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PEROXIDES-XI

Benzoyl Peroxide–Tetraalkylammonium Iodide System As an Initiator of the Low-Temperature Oxidation of Cumene

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Abstract—The initiating effect of the benzoyl peroxide–tetraalkylammonium iodide system in the low-temperature liquid-phase oxidation of cumene at 313 K is studied. The reaction proceeds by a nonbranching-chain radical mechanism. At the initial stage, the kinetics of the process is described by a first-order equation. The parameters of the kinetic equation are determined at various substrate concentrations and component proportions in the initiating system. Addition to the reaction mixture of benzoic acid, cumene hydroperoxide, and iodine in amounts that can accumulate during the reaction produces only a slight effect on the oxidation rate.

The kinetics of oxidation of organic compounds by oxygen gas is governed, to a considerable extent, by the rate of chain initiation. Dinitriles and peroxides are usually used as initiators [1]. The catalysis of cumene oxidation and homolytic decomposition of cumene hydroperoxide by onium salts at low temperatures (333–363 K) was discovered in [2, 3]. In particular, alkylammonium halides, which initiate radical decomposition of hydroperoxides, can play the role of catalysts in hydrocarbon oxidation [4, 5]. Peroxide–onium salt binary mixtures are an interesting modification to this type of initiating system. For example, a mixture of benzoyl peroxide and tetraalkylammonium bromide exhibits initiating properties during cumene oxidation at low temperatures (313 K) [6].

Tetraalkylammonium iodides, which drastically affect the rate of benzoyl peroxide decomposition in organic solvents [7], hold a special place among tetraalkylammonium halides. Iodides are widely used in the development of analytical methods for peroxide determination [8, 9]. Considerable study has also been given to other aspects of iodide–peroxide reactions and the significant role that they play in biochemical processes [10, 11].

Many of the mechanisms suggested for the reactions between the iodide ion and peroxides do not include the formation of reactive free radicals [9–11]. However, alkylammonium iodides, like other alkylammonium halides, can catalyze hydrocarbon oxidation by initiating the radical decomposition of hydroperoxides, and their effectiveness in chain initiation depends on their structure [4, 5].

The purpose of this work is to study the initiation of the liquid-phase low-temperature chain radical oxidation of hydrocarbons by the benzoyl peroxide–tetraammonium iodide system.

Cumene (Cum) is used as the oxidized substrate, because its radical oxidation is well understood and the rate constants of the elementary steps have been determined [12].

EXPERIMENTAL

Cumene purification and the experimental procedures (oxidation rate measurements, titration of hydroperoxides, IR spectroscopic determination of benzoyl peroxide content) were described in [6]. Tetrabutylammonium iodide (Bu_4NI) and tetraethylammonium iodide (Et_4NI) were purified by repeated precipitation from acetonitrile into water-free diethyl ether. Next, the salts were dried at a reduced pressure and a temperature of 329.0 ± 0.5 K and were stored in a dry box with phosphorus(V) oxide. Halide solutions were prepared in acetonitrile (AcN); therefore, AcN (10 vol %) was always present in the reaction mixture. The kinetics of cumene oxidation were also studied in the presence of chlorobenzene (PhCl). When measuring the oxidation rate as a function of cumene concentration, certain amounts of cumene were replaced with an equal volume of chlorobenzene for the polarity of the medium to be constant. In this case, the composition of the solution (in volume fractions) can be represented as (Cum + PhCl)/AcN = 0.9 : 0.1. Oxidation at varied salt and benzoyl peroxide concentrations was studied in two types of solutions, namely, Cum : AcN = 0.5 : 0.5 and Cum : AcN/PhCl = 0.5 : 0.1 : 0.4.[1]

RESULTS AND DISCUSSION

The measurement of oxygen consumption in the presence of benzoyl peroxide (BP) and Bu_4NI or Et_4NI

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[1] These compositions are hereafter referred to as acetonitrile and chlorobenzene.

demonstrated that, at 313 K, cumene oxidizes at a detectable rate without an induction period. The instant that the reactor with the reaction mixture was immersed into the thermostat was taken to be the onset time of the reaction. Figure 1 plots oxygen consumption curves for cumene oxidation. The maximum oxidation rate ($w_{\max}$) is observed at the initial stage of the process. Afterwards, the rate gradually slows down.

In the presence of BP alone (without iodide), cumene is not oxidized at 313 K over several hours. Testing various kinds of cations showed that even considerable changes in cation structure (passing from ammonium to phosphonium salts) or in the size of substituents (Bu_4NI, Et_4NI) produce only a slight effect on the rate of cumene oxidation (Table 1). A comparison between kinetic data for tetraalkylammonium iodides and tetraalkylammonium bromides [6] demonstrates that the bromides are more active in cumene oxidation (Table 1). In the case of the bromides, the effect of cation structure is more pronounced.

Particular attention was given to cumene oxidation initiated by the BP—tetraalkylammonium iodide (Bu_4N or Et_4N) system at 313 K for the reason that, at this temperature, the decomposition rates of cumene hydroperoxide and BP in the absence of an ammonium salt are negligible.

The time dependence of oxygen consumption ($[O_2]$) (mol/l) is adequately described by the equation

$$[O_2]_t = a(1 - b\exp(-kt)), \qquad (1)$$

where a, b, and k are empirical parameters. It is evident from Fig. 1 that the curves calculated by Eq. (1) fit the experimental data well. The fact that Eq. (1) includes a coefficient b somewhat differing from unity is explained by the following problem in the determination of the onset time of the reaction: the preparation of the manometric device for oxygen uptake measurements takes some time, so the instant the reactants are mixed and the instant the run is begun (the reactor is immersed into the thermostat) are separated by about 2 min.

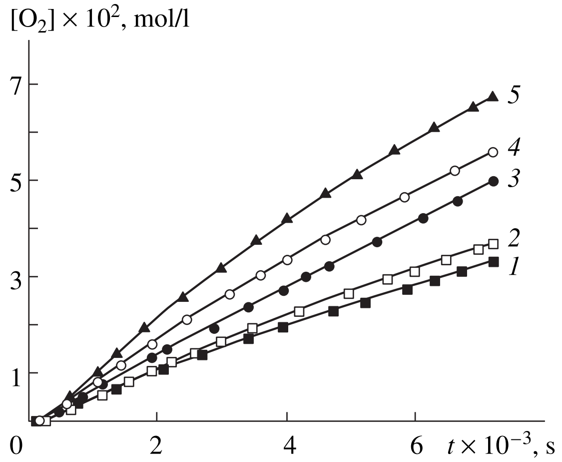

Fig. 1. Oxygen consumption curves for cumene oxidation in the presence of benzoyl peroxide and tetrabutylammonium iodide at 313 K. $[Cum]_0 = 3.58$ mol/l; $[BP]_0 \times 10^2 =$ (*1*, *4*, *5*) 2.0, (*2*) 1.0, and (*3*) 8.0 mol/l; $[Bu_4NI]_0 \times 10^3 =$ (*1*) 1.26, (*2*) 1.31, (*3*) 1.35, (*4*) 4.09, and (*5*) 14.80 mol/l; the solvent is (*1*, *5*) chlorobenzene and (*2*–*4*) acetonitrile. The points stand for experimental data, and the lines represent data calculated using Eq. (1).

Knowing a, b, and k, we can calculate the initial (maximum) rate of the reaction:

$$w_{\max} = \left(\frac{d[O_2]}{dt}\right)_{t \to 0} = kab. \qquad (2)$$

Statistical processing of the oxygen consumption curves obtained for a wide range of concentrations of the substrate (1.8–6.5 mol/l), BP (0.005–0.1 mol/l), and ammonium salts (0.001–0.015) showed that these curves are adequately described by Eq. (1). In all

Table 1. Kinetic parameters of cumene oxidation initiated by the benzoyl peroxide–tetraalkylammonium (tetraalkylphosphonium) halide mixture at 313 K

Salt	$[Salt] \times 10^3$, mol/l	$[O_2]_{t=2} \times 10^2$, mol/l	$w_{\max} \times 10^5$, mol l^{-1} s^{-1}
$C_2H_5(C_6H_5)_3PI$	2.09	4.8	0.72
Bu_4NI	2.03	4.9	0.86
Et_4NI	2.38	5.0	0.85
$(CH_3)_4NI$	2.36	5.1	0.83
$(C_6H_5)_4PI$	2.30	5.2	0.91
Bu_4NBr	1.25	6.4	1.30
Et_4NBr	1.31	7.8	1.51

Note: $[Cum]_0 = 3.58$; $[BP]_0 = 2.0 \times 10^{-2}$ mol/l; $[O_2]_{t=2}$ is the amount of oxygen consumed per liter of solution in 2 h.

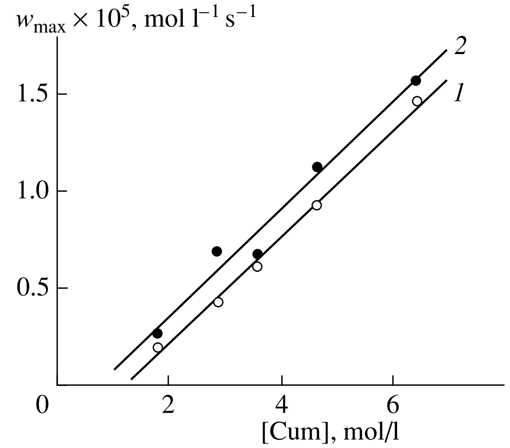

Fig. 2. Dependence of the maximum cumene oxidation rate (w_{max}) on cumene concentration in the presence of benzoyl peroxide (0.02 mol/l) and tetrabutylammonium iodide (1.31×10^{-3} mol/l) at 313 K; the solvent is (*1*) chlorobenzene and (*2*) acetonitrile.

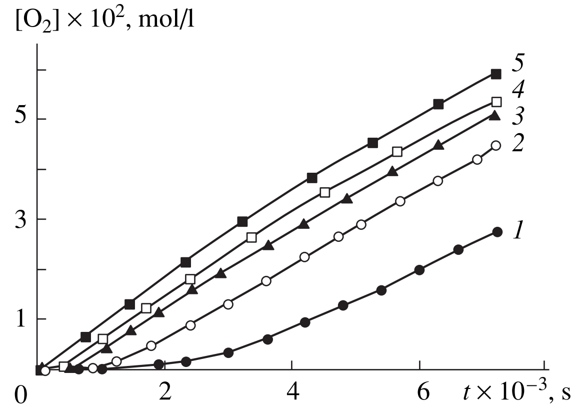

Fig. 3. Effect of cumene hydroperoxide (CHP), iodine (I_2) and benzoic acid (BA) on the kinetics of cumene (3.58 mol/l) oxidation in the presence of benzoyl peroxide (0.02 mol/l) and tetraethylammonium iodide (4.0×10^{-3} mol/l) in acetonitrile: (*1*) [BA] = 0.4 mol/l, (*2*) [BA] = 1.0 mol/l, (*3*) $[I_2]$ = 0.2 mol/l, (*4*) [CHP] = 2.0 mol/l, and (*5*) no additive.

instances, the correlation coefficient was equal to or greater than 0.999.

The maximum initial rates calculated as a product of fitted empirical parameters using Eq. (2) are given in Tables 2 and 3. It follows from these data that both the calculated rates and parameters *a* and *k* depend crucially on the concentrations of the substrate, PB, and the salts.

Table 2 lists w_{max} data for various $[R_4NI]_0$ values for the PhCl–AcN mixture and pure AcN. An increase in the AcN content raises the initial rate of the process. w_{max} rises as the concentration of the salt increases to ~0.015 mol/l. At higher salt concentrations, BP begins to react readily with iodide during the preparation of the reaction mixture, causing considerable difficulties in recording oxygen consumption curves. In addition, the solution turns yellow, because I_2 is released.

The kinetic parameters calculated from the oxygen consumption curves for various cumene concentrations and constant initial concentrations of BP and Bu_4NI (or Et_4NI) are listed in Table 3. According to these data, the dependence of w_{max} on $[RH]_0$ is linear for both iodides, with a correlation coefficient of 0.99. A similar linear dependence is observed for AcN, although the polarity of the medium increases with decreasing cumene content. In this case, the w_{max} values are higher than those for PhCl and the correlation coefficient is 0.98 (Fig. 2).

Raising the BP concentration from 0.005 to 0.06 mol/l at constant concentrations of the substrate and salt causes an increase in w_{max} and the amount of oxygen consumed (Table 3). As $[BP]_0$ is further increased, the oxidation rate ceases to grow and then drops. Most of the experiments were performed at $[BP]_0 = 2.0 \times 10^{-2}$ mol/l, the concentration optimal for sustaining high initiation rates.

Iodometric titration data suggest that the concentration of peroxide compounds rises in the course of the process, owing to the formation of cumene hydroperoxide (CHP) (Table 4). However, titration allowed us to determine the total amount of peroxide groups [O–O] because both CHP and BP were titrated. To determine $[BP]_t$, we studied the kinetics of BP decomposition by IR spectroscopy, measuring the intensity of the carbonyl (1764 cm^{-1}) absorption band. Thus, at $[BP]_0 = 2.0 \times 10^{-2}$ mol/l, $[Et_4NI]_0 = 4.0 \times 10^{-3}$ mol/l, and $[Cum]_0$ = 3.58 mol/l in AcN, the BP concentration decreased to 0.8×10^{-2} mol/l within 2 h. To evaluate the yield of CHP, we compared these results with the data of run 9 (Table 4).

The CHP concentration is

$$[CHP]_t = [O\text{–}O]_t - [BP]_t.$$

The selectivity of CHP with respect to consumed oxygen is

$$S = ([CHP]_t/[O_2]_t) \times 100\%.$$

For run 9, *S* = 85%; thus, CHP is the primary product of the reaction. It is evident from the data in Table 4 that the total amount of peroxide groups decreases drastically (as compared to the amount of oxygen consumed) with increasing iodide concentration. When the salt concentration is small, the peroxides decompose at substantially lower rates (Table 4, runs 1–3 and 9–11).

The study of the effect of the reaction products on the cumene oxidation rate provided the following results. Benzoic acid, CHP, and iodine introduced into the reaction mixture in amounts that might result from the process slightly retard oxidation (Fig. 3). The formation of benzoic acid was confirmed by IR spectroscopy, specifically the growth of the intensity of the absorption band at 1721 cm^{-1} (the characteristic band

Table 2. Kinetic data for cumene oxidation in the presence of tetraalkylammonium iodides at 313 K

Solvent	$[R_4NI]_0 \times 10^3$, mol/l	$[O_2]_{t=2} \times 10^2$, mol/l	a	b	$k \times 10^4$, s^{-1}	$w_{max} \times 10^5$, mol l^{-1} s^{-1} (calculated using Eq. (2))
Tetrabutylammonium iodide						
Chlorobenzene (Cum : AcN/PhCl = 0.5 : 0.1 : 0.4	1.26	3.29	0.0887	1.010	0.650	0.58
	1.31	3.46	0.0937	1.008	0.642	0.61
	3.60	4.08	0.1161	1.009	0.643	0.75
	8.39	5.92	0.1059	1.035	1.19	1.30
	14.8	6.70	0.1414	1.024	0.927	1.34
	1.25*	5.76				1.14**
Acetonitrile (Cum : AcN = 0.5 : 0.5)	1.26	4.03	0.1322	1.021	0.534	0.72
	1.31	4.24	0.1249	1.030	0.611	0.79
	2.03	4.68				0.83**
	4.09	5.58	0.1460	1.015	0.686	1.02
	6.55	5.93	0.1569	1.039	0.714	1.16
	11.5	7.23	0.2730	1.007	0.440	1.21
	1.25*	6.40				1.30**
Dimethyl sulfoxide (Cum : DMSO = 1 : 1)	1.25*	0.95				0.17**
Tetraethylammonium iodide						
Chlorobenzene (Cum : AcN/PhCl = 0.5 : 0.1 : 0.4)	0.68	2.70	0.0831	1.011	0.542	0.46
	1.36	3.22	0.0893	1.025	0.654	0.60
	3.89	5.30	0.1113	1.009	0.912	1.02
	7.38	6.10				1.05**
	8.56	6.34	0.1220	1.009	1.01	1.24
	10.4	6.55	0.1129	1.034	1.24	1.45
Acetonitrile (Cum : AcN = 0.5 : 0.5)	0.68	3.64	0.1174	1.017	0.543	0.65
	1.36	4.02	0.1958	1.009	0.330	0.65
	2.38	4.95	0.1353	1.003	0.628	0.85
	4.28	6.10	0.1844	1.000	0.556	1.03
	7.00	7.10	0.1976	1.025	0.647	1.31
	20.6	8.24	0.1129	1.034	1.24	1.45
Dimethyl sulfoxide (Cum : DMSO = 1 : 1)	4.07	5.88				0.99**

Note: $[Cum]_0 = 3.58$; $[BP]_0 = 2.0 \times 10^{-2}$ mol/l.

* The catalyst is tetrabutylammonium bromide, Bu_4NBr.

** The rates are determined from the slope of the initial portion of the oxygen consumption curve.

Table 3. Kinetic data for cumene oxidation at various concentrations of benzoyl peroxide (313 K)

Solvent*	$[\mathrm{Cum}]_0$, mol/l	$[\mathrm{BP}]_0 \times 10^2$, mol/l	$[\mathrm{O_2}]_t \times 10^2$, mol/l	a	b	$k \times 10^4$, $\mathrm{s^{-1}}$	$w_{\max} \times 10^5$, mol $\mathrm{l^{-1}}$ $\mathrm{s^{-1}}$ (calculated using Eq. (2))
Tetrabutylammonium iodide							
Chlorobenzene	1.79	2.00	1.24	0.0790	1.006	0.246	0.20
	2.87	2.00	2.39	0.0666	1.025	0.649	0.44
	3.58	2.00	3.46	0.0937	1.008	0.642	0.61
	4.66	2.00	4.64	0.0958	1.024	0.942	0.92
	5.38	2.00	5.56	0.1147	1.018	0.930	1.08
	6.45	2.00	7.22	0.1368	0.9938	1.00	1.36
	3.58	1.00	3.03	0.0714	1.015	0.782	0.57
	3.58	4.05	3.62	0.1507	1.021	0.410	0.63
	3.58	6.04	3.67	0.1021	1.028	0.654	0.69
	3.58	8.00	4.30	0.1246	1.009	0.600	0.75
Acetonitrile	3.58	1.00	3.65	0.0973	1.018	0.676	0.67
	3.58	2.00	4.24	0.1249	1.030	0.611	0.79
	3.58	4.00	4.45	0.1462	1.013	0.568	0.84
	3.58	6.00	4.73	0.1260	1.019	0.708	0.91
	3.58	8.00	4.96	0.3780	1.006	0.214	0.81
Tetraethylammonium iodide							
Chlorobenzene	1.79	2.00	1.27	0.0767	1.010	0.264	0.20
	2.87	2.00	2.52	0.0807	1.010	0.524	0.43
	3.58	2.00	3.22	0.0893	1.025	0.654	0.60
	4.66	2.00	4.50	0.1238	1.034	0.675	0.86
	6.45	2.00	7.30	0.1945	1.002	0.672	1.31
	3.58	0.51	3.04	0.0553	1.000	1.070	0.59
	3.58	1.00	3.16	0.0762	1.023	0.760	0.60
	3.58	4.00	4.20	0.1272	1.011	0.576	0.74
	3.58	6.00	4.46	0.1057	0.9972	0.791	0.83
	3.58	8.00	4.30	0.1270	1.016	0.600	0.74
	3.58	10.1	3.89				0.64**
Acetonitrile	3.58	0.50	3.40	0.0760	1.020	0.840	0.66
	3.58	1.00	3.89	0.1328	1.012	0.498	0.67
	3.58	2.00	4.02	0.1958	1.009	0.330	0.65
	3.58	4.00	4.34	0.1709	1.020	0.476	0.83
	3.58	6.00	4.95	0.1795	1.017	0.467	0.85
	3.58	8.00	4.71	0.1462	1.025	0.591	0.89

Note: $[\mathrm{Bu_4NI}]_0 = 1.31 \times 10^{-3}$ mol/l; $[\mathrm{Et_4NI}]_0 = 1.36 \times 10^{-3}$ mol/l.

* See Table 1.

** The rates are determined from the slope of the initial portion of the oxygen consumption curve.

Table 4. Total concentration of peroxide groups [O–O] in the reaction mixture in relation to the amount of oxygen ($[O_2]_{t=2}$) consumed in cumene oxidation at 313 K

Run no.	Solvent*	$[PB]_0 \times 10^2$, mol/l	$[Alk_4NI]_0 \times 10^3$, mol/l	$[O_2]_{t=2} \times 10^2$, mol/l	$[O\text{–}O]_t \times 10^2$, mol/l
			Bu_4NI		
1	Acetonitrile	2.0	4.03	5.76	5.82
2		2.0	6.55	5.93	5.53
3		2.0	11.5	7.23	5.31
4		6.0	1.31	4.72	9.45
5		8.0	1.31	5.22	11.3
			Bu_4NI		
6	Chlorobenzene	2.0	14.8	6.70	4.36
7		8.0	1.31	4.30	11.0
			Et_4NI		
8	Chlorobenzene	1.0	1.36	3.16	2.79
9		2.0	3.89	5.30	5.29
10		2.0	7.38	6.10	5.17
11		2.0	10.4	6.55	4.54
12		6.0	1.36	4.64	9.23

Note: $[Cum]_0 = 3.58$ mol/l.

* See Table 1.

of the carbonyl group of BA) in the course of the reaction.

The high yield of CHP and the first order reaction with respect to cumene are indicative of initiated nonbranching-chain radical oxidation [1]. The effect of an oxidation inhibitor (ionol, InH) is further evidence of this mechanism. With ionol added to the reaction mixture, we observed an induction period (Fig. 4). From the curves presented in Fig. 4, we calculated the rate of inhibition:

$$w_{InH} = \tau[InH]_0 = 0.7 \times 10^{-6} \text{ mol l}^{-1} \text{ s}^{-1},$$

where τ is the induction period.

In view of the fact that the efficiency of inhibition by ionol is 2 [1], the rate of initiation can be written as $2w_{InH}$ and is equal to 1.4×10^{-6} mol l^{-1} s^{-1}.

The rate of hydrocarbon oxidation by the chain radical mechanism (w) is given by the equation

$$w = -d[O_2]/dt = k_p k_t^{-1/2} w_i^{1/2} [RH]. \quad (3)$$

We calculated the initiation rate using Eq. (3), taking $k_p k_t^{-1/2} = 2.0 \times 10^{-3}$ l$^{-1/2}$ mol$^{-1/2}$ s$^{-1/2}$ at 313 K [13], $w_{max} = 0.9 \times 10^{-5}$ mol l^{-1} s^{-1}, and $[RH]_0 = 3.58$ mol/l, to obtain $w_i = 1.6 \times 10^{-6}$ mol l^{-1} s^{-1}. Thus, the w_i values calculated by two methods are in good agreement.

Based on the above experimental data, the process may be described by the following reaction scheme:

$$ROOR \xrightarrow{Cat} r^{\bullet} \quad (w_i) \quad (I)$$

$$r^{\bullet} + RH \longrightarrow rH + R^{\bullet}, \quad (II)$$

$$R^{\bullet} + O_2 \longrightarrow ROO^{\bullet}, \quad (III)$$

$$ROO^{\bullet} + RH \longrightarrow ROOH + R^{\bullet} \quad (k_p), \quad (IV)$$

$$ROO^{\bullet} + ROO^{\bullet} \longrightarrow \text{molecular products} + O_2 \quad (k_t). \quad (V)$$

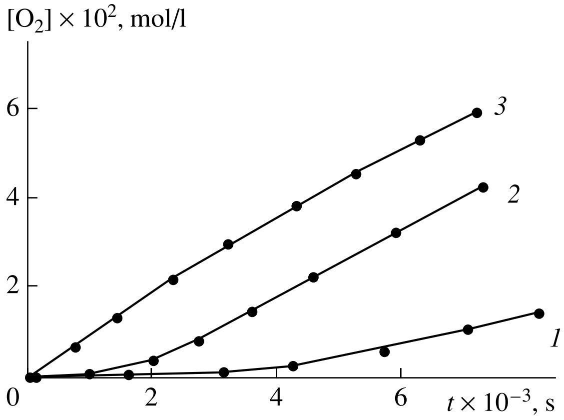

Fig. 4. Oxygen consumption curves for cumene (3.58 mol/l) oxidation at 313 K in acetonitrile in the presence of benzoyl peroxide ($[BP]_0 = 0.02$ mol/l), tetraethylammonium iodide ($[Et_4NI]_0 = 4.0 \times 10^{-3}$ mol/l), and ionol. The ionol concentration (mol/l) is (*1*) 3.05×10^3, (*2*) 1.4×10^3, and (*3*) 0.00.

Here, Cat is the onium salt, RH is the oxidized hydrocarbon, $r^{\bullet}$ is the radical arising from the catalytic decomposition of BP, $ROO^{\bullet}$ is the cumyl peroxy radical, and k_p and k_t are the rate constants of chain propagation and chain termination, respectively, with the participation of $ROO^{\bullet}$ radicals.

Note that initiation reaction (I) is described by a complicated rate law, as is demonstrated by the fact that the dependence of w_{max} on the initial concentration of BP (0.01–0.10 mol/l) passes through a maximum at $BP_0 \approx 0.06$ mol/l and constant concentrations of the substrate and salt. The dependence of the cumene oxidation rate on the iodide concentration also has an extremum (Table 2).

The study of the effect of the medium on the cumene oxidation rate showed that passing from a solution containing PhCl to pure AcN (Tables 2, 3) causes a modest increase in w_{max} and $[O_2]_t$ in the presence of the iodide. With the bromide, the oxidation rate is more strongly influenced by the medium [6]. Note the specific effect of dimethyl sulfoxide; replacing AcN with this solvent exerts only a light effect on the rate of cumene oxidation in the presence of the iodide and reduces the oxidation rate by one order of magnitude in the presence of the bromide (Table 2). The study of the temperature dependence of the oxidation rate between 281 and 328 K showed that the volume of the tetraalkylammonium cation influences the activation parameters of the process only slightly. Thus, the effective activation energy of the reaction in PhCl is 55 and 60 kJ/mol for the ethyl and butyl substituents, respectively; in AcN, the respective values are 62 and 67 kJ/mol.

Comparison of the activities of the above two tetraalkylammonium iodides and their bromide counterparts [6] leads to the following conclusions. The initiating effect of the iodides depends less strongly on the nature of the cation than that of the bromides. The rate of cumene oxidation in the presence of tetraalkylammonium iodides is nearly two times lower than that in the presence of the bromides.

Thus, the interaction of benzoyl peroxide with tetraalkylammonium iodide yields radicals. The capacity of the benzoyl peroxide–tetraalkylammonium iodide system to initiate the chain radical process at fairly low temperatures is rather high, but it is lower than that of the benzoyl peroxide–tetraalkylammonium bromide system [6]. The initiating capacity of the benzoyl peroxide–tetraalkylammonium salt system depends more strongly on the nature of the anion than on the nature of the cation. The retardation of the process appears to be due to not only the decrease in the concentration of the components of the initiating system in the course of the reaction but also the accumulation of benzoic acid, cumene hydroperoxide, and iodine.

REFERENCES

1. Emanuel', N.M., Denisov, E.T., and Maizus, Z.K., *Tsepnye reaktsii okisleniya uglevodorodov v zhidkoi faze* (Liquid-Phase Chain Oxidation of Hydrocarbons), Moscow: Nauka, 1965.
2. Fukui, K., Ohkubo, K., and Yamabe, T., *Bull. Chem. Soc. Jpn.*, 1969, vol. 42, no. 2, p. 312.
3. Ohkubo, K., Yamabe, T., and Fukui, K., *Bull. Chem. Soc. Jpn.*, 1970, vol. 43, no. 1, p. 1.
4. Opeida, I.A., Zalevskaya, N.M., Titskii, G.D., and Vasil'ev, A.Yu., *Ukr. Khim. Zh.*, 1993, vol. 59, no. 10, p. 1072.
5. Opeida, I.A., Zalevskaya, N.M., Vasil'ev, A.Yu., Turovskii, N.A., and Tselinskii, S.Yu., *Neftekhimiya*, 1992, vol. 32, no. 6, p. 509.
6. Opeida, I.A., Zalevskaya, N.M., Turovskaya, E.N., and Sobka, Yu.I., *Neftekhimiya*, 2002, vol. 42, no. 5, p. 31.
7. Sucyinashi, G.T., Miyajmi, S., Otsu, T., Matsusima, M., and Simamira, O., *Tetrahedron Lett.*, 1965, vol. 21, p. 1039.
8. Antonovskii, V.L. and Buzlanova, M.M., *Analiticheskaya khimiya organicheskikh peroksidnykh soedinenii* (Analytical Chemistry of Organic Peroxides), Moscow: Khimiya, 1978.
9. Bel'skii, V.E. and Bezzubova, N.N., *Zh. Anal. Khim.*, 1968, vol. 23, no. 7, p. 1084.
10. Magnusson, R.P., Taugor, A., and Dorris, M.L., *J. Biol. Chem.*, 1984, vol. 259, no. 2, p. 197.
11. Chang, H.C. and Bumpus, J.A., *Proc. Natl. Sci. Counc. ROC (B)*, 2001, vol. 25, no. 2, p. 82.
12. Denisov, E.T., *Konstanty skorosti gomoliticheskikh zhidkofaznykh reaktsii* (Rate Constants of Homolytic Liquid-Phase Reactions), Moscow: Nauka, 1971.
13. Opeida, I.A., Shendrik, A.N., Dubina, V.N., and Kachurin, I.O., *Molekulyarnye vzaimodeistviya, struktura i reaktsionnaya sposobnost' organicheskikh soedinenii* (Molecular Interaction, Structure, and Reactivity of Organic Compounds), Kiev: Naukova Dumka, 1989, p. 129.