

Research Article

Polyethylene Glycols as Efficient Media for Decarboxylative Nitration of α,β -Unsaturated Aromatic Carboxylic Acids by Ceric Ammonium Nitrate in Acetonitrile Medium: A Kinetic and Mechanistic Study

K. Ramesh, S. Shylaja, K. C. Rajanna, P. Giridhar Reddy, and P. K. Saiprakash

Department of Chemistry, Osmania University, Hyderabad, Andhra Pradesh 500 007, India

Correspondence should be addressed to K. C. Rajanna; krajannaou@yahoo.com

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Polyethylene glycols (PEGs) were found to be efficient media for decarboxylative nitration of α,β -unsaturated aromatic carboxylic acids by ceric ammonium nitrate (CAN) in acetonitrile to give β -nitrostyrene derivatives. Kinetics of the reaction exhibited second order kinetics with a first order dependence on [CAN] and [substrate]. Reactions were too sluggish to be studied in the absence of PEG; therefore detailed kinetics were not taken up. Reaction times were reduced from 24 hrs to few hours. The catalytic activity was found to be in the increasing order PEG-300 > PEG-400 > PEG-600 > PEG-200. Mechanism of PEG-mediated reactions was explained by Menger-Portnoy's scheme as applied in micellar kinetics.

1. Introduction

Cerium (IV) ammonium nitrate (CAN) is one of the most important reagents used for organic synthesis [1–4]. The formula of cerium (IV) ammonium nitrate, $[(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6]$, reflects that the cerium (IV) ion is surrounded by six nitrate groups and the ammonium ions are counterions to compensate for the negative charge of the hexanitratocerate (IV) coordinating unit. CAN is a one-electron oxidation reagent. Cerium (IV) ammonium nitrate can also be used as a nitrating agent [5, 6], initiator for radical polymerization reactions [7], and also as a reagent to remove protecting groups [8]. Even though cerium (IV) reagents are milder oxidation reagents than the other metal-based oxidation reagents such as Mn(VII) and Cr(VI) salts, they are relatively much less toxic. Because of their high molecular mass, large quantities of cerium (IV) salts are required for stoichiometric reactions. Therefore, indirect and catalytic reactions using Ce(IV) have been developed [9, 10]. The main advantage of CAN over other cerium (IV)

reagents is its higher solubility in organic solvents. The most popular solvents are (in decreasing order of importance) water, acetonitrile, dichloromethane, THF, and methanol [11]. Often mixtures of these solvents are also used as reaction medium. Other solvents have found only marginal use for this type of reactions.

Being good Michael acceptors, α,β -unsaturated nitroalkenes are widely applied in organic synthesis [12]. Among various methods reported for their preparation, a method involving the use of CAN provides a practical way to the synthesis of α,β -unsaturated "nitroalkenes" in good-to-excellent yields [13–23]. Recently polyethylene glycols (PEGs) have been used as catalysts and catalyst supports and also have been found to be an inexpensive, nontoxic, and environmentally friendly reaction medium, which avoid the use of acid or base catalysts. Moreover PEG can be recovered after completion of the reactions and recycled/reused [24–29] in another batch. Inspired by the striking features of PEG the author wants to use it as a catalyst by avoiding the use of acid in the present study; namely, ceric ammonium

TABLE 1: Binding constants of [CAN-PEG] at 303°K using Benesi-Hildebrand method.

S. N	PEG	Benesi-Hildebrand equation	K dm ³ /mol	ϵ dm ³ /mol/cm	-ΔG (kJ/mol)
1	PEG-200	$y = 7E - 05x + 0.052$	743	19.23	16.7
2	PEG-300	$y = 9E - 05x + 0.055$	611	18.18	16.2
3	PEG-400	$y = 5E - 05x + 0.071$	1420	14.08	18.3

TABLE 2: Activation parameters of cinnamic acid in different PEG media. Units of $k'' = \text{dm}^3 \text{ mol}^{-1} \text{ min}^{-1}$.

Type of PEG	PEG % (V/V)	k'' at 300 K	Equation	R ²	ΔH [#] kJ/mol	ΔG [#] kJ/mol	ΔS [#] J/K/mol
PEG-200	0.5	0.01	$y = -13.32x + 34.09$	0.999	110	84.2	85.9
	1.0	0.02	$y = -9.181x + 20.97$	0.999	76.3	83.3	-23.2
	2.0	0.03	$y = -8.399x + 18.75$	0.995	70.0	95.5	-41.7
	3.0	0.04	$y = -8.625x + 19.84$	0.998	91.8	81.8	-32.6
	4.0	0.08	$y = -7.047x + 15.06$	0.999	58.6	55.6	-72.3
PEG-300	5.0	0.1	$y = -8.112x + 19.01$	0.995	67.5	39.7	39.5
	0.5	0.01	$y = -22.79x + 64.43$	0.997	189	87.6	338
	1.0	0.03	$y = -4.655x + 6.308$	0.996	38.7	82.3	-145
	2.0	0.04	$y = -5.385x + 8.930$	0.999	44.8	81.8	-123
	3.0	0.05	$y = -2.684x + 0.252$	0.998	22.4	81.0	-195
PEG-400	4.0	0.06	$y = -8.743x + 20.63$	0.999	72.7	80.5	-20.0
	5.0	0.08	$y = -7.750x + 17.60$	0.999	64.5	80.0	-51.3
	0.5	0.02	$y = -6.979x + 13.65$	0.999	58.0	83.3	-84.0
	1.0	0.03	$y = -6.106x + 11.05$	0.997	50.8	82.5	-105
	2.0	0.04	$y = -9.224x + 21.84$	0.999	76.7	81.5	-16.0
PEG-600	3.0	0.06	$y = -8.718x + 20.54$	0.999	72.5	38.0	-80.5
	4.0	0.07	$y = -7.054x + 15.38$	0.999	58.7	80.1	-69.7
	5.0	0.1	$y = -7.687x + 17.63$	0.999	64.0	79.3	-51.0
	0.5	0.02	$y = -5.421x + 8.550$	0.998	45.0	83.0	-126
	1.0	0.03	$y = -4.644x + 6.274$	0.999	38.6	82.2	-145
	2.0	0.04	$y = -3.131x + 1.542$	0.999	26.0	81.4	-184
	3.0	0.05	$y = -5.555x + 9.813$	0.999	46.2	81.0	-115
	4.0	0.07	$y = -3.622x + 3.753$	0.998	30.1	80.0	-166
	5.0	0.1	$y = -4.247x + 5.956$	0.999	35.3	80.0	-148

nitrate (CAN) triggered decarboxylative nitration of α,β -unsaturated aromatic carboxylic acids. Acetonitrile is used as solvent in order to facilitate kinetic studies.

2. Experimental Details

2.1. Materials. Cinnamic acid, ceric ammonium nitrate (CAN), and polyethylene glycols were obtained from SD Fine Chemicals or Loba. Substituted cinnamic acids were prepared by Perkins reaction as cited in the literature [30, 31].

2.2. General Procedure for PEG-Mediated β -Nitrostyrenes Synthesis. In a typical solid state synthesis, cinnamic acid (0.01 mol), PEG (0.02 mmol), and CAN (0.012 mmol) are placed in a clean two-necked R. B. flask containing acetonitrile (MeCN) and stirred for certain time. Progress of the reaction is periodically monitored by thin layer chromatography (TLC). After completion, the reaction mixture is

treated with 2% sodium carbonate solution, followed by the addition of “dichloromethane” (DCM) or “dichloroethane” (DCE). The organic layer was separated, dried over Na_2SO_4 and evaporated under vacuum, and purified with column chromatography using ethyl acetate : hexane (3 : 7) as eluent to get pure product. The products were characterized by IR, $^1\text{H-NMR}$, mass spectra, and physical data with authentic samples and found to agree well with earlier reports (Table 1). The yields of major products are compiled in Table 2.

2.3. Kinetic Method of Following the Reaction. Thermostat was adjusted to desired reaction temperature. Flask containing known amount of ceric ammonium nitrate (CAN) in acetonitrile solvent and another flask containing the substrate (α,β -unsaturated acid) and suitable amount of PEG solutions were clamped in a thermostatic bath. Reaction was initiated by mixing requisite amount of CAN with the other contents of the reaction vessel. The entire reaction mixture was

TABLE 3: Activation parameters of crotonic acid in different PEG media. Units of $k'' = \text{dm}^3 \text{ mol}^{-1} \text{ min}^{-1}$.

Type of PEG	PEG % (V/V)	k'' at 300 K	Equation	R^2	$\Delta H^\#$ kJ/mol	$\Delta G^\#$ J/K/mol	$\Delta S^\#$
PEG-200	0.5	0.01	$y = -9.907x + 22.7$	0.999	82.4	85.1	-9.0
	1.0	0.02	$y = -6.742x + 12.86$	0.999	56.0	83.3	-91.0
	2.0	0.03	$y = -5.069x + 7.688$	0.999	42.1	82.3	-134
	3.0	0.04	$y = -6.020x + 11.13$	0.999	50.0	81.5	105
	4.0	0.05	$y = -7.664x + 16.87$	0.999	64.0	81.2	-57.3
PEG-300	5.0	0.06	$y = -7.062x + 14.92$	0.999	59.0	81.0	-73.5
	0.5	0.01	$y = -9.797x + 22.35$	0.999	81.4	85.0	-12.0
	1.0	0.02	$y = -8.070x + 17.25$	0.999	67.0	83.2	-54.2
	2.0	0.04	$y = -4.233x + 5.180$	0.998	35.2	81.5	-154
	3.0	0.05	$y = -6.852x + 14.13$	0.999	54.6	79.0	-80.0
PEG-400	4.0	0.06	$y = -6.564x + 13.36$	0.999	54.5	80.4	-86.5
	5.0	0.08	$y = -9.440x + 23.13$	0.999	78.5	80.0	-5.3
	0.5	0.01	$y = -9.759x + 22.23$	0.999	81.2	85.0	-13.0
	1.0	0.02	$y = -7.864x + 16.59$	0.999	65.4	83.3	-57.0
	2.0	0.04	$y = -4.189x + 5.034$	0.999	35.0	82.0	-155
PEG-600	3.0	0.05	$y = -8.018x + 17.93$	0.999	67.0	81.5	-48.5
	4.0	0.06	$y = -5.394x + 9.454$	0.999	45.0	80.7	-119
	5.0	0.08	$y = -8.250x + 19.25$	0.998	68.6	80.0	-37.5
	0.5	0.01	$y = -9.630x + 21.81$	0.998	80.0	85.0	-16.3
	1.0	0.02	$y = -5.541x + 8.852$	0.998	46.0	83.2	-123
PEG-300	2.0	0.03	$y = -5.256x + 8.404$	0.999	44.0	82.3	-128
	3.0	0.04	$y = -5.421x + 9.243$	0.998	45.0	81.2	-120
	4.0	0.06	$y = -4.492x + 6.466$	0.997	37.4	80.5	-144
	5.0	0.09	$y = -6.254x + 12.73$	0.999	52.0	80.0	-91.8

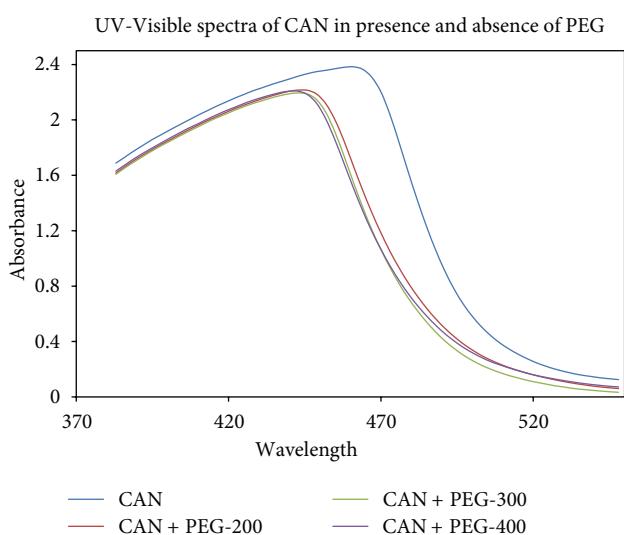


FIGURE 1: UV-Visible spectra of CAN in presence and absence of PEG in MeCN medium.

mixed thoroughly. Flask was coated black from the outside to prevent photochemical effects. Aliquots of the reaction

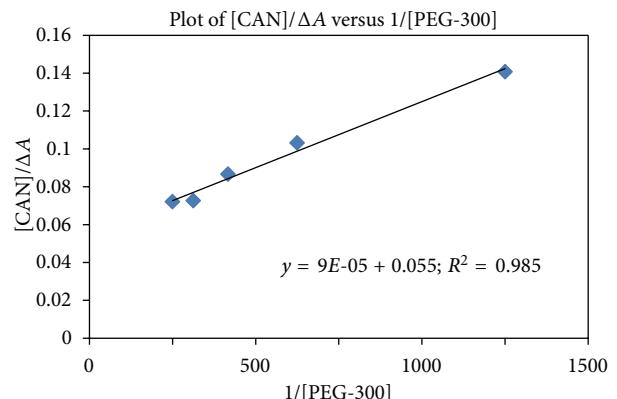


FIGURE 2: Benesi-Hildebrand plot of PEG-300 interaction with CAN.

mixture were withdrawn into a cuvette and placed in the cell compartment of the laboratory visible spectrophotometer. Cell compartment was provided with an inlet and an outlet for circulation of thermostatic liquid at a desired temperature. The CAN content could be estimated from the previously constructed calibration curve showing absorbance (A) versus $[CAN]$. Absorbance values were in agreement with each other with an accuracy of $\pm 3\%$ error.

TABLE 4: Activation parameters of methoxy cinnamic acid in different PEG media. Units of $k'' = \text{dm}^3 \text{ mol}^{-1} \text{ min}^{-1}$.

Type of PEG	PEG % (V/V)	k'' at 300 K	Equation	R^2	$\Delta H^\#$ kJ/mol	$\Delta G^\#$ J/K/mol	$\Delta S^\#$ J/K/mol
PEG-200	0.5	0.01	$y = -12.85x + 32.55$	0.996	107	85.0	73.0
	1.0	0.02	$y = -13.90x + 36.01$	0.998	115	84.4	102
	2.0	0.04	$y = -6.038x + 11.21$	0.999	50.2	81.50	-104
	3.0	0.06	$y = -5.027x + 8.448$	0.999	42.0	80.2	-127
	4.0	0.08	$y = -3.844x + 4.748$	0.999	32.0	80.0	-158
PEG-300	5.0	0.12	$y = -4.403x + 6.945$	0.999	37.0	79.0	-140
	0.5	0.01	$y = -10.36x + 14.11$	0.997	86.0	35.3	110
	1.0	0.03	$y = -3.532x + 2.653$	0.999	46.0	98.5	-175
	2.0	0.04	$y = -5.385x + 8.930$	0.959	45.0	82.0	-123
	3.0	0.05	$y = -2.423x - 0.582$	0.999	20.2	78.0	-192
PEG-400	4.0	0.06	$y = -8.743x + 20.63$	0.999	73.0	81.0	-26.0
	5.0	0.08	$y = -7.965x + 18.28$	0.999	66.2	80.0	-46.0
	0.5	0.02	$y = -7.638x + 15.83$	0.999	63.5	83.3	-66.0
	1.0	0.03	$y = -10.01x + 24.07$	0.999	83.2	77.0	21.3
	2.0	0.04	$y = -9.756x + 23.58$	0.999	81.0	81.4	-2.0
PEG-600	3.0	0.06	$y = -8.022x + 18.16$	0.999	67.0	80.0	-41.0
	4.0	0.08	$y = -6.000x + 11.86$	0.999	50.0	80.0	-99.0
	5.0	0.10	$y = -9.302x + 22.89$	0.999	77.3	79.5	-7.3
	0.5	0.02	$y = -7.936x + 16.83$	0.999	66.0	83.3	-58.0
	1.0	0.03	$y = -5.955x + 10.61$	0.998	49.5	82.3	-110
PEG-600	2.0	0.05	$y = -4.894x + 7.616$	0.999	41.0	81.3	-134
	3.0	0.06	$y = -6.259x + 12.33$	0.999	52.0	80.5	-95.0
	4.0	0.08	$y = -5.659x + 10.63$	0.999	47.0	38.72	-110
	5.0	0.1	$y = -6.719x + 14.05$	0.998	56.0	80.3	-81.0

2.4. [CAN-PEG] Binding Study. Spectrophotometric studies were performed in order to throw light on CAN binding with PEG (polyethylene glycol). UV-Visible spectrum of CAN in MeCN indicated a band at 459 nm. It underwent a hypsochromic shift (blue shift) of about 17 to 18 nm (band-shifted from 441 to 442 nm) in presence of PEG (Figure 1), followed by hypochromic shift. This observation indicates the formation of [CAN-PEG] complex. The CAN-PEG binding constants (K) were evaluated by the method of Benesi-Hildebrand [32]. When the equilibrium for molecular complexation is taken into consideration,



The equilibrium constant $K = [C]/[\text{CAN}][\text{PEG}]$, where [CAN], [PEG], and [C] are equilibrium concentrations of acceptor (CAN), donor (PEG), and complex, respectively. If $[\text{CAN}]_0$ and $[\text{PEG}]_0$ represent initial concentrations of CAN and PEG, respectively, then

$$K = \frac{[C]}{([\text{CAN}]_0 - [C])([\text{PEG}]_0 - [C])}. \quad (2)$$

Under condition that $[\text{PEG}]_0 \gg [\text{CAN}]_0 \Rightarrow [\text{PEG}]_0 \gg [C]$ and $([\text{PEG}]_0 - [C]) \sim [\text{PEG}]_0$

$$\begin{aligned} K &= \frac{[C]}{([\text{CAN}]_0 - [C])([\text{PEG}]_0)} \\ \Rightarrow K &= \frac{[C]}{([\text{CAN}]_0 [\text{PEG}]_0 - [C] [\text{PEG}]_0)}, \\ [C](1 + K[\text{PEG}]_0) &= K[\text{CAN}]_0[\text{PEG}]_0 \\ \Rightarrow [C] &= \frac{K[\text{CAN}]_0[\text{PEG}]_0}{(1 + K[\text{PEG}]_0)}. \end{aligned} \quad (3)$$

But according to Lambert-Beer's law absorbance ($A = ecl$).

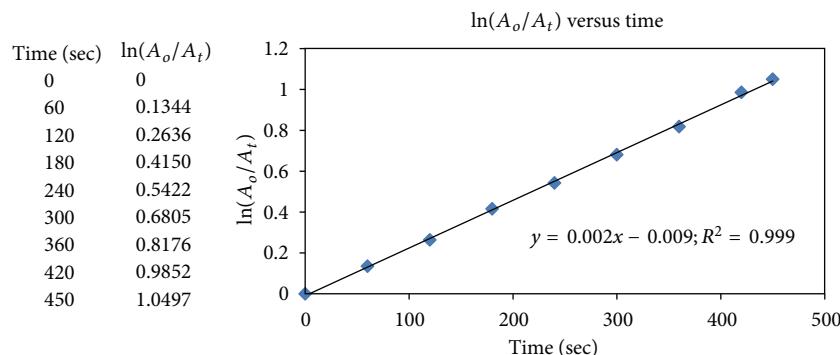
In the previous equations, l is path length, A is absorbance, ϵ is the molar extinction coefficient, and K is formation constant of the complex, respectively,

$$[C] = \frac{A}{\epsilon l} = \frac{K[\text{CAN}]_0[\text{PEG}]_0}{(1 + K[\text{PEG}]_0)}. \quad (4)$$

According to this plot of absorbance (A) as a function of donor concentration ($[\text{PEG}]_0$) the plot indicated a linear increase in the value of (A) with an increase in ($[\text{PEG}]_0$) with

TABLE 5: Activation parameters of nitrocinnamic acid in different PEG media. Units of $k'' = \text{dm}^3 \text{ mol}^{-1} \text{ min}^{-1}$.

Type of PEG	PEG % (V/V)	k'' at 300 K	Equation	R^2	$\Delta H^\#$ kJ/mol	$\Delta G^\#$	$\Delta S^\#$ J/K/mol
PEG-200	0.5	0.01	$y = -12.00x + 29.73$	0.999	100	85.0	50.0
	1.0	0.02	$y = -10.87x + 26.63$	0.999	90.3	83.1	24.0
	2.0	0.04	$y = -4.711x + 6.807$	0.999	39.2	37.05	-141
	3.0	0.06	$y = -5.506x + 9.842$	0.999	46.0	38.04	-116
	4.0	0.07	$y = -5.012x + 8.347$	0.999	42.0	38.40	-128
PEG-300	5.0	0.09	$y = -3.923x + 4.963$	0.998	33.0	38.99	-156
	0.5	0.01	$y = -9.764x + 22.25$	0.999	81.2	85.0	-13.0
	1.0	0.02	$y = -7.861x + 16.58$	0.999	65.4	83.3	-60.0
	2.0	0.04	$y = -4.270x + 5.297$	0.999	35.5	37.0	-153
	3.0	0.05	$y = -6.852x + 14.13$	0.999	57.0	81.0	-80.0
PEG-400	4.0	0.06	$y = -6.545x + 13.3$	0.998	54.4	81.2	-89.5
	5.0	0.08	$y = -9.042x + 21.84$	0.999	75.1	80.0	-16.0
	0.5	0.02	$y = -7.717x + 16.10$	0.977	64.1	83.2	-64.0
	1.0	0.03	$y = -5.321x + 8.612$	0.999	44.2	82.0	-126
	2.0	0.04	$y = -8.683x + 20.01$	0.999	72.1	81.4	-31.2
PEG-600	3.0	0.06	$y = -8.718x + 20.54$	0.999	72.4	80.4	-27.0
	4.0	0.07	$y = -7.947x + 18.23$	0.998	66.0	80.0	-46.0
	5.0	0.10	$y = -7.687x + 17.63$	0.999	64.0	79.3	-51.0
	0.5	0.01	$y = -9.635x + 21.82$	0.998	80.1	85.0	-16.2
	1.0	0.02	$y = -8.534x + 18.80$	0.997	71.0	83.4	-41.3
PEG-600	2.0	0.04	$y = -4.071x + 4.648$	0.999	34.0	82.0	-159
	3.0	0.06	$y = -4.703x + 7.167$	0.999	39.1	80.5	-138
	4.0	0.08	$y = -3.635x + 3.891$	0.999	30.2	80.0	-165
	5.0	0.10	$y = -5.600x + 10.65$	0.999	46.5	79.2	-109

FIGURE 3: Pseudo first order plot of cinnamic acid ($\ln(A_o/A_t)$ versus time) at 323 K. $[\text{CA}] = 1.00 \times 10^{-2} \text{ mol dm}^{-3}$; $[\text{CAN}] = 4.00 \times 10^{-3} \text{ mol dm}^{-3}$; $[\text{PEG-300}] = 9.99 \times 10^{-1} \text{ mol dm}^{-3}$.

a limiting value at its higher concentrations. Further, taking the reciprocals to the previous equation, it rearranges to

$$\left(\frac{[\text{CAN}]_0}{Al} \right) = \left(\frac{1}{K[\text{PEG}]_0 \epsilon} \right) + \left(\frac{1}{\epsilon} \right). \quad (5)$$

For one cm path length, the aforementioned equation can be written as

$$\left(\frac{[\text{CAN}]_0}{A} \right) = \left(\frac{1}{K[\text{PEG}]_0 \epsilon} \right) + \left(\frac{1}{\epsilon} \right). \quad (6)$$

But the absorbance of CAN and [CAN-PEG] absorbs in the same region significantly; therefore the observed absorbance (A) could be written as

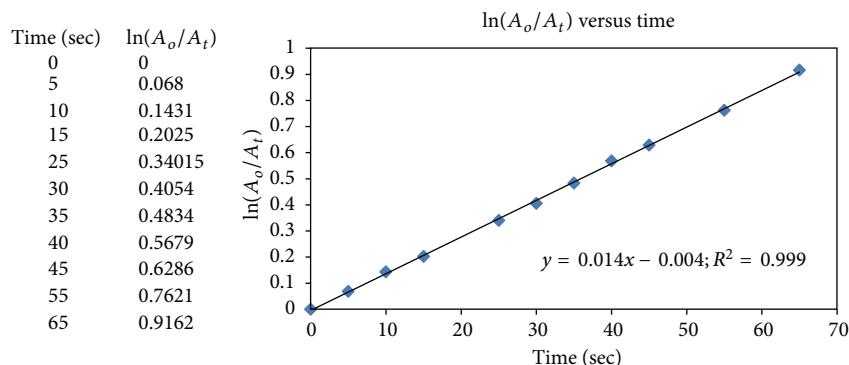
$$A = A_{(\text{CAN})} + A_{(\text{Complex})}. \quad (7)$$

Now the true absorbance of [CAN-PEG] adduct is the difference between observed absorbance and absorbance of CAN:

$$\Rightarrow A_{(\text{Complex})} = \Delta A = A \sim A_{(\text{CAN})}. \quad (8)$$

TABLE 6: Activation parameters of acrylic acid in different PEG media. Units of $k'' = \text{dm}^3 \text{ mol}^{-1} \text{ min}^{-1}$.

Type of PEG	PEG % (V/V)	k'' at 300 K	Equation	R^2	$\Delta H^\#$ kJ/mol	$\Delta G^\#$ J/K/mol	$\Delta S^\#$ J/K/mol
PEG-200	0.5	0.01	$y = -11.85x + 29.21$	0.999	98.5	85.0	45.3
	1.0	0.02	$y = -8.384x + 18.31$	0.998	70.0	84.0	-45.3
	2.0	0.03	$y = -7.860x + 16.98$	0.998	65.3	82.2	-57.0
	3.0	0.04	$y = -8.164x + 18.27$	0.997	68.0	82.0	-47.0
	4.0	0.06	$y = -6.581x + 13.42$	0.999	55.0	81.0	-86.0
PEG-300	5.0	0.08	$y = -6.061x + 11.96$	0.998	51.0	80.5	-98.2
	0.5	0.01	$y = -11.85x + 29.21$	0.999	98.5	85.0	46.0
	1.0	0.02	$y = -11.43x + 28.49$	0.998	95.0	83.2	39.3
	2.0	0.03	$y = -10.67x + 26.25$	0.997	89.0	83.0	21.0
	3.0	0.04	$y = -9.163x + 21.61$	0.999	76.2	82.0	-18.0
PEG-400	4.0	0.05	$y = -6.125x + 11.72$	0.999	51.0	81.0	-100
	5.0	0.07	$y = -5.443x + 9.792$	0.998	45.3	80.2	-116
	0.5	0.02	$y = -8.314x + 18.07$	0.997	69.2	83.4	-47.4
	1.0	0.03	$y = -9.364x + 21.98$	0.998	78.0	82.5	-15.0
	2.0	0.04	$y = -9.756x + 23.58$	0.999	81.2	82.0	-1.6
PEG-600	3.0	0.06	$y = -7.889x + 17.76$	0.997	66.0	81.0	-50.0
	4.0	0.08	$y = -6.573x + 13.69$	0.998	55.0	80.2	-84.0
	5.0	0.10	$y = -8.507x + 20.35$	0.999	71.0	80.0	-28.4
	0.5	0.01	$y = -9.947x + 22.82$	0.998	83.0	85.4	-8.0
	1.0	0.02	$y = -6.653x + 12.57$	0.997	55.4	83.3	-93.0
PEG-600	2.0	0.03	$y = -6.334x + 11.88$	0.997	53.0	83.0	-99.0
	3.0	0.05	$y = -2.362x - 0.780$	0.998	20.0	77.4	-191
	4.0	0.07	$y = -3.078x + 1.893$	0.998	26.0	80.5	-182
	5.0	0.09	$y = -4.666x + 7.455$	0.998	39.0	80.0	-135

FIGURE 4: Pseudo first order plot of acrylic acid ($\ln(A_o/A_t)$ versus time) at 315 K. $[\text{AA}] = 1.00 \times 10^{-2} \text{ mol dm}^{-3}$; $[\text{CAN}] = 4.00 \times 10^{-3} \text{ mol dm}^{-3}$; $[\text{PEG-300}] = 13.32 \times 10^{-2} \text{ mol dm}^{-3}$.

Therefore, a plot of $([\text{CAN}]_0/\Delta A)$ versus $1/[\text{PEG}]_0$ should give a straight line according to the previous equation. These plots (Figure 2) have been realized in the present study. Formation constant (K) has been calculated from the ratio of intercept to slope, while inverse of the intercept gave molar extinction coefficient (e) and is represented in Table 1.

3. Results and Discussion

3.1. Determination of the Order of Reaction. General form of the rate law for a nitrodecarboxylation (nitro-Hunsdiecker

reaction) reaction could be represented by considering the following general scheme:



where CAN = ceric ammonium nitrate and S = α,β -unsaturated carboxylic acid:

$$V = k_1 [\text{CAN}]^x [\text{CAN}]^y. \quad (10)$$

Reactions were conducted under two different conditions. Under pseudo first order conditions $[\text{CAN}] \gg [\text{CAN}]$,

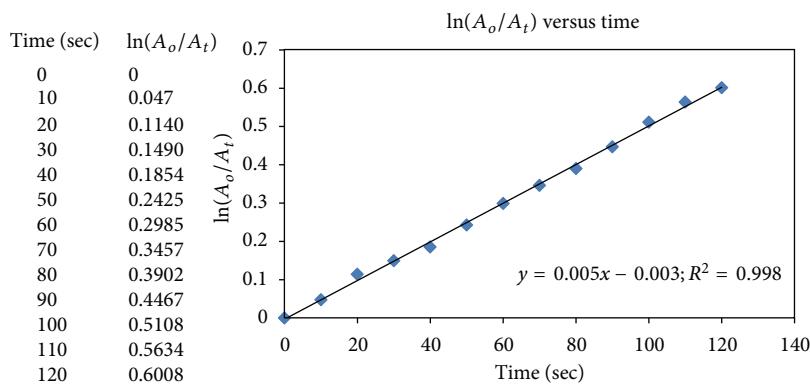


FIGURE 5: Pseudo first order plot of nitrocinnamic acid ($\ln(A_o/A_t)$ versus time) at 315 K. $[NCA] = 1.00 \times 10^{-2} \text{ mol dm}^{-3}$; $[CAN] = 4.00 \times 10^{-3} \text{ mol dm}^{-3}$; $[PEG-400] = 1.25 \times 10^{-1} \text{ mol dm}^{-3}$.

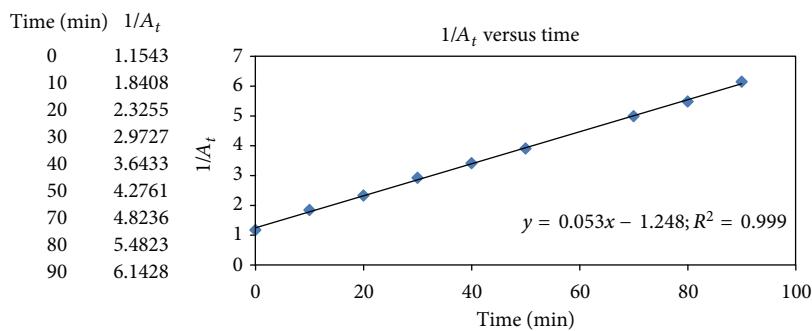


FIGURE 6: Second order kinetic plot of cinnamic acid ($1/A_t$ versus Time) at 310 K. $[CA] = 4.00 \times 10^{-2} \text{ mol dm}^{-3}$; $[CAN] = 4.00 \times 10^{-2} \text{ mol dm}^{-3}$; $[PEG-200] = 5.00 \times 10^{-1} \text{ mol dm}^{-3}$.

plots of $\ln(A_o/A_t)$ versus time were straight lines with a negative slope indicating order (x) with respect to $[CAN]$ to be unity. As typical examples pseudo first order plots are shown in Figures 3, 4, and 5. First order rate constant (k') was obtained from the slopes of line plots cited (k').

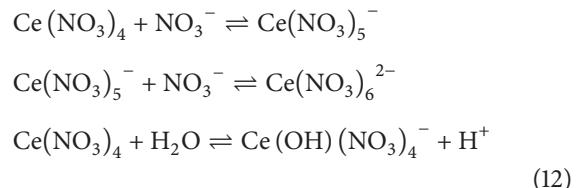
The reaction is also conducted under second order conditions with equal concentrations of $[CAN]_0 = [CAN]_0$. Kinetic plots of $[1/(a-x)]$ or $[1/(A_t)]$ versus time (Figures 6, 7, and 8) have been found to be linear with a positive gradient and definite intercept on ordinate (vertical axis), indicating overall second order kinetics.

In the present study, kinetic data have been collected at three to four different temperatures within the range of 300–315 K. Activation parameters such as $\Delta H^\#$ and $\Delta S^\#$ have been evaluated from Eyring's plots (Figures 9 and 10). Free energy of activation ($\Delta G^\#$) is obtained from Gibbs-Helmholtz equation:

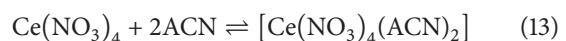
$$\Delta G^\# = \Delta H^\# - T\Delta S^\#. \quad (11)$$

3.2. Mechanism of Nitrodecarboxylation of Unsaturated Acids by Ce(IV) Nitrate (CAN) in MeCN Medium. In order to gain an insight into the mechanistic aspects of CAN-CA reaction in MeCN medium, the knowledge of distribution of CAN species in HNO_3 medium could be useful. In HNO_3 Ce(IV) mainly exists as $Ce(NO_3)_6^{2-}$, $Ce(NO_3)_5^-$, $Ce(OH)(NO_3)_4^-$,

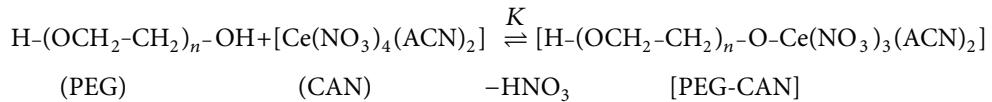
$Ce(NO_3)_4$, which could arise from the following equilibria as cited in the literature reports [33–36]:



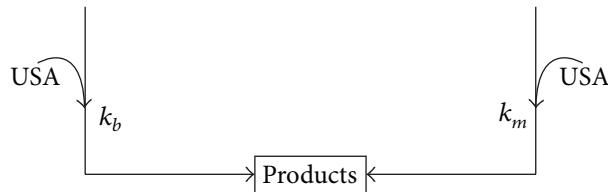
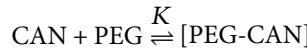
But the CAN species in the present study could be entirely different because the reactions are conducted in MeCN medium, which is large excess over [CAN]. MeCN may penetrate into the coordination spheres of Ce(IV) and form solvated CAN species according to the following equilibrium:



When unsaturated acid (USA) is added to the reaction mixture containing solvated CAN, it may form [Ce(IV) carboxylate] precursor which dissociates and releases HNO_3 *in situ*. The HNO_3 thus released in turn may combine with another solvated CAN to form nitronium ion (NO_2^+) which

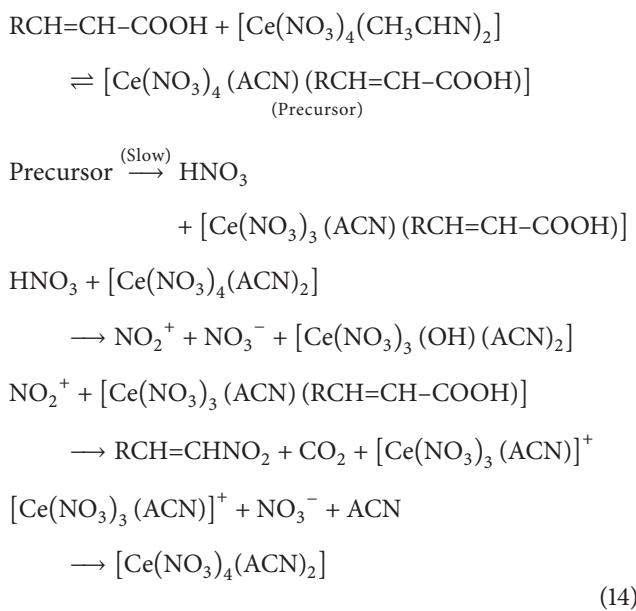


SCHEME 1



SCHEME 2

finally reacts with coordinated USA to afford β -nitrostyrene as shown in the following sequence of steps:



3.3. Mechanism of Nitrodecarboxylation in PEG Media. Progress of the reaction has been studied in the presence of a set of polyoxyethylene compounds (PEGs) with varied molecular weights ranging from 200 to 600 units, and it was found that the reaction is enhanced remarkably in all PEGs. Reaction times were reduced from 24 hrs to few hours. The catalytic activity was found to be in the increasing order PEG-300 > PEG-400 > PEG-600 > PEG-200. Further, it is also interesting to note that the absorbance of solvated Ce(IV) species is increased when PEG is added to [CAN] solution. This observation may indicate that solvated [CAN] species could bind with PEG to form *PEG supported CAN species* according to the equilibrium shown in Scheme 1.

The plots of k_m (rate constant of PEG reaction) versus C_{PEG} (concentration of PEG) indicated a rate maxima nearly in the vicinity of 1.50 mol dm^{-3} PEG-200, 0.99 mol dm^{-3} PEG-300, 0.99 mol dm^{-3} PEG-400, $0.500 \text{ mol dm}^{-3}$ PEG-600. Efforts have been made to interpret PEG effect on the mechanism of CAN-USA reaction. Mechanism of PEG-mediated reactions was explained in the lines of micellar catalysis because PEG resembles the structure of Triton-X. The first and widely applied model is that of Menger and Portnoy [37] which closely resembles that of an enzymatic Catalysis. According to this model, formation of PEG bound reagent (PEG-CAN) could occur in the preequilibrium step due to the interaction of Ce(IV) with PEG. The complex thus formed may possess higher or lower reactivity to give products. A general mechanism is proposed by considering the bulk phase and micellar phase reactions as shown in Scheme 2, where k_m and k_0 or (k_b) represents rate constants for PEG and bulk phases, respectively, and K is the [PEG-CAN] binding constant. For the previous mechanism, rate law could be derived according to the following sequence of steps in the lines of micellar catalyzed reactions.

Considering the total concentration of (C_s) as the algebraic sum of free species and PEG bound substrate complex (CAN-PEG) species,

$$C_s = [\text{CAN}] + [\text{CAN-PEG}] \tag{15}$$

From micelle-substrate binding equilibrium,

$$\begin{aligned}
 K &= \frac{[\text{CAN-PEG}]}{[\text{PEG}][\text{CAN}]}, \quad \text{or} \\
 [\text{CAN}] &= \frac{[\text{CAN-PEG}]}{K[\text{PEG}]}.
 \end{aligned} \tag{16}$$

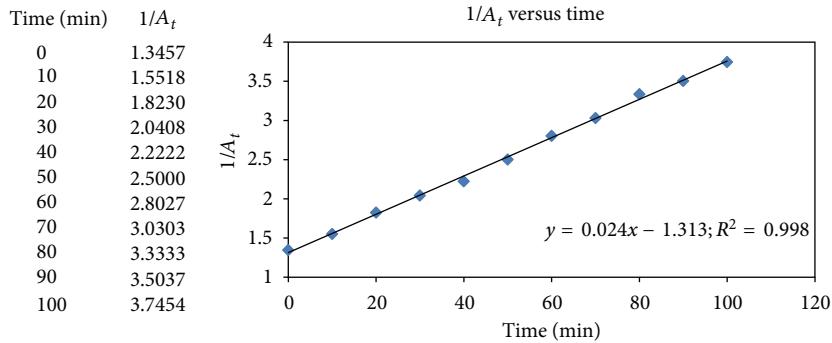


FIGURE 7: Second order kinetic plot of acrylic acid ($1/A_t$ versus Time) at 310 K. $[AA] = 4.00 \times 10^{-2}$ mol dm $^{-3}$; $[CAN] = 4.00 \times 10^{-2}$ mol dm $^{-3}$; $[PEG-300] = 3.33 \times 10^{-1}$ mol dm $^{-3}$.

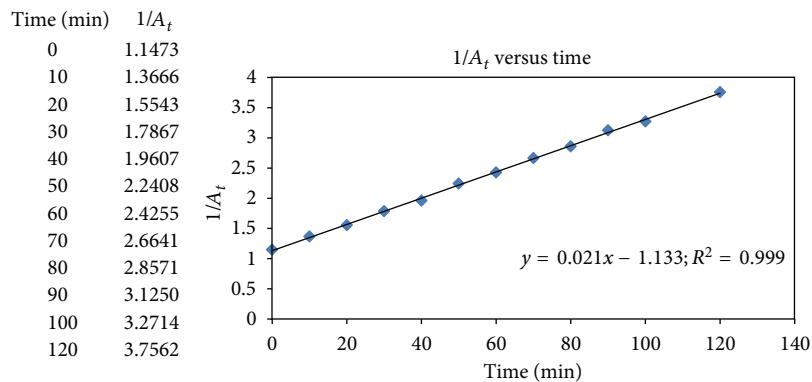


FIGURE 8: Second order kinetic plot of nitrocinnamic acid ($1/A_t$ versus time) at 310 K. $[NCA] = 4.00 \times 10^{-2}$ mol dm $^{-3}$; $[CAN] = 4.00 \times 10^{-2}$ mol dm $^{-3}$; $[PEG-600] = 3.32 \times 10^{-1}$ mol dm $^{-3}$.

Substitution of $[CAN]$ in (15) gives

$$\begin{aligned} C_S &= \frac{[CAN-PEG]}{K [PEG]} + [CAN-PEG] \\ &= \frac{[CAN-PEG] + K [PEG] [CAN-PEG]}{K [PEG]} \quad \text{or} \quad (17) \\ [CAN-PEG] &= \frac{K [PEG] C_S}{1 + K [PEG]}. \end{aligned}$$

Similarly free substrate $[CAN]$ is written as $[CAN] = C_S - [CAN-PEG]$

$$[CAN] = C_S - \frac{K [PEG] C_S}{1 + K [PEG]}. \quad (18)$$

After simplification, the previous equation reduces to

$$[CAN] = \frac{C_S}{1 + K [PEG]}. \quad (19)$$

Substitution of $[CAN-PEG]$ and $[CAN]$ in (15) gives

$$\begin{aligned} k' &= \frac{k_0 C_S}{1 + K [PEG]} + \frac{k_m K [PEG] C_S}{1 + K [PEG]} \quad \text{or} \\ k_\varphi &= \frac{(k_0 + k_m K [PEG])}{1 + K [PEG]} \quad (20) \\ k_\varphi &= \frac{(k_0 + k_m K [PEG])}{1 + K [PEG]}, \end{aligned}$$

where $k_\varphi = (k'/[CAN])$, the second order rate constant in PEG media. Subtracting k_0 from both sides of equation and rearranging

$$k_\varphi - k_0 = \frac{(k_m - k_w) K [PEG]}{1 + K [PEG]}. \quad (21)$$

But, since the reactions are too sluggish in the absence of $[PEG]$, the rate constant (k_0) would be much smaller than $(k_m K [PEG])$; that is, $(k_0 \ll k_m K [PEG])$. Therefore the (k_0) term could be neglected in the previous equation. The rate law (21) could be then considered as

$$k_\varphi = \frac{k_m K [PEG]}{1 + K [PEG]}. \quad (22)$$

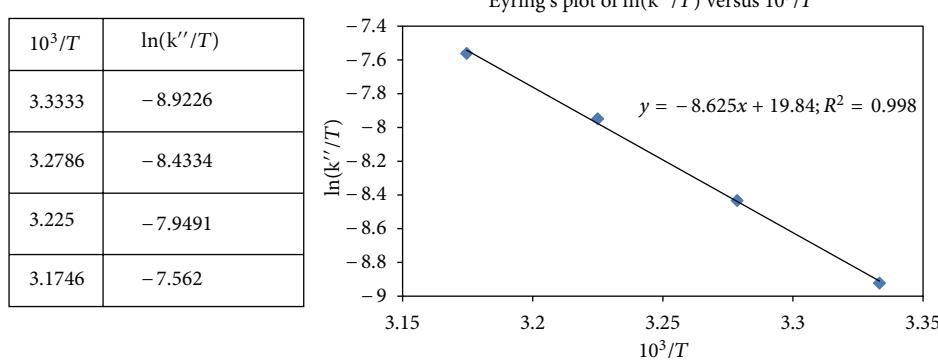


FIGURE 9: Eyring's plot of cinnamic acid ($\ln(k''/T)$) versus $10^3/T$. Kinetic study with $[PEG-200] = 2.00 \text{ mol dm}^{-3}$.

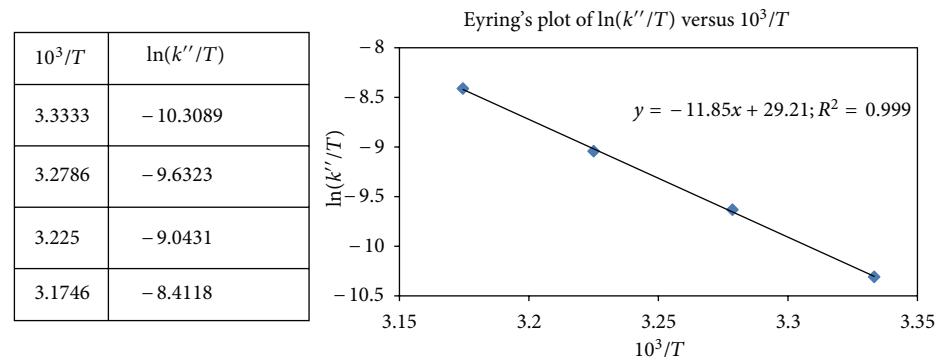


FIGURE 10: Eyring's plot of acrylic acid ($\ln(k''/T)$) versus $10^3/T$. Kinetic study $[PEG-300] = 13.32 \times 10^{-1} \text{ mol dm}^{-3}$.

This rate-law resembles Michaelis-Menten type rate law that is used for enzyme kinetics. Interestingly the plots of rate constant (k_φ), that is, second order rate constant of PEG-mediated reaction versus [PEG], indicated either Hill type curve (i.e., a gradual increase with an increase in [PEG] passing through a maximum point in the profile). This observation could be explained due to the CAN-PEG binding interactions to give [CAN-PEG] species which is responsible for rate accelerations in PEG-mediated reactions. Formation of [CAN-PEG] species has also been established by UV-Visible spectroscopic studies, and binding constants are compiled in Table 1. These observations strengthened us to take up detailed reaction kinetics at various PEG concentrations in order to have an insight into the variation in the enthalpies and entropies of activation with [PEG].

3.4. Effect of Structure on the Reactivity, Enthalpy, and Entropy Changes. The enthalpy ($\Delta H^\#$) and entropy of activation ($\Delta S^\#$) are the two parameters typically obtained from the temperature dependence of a reaction rate, when these data are analyzed using Eyring's equation. Both of these values are obtained from Eyring's plots according to standard procedures [37–39]. Typical plots are shown in Figures 9 and 10. The entropy of activation ($\Delta S^\#$) provides clues about the molecularity of the rate determining step in a reaction, that

is, whether the reactants are bonded to each other or not. Even though structural change in the cinnamic acid exhibits slight variation on its reactivity, no quantitative conclusions could be obtained from rate constant data. However, the observed positive $\Delta S^\#$ values in lower PEG concentration (0.1 M PEG) decreased with an increase in [PEG] and are becoming more negative for all the unsaturated acids which probably indicates that PEG is tightly bound to CAN and lends support that PEG bound CAN is the active species in PEG-mediated reactions. The observed negative $\Delta S^\#$ values are in consonance with the concept that for associative mechanism, entropy decreases upon achieving the transition state, and values near zero are difficult to interpret [38–40]. By and large similar magnitude of observed free energy of activation ($\Delta G^\#$) in this reaction series (Tables 2, 3, 4, 5, 6) indicates a similar type of mechanism which is operative in the present study. The observed negative magnitude of ΔG (Table 1) indicates the spontaneity of complexation of [CAN-PEG] due to PEG binding with CAN.

4. Conclusions

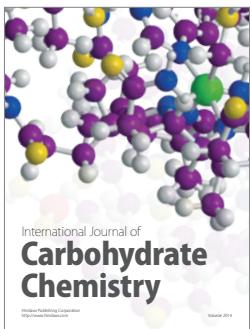
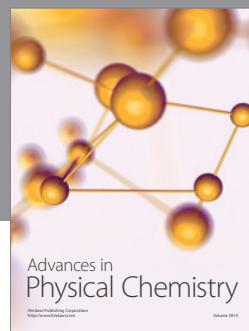
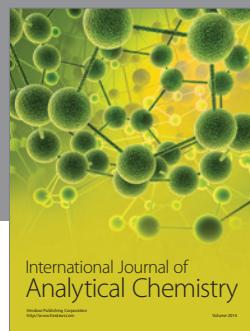
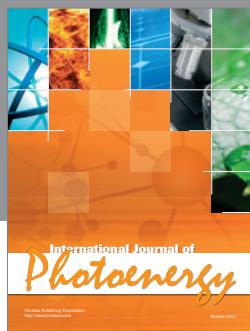
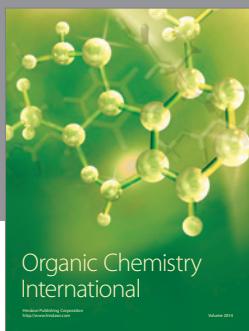
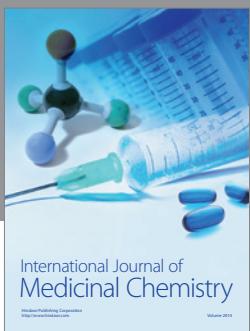
Being a versatile chemical reagent CAN has been applied to organic reactions in catalytic or stoichiometric amounts. Our research group has succeeded in using CAN to perform

nitrodecarboxylation of α,β -unsaturated aromatic carboxylic acids to give β -nitrostyrene derivatives. Furthermore, use of PEG supported CAN could effectively initiate the decarboxylation of carboxyl group followed by nitration. Because the CAN reagent is cost effective, we believe that the present protocol offers a rapid and clean alternative and reduces reaction times.

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