



Photochemically induced fluorescence studies of 1,3-diethyl-1,3-diphenylurea as stabilizer and its quantitative determination



Alireza Farokhchah, Naader Alizadeh*

Department of Chemistry, Faculty of Science, Tarbiat Modares University, PO Box 14115-175, Jalale Ale Ahmad, Tehran, Iran

ARTICLE INFO

Article history:

Received 27 December 2013
Received in revised form 2 April 2014
Accepted 8 April 2014
Available online 15 April 2014

Keywords:

Ethyl centralite
UV irradiation
Photochemically induced fluorescence
Stabilizer

ABSTRACT

The photochemically induced fluorescence (PIF) studies of 1,3-diethyl-1,3-diphenylurea or ethyl centralite (EC) as stabilizer have been carried out under various conditions. Influences of solvent type (water, methanol, acetonitrile and chloroform), oxygen dependence and UV irradiation time on the spectroscopic properties of EC were studied. In order to obtain a better understanding of the photochemical mechanism, products were identified by mass spectrometry study. A novel fluorimetric method has been developed for the determination of EC based on the PIF. The method is based on the use of UV irradiation to produce fluorescent derivatives from EC as a non-fluorescent molecule. The determination is carried out by UV irradiation for 4 min through measuring the fluorescence intensity in 354 nm when an excitation wavelength of 227 nm was used. Parameters related to the analytical signal and to the PIF are optimized. The linear range for determination of EC was 4×10^{-8} to 2×10^{-6} mol L⁻¹ and the limit of detection (LOD) was 2×10^{-8} mol L⁻¹ with relative standard deviation (R.S.D.) of 3% ($n = 5$). Finally, the proposed method was successfully applied for the determination of EC in real propellant samples and the acquired results were favorably compared to those obtained with HPLC method.

© 2014 Elsevier Ireland Ltd. All rights reserved.

1. Introduction

Photochemically induced fluorescence (PIF), based on the conversion upon UV irradiation of non-fluorescent analytes into strongly fluorescent photoproducts, and is a recent approach applied to quantitative analysis in different areas [1–5]. The PIF method has been established upon the direct UV irradiation of stationary liquid solution or dynamic flow containing a non-fluorescent or weakly fluorescent analyte, and photoconversion into strongly fluorescent photoproducts. As compared to chemical derivatization, photochemical reactions are relatively rapid allowing determination of numerous compounds, offer advantages such as simplicity, high sensitivity, high selectivity and cleanliness over other derivatization methods. Moreover, this method can be coupled with chromatographic methods [5–7]. Among the various parameters controlling the analyte conversion photoreaction and method sensitivity, two are particularly important, namely the optimum UV irradiation time (optimum time of irradiation,

corresponding to the maximum PIF signal) and the type of solvent [1,8]. Time of optimum irradiation and PIF intensity values vary significantly with the solvent polarity and its protic or aprotic character. For analytical purposes, the selected solvent should be the one giving the shortest time of optimum irradiation and the largest PIF signal.

Stabilizers are added to smokeless gun powders to prevent the decomposition of species.

As nitrate ester-based propellants decompose, they release nitrogen oxides. If the nitrogen oxides are left free to react in the propellant, they can react with the nitrate ester, causing further decomposition and additional release of nitrogen oxides. The reaction between the nitrate ester and the nitrogen oxides is exothermic, i.e. the reaction produces heat. The exothermic nature of the reaction creates a problem if sufficient heat is generated to initiate combustion. Stabilizers are added to propellant formulations to react with free nitrogen oxides to prevent their attack on the nitrate esters in the propellant. Another decomposition pathway is the neutralization by acid hydrolysis of the nitrate esters. The reaction is catalyzed by moisture and residual acids, or by water and acids formed during the decomposition process. The stabilizers are scavengers that act rather like sponges, and once they become “saturated they are no longer able to remove nitrogen

* Corresponding author. Tel.: +98 21 82883455/+98 21 82883409; fax: +98 21 82883455.

E-mail address: alizaden@modares.ac.ir (N. Alizadeh).

oxides from the propellant. At this point self-heating of the propellant can occur unabated. Once begun, the self-heating may become sufficient to cause autoignition [9–14]. Among many components, diphenylamine (DPA), ethyl centralite (EC) and methyl centralite (MC) appear to be the most commonly used stabilizers to control the thermal degradation of propellants but due to the application of DPA in pesticides and agriculture, pharmaceutical and rubber production, its application in analysis of propellant has been limited [15]. The techniques which have been most frequently used to determine stabilizers are as follows: high-performance liquid chromatography with electrochemical detection (LCEC) [16], capillary electrophoresis [17], tandem MS method [18], time-of-flight secondary ion mass spectrometry (TOF-SIMS) [19] fluorescence method [20] and high-performance liquid chromatography with fluorescence detection [21]. On one hand, chromatographic methods require cleanup steps and derivatization after extraction, on the other hand, fluorescence-based methods are highly sensitive and simple as compared to the chromatographic methods. However, many of the present organic compounds as stabilizer are, in general, non-fluorescent. For this reason, a number of analysis methods with derivatization process have been developed to convert non-fluorescent stabilizer into highly fluorescent derivatives for the purposes of detection. However, derivative techniques are considered as the most challenging and time-consuming step in the analytical process. As a result, employing fluorimetric method for determination of stabilizer has received less attention.

In our previous studies, PIF and synchronous fluorimetry using double scans method were utilized for simultaneous determination of diphenylamine and nitrosodiphenylamine as stabilizer [22]. In the current work, after investigating of the effect of various physicochemical parameters, including solvent system, oxygen dependence and UV irradiation time, a PIF method was utilized for the analysis of EC. Although, few chromatographic methods have been proposed for EC analysis in different samples. To the best of our knowledge, no direct fluorimetric method has been reported for determination of EC in propellant samples. The method developed allows a very sensitive and selective determination of stabilizer in propellant samples without any previous treatment of the sample.

2. Materials and methods

2.1. Materials

Ethyl centralite was purchased from Sigma-Aldrich, Germany. Other used reagents were of analytical grade. Double-distilled water was used throughout. Stock solutions of EC at the concentration of 10^{-3} mol L⁻¹ were prepared in acetonitrile and kept in the dark at 4 °C for no longer than 3 weeks. Working concentrations of EC were prepared from the stock solution by appropriate dilution before use. All solutions were protected against light with aluminum foil and stored in a refrigerator. The stabilizer solution was placed in a quartz cuvette and irradiated for a certain time at room temperature prior to fluorescence measurements.

2.2. Apparatus

All PIF measurements were performed at room temperature on a Perkin-Elmer model LS 50B spectrofluorimeter equipped with a thermostated cell compartment. The EC fluorescence intensity was measured at the maximum emission wavelength of 350 nm after excitation of solutions at 230 nm. The excitation and emission slits were both maintained at 10 nm. All measurements were performed in 10 mm quartz cells at 25 ± 0.1 °C by use of a thermostatic

cell holder and a Thermomix thermostatic bath. Mass spectra were obtained via a Finnigan-mat gas chromatograph/mass spectrometer (Bremen, Germany), magnetic sector, high resolution, double focusing and model 8430. It was operated in the 70 eV positive ionization mode. Instrument calibration was performed routinely using the calibration compound, perfluorokerosene (PFK) through the reference inlet system. All samples were introduced to the ion source through the introduction solid probe system. The scanning rate of the mass spectrometer was fixed at 1 s/decade at a mass range of 33–600 a.m.u. All mass spectra were taken by the manufacturer's software SS300. Absorption spectra were obtained using a Sinco (model UVS-2100) UV–vis spectrophotometer. Prior to each fluorescence measurement, the working solutions were analyzed by recording UV–visible spectrum from 200 to 800 nm. Solutions were purged with N₂ for 20 min before use and were introduced into the photolysis optical cell under a positive pressure of N₂. The photochemical set-up included a light-box consisting of a mercury lamp (8 W). A standard Hellma (Mullheim, Germany) 1 cm path-length quartz fluorescence cuvette was placed on an optical bench at 30 cm from the mercury lamp.

2.3. Calibration curve for PIF measurement

Standard solution of EC was prepared in acetonitrile and (in the working concentration range) was transferred into a two separate series of 20 mL volumetric flasks and diluted to the volume by acetonitrile. EC solution was excited at 227 nm and fluorescence intensity measurements were made at the maximum of 354 nm after UV irradiating for 4 min at room temperature.

2.4. Sample preparation

Four different propellant samples were analyzed. In order to prepare each propellant sample, an amount of 50 mg grinded sample was placed in a 25 mL beaker and then samples were extracted three times with 10 mL of methanol. Extraction time was 10 min and the mixture was agitated in the ultrasonic bath in each step. Extracts were filtrated immediately after each extraction step through a Whatman no. 1 filter before further use. The prepared samples were kept in the dark before analysis [23].

2.5. Chromatography

The liquid chromatographic analysis was performed on a HPLC system with UV PDA detector, model Smart line 2600 (Knauer, Germany). A C18 column 4.6 i.d. × 250 mm, 5.0 mm (Knauer, Germany) was used for separations. The mobile phase was acetonitrile/water (67:33 v/v) and operated at 0.9 mL min⁻¹. The absorption detector was fixed at 283 nm and the peak area of sample injection volume was used as the quantification parameter [21,23].

3. Results and discussion

3.1. Influence of UV irradiation on the absorption spectra of EC

The absorption spectra of virgin and irradiated EC solution are shown in Fig. 1. Prior to UV irradiation, optical absorption spectra of the virgin sample exhibit two absorption maxima, one peak in the region 200–230 nm and another a wide peak in 220–280 nm. For the region at 200–230 nm, the molar absorption coefficient (ϵ_{\max}) values were larger than or close to 10^4 L mol⁻¹ cm⁻¹, indicating that this band correspond to π – π^* electronic transitions of the aromatic system.

However, after UV irradiation of the EC solution, a notable increase was detected in the overall absorption in the region

Download English Version:

<https://daneshyari.com/en/article/95579>

Download Persian Version:

<https://daneshyari.com/article/95579>

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