Oxidation of Alcohols by Hydroperoxides in the Presence of Polymer-Supported Catalysts: Tetrabromooxomolybdate Supported on a Cationic Polymer

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OXIDATION OF ALCOHOLS BY HYDROPEROXIDES IN THE PRESENCE OF POLYMER-SUPPORTED CATALYSTS: TETRABROMOOXOMOLYBDATE SUPPORTED ON A CATIONIC POLYMER

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ABSTRACT

The immobilization of Br_4MoO^- in both poly-p-vinylpyridine with a flexible backbone and silica as a rigid polymer support was carried out. The oxidation of alcohols by t-butyl hydroperoxide (t-BuOOH) was then studied in the presence of the polymer-supported complexes obtained. The differences of the reactivity between catalysts supported by organic and inorganic polymers are discussed. The best carrier for Br_4MoO^- as an oxidation catalyst is a silica modified with silane coupling reagent (dimethyloctadecyl-[3-(trimethoxysilyl)propyl] ammonium chloride).

INTRODUCTION

Oxidation by hydroperoxide in the presence of molybdenum compounds has recently aroused wide interest [1]. Tetrabromooxomolybdate (Br_4MoO^-) complex can be used as a chemoselective catalyst for epoxidation of olefins and for oxidation of alcohols with t-butyl hydroperoxide (t-BuOOH) [2]. In order to expand the application of this active species, we attempted the im-

mobilization of Br_4MoO^- by alkylammonium cation type polymers obtained from the reaction of poly(p-chloromethylstyrene-co-divinylbenzene and styrene) with amines [3]. Low molecular weight ammonium tetrabromooxomolybdate is hygroscopic and unstable. These defects can be improved by the immobilization of Br_4MoO^- in the cationic polymers. Major advantages of this approach are: (a) easy work-up of the reaction mixtures, (b) convenient preparation of the catalyst, (c) re-use of the valuable metal, and (d) an effect of the neighboring groups observed as "polymer effect." In this work we used a cationic polymer obtained easily from quaternization of poly(p-vinylpyridine) for the immobilization of Br_4MoO^-, and we investigated the catalytic activity for the oxidation of alcohols by t-BuOOH. Preparation of the immobilized catalyst is shown in Scheme 1.

As this route did not proceed quantitatively, [I] contained various functional groups, i.e., pyridinium, pyridinium tetrabromooxomolybdate, and pyridine. The ratio of the reactive groups was estimated on the basis of elemental analyses of halogen and molybdenum. In this paper we report on the oxidation of various alcohols with t-BuOOH in the presence of Br_4MoO^- immobilized on poly(p-vinylpyridinium) salt. The influence of the counteranion in the polymer must be considered because of the low selectivity for the oxidation of alcohol by t-BuOOH. In this connection we found that rigid inorganic polymers such as silica showed much better characteristics than organic polymers, which possess a flexible backbone and swell in the organic solvents.

EXPERIMENTAL

Materials

The polymer used in this investigation was poly-p-vinylpyridine, which was a gift of Koei Chemicals Co. It had a molecular weight of 100 000. The polymer was reprecipitated from a methanol-ether system, then dried at 60°C for 24 h.
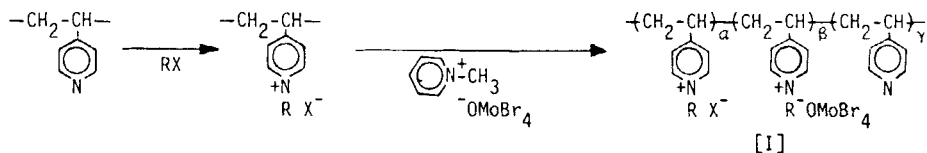
SCHEME 1.

t-Butyl hydroperoxide (*t*-BuOOH), purchased from Nippon Oils & Fats Co., was used after purification by vacuum distillation.

Silica (AS-380, 323 m^2/g) was a gift from Nikki Chemical Co.

Silane coupling reagent (octadecyl[3-(trimethoxysilylpropyl] ammonium chloride was a gift of Toray-Silicone Co.

All other chemicals, except those used for quantitative analysis, were reagent grade and were used as received. Guaranteed reagents were used for quantitative analyses.

Preparation of Modified Silica

Silica was activated by 6 *M* hydrochloric acid under reflux with stirring for 24 h, washed thoroughly with water, and finally dried under a vacuum. A mixture of 3 g silica and 25 g octadecyldimethyl[3-(trimethoxysilylpropyl]- ammonium chloride in methanol (50 cm^3) and toluene (5 cm^3) was heated at 70°C with stirring for 24 h. After being separated from the mixture, the modified silica was washed with methanol and dried at 70°C under a vacuum.

Immobilization of Br$_4$MoO$^-$ in Poly-*p*-vinylpyridine

Poly-*p*-vinylpyridine (2 g) was dissolved in DMF (20 cm^3), and an appropriate alkyl halide (5-20 cm^3) was added. The reaction was carried out at 80°C for 20 h. After this process, the following processes, (A) and (B), were carried out for immobilization: (A) The polymer obtained was added to a hydrobromic acid solution of molybdenum trioxide. After the solution was stirred, the precipitate was filtered and washed with methanol. (B) The poly-4-vinylpyridinium salt was added to a methanol solution of *N*-methyl pyridinium tetrabromooxomolybdate. After overnight stirring, the polymer was filtered off and washed with methanol, and then dried under vacuum. The halogen content was obtained by the Volhard method. Molybdenum was analyzed by the EDTA method.

The modified silica was used for the immobilization of Br$_4$MoO$^-$. The immobilization was carried out by the method described previously.

Oxidation of Alcohol

The general procedure was as follows: alcohol (3 mmol), *t*-BuOOH (3 mmol), immobilized catalyst (0.3 mmol), and benzene (3 cm^3) were added to a screw-capped test tube and reacted at 60°C in an aluminum-block thermostat. After an appropriate time, a small portion of the reaction mixture was analyzed on a gas chromatograph using a 2-m PEG 20M column at 170°C.

The remaining immobilized polymer catalyst was filtered off and washed with ethyl ether. The filtrate and the washings were evaporated. The precipitate or condensate obtained was purified by column chromatography and identified by comparison with an authentic sample by IR and NMR.

RESULTS AND DISCUSSION

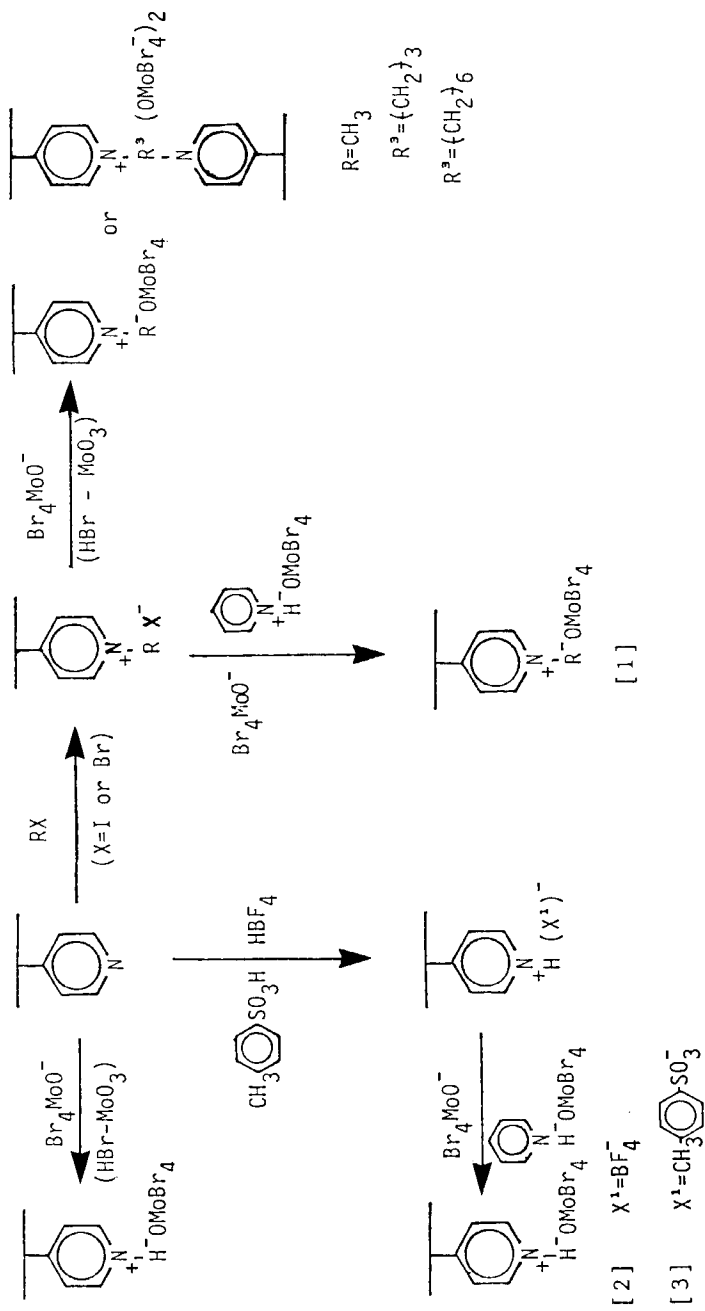### Preparation of Immobilized Polymer

a. From Poly(p-vinylpyridine)

Immobilization of Br_4MoO^- was carried out with N-alkylpyridinium polymer obtained by the reaction of poly-p-vinylpyridine with alkyl halide in dimethylformamide (DMF) or acetonitrile. This route is shown in Scheme 2.

In a previous paper [3] we reported that halide ion as a counteranion, which was attached to the polymer chain, decomposed hydroperoxide without the oxidation of alcohol.

Br_4MoO^--HBr solution was synthesized by the reaction of MoO_3 with HBr. When the polymer was added to this solution, pyridinium bromide groups were produced along with pyridinium tetrabromooxomolybdate groups on the polymer chain. The former groups were found to be ineffective for the oxidation of alcohol. The reason will be described later. In order to minimize the halide, we carried out the anion-exchange reaction of poly-p-vinylpyridinium halide with N-methylpyridinium tetrabromooxomolybdate or pyridinium tetrabromooxomolybdate. The halide ion of the polymer was exchanged with N-methylpyridinium tetrabromooxomolybdate to immobilize Br_4MoO^- in N-alkylpyridinium polymer. Also, poly-p-vinylpyridine was treated with tetrafluoroboric acid or p-toluenesulfonic acid so that we could obtain poly-p-vinylpyridinium BF_4^- or poly-p-vinylpyridinium p-toluenesulfonate, which were exchanged with pyridinium tetrabromooxomolybdate to immobilize Br_4MoO^-.

The composition of the immobilized catalyst is shown in Table 1; the findings can be summarized as follows. In the case of the reaction with methyl iodide or butyl bromide, complete N-alkylation of the pyridine nucleus was observed. On the other hand, octyl iodide or dodecyl iodide did not react with all nitrogen atoms in pyridine rings under the same conditions. In the anion-exchange reaction with N-methylpyridinium tetrabromooxomolybdate or pyridinium tetrabromooxomolybdate, all halide ions were not replaced, and pyridinium bromide groups remained in the main chain.

$R^- OMoBr_4^-$

$R^3 (OMoBr_4^-)_2$

or

Br_4MoO^-
$\overline{(HBr - MoO_3)}$

$R^- OMoBr_4^-$

$R=CH_3$

$R^3 = \{CH_2\}_3$

$R^3 = \{CH_2\}_6$

$R X^-$

$\overline{H^- OMoBr_4}$

Br_4MoO^-

$R^- OMoBr_4^-$

[1]

RX

(X=I or Br)

Br_4MoO^-
$\overline{(HBr-MoO_3)}$

$H^- OMoBr_4^-$

$CH_3 \langle SO_3H \rangle \quad HBF_4$

$+H \; (X^1)^-$

Br_4MoO^-

$\overline{H^- OMoBr_4} \quad H^- OMoBr_4^-$

[2] $X^1 = BF_4^-$

[3] $X^1 = CH_3\langle\;\rangle SO_3^-$

SCHEME 2.

TABLE 1. Composition of Polymer 1 and Oxidation of Borneol[a] with
t-BuOOH

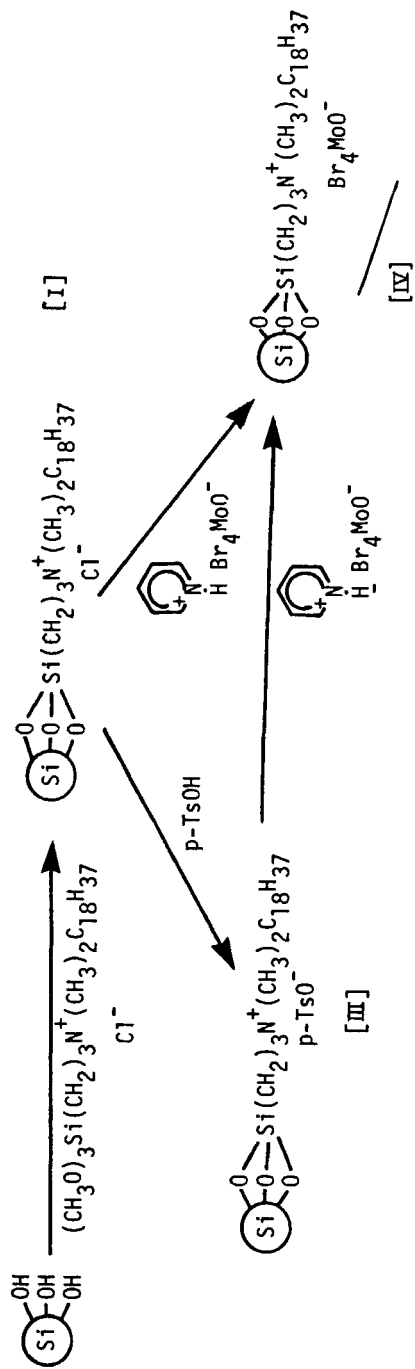| R	α[c]	β	γ	Yield of camphor, %	Reaction time, d[b]
—H	100	0	0	39	7
	82	17	0	71	2
	6	5	89	79	11
—CH$_3$	100	0	0	28	6
	74	26	0	52	12
	59	41	0	39 (70)	2 (2)
	36	25	39	73	13
—C$_4$H$_9$	56	44	0	66	2
	48	52	0	69	2
	20	34	46	78	4
—C$_8$H$_{17}$	15	37	48	53	1
	6	25	69	78 (81)	1 (1)
—C$_{12}$H$_{25}$	22	45	33	58	1
	3	26	71	86	1

[a]Yields and times for isoborneol in parentheses.
[b]Time for disappearance of t-BuOOH.
[c]X = Br, except for R = —CH$_3$ where X = I.

b. From Silica

Silica was functionalized with dimethyloctadecyl[3-(trimethoxysilyl)pro-
pyl] ammonium chloride. The functionalized silica was used as a support.
Br$_4$MoO$^-$ was immobilized in the silica modified by the same method as used
for poly-p-vinylpyridinium salts. The reaction is shown in Scheme 3. In this
case the exchange reaction of Br$_4$MoO$^-$ proceeded quantitatively, that is,
chloride or tosylate ion was stoichiometrically changed to Br$_4$MoO$^-$. It is
easy to appreciate why the reaction proceed quantitatively by considering
that the reactive sites on the silica are mainly confined to the surface [4] and
are more accessible to the reactants.

Si—OH
—OH
—OH

$(CH_3O)_3Si(CH_2)_3N^+(CH_3)_2C_{18}H_{37}$
Cl^-

Si=O
—O
—O
$Si(CH_2)_3N^+(CH_3)_2C_{18}H_{37}$
Cl^-

[I]

Si=O
—O
—O
$Si(CH_2)_3N^+(CH_3)_2C_{18}H_{37}$
p-TsO^-

[III]

p-TsOH

Si=O
—O
—O
$Si(CH_2)_3N^+(CH_3)_2C_{18}H_{37}$
Br_4MoO^-

[IV]

$\overset{+}{N}$
H Br_4MoO^-

$\overset{+}{N}$
H Br_4MoO^-

SCHEME 3.

Oxidation of Various Alcohols with t-BuOOH in the Presence of the Immobilized Catalyst

The results of the oxidation of borneol and isoborneol with t-BuOOH in the presence of the immobilized polymer are shown in Table 1. Halide ion as a counteranion of pyridinium accelerated the decomposition of t-BuOOH to depress the yield of camphor. Therefore, in order to investigate the difference between the oxidation of alcohol with t-BuOOH and the decomposition of t-BuOOH that was not followed by the oxidation of alcohol, we carried out the following experiment. When 2,6-dimethylphenol and 2,6-di-t-butylphenol were used as radical scavengers in the decomposition of t-BuOOH in the presence of poly-p-vinyl-N-methylpyridinium halide, the decomposition was restricted to a great extent. Consequently, this decomposition may be a radical-induced reaction.

The oxidation of alcohol was also carried out ionically as previously reported [2]. The selectivity for oxidation with t-BuOOH was dependent on the counteranion; the lower the contents of halide ion, the higher the selectivity for the oxidation of alcohols because of the depression of self-decomposition without the oxidation of alcohol. When Br_4MoO^- was immobilized in the polymer by the anion-exchange reaction with N-methylpyridinium tetrabromooxomolybdate, the halide content of the immobilized catalyst became smaller than that of the polymer reacted in the hydrogen bromide solution of Br_4MoO^-. The chain lengths of alkyl groups in N-alkylpyridinium groups exerted a favorable influence of the reactivity; the longer the carbon chain of the alkyl group, the higher the yield of camphor. Moreover, if the contents of bromide ion were low, the yield of camphor became higher. Also, for the dodecyl group under this reaction condition, the best results were observed because the dodecyl group acted as a hydrophobic group. Free pyridine nuclei were desirable for oxidation of alcohols, because pyridine nuclei were effective for association of hydrogen bromide generated from the decomposition of Br_4MoO^- and for the abstraction of the hydrogen of the hydroxyl group. Also, it may be considered that each pyridine group supports the activity of the immobilized molybdenum complex by abstracting protons from the alcohol-Br_4MoO^--t-BuOOH complex in a way similar to that proposed by Trost and Masuyama [5].

In order to oxidize alcohols effectively, it is essential to take an ionic reaction route rather than a radical one. When there were free pyridine nuclei in the polymer and the N-alkyl group was larger (dodecyl in this case), selectivity for alcohol oxidation became high. The relation between polymer structure and the oxidation of alcohol was examined, and the results are summarized in Table 2(a).

TABLE 2. Yields for Oxidation of Various Alcohols[a,b]

(a)

	Reaction time				
	24 h	2 d	12 h	2 d	1 d
A, %	12		47	39	78[c]
B, %	78	78[c]	81		81[c]

(b)

	Reaction time					
	24 h	2 d	3 d	24 h	5 d	13 d
A, %	14		21[c]	11		20[c]
B, %	23	28[c]		13	23[c]	

$C_6H_5COCHC_6H_5$ (OH) $\longrightarrow$ $C_6H_5CO-COC_6H_5$ (yield 93%, 3 d)[c]

[a] Reaction conditions: substrate, 3 mmol; t-BuOOH, 3 mmol; catalyst, 0.3 mmol; benzene, 3 cm^3.
[b] A: R = CH_3, $\alpha = 59$, $\beta = 41$, $\gamma = 0$. B: R = C_8H_{17}, $\alpha = 6$, $\beta = 25$, $\gamma = 69$.
[c] Time for disappearance of t-BuOOH.

Oxidation with the immobilized catalyst containing N-methyl groups showed the difference between borneol and isoborneol, as the activity of this immobilized catalyst was not very high. This difference can be understood when we consider that the steric rate acceleration came from strain differences in the transition state between borneol and isoborneol in a way similar to the chromic acid oxidation of alcohols [6]. But in the case of the immobilized polymer containing N-octyl groups, borneol and isoborneol were oxidized at similar rates. This behavior shows that the octyl group acts as a hydrophobic group and accelerates the oxidation of borneol and isoborneol. Also, free pyridinium groups may be available for the acceleration of borneol oxidation. We could not find any difference in the oxidation of menthol and isomenthol shown in Table 2(b), for the abstraction of hydride ions was hindered by the isopropyl group adjacent to the hydroxyl group and many difficulties arose in constituting a reactive intermediate among the immobilized catalyst, substrate, and hydroperoxide. The hydroxyl group of the benzyl position was easily oxidized. Thus, the reaction of benzoin afforded benzil in 93% yield, as shown in Table 2(b).
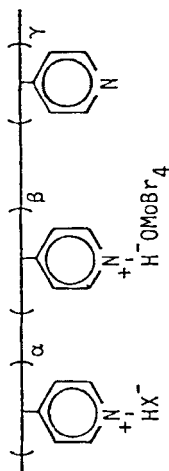
The Effect of the Counteranion

In order to minimize the content of halide in the immobilized catalyst, we treated poly-p-vinylpyridine with p-toluenesulfonic acid or tetrafluoroboric acid before anion exchange with pyridinium tetrabromooxomolybdate. This reaction is shown in Scheme 2. The structure of the immobilized polymer was confirmed by elemental analysis.

The results of oxidation of borneol by t-BuOOH in the presence of 2 or 3 are summarized in Table 3. High selectivity for the alcohol oxidation was obtained. The random radical decomposition could be suppressed by this exchange reaction.

Oxidation of Borneol by t-BuOOH in the Presence of Silica-Immobilized Br_4MoO^-

The results are summarized in Table 4. The counteranions were changed quantitatively. The activity for oxidation is relatively high. This is because inorganic polymers such as silica neither shrink nor swell in organic solvents because of their rigidity. On organic polymers which possess flexible backbones and swell with the reaction conditions, not all active groups are utilized. On the other hand, the active species on the rigid inorganic polymers, such as silica, are fully available because they are immobilized on the surface.

TABLE 3. Composition of the Polymer and Oxidation of Borneol and 1-Phenylethanol[a]

X⁻	α	β	γ	Camphor		Acetophenone, yield, %
				Yield, %	Selectivity,[b] %	
Cl⁻	38	22	39	36[c]	37	
BF_4^- 2	38	22	39	30[c]	98	74[e]
$p\text{-}CH_3C_6H_4SO_3^-$ 3	75	22	3	38[d]	92	59[e]

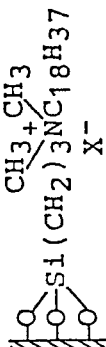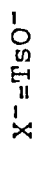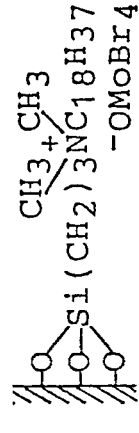[a]t-BuOOH, 3 mmol; substrate, 3 mmol; benzene, 3 cm³; catalyst, 0.07 g.
[b][Yield of camphor (%)/Decomposition of t-BuOOH (%)] × 100.
[c]Reaction time: 6 days.
[d]Reaction time: 5 days.
[e]Reaction time: 3 days.

TABLE 4. Oxidation of Borneol and Decomposition of t-BuOOH[a]

Catalyst		(A) Yield of camphor (%)[b]	(B) Decomposition of t-BuOOH (%)[b]	(A)/(B) × 100
$\underset{\text{Si(CH}_2)_3\text{NC}_{18}\text{H}_{37}}{\overset{\text{CH}_3\text{+CH}_3}{\diagdown\diagup}}$ X⁻ X⁻=Cl⁻	[II]	30	92	33
X⁻=TsO⁻	[III]	7	8	88
$\underset{\text{Si(CH}_2)_3\text{NC}_{18}\text{H}_{37}}{\overset{\text{CH}_3\text{+CH}_3}{\diagdown\diagup}}$ ⁻OMoBr₄	[IV]	89	100	89

[a]Substrate, 3 mmol; t-BuOOH, 3 mmol; catalyst, 0.15 mmol; benzene, 7 mL; 60°C; reaction time, 24 h.
[b]Yields were determined by GC.

Because of this reactivity difference, the exchange (immobilization) of Br_4MoO^- proceeded quantitatively, and the reactivity for the oxidation of alcohol was higher than that of the organic polymer supports.

CONCLUSIONS

By the immobilization of Br_4MoO^- in polyvinylpyridine or modified silica, we could obtain a good catalyst for oxidation by t-BuOOH. In order to oxidize alcohols effectively, it is essential to take an ionic reaction route rather than a radical one. When there are free pyridine nuclei in the polymer and the N-alkyl group is larger (dodecyl group in this case), activity and selectivity for alcohol oxidation became high. For inorganic polymer as carrier, all active groups are well utilized in the reaction and high activity is observed. The best carrier for the oxidation catalyst Br_4MoO^- is a silica modified with a silica coupling reagent (octadecyldimethyl[3-(trimethoxysilyl)propyl] ammonium chloride).

ACKNOWLEDGMENT

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