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Kinetics of Oxy-chemiluminescence and Its Use in the Analysis of Antioxidants

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Abstract—The influence of the antioxidant (chroman C_1, a synthetic analog of tocopherol) on the chemiluminescence kinetics during diphenylmethane and cumene oxidation is studied. Principles are considered for choosing a standard oxidized mixture in which the concentration and reactivity of an antioxidant are determined most reliably. The results of exact computer simulations and analytical calculations assuming quasi-stationarity with respect to different types of radicals are compared. A strategy is proposed to interpret the results and choose the experimental conditions (model oxidation system, type of hydrocarbon, interval of initiation rates) under which the antioxidant concentration and reactivity can be determined most reliably. The chemiluminescence method is used to study natural antioxidants in sunflower and corn oil.

INTRODUCTION

The liquid-phase oxidation of hydrocarbons (RH) by molecular oxygen is a radical-chain reaction involving many elementary acts (more than 40 for alkylaromatic hydrocarbons at 400 K [1]). However, our consideration can be restricted to 18 steps (and, under some conditions, by simpler schemes) without substantial loss in accuracy [2]. For example, at moderate temperatures, hydroperoxide is the final product, and the reaction is nonbranched (see scheme). Weak chemiluminescence (CL), which can be called oxy-chemiluminescence, is excited in the chain termination step. Chemiluminescence is used as a convenient kinetic method, because its intensity (I) is proportional to $k_6[ROO^{\cdot}]^2$ [3].

Antioxidants (InH) trap peroxide radicals and quench CL. Chemiluminescence quenching forms the basis for the quantitative determination of antioxidants, which are present in (or specially added to) artificial and natural compositions, drugs, food products, etc., and prevent them from oxidation. The effect of CL quenching only depends on the concentration and reactivity of the antioxidant, that is, on the property that makes it an antioxidant, and does not directly depend on its chemical structure [3–5].

In this work, we studied chemiluminescence in the oxidation of diphenylmethane and cumene. The kinetics of the CL intensity and concentrations of InH, $ROO^{\cdot}$, and $In^{\cdot}$ were simulated. Methods of determining the concentration and reactivity of InH were considered. The problem of choosing a standard chemiluminescent mixture was considered theoretically. The determination of the concentration of tocopherols in vegetable oil samples is presented as an example.

EXPERIMENTAL

The oxidation of a hydrocarbon (a component of a standard mixture) was initiated by the thermal decomposition of azobisisobutyronitrile (AIBN). The initiator, solvents (benzene and chlorobenzene), antioxidant (chroman C_1), and hydrocarbons (diphenylmethane, cumene) were purified by standard procedures. When diphenylmethane emitted chemiluminescence without an initiator additive (this indicated the presence of an admixture of a "contaminating initiator," probably peroxide), the hydrocarbon was additionally passed through an alumina layer [6]. The reaction mixture (5 ml) was placed in a temperature-controlled vessel of a chemiluminometer [7]. The mixture was saturated with oxygen by air bubbling.

The weak triplet-singlet emission of the excited carbonyl product (benzophenone in the case of diphenylmethane oxidation) was enhanced due to the energy transfer (see scheme) to luminophore A (europium chelate, europium(III) tris(thenoyltrifluoroacetonate)-1,10-phenanthroline). The emission from A (in the narrow band at 612 nm) was detected by an FEU-38 photomultiplier with a multialkali cathode. The amplification coefficient of the CL signal $\Phi_A\Phi_{et}/\Phi_{R(-H)=O} = \Phi_A/\{1 + (k_{et}\tau_{R(-H)=O}[A])^{-1}\}\Phi_{R-H=O}$ was 10^3 to 10^4 at [A] = 10^{-3} mol/l and, correspondingly, the CL yield ($\Phi_{CL} = \Phi_A\Phi_{et}\Phi^* = 0.28 \times 0.3 \times 0.003$) reached 2.5×10^{-4} (here specially measured [8] Φ_A and Φ^* values are given). This made it possible to detect the oxy-CL of diphenylmethane (the sensitivity of the chemiluminometer being 10^4–10^5 photon/s) at w_i values as low as 10^{-12} mol l^{-1} s^{-1}.

Absolute CL intensities $I = b(2k_6)[ROO^{\cdot}]^2$ are not necessarily measured experimentally. (This is a very difficult task, because the instrumental factor (b)

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Oxidation of hydrocarbon and chemiluminescence

Step	Equation	Rate constants and/or yield
	Chemical reactions	
Chain initiation	$Y\ (+RH, O_2) \longrightarrow ROO^{\bullet}$	Rate w_i
Chain propagation	$R^{\bullet} + O_2 \longrightarrow ROO^{\bullet}$	k_1 (rapidly)
	$ROO^{\bullet} + RH \longrightarrow ROOH + R^{\bullet}$	k_2
Quadratic or linear chain termination	$2ROO^{\bullet} \longrightarrow R(-H)=O + Products$	k_6
	$ROO^{\bullet} + InH \longrightarrow ROOH + In^{\bullet}$	k_7
	$ROO^{\bullet} + In^{\bullet} \longrightarrow Products$	k_8
	$In^{\bullet} + In^{\bullet} \longrightarrow InH + Product$	k_9, α
	$In^{\bullet} + In^{\bullet} \longrightarrow Products$	$k_9, 1 - \alpha$
Chemiexcitation	$2\ ROO^{\bullet} \longrightarrow R(-H)=O^* + Products$	$\Phi^* k_6$
	Chemiluminescence emission and secondary physical processes	
Chemiluminescence	$R(-H)=O^* \longrightarrow R(-H)=O + h\nu$	$\Phi_{R(-H)=O}$
Quenching	$R(-H)=O^*(+Q) \longrightarrow R(-H)=O(+Q)$	$k_q = 1/\tau_{R(-H)=O}$
Energy transfer to A	$R(-H)=O^* + A \longrightarrow R(-H)=O + A^*$	Φ_{et}
Emission of A	$A^* \longrightarrow A + Light$	Φ_A

Note: Y is the initiator, InH is the antioxidant, and activator (CL intensifier) A and quencher Q are specially added substances. The role of quenchers can also be played by RH, A, Y, and dissolved oxygen. Quadratic termination ($ROO^{\bullet} + ROO^{\bullet}$) occurs through the intermediate tetroxide ROOOOR; α is the recovery coefficient of the inhibitor.

Scheme.

depends on the absolute spectral sensitivity of the photomultiplier, CL spectrum, and the efficiency of light gathering.) Instead, relative intensities (i), which are the ratios of photocurrent with and without an antioxidant, were measured

$$i = I/I_0 = 2k_6[ROO^{\bullet}]^2/w_i = [ROO^{\bullet}]^2/[ROO^{\bullet}]_0^2 = r^2 \quad (1)$$

(i and r change from 0 to 1) or

$$[ROO^{\bullet}] = (w_i/2k_6)^{1/2} i^{1/2} = (w_i/2k_6)^{1/2} r, \quad (2)$$

where I and I_0 are the current (in the presence of InH) and maximum (initial or final) photocurrent expressed in arbitrary units. Formula (2) shows that the $i^{1/2}$ value is equal to the relative concentration of peroxide radicals, and their absolute concentration can be calculated when w_i and k_6 are known. The photocurrent is continuously recorded, which makes it possible to continuously monitor the $ROO^{\bullet}$ concentration and its changes during experiment.

The following procedure was used for determining the antioxidant concentration in samples. An additive (ΔV) of the sample containing InH was introduced into a solution with a V_0 volume containing hydrocarbon and a known amount of an initiator. The CL kinetics of mixture oxidation was studied. The initial concentration of InH ($[InH]_0$) in the CL mixture was calculated by formula (8) (see below). Then the concentration of InH was calculated: $[InH] = [InH]_0(V_0 + \Delta V)/\Delta V$. The initiation rate ($w_i$) was determined directly in the reaction mixture before and after experiments on the CL kinetics (by formula (8)) after a known amount of the standard inhibitor (chroman C_1) was added.

RESULTS AND DISCUSSION

Chemiluminescence Kinetics and the Concentration of Peroxide Radicals in the Presence of Antioxidant

The scheme presented above corresponds to the system of equations (3) describing the CL kinetics

$$d[ROO^{\bullet}]/dt = w_i - 2k_6[ROO^{\bullet}]^2 - k_7[InH][ROO^{\bullet}] - k_8[ROO^{\bullet}][In^{\bullet}], \quad (3a)$$

$$d[In^{\bullet}]/dt = k_7[InH][ROO^{\bullet}] - k_8[ROO^{\bullet}][In^{\bullet}] - 2k_9[In^{\bullet}]^2, \quad (3b)$$

$$d[InH]/dt = -k_7[ROO^\bullet][InH] + (\alpha/2)2k_9[In^\bullet]^2, \quad (3c)$$

$$I = b(2k_6)[ROO^\bullet]^2, \quad (3d)$$

where b is the instrumental factor.

In the absence of InH, a stationary concentration of radicals $[ROO^\bullet]_0$ and the respective constant CL intensity are established in a solution. An antioxidant introduced into a solution creates new channels for chain termination. The $ROO^\bullet$ concentration, oxidation rate (proportional to $[ROO^\bullet][RH]$), and CL intensity decrease. Then, the CL is gradually recovered with antioxidant consumption. The experimental data on CL kinetics and changes in the reactant concentrations with time calculated by Eqs. (3) are presented in Fig. 1.

Determination of the Antioxidant Concentration

We obtain from Eqs. (3)

$$d[ROO^\bullet] - d[In^\bullet] - 2d[InH] = (w_i - 2k_6[ROO^\bullet]^2)dt + (1-\alpha)2k_9[In^\bullet]^2 dt. \quad (4)$$

Integrating from $t = 0$ to $t = \infty$ and taking into account Eqs. (1) and (2) that $[ROO^\bullet]_0 = [ROO^\bullet]_\infty = (w_i/2k_6)^{1/2}$, $[In^\bullet]_0 = [In^\bullet]_\infty = 0$, $[InH]_0$ is the concentration of the antioxidant introduced into a solution, and $[InH]_\infty = 0$, we have the integrated form of Eq. (4)

$$2[InH]_0 = w_i\int_0^\infty (1-i)dt - (\alpha-1)\int_0^\infty 2k_9[In^\bullet]^2 dt. \quad (5)$$

Equation (5) can conveniently be used to determine $[InH]_0$ from the kinetics of CL intensity, if the term $(\alpha-1)\int_0^\infty 2k_9[In^\bullet]^2 dt$ can be neglected. This is possible in two cases

1. $\alpha = 1$, which implies the complete recovery of InH in the reaction $In^\bullet + In^\bullet$. This is the case, for example, for hydroquinone and some other phenols. Recovery occurs through the elimination of the hydrogen atom by one $In^\bullet$ from another and the transformation of the latter into the quinoid form. However, for many antioxidants $\alpha < 1$.

2. $k_9 = 0$, which means low relative contribution (let it be denoted by ε) of the $In^\bullet + In^\bullet$ reaction to the general balance of chain initiation (w_i) and termination. Let us show that this more general case takes place. Consider the quasi-stationary conditions with respect to the radicals ($d[ROO^\bullet]/dt = 0$ and $d[In^\bullet]/dt = 0$). By summing (3a) and (3b), we have

$$w_i = 2k_6[ROO^\bullet]^2 + 2k_8[ROO^\bullet][In^\bullet] + 2k_9[In^\bullet]^2. \quad (6)$$

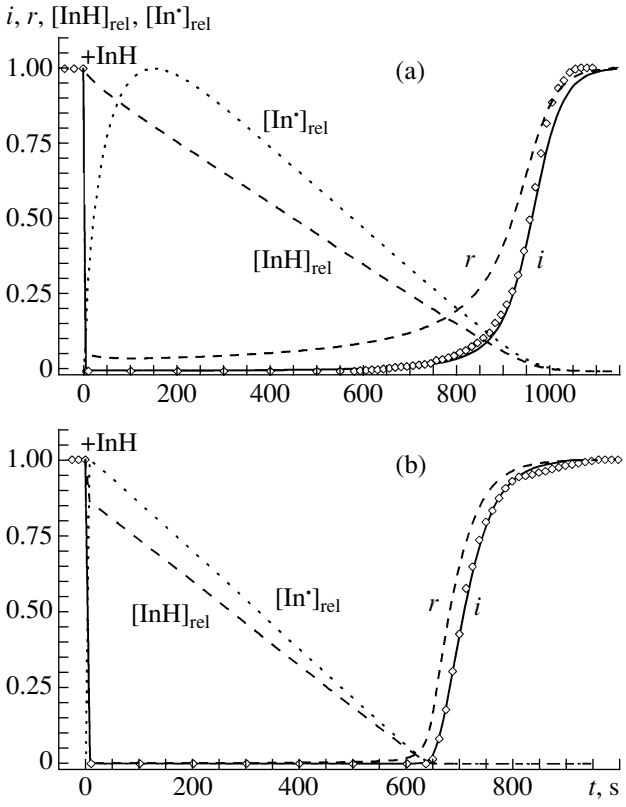

Fig. 1. Kinetics of the relative chemiluminescence intensity (i) and relative concentrations of peroxide radicals (r), antioxidant ($[InH]_{rel}$), and antioxidant radicals ($[In^\bullet]_{rel}$): (a) for diphenylmethane oxidation (10.2 vol % in benzene, $w_i = 2.15 \times 10^{-9}$ mol l^{-1} s^{-1}, 333 K); "+InH" is the moment of antioxidant (chroman C_1) introduction, $[InH]_0 = 1.01 \times 10^{-6}$ mol/l; points are experiment, and lines are computer calculated at $2k_6 = 1.32 \times 10^8$ l mol^{-1} s^{-1} and $k_7 = 7.6 \times 10^6$ l mol^{-1} s^{-1} obtained from the $F(t)$ anamorphosis (see Eq. (10) and Fig. 3); (b) for cumene oxidation (52.1 vol % in benzene, $w_i = 5.69 \times 10^{-9}$ mol l^{-1} s^{-1}, 333 K; $[InH]_0 = 2.04 \times 10^{-6}$ mol/l; $2k_6 = 4.0 \times 10^4$, $k_7 = 3.0 \times 10^6$ l mol^{-1} s^{-1}).

Assuming that $2k_9[In^\bullet]^2 \le (2k_9)_{max}[In^\bullet]^2 = \varepsilon w_i$ and substituting $[In^\bullet] = (\varepsilon w_i/(2k_9)_{max})^{1/2}$ and $[ROO^\bullet] = (w_i/2k_6)^{1/2} i^{1/2}$ into Eq. (6), we find a criterion whose fulfillment makes it possible to neglect the $In^\bullet + In^\bullet$ reaction, namely, its contribution ε to the chain termination rate is low at the following ratio of rate constants:

$$2k_9 \le (2k_9)_{max} = (k_8^2/2k_6)(4\varepsilon i/(1-\varepsilon-i)^2). \quad (7)$$

It can bee seen that $(2k_9)_{max}$ depends on k_6 (i.e., on the choice of hydrocarbon), k_8, and the considered region of the CL recovery curve: at low i the contribution of the $In^\bullet + In^\bullet$ process is higher than that at higher i, where the $[ROO^\bullet]$ values are high. The esti-

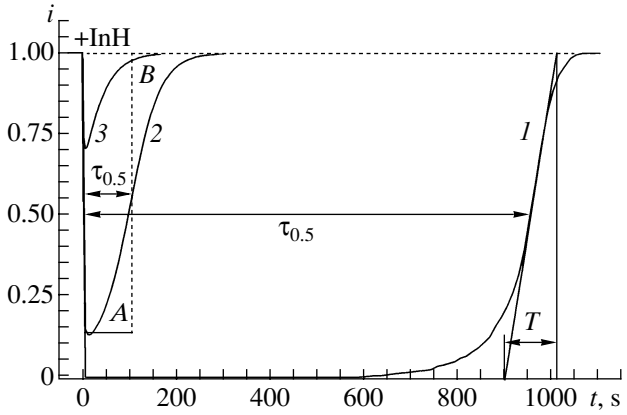

Fig. 2. Chemiluminescence kinetics for diphenylmethane oxidation (10.2 vol % in benzene, $w_i = 2.15 \times 10^{-9}$ mol l^{-1} s^{-1}, 333 K) after introducing different amounts of chroman C_1: $[InH]_0$ = (*1*) 1.01×10^{-6}, (*2*) 1.01×10^{-7}, and (*3*) 1.52×10^{-8} mol/l. (Illustrates the parameters of the kinetic curve (inverse slope T and induction period $\tau_{0.5}$) and the possibility to replace the $\int_0^\infty (1 - i)dt$ area by the area of a rectangle with sides $\tau_{0.5}$ and Δi.)

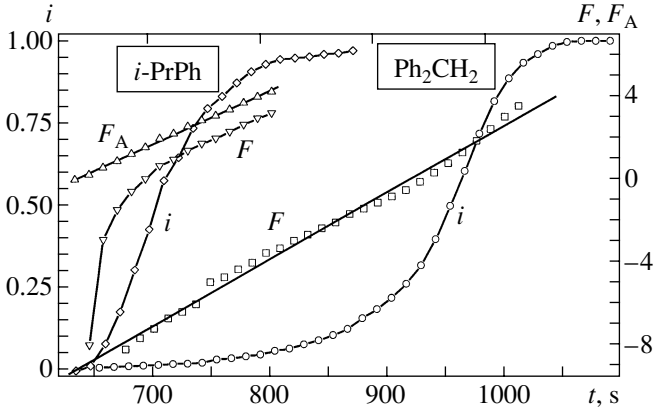

Fig. 3. Final regions of the kinetic curves presented in Figs. 1a and 1b and their anamorphoses F and F_A.

mates of $(2k_9)_{max}$ for several real cases are presented in Table 1. It is accepted that the contribution of the $In^{\cdot} + In^{\cdot}$ reaction to the total chain termination rate (ε) is 10% and $k_8 = 2 \times 10^8$ l mol^{-1} s^{-1} [9]. The rate constants $2k_9$ measured at 323 K for thirty phenoxy radicals vary over a wide range from 0.5 to 3×10^5 l mol^{-1} s^{-1} [10], that is, they are much lower than $(2k_9)_{max}$. Therefore, the second term in Eq. (5) can be neglected, and the equation takes the simple form

$$2[InH]_0 = w_i \int_0^\infty (1 - i)dt. \quad (8)$$

The integral $\int_0^\infty (1 - i)dt$ is the area above the kinetic curve of CL (chemiluminescence lightsum) "stolen" by the antioxidant and its radical in equal parts according to the simple scheme and Eqs. (3). In the case of a more complicated mechanism, the coefficient f (inhibition efficiency) appears instead of the coefficient 2. The coefficient f reflects other reactions of radicals and the antioxidant, which were ignored in the scheme: $f[InH]_0 = w_i \int_0^\infty (1 - i)dt$. Usually $1 < f < 2$. However, for some antioxidants containing several active groups, the coefficient f can be several units. Note that the f[InH] quantity rather than [InH] characterizes the antioxidant effect of the reactant under study.

The integral is measured in the units of time. Let us replace the *S*-shaped curve by a rectangle with a height Δi and length $\tau_{0.5}$, which is the time required to achieve $0.5\Delta i$, that is, the time of chemiluminescence "half-recovery" (Fig. 2, curve *2*). Sometimes $\tau_{0.5}$ is called the induction period or effective induction period [3]. Then, the antioxidant concentration is determined by the simple formula

$$2[InH]_0 = w_i \tau_{0.5}. \quad (8a)$$

The coincidence of the true and measured antioxidant concentrations depends on the difference between the A and B areas (Fig. 2, curve *2*). Analysis shows [11]

Table 1. Rate constants $(2k_9)_{max}$ at 333 K*

RH	$2k_6$, l mol^{-1} s^{-1}	$(2k_9)_{max}$, l mol^{-1} s^{-1}		
		$i = 0.1$	$i = 0.2$	$i = 0.5$
Cumene	4.0×10^4	6.3×10^{10}	1.6×10^{11}	1.3×10^{12}
Cyclohexane	1.6×10^6	1.6×10^9	4.1×10^9	3.1×10^{10}
Ethylbenzene	1.9×10^7	1.3×10^8	3.4×10^8	2.6×10^9
Diphenylmethane	1.32×10^8	1.9×10^7	4.9×10^7	3.8×10^8

* Calculated by Eq. (7) for several standard CL mixtures with different rate constants of chain termination $2k_6$ at $\varepsilon = 0.1$ and different levels of CL quenching by the antioxidant (from 90 ($i = 0.1$) to 50% ($i = 0.5$)).

that the overestimation of $[InH]_0$ does not exceed 2%, if $\tau_{0.5} \geq 3T$, where T is the inverse slope at the inflection point (see below, Eq. (11)). The procedure with area measuring is applied at low concentrations of the introduced antioxidant, when the CL inhibition is low (Fig. 2, curves *2*, *3*).

For example, in the experiment on the determination of the chroman C_1 concentration in a benzene solution of diphenylmethane (Figs. 1a, 2, curves *1*), it was found that $\int_0^\infty (1-i)\mathrm{d}t = 938$ s and, hence, $[InH]_0 = 1.01 \times 10^{-6}$ mol/l. The measured $\tau_{0.5}$ value is equal to 956 s and, thus, $[InH]_0 = 1.03 \times 10^{-6}$ mol/l; the concentration is somewhat overestimated compared to the true value. The 2% divergence is the systematic error, which is exactly 2% at $\tau_{0.5} \geq 3T$ (here $\tau_{0.5} = 7.6T$) (see above). Therefore, it is quite admissible, especially at high $\tau_{0.5}/T$ ratios (i.e., at high $[InH]_0$), to replace the measurement of the area by the measurement of $\tau_{0.5}$.

In the case of cumene (Fig. 1b), $\int_0^\infty (1-i)\mathrm{d}t = 717$ s and, hence, $[InH]_0 = 2.04 \times 10^{-6}$ mol/l. Unlike diphenylmethane, the calculation with $\tau_{0.5}$ (703 s) gives an underestimated $[InH]_0$ value (2.00×10^{-6} mol/l) instead of the overestimated value. This is explained by the fundamental difference between the reaction mechanisms in the region of CL recovery (see below), resulting in different shapes of the kinetic curve: *S*-shaped symmetric and sharply asymmetric for diphenylmethane and cumene, respectively.

Thus, the replacement of the $\int_0^\infty (1-i)\mathrm{d}t$ area with the $\tau_{0.5}$ time results in an acceptable error of about 2%. This is practically important, because there may be cases where, after the complete consumption of the antioxidant, the chemiluminescence intensity does not attain the initial value (see, e.g., Fig. 4) for many reasons (involvement of some components introduced with the antioxidant into the reaction, quenching of excited states and (or) light filtration by these components or products, and other factors). In this case, the calculation of the "area above the kinetic curve" somewhat loses a clear kinetic sense. At the same time, the $\tau_{0.5}$ value retains the meaning of effective time during which the antioxidant is consumed almost completely.

Simultaneous Determination of Concentration and Reactivity

Assuming quasi-stationarity with respect to the $ROO^\bullet$ and $In^\bullet$ radicals and under the condition of a small contribution of the $In^\bullet + In^\bullet$ process, we find from Eq. (3) a relationship between the relative intensity (i) and the current inhibitor concentration in a solution, as well as the kinetics of the CL intensity, [12]

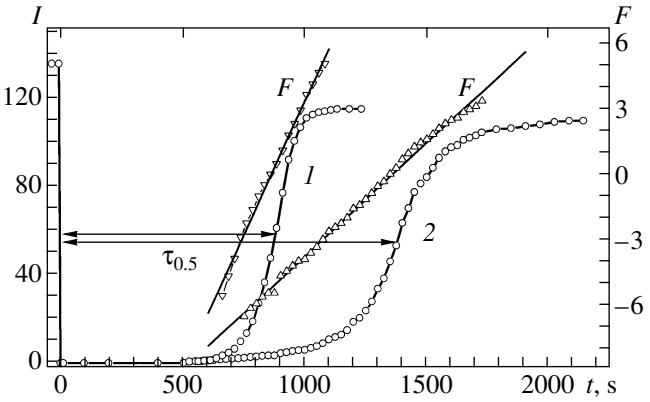

Fig. 4. Chemiluminescence kinetics for diphenylmethane oxidation after the (*1*) sunflower and (*2*) corn oil samples were introduced. For experimental conditions and results, see Table 2.

$$i^{-1/2} - i^{1/2} = 2k_7[InH](w_i 2k_6)^{-1/2}, \quad (9)$$

$$F(t) = \ln(1 + i^{1/2}) - \ln(1 - i^{1/2}) - i^{-1/2} = (k_7/(2k_6)^{1/2})w_i^{1/2}t + \text{const}. \quad (10)$$

The slope of the $i(t)$ kinetic curve at the inflection point equals

$$(\mathrm{d}i/\mathrm{d}t)_{max} = 1/T = 0.237(k_7/(2k_6)^{1/2})w_i^{1/2}, \quad (11)$$

and the inflection point itself is at a height $i_{max} = 0.535$.

Processing the kinetic chemiluminescence curve, one can either use the linear anamorphosis of the plot of i vs. t ($F(t)$) or measure the maximum slope of the CL buildup: $(\mathrm{d}i/\mathrm{d}t)_{max}$. In any case, we determine $(k_7/(2k_6)^{1/2})w_i^{1/2}$. Knowing w_i and $2k_6$, we find k_7.

Thus, both the initial concentration of the inhibitor $[InH]_0$ and its reactivity k_7 can be found in a single experiment if the $2k_6$ rate constant is known.

The most reliable results are obtained when the following experimental conditions are fulfilled (w_i, $[InH]_0$, and $2k_6$ (i.e., type of RH) are chosen).

1. Substantial suppression of chemiluminescence (at least by half): $i \leq 0.5$; then, we have from Eq. (9)

$$8k_7^2[InH]_0^2/(2k_6) \geq w_i. \quad (12)$$

2. A reasonable, although not too long, time of CL recovery, for example, $T \leq 1500$ s; then, it follows from (11) that

$$w_i \geq 8 \times 10^{-6}(2k_6)/k_7^2. \quad (13)$$

3. Quasi-stationarity with respect to radicals $ROO^{\bullet}$ and $In^{\bullet}$; it holds [13] when

$$2k_6 \geq 10k_7; \quad (14)$$

otherwise (for example, for the cumene–chroman C_1 combination) the kinetics of CL recovery are determined by the k_6 rate constant but are independent of k_7 (see below, Fig. 3). When conditions (12), (13), and (14) are fulfilled, a combination of them gives the following inequality:

$$10^3 k_7^2 [InH]_0 \geq 2k_6 \geq 10k_7, \quad (15)$$

which allows one to estimate the lowest concentration of the antioxidant determinable in a given experiment

$$k_7[InH]_0 \geq 10^{-2}. \quad (16)$$

Generally speaking, in the considered variant of $[InH]_0$ measurement, the constraint $i \leq 0.5$ can be decreased, that is, strong inhibition of CL by InH is not necessary. Assuming, for example, that $i \leq 0.8$ (inhibition by 20%), we obtain

$$k_7[InH]_0 \geq 3.2 \times 10^{-3}, \quad (16a)$$

instead of condition (16), that is, threefold lower $[InH]_0$ values can be measured. However, in this case, the accuracy decreases, because the area above the kinetic CL curve decreases and, correspondingly, the contribution of photocurrent noises to the area increases.

Conditions (12)–(15) show the boundaries of applicability of the method and also make it possible to rapidly choose an appropriate model oxidation system.

Let us assume, for example, that one has to determine an antioxidant in a sample with k_7 of an order of magnitude of 10^6 l mol^{-1} s^{-1}, and the expected InH content, after the sample was added to a standard solution, is ~10^{-7} mol/l. What model can be used for its analysis? It follows from inequality (15) that $10^8 \geq 2k_6 \geq 10^7$ l mol^{-1} s^{-1}; that is, for instance, ethylbenzene with $2k_6 \approx 2 \times 10^7$ l mol^{-1} s^{-1} can be an appropriate hydrocarbon. Then using inequalities (12) and (13), we find the range of initiation rates: $4 \times 10^{-9} \geq w_i \geq 1.6 \times 10^{-10}$ mol l^{-1} s^{-1}. When the order of magnitude of k_7 is unknown, one has to perform experiments with several hydrocarbons with different $2k_6$ rate constants (for example, cumene, ethylbenzene, or diphenylmethane, see Table 1). When the condition $2k_6 \geq 10k_7$ is met, close k_7 values should be obtained. When this condition is not met, the values of k_7 are underestimated according to [13]. In the limiting case where $k_7 \gg 2k_6$, in fact, $k_7 \geq 10(2k_6)$, the CL intensity is recovered according to the law

$$F_A(t) = \ln(1 + i^{1/2}) - \ln(1 - i^{1/2}) = 2(w_i(2k_6))^{1/2} t + \text{const}, \quad (17)$$

from which we can obtain only the $2k_6$ rate constant, that is, the inhibitory buildup transforms into nonstationary kinetics only with respect to the $ROO^{\bullet}$ radicals (in other words, the CL kinetics are determined by the quadratic chain termination rather than by InH consumption). The physical meaning of this is as follows: the antioxidant is so strong that it inhibits CL down to the almost complete disappearance of InH, and CL is recovered in the absence of the antioxidant (naturally, without its influence) and is controlled by the nonstationary law $F_A(t)$ rather than the stationary law $F(t)$.

Figure 3 demonstrates the influence of the k_6/k_7 parameter on the kinetics of chemiluminescence recovery. For cumene, $2k_6 < k_7$ and, therefore, law (10) is not fulfilled; if the mean value of the $F(t)$ function derivative is calculated, it gives a strongly underestimated value of 1.3×10^5 l mol^{-1} s^{-1} for k_7 and, hence, cumene is inappropriate for determining the k_7 of strong antioxidants. However, law (17) is well obeyed, and the $F_A(t)$ function gives $2k_6 = 2.7 \times 10^4$ l mol^{-1} s^{-1} close to the value presented in Table 1. In the case of diphenylmethane, $2k_6 > k_7$; law (10) can successfully be applied, and $k_7 = 7.6 \times 10^6$ l mol^{-1} s^{-1}, following from the $F(t)$ anamorphosis, which agrees with the previously obtained values (6.0×10^6 and 6.8×10^6 l mol^{-1} s^{-1} in benzene and chlorobenzene solutions, respectively [7]). A close value ($k_7 = 3.2 \times 10^6$ l mol^{-1} s^{-1}) was found by the chemiluminescence method for the reaction of chroman C_1 with peroxide radicals of ethylbenzene [16].

However, a solution of cumene is well suited for antioxidants with low k_7 values (<10^4): due to the low k_6 values, the stationary concentration of peroxide radicals is high (for example, compared to diphenylmethane at the same w_i), which results in the noticeable CL quenching even by weak antioxidants. Indeed, it follows from formula (9) that CL inhibition, after the antioxidant was introduced, is inversely proportional to $k_6^{1/2}$.

When only $[InH]_0$ (not k_7) is to be determined, any ratio between the k_6 and k_7 rate constants is acceptable. Recall that formula (8) was obtained without assumption of the quasi-stationary character of the process.

Chemiluminescence Analysis of Natural Antioxidants (Tocopherols) in Vegetable Oil

According to the published data [14, 15], tocopherols from sunflower oil contain 90% α-tocopherol (5,7,8-trimethyltocol), with the remaining 10% being a mixture of δ-tocopherol (8-methyltocol) and γ-tocopherol (7,8-dimethyltocol). Tocopherols of corn oil consist of γ- (90%) and α-tocopherols (10%).

The k_7 values of tocopherols are known [16, 17] to be high (approximately 10^6 l mol^{-1} s^{-1}), and k_7 depends on the number and position of methyl groups in the benzene ring. On the contrary, the length of the lateral aliphatic chain has no substantial effect on k_7 (for example, k_7 are the same for α-tocopherol and its synthetic analog chroman C_1 with a minimum length of the aliphatic chain).

Table 2. Experimental conditions and results of chemiluminescence analysis of the sunflower and corn oil samples

RH	[RH], vol %	$w_i \times 10^9$, mol l^{-1} s^{-1}	[A] $\times 10^4$, mol/l	C, vol %	I_0, rel. units	I/I_0	$[InH]_0 \times 10^6$, mol/l	[InH] $\times 10^3$, mol/l	$k_7^{app} \times 10^{-6}$, l mol^{-1} s^{-1}
Sunflower oil									
Cumene	50	104.0	2.0	2.0	137.0	0.25	33.8	1.7	–
Cumene	50	5.2	2.0	0.1	12.6	0.56	1.9	1.9	(0.071)*
Diphenylmethane	10	2.1	0.5	0.05	155.0	0.71	0.9	1.8	6.0
Corn oil									
Cumene	50	101.0	2.0	2.0	136.0	0.15	63.0	3.1	–
Cumene	50	5.7	2.0	0.1	13.5	0.56	2.6	2.6	(0.057)*
Diphenylmethane	10	2.0	0.5	0.05	159.0	0.72	1.4	2.8	2.6

Note: A (Eu(III) tris(thenoyltrifluoroacetonate)-1,10-phenanthroline) is the CL enhancing agent, C is the oil concentration in a solution, $[InH]_0$ is the antioxidant concentration in a chemiluminescent solution, [InH] is the antioxidant concentration in the oil sample, I_0 is the initial CL intensity (until the antioxidant was introduced), and I is the intensity at the end of the experiment (after the antioxidant was completely consumed).

* The k_7^{app} values were formally obtained from the maximum slope of the kinetic CL curve using formula (11), which, however, is inappropriate for cumene, because $(2k_6) < 10k_7$ and the kinetics are independent of k_7. The high cumene concentration was taken because the k_6 apparent rate constant of chain termination (which has a complicated mechanism) stops increasing with an increase in [RH] at [RH] ≈ 50 vol % [21].

The concentration of tocopherols was determined for the systems of cumene and diphenylmethane oxidation at several oil concentrations in a chemiluminescent solution (Fig. 4 and Table 2). The intensity after the induction period is somewhat lower than the initial value. This is especially pronounced at the 2% concentration of oil in a solution, which can be related to the quenching of CL by both oil components and products of the reaction of tocopherol with peroxide radicals [18]. Therefore, the $\tau_{0.5}$ value was used in the calculation instead of the $\int_0^\infty (1 - i)\mathrm{d}t$ integral. The content of tocopherols in the oil samples (Table 2) corresponds to the published data [15, 19].

The reactivity was only determined in a diphenylmethane–benzene mixture, because conditions (12)–(15) are valid for it. The $F(i, t)$ anamorphosis of CL recovery (Fig. 4) is almost linear and gave k_7^{app} for corn and sunflower oil (Table 2). These values are close to (somewhat higher than) the published k_7 values for γ- and α-tocopherols in the reactions with peroxide radicals of ethylbenzene, namely, 1.4×10^6 and $(3.1–3.6) \times 10^6$ l mol^{-1} s^{-1}, respectively [16, 17].

When the condition $k_7 \le 0.1(2k_6)$ is not fulfilled, a systematic error (underestimation) appears for the experimentally determined k_7 value. This effect, observed for the model system (see above, Fig. 3), is manifested in the case of vegetable oil. For example, for cumene oxidation we obtained k_7 of an order of 10^5 l mol^{-1} s^{-1} by the CL method (in parentheses in the last column in Table 2). The authors of [19, 20] also obtained an underestimated value of 2.5×10^5 l mol^{-1} s^{-1} for tocopherols of sunflower oil (by oxygen absorption).

CONCLUSION

Thus, the kinetic method based on the inhibition of hydrocarbon oxidation and chemiluminescence by antioxidants is efficient in studying the mechanisms of the antioxidant effect and determining their concentration. The *S*-shaped chemiluminescence recovery curve reflects the rate constant (k_7) of the reaction of the antioxidant with the peroxide radical, that is, the individual kinetic characteristics of the antioxidant (but not its structure), whereas the area above the kinetic curve is proportional to the initial antioxidant concentration only and is independent of k_7. However, reliable k_7 and $[InH]_0$ values can only be obtained under proper experimental conditions (the composition of a model chemiluminescent solution, the type of hydrocarbon, the initiation rate, and the ratio of the k_7 and k_6 rate constants).

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