# Recoverable aqueous-ionic liquid biphasic catalyst system for the oxidation of *n*-octane

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### ABSTRACT

This study seeks to address the need for the development of highly active paraffin activation catalysts that are reusable and based on cheap earth abundant metals. Hence, a series of related halide-free 1,3,4-trisubstituted-1,2,3-triazolium ionic liquids (IL)(**3a–3f**) bearing a variety of substituents were synthesized and fully characterized by spectroscopic and analytical techniques. Crystal structure of the halide derivative, compound **2f** is also reported. With the IL as solvents for the dissolution of $FeCl_2$, $FeCl_3$, $CoCl_2$, and $NiCl_2$, a series of catalyst systems were developed and used to activate the catalytic oxidation of *n*-octane in the presence of $H_2O_2$ as the oxidant in a biphasic $IL/H_2O$ system. All systems tested were found to be active under optimum conditions yielding oxygenated products (mainly octanones). The role of the substituents around the triazole ring was to influence catalytic efficiency in terms of conversion of the substrate *n*-octane and selectivity to oxygenated products (octanols, octanal, octanones, and octanoic acid). In a test for recyclability, recovered IL dissolved catalysts were found to be effective up to three cycles without any significant loss of catalytic activity before leaching to the aqueous phase resulted in loss of activity.

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## 1. Introduction

Selective activation of chemically inert alkane C—H bonds is a challenging field of research to academia which enjoys unwavering interest from global chemical industry due to the potential for huge economic benefits [1]. Currently, the enormous volumes of paraffins emanating from both petroleum refining and natural gas exploration are mainly used as fuel for energy generation. Only a very limited amount is exploited as feedstock for high temperature bulk chemical production that often proceed via multi-step reactions that are inefficient, environmentally damaging, and to a large extent, economically unviable [2,3]. The oxidation of relatively abundant alkanes into value-added products (alcohols, carboxylic acids, and alkenes) under controlled catalytic conditions can offer large economic benefits as feedstock, additives, and solvents for the pharmaceutical and fine chemical manufacturing industries [4]. Metal-mediated C—H activation is of considerable interest to chemical research globally; however, the well-known chemical catalysts for this process suffer from various disadvantages including difficulty of recovery, high cost, poor stability at moderate temperatures, and high reactivity that often leads to a wide range of side-products [5]. Circumventing some of these challenges by the development of cheap, abundant, relatively stable, and recyclable oxidation catalyst systems that combine the advantages of both homogeneous (catalyst modulation) and heterogeneous (catalyst recycling) catalysis has remained a subject of intense research interest [6].

Toward the attainment of these goals, the applications of ionic liquids (IL) in catalysis has received a lot of attention due to their exceptional properties especially for the stabilization of the catalyst in the IL medium that allows for recycling of tandem catalyst/solvent systems [7]. Moreover, IL have also been reported to have non-benign effects in some catalytic reactions that include the generation of the active metal species and their stabilization (much like the role of ligands in metal complexes) [8,9]. The potential of IL in oxidation reactions is huge and growing interest has led to a surge in the number of publications describing their application in this sphere [10–13]. However, it is interesting to note that the vast majority of work in this field has focused mainly on IL developed from alkylimidazoles [14–17]. The successful industrial applications [18,19] of imidazolium IL systems have stimulated more interest in exploring other azolium species as potential sources of even more stable IL solvents. Hence, since the first report on stable and easily tuneable 1,2,3-triazolium salts, their application as supporting ligand precursors has received a lot of attention. Surprisingly, these have been neglected as potential IL sources with only a handful of applications utilizing the ionic liquid property of 1,3,4-trialkyl-1,2,3-triazolium salts reported to date [20]. Hence, in this report, we present the first use of simple metal salts in triazolium IL systems ($M^{2+}$–IL) as recyclable catalysts for the oxidation of alkanes using $H_2O_2$ as oxidant to yield oxygenated products in a biphasic system with water.

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## 2. Experimental section

### 2.1. General

Solvents were dried according to established methods [21] and purged with high purity nitrogen gas prior to use. All reagents were purchased from commercial suppliers and were used without further purification. All glassware were oven dried at 110 °C. $^1$H and $^{13}$C NMR experiments were conducted in deuterated solvents on a 400 MHz Bruker ultrashield spectrometer with chemical shifts ($\delta$, ppm) reported with respect to tetramethylsilane (TMS) as the internal standard. Infrared spectra (FTIR) were recorded on a Perkin Elmer FT-IR 1600 spectrophotometer with vibrational frequencies expressed in cm$^{-1}$. The 1,4-triazoles 1(a–f) [22,23] and the corresponding triazolium salts 2(a–f) [24] were synthesised according to published procedure (Scheme 1).

### 2.2. Synthesis of triazolium ionic liquids 3

A generic procedure is described: To a solution of 2 (1 equiv. mmol) in dry DCM (20 mL) was added a solution of AgNO$_3$ (1 equiv. mmol) in DCM (10 mL). The resulting mixture was then allowed to stir at room temperature overnight. The precipitated AgX (X = I or Br) was filtered through Celite and the solvent was evaporated and the residue was washed with diethyl ether and allowed to dry under vacuum.

### 2.3. 3-methyl-1,4-diphenyl-1 H-1,2,3-triazol-3-ium nitrate (3a)

The starting materials 2a (5.21 g, 14.3 mmol) and AgNO$_3$ (3.98 g, 1 equiv.) were used. Light yellow oily product (3.98 g, 33%). $^1$H NMR (CDCl$_3$ 400 MHz): $\delta$ 9.65 (s, 1 H, triazole —C=CH), 7.52–8.17 (m, 10 H, Ar), 4.44 (s, N—CH$_3$). $^{13}$C NMR (CDCl$_3$ 400 MHz): $\delta$ 144.2, 134.6, 132.0, 132.0, 132.0, 129.6, 127.3, 122.0, 121.3, 39.8. IR $\nu_{max}$ (cm$^{-1}$):3433 (s) 2927 (m), 2660 (m), 1695 (s), 1622 (m), 1530 (s), 1450 (m), 1384 (m), 1073 (m), 780 (s), 698 (m). HRMS (ESI) m/z for C$_{15}$H$_{14}$N$_3$ [M—NO$_3$]$^+$: calculated: 236.1188, found: 236.1183.

### 2.4. 3-benzyl-1,4-diphenyl-1 H-1,2,3-triazol-3-ium nitrate (3b)

The starting materials 2b (4.18 g, 10.7 mmol) and AgNO$_3$ (1.81 g, 1 equiv.) were used. Light brown oily product (3.52 g, 88%). $^1$H NMR (CDCl$_3$ 400 MHz): $\delta$ 10.38 (s, 1 H, triazole —C=CH), 7.13–7.92 (m, 15 H, Ar), 5.95 (s, N—CH$_2$—). $^{13}$C NMR (CDCl$_3$ 400 MHz): $\delta$ 144.2, 134.6, 132.1, 132.0, 130.4, 130.0, 129.6, 127.3, 127.3, 122.0, 121.3, 39.8. IR $\nu_{max}$ (cm$^{-1}$): 3412 (m), 3001 (m), 2928 (m), 1753 (s), 1604 (m), 1555 (m), 1465 (m), 1172 (m), 777 (s), 722 (m), 694 (s), 501 (m).

HRMS (ESI) m/z for C$_{15}$H$_{14}$N$_3$ [M—NO$_3$]$^+$: calculated: 312.1501, found: 312.1501.

### 2.5. 1-benzyl-3-methyl-4-phenyl-1 H-1,2,3-triazol-3-ium nitrate (3c)

The starting materials 2c (3.89 g, 10.3 mmol) and AgNO$_3$ (1.74 g, 1 equiv.) were used. Light brown oily product (2.76 g, 86%). $^1$H NMR (CDCl$_3$ 400 MHz): $\delta$ 8.99 (s, 1 H, triazole —C=CH), 7.35–7.58 (m, 10 H, Ar), 5.80 (s, 2 H, Ar—CH$_2$—), 4.22 (s, 3 H, N—CH$_3$); $^{13}$C NMR (CDCl$_3$ 400 MHz): $\delta$ 143.3, 131.7, 131.6, 129.7, 129.6, 129.6, 129.3, 128.8, 121.9, 57.4, 38.6. IR $\nu_{max}$ (cm$^{-1}$): 3442 (s), 3334 (b), 3214 (s), 1627 (m), 1614(m), 1501(s), 1435 (s), 1358 (s), 805(s), 758(s), 724 (m), 523(m), 484(m). HRMS (ESI) m/z for C$_{16}$H$_{13}$N$_3$[M—NO$_3$]$^+$: calculated: 250.1344, found: 250.1340.

### 2.6. 1-(2-ethoxy-2-oxoethyl)-3-methyl-4-phenyl-1 H-1,2,3-triazol-3-ium nitrate (3d)

The starting materials 2d (3.12 g, 13.5 mmol) and AgNO$_3$ (2.30 g, 1 equiv.) were used. Clear oily product (4.201 g, 83%). $^1$H NMR (CDCl$_3$ 400 MHz): $\delta$ 9.18 (s, 1 H, triazole —C=CH), 7.53–7.62 (m, 5 H, Ar), 5.69 (s, 2 H, Ar—CH$_2$—), 4.37 (s, 3 H, N—CH$_3$), 4.30 (m, 5 H, N—CH$_3$, —CH$_2$—), 1.30–1.33 (d, 3 H, —CH$_3$); $^{13}$C NMR (CDCl$_3$ 400 MHz): $\delta$ 165.0, 143.3, 131.9, 130.0, 129.7, 129.6, 121.8, 63.2, 53.8, 38.7, 13.9. IR $\nu_{max}$ (cm$^{-1}$): 3134 (m) 2993 (m), 2948 (m), 1752 (s), 1711(m), 1466 (m), 1346 (m), 1197 (m), 763 (s), 692 (s), 511 (m). HRMS (ESI) m/z for C$_{12}$H$_{13}$N$_3$O$_2$[M—NO$_3$]$^+$: calculated: 246.1243, found: 246.1240.

### 2.7. 1-hexyl-3-methyl-4-phenyl-1 H-1,2,3-triazol-3-ium nitrate (3e)

The starting materials used: 2e (3.19 g, 8.60 mmol) and AgNO$_3$ (1.46 g, 1 equiv.). Yellow oily product (2.32 g, 88%). $^1$H NMR (MeOD 400 MHz): $\delta$ 9.02(s, 1 H, triazole —C=CH), 7.82 (d, 2 H, Ar), 7.68 (m, 3 H, Ar), 4.76 (m, 2 H, —CH$_2$—), 4.34 (s, 3 H, N—CH$_3$), 2.15–2.11 (m,2 H, —CH$_2$—), 1.51–1.40 (m, 6 H, —CH$_2$—), 0.95 (d, 3 H, —CH$_3$); $^{13}$C NMR (MeOD, 400 MHz): 144.6, 132.9, 130.9, 130.7, 130.1, 124.0, 55.4, 39.9, 32.3, 30.3, 27.0, 23.5, 14.5.IR $\nu_{max}$ (cm$^{-1}$): 3150 (m), 3086 (m), 2956 (m), 2874 (m), 1745 (s), 1608 (s), 1512 (s), 1339 (s), 1258 (m), 751 (s), 690 (s), 499 (m). HRMS (ESI) m/z for C$_{15}$H$_{22}$N$_3$[M—NO$_3$]$^+$: calculated: 244.1814, found: 244.1806.

### 2.8. 3-benzyl-1-hexyl-4-phenyl-1H-1,2,3-triazol-3-ium nitrate (3f)

The starting materials 2f (5.381 g, 13.4 mmol) and AgNO$_3$ (2.271 g, 13.4 mmol) were used. Brown oily product (5.104 g, 82%). $^1$H NMR (CDCl$_3$ 400 MHz): $\delta$ 9.02 (s, 1 H, triazole C=CH), 7.61–6.65 (m, 5 H,
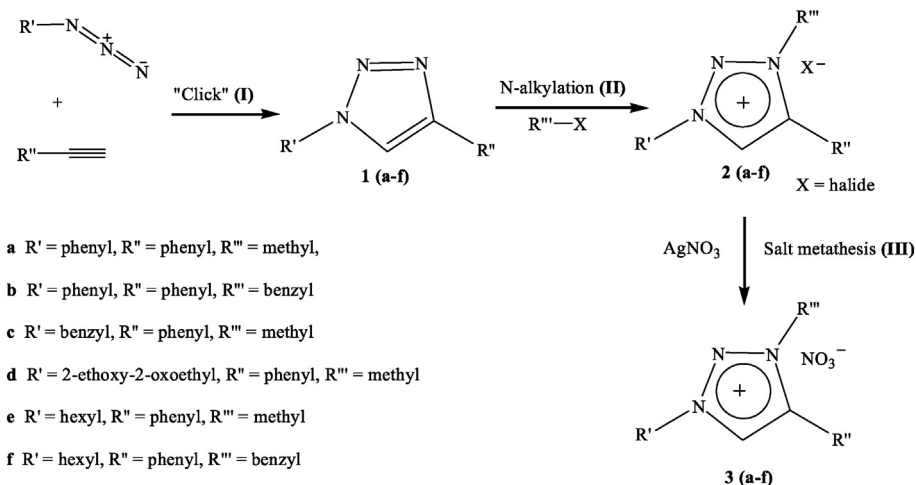


**Scheme 1.** Schematic route to the synthesis of 1,2,3-triazolium ionic liquids (3a–f).

a  R' = phenyl, R" = phenyl, R'" = methyl,

b  R' = phenyl, R" = phenyl, R'" = benzyl

c  R' = benzyl, R" = phenyl, R'" = methyl

d  R' = 2-ethoxy-2-oxoethyl, R" = phenyl, R'" = methyl

e  R' = hexyl, R" = phenyl, R'" = methyl

f  R' = hexyl, R" = phenyl, R'" = benzyl