

Note

Isolation and characterization of an iodide bridged dimeric palladium complex in carbonylation of methanol

Sunil S. Tonde^a, Ashutosh A. Kelkar^a, Mohan M. Bhadbhade^b,
Raghunath V. Chaudhari^{a,*}

^a Homogeneous Catalysis Division, National Chemical Laboratory, Homi Bhabha Road, Pune 411 008, India

^b Center for Materials Characterization (X-ray Facility), National Chemical Laboratory, Pune 411 008, India

Received 14 October 2004; accepted 6 January 2005

Available online 1 February 2005

Abstract

Palladium-catalyzed carbonylation of methanol in presence of iodide promoters was investigated. Iodide bridged palladium dimeric complex, $[\text{PPh}_3\text{CH}_3]_2[\text{Pd}_2\text{I}_6]$ was isolated from the carbonylation reaction mixture and characterized using X-ray crystallography. Reaction mechanism was proposed based on IR and UV spectroscopic characterizations of catalytic species involved in the catalytic cycle. The isolated dimeric palladium species, $[\text{Pd}_2\text{I}_6]^{2-}$ underwent carbonylation to give monomeric species $[\text{PdI}_3\text{CO}]^-$ at atmospheric pressure of carbon monoxide. It was also observed that PPh_3 plays an important role to avoid catalyst deactivation at higher temperatures. Turnover frequency (TOF) of 1052 h^{-1} was achieved using $\text{Pd}(\text{OAc})_2\text{-HI-PPh}_3$ catalyst system at $175 \text{ }^\circ\text{C}$. © 2005 Elsevier B.V. All rights reserved.

Keywords: Methanol carbonylation; Palladium catalyst; Dimeric palladium; UV; IR spectroscopy; Reaction mechanism

1. Introduction

Acetic acid is one of the most important commodity chemicals used in the manufacture of synthetic fibers, resins, acetic anhydride, vinyl acetate and as a solvent in polyester fiber production [1]. Carbonylation of methanol is the preferred route for the production of acetic acid after the successful development of cobalt catalyst by BASF in 1960s [2]. Iodide promoted cobalt catalyst operated at high temperatures ($250 \text{ }^\circ\text{C}$) and high pressures (68 MPa), giving 90% selectivity to the product acetic acid based on methanol. Rhodium-catalyzed iodide promoted carbonylation of methanol, discovered by Monsanto in 1970s [3], gave a high selectivity (>99% based on methanol) at milder operating condi-

tions ($150\text{--}200 \text{ }^\circ\text{C}$ temperature and 3–6 MPa pressure). In 1996, Iridium/iodide catalyzed process named Cativa process was announced by BP Chemicals [4]. The Cativa process is operated at lower water concentration but gives high reaction rates, improved selectivity based on carbon monoxide and minimum liquid by-products. Ru, Ni, Pd, Pt were also found to be active for carbonylation of methanol [5]. Carbonylation of methanol with palladium catalyst, patented by Shell, used the severe operating conditions ($182 \text{ }^\circ\text{C}$, 11 MPa CO) with sulfolane as a solvent and nitrogen-containing ligands to give high activity (0.34 kg/L/h) [5d]. Palladium and platinum-catalyzed carbonylation of methyl iodide has been reported by Maitlis and coworkers [5c], where the activity was observed to be very low (turnover frequency (TOF) = 7 h^{-1}). These authors have proposed a catalytic cycle containing $[\text{PdI}_3\text{CO}]^-$ as an intermediate species based on analogy with Pt-catalyzed carbonylation of methanol, but no direct evidence for this species

* Corresponding author. Tel.: +91 20 5893260/+91 20 25893163; fax: +0091 20 5893260.

E-mail address: rvc@ems.ncl.res.in (R.V. Chaudhari).

was reported [5c]. In this paper, we demonstrate that conditions for the Pd(OAc)₂-HI-PPh₃ catalyst can be optimized to give high TOF (in the range of 1052 h⁻¹). Further, we report characterization of a [PPh₃CH₃]₂[Pd₂I₆] complex as an intermediate species formed during carbonylation of methanol. The iodide bridged dimeric Pd-complex catalyst was isolated from the reaction mixture for the first time and characterized using single crystal X-ray analysis.

2. Results and discussion

Preliminary catalytic reactions were carried out at 115 °C and 5.4 MPa pressure of carbon monoxide using Pd(OAc)₂ as a catalyst, toluene-4-sulphonic acid (TsOH) and an alkali metal iodide as promoters in presence of water and 2-butanone as a solvent. Effect of LiI, NaI and KI was examined with TsOH using Pd(OAc)₂ at 4% water concentration. The results are summarized in Table 1. Alkali metal iodides LiI, NaI and KI as promoters showed comparable activity giving a TOF in the range of 23–25 h⁻¹ at 4% water concentration (Table 1, runs #1–3). A significant effect of water concentration was observed. An increase in water concentration from 4% to 20% doubled the catalytic TOF, when KI was used as a promoter in presence of TsOH and Pd(OAc)₂ (Table 1, run #4). At lower water concentration (4%), the precipitation of a white salt, KOTs, was observed when the reactor was discharged, unlike at higher water concentration due to its solubility in water. Comparable activity of alkali metal iodide promoters and the precipitation of alkali metal salts of TsOH at low water concentration, liberating HI in the solution encouraged us to develop a catalytic system with HI as the only promoter for Pd-catalyzed carbonylation of methanol. When the carbonylation reaction was carried out using Pd(OAc)₂ as a catalyst and HI as a promoter at 20% water concentration, marginal increase in selectivity was achieved over Pd(OAc)₂-KI-TsOH catalyst system

at the cost of conversion maintaining the catalytic TOF (Table 1, run #5^b). Further, when gas phase was analyzed by gas chromatography, other gaseous components like CO₂, CH₄ were traced below 1% of the total gas phase, indicating minor tendency of the catalyst system towards water gas shift reaction. Other palladium catalysts like PdCl₂, Pd(acac)₂ and [Pd(Pyca)(PPh₃)(OTs)] [6] were examined for methanol carbonylation using TsOH and LiI as promoters at 4% water concentration and were found to give activity comparable to Pd(OAc)₂ (Table 1, runs #6–8).

In order to increase the catalytic activity of Pd(OAc)₂-HI catalyst system, higher temperatures were employed. When the reaction was carried out at 145 °C and 10% water concentration using Pd(OAc)₂ as a catalyst and HI as a promoter, CO intake of the reaction was found to slow down after 45 min (~17% conversion of methanol) indicating deactivation of the catalyst. Deactivation of the catalyst seems to occur significantly at higher temperatures (>115 °C) and a considerable amount of palladium black was found precipitated when the reactor was discharged. (Table 2, run #3^b). However, at higher temperatures, addition of PPh₃ with Pd(OAc)₂ and HI allowed the palladium catalyst to remain in solution as an active catalyst. At 145 °C, 2.7 times increase in conversion with 9 times increase in TOF was observed by addition of PPh₃ (40 equiv. to Pd) to Pd(OAc)₂-HI catalyst system without any catalyst precipitation at the end of reaction (Table 2, runs #3^b and 4). Further increase in temperature in Pd(OAc)₂-HI-PPh₃ catalyst system increased the conversion levels and TOF significantly without catalyst precipitation. At 175 °C, the highest TOF was observed as 1052 h⁻¹. Thus, Pd-catalyst gave the high activity by selecting optimum operating conditions.

An attempt was made to isolate a catalytic intermediate [PPh₃CH₃]₂[Pd₂I₆] from the reaction mixture of Pd(OAc)₂-HI-PPh₃ catalyst system (see details in Section 3) and the intermediate was characterized using single crystal X-ray diffraction (Fig. 1) [7]. In order to

Table 1
Effect of promoters and water concentration in palladium-catalyzed carbonylation of methanol to acetic acid

Run no.	Water, v/v (%)	Catalyst	Promoter	Conversion (%) ^a	Selectivity A (%) ^a	TOF (h ⁻¹)
1	4	Pd(OAc) ₂	LiI	97.25	64.99	23
2	4	Pd(OAc) ₂	NaI	97.06	78.89	25
3	4	Pd(OAc) ₂	KI	97.07	73.96	24
4	20	Pd(OAc) ₂	KI	92.86	89.86	50
5 ^b	20	Pd(OAc) ₂	HI	78.80	94.83	50
6	4	PdCl ₂	LiI	96.37	67.74	23
7	4	Pd(acac) ₂	LiI	97.36	67.55	24
8	4	Pd(Pyca)(PPh ₃)(OTs)	LiI	93.84	72.54	23

Catalyst: 0.1 mmol; Promoter: 10 mmol; TsOH: 10 mmol; Substrate (CH₃OH): 31.2 mmol; Solvent (2-butanone): 21 mL; Temperature: 115 °C; P_{CO}: 5.4 MPa; Time: 10 h; A: acetic acid.

^a Calculated based on GC analysis (see Supplementary material).

^b Without TsOH.

Table 2
Effect of temperature on Pd(OAc)₂-HI-PPh₃ catalyzed carbonylation of methanol

Run no.	Temperature (°C)	Time (h)	Conversion (%) ^a	Selectivity (%) ^a		TOF (h ⁻¹)
				A	B	
1	115	2	20.54	17.10	56.66	100
2	130	1	26.77	21.23	52.77	260
3 ^b	145	2	17.28	15.43	80.31	59
4	145	1	46.46	28.45	57.46	533
5 ^c	145	1	47.52	25.42	52.42	565
6	160	1	62.34	54.39	42.45	863
7	175	1	64.77	61.33	33.74	1052

Pd(OAc)₂: 0.05 mmol; PPh₃: 2 mmol; HI: 5 mmol; Substrate (CH₃OH): 100 mmol; H₂O: 10% (v/v); Solvent (2-butanone): 20 mL; P_{CO}: 5.4 MPa; A: acetic acid; B: methyl acetate.

^a Calculated based on GC analysis (see Supporting information).

^b Without PPh₃.

^c Isolated compound [PPh₃CH₃]₂[Pd₂I₆] as catalyst.

investigate the mechanism of carbonylation of methanol using Pd-catalysts, intermediate species generated through stoichiometric reactions of catalyst, promoters and carbon monoxide were characterized using UV and IR spectroscopy. These stoichiometric reactions were based on three different catalyst systems viz., Pd(OAc)₂-alkali metal iodide-TsOH, Pd(OAc)₂-HI, and [PPh₃CH₃]₂[Pd₂I₆] and their reactions with carbon monoxide. It was noted that all the catalyst systems studied followed the same mechanism and involve [Pd₂I₆]²⁻ and [PdI₃CO]⁻ as catalytic intermediates.

When the isolated complex [PPh₃CH₃]₂[Pd₂I₆] was dissolved in 2-butanone and examined by UV-Vis spectroscopic analysis at room temperature, the characteristic absorption at 342 nm was noted (Fig. 2(a), ▲) that was assigned for the dimeric palladium species [Pd₂I₆]²⁻, which is in good agreement with the literature [8]. Similar UV-Vis spectroscopic observations were recorded

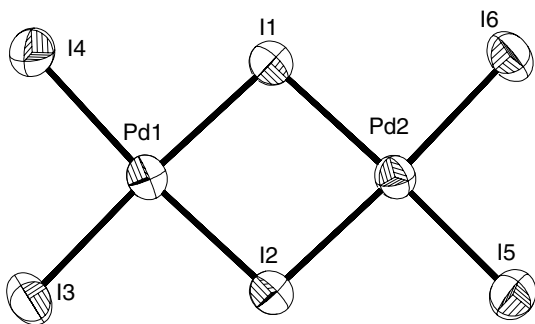


Fig. 1. X-ray structure of [Pd₂I₆]²⁻ anion Bond lengths (Å) and angles (°): I(1)-Pd(1) 2.5898(5), I(1)-Pd(2) 2.5910(5), Pd(2)-I(5) 2.5830(5), Pd(2)-I(6) 2.5897(5), Pd(2)-I(2) 2.5995(5), I(2)-Pd(1) 2.6074(5), Pd(1)-I(3) 2.5923(5), Pd(1)-I(4) 2.5986(5); Pd(1)-I(1)-Pd(2) 94.500(14), I(5)-Pd(2)-I(6) 93.042(15), I(5)-Pd(2)-I(1) 174.958(15), I(6)-Pd(2)-I(1) 90.178(14), I(5)-Pd(2)-I(2) 91.242(14), I(6)-Pd(2)-I(2) 173.629(15), I(1)-Pd(2)-I(2) 85.878(14), Pd(2)-I(2)-Pd(1) 93.881(14), I(1)-Pd(1)-I(3) 176.574(15), I(1)-Pd(1)-I(4) 89.847(14), I(3)-Pd(1)-I(4) 93.405(14), I(1)-Pd(1)-I(2) 85.737(14), I(3)-Pd(1)-I(2) 91.055(14), I(4)-Pd(1)-I(2) 175.037(14).

for the solutions containing Pd(OAc)₂-HI in 2-butanone and Pd(OAc)₂-TsOH-NaI in 2-butanone (Fig. 2) and it was observed that the formation of the species [Pd₂I₆]²⁻ was consistent in all of the cases. Olsson [9] has already reported the formation of dimeric palladium species, [Pd₂I₆]²⁻ from [PdI₄]²⁻ in organic solvents. When carbon monoxide was bubbled through the solution containing [Pd₂I₆]²⁻, and analyzed by UV spectroscopy, the characteristic peak at 342 nm disappeared meaning that the [Pd₂I₆]²⁻ was converted to the active Pd-CO species by reaction with carbon monoxide (Figs. 2(b) and (d)). In presence of carbon monoxide, the dimeric

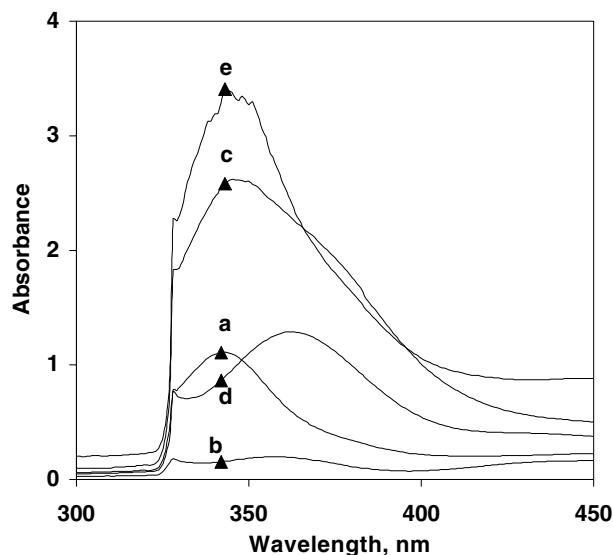
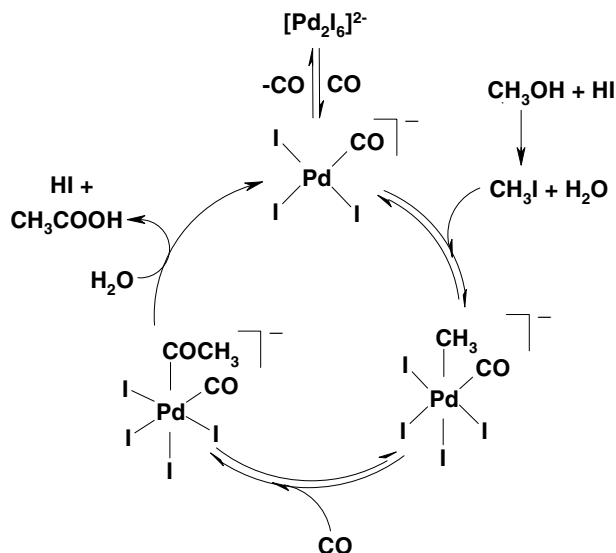


Fig. 2. UV spectroscopic analysis of Pd-catalysts in 2-butanone at room temperature: (a) 0.5×10^{-4} M palladium solution using the isolated complex, [PPh₃CH₃]₂[Pd₂I₆] in 2-butanone; (b) CO was bubbled for 5 min in the solution (a); (c) 1×10^{-4} M palladium solution using Pd(OAc)₂ in 2-butanone with 4 equiv. of HI per Pd; (d) CO was bubbled for 5 min in the solution (c); (e) 1.5×10^{-4} M palladium solution using Pd(OAc)₂ in 2-butanone with 4 equiv. of NaI and TsOH each per Pd.

anionic species $[\text{Pd}_2\text{I}_6]^{2-}$ was converted to the monomeric palladium species $[\text{PdI}_3\text{CO}]^-$, as evidenced by IR spectroscopic analysis at room temperature, which showed a strong carbonyl frequency at 2094 cm^{-1} , consistent with the literature [10] (see Supplementary material, Figure 1). Maitlis and coworkers [5c] also have proposed the formation of $[\text{PdI}_3\text{CO}]^-$, as an active catalytic species in the carbonylation of methyl iodide, but the direct evidence for this species was not shown. In order to check the stability of $[\text{PdI}_3\text{CO}]^-$ species at the reaction conditions, the isolated complex, $[\text{PPh}_3\text{CH}_3]_2[\text{Pd}_2\text{I}_6]$ was dissolved in 2-butanone, heated at $145\text{ }^\circ\text{C}$, pressurized with 5.4 Mpa CO and stirred for 30 min. IR analysis of the reaction mixture after cooling to room temperature and reducing the pressure to 1 atmosphere, showed the characteristic peak of $[\text{PdI}_3\text{CO}]^-$ ($\nu_{\text{CO}} = 2094\text{ cm}^{-1}$) without any change. This indicates that the palladium catalyst would be stable even at higher temperature. A possible reaction mechanism has been proposed in Scheme 1, which involves $[\text{PdI}_3\text{CO}]^-$ as an active catalytic species formed from $[\text{Pd}_2\text{I}_6]^{2-}$ generated in situ in the carbonylation reaction mixtures (in $\text{Pd}(\text{OAc})_2$ -alkali metal iodide-TsOH, $\text{Pd}(\text{OAc})_2$ -HI and $\text{Pd}(\text{OAc})_2$ -HI- PPh_3 catalyst systems).

3. Experimental

Carbonylation reactions were carried out in a 50 mL Parr autoclave provided with digital temperature and pressure display. Liquid reactants, products and gaseous components were analyzed using HP 6890 Gas Chromatograph [11]. UV spectroscopic analysis was done on PerkinElmer Lambda 25 UV/VIS Spectrometer [12]. IR analysis of samples in 2-butanone were obtained



Scheme 1. Mechanism of Pd-catalyzed carbonylation of methanol.

on Bio Rad FTS 175C spectrophotometer. Solvent 2-butanone and reactant methanol were distilled prior to use. $[\text{Pd}(\text{Pyca})(\text{PPh}_3)(\text{OTs})]$ was prepared as reported elsewhere [6]. The following materials were used as received from their commercial sources: $\text{Pd}(\text{OAc})_2$, $\text{Pd}(\text{acac})_2$ and PdCl_2 from Aldrich Chemicals (Milwaukee, WI), 57% HI from Fluka Chemicals, LiI, NaI, KI, TsOH, PPh_3 and CH_3I from SD Fine Chemicals (Mumbai, India).

3.1. Isolation of $[\text{PPh}_3\text{CH}_3]_2[\text{Pd}_2\text{I}_6]$ from reaction mixture

A solution from a set of reactions at $145\text{ }^\circ\text{C}$ ($\text{Pd}(\text{OAc})_2$ -HI- PPh_3 catalyst system) was allowed to evaporate at room temperature, from where black crystalline solid was obtained. The solid was washed with water and diethyl ether and then dried in vacuum. Black crystals were grown from dimethyl ketone and characterized by X-ray crystallography [7] (Fig. 1) as $[\text{PPh}_3\text{CH}_3]_2[\text{Pd}_2\text{I}_6]$, a iodide bridged dimeric palladium complex. ^{13}C NMR (50.32 MHz, acetone- d_6): δ (ppm) 136.1, 134.4, 134.2, 131.4, 131.1, 121.5, 119.7, 9.6, 8.5; ^{31}P NMR (81.02 MHz, acetone- d_6): δ (ppm) 27.62. Anal. Calc. for $\text{C}_{38}\text{H}_{36}\text{P}_2\text{Pd}_2\text{I}_6$: C, 29.80; H, 2.30; I, 49.80. Found: C, 29.82; H, 2.50; I, 50.0.

4. Conclusion

In conclusion a dimeric $[\text{PPh}_3\text{CH}_3]_2[\text{Pd}_2\text{I}_6]$ species was isolated and characterized using single crystal X-ray diffraction during carbonylation of methanol. Under carbonylation reaction conditions the dimeric palladium species forms monomeric $[\text{PdI}_3\text{CO}]^-$ species. Palladium-catalyzed carbonylation of methanol with $\text{Pd}(\text{OAc})_2$ -HI- PPh_3 catalytic system showed high catalytic activity (TOF = 1052 h^{-1}) at $175\text{ }^\circ\text{C}$.

Acknowledgement

S.S.T. thanks Council of Scientific and Industrial Research (CSIR), India for fellowship.

Appendix A. Supplementary material

Formulas for calculations of conversion and selectivities, FTIR spectra of carbonylation of $[\text{Pd}_2\text{I}_6]^{2-}$ to $[\text{PdI}_3\text{CO}]^-$ (Fig. 1), Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CSD No. 414452, for compound $[\text{PPh}_3\text{CH}_3]_2[\text{Pd}_2\text{I}_6]$. Supplementary data associated with this article can be found, in the online version at doi:10.1016/j.jorganchem.2005.01.010.

References

- [1] Aguilo, C.C. Hobbs, fifth ed. Ullmann's Encycl. Ind. Chem., vol. A1, 1987.
- [2] H. Hohenschutz, N. von Kutepow, W. Himmele, Hydrocarbon Process. 45 (1966) 141.
- [3] F.E. Paulik, J.F. Roth, Chem. Commun. (1968) 1578.
- [4] C.S. Garland, M.F. Giles, J.G. Sunley, Eur. Pat. 643034, 1995.
- [5] (a) A.A. Kelkar, D.S. Kolhe, R.V. Chaudhari, J. Organomet. Chem. 430 (1992) 111;
 (b) A.A. Kelkar, R.S. Ubale, R.M. Deshpande, R.V. Chaudhari, J. Catal. 156 (1995) 290;
 (c) J. Yang, A. Haynes, P.M. Maitlis, Chem. Commun. (Cambridge) (1999) 179;
 (d) P.W.N. Van Leeuwen, Eur. Pat. 0090443, 1983;
 (e) D. Eit, Eur. Pat. 0124160, 1984;
 (f) P.W.N. Van Leeuwen, R.C. Franciscus, Eur. Pat. 0133331, 1985;
 (g) P.W.N. Van Leeuwen, Jp. Pat. 60042341, 1985.
- [6] (a) A.M. Seayad, S. Jayashree, R.V. Chaudhari, Catal. Lett. 61 (1999) 99;
 (b) R.V. Chaudhari, S. Jayashree, A.M. Seayad, US Pat. 6093847, 2000.
- [7] Crystal data for $(C_{19}H_{18}P)_2(Pd_2I_6)$; $M = 1528.81$, crystal dimensions $0.46 \times 0.36 \times 0.15$ mm, crystal system: triclinic, space group $P\bar{1}$, $a = 10.0013(17)$, $b = 12.674(2)$, $c = 18.552(3)$ Å, $\alpha = 101.540(3)^\circ$, $\beta = 90.930(3)^\circ$, $\gamma = 103.252(3)^\circ$, $V = 2237.9(7)$ Å³, $Z = 2$, $D_c = 2.269$ g cm⁻³, μ (Mo K α) = 5.039 mm⁻¹, $T = 293(2)$ K, 21,394 reflections collected, 6742 unique [$I > 2\sigma(I)$], R value = 0.0300, $wR_2 = 0.0778$ (all data $R = 0.0350$, $wR_2 = 0.0813$). All data were measured on Bruker SMART APEX CCD Single Crystal Diffractometer.
- [8] L.I. Elding, L.F. Olsson, Inorg. Chem. 16 (1977) 2789.
- [9] L.F. Olsson, Inorg. Chem. 25 (1986) 1697.
- [10] B.P. Andreine, D. Belli Dell'Amico, F. Calderazzo, G. Pelizzi, J. Organomet. Chem. 354 (1988) 369.
- [11] Liquid components were analyzed with HP1 methyl siloxane capillary column (length 30 m, diameter 30 μ m, film thickness 0.25 μ m): column temperature: 30–250 °C (programmed), split inlet (split ratio was 100:1) temperature: 250 °C, FID: 250 °C, carrier gas (helium) flow: 1 mL/min; gaseous components were analyzed with Hayesep and molecular sieve packed column (operated through programmed valve switching), temperature: 250 °C, TCD temperature: 200 °C, carrier gas (helium) flow: 1 mL/min.
- [12] Absorbance of the solutions (in 2-butanone) with known concentration was obtained using 2-butanone as a reference. Scan range: 450–300 nm; scan speed: 960 nm/min; data interval: 1 nm; slit width: 1 nm.