CHEMILUMINESCENCE INVESTIGATION OF HYDROPEROXIDES DECOMPOSITION IN PRESENCE OF SOME SULFUR INHIBITORS

S.K.Ivanov, V.S.Yuritsin and D.Shopov

Institute of Organic Chemistry,
Bulgarian Academy of Sciences, Sofia 13, Bulgaria

The kinetics and mechanism of homolytic decomposition of tetralyl-, cumyl-, and tert-butyl-hydroperoxides in the presence of some sulfur containing antioxidants (zinc diisopropyl dithiophosphate, zinc ethylphenyl dithiocarbamate and tetramethylthiuram disulfide) were studied by the chemiluminescence method in an inert solvent (chlorobenzene) at 70°C. The formation of an intermediate complex between tetralyl hydroperoxide and zinc diisopropyl dithiophosphate was established and its equilibrium constant determined (K 1,6 . 10^6 l/mol). 1-Tetraline was shown as the probable emitter of chemiluminescence in this reaction. The emitter formation out of solvent "cage" was demonstrated.

Although sulfur containing inhibitors, especially dithiophosphoric and dithiocarbamic salts have been widely used as antioxidants, the mechanism of their action is still not clear enough. The inhibition effect of dithiophosphates and dithiocarbamates is accomplished by two mechanisms — a radical type and a peroxide decomposition[1−6]. Burn[5] postulated the formation of a coordinative complex between dithiophosphate and cumyl hydroperoxide, followed by its heterolytic decomposition (reaction (A)): However, this mechanism does not explain some experimental facts as, for example, the "prooxidative" effect[7], *i.e.* the increase of hydroperoxide homolytic decomposition by means of dithiophosphates. In a recent study[6], a homolytic and a heterolytic mechanism were postulated for the hydroperoxide decomposition in the presence of zinc diisopropyl dithiophosphate (*I*).

In the present study the Michaelis–Menten[8] formula with some modification was used with the view to achieve a quantitative interpretation of the experimental results. The homolytic action of *I* was examined by the chemiluminescence method, which provides direct physical evidence of the intensive radical recombination. The chemiluminescence intensity (*J*) for a thermal homolytic peroxide decomposition is proportional to the rate of hydroperoxide decomposition (R_d), as Zacharov and Šljapintoch[9] have shown:

$$J = \eta R_d = \eta K_t [RO_2^\bullet]^2 , \tag{1}$$

where η is the quantum yield of chemiluminescence and K_t the terminate rate constant for $RO_2^\bullet$ peroxide radicals. In the present work zinc diisopropyl dithiophosphate (*I*), zinc dithiocarbamate (*II*) and tetramethylthiuram disulfide (*III*) were used as peroxide decomposers. All these compounds are homolytic peroxide decomposers[10].

EXPERIMENTAL

Apparatus. The weak chemiluminescence intensities were recorded with the aid of a SNK 7 photometric installation with very high sensitivity[11]. The luminescence spectra were measured on a Beckman DB spectrophotometer, supplied with an 80 W mercury high pressure lamp (Zeiss, Jena) and a 366 nm light filter for exciting of luminescence in the samples.

Materials. The inert solvent, chlorobenzene, was purified as described in[12]. Tert-butyl hydroperoxide and cumyl hydroperoxide (Schuchardt, *purum*) were purified by the described method[13]. Tetralyl hydroperoxide was synthetised according to [6]. Zinc diisopropyl dithiophosphate was prepared also by the method described in[6]. The purification of zinc ethylphenyldithiocarbamate and tetramethylthiuramdisulfide was given in[10]. The melting and boiling points, respectively are presented in Table I. The compounds and 9,10-dibromoanthracene (Fluka or Schuhard, p.a.) were recrystallised twice from benzene or toluene.

Measurements. All experiments were performed at the temperature of $70 \pm 0.1°C$ in a glass double-wall reactor, supplied with a water cooled reflux condenser and a special container for the peroxide decomposer solution. The reactor had a nitrogen inlet for inert atmosphere and mixing. After adding hydroperoxide solution in chlorobenzene (and *IV* as activator) to the reactor, a very weak chemiluminescence was registered. Then a solution of peroxide decomposer in chlorobenzene was introduced from the pneumatically controlled special container to the reactor with hydroperoxide. During the experiments, nitrogen was passed through the solution, or a few tests were carried out with air, instead of nitrogen. The temperature was maintained constant with an U 10 Ultra Thermostat.
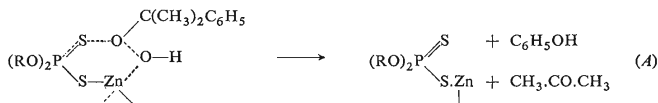
RESULTS

Most experiments were carried out with tetralyl hydroperoxide, because of its highest quantum yield (η), however cumyl- and tert-butyl hydroperoxides were used as well.

TABLE I

Properties of the Compounds Used

Compound	B.p., °C lit.	M.p., °C lit.	B.p., °C found	M.p., °C found
Chlorobenzene	132·1	—	130—131	—
Tetralyl hydroperoxide	—	54—55	—	54·8—55
Cumyl hydroperoxide	74/1 Torr	—	87/3 Torr	—
Tert-butyl hydroperoxide	35—37/17 Torr	—	34—35/17 Torr	—
Zinc diisopropyl dithiophosphate	—	140—141	—	140—141
Tetramethylthiuram disulfide	—	155—156	—	155—156
Zinc ethylphenyldithio-carbamate	—	202—205	—	210—211
9,10-Dibromoanthracene	—	221—222	—	221—221·5

As shown in Fig. 1 the kinetic curves obtained with the three hydroperoxides are qualitatively similar. Before introduction of I, the chemiluminescence intensity is very low. After addition of I, intensity increases to a maximum (J_{max}) and then decreases exponentially to J_t. Obviously the hydroperoxide decomposes, since its concentration after reaching J_t is lower than initial concentration as shown by iodometric titration. For example, in one of the experiments the initial concentrations equaled to 0·3330 mol/l and after adding $3 . 10^{-3}$ mol/l of I and decrease of the intensity from J_{max} to J_t, the concentration of tetralyl hydroperoxide changed to 0·3290 mol/l. Therefore, the quantity of decomposed hydroperoxide in the J_{max} to J_t period of time is approximatively equivalent to initial concentration of I. The kinetic curves, obtained in the presence of the other two decomposers II and III with tert-butyl hydroperoxide — are qualitatively similar — they exhibit a quick increase to J_{max} and, after that, a decrease to J_t (Fig. 1). The products of the interaction of these two compounds with hydroperoxides caused chemiluminescence reabsorption and this was the reason for the use of only I in our further experiments.

$$\begin{array}{c} \text{C(CH}_3)_2\text{C}_6\text{H}_5 \\ \text{(RO)}_2\text{P} \overset{\displaystyle S\text{----O}}{\underset{\displaystyle S\text{---Zn}}{\diagup}} \overset{\displaystyle}{\diagdown} \text{O---H} \end{array} \longrightarrow \begin{array}{c} \text{(RO)}_2\text{P} \overset{\displaystyle S}{\underset{\displaystyle S.\text{Zn}}{\diagup}} \quad + \text{ C}_6\text{H}_5\text{OH} \\ \qquad\qquad + \text{ CH}_3.\text{CO.CH}_3 \end{array} \qquad (A)$$

With the view of getting a more detailed picture of the mechanisms and nature of chemiluminescence experiments with radical scavengers were carried out. The results with ionol, 1-naphthol and 2,2,6,6-tetramethylpiperidine-1-oxyl[14] as scavengers are given in Fig. 2. These compounds are not physical quenchers, as was established by special experiments. The curve 4 in Fig. 2 represents chemiluminescence without radical trapping. Curves 1—3 show that chemiluminescence intensity decreases and J equals zero for scavengers concentrations exceeding 10^{-2} mol/l. It can be concluded from these results that generation of chemiluminescence takes place by out of "cage" recombination of radicals. It is of interest to note that in similar experiments carried out with tert-butylhydroperoxide and trialkyl phosphites as decomposers, in the presence of 2,2,6,6-tetramethylpiperidine-1-oxyl, Pobedimskij and coworkers[15] observed chemiluminescence by in the "cage" recombination of radicals for low concentration of scavenger $(\approx 10^{-3}$ mol/l$)$. In Fig. 3 the dependence of J_{max} on the hydroperoxide concentration is given. When the hydroperoxide concentration is greater than concentration of I, J_{max} becomes constant.

The J_{max}–$[I]$ relationship is more complex. When the concentration of I increases, J_{max} increases too. However, after it higher than the concentration of the hydroperoxide, the intensity begins to decrease. This phenomenon, as shown with special

experiments, has no physical causes (chemiluminescence quenching or a growth in light reabsorption in the solution).

Fig. 1 shows fourfold increase in chemiluminescence intensity after substituting air for nitrogen in the presence of tetralin. Explanation of this phenomenon lies in the increase of $RO_2^\bullet$ concentration, since all other types of radicals yield the peroxide $RO_2^\bullet$ radicals in the presence of O_2 and a hydrocarbon. $RO_2^\bullet$ recombination leads to the formation of a ketone in excited triplet state which on deactivation emits a quantum of chemiluminescence light[16] (reaction (B)).

The following experiments were performed with the aim of obtaining evidence that in our case the scheme (B) is valid. The spectral chemiluminescence band was determined as to be approximatively at $380 - 500$ nm, by means of light filters, without any activator. For a more precise determination of the band and the level
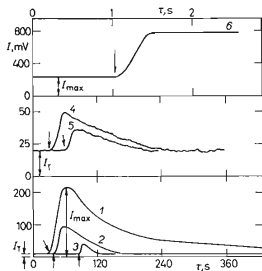
Fig. 1

Time Dependence of Chemiluminescence Intensity J of Hydroperoxides Solution in Chlorobenzene

The moment of decomposer addition is marked with an arrow. 9,10-Dibromoanthracene (10^{-3} mol/l) was used as chemiluminescence intensity activator. 1 ROOH 0·108 mol/l, I 0·011 mol/l. 2 Cumyl hydroperoxide 0·5 mol/l, I 0·01 mol/l. 3 Tert-butyl hydroperoxide 0·6 mol/l, I 0·01 mol/l. 4 Tertbutyl hydroperoxide 0·4 mol/l, zinc ethylphenyldithiocarbamate 0·02 mol/l. 5 Tertbutyl peroxide 0·4 mol/l, tetramethylthiuramdisulfide 0·05 mol/l. 6 ROOH 0·1 mol/l, I 0·01 mol/l, tetralin 1·0 mol/l. In the moment signed with an arrow air entered into the solution.
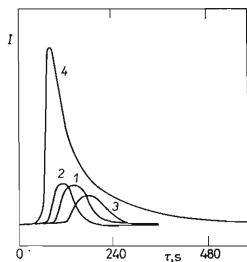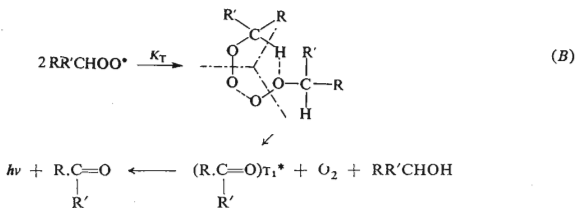

Fig. 2

Chemiluminescence Intensity for Mixture of I 0·01 mol/l, ROOH 0·25 mol/l and Added of Peroxide Radicals Scavengers c. 0·01 mol/l: 1 Ionol, 2 1-Naphthol, 3 2,2,6,6-Tetramethyl piperidine-1-oxyl, 4 no Scavenger

$$2 \, RR'CHOO^{\bullet} \xrightarrow{K_T}$$ (B)

$$h\nu + \underset{\underset{R'}{|}}{R.C{=}O} \longleftarrow (R.C{=}O)_{T_1}^* + O_2 + RR'CHOH$$

of excitation of the emitting particles, measurements of J_{max} were made (Table II) with a series of acceptors with known excited state levels. Obviously, energy transfer takes place only for acceptors with E_t 69 kcal, therefore, the minimum of chemiluminescence emitters is near to 414 nm, with an energy transfer of less than 69 to 70 kcal. Luminescence spectra were obtained of the mixture and individual compounds present in the hydroperoxide–I reaction system. Some of these spectra are shown in Fig. 4. From the spectral data it follows, that only 1-tetralone (or its exiplex with I) had luminescence in the 414 nm band (Fig. 4). Therefore, 1-tetralone or its exiplex with I, are most probable emitters. In the presence of the activator 9,10-di-
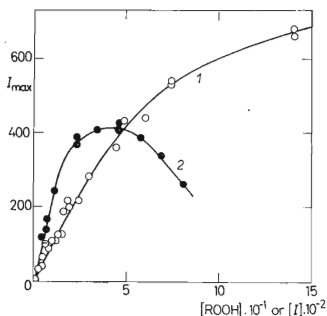

FIG. 3

Dependence of Maximum Chemiluminescence Intensity J_{max}: 1 On concentration of ROOH ($[I] = 2\cdot3 \cdot 10^{-3}$ mol/l) and 2 on concentration of I ([ROOH] = 0·025 mol/l)
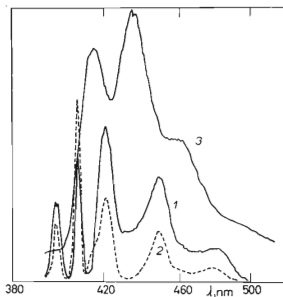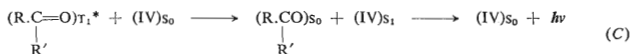
FIG. 4

Luminescence Spectra

1 1-Tetralone (0·001 mol/l) at 77 K and 2 1-tetralone (0·001 mol/l) + I c. (0·001 mol/l) at 77 K. 3 9,10-Dibromoanthracene (10^{-4} mol/l) in chlorobenzene solution at room temperature.

TABLE II

Results of Experiments for Physical Quenching of Chemiluminescence with Some Acceptors
The sign $+$ means presence of quenching.

Compound	λ, nm	E_T, Kcal triplet excited range	Result
Anthracene	680·8	42	$+$
9,10-Dibromoanthracene	—	—	$+$
Pyrene	583·5	49	$+$
Phenanthrene	461·2	62	$+$
Benzophenone	414·4	69	—
Acetophenone	386·4	74	—

bromoanthracene (IV), the latter molecule emits, because IV quenches the excited state of the ketone particles, according to the scheme[17] (C).

$$(R.C{=}O)T_1{}^* + (IV)s_0 \longrightarrow (R.CO)s_0 + (IV)s_1 \longrightarrow (IV)s_0 + h\nu \qquad (C)$$
$$\quad\; |$$
$$\quad R'$$
$$\qquad\qquad\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\qquad\qquad\qquad R'$$

The light emission in the presence of the activator IV is significantly more intensive because of the higher probability of optical conversion. In this case the chemiluminescence and luminescence spectra of IV (Fig. 4) are identical. The mechanism of quenching with IV is of an exchange-resonance type[18] and the following expression is valid:

$$(J_b/J_k)^{-1} = [(\eta_s K_{ts}/f_k \tau_k K_{kb}) - 1]^{-1} + [K_{ts}/f_k \tau_k^0 K_{kb}]^{-1} (K_{kb}\tau_k[IV])^{-1}. \qquad (2)$$

The dependence (J_b/J_k^0)–$[IV]^{-1}$ is linear. The slope $K_{kb}\tau_k$ amounts to $8{,}66 . 10^4$ l/mol. K_{diff} for the exchange-resonance mechanism limits the constant K_{kb}. At the temperature of 70°C in chlorobenzene solution K_{diff} $1{\cdot}9 . 10^9$ l/mol s. Then $\tau_k \approx$ $\approx 4{\cdot}6 . 10^{-5}$ s. This value is in agreement with the life time of the excited state of aromatic ketones[19] and shows that triplet excited 1-tetralone is the most likely emitter. On the basis of the simplified kinetic scheme (D), the following expression can be deduced
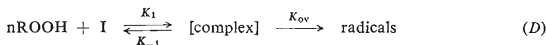
$$R_d = KK_{0v}[ROOH]^n [I]/(1 + K[ROOH]^n), \qquad (3)$$

where $K = K_1/K_{-1}$ is the equilibrium constant of complex formation and K_{0v} is the value of the rate constant of homolytic decomposition of the complex. The chemiluminescence intensity $J = \eta R_d = \eta K_t[RO_2^\bullet]^2$ (see reactions (B)); therefore

$$(J_{max})_\infty = \eta K K_{0v}[ROOH]^n [I]/(1 + K[ROOH]^n) . \qquad (4)$$

For high ROOH concentrations $(J_{max}) = \eta(R_d)_\infty = \eta K_{0v}[I]$, when $[ROOH] \rightarrow \infty$. Then

$$\log\left[(J_{max})^{-1} - (J_{max})_\infty^{-1}\right]/(J_{max})_\infty = \log(1/K) - n\log[ROOH] . \qquad (4b)$$

$$nROOH + I \underset{K_{-1}}{\overset{K_1}{\rightleftarrows}} [\text{complex}] \overset{K_{0v}}{\longrightarrow} \text{radicals} \qquad (D)$$

From the graphic expression of Eq. (4b) the slope gives n and the intercept $\log(1/K)$, thus allowing the number of the ROOH molecules, included in a complex with I, and the equilibrium constant of it formation to be calculated. Giving $K = 1.6$. $.10^6$ l/ml, $n = 1.2$. The following expression for J for equal concentrations of ROOH and I can be used[15].

$$J^{-1/2} = K_1[ROOH]_0 \tau \qquad (5)$$

In Fig. 5 the $J - \tau$ and $J^{-1/2} - \tau$ dependences are shown. The slope of line 2 permits to calculate K_1 $4.3 . 10^{-2}$ l mol s.
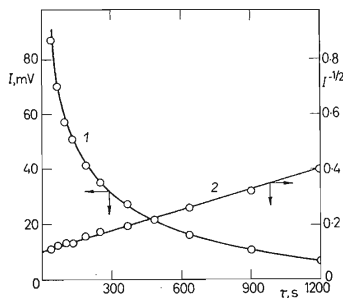

Fig. 5

a) Dependence of $[(J_a/J_k) - 1]$ from Reciprocal IV Concentration; b) Logarithmic Dependence of $[(J_{max})^{-1} - (J_{max})_\infty^{-1}]/(J_{max})_\infty$ from [ROOH]; c, d) Time Dependence of Chemiluminescence Intensity J and $(J)^{-1/2}$, resp. In this experiment [ROOH] = $= [I] = 0.04$ mol/l in chlorobenzene.)

DISCUSSION

The earlier proposed[7] kinetic scheme of hydroperoxide decomposition in the presence of I can be used taking into consideration the present experimental results (reactions $(E)-(K)$). As shown above, chemiluminescence is emitted in reaction (G). The intensity in the presence of O_2 and tetralin is about four times higher because under these conditions reactions $(L)-(M)$ take place. Therefore, it can be concluded that

all RO· radicals are converted into $RO_2^•$ radicals and the concentration of the latter particles is twice as high. In accordance with the Eq. (1) J is four times higher.

$$(E\text{-}a)$$

$$(E\text{-}b)$$

$$(E\text{-}c)$$

$$(F)$$
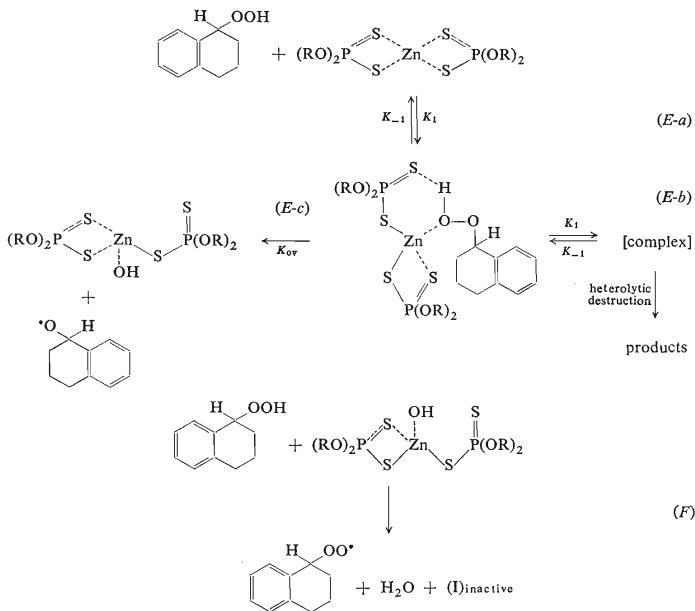
The type of emitter in this case throws light on the nature of the observed weak chemiluminescence and on by it generated $RO_2^•$ recombination. The results given in Figs 3 and 5 prove the formation of a complex, with equilibrium constant K $1 \cdot 6 \cdot 10^6$ l/mol, from one molecule of tetralylhydroperoxide and one molecule of I $(n = 1, 2)$. In scheme $(E)-(K)$ the formation of the second complex (Eb) is shown, which decomposes heterolytically. This stage has been investigated in detail recently[6]. Since, however, not enough information has been collected regarding these intermediate complexes, proposed by us or other authors[4-6] and it will be reasonable to abstain from detailed discussion at present.

The value of thermal hydroperoxide decomposition (K_t) was calculated from[20] and $K_t = 5 \cdot 16 \cdot 10^{-7}$ s^{-1} at 70°C in tetralin, for purpose of estimation of K_{ov}. This value is valid for a chlorobenzene solution as well because the nature of the solvent

$$(G\text{-}a)$$

$$(G\text{-}b)$$

$$\xrightarrow{K_{T_3}} \text{products} \qquad (H)$$
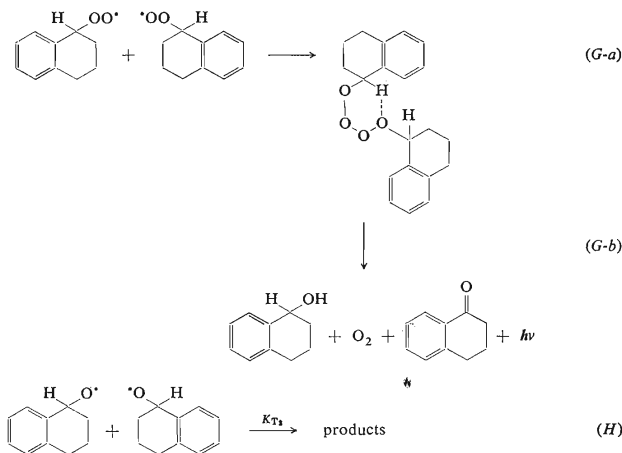
influences slightly the tetralylhydroperoxide thermal decomposition. We then have that the initial rate of thermal decomposition $R_{T_0} = K_T[\text{ROOH}]_0$ and $J_T = \eta K_T[\text{ROOH}]_0$, where J_T is the chemiluminescence intensity before adding I. From Eq. 4 for the case when $[\text{ROOH}] > [I]$ we get:

$$K_{0v} = K_t[\text{ROOH}]_0 \, (J_{\max})_\infty / [I] \, J_t \, . \qquad (6)$$

Eq. (6) permits to obtain for K_{0v} the value of $4.7 \cdot 10^{-2} \text{ s}^{-1}$. It is worth note the essential difference between equilibrium constants for reaction (Ea) $(K = 1.6 \cdot 10^6$ l/mol$)$ and reaction (Eb) $(K = 8.9 \cdot 10^2 \, \text{l}^2/\text{mol}^2)^6$. A catalytic effect was observed, e.g. one molecule of I decomposed c. 340 molecules of hydroperoxide in heterolytic destruction effect. As shown above for the homolytic decomposition path, the quantity of decomposed hydroperoxide is aproximatively equivalent to the molar amount of I added. Therefore I was quickly inactivated by reaction (F) as homolytic peroxide decomposer. The formation of a exiplex between 1-tetralone and I can be seen from spectra in Fig. 4; an essential change in the symmetry of emitting molecules has taken place. These properties of I ("prooxidative" effect) disappear relatively quickly but its products, formed by reaction $(E)-(G)$, continue the heterolytic decomposition, thus making the antioxidative action of I to last longer then the prooxidative effect. The curves in Fig. 1 permit us to conclude, that the other two decomposers follow qualitatively similar mechanism of decomposition.

$$ (K) $$

$$ (L) $$

$$ (M) $$

$$ (N) $$
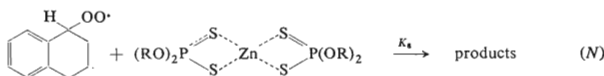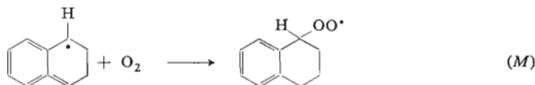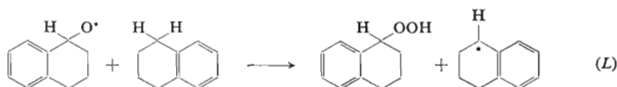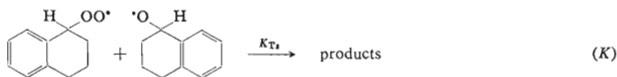
It can be seen from Fig. 3 an other interesting feature of I as an antioxidant. When $[ROOH] > [I]$, all I is tied in a complex with ROOH and thus withdrawn from the reaction with the $RO_2^\bullet$ radicals, or allowed to react very slowly, since the chemiluminescence intensity is not less than J_t (Fig. 1). However, when $[I] > > [ROOH]$, enough free molecules of I are present in the system and, as a radical type inhibitors they react with $RO_2^\bullet$ and lead to a decrease in chemiluminescence intensity. This is the explanation of the phenomena, observed in Fig. 3, when $[I] = = 4 . 10^{-2}$ mol/l and a J_{max} decrease instead of an increase takes place. Free I is a scavenger of $RO_2^\bullet$ radicals and when it is present the $RO_2^\bullet$ concentration decreases. In this case reaction[5] (N) must be added to the kinetic scheme. As recently reported[10], the K_s value at 60°C in cumene is $1 . 10^4$ l/mol s.

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