dot{O}$ to the alkyl radicals $\dot{r}$, which are converted into peroxide radicals in the presence of O_2 with the rate constant $k \simeq 10^8$ liters/mole·sec [14]. Thus, the isomerization of alkoxy radicals with the transfer of the free valence to a C atom was established in the case of the photooxidation of C_4–C_6 alkanes [15]. If it is assumed that the isomerization of the $R\dot{O}$ radical occurs according to a mechanism involving the migration of an H atom, the formation of peroxyhydroxycyclohexyl radicals in the system should be expected, and H_2O_2 should be present in the oxidation products of RH, since the disproportionation of peroxyhydroxycyclohexyl radicals results in the formation of R'O and H_2O_2 in a 2:1 ratio. This is not consistent with our experimental data. Therefore, it may be assumed that under our conditions the cyclohexoxy radicals isomerize with cleavage of a C—C bond, as was pointed out in [16].

The set of results obtained in the present work and in [4, 6], as well as the literature data, allow us to propose the following scheme for the photochemical oxidation of cyclohexane:

$$RH + O_2 \rightleftarrows \overset{\delta+}{RH} \ldots \overset{\delta-}{O_2} \tag{1}$$

$$\overset{\delta+}{RH} \ldots \overset{\delta-}{O_2} \xrightarrow{h\nu} \begin{cases} \dot{R} + H\dot{O}_2 \\ ROOH \end{cases} \tag{2}$$

$$ROOH \xrightarrow{h\nu} R\dot{O} + H\dot{O} \tag{3}$$

$$R\dot{O} + RH \rightarrow ROH + \dot{R} \tag{4}$$

$$H\dot{O} + RH \rightarrow H_2O + \dot{R} \tag{5}$$

$$R\dot{O} \rightarrow \dot{r} \tag{6}$$

$$\dot{R} + O_2 \rightarrow R\dot{O}_2 \tag{7}$$

$$\dot{r} + O_2 \rightarrow rO_2 \tag{8}$$

$$R\dot{O}_2 + RO_2 \rightarrow ROH + R'O + O_2 \tag{9}$$

$$r\dot{O}_2 + r\dot{O}_2 \rightarrow \text{Products} \tag{10}$$

$$R\dot{O}_2 + r\dot{O}_2 \rightarrow \text{Products} \tag{11}$$

$$R\dot{O}_2 + H\dot{O}_2 \rightarrow ROOH + O_2 \tag{12}$$

$$r\dot{O}_2 + H\dot{O}_2 \rightarrow \text{Products} \tag{13}$$

According to the proposed scheme, the step preceding initiation is the formation of a complex of RH with O_2. Solutions of O_2 in cyclohexane absorb light with $\lambda < 260$ nm [1-3] owing to the existence of the contact charge-transfer complex $[RH^+ \ldots O_2^-]$ [17]. The step initiating the photooxidation of RH is the decomposition of the complex to form $\dot{R}$, $H\dot{O}_2$, and ROOH according to reaction (2). Under the conditions of the photochemical process, the hydroperoxide can rapidly dissociate homolytically under the action of light according to reaction (3) (in the opinion of some investigators [1], reaction (3) is the only path for the formation of ROH and R'O) and regenerated according to reaction (12). The other path for the formation of ROOH, viz., $R\dot{O}_2 + RH \rightarrow ROOH + \dot{R}$, is practically not realized under the conditions of our experiments (22°C) [14].

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CONCLUSIONS

1. The kinetics of the accumulation of the photooxidation products of cyclohexane have studied, and a radical mechanism for their formation has been proposed. The effective rate

constant for the recombination of peroxide radicals and their extinction coefficient have been measured.

2. The contribution of the disproportionation of peroxycyclohexyl radicals to the overall process of the destruction of the peroxide radicals amounts to ∿30%. It has been postulated that one of the main paths for the formation of peroxide radicals other than peroxycyclohexyl radicals is the isomerization of the cyclohexoxy radical with cleavage of the C–C bond.

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OXIDATION OF AMINES BY MOLECULAR OXYGEN.

11. MECHANISM OF THE OXIDATION OF N-METHYLPIPERIDINE

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The liquid-phase oxidation of acyclic N-alkylamines proceeds according to a radical chain mechanism [1]. As a continuation of the investigation of the connection between the structure and reactivity, in the present work we studied the oxidation of a cyclic amine, viz., N-methylpiperidine.

EXPERIMENTAL

The amine, which was dried by KOH, was vacuum distilled at ∿40°C and then distilled at atmospheric pressure in Ar over K. The purification was carried out by passage through Al_2O_3 or maintenance for 24 h with paraformaldehyde or for 1 week with p-quinone in an O_2 atmosphere. In all cases, after the vacuum distillation, the amine was oxidized with linear chain termination. Additional purification by activated charcoal [2] removed the inhibiting impurities. The oxidation rate was measured volumetrically according to the absorption of O_2 and according

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