

# Oxidative Bromination of Alkenes Mediated with Nitrite in Ionic Liquids

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**Abstract** The oxidative bromination of C<sub>2</sub>–C<sub>8</sub> alkenes with HBr–NaNO<sub>2</sub>–O<sub>2</sub> in solutions of BMImBr, HMImBr or BMImBF<sub>4</sub> containing 16–28 wt% H<sub>2</sub>O was studied using volumetric method, GC–MS analysis, <sup>14</sup>N NMR and UV–VIS spectroscopy. The optimal conditions to conduct the reaction at high selectivity for 1,2-dibromoalkanes in BMImBr were determined. The composition of ionic liquid affects the catalytic performance. Although in BMImBF<sub>4</sub> the reaction runs with equal rate as in bromide ionic liquid, the fraction of bromohydrin in the reaction products increases to 20 %. Generated from NaNO<sub>2</sub>, NO<sub>x</sub> operated as a catalyst in the oxidation of Br<sup>−</sup> and was oxidized to catalytically inert NO<sub>3</sub><sup>−</sup> anions when complete conversion of HBr was attained.

**Keywords** Bromination · Alkene · Ionic liquids · Hydrobromic acid · Sodium nitrite · Oxygen · Dibromoalkanes

## 1 Introduction

Bromination of alkenes and aromatic compounds is an effective method for functionalization of hydrocarbons under mild conditions. Apart from reactions with Br<sub>2</sub>, the oxidative bromination with hydrobromic acid or bromides in combination with an oxidant is used for this purpose. As a more advanced method, the oxidative bromination

excludes contact with hazardous Br<sub>2</sub> and provides bromine recycling in cases where bromination products undergo further processing with a release of bromide anions. Being intensively developed a quarter of a century ago [1–4], the study of the oxidative bromination is currently concentrated on the choice of oxidant and conditions for an efficient generation of electrophilic agent from hydrobromic acid or bromide.

Unlike the peculiar oxidants such as NaBO<sub>3</sub> [5] and NaIO<sub>4</sub> [6], the ordinary ones, H<sub>2</sub>O<sub>2</sub> and O<sub>2</sub>, require catalysts to react with bromide ions [7]. Typical vanadium and molybdenum activators of peroxide are often used as the catalysts in bromination with H<sub>2</sub>O<sub>2</sub> [8–10], whereas the bromination with molecular oxygen is carried out in the presence of RuCl<sub>3</sub> [11], Pd–Cu [12], H<sub>3+n</sub>PMo<sub>12–n</sub>V<sub>n</sub>O<sub>40</sub> [2], and NH<sub>4</sub>VO<sub>3</sub> [13–15] catalysts. According to a common tendency, much attention in the oxidative bromination is paid to non-metallic catalysts, in particular, to nitrogen oxy compounds. Nitric acid is known to be applicable as a stoichiometric oxidant for the oxidative bromination in strongly acidic media [16, 17] or as a catalyst for oxidative bromination or chlorination of aromatic compounds in the presence of O<sub>2</sub> and Brønsted acid [4, 18, 19]. Nitrites of alkali metals were used in catalytic amounts for bromination of aromatic compounds and aryl ketones [20] as well as substituted alkenes [21] in weakly acidic media. In the acidic solutions, the nitrite anions are known to produce nitrogen oxides, which involve oxygen in the catalytic cycle as a terminal oxidant of bromide anions [20, 21].

Bromination with Br<sub>2</sub> is performed in organic solvents which have recently included ionic liquids (paper [22] and references therein). Ionic liquids are considered as the solvents with good stability to aggressive reaction mixtures, and their non-volatility facilitates easy separation of the brominated products from the solvent. Being good

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solvents not only for hydrocarbon substrates but also for inorganic reagents and catalysts, ionic liquids have already been used in the oxidative bromination, where they exhibited interesting properties. It was reported, for example, that ionic liquids affected the products composition in bromination of styrene [23]. Ionic liquids were able to mobilize the catalyst in the oxidative bromination and chlorination [18, 19, 24].

We investigated the use of imidazolium ionic liquids BMImBr, HMImBr and BMImBF<sub>4</sub> for the oxidative bromination of alkenes with HBr, sodium nitrite catalyst, and oxygen as a terminal oxidant. The catalytic systems of similar composition were tested earlier in halogenation of aromatics and activated alkenes [20, 21]. We compared properties of gaseous and liquid C<sub>2</sub>–C<sub>8</sub> alkenes and properties of the three ionic liquids in the HBr–NaNO<sub>2</sub>–O<sub>2</sub> brominating system. Particular attention was paid to transformations of the catalyst during the bromination runs.

## 2 Experimental

### 2.1 Reagents

1-Buthyl-3-methylimidazolium bromide (BMImBr, Merck), 1-buthyl-3-methylimidazolium tetrafluoroborate (BMImBF<sub>4</sub>, Aldrich), 1-octene (Reachim, distilled just before use), 2-methylpropene and 2,3-dimethyl-2-butene (Aldrich), ethylene (99.99 %), propene (99.8 %), 1-butene (99.6 %), NaNO<sub>2</sub>, 48 % HBr (Reachim) and HClO<sub>4</sub> (Reachim) were used. 1-Methylimidazolium bromide (HMImBr) was obtained by the reaction of 1-methylimidazole (Acros) with HBr [25].

### 2.2 Catalytic Testing and Analysis

The oxidative bromination of olefins was carried out in a thermostated glass reactor at ambient pressure. The reactor was loaded with the solvent and HBr, purged with air or a gas containing oxygen and gaseous alkene. Liquid alkenes were introduced in the reactor after purging with air. NaNO<sub>2</sub> was added last, and agitation of the reactor contents with a magnetic stirrer was started. Volume of the gases consumed (gaseous alkene and O<sub>2</sub> in 2/1 ratio or O<sub>2</sub> in case of liquid alkene) was measured by a calibrated gas burette connected to the reactor. To maintain a constant composition of gas in the reactor, the gas burette was filled with a 2/1 mixture of alkene and O<sub>2</sub> or with pure O<sub>2</sub>, respectively, in case of gaseous or liquid alkene. In a stepwise mode, HBr was oxidized with air to Br<sub>2</sub> that further reacted with the gas containing alkene or with liquid alkene. The reactions were monitored by gas uptake. At some point, the process was stopped, and the reactor was cooled to 10 °C.

**Table 1** Consumption of reagents and yield of products in the oxidative bromination of C<sub>2</sub>H<sub>4</sub> 1,2-dibromoethane (Br,Br) and 2-bromoethanol (OH, Br)

Entry	$\tau$ (min)	H <sub>2</sub> O (wt%)	Reagents consumed (mmol)		Products (mmol)	
			HBr	C <sub>2</sub> H <sub>4</sub>	Br,Br	OH,Br
1	180	8	0.97	0.47	0.51	0.004
2 <sup>a</sup>	125	28	0.97	0.50	0.47	0.050

The reaction conditions 1 g (1) or 0.78 g (2) BMImBr, 5 mg NaNO<sub>2</sub> (0.072 mmol)

0.112 mL 48 % HBr (1 mmol), C<sub>2</sub>H<sub>4</sub>/O<sub>2</sub> = 2/1 (v/v), 40 °C

<sup>a</sup> 0.2 g H<sub>2</sub>O

The rest HBr was neutralized by KOH solution. Consumption of HBr was determined as the difference between initial HBr and KOH spent for the neutralization. The reaction products and unreacted alkene were extracted with diethyl ether cooled to 10–15 °C (to prevent its evaporation), and the ether solution was analyzed by GC (Kristall 2000 M instrument with FID and an SPB<sup>TM</sup>–1000 capillary column 30 m × 530 μm) and GC–MS (Agilent Technologies 7000 GC/MS Triple Quad instrument, GC System 7890A with HP-5MS Phenyl Methyl Silox 325 °C column 30 m × 250 μm × 0.25 μm). Amounts of the products and liquid alkenes were determined using the standard calibration relationships. The selectivity of the bromination was calculated as a molar ratio of dibromo compound to GC detected products (for gaseous alkenes) or alkene consumed (for liquid alkene).

### 2.3 Spectral Studies

The <sup>14</sup>N NMR spectra of the reaction solutions were recorded on an AWANCE-400 spectrometer at NMR frequency 28.9 MHz, at room temperature and 40 °C, with accumulation frequency 100 ms. Chemical shifts were counted from the signal of external standard, 4 M Mg(NO<sub>3</sub>)<sub>2</sub> aqueous solution.

The UV–VIS spectra of solutions were recorded with a UV-2501 PC spectrometer (Shimadzu, Japan) in a region of 200–900 nm using a quartz cuvette with 0.06 mm optical layer.

## 3 Results and Discussion

### 3.1 Bromination of Ethylene

Ethylene was brominated under the action of HBr, O<sub>2</sub> and NaNO<sub>2</sub> catalyst precursor in a BMImBr–H<sub>2</sub>O solution to form mainly dibromoethane. The molar amount of the

**Table 2** Effect of reaction variables on initial rate of bromination ( $W_{in}$ ), contact time for 90 % conversion of HBr ( $\tau_{90}$ ), and resulting molar ratio of 1,2-dibromoethane (Br,Br) to 2-bromoethanol (OH,Br)

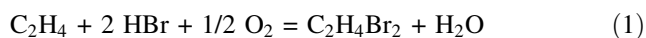
Entry	NaNO <sub>2</sub> (mmol)	C <sub>2</sub> H <sub>4</sub> :O <sub>2</sub> :N <sub>2</sub> (v/v)	$W_{in}$ (mmol · min <sup>-1</sup> )	$\tau_{90}$ (min)	Br,Br/OH,Br (mol %)
1	0.036	0.67:0.33:0	0.015	146	99.7:0.3
2	0.072	The same	0.028	72	99.1:0.9
3	0.145	The same	0.055	57	98.8:1.2
4	0.290	The same	0.079	47	98.7:1.3
5 <sup>a</sup>	0.145	The same	0.057	65	~ 100:0
6	0.145	0.33:0.33:0.33	0.042	89	99.3:0.7
7	0.145	0.67:0.16:0.17	0.039	61	99.1:0.9
8 <sup>b</sup>	0	0.67:0:0.33	0.045	55	99.2:0.8

The reaction conditions: 2 g BMImBr, 0.224 mL 48 % HBr (2 mmol HBr), 0.2 g H<sub>2</sub>O

<sup>a</sup> 0.2 g HClO<sub>4</sub> instead of H<sub>2</sub>O

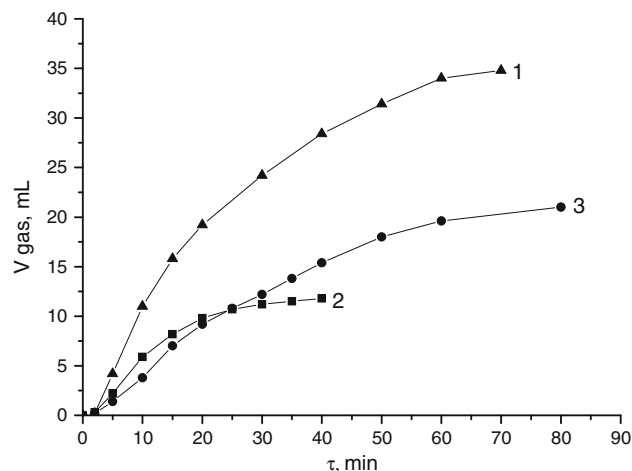
<sup>b</sup> 2 mmol HBr and 0.145 mmol NaNO<sub>2</sub> were pre-oxidized with O<sub>2</sub>

product well agreed with those of HBr and ethylene consumed (calculated as 2/3 of C<sub>2</sub>H<sub>4</sub>/O<sub>2</sub> gas consumed) (Table 1). The production of 2-bromoethanol was negligible at a small water content, and remained low even when the water content was increased to ~30 %. Bromoethane was not detected by GC-MS, thus indicating that the acid-catalyzed addition of HBr to the double bond did not occur under the operating conditions. Thus, the bromination exactly followed equation (1):



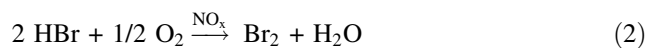
Data in Table 2 show the effect of variables on the bromination of ethylene. One can see that the NaNO<sub>2</sub> loading affected more strongly the initial rate determined in 5–10 min interval after starting the bromination than the contact time required for 90 % conversion of HBr (Table 2, entries 1–4). A decrease in the partial pressure of ethylene changed more strongly the contact time than the initial rate of bromination (compare entries 3 and 6). On the contrary, a similar decrease in the partial pressure of oxygen affected mostly the initial rate and exerted a small effect on the contact time (entries 3 and 7). The changes in conditions did not produce a noticeable effect on the selectivity of the bromination. 1,2-Dibromoethane remained the main product with no more than 1.0–1.5 % admixture of 2-bromoethanol. The addition of a strong acid (HClO<sub>4</sub>) changed neither the rate nor the selectivity of the bromination (entry 5).

The effects observed were in agreement with the mechanism of the oxidative bromination catalyzed by nitrogen oxides NO<sub>x</sub>, which appeared from decomposition of NO<sub>2</sub><sup>-</sup> anions in acidic medium and were responsible for



**Fig. 1** Gas consumption versus time curves 1, 2 BMImBr 2 g, NaNO<sub>2</sub> 0.145 mmol, 48 % HBr 0.224 mL (2 mmol HBr), H<sub>2</sub>O 0.2 g, C<sub>2</sub>H<sub>4</sub>/O<sub>2</sub> = 2/1 (1), Ar/O<sub>2</sub> = 2/1 (2), 40 °C, 3 solution (2), C<sub>2</sub>H<sub>4</sub>/Ar = 2/1, 40 °C

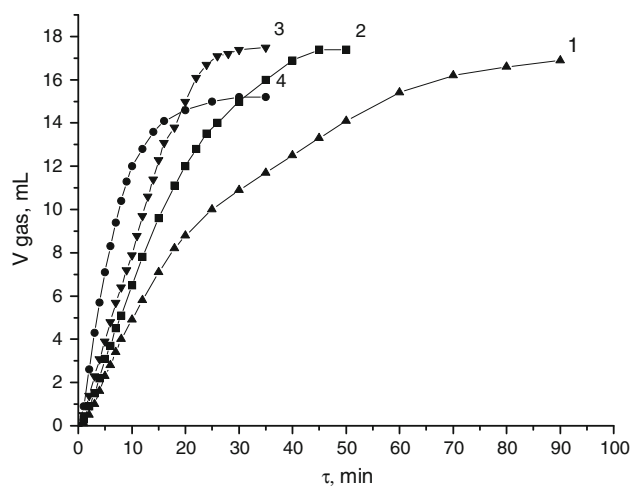
catalysis in the oxidative bromination reactions [20, 21]. The mechanism includes two steps: the catalytic generation of a brominating reagent, probably Br<sub>2</sub> and its interaction with hydrocarbon substrate.



A specificity of the HBr–NaNO<sub>2</sub>–O<sub>2</sub> brominating system studied here is rapid generation of Br<sub>2</sub> in BMImBr solution in the first step (2) and slow electrophilic addition of Br<sub>2</sub> to non-activated double bond of ethylene in the second step (3). When both reactions occurred simultaneously (Table 2, entries 1–6), the initial gas uptake was caused mostly by the reaction of bromide with O<sub>2</sub>, while duration of the total reaction was determined by the reaction of ethylene. In the stepwise mode, the reactions (2) and (3) were performed separately (Table 2, entry 8). In this case, reaction (3) required the same contact time as the total reaction (entry 3). Curves 1–3 in Fig. 1 illustrate the gas uptake during generation of Br<sub>2</sub>, bromination of ethylene, and total reaction. All these data show that the NO<sub>x</sub> catalyst and BMImBr solvent enable accumulation of the reactive Br<sub>2</sub> in the solution. Bromination of alkene can be combined with oxidation of Br<sup>-</sup> or performed in the absence of oxygen after accumulation of sufficient Br<sub>2</sub>. The yield of 1,2-dibromoethane did not depend on the bromination mode.

### 3.2 Bromination of C<sub>3</sub>–C<sub>8</sub> Alkenes

C<sub>3</sub> and C<sub>4</sub> alkenes were brominated more readily than ethylene, and the time required for consumption of an



**Fig. 2** Gas absorption versus time curves obtained in bromination of ethylene (1), propylene (2), 1-butene (3), 2-methylpropene (4), BMImBr 1 g, NaNO<sub>2</sub> 5 mg (0.072 mmol), 48 % HBr 0.112 mL (1 mmol HBr), H<sub>2</sub>O 0.1 g, alkene/O<sub>2</sub> = 2/1, 40 °C

assigned volume of gaseous reagents decreased in order of ethylene, propene, 1-butene, 2-methylpropene (Fig. 2). The influence of nucleophilic alkyl groups on the reactivity of alkenes is pronounced for the electrophilic addition of Br<sub>2</sub> [26]. Furthermore, solubility of the light alkenes in BMImBr increased in the same order, which was confirmed

by different absorption of the gaseous alkenes by BMImBr in the absence of NaNO<sub>2</sub> (no reaction of the alkenes). The overall effect of solubility and reactivity produced a three-fold decrease in the reaction time if comparing 1-butene with ethylene (curves 1 and 3 in Fig. 2). In cases of propene and 1-butene as well as ethylene the complete conversion of HBr (curves 2 and 3) resulted in formation of the corresponding 1,2-dibromoalkanes with a high selectivity (Table 3, entries 1 and 2). The bromination of 2-methylpropene was faster than that of 1-butene, but terminated at incomplete conversion of HBr (curve 4), probably due to expense of the NO<sub>x</sub> catalyst. In addition to 1,2-dibromo-2-methylpropane, 1-bromo-2-methylpropane-2-ol and a product of its dehydration, 1-bromo-2-methylpropene, was detected (Table 3, entry 3).

The bromination of cyclohexene resulted in complete conversion and good selectivity to trans-1,2-dibromocyclohexane at 30 °C, in air (Table 3, entry 4), but the reaction at 40 °C had ceased before complete conversion of alkene and HBr was reached. In case of 1-octene, the deactivation of the catalyst resulted in incomplete conversion even at 30 °C (entry 5). However, deactivation of the catalyst was observed in bromination of 2,3-dimethyl-2-butene. The reaction stopped soon after beginning, and only a 15 % conversion of 2,3-dimethyl-2-butene was achieved (Table 3, entry 6). The GC-MS analysis revealed the formation of 2,3-dimethyl-2,3-dinitrobutane together

**Table 3** Data on bromination of C<sub>3</sub>-C<sub>8</sub> alkenes

Entry	Alkene	Reagents consumed (mmol)		Products	
		Alkene	HBr	Dibromoalkane (selectivity, %) <sup>d</sup>	Other products
1 <sup>a</sup>	CH <sub>3</sub> CH=CH <sub>2</sub>	0.48	0.96	CH <sub>3</sub> CH(Br)-CH <sub>2</sub> (Br) (96)	CH <sub>3</sub> CH(OH)-CH <sub>2</sub> (Br)
2 <sup>a</sup>	(C <sub>2</sub> H <sub>5</sub> )CH=CH <sub>2</sub>	0.49	0.97	(C <sub>2</sub> H <sub>5</sub> )CH(Br)-CH <sub>2</sub> (Br) (96)	(C <sub>2</sub> H <sub>5</sub> )CH(OH)-CH <sub>2</sub> (Br)
3 <sup>a</sup>	(CH <sub>3</sub> ) <sub>2</sub> C=CH <sub>2</sub>	0.42	0.72	(CH <sub>3</sub> ) <sub>2</sub> C(Br)-CH <sub>2</sub> (Br) (88)	(CH <sub>3</sub> ) <sub>2</sub> C(OH)-CH <sub>2</sub> (Br), $\begin{array}{c} \text{CH}_2 \\    \\ \text{CH}_3\text{C}-\text{CH}_2(\text{Br}) \end{array}$
4 <sup>b</sup>	C <sub>6</sub> H <sub>10</sub>	0.48	0.81	C <sub>6</sub> H <sub>10</sub> Br <sub>2</sub> (82)	C <sub>6</sub> H <sub>10</sub> (OH)Br, C <sub>6</sub> H <sub>11</sub> Br
5 <sup>b</sup>	(n-C <sub>6</sub> H <sub>13</sub> )CH=CH <sub>2</sub>	0.39	0.80	(n-C <sub>6</sub> H <sub>13</sub> )CH(Br)-CH <sub>2</sub> (Br) (98)	(n-C <sub>6</sub> H <sub>13</sub> )CH(OH)-CH <sub>2</sub> (Br)
6 <sup>b</sup>	(CH <sub>3</sub> ) <sub>2</sub> C=C(CH <sub>3</sub> ) <sub>2</sub>	–	0.29	(CH <sub>3</sub> ) <sub>2</sub> C(Br)-C(Br)(CH <sub>3</sub> ) <sub>2</sub>	(CH <sub>3</sub> ) <sub>2</sub> C(NO <sub>2</sub> )-C(NO <sub>2</sub> )(CH <sub>3</sub> ) <sub>2</sub>
7 <sup>b,c</sup>	(CH <sub>3</sub> ) <sub>2</sub> C=C(CH <sub>3</sub> ) <sub>2</sub>	0.50	0.84	(CH <sub>3</sub> ) <sub>2</sub> C(Br)-C(Br)(CH <sub>3</sub> ) <sub>2</sub> (83)	$\begin{array}{c} \text{O} \\   \\ (\text{CH}_3)_2\text{C}-\text{C}(\text{CH}_3)_2 \end{array}$

The reaction conditions: BMImBr 1 g, 48 % HBr 0.112 mL (1 mmol HBr), H<sub>2</sub>O 0.1 g

<sup>a</sup> NaNO<sub>2</sub> 5 mg (0.072 mmol), alkene/O<sub>2</sub> = 2/1, 40 °C, the reaction times correspond to overall absorption of alkene/O<sub>2</sub> mixture in Fig. 2

<sup>b</sup> NaNO<sub>2</sub> 10 mg (0.145 mmol), liquid alkene 0.5 mmol, air, 30 °C, time 1 h

<sup>c</sup> Stepwise mode: 1 h with air, 1 h with alkene

<sup>d</sup> Referred to the reacted alkene

with 2,3-dimethyl-2,3-dibromobutane. 2,3-Dimethyl-2,3-dinitrobutane was detected as a small impurity only. Analogous dinitro derivatives of 1-octene and 2-methylpropene were not detected. The detection of small amounts of thermally unstable compounds, such as dinitro compounds, by GC is a difficult problem. Meanwhile, the formation of nitro compounds is very probable under the bromination conditions [27]. Therefore, we suggested conversion of  $\text{NO}_x$  to the nitro compound to give rise to the catalyst deactivation.

A complete conversion of 2,3-dimethyl-2-butene was achieved when the reaction was performed in the stepwise mode. 2,3-Dimethyl-2,3-dibromobutane was obtained with admixtures of tetramethyloxirane (Table 3, entry 6) and unidentified compound with higher molecular mass. The first one formed through conversion of alkene to bromohydrin and then to epoxide, as suggested in paper [28]. The bromohydroxy compounds usually appeared in neutral solutions, which is consistent with nearly complete conversion of HBr (entry 7). The results obtained in bromination of 2,3-dimethyl-2-butene have shown that the stepwise procedure is preferable in the case of strongly nucleophilic alkenes.

### 3.3 $^{14}\text{N}$ NMR Analysis of the Catalyst Transformations

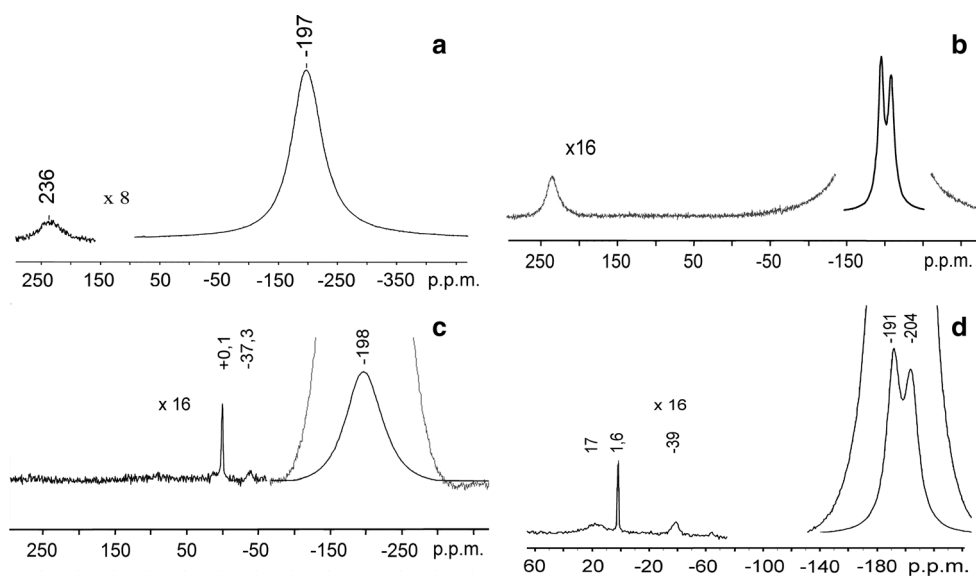
The  $^{14}\text{N}$  NMR spectrum of the  $\text{NaNO}_2$  solution without HBr showed the broad peaks of BMImBr ( $-197$  ppm) and  $\text{NO}_2^-$  anions ( $236$  ppm) (Fig. 3, spectrum a). Dilution of the solution with water decreased the viscosity; that resulted in appearance of two narrow peaks from non-equivalent nitrogen atoms of the BMIm $^+$  cation at  $-191$  and  $-205$  ppm (spectrum b). 2 min after addition of HBr and starting the reaction with cyclohexene in an  $\text{O}_2/\text{Ar} = 1/2$  atmosphere, at  $40^\circ\text{C}$  the signal of the  $\text{NO}_2^-$  anion disappeared. Paramagnetic molecules NO and  $\text{NO}_2$ , which formed in the presence of acid, were not observed. At the same time, low-intensity peaks appeared in the region of  $20$  to  $-40$  ppm, the intensity of which increased by the end of the bromination (in 1 h, spectra c and d). The narrow peak at about  $0$  ppm coincided with the peak of  $\text{NaNO}_3$  added to the solution, therefore, it was attributed to  $\text{NO}_3^-$  anions. The broad peaks appeared in the presence of cyclohexene, but were absent when oxidation of HBr (reaction (2)) proceeded without alkene. Therefore, the broad peaks were tentatively assigned to the nitro compounds formed from cyclohexene. If the peaks observed in spectrum d, Fig. 3 were normalized to intensity of the signal of BMImBr, ca. 30 % of nitrogen initially introduced as  $\text{NaNO}_2$  was observed in the spectrum. The remaining nitrogen was probably in the form of undetectable NO and  $\text{NO}_2$  molecules. Similar spectra of solution were observed under bromination of ethylene, except for

much lower intensity of the signals attributed to nitro compounds even after repeated addition of HBr and a long-time reaction with ethylene. No additional signals from NOBr [21] or other possible intermediates were detected during the oxidation of HBr in the absence of alkene. The spectra recorded after the oxidation of HBr in the absence of alkene indicated a complete conversion of nitrite to nitrate. Although nitrate was used as the stoichiometric oxidant or catalyst in oxidative halogenation at high temperature and acidity of the medium [16, 18],  $\text{NaNO}_3$  showed no catalytic activity under our operating conditions. That means nitrate is the second after nitro compounds product of transformation of the  $\text{NO}_x$  catalyst. Deactivation of the catalysts owing to formation of the nitro compounds proceeded readily in reaction with nucleophilic alkenes, whereas oxidation of the catalyst was facilitated by the lack of reactivity or absence of alkene. As shown, formation of the nitro compounds can be avoided if conducting the bromination in the stepwise mode (Table 3, entry 7). On the other hand, deactivation does not create an essential limitation for application of  $\text{NO}_x$  catalyst. The conversion of nitrite finally into nitrate can be regarded as a positive process, because it prevents contacting with volatile nitrogen oxides under processing the reaction solutions.

### 3.4 Comparative Properties of BMImBr, BMImBF<sub>4</sub> and HMImBr as Solvents for the HBr– $\text{NaNO}_2$ – $\text{O}_2$ Brominating System

The brominating systems based on different ionic liquids were tested in three cycles when equal portions of HBr were added at the beginning of the process and after consuming the  $\text{C}_2\text{H}_4/\text{O}_2$  gas volume, which corresponded to nearly complete conversion of the previous portion of HBr. In the first cycle, the initial rates and durations of the bromination were close in different imidazolium ionic liquid solutions, but deactivation of the catalytic system with each new portion of HBr proceeded more intensively in HMImBr solution (Table 4). Similar to BMImBr, HMImBr provided selectivity to 1,2-dibromoethane of over 98 % in the first cycle, and a small loss in the selectivity in subsequent cycles. In BMImBF<sub>4</sub> solution, the selectivity to 1,2-dibromoethane was lower due to increasing the portion of 2-bromoethanol to 20 % in the first cycle, 22 % in the third cycle, and 23 % in the stepwise bromination (Table 4). As reported by Chiappe et al. [29], the bromination of alkenes with  $\text{Br}_2$  in BMImBr and BMImBF<sub>4</sub> ionic liquids produced dibromide, whereas two products—bromohydrin and dibromide—were observed by Conte et al. [23] in the oxidative bromination of styrene in water-containing solutions. In the brominating systems tested here, water content of 16–28 wt% did cause the appearance

**Fig. 3**  $^{14}\text{N}$  NMR spectra of reaction solutions, **a** BMImBr 2 g (9.1 mmol),  $\text{H}_2\text{O}$  0.2 g,  $\text{NaNO}_2$  20 mg (0.28 mmol), **b** solution (a) diluted 1:1 with water, **c** solution (a) after reaction with cyclohexene 0.1 mL (1 mmol), 48 % HBr 0.224 mL (2 mmol HBr) in Ar/ $\text{O}_2 = 2/1$  at 40 °C for 1 h, **d** solution c diluted 1:1 with water



**Table 4** Effect of the ionic liquid composition on initial rate of  $\text{C}_2\text{H}_4/\text{O}_2$  mixture absorption ( $W_{\text{in}}$ ), contact time for 90 % conversion of HBr ( $\tau_{90}$ ), and amount of products 1,2-dibromoethane (Br,Br) and 2-bromoethanol (OH,Br)

Ionic liquid	Cycle	$W_{\text{in}}$ (mmol·min $^{-1}$ )	$\tau_{90}$ (min)	Br,Br (mmol)	OH,Br (mmol)
BMImBr	1	0.049	48	0.88	0.011
	2	0.033	49	n.d.	n.d.
	3	0.026	75	3.05	0.14
HMImBr	1	0.042	45	0.83	0.022
	2	0.022	110	n.d.	n.d.
	3	0.005 <sup>a</sup>	–	1.7	0.052
BMImBF <sub>4</sub>	1	0.055	43	0.92	0.23
	2	0.045	40	n.d.	n.d.
	3	0.048	38	2.51	0.71
BMImBF <sub>4</sub>	Stepwise	–	–	0.92	0.28
(n-Bu) <sub>4</sub> NBr	1	0.022	80	1.09	0.01

The reaction conditions: 2.0 g BMImBr or HMImBr, or BMImBF<sub>4</sub>, or (n-Bu)<sub>4</sub>NBr, 10 mg  $\text{NaNO}_2$  (0.145 mmol), 0.2 g  $\text{H}_2\text{O}$ ,  $\text{C}_2\text{H}_4/\text{O}_2 = 2/1$ , 40 °C; 0.224 mL 48 % HBr (2 mmol HBr) was added in each cycle

<sup>a</sup> Conversion of HBr ~ 10 %

of 2-bromoethanol in BMImBF<sub>4</sub>, but addition of  $\text{OH}^-$  groups and formation of 2-bromoethanol were suppressed by the exceeding concentration of  $\text{Br}^-$  in BMImBr solution. That means the concentration of  $\text{Br}^-$  is a critical factor which determines the selectivity of bromination in the ionic liquids containing water.

Besides of the imidazolium ionic liquids, (n-Bu)<sub>4</sub>NBr was tested in the  $\text{NO}_x$  catalyzed bromination, as the salts with organic cations, other than imidazolium, were used in brominating systems [30]. Similar to BMImBr, (n-Bu)<sub>4</sub>NBr

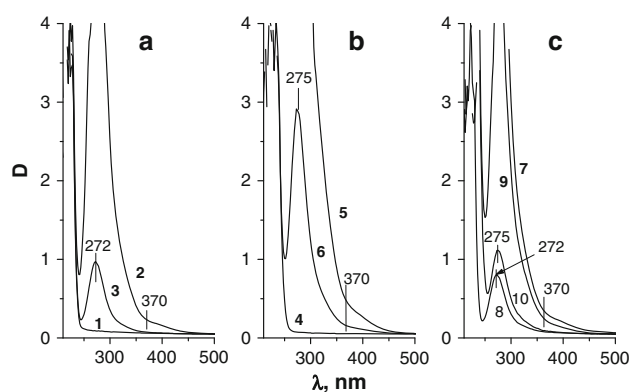
based catalytic system provided selective formation of dibromoethane, but showed lower activity in the first cycle (Table 4). Although activity of the system was not remarkably changed in subsequent two cycles, appearance of tributylamine after the 1-st cycle and its accumulation in the following cycles (detected by GCMS) showed degradation of the (n-Bu)<sub>4</sub>N<sup>+</sup> cation under the reaction conditions.

In contrast to  $\text{CH}_3\text{CN}$  solvent used before [21], bromide ionic liquid creates high  $\text{Br}^-$  concentration in the reaction medium. It enables to carry out dibromination selectively at higher concentration of water that is added with HBr and accumulated during reaction. As shown, high selectivity to dibromoalkane maintained when the  $\text{H}_2\text{O}$  concentration in BMImBr raised from 16 to 28 wt%, whereas in  $\text{CH}_3\text{CN}$  water concentration was 2.4 or 10 wt% [21]. Thereby, complete removing of water is not required under regeneration of ionic liquid, that can be done, for example, by low-power method [31].

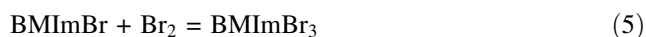
The positive effect of  $\text{Br}^-$  on selective formation of dibromoalkanes has been established earlier in brominations performed in a  $\text{H}_2\text{O}/\text{THF}$  [12] and  $\text{CH}_3\text{CN}$  [21] medium. This phenomenon was explained by specific reactivity of  $\text{HBr}_3$  particles [21], which could occur in the bromide containing solutions by reaction (4).



In other studies, pre-synthesized salts of the  $\text{Br}_3^-$  anions and Zn(II) or organic cations were used in the bromination of aromatics [32–34] and alkenes [30]. A similar reaction (5) presumably proceeds in the  $\text{Br}^-$ -containing ionic liquids when the  $\text{NO}_x$  catalyzed oxidation of HBr produces  $\text{Br}_2$ .



**Fig. 4** UV-VIS spectra of solutions of ionic liquids and HBr reacted with oxygen (**a**, **b**) and with  $C_2H_4/O_2$  (**c**), 1 BMImBF<sub>4</sub> 2.06 g, H<sub>2</sub>O 0.2 mL, 2 (1), HBr 2 mmol, NaNO<sub>2</sub> 0.145 mmol, Ar/O<sub>2</sub> = 2/1, 40 °C, 1 h, diluted 1:9 with (1), 3 (1), HBr 2 mmol, NaNO<sub>2</sub> 0.145 mmol, Ar/O<sub>2</sub> = 2/1, 40 °C, 1 h, diluted 1:49 with (1), 4 BMImBr 2.0 g, H<sub>2</sub>O 0.2 mL, 5 (4), HBr 2 mmol, NaNO<sub>2</sub> 0.145 mmol, Ar/O<sub>2</sub> = 2/1, 40 °C, 1 h, diluted 1:9 with (4), 6 (4), HBr 2 mmol, NaNO<sub>2</sub> 0.145 mmol, Ar/O<sub>2</sub> = 2/1, 40 °C, 1 h, diluted 1:49 with (4), 7 (1), HBr 2 mmol, NaNO<sub>2</sub> 0.145 mmol,  $C_2H_4/O_2$  = 2/1, 40 °C, 10 min, 8 (7) diluted 1:9 with (1), 9 (4), HBr 2 mmol, NaNO<sub>2</sub> 0.145 mmol,  $C_2H_4/O_2$  = 2/1, 40 °C, 10 min, diluted 1:9 with (4), 10 (4), HBr 2 mmol, NaNO<sub>2</sub> 0.145 mmol,  $C_2H_4/O_2$  = 2/1, 40 °C, 10 min, diluted 1:49 with (4)



This assumption was verified by means of UV–VIS spectroscopy used for characterization of the reaction solutions. The oxidation of HBr with O<sub>2</sub> according to reaction (3) in a BMImBF<sub>4</sub> or BMImBr medium resulted in appearance of a broad band with a maximum near 370 nm and strong bands at 272 or 275 nm (spectra 2, 3 and 5, 6 in Fig. 4). We attributed these bands to Br<sub>2</sub> based on their similarity to the bands at 370 and 269 nm reported in paper [21] for CH<sub>3</sub>CN solution of Br<sub>2</sub>. At identical concentrations of Br<sub>2</sub> in the BMImBF<sub>4</sub> and BMImBr solutions, the spectrum of the latter showed a higher intensity and a small shift of the absorption band maximum. (The spectral characteristics of Br<sub>2</sub> solutions are represented in Table 5). The different absorption peak position and apparent extinction coefficient of Br<sub>2</sub> in the two ionic liquids can be explained by the formation of a charge-transfer complex [BMIm]<sup>+</sup>Br<sup>−</sup>Br<sub>2</sub> (reaction (5)).

The same spectra were observed for the reaction solutions recorded after interruption of the oxidative bromination of ethylene (Fig. 4c, 10 % conversion of HBr). The spectra showed the same maxima at 272 nm in BMImBF<sub>4</sub> and 275 nm in BMImBr, the latter maximum having a higher intensity. Thus, the spectral data confirmed the formation of the [BMIm]<sup>+</sup>Br<sup>−</sup>Br<sub>2</sub> species in BMImBr at conditions which provided the best selectivity to 1,2-dibromoethane. However, these species do not affect the rate of bromination under operating conditions, as close

**Table 5** Spectral band characteristics of Br<sub>2</sub> in different solvents

Solvent	$\lambda_{max}$ , nm	$\epsilon$ , <sup>a</sup> L·mol <sup>−1</sup> ·cm <sup>−1</sup>	Reference
CH <sub>3</sub> CN	269	No data	[21]
BMImBF <sub>4</sub>	272	1.6 10 <sup>4</sup>	This work
BMImBr	275	4.8 10 <sup>4</sup>	This work

<sup>a</sup> Apparent extinction coefficient

values of the rate and contact time (for 90 % conversion of HBr) were observed for bromination of ethylene in the different ionic liquids (Table 4).

More or less intensive deactivation of the catalytic systems was observed in long-term testing (Table 4). As was discussed above, the most probable reason of the deactivation in bromination of ethylene is the oxidation of NO<sub>x</sub> catalyst to NO<sub>3</sub><sup>−</sup>. We assumed that additional deactivation might be connected with degradation of the ionic liquids. The oxidation of the imidazolium cation in radical oxidation with H<sub>2</sub>O<sub>2</sub> [35] and chlorination of the imidazolium ring in the system HMIm(NO<sub>3</sub>)–HCl–O<sub>2</sub> [18] were observed earlier. In the brominating system studied here, possible transformations of the ionic liquids were followed by GC–MS analysis of ether extracts of the neutralized reaction solutions. No anticipated products of the ionic liquids decomposition were detected in the solutions after bromination of alkenes in nearly optimal conditions (e.g., the runs in Table 3), which indicated a sufficient stability of the ionic liquids.

However, the degradation of the ionic liquids was actually observed when the reaction conditions were far from optimal, as indicated in Table 6. At a small water content in run 1, the bromination of alkenes proceeded slowly and was accompanied by the destruction of BMIm<sup>+</sup> cation through abstraction of alkyl (mainly butyl) groups from the ring to yield 2,3-dibromobutane and 1,3-dibromobutane, which constituted a few percent of 1,2-dibromobutane that formed from 1-butene in two brominating cycles with repeated addition of HBr (Table 6, entry 1). The process was more intensive and involved methyl group at the increased concentration of HBr, as it was shown upon bromination of propene (entry 2). In the absence of substrate, small amounts of the products of BMIm<sup>+</sup> cation destruction were also detected (entry 3). In contrast to BMIm<sup>+</sup>, the destruction of HMIm<sup>+</sup> was rather intensive and involved bromination of the methylimidazole aromatic ring (entry 4). That indicated butyl group to provide a higher stability of the BMIm<sup>+</sup> cation.

## 4 Conclusion

The alkyimidazolium ionic liquids have been successfully applied in the oxidative bromination of alkenes with

**Table 6** GC–MS products of degradation of the ionic liquids during oxidative bromination under critical conditions

Entry	Critical conditions	Composition of gas (v/v)	Time (min)	GC–MS detected compounds (relative area units) <sup>a</sup>		
1	Small initial amount of H <sub>2</sub> O 8wt%	Butene-1/O <sub>2</sub> = 2/1	240	2,3-Dibromobutane (2.1)	1,3-Dibromobutane (5.5)	
2	High initial amount of HBr	Propylene/O <sub>2</sub> = 2/1	120	2,3-Dibromobutane (8.0)	1,3-Dibromobutane (5.6)	Tribromomethane (2.7)
3	Without substrate (BMImBr)	Ar/O <sub>2</sub> = 2/1	60	2,3-Dibromobutane (2.6)	1,3-Dibromobutane (1.6)	1,2-Dibromobutane (traces)
4	Without substrate (HMImBr)	Ar/O <sub>2</sub> = 2/1	20	2,4-Dibromo-1-methylimidazole (5.2)	2,4,5-Tribromo-1-methylimidazole (25)	

The reaction conditions: 1 g BMImBr (1–3) or 1 g HMImBr (4), 0.072 mmol (1, 2) or 0.145 mmol (3, 4) NaNO<sub>2</sub>, 48 % HBr 0.112 mL × 2 (2 mmol) was added in two steps (1), or at once (2), and 112 mL (1 mmol) was added at once (3, 4), 40 °C

<sup>a</sup> GC-MS peaks were normalized to the solvent

NaNO<sub>2</sub> as the NO<sub>x</sub> catalyst precursor, and air as terminal oxidant. The selectivity to dibromoalkanes of 96–99 % was obtained for ethylene, propene, 1-butene and 1-octene, and 82–88 % in case of more susceptible to electrophilic attack branched alkenes. The process included two reactions: the NO<sub>x</sub> catalyzed oxidation of HBr to Br<sub>2</sub> and the bromination of alkene, which could be carried out in simultaneous or stepwise modes. The stepwise performance eliminated the contact of alkene with nitrogen oxides, thus preventing the formation of nitro compounds. BMImBr solvent was shown to possess excellent characteristics in the NO<sub>x</sub> catalyzed bromination. Large concentration of Br<sup>−</sup> anions was an important factor to keep high selectivity to dibromoalkane even at the H<sub>2</sub>O content as large as 16–28 wt%. The BMIm<sup>+</sup> cation exhibited high stability under favorable for bromination conditions. In terms of safety and environmental protection, the brominating system based on air and NaNO<sub>2</sub> has advantageous characteristics such as complete consumption of HBr and neutralization of hazardous NO<sub>x</sub> gases to form NO<sub>3</sub><sup>−</sup> anions dissolved in the ionic liquid.

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