Polyethylene Glycols as Efficient Catalysts for the Oxidation of Bicyclic Monoterpenes by Ceric Ammonium Nitrate in Acetonitrile under Acid-Free Conditions: Kinetic and Mechanistic Approach

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Received 15 October 2017; revised 26 January 2018; accepted 25 February 2018

DOI 10.1002/kin.21168
Published online 26 March 2018 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: Polyethylene glycols (PEG) acts as efficient catalysts for the oxidation of bicyclic monoterpenes such as borneol, isoborneol, and camphor by ceric ammonium nitrate (CAN), a laboratory desktop reagent, in acetonitrile medium under mineral acid-free conditions. The kinetics of the reactions revealed first-order dependence on in both [CAN] and [bicyclic terpene]. The rate of oxidation is accelerated with an increase in [PEG] linearly, which could be explained by considering PEG-bound oxidant (PEG-CAN) as more reactive species than (CAN) itself. The mechanism of oxidation in PEG media has been explained through the participation of PEG-bound oxidant (PEG-CAN) and bicyclic monoterpene in the slow step. © 2018 Wiley Periodicals, Inc. Int J Chem Kinet 50: 383–396, 2018

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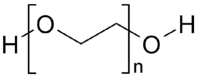
INTRODUCTION

The camphor is a bicycle monoterpenoid ketone, which is well known for its uses in medicine and as a plasticizer for nitrocellulose. For several years, camphor was extracted mainly from the Formosan camphor tree, but it is now synthesized on a large scale from α-pinene through isobornyl ethanoate and isoborneol intermediates. Isobornyl ethanoate upon hydrolysis affords isoborneol, which upon oxidation gives camphor. On the other hand, oxidation of borneol also gives camphor [1,2]. Camphor upon oxidation is known to form camphoronic acid [3]. During the past few decades, single-electron transfer (SET) oxidation has received considerable attention as a means to promote bond-forming reactions in organic synthesis [2–4]. Oxidation of an organic substrate by a SET reagent generally proceeds through a radical or radical–ion followed by the reduction of oxidizing reagent [5–9]. More so, cerium(IV) ammonium nitrate (CAN) has recently emerged as a versatile reagent for oxidative electron transfer; the overwhelming number of reports serve as a testimony to the unparalleled utility of CAN in a variety of transformations of synthetic importance [10–19]. Polyethylene glycol (PEG) is a polyoxyethylene, which exhibits a broad spectrum of applications from industrial manufacturing to medicine. It is a condensation polymer of ethylene oxide and water (polyethylene oxide (PEO)) with the general formula [$H(OCH_2CH_2)_nOH$], where n is the average number of repeating oxyethylene groups typically from 4 to about 180. It is a neutral, less expensive, and easily available hydrophilic polyether. The structure of PEG is shown below:



In recent past, PEG has been used as catalysts, catalyst supports, and also have been found as inexpensive, nonionic, nontoxic, environmentally friendly reaction medium, which avoids the use of acid or base catalysts [20–23].

A perusal of literature shows that the kinetics of oxidation of bicyclic terpenoids (BCT), such as borneol (BORN), isoborneol (IBORN), and camphor (CAMP) by CAN have not been attempted so far. Inspired by this aspect coupled with the striking features of PEG as a green acid-free catalyst/reaction medium, we have used the PEG to assist the present study in acetonitrile medium. It is of interest to note that native CAN oxidation of BCT compounds in a pure acetonitrile medium did not proceed smoothly and gave reproducible results. This study does not require Bronsted acid to onset the reaction.

EXPERIMENTAL

All chemicals used were of analytical grade. Doubly distilled water (distilled over alkaline $KMnO_4$ and acid dichromate in a glass apparatus) was used whenever required. Acetonitrile and other solvents were HPLC grade and used as such throughout the work. CAMP was procured from Aldrich (India). CAN, polyethylene glycols (PEGs: PEG–200, PEG–300, PEG–400, and PEG–600) were purchased from Avra or SD-fine chemicals (Mumbai, India).

Kinetic Method

For a typical first-order reaction, a flask containing centimolar (0.01 mol/dm^3) CAN prepared in acetonitrile (MeCN) solvent was clamped in a thermostat at a desired temperature. In another stoppered cylindrical tube, BCT (2.0 mL of 0.10 mol/dm^3), suitable amount of PEG (0.50–5.0 mL depending on the reaction), and the remaining amount was adjusted to 10.0 mL with acetonitrile (MeCN). This tube was also clamped in the thermostatic bath for about few minutes until it attained desired temperature. Reaction was initiated by transferring 2.0 mL of CAN to the other contents present in the cylindrical tube. The entire reaction mixture was mixed thoroughly. Aliquots of the reaction mixture were withdrawn into a cuvette and placed in the cell compartment of the laboratory visible spectrophotometer, which was provided with an inlet and an outlet for circulation of thermostatic liquid at a desired temperature. Absorbance (A) values of the CAN content were recorded at 400 nm at different time intervals. Absorbance values were in agreement with each other with an accuracy of $\pm 3\%$ error. However, for a second-order reaction, equimolar (0.01 mol/dm^3) CAN and BCT were used.

RESULTS AND DISCUSSION

The kinetic study was taken-up in acetonitrile medium under acid-free conditions. BCT–CAN reaction kinetics could not be followed smoothly in the absence of PEG. An irregular trend was obtained. However, the reaction was smooth, when we conducted the reactions in PEG–MeCN media.

Determination of the Order of Reaction and Salient Kinetic Features

1. Reactions were conducted under two different conditions. Under the conditions

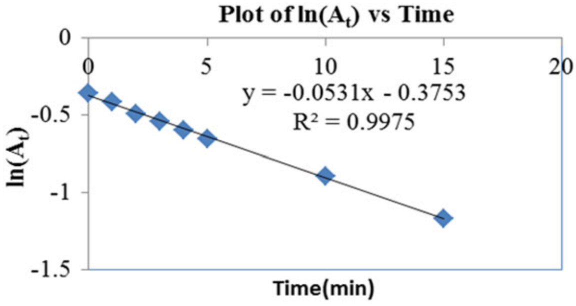


Figure 1 First-order plot of [CAN] in the PEG-mediated CAN-camphor reaction at 310 K [CAN] = 1.67 × 10^{-3} mol/dm^3; [PEG-200] = 0.50 mol/dm^3; [Camphor] = 1.67 × 10^{-2} mol/dm^3. [Color figure can be viewed at wileyonlinelibrary.com]

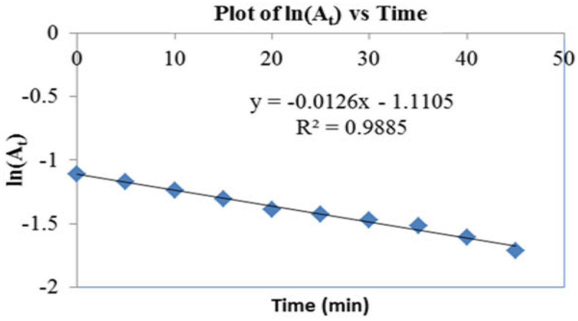


Figure 2 First-order plot of [CAN] in the PEG-mediated CAN–IBORN reaction at 315 K [CAN] = 1.67 × 10^{-3} mol/dm^3; [PEG-300] = 0.30 mol/dm^3; [IBORN] = 1.67 × 10^{-2} mol/dm^3. [Color figure can be viewed at wileyonlinelibrary.com]

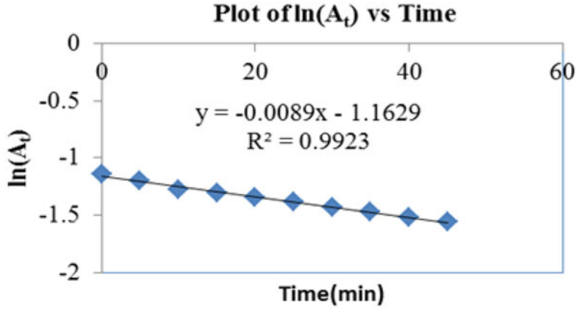


Figure 3 First-order plot of [CAN] in the PEG-mediated CAN–BORN reaction at 305 K [CAN] = 1.67 × 10^{-3} mol/dm^3; [PEG-400] = 0.25 mol/dm^3; [BORN] = 1.67 × 10^{-2} mol/dm^3. [Color figure can be viewed at wileyonlinelibrary.com]

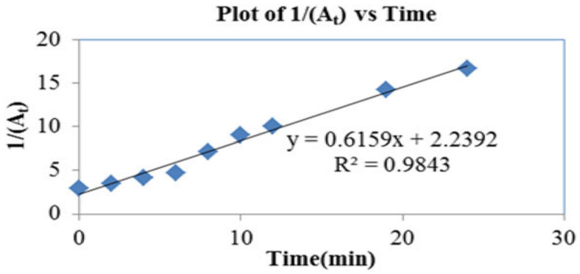


Figure 4 Second-order plot of the PEG-mediated CAN–Camphor reaction at 320 K [CAN] = 1.67 × 10^{-3} mol/dm^3; [PEG-200] = 0.5 mol/dm^3; [Camphor] = 1.67 × 10^{-3} mol/dm^3. [Color figure can be viewed at wileyonlinelibrary.com]

[BCT] ≫ [CAN], plots of ln (A_t) versus time were straight lines with a negative slope, indicating first order with respect to [CAN] to be unity (Figs. 1–3). First rate constants (k') are obtained from slopes of these plots.

2. This reaction is also conducted under second-order conditions with equal concentrations of $[BCT]_0 = [CAN]_0$. Kinetic plots of [1/(A_t)] versus time have been found to be linear with a positive gradient and definite intercept on ordinate (vertical axis), indicating overall second-order kinetics (Figs. 4–6). Since the order with respect [CAN] is already verified as one under pseudoconditions, this observation suggests that order in [BCT] is also one.
3. CAN oxidation of BCT compounds in pure acetonitrile medium was generally fast, but kinetics could not be followed smoothly and obtained results were not reproducible. Therefore, we have taken up kinetic studies only in PEG-mediated reactions. The addition of small amounts of PEG to CAN in acetonitrile medium increases the intensity of CAN color, indicating a hyperchromic shift. An increase in the [PEG] increased the reaction rates depending on the nature of PEG. By and large, reaction rates were found high in PEG-300 media over other PEGs in increasing order: PEG-300 > PEG-400 ≥ PEG-600 > PEG-200.
4. The addition of DPPH (2,2-diphenyl-1-picrylhydrazyl) to the reaction mixture decreased the reaction rate substantially, because it is an efficient radical trap [24]. The DPPH has a deep violet color in solution and showed a strong absorption band at about 520 nm, became colorless by trapping substrate-free radical formed during the course of the reaction [25].

Computation of Activation Parameters

Kinetic studies have been taken up at various temperatures in the temperature range 300–325 K. The free

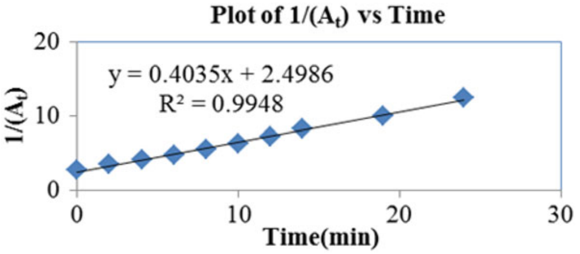


Figure 5 Second-order plot of the PEG-mediated CAN–IBORN reaction at 320 K [CAN] = 1.67×10^{-3} mol/dm^3; [PEG-200] = 0.5 mol/dm^3; [IBORN] = 1.67×10^{-3} mol/dm^3. [Color figure can be viewed at wileyonlinelibrary.com]

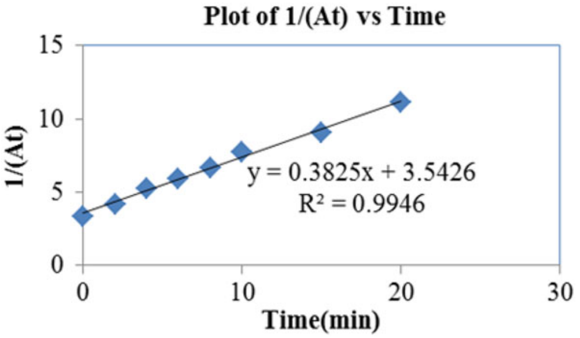


Figure 6 Second-order plot of the PEG-mediated CAN–IBORN reaction at 310 K [CAN] = 1.67×10^{-3} mol/dm^3; [PEG-600] = 0.17 mol/dm^3; [IBORN] = 1.67×10^{-3} mol/dm^3. [Color figure can be viewed at wileyonlinelibrary.com]

energy of activation ($\Delta G^{\#}$) at various temperatures is calculated using Eyring's equation according to the well-known theory of reaction rates [25,26]

$$\Delta G^{\#} = RT \ln \left(RT/Nhk \right)$$

Substituting the values for rate constant (k), R (8.314 J mol^{-1} K^{-1}), N (6.022×10^{23} mol^{-1}), h (6.626×10^{-34} J s), and T (Kelvins), respectively, free energy of activation ($\Delta G^{\#}$) can be obtained. Enthalpy and entropies of activation ($\Delta H^{\#}$ and $\Delta S^{\#}$) were obtained from ($\Delta G^{\#}$) versus (T) plots (Figs. 7–9), according to the Gibbs–Helmholtz equation [25,26]:

$$\Delta G^{\#} = \Delta H^{\#} - T\Delta S^{\#}$$

The data related to activation parameters are compiled in Tables I–IV.

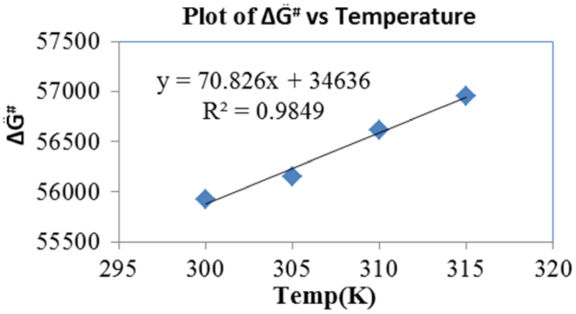


Figure 7 $\Delta G^{\#}$ versus temperature graph Isoborneol-PEG-300 (4.0 mL). [Color figure can be viewed at wileyonlinelibrary.com]

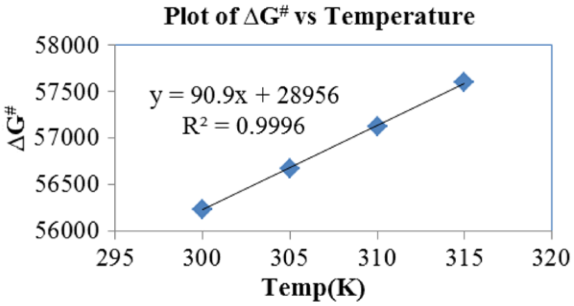


Figure 8 $\Delta G^{\#}$ versus temperature graph isoborneol-PEG-200 (2.0 mL). [Color figure can be viewed at wileyonlinelibrary.com]

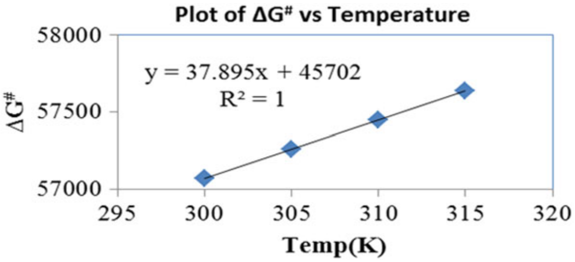


Figure 9 $\Delta G^{\#}$ versus temperature graph borneol-PEG-600 (3.0 mL). [Color figure can be viewed at wileyonlinelibrary.com]

Reactive Species and Mechanism of Oxidation of Bicyclic Terpenes by CAN

In aqueous nitric acid CAN is known to form different types of reactive species such as $Ce(NO_3)_6{}^{2-}$, $Ce(NO_3)_5{}^{-}$, $Ce(OH)(NO_3)_4{}^{-}$, $Ce(NO_3)_4$, $[Ce(NO_3)_4(H_2O)_2]$, and $Ce(OH)^{3+}$ as reported by earlier workers [10–20]. However, our aim is to study the reactions under acid-free conditions. Therefore, we studied the kinetics of the reactions in moderately a green acetonitrile (MeCN) solvent. Therefore, the reactive

Table I Second-Order Rate Constants (k) and Activation Parameters for Bicyclomonoterpenes in MeCN/PEG-200

		Camphor				Isoborneol				Borneol			
[PEG-200] % (V/V)	Temperature (K)	k	$\Delta G^{\neq}$ (k J/mol)	$\Delta H^{\neq}$ (k J/mol)	$-\Delta S^{\neq}$ (J/K/mol)	k	$\Delta G^{\neq}$ (k J/mol)	$\Delta H^{\neq}$ (k J/mol)	$-\Delta S^{\neq}$ (J/K/mol)	k	$\Delta G^{\neq}$ (k J/mol)	$\Delta H^{\neq}$ (k J/mol)	$-\Delta S^{\neq}$ (J/K/mol)
0.5	300	0.192	77.6	44.5	110	534	56.8	39.3	58.2	1325	54.5	34.6	66.5
	305	0.287	77.8			704	57.1			1694	54.8		
	310	0.389	78.5			917	57.3			2136	55.2		
	315	0.491	79.2			1187	57.6			2697	55.5		
1.0	300	0.515	74.1	4.27	233	627	56.4	30.6	85.9	1457	54.3	31.1	77.5
	305	0.545	75.2			803	56.7			1705	54.8		
	310	0.569	76.4			962	57.2			2246	55.0		
	315	0.587	77.6			1190	57.6			2711	55.5		
2.0	300	0.611	73.7	17.7	186	659	56.2	29.0	90.9	1471	54.2	30.8	78.2
	305	0.761	74.4			814	56.7			1708	54.8		
	310	0.874	75.3			999	57.1			2269	55.0		
	315	0.898	76.5			1201	57.6			2716	55.5		
3.0	300	0.970	72.5	6.28	221	698	56.1	26.3	99.4	1521	54.2	29.0	83.9
	305	1.00	73.7			855	56.6			1765	54.7		
	310	1.02	74.9			1012	57.1			2285	55.0		
	315	1.16	75.8			1214	57.6			2722	55.5		
4.0	300	1.29	71.8	24.2	159	727	56.0	32.4	79.0	1555	54.1	27.4	89.1
	305	1.60	72.5			887	56.5			1881	54.6		
	310	1.82	73.4			1106	56.9			2289	55.0		
	315	2.17	74.1			1416	57.2			2744	55.4		
5.0	300	2.64	70.0	7.92	207	766	55.9	31.6	81.1	1660	53.9	31.0	76.5
	305	2.83	71.0			905	56.4			2068	54.3		
	310	3.13	72.0			1122	56.8			2560	54.7		
	315	3.19	73.1			1471	57.1			3144	55.1		

Table II Second-Order Rate Constants (k) and Activation Parameters for Bicyclomonoterpenes in MeCN/PEG-300

		Camphor				Isoborneol				Borneol			
PEG-300 % (V/V)	Temperature (K)	k	$\Delta G^{\neq}$ (k J/mol)	$\Delta H^{\neq}$ (k J/mol)	$-\Delta S^{\neq}$ (J/K/mol)	k	$\Delta G^{\neq}$ (k J/mol)	$\Delta H^{\neq}$ (k J/mol)	$-\Delta S^{\neq}$ (J/K/mol)	k	$\Delta G^{\neq}$ (k J/mol)	$\Delta H^{\neq}$ (k J/mol)	$-\Delta S^{\neq}$ (J/K/mol)
0.5	300	0.329	75.2	2.89	241	613	56.4	35.0	71.5	342	57.9	49.9	26.4
	305	0.335	76.5			782	56.8			483	58.0		
	310	0.347	77.7			1043	57.0			675	58.1		
	315	0.365	78.8			1236	57.5			932	58.3		
1.0	300	0.449	74.4	11.0	211	631	56.3	34.8	71.8	401	57.5	45.1	41.2
	305	0.533	75.3			810	56.7			548	57.7		
	310	0.569	76.4			1071	57.0			743	57.9		
	315	0.587	77.6			1271	57.5			996	58.1		
2.0	300	0.593	73.7	2.54	237	647	56.3	37.1	63.9	426	57.3	42.3	50.0
	305	0.635	74.8			866	56.5			572	57.6		
	310	0.641	76.1			1136	56.8			762	57.8		
	315	0.659	77.3			1373	57.3			1003	58.1		
3.0	300	0.665	73.5	0.608	243	668	56.2	38.8	57.7	431	57.3	48.5	29.5
	305	0.677	74.7			924	56.4			602	57.5		
	310	0.689	75.9			1183	56.7			832	57.6		
	315	0.707	77.1			1480	57.1			1140	57.7		
4.0	300	0.755	73.1	1.40	239	727	56.0	34.7	70.8	465	57.1	45.6	38.4
	305	0.778	74.3			999	56.2			616	57.4		
	310	0.796	75.5			1192	56.7			844	57.6		
	315	0.814	76.7			1512	57.0			1163	57.7		
5.0	300	0.826	72.9	20.5	174	746	55.9	34.5	71.2	472	57.1	45.7	37.9
	305	1.06	73.5			1008	56.1			648	57.3		
	310	1.17	74.5			1215	56.6			879	57.5		
	315	1.31	75.5			1539	57.0			1185	57.6		

Table III Second-Order Rate Constants (*k*) and Activation Parameters for Bicyclomonoterpenes in MeCN/PEG-400

		Camphor				Isoborneol				Borneol			
PEG-400 % (V/V)	Temperature (K)	k	$\Delta G^{\neq}$ (k J/mol)	$\Delta H^{\neq}$ (k J/mol)	$-\Delta S^{\neq}$ (J/K/mol)	k	$\Delta G^{\neq}$ (k J/mol)	$\Delta H^{\neq}$ (k J/mol)	$-\Delta S^{\neq}$ (J/K/mol)	k	$\Delta G^{\neq}$ (k J/mol)	$\Delta H^{\neq}$ (k J/mol)	$-\Delta S^{\neq}$ (J/K/mol)
0.5	300	0.234	76.1	10.1	220	1174	54.8	33.0	72.8	684	56.1	47.4	29.1
	305	0.270	77.0			1477	55.2			949	56.3		
	310	0.287	78.1			1833	55.6			1304	56.4		
	315	0.299	79.3			2321	55.9			1773	56.6		
1.0	300	0.305	75.4	3.77	239	1218	54.7	33.8	69.9	725	56.0	47.1	29.7
	305	0.329	76.5			1487	55.2			1004	56.2		
	310	0.335	77.7			1904	55.5			1377	56.3		
	315	0.347	79.0			2421	55.8			1868	56.5		
2.0	300	0.383	74.8	−1.55	250	1357	54.4	28.1	87.9	746	55.9	51.8	13.9
	305	0.389	76.1			1587	55.0			1064	56.0		
	310	0.395	77.3			1915	55.5			1505	56.1		
	315	0.401	78.6			2436	55.8			2101	56.1		
3.0	300	0.437	74.5	5.00	232	1375	54.4	29.0	84.8	764	55.9	53.6	7.70
	305	0.473	75.6			1662	54.9			1103	55.9		
	310	0.485	76.8			2029	55.3			1576	56.0		
	315	0.509	77.9			2510	55.7			2230	56.0		
4.0	300	0.623	73.6	14.7	197	1452	54.3	25.5	95.7	816	55.7	50.7	16.5
	305	0.641	74.8			1801	54.7			1163	55.8		
	310	0.737	75.7			2275	55.0			1651	55.8		
	315	0.856	76.6			3160	55.8			2250	56.0		
5.0	300	0.898	72.7	27.8	149	1462	54.3	25.3	96.2	887	55.5	52.2	11.1
	305	1.13	73.4			1822	54.6			1270	55.6		
	310	1.43	74.0			2319	55.0			1799	55.6		
	315	1.59	75.0			6813	55.8			2520	55.7		

Table IV Second-Order Rate Constants (k) and Activation Parameters for Bicyclomonoterpenes in MeCN/PEG-600

		Camphor				Isoborneol				Borneol			
PEG-600 % (V/V)	Temperature (K)	k	$\Delta G^{\neq}$ (k J/mol)	$\Delta H^{\neq}$ (k J/mol)	$-\Delta S^{\neq}$ (J/K/mol)	k	$\Delta G^{\neq}$ (k J/mol)	$\Delta H^{\neq}$ (k J/mol)	$-\Delta S^{\neq}$ (J/K/mol)	k	$\Delta G^{\neq}$ (k J/mol)	$\Delta H^{\neq}$ (k J/mol)	$-\Delta S^{\neq}$ (J/K/mol)
0.5	300	0.210	76.3	11.4	216	698	56.1	42.0	46.9	572	56.6	36.2	68.0
	305	0.240	77.3			944	56.3			738	56.9		
	310	0.258	78.4			1291	56.5			959	57.3		
	315	0.275	79.6			1619	56.8			1199	57.6		
1.0	300	0.305	75.4	3.30	240	771	55.9	40.1	52.5	677	56.2	35.5	68.9
	305	0.311	76.6			1019	56.1			864	56.5		
	310	0.323	77.8			1337	56.4			1108	56.9		
	315	0.341	79.0			1740	56.6			1398	57.2		
2.0	300	0.353	75.0	5.60	232	778	55.8	42.4	44.9	718	56.0	34.5	71.7
	305	0.365	76.2			1044	56.1			905	56.4		
	310	0.383	77.4			1389	56.3			1161	56.7		
	315	0.413	78.5			1833	56.5			1452	57.1		
3.0	300	0.425	74.6	20.8	180	809	55.7	44.3	38.2	727	56.0	38.1	59.7
	305	0.455	75.7			1100	55.9			917	56.4		
	310	0.509	76.7			1482	56.1			1229	56.6		
	315	0.671	77.2			1977	56.3			1560	56.9		
4.0	300	0.689	73.4	0.608	222	839	55.6	43.8	39.4	750	55.9	39.0	56.5
	305	0.737	74.5			1140	55.8			985	56.2		
	310	0.755	75.7			1528	56.0			1281	56.5		
	315	0.832	76.7			2033	56.2			1655	56.8		
5.0	300	0.844	72.9	11.5	205	848	55.6	43.7	39.6	796	55.8	47.8	26.5
	305	0.874	74.0			1149	55.8			1107	55.9		
	310	0.910	75.2			1544	56.0			1525	56.0		
	315	1.120	75.9			2052	56.2			2081	56.2		

could be entirely different in the MeCN medium. Since MeCN is very large excess over [CAN], MeCN may penetrate into the coordination spheres of Ce(IV) and form *solvated CAN species* with replacement of water molecules according to the following equilibrium:

$$\underset{\text{(CAN)}}{\mathrm{Ce(NO_3)_4\,(H_2O_2)}} + 2(\mathrm{CH_3CN})_2$$

$$\rightleftharpoons \underset{\text{[Solvated CAN]}}{\left[\mathrm{Ce(NO_3)_4\,(CH_3CN_2)}\right]} + 2\mathrm{H_2O}$$

When bicyclic terpene is added to the reaction mixture, kinetics could not be followed smoothly by (solvated CAN), and an irregular trend was obtained. However, in polyethylene glycol–acetonitrile media, the kinetic studies were smooth, and the reaction is enhanced remarkably in all PEGs A set of polyoxy ethylene glycols (PEGs) with varied molecular weights ranging from 200 to 600. Reaction times were reduced from 24 h to few hours. The catalytic activity was found to increase in the order: PEG-300 > PEG-400 ≥ PEG-600 > PEG-200. Furthermore, it is also interesting to note that the absorbance (A) of solvated Ce(IV) species is increased when PEG is added to the CAN solution. This observation may indicate that solvated –CAN species could bind with PEG to form PEG-supported CAN species according to the following equilibrium:

$$\underset{\text{(PEG)}}{\mathrm{H-(OCH_2-CH_2)_n-OH}} + \underset{\text{(CAN)}}{\left[\mathrm{Ce(NO_3)_4(CH_3CN)_2}\right]}$$

$$\rightleftharpoons \underset{\text{[PEG}-\text{CAN]}}{\mathrm{H-(OCH_2-CH_2)_n-O\,(H)-Ce(NO_3)_4(CH_3CN)_2]}}$$

Spectrophotometric Determination of Binding Constants (K) by the Benesi–Hildebrand Method

The PEG–CAN interaction studies are established, and binding constants are evaluated using the Benesi-Hildebrand method [28–30]. The equilibrium for the molecular complexation is generally written as in the following equation when donor (D) is assumed to interact with an acceptor (A):

$$\mathrm{D + A} \overset{K}{\rightleftharpoons} \mathrm{(D-A)}\ \text{adduct}$$

The equilibrium constant K = [C]/[A] [D], where [A], [D], and [C] are the equilibrium concentrations of acceptor, donor, and complex, respectively. If the initial concentrations of A and D are $[\mathrm{A}]_0$ and $[\mathrm{D}]_0$, then $K = [\mathrm{C}]/([\mathrm{A}]_0 - [\mathrm{C}])\,([\mathrm{D}]_0 - [\mathrm{C}])$. Under the condition that $[\mathrm{D}]_0 \gg [\mathrm{A}]_0$, the Benesi-Hildebrand equation becomes

$$([\mathrm{A}]_0/d) = (1/K[\mathrm{D}]_0\epsilon) + (1/\epsilon)$$

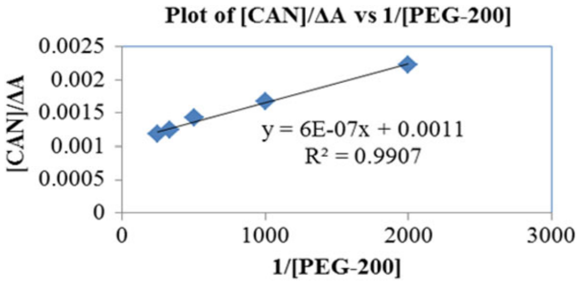


Figure 10 Benesi–Hildebrand plot for PEG-200. [Color figure can be viewed at wileyonlinelibrary.com]

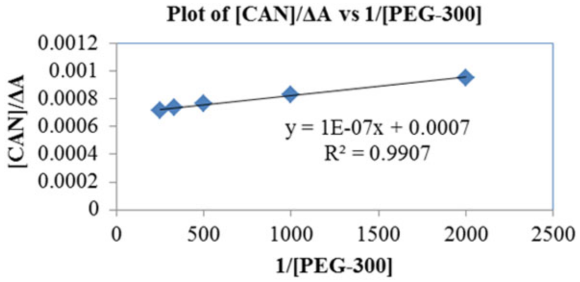


Figure 11 Benesi–Hildebrand plot for PEG-300. [Color figure can be viewed at wileyonlinelibrary.com]

For the PEG-bound CAN equilibrium, A = CAN, therefore, $[\mathrm{A}]_0 = [\mathrm{CAN}]_0$ and $[\mathrm{D}]_0$ = PEG and in this case the above equation reduces to

$$([\mathrm{CAN}]_0/d) = (1/K[\mathrm{PEG}]_0\epsilon) + (1/\epsilon)$$

However, the absorbance of CAN and PEG-bound CAN adduct ([PEG-CAN]) absorb in the same region significantly; therefore, the observed absorbance (d) could be written as

$$\mathrm{d = d_{CAN} + d_{[PEG-CAN]} \Rightarrow d_{[PEG-CAN]}}$$

$$\mathrm{= (d_{\sim}d_{CAN}) = \Delta A}$$

Thus, a plot of $([\mathrm{CAN}]_0/\Delta A)$ versus (1/[PEG]) afforded a straight line according to the above equation. Representative Benesi-Hildebrand plots are given in Figs. 10–13. PEG-CAN binding constants (K) and corresponding thermodynamic parameters are given Table V. Free energy of complexation (binding constant) are obtained from van't Hoff's isotherm, whereas enthalpy and entropy of complexation were calculated from Gibbs–Helmholtz plots as shown in Figs. 14 and 15.

Observed kinetic features together with the positive test for the formation free radical intermediates

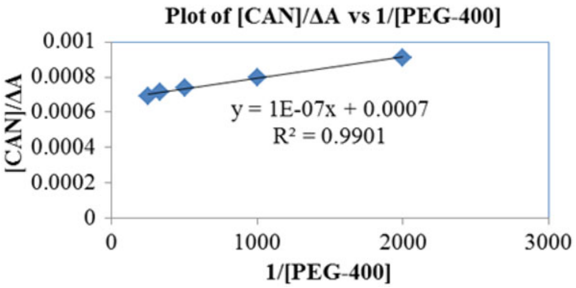


Figure 12 Benesi–Hildebrand plot for PEG-400. [Color figure can be viewed at wileyonlinelibrary.com]

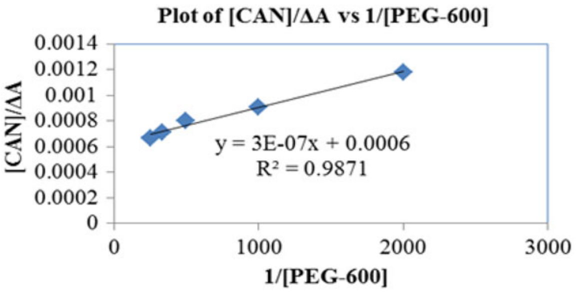


Figure 13 Benesi–Hildebrand plot for PEG-600. [Color figure can be viewed at wileyonlinelibrary.com]

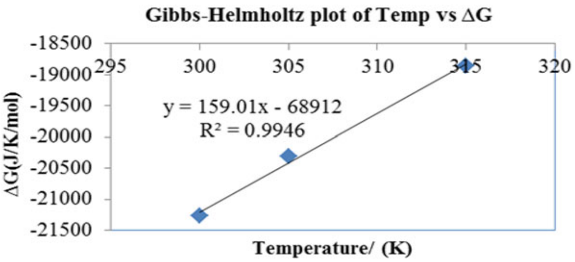


Figure 14 Gibbs–Helmholtz plot for CAN-PEG-300 interactions. [Color figure can be viewed at wileyonlinelibrary.com]

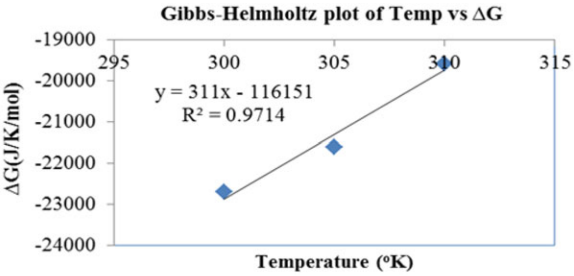
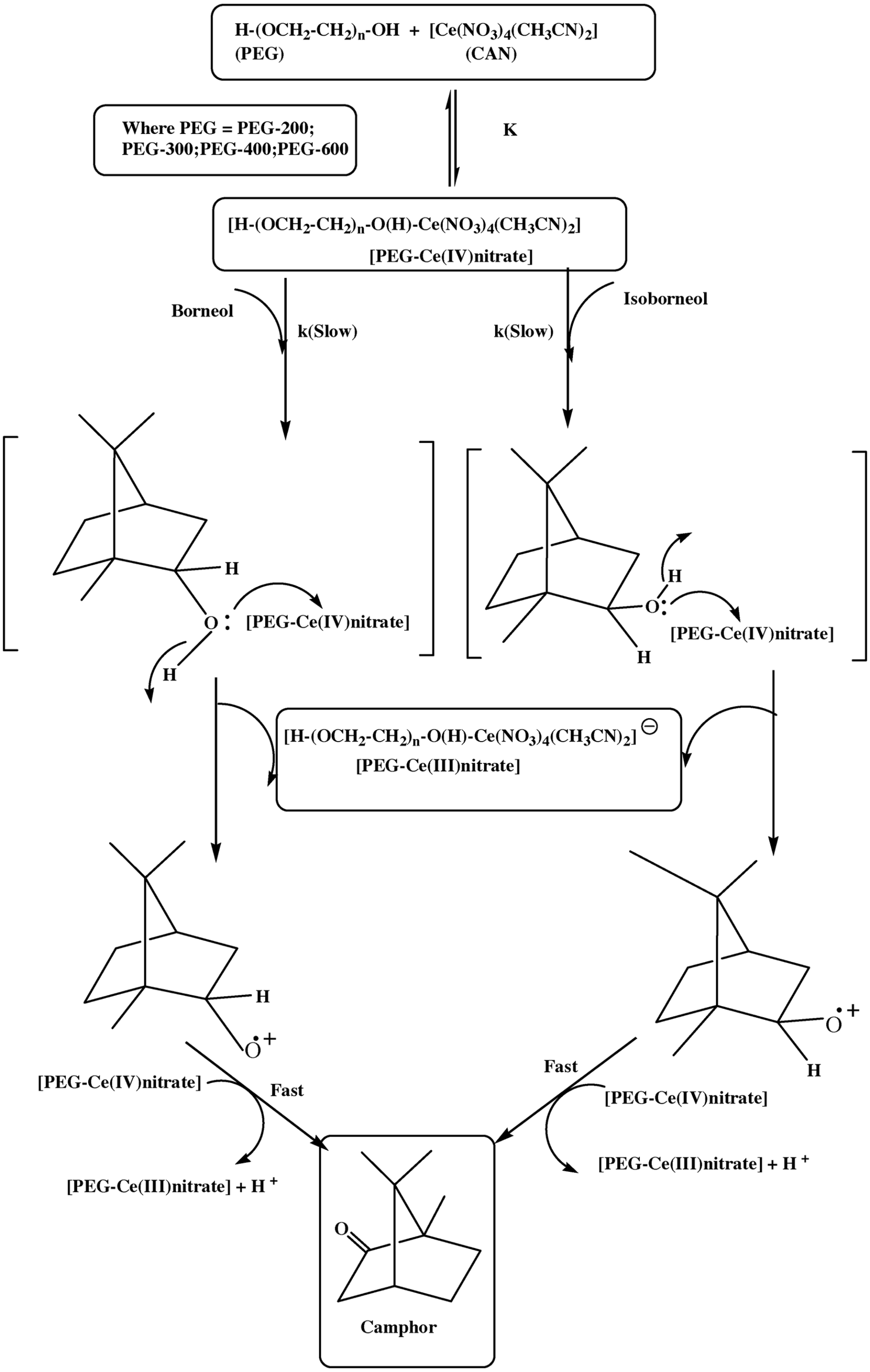


Figure 15 Gibbs–Helmholtz plot for CAN-PEG-600 interactions. [Color figure can be viewed at wileyonlinelibrary.com]

substantiate the most plausible mechanism as shown in Scheme 1. The mechanism of the reaction shows the interaction of PEG-bound Ce(IV) forming a transient complex [PEG-Ce(IV)nitrtate], i.e., [H-(OCH$_2$-CH$_2$)$_n$-O(H)-Ce(NO$_3$)$_4$(CH$_3$CN)$_2$], which decomposes to give substrate radical-ion (borneol radical-ion or isoborneol radical-ion) followed by the reduction of Ce(IV) species to Ce(III) species ([PEG-Ce(III)nitrtate], i.e., [H-(OCH$_2$-CH$_2$)$_n$-O-Ce(NO$_3$)$_4$(CH$_3$CN)$_2$]–, through SET. Substrate radical-ion upon thus formed is then oxidized by another Ce(IV) species ([PEG-Ce(IV)nitrtate]) to afford camphor. On the other hand, the kinetic features together with the detection of free radical intermediates (as evidenced through the conversion of acrylamide monomer to polyacrylamide (polymer), the most plausible mechanism for the oxidation of camphor could be given as in Scheme 2.

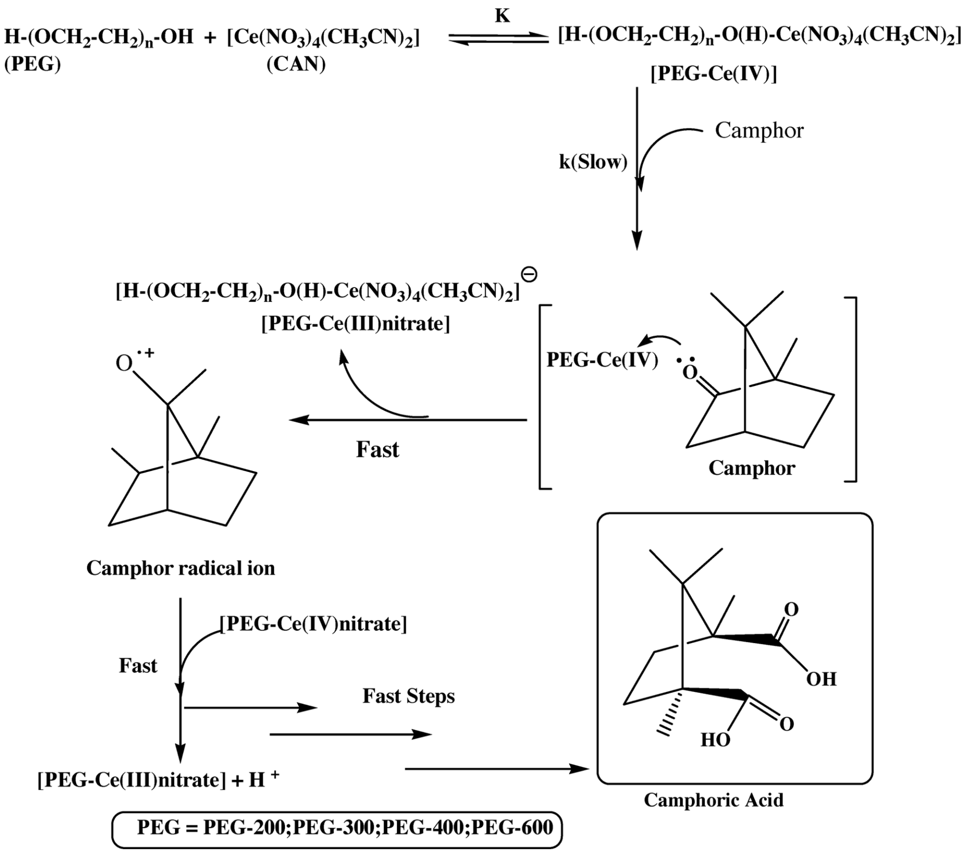
Table V PEG–CAN Binding Constants (K) and Corresponding Thermodynamic Parameters

PEG	Temperature (K)	K (dm^3 /mol)	$\Delta\varepsilon$ (dm^3/mol.cm)	$-\Delta G$ (k J/mol)	ΔH (k J/mol)	ΔS (J/K/mol)	R^2
PEG-200	300	3500	1428	20.4	48.5	94.2	0.954
	305	2250	1111	19.6			
	310	1833	909	19.3			
	315	1333	833	18.9			
PEG-300	300	7000	1428	21.3	68.5	159	0.995
	305	3000	1111	20.3			
	315	1333	833	18.9			
PEG-400	300	7000	1428	21.3	116	311	0.972
	305	5500	909	20.3			
	310	4000	833	18.9			
PEG-600	300	9000	1111	22.7	43.3	70.7	0.967
	305	5000	1000	21.6			
	310	2000	1250	19.6			

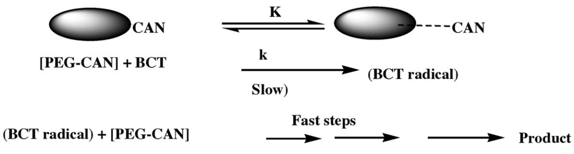


Scheme 1 PEG-mediated CAN oxidation of borneol and isoborneol.

The mechanism of the reaction as shown in Scheme 2 is largely similar to Scheme 1, wherein camphor upon oxidation gives camphoric acid through the formation of the camphor radical. The general mechanism and rate law for the above schemes are shown in the following sequential steps:



Scheme 2 PEG-mediated CAN oxidation of camphor.



For the above mechanisms, the rate can be written as

$$(-\mathrm{d}\,[\mathrm{CAN}]/\mathrm{d}t) = k\,[\mathrm{PEG}-\mathrm{CAN}]\,[\mathrm{BCT}] \qquad (1)$$

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

$$C_{\mathrm{CAN}} = [\mathrm{CAN}] + [\mathrm{PEG}-\mathrm{CAN}] \qquad (2)$$

From PEG-CAN binding equilibrium,

$$K = [\mathrm{PEG}-\mathrm{CAN}]\,/\,[\mathrm{PEG}]\,[\mathrm{CAN}]$$
$$\text{or } [\mathrm{CAN}] = [\mathrm{PEG}-\mathrm{CAN}]\,/K\,[\mathrm{PEG}]$$

Substitution of [CAN] in Eq. (2) gives

$$\begin{aligned} C_{\mathrm{CAN}} &= \frac{[\mathrm{PEG}-\mathrm{CAN}]}{K\,[\mathrm{PEG}]} + [\mathrm{PEG}-\mathrm{CAN}] \\ &= \frac{[\mathrm{PEG}-\mathrm{CAN}] + K\,[\mathrm{PEG}]\,[\mathrm{PEG}-\mathrm{CAN}]}{K\,[\mathrm{PEG}]} \\ \Rightarrow [\mathrm{PEG}-\mathrm{CAN}] &= \frac{K\,[\mathrm{PEG}]\,C_{\mathrm{CAN}}}{1+K\,[\mathrm{PEG}]} \end{aligned}$$

Substituting for [PEG-CAN] in Eq. (1)

$$\frac{-\mathrm{d}\,[\mathrm{CAN}]}{\mathrm{d}t} = \frac{kK\,[\mathrm{PEG}]\,[\mathrm{BCT}]\,[\mathrm{CAN}]}{1+K\,[\mathrm{PEG}]} \qquad (3)$$

This rate-law explains first-order dependence on [CAN], [BCT], and complex order in [PEG]. At constant [PEG], the rate law becomes

$$-\mathrm{d}\,[\mathrm{CAN}]\,/\mathrm{d}t = k''\,[\mathrm{CAN}]\,[\mathrm{BCT}]$$

Binding constants for [PEG-CAN] have been calculated spectrophotometrically as detailed in earlier sections. Thermodynamic data presented in Table I show that (PEG-CAN) formation constants (K) are far greater than unity (very higher magnitudes). The corresponding free energy values (ΔG) are negative, indicating spontaneous nature of the equilibrium (PEG-CAN) adducts. A further insight into the activation parameters presented in Tables I–IV shows that entropy of activation ($\Delta S^{\#}$) is negative. Negative entropy of activation ($\Delta S^{\#}$) reorganization of the transition state and shows the associative mechanism, whereas positive values for $\Delta S^{\#}$ often indicate a dissociative mechanism and suggest that entropy increases upon achieving the transition state. Observed negative $\Delta S^{\#}$ values in this study indicate that entropy decreases upon achieving the transition state, depicting on the associative mechanism [27–29]. These results probably support the release of proton from PEG and nitrate from CAN moieties, which readily bring about changes in the transition state and cause simultaneous association and dissociation of species causing a greater disorderness in the transition state leading to a chemical reaction. A similar type of trends is recorded in all the PEGs used in this study.

CONCLUSIONS

In summary, the authors studied oxidation of bicyclic monoterpenes such as BORN, IBORN, and CAMP in aqueous acetonitrile medium using a common laboratory desktop reagent CAN in catalytic amounts under mineral acid-free conditions. The reaction underwent smoothly in the presence of PEG, and followed first order in both [CAN] and [Bicyclic terpene]. The rate of oxidation is accelerated with an increase in [PEG] linearly. The mechanism of oxidation in PEG media has been explained through the participation of PEG-bound oxidant (PEG-CAN) and terpene, and PEG-bound oxidant (PEG-CAN) as more reactive species than (CAN) itself.

The authors thank the Principal, Nizam College (Osmania University) Hyderabad, and the Head, Department of Chemistry (Osmania University) for encouragement and facilities.

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