CHEMILUMINESCENCE IN THE OXIDATION OF UNSATURATED ORGANIC COMPOUNDS
IN SOLUTION

V. A. Belyakov, R. F. Vasil'ev, and G. P. Fedorova

The oxidation of organic materials by molecular oxygen in solution is often accompanied by low-intensity chemiluminescence (CL) [1]. In [2, 3] the quantitative properties of CL were obtained for the oxidation of alkylaromatics and of some other hydrocarbons that are oxidized at a secondary carbon atom. The present work is a study of CL in the oxidation of unsaturated compounds.

In the quantitative study of CL, certain additives are added to the solution of hydrocarbon to be oxidized, and the change in CL intensity, \( I \), is followed [4]. The activators, \( A \) — strongly chemiluminescent acceptors of electron excitation energy — intensify CL. This permits the photophysical parameters to be determined: \( \phi_p \), the yield; \( f_p \), the rate constant, of the light emission; and \( k_{e,t} \), the rate constant of energy transfer. Addition of the quencher \( Q \) enables the actual lifetime of the CL emitter, \( \tau_p \), to be determined; dissolved oxygen can act as quencher. The addition of an initiator, a source of free radicals, makes it possible to obtain a definite rate of CL excitation, and to obtain \( \phi^* \), the excitation yield, and \( \phi_{CL} \), the absolute CL yield, which is equal to \( \phi_p \phi^* \).

In the oxidation of \( RH_2 \) hydrocarbons that contain secondary C-H bonds, the source of CL excitation is the decomposition of tetroxide that forms when peroxy radicals meet, and the primary excitation carrier (i.e., CL emitter) is a carbonyl compound, \( R = O \) [1-3].

here \( k_q \) is the quenching rate constant, and \( \psi_A \) is the quantum yield of activator luminescence.

As follows from this scheme, the intensities of the total, direct, and activated CL are expressed by the following equations:

\[
I = I^p + I^A \quad (1)
\]

\[
I^p = \Phi_{CL} w^p = \Phi_i \Phi^* w \quad (2)
\]

\[
I^A = \psi_A \Phi_{CL} \Phi^* w \quad (3)
\]

here \( w \) is the rate of formation of \( R = 0 \) product; and \( \Phi_{CL} \) is the yield of energy transfer.

\[
w = w_i/2
\]

\[
w_i = k_i[HROO] = kK[HROO] = 2f_{CL} k_{[Initiator]}
\]

\[
\Phi_{CL} = \Phi_{CL} = (1 - k_{CL} TP [A]/(1 - k_{CL} TP [A])
\]

here \( w_i \) is the initiation rate; \( k_i \) is the rate constant for chain breakage; \( k_a \) is the rate constant for overall decomposition of initiator; \( f_{CL} \) is the efficiency of initiation; and \( \Phi_{CL} \) is the yield of energy transfer.

In the absence of an initiator \( (w = 0) \) CL is negligible, the inhibitor antioxidants suppress CL almost completely \( ([HROO] = 0) \), and activators such as anthracene derivatives of europium complexes are chemically inert and only increase CL intensity without affecting the kinetics \( \psi_A \gg \Phi_i; \Phi_{CL} \) approaches unity as the activator concentration increases.

In the present work we have tried to clarify the extent to which the above simple scheme is applicable to the oxidation of unsaturated hydrocarbons, and to determine the quantitative properties of CL excitation and emission. We studied the CL of sixteen unsaturated hydrocarbons. Data on the CL of four olefins are contained in the previous communication [5].

EXPERIMENTAL

The photometric apparatus, the working procedure, and the methodology of the determination of the quantitative properties of CL have been described in [4]. Most of the unsaturated hydrocarbon samples were obtained from the K. Schorlemmer Technical University, Merseburg, German Democratic Republic. Cyclohexene was synthesized by dehydration of cyclohexanol with orthophosphoric acid and then redistilled. The materials were stored in evacuated and sealed ampules. Benzene and chlorobenzene were the solvents. The tests were carried out at 50 and 60°C.

DISCUSSION OF RESULTS

In olefin oxidation, CL behaves quite differently than in the oxidation of secondary hydrocarbons, and it must be concluded that there are several routes of CL excitation.

First of all, a perceptible CL is recorded in the absence of initiator and activator; during this time its intensity is practically constant. We call it inherent CL. The addition of an initiator that decomposes to radicals induces radical oxidation and invariably increases CL intensity. The contributions of initiated and inherent CL are different for different olefins. Below we shall discuss each component of CL, as exemplified by those olefins for which it is most distinctly exhibited.