CHEMILUMINESCENCE DETERMINATION OF CHROMIUM(VI), MOLYBDENUM(VI), AND VANADIUM(V) WITH BIS-(2,4,6-TRICHLOROPHENYL) OXALATE AND PERYLENE

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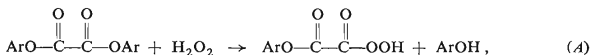
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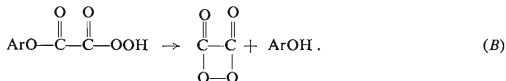*Prague Institute of Chemical Technology, 166 28 Prague 6*

The effect of the experimental conditions (pH, ionic strength, hydrogen peroxide concentration) and of various metal salts on the chemiluminescence occurring during oxidation of bis-(2,4,6-tri-chlorophenyl) oxalate (TCPO) with hydrogen peroxide in the presence of perylene was studied in water–methyl acetate solutions. The spectrum of the emitted radiation was found practically identical with the fluorescence spectrum of perylene. The observed catalytic effect of Cr(IV), Mo(VI), and V(V) on the chemiluminescence reaction in question can be explained so that these elements form peroxo acids with hydrogen peroxide, thereby facilitating the oxygen transfer from the latter to TCPO. Based on this phenomenon, a method is suggested for the determination of the above elements in concentrations about 10^{-3} to 10^{-4} mol l^{-1}; its precision, represented by the relative standard deviation, is about 3—4%, the limits of determination of Cr(VI), Mo(VI), and V(V) are approximately 5—10 µg.

Of a number of chemiluminescence reactions employed for trace analysis, oxidation of oxalates by hydrogen peroxide in the presence of aromatic polycyclic hydrocarbons has recently received attention. By measuring the intensity of the emitted radiation, perylene, for instance, can be determined[1] in concentrations 10^{-8} mol l^{-1}, hydrogen peroxide[2] in concentrations $2 \cdot 10^{-8}$ mol . l^{-1}.
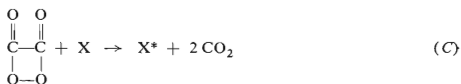
The mechanism of the chemiluminiscence process has been suggested to be as follows[3]: the ester is oxidized by hydrogen peroxide to the corresponding peroxo acid

$$ArO-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-OAr + H_2O_2 \rightarrow ArO-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-OOH + ArOH, \qquad (A)$$

which decomposes to give an unstable intermediate:

$$ArO-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-OOH \rightarrow \underset{\underset{O-O}{|\quad|}}{\overset{\overset{O\quad O}{\|\quad\|}}{C-C}} + ArOH. \qquad (B)$$

This species, rich in energy, gives up the excess energy to the aromatic hydrocarbon X and converts to carbon dioxide. On transition to its ground state, the excited hydrocarbon X* emits the excess energy as chemiluminescence radiation:

$$\begin{array}{c} O \quad O \\ \parallel \quad \parallel \\ C{-}C \\ \mid \quad \mid \\ O{-}O \end{array} + X \;\rightarrow\; X^* + 2\,CO_2 \qquad\qquad (C)$$

$$X^* \;\rightarrow\; X + h\nu \qquad\qquad (D)$$

In a study of the effect of the experimental conditions and of the presence of various inorganic salts[4] we have found that chromate, molybdate, and vanadate accelerate the chemiluminescence reaction, hence act in it as catalysts. We have made use of this fact for working out a method making it possible to determine Cr(VI), Mo(VI), and V(V) in concentrations approximately $10^{-3} - 10^{-4}$ mol l^{-1} with a precision represented by the relative standard deviation of $3-4\%$.

EXPERIMENTAL

Chemicals

The inorganic chemicals were reagent grade purity, their solutions were made up using deionized water. The pH values of the aqueous solutions were adjusted with buffers[5] (Britton–Robinson) of a constant ionic strength I 0·15. Dried rectified methyl acetate served as the solvent for the organic substances, its purity was checked gas chromatographically. Perylene was an imported preparation supplied by Lachema, Brno.

Bis(2,4,6-trichlorophenyl) oxalate (TCPO) was synthesized according to ref.[3] The observed unsharp melting point of the preparation recrystallized from chloroform, 188—190°C, approaches the value of 190—192°C reported in ref.[3], but differs from another published value[6], 196—198°C. Chromatographic treatment on a Silufol thin layer using benzene with 0·25% formamide as the mobile phase (detection with a basic permanganate solution) revealed the presence of a small quantity of oxalic acid and other unidentified components. After an additional recrystallization from benzene or chloroform the melting point was somewhat higher (189—192°C or 195—198°C, respectively), still, as the corresponding chromatograms demonstrate, the substance was not absolutely pure (decomposition took probably place during the chromatographic treatment). Although the chemical was stored in a dessicator in darkness, it was found partly decomposed after several months.

Fresh TCPO solutions in anhydrous methyl acetate were prepared daily, because it decomposes too. An enhanced content of humidity in the solvent promotes the decomposition, and so does boiling of the solution. The chemiluminescence intensity of a mixture with a fresh solution as compared with that of a mixture containing a solution stored for 100 h (in otherwise identical experimental conditions) amounted to only about 75% of the initial value.

Measuring Apparatus

The chemiluminescence intensity of the reaction mixtures was measured in a glass tubular cell 20 mm in diameter on a Spekol spectrometer (Carl Zeiss, Jena) with a Ti attachment enabling the mixture to be stirred with a magnetic stirrer. After amplification, the signal was recorded in dependence on time on an X-Y plotter. The time base of the plotter was provided by an Aminco-Bowman spectrophotofluorimeter (Silverspring, U.S.A.), which served also for scanning the chemi-

luminescence, fluorescence, and excitation spectra. The recorder chart speed was 2 cm/min. The small volumes of hydrogen peroxide were dosed by using a 10 ml plunger burette of Metrohm, Herisau.

Working Procedure

0·5 ml of the buffer, 0·5 ml of aqueous solution of the substance under study (or water), 0·5 ml of a 10^{-3}M solution of TCPO in methyl acetate, and 0·5 ml of a 10^{-3}M solution of perylene in methyl acetate were placed successively in the cell, the mixture was stirred at $20 \pm 1°C$, 0·1 ml of aqueous solution of hydrogen peroxide of a chosen concentration was added and the emitted radiation was recorded, the system being constantly stirred.

Evaluation of the Record of the Chemiluminescence Intensity in Dependence on Time

In preliminary experiments, two procedures were used: the area enclosed by the curve recorded after 6 min was measured (planimetrically), and the signal height after 2 min was read off. The relative standard deviations from three parallel measurements for three pH values, *viz.* pH 6, pH 7, and pH 8, were 6—8% for both methods. In subsequent experiments, only the signal heights after 2 min (or the heights of the maxima) were measured, this method being simpler than the planimetric evaluation.
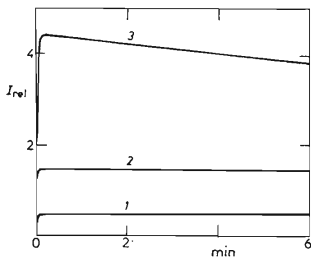

FIG. 1

Time dependence of the chemiluminescence intensity for various pH values of the aqueous phase. 3% H_2O_2, 10^{-3}M-TCPO and 10^{-3}M perylene in methyl acetate, I 0·15. I_{rel} is the relative chemiluminescence intensity. Curves: *1* pH 6, *2* pH 7, *3* pH 8
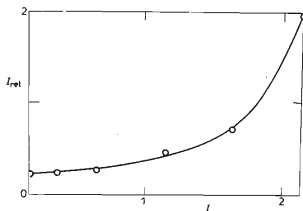
FIG. 2

Effect of the ionic strength on the chemiluminescence intensity. 3% H_2O_2, pH 7. I_{rel} is the relative chemiluminescence intensity, I is the ionic strength of the aqueous phase ($NaClO_4$)

RESULTS AND DISCUSSION

Effect of the Reaction Mixture Composition on the Radiation Intensity

A typical record of the dependence of the chemiluminescence intensity on time for various pH values of the reaction mixtures are shown in Fig. 1. At a constant pH, the radiation intensity increases with increasing concentration of hydrogen peroxide. The effect of the ionic strength is apparent from Fig. 2, the chemiluminescence, fluorescence, and excitation spectra are reproduced in Fig. 3.

If the content of water in the mixture (pH 7) is lowered a half, the emission intensity increases approximately twice. Oxidants used in place of hydrogen peroxide — $K_2S_2O_8$ + $AgNO_3$, potassium permanganate, dibenzoyl peroxide, or perhydrite — did not induce chemiluminescence of the system.

Of the salts tested: Ag, Cu, Fe(II), Fe(III), UO_2(II), Co, Ni, Mn, Cr(III), Mg, Na, and K nitrates, perchlorates, and chlorides; EDTA, NH_4VO_3, $(NH_4)_2CrO_4$, $(NH_4)_6Mo_7O_{24}$, and Na_2WO_4, practically only Cr(VI), Mo(VI), V(V), and U(VI)
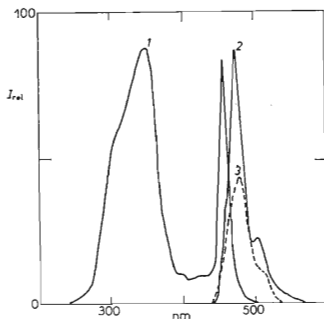

Fig. 3

The chemiluminescence, fluorescence, and excitation spectra of the reaction mixture containing 10^{-3}M-TCPO and 10^{-3}M perylene in methyl acetate, 3% H_2O_2; pH 6, I 0·15. I_{rel} is the relative intensity of the emitted radiation. Curves: *1* excitation spectrum (λ_{em} 470 nm), *2* fluorescence spectrum (λ_{exc} 345 nm), *3* chemiluminescence spectrum
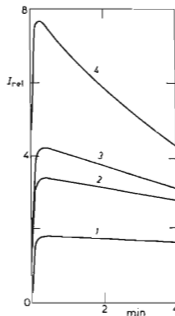

Fig. 4

Effect of molybdenum(VI) on the time dependence of the chemiluminescence intensity. 10^{-3}M-TCPO and 10^{-3}M perylene in methyl acetate, 3% H_2O_2, pH 7, I 0·15. Concentration of $Mo_7O_{24}^{6-}$ (mmol l^{-1}): *1* 0, *2* 0·24, *3* 0·48, *4* 0·95

compounds affected the emission of radiation. The three former accelerated the chemiluminescence reaction, thereby increasing the emission intensity. Tungsten behaved likewise only in the presence of vanadium(V). The UO_2^{2+} cation lowered the emission intensity (a precipitate separated from the mixture).

A typical record of the time dependence of light emission for mixtures containing Mo(VI) (pH 7) relative to a blank is shown in Fig. 4. The optimum pH value or H_2O_2 concentration for which the emission intensity ratios of mixtures containing V(V) to blank experiments are highest can be read from Figs 5 and 6, respectively.

Calibration Curves for the Determination of Vanadium(V), Molybdenum(VI), and Chromium(VI)

The calibration curves[7] were constructed based on the results of triplicate chemiluminescence intensity measurements for six different concentrations of the element under study in the region of 0 to 2·4 mmol l^{-1} (Fig. 7). The following straight line equations were obtained by calculation on an ICL 4-72 computer by using the POLGR program:

$$I_{Mo} = 75·3 + 2·22 . 10^5 c_{Mo} - 2·99 . 10^7 c_{Mo}^2 \qquad (1)$$

$$I_V = 112 + 9·62 . 10^4 c_V - 1·70 . 10^7 c_V^2 , \qquad (2)$$

where I_{Mo} and I_V are the light emission intensities of the reaction mixtures containing Mo(VI) and V(V), respectively, and c_{Mo} and c_V are the molar concentrations of the corresponding compounds in the reaction mixture.
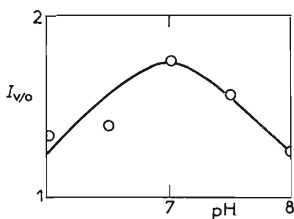

Fig. 5

Dependence of the chemiluminescence intensity ratio in the presence and in the absence of vanadium ($I_{V/o}$) on pH. 3% H_2O_2, $c_{NH_4VO_3} = 10^{-2}$ mol l^{-1}, I 0·15
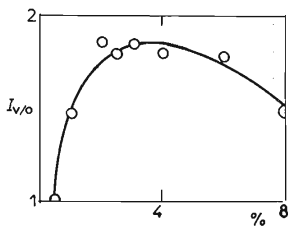
Fig. 6

Dependence of the chemiluminescence intensity ratio in the presence and in the absence of vanadium ($I_{V/o}$) on the concentration of hydrogen peroxide. $c_{NH_4VO_3} = 10^{-2}$ mol . . l^{-1}, pH 7, I 0·15

For chromium(VI), the calibration curve could not be represented even by a 4th degree polynomial (according to the value of the F-criterion for a 95% level of significance).

The precision, represented by the relative standard deviation, lay in the region of approximately 2—5%. The limits of determination, evaluated as the element weights corresponding to the triple standard deviations of averages of the chemiluminescence intensities for the blanks, fell within the region of approximately 5—10 µg.

The sensitivity, precision, as well as the limit of determination grow poorer on increasing the ionic strength of the reaction mixture.

CONCLUSIONS

The position of the maximum in the chemiluminescence spectra of the studied reaction mixtures in the water–methyl acetate systems, λ 475 nm, practically coincides with that in the fluorescence spectrum of perylene in methyl acetate, λ 470 nm; hence, this hydrocarbon is the emitting species. Only those substances that are known to form peroxo compounds with hydrogen peroxide appeared to act as catalysts in the chemiluminescence reaction in question. Probably, the peroxo compounds facilitate the formation of the energy-rich $(C_2O_4)^*$ species whose transient existence in the chemiluminescence mechanism mentioned is assumed. The limits of determination of molybdenum (VI), chromium(VI), and vanadium(V) might possibly be further improved by chosing a solvent more suitable than methyl acetate, in which the TCPO reagent is not very stable.
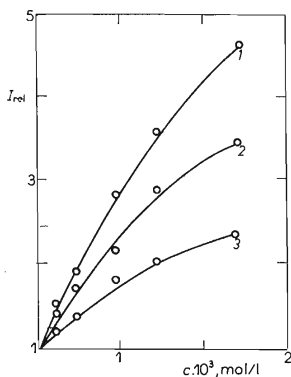

Fig. 7

Calibration curves for the determination of molybdenum(VI), chromium(VI), and vanadium(V). 3% H_2O_2, pH 7, I 0·15. I_{rel} is the relative chemiluminescence intensity, c the molar concentration of the salt. Curves: 1 $(NH_4)_6Mo_7O_{24}$, 2 $(NH_4)_2CrO_4$, 3 NH_4VO_3

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