



Luminol chemiluminescence under interaction with heteropoly acids

Oleg Zui^{a,*}, Hiroki Takahashi^b, Toshitaka Hori^b, Teruo Hinoue^c

^a A.V. Dumansky Institute of Colloid Chemistry and Water Chemistry of the National Academy of Sciences of Ukraine, 03680 Kyiv-142, Vernadsky Prospect 42, Ukraine

^b Graduate School of Human and Environmental Studies, Kyoto University, Kyoto 606-8501, Japan

^c Department of Chemistry, Faculty of Science, Shinshu University, 3-1-1 Asahi, Matsumoto, Nagano 390-8621, Japan

ARTICLE INFO

Article history:

Received 25 July 2008

Received in revised form 15 January 2009

Accepted 23 January 2009

Available online 4 February 2009

Keywords:

Heteropoly acids

Luminol

Chemiluminescence

Reaction mechanism

ABSTRACT

Interaction of luminol with phosphomolybdic, phosphovanadomolybdic and silicomolybdic acids was studied by examination of chemiluminescence spectra, measurement of ESR spectra, investigation of reaction order, and elucidation of inhibition effects. A scheme of the reaction mechanism is proposed.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Heteropoly acids (HPA) are in a wide class of coordination compounds. HPA molecule consists of a central atom and assemblies of metal–oxygen polyhedrons, including components of molybdenum, tungsten or fragments of oxide crystal grating [1]. Having strong electron-acceptor properties, HPA are readily reduced to form blue products isostructural with the initial acids. Examination of HPA in the reduced state by different methods has shown that they contain some tungsten or molybdenum ions in the (5+) valence state. Chemiluminescence (CL) of luminol with phosphovanadomolybdic and silicomolybdic HPA was first described in 1974 [2], and then determination of germanovanadomolybdic and arsenovanadomolybdic acids was reported via luminol chemiluminescence [3,4]. Later, ion chromatographic separation of phosphate, arsenate, silicate and germanate ions was coupled with CL detection of corresponding HPA in the oxidized state [5]. These chemiluminescence methods gave detection limits at the level of 1–50 $\mu\text{g/L}$ for HPA with central atoms P, As, Ge and Si. Improvement in sensitivity and selectivity was achieved by application of sorption preconcentration of P–V–Mo HPA or its ion associates (IAs) [6], with a detection limit of 20 ng/L for phosphorus. Further, flow-injection methods for phosphate [7,8] and silicate [9] were proposed, based on luminol CL detection of HPA. A flow-through solid-phase-based optical sensor for orthophosphate in water, which also relies on sorption preconcentration of HPA with subsequent CL detection,

was proposed [10]. All methods mentioned include HPA formation (or its ion pair with cationic surfactant) and CL reaction with luminol; however, the oxidation mechanism of luminol by HPA has not been studied up to now. In addition, there are no data on the nature of products of this CL reaction [11], in particular, on reduced heteropoly compounds in the literatures. The main purpose of the present research is to investigate products and intermediates of CL reaction in the system of luminol–HPA by electron spin resonance (ESR) spectroscopy and the chemiluminescence inhibition method.

2. Experimental

2.1. Reagents

Luminol, osmium tetroxide, 4-aminophenol, methyl isobutyl ketone (MIBK, 4-methyl-2-pentanone, Aldrich, USA), phosphomolybdic acid, sodium hydroxide (Wako Chemicals, Japan), paper filters (ADVANTEC MFS, Japan), phosphovanadomolybdic acid (Nippon Inorganic Color & Chemical Co., Japan), silicomolybdic acid (Strem Chemicals, Japan), tetraethyl orthosilicate (Acros Organics, Japan), catalase from bovine liver (Sigma, USA) were used as received. Ion-exchanged water (Millipore, USA) was used throughout the experiments.

2.2. Equipment and procedures

Electron spin resonance spectra were recorded on a JEOL JES-RE3X ESR spectrometer. A solution of HPA was placed on a narrow

* Corresponding author. Tel.: +380 44 4243175; fax: +380 44 4238224.

E-mail address: olegzuy@hotmail.com (O. Zui).

strip of filter paper situated inside a fused silica tube (3–4 mm inner diameter) so that the solution was completely absorbed by the strip in the tube, and then frozen in liquid nitrogen. After a “blank” ESR spectrum was recorded, the fused silica tube was taken out of the instrument cavity and left at room temperature for equilibration. One drop of alkaline luminol solution was put into the tube, allowed to reach the strip of filter paper and to be absorbed on it. After freezing in liquid nitrogen (123 K), the ESR spectrum of luminol–HPA mixture on the strip was recorded. Experimental conditions: X-field sweep; center field, 3300.0 G; sweep width, 500 G; frequency, 9.08900 GHz; power, 1.000 mW; modulation width, 3.2 G; time constant, 0.3 s; sweep time, 5.0 min. The concentration of HPA was 0.05 M, and 0.05 M luminol solution was prepared with 1 M NaOH.

Chemiluminescence spectra were measured on a JASCO FP-750 spectrofluorometer in the range of 350–600 nm without excitation light, using 0.01 M luminol solution in 0.1 M NaOH, and 0.01 M or 0.001 M HPA solution at pH 3.0. As direct measurement of chemiluminescence spectra in aqueous solution was difficult, because of very short-term light emission, a CL spectrum was measured in the following manner. HPA was dissolved in MIBK, and HPA solution was added to an optical cell containing aqueous alkaline luminol solution. Under the condition with a MIBK–water interface, the CL reaction proceeded more slowly. Measurements of CL intensity were carried out using a Triathler luminometer (Finland).

3. Results and discussion

3.1. ESR measurements

When one drop of 0.05 M luminol in 1 M NaOH reached the filter paper impregnated with 0.05 M phosphomolybdic acid in the fused silica tube, an intense blue color developed instantly. The ESR spectrum of this blue species at 123 K showed an isotropic signal (Fig. 1). This signal is attributed to a one-electron reduction compound in which one molybdenum atom is in a (5+) valence state [12]. Heating the frozen solution leads to a decrease in signal intensity of the ESR spectrum, and no ESR signal was observed at temperatures higher than 130 K. In Ref. [12], where ESR spectroscopy was used to investigate phosphomolybdic blue obtained from the reduction of phosphomolybdic acid by ethylene in the presence of Pd(II), it was shown that an ESR spectrum of frozen solution of the reduced phosphomolybdic HPA arises from the presence of a solely one-electron reduction compound in aqueous solution. As we obtained an ESR signal identical to that of Ref. [12], phosphomolybdic HPA appears to be one-electron oxidant to luminol. Consequently, the formation of short-lived radical species would be expected to be the intermediate products.

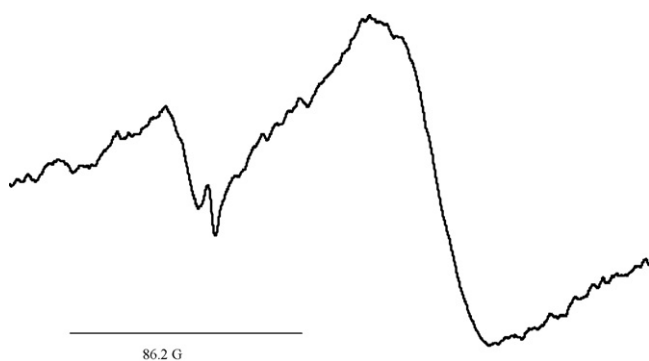


Fig. 1. ESR spectrum obtained during the reaction of phosphomolybdic HPA with luminol in alkaline solution at a temperature of 123 K.

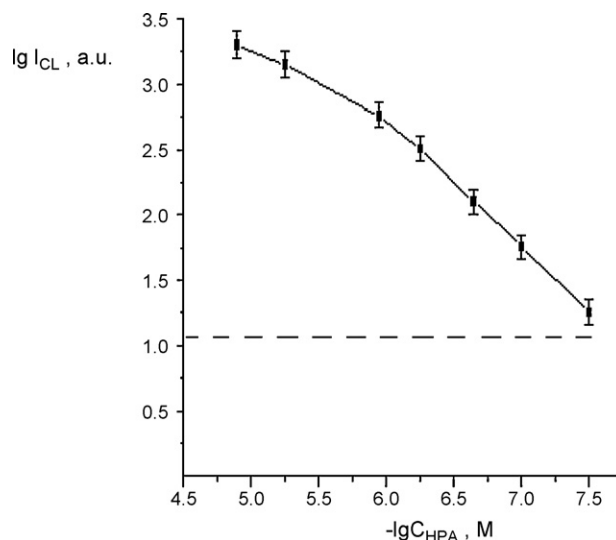


Fig. 2. Dependence of maximum intensity of chemiluminescence in the reaction of phosphomolybdic HPA with luminol on HPA concentration. Luminol concentration is 2×10^{-4} M, pH 12.0. Dashed line shows the value of the blank light emission.

3.2. Examination of dependence of light emission intensity in HPA–luminol reaction on HPA concentration

Optimum pH for the CL luminol–HPA reaction was 12.0, as described later. In order to examine the dependence of CL intensity in the luminol–P–Mo HPA system at pH 12.0 on HPA concentration, CL intensity was plotted against HPA concentration in logarithmic coordinates, as shown in Fig. 2. As can be seen in this figure, the dependence was a straight line in the concentration range of 1×10^{-7} M to 1×10^{-6} M, and at HPA concentrations higher than 1×10^{-6} M, the dependence showed a tendency to level off. The slope of the straight line in the HPA concentration range between 1×10^{-7} M and 1×10^{-6} M was approximately 1, which means that I_{CL} is directly proportional to C_{HPA} , indicating that a first-order reaction takes place. At HPA concentrations higher than 1×10^{-6} M, it is assumed that the reaction order changes. The reaction order also changed with changing pH. Similar dependences were observed by Seitz and Hercules [13,14] in iodine–luminol and chlorine–luminol reactions.

3.3. Examination of inhibitor effect

In Refs. [15,16], the reaction mechanism was investigated for luminol oxidation by one-electron oxidants. In one-electron oxidation, the formation of superoxide radical and/or hydrogen peroxide is possible as well as semiquinone radical of luminol as intermediate products. As these intermediates are characterized by a very short half-decay period, their direct ESR registration is difficult.

Indirect data on the nature of intermediate products in a reaction between luminol and HPA may be obtained by applying selective inhibitors, i.e., radical scavengers, for example, superoxide radical scavengers such as OsO_4 and *p*-aminophenol [17,18]. In our experiments, OsO_4 at a concentration of 1×10^{-7} M or *p*-aminophenol at a concentration of 1×10^{-6} M completely inhibited light emission in the reaction of 2.2×10^{-6} M P–V–Mo HPA or P–Mo HPA with 2×10^{-4} M luminol. The experimental results obtained clearly indicate the formation of superoxide radicals as intermediate products. Further, the effect of catalase on the luminol–HPA reaction was examined: catalase is an enzyme serving as a hydrogen peroxide deactivator which promotes H_2O_2 decomposition [19]. Catalase at a concentration of 1×10^{-6} M did not inhibit light emission in

Download English Version:

<https://daneshyari.com/en/article/1244965>

Download Persian Version:

<https://daneshyari.com/article/1244965>

[Daneshyari.com](https://daneshyari.com)