

# Anion activation by quaternary onium salts and polyether ligands in homogeneous and heterogeneous systems

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**Abstract** - Anion activation realized by quaternary onium salts or complexes of lipophilic polyetheral ligands is particularly high in low polarity media due to the low interaction with the bulky cation and the scarce solvation. Reactivity follows the order: quaternary salt < crown ether < cryptand. Under liquid-liquid phase-transfer catalysis (LL-PTC) conditions the reactivity observed is mainly determined by the specific solvation of the anion by a limited number of water molecules. Removal of this hydration sphere remarkably increases anionic reactivity, especially for anions with high charge density (OH<sup>-</sup>, F<sup>-</sup>).

## INTRODUCTION

Anion promoted reactions represent a large and important part of organic chemistry and include aliphatic and aromatic nucleophilic substitutions, eliminations, C-, O- and N-alkylations, oxidations, reductions, etc..

These reactions are usually performed in homogeneous media that solubilize both the substrate and the salt source of the anion. Under these conditions the solvent (protic, dipolar aprotic) is found to play a major role in determining the anionic reactivity (1). Often an appropriate choice of the medium leads to remarkable enhancements in the reaction rate.



Passing from the polar protic solvent water to the dipolar non-hydrogen bond donor DMF the rate constant of the reaction 1 increases by 5 powers of ten, mainly because of the reduced solvation of the anion in the latter medium. On the other hand nucleophilicity of the chloride, solvated by DMF or water, is 10-15 orders of magnitude lower than that of the corresponding "naked" Cl<sup>-</sup> in gas-phase (1). Comparison of the activation energy in water (103 kJ mol<sup>-1</sup>) and the gas phase (11 kJ mol<sup>-1</sup>) indicates that reaction rates in solution are primarily determined by the quantity of energy necessary to destroy the solvation shell of the anion in the activation process and, to a lesser extent, by the intrinsic properties of the reactants (1).

The association with the corresponding cation has proved to be another important factor that affects anionic reactivity. The ion paired anion is usually found to be less reactive than the corresponding free ion (1).

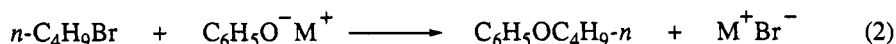
## ANIONIC REACTIVITY IN HOMOGENEOUS MEDIA

According to Coulomb's law, in solvents of low dielectric constant, where ion pair or ion pair aggregates are mostly present, the interaction energy between cation and anion can be minimized by increasing the interionic distance. This can be realized by using: (i) bulky quaternary onium instead of small metal cations; (ii) specific cation solvators (EPD solvents of high Lewis basicity); (iii) cation complexing agents [macro(poly)cyclic ligands such as crown ethers, cryptands].

As a consequence the reactivity of the anion is expected to increase (1).

The use of lipophilic quaternary onium salts in low polarity media allows the study of anionic reactivity under conditions that approach those of the gas phase.

As found by Ugelstad *et al.* (2) the rate of reaction 2 is always higher with the quaternary Bu<sub>4</sub>N<sup>+</sup> than with the potassium cation whatever the solvent (Table 1).



Moreover whereas with potassium phenoxide the rate constants greatly depend on the dielectric constant ( $\epsilon$ ) of the solvent, they are independent of the medium with Bu<sub>4</sub>N<sup>+</sup>C<sub>6</sub>H<sub>5</sub>O<sup>-</sup>. This means that, in dioxane, phenoxide anion associated with the bulky quaternary ammonium cation is already very reactive as an ion pair.

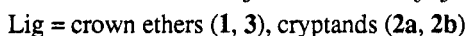
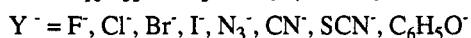
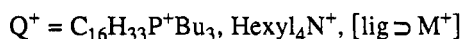
TABLE 1. Influence of interionic distance ( $r$ ) and dielectric constant ( $\epsilon$ ) on the reactivity of C<sub>6</sub>H<sub>5</sub>O<sup>-</sup>M<sup>+</sup> (M<sup>+</sup> = K<sup>+</sup>, Bu<sub>4</sub>N<sup>+</sup>) ion pairs [reaction 2].

Solvent	$\epsilon$	$k \times 10^5/\text{M}^{-1}\text{s}^{-1}$		$k_{\text{Bu}_4\text{N}^+}/k_{\text{K}^+}$
		K <sup>+</sup>	Bu <sub>4</sub> N <sup>+</sup>	
Dioxane	2.2	0.01	330	33,000
Acetonitrile	36	40	300	7.5

TABLE 2. Relative reactivities ( $k_{\text{soln}}/k_{\text{DMSO}}$ ) in solvents of different polarity in the reaction of *n*-octyl methanesulphonate with C<sub>16</sub>H<sub>33</sub>P<sup>+</sup>Bu<sub>3</sub>Y<sup>-</sup>, at 60 °C.

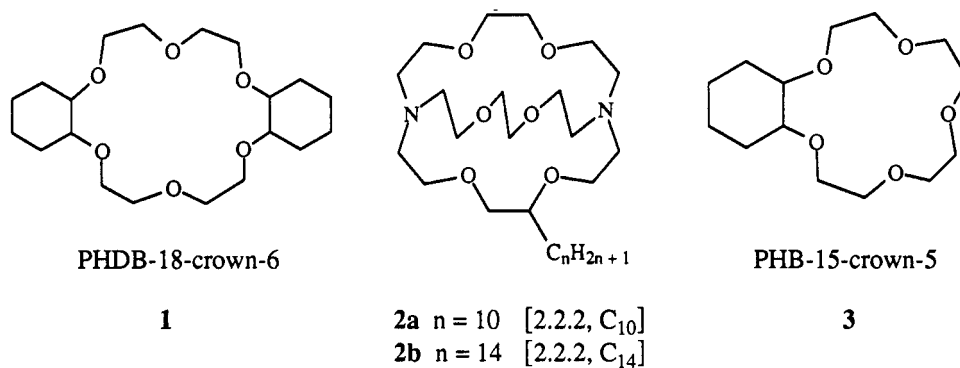
Y <sup>-</sup>	DMSO ( $E_{\text{T}}^{\text{N}} = 0.444$ )	C <sub>6</sub> H <sub>5</sub> Cl ( $E_{\text{T}}^{\text{N}} = 0.188$ )	Cyclohexane ( $E_{\text{T}}^{\text{N}} = 0.006$ )
N <sub>3</sub> <sup>-</sup>	1	6	33
CN <sup>-</sup>	1	2.7	19
Cl <sup>-</sup>	1	5.5	30
Br <sup>-</sup>	1	4	18
I <sup>-</sup>	1	5.5	31
SCN <sup>-</sup>	1	3	13

Nucleophilicity of a series of tributylhexadecylphosphonium salts has been measured in the aliphatic S<sub>N</sub>2 reaction 3 in solvents of different polarity (3, 4).



Data of Table 2 indicate that reactivity of all the anions increases about 3-6 times passing from DMSO to chlorobenzene. More pronounced enhancements (up to 33 fold) are found in the even less polar cyclohexane. Since quaternary salts are mostly dissociated in DMSO (5, 6), whereas they are present as ion-pairs or ion-pair aggregates in solvents of low polarity, the results emphasize the remarkable reactivity of these "loose" ion-pairs in scarcely solvating media. This largely overcomes the unfavourable effects of the ion pairing (4).

Lipophilic polyether ligands (crown ethers, cryptands such as 1-3) are known to form stable inclusion complexes with alkali and alkaline-earth metal salts in weakly polar solvents. In the complexation process a small metal cation M<sup>+</sup> is transformed into a voluminous cation, [Lig ⊃ M<sup>+</sup>], which is much more soluble in organic medium. The associated anion is expected to be noticeably activated since both ion pairing with the bulky complexed cation and the scarce interaction with the solvent provide only little stabilization.



Nucleophilic reactivity of the complexes of crown ether PHDB-18-crown-6 (**1**) and cryptand [2.2.2, C<sub>14</sub>] (**2b**) with potassium salts KY (Y = N<sub>3</sub>, Cl, Br, I, SCN) in chlorobenzene have been compared with that of the corresponding quarternary phosphonium salts C<sub>16</sub>H<sub>33</sub>P<sup>+</sup>Bu<sub>3</sub>Y<sup>-</sup> [reaction 3] (Table 3) (3, 7-9).

TABLE 3. Anion reactivity of quarternary salts C<sub>16</sub>H<sub>33</sub>P<sup>+</sup>Bu<sub>3</sub>Y<sup>-</sup> and complexes (Lig ⊃ K<sup>+</sup>) Y<sup>-</sup> in the S<sub>N</sub>2 reaction 3 in chlorobenzene, at 60 °C.

Y <sup>-</sup>	k × 10 <sup>3</sup> /M <sup>-1</sup> s <sup>-1</sup>		
	C <sub>16</sub> H <sub>33</sub> P <sup>+</sup> Bu <sub>3</sub>	(PHDB-18-crown-6 ⊃ K <sup>+</sup> )	(2.2.2, C <sub>14</sub> ⊃ K <sup>+</sup> )
N <sub>3</sub> <sup>-</sup>	70 <sup>a</sup>	89 <sup>b</sup>	150 <sup>c</sup>
Cl <sup>-</sup>	20 <sup>a</sup>	12 <sup>d</sup>	51 <sup>c</sup>
Br <sup>-</sup>	8.1 <sup>a</sup>	13 <sup>b</sup>	37 <sup>c</sup>
I <sup>-</sup>	3.0 <sup>a</sup>	9.2 <sup>b</sup>	14.5 <sup>d</sup>
SCN <sup>-</sup>	0.75 <sup>a</sup>	1.1 <sup>b</sup>	1.5 <sup>c</sup>

<sup>a</sup> From ref. 3 <sup>b</sup> From ref. 7 <sup>c</sup> From ref. 8 <sup>d</sup> Unpublished results, see ref. 9

Results show that by replacing the quarternary C<sub>16</sub>H<sub>33</sub>P<sup>+</sup>Bu<sub>3</sub> cation with the bulkier [Lig ⊃ K<sup>+</sup>] the nucleophilicity of the anions generally increases, up to 2-5 times in the case of the lipophilic cryptates [(2.2.2, C<sub>14</sub>) ⊃ K<sup>+</sup>]Y<sup>-</sup>. The enhancements found, in the order: quarternary salt < crown ether < cryptand, are mainly due to the increased cation-anion separation induced by these ligands. The nucleophilicity scale obtained with cryptates of **2b** (N<sub>3</sub><sup>-</sup> > Cl<sup>-</sup> > Br<sup>-</sup> > I<sup>-</sup> > SCN<sup>-</sup>), the same as for quarternary phosphonium salts, is slightly modified with complexes of crown ether **1** (N<sub>3</sub><sup>-</sup> > Br<sup>-</sup> ~ Cl<sup>-</sup> > I<sup>-</sup> > SCN<sup>-</sup>). Moreover with the latter ligand the reactivity spans a very narrow range, especially for halide ions (Cl<sup>-</sup>:Br<sup>-</sup>:I<sup>-</sup> = 1.3:1.4:1). Such behaviour is mainly due to the different topology of polyethers. Cryptates, where the metal cation is fully wrapped in the cavity of the ligand which replaces its first sphere of solvation, give rise to a very reactive "solvent-separated" ion pair. Conversely, in the crown ether complexes the ligand does not induce a large cation-anion separation. In this case the complexed cation is still accessible for interaction with the anion in a tighter "crown-separated" ion pair. By increasing the charge density of cation and/or anion the ion pair becomes progressively more intimate and hence less reactive, as found (Table 3) in the series of potassium halides (10).

These ligands have proved to be an effective tool for ascertaining the participation of the metal cation in anion-promoted reactions. In fact, if a cation catalyzes a reaction, its complexation is expected to decrease reaction rates. Again, the topology of the polyether plays a determinant role. As reported in

Table 4 the rate constants of reaction 3 promoted by cryptates  $[(2.2.2, C_{10}) \supset M^+]I^-$  ( $M^+ = Li^+, Na^+, K^+$ ) are independent of the cation whereas they increase, up to 8 times, with the complexes of PHB-15-crown-5 (3) in the order  $k_{KI} < k_{NaI} < k_{LiI}$  (9). Since cryptands are well known to be among the best anion activators the lower rate constant values observed in this case are clear proof of the electrophilic assistance of the metal cation. Moreover it is important to emphasize (Table 4) the much higher reactivity (about 130 times), due to cation assistance, of the ion pair  $[(PHB-15-crown-5) \supset Li^+] I^-$  in toluene with respect to that of the free  $I^-$ , solvated by DMF (9).

TABLE 4. Effect of the metal cation in the reaction 3 promoted by complexes  $(PHB-15-crown-5 \supset M^+) I^-$  and  $(2.2.2, C_{10} \supset M^+) I^-$  in chlorobenzene, at 60 °C<sup>a</sup>.

Lig	$k \times 10^3/M^{-1}s^{-1}$		
	Li <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>
PHB-15-crown-5 3	126 <sup>b</sup> (230) <sup>c</sup>	22 <sup>b</sup> (59) <sup>c</sup>	18 <sup>b</sup>
2.2.2, C <sub>10</sub> 2a	15.3	14.6	14.5

<sup>a</sup> Unpublished results, see ref. 9 <sup>b</sup> In DMF the same rate constants are found for LiI, NaI, and KI, *ie*  $k = 1.8 \times 10^{-3}/M^{-1}s^{-1}$

<sup>c</sup> Data in toluene, see ref. 9.

TABLE 5. Anionic reactivity under PTC conditions and in anhydrous chlorobenzene in the reaction of *n*-octyl methanesulphonate with various nucleophiles ( $Y^-$ ), at 60 °C.

Y <sup>-</sup>	Hydration number <i>n</i> , of $Q^+Y^- \cdot n H_2O$	$k \times 10^3/M^{-1}s^{-1}$	
		PTC (C <sub>6</sub> H <sub>5</sub> Cl-H <sub>2</sub> O)	anhydr. C <sub>6</sub> H <sub>5</sub> Cl
F <sup>-</sup>	8.5 <sup>b</sup>	2.3	1890
Cl <sup>-</sup>	3.4 <sup>c</sup>	1.8	19.7
Br <sup>-</sup>	2.1 <sup>c</sup>	3.2	8.1
I <sup>-</sup>	1.0 <sup>c</sup>	2.8	3.0
CN <sup>-</sup>	5.0 <sup>c</sup>	11.7	86.7
C <sub>6</sub> H <sub>5</sub> O <sup>-</sup>	4.0 <sup>d</sup>	8.7	650

<sup>a</sup> From C<sub>16</sub>H<sub>33</sub>P<sup>+</sup>Bu<sub>3</sub>Y<sup>-</sup> or Hexyl<sub>4</sub>N<sup>+</sup>Y<sup>-</sup>. <sup>b</sup> From ref. 17.

<sup>c</sup> From ref. 3. <sup>d</sup> From ref. 10.

#### ANIONIC REACTIVITY UNDER LIQUID-LIQUID PHASE-TRANSFER CATALYSIS (LL-PTC) CONDITIONS

Anion-promoted reactions can also be performed in water/organic two-phase systems under conditions of phase-transfer catalysis. The mechanism of LL-PTC was initially proposed by Starks (11) and then fully explained through liquid membranes (12) and kinetic experiments (3, 10, 13). Following this mechanism a quaternary salt or a lipophilic cation complexing agent, present in catalytic amounts, transfers the water soluble anionic species across the interface into the organic phase where the reaction occurs. Under these conditions anions are extracted into the organic medium specifically solvated by a limited number (1-11 moles *per* mol of  $Q^+Y^-$ ) of water molecules. This hydration sphere, characteristic of each anion, always reduces, more or less noticeably, anionic reactivity. As shown in Table 5, changing from PTC (chlorobenzene-water) to anhydrous homogeneous (chlorobenzene) conditions, nucleophilicity of a representative series of quaternary salts increases, particularly in the case of anions with high charge density and hence more hydrated (3, 10).

Reactivity of the homogeneous anhydrous phase can be reproduced under LL-PTC conditions by using concentrated aqueous alkaline solutions. These solutions (50% aq NaOH, 60% aq KOH), where the water activity  $[a(H_2O)]$  tends to zero, were found to be very efficient systems for extracting into the organic phase anions largely or completely "nonhydrated" (Table 6) (10, 14).

TABLE 6. Second-order rate constants for the reaction of *n*-octyl methanesulphonate with various nucleophiles (Y<sup>-</sup>)<sup>a</sup> in C<sub>6</sub>H<sub>5</sub>Cl-H<sub>2</sub>O and C<sub>6</sub>H<sub>5</sub>Cl-50% aq NaOH two-phase systems and in anhydrous chlorobenzene at 35 °C.

Y <sup>-</sup>	k x 10 <sup>3</sup> /M <sup>-1</sup> s <sup>-1</sup>		
	PTC		
	C <sub>6</sub> H <sub>5</sub> Cl-H <sub>2</sub> O	C <sub>6</sub> H <sub>5</sub> Cl-50% aq NaOH	anhydr. C <sub>6</sub> H <sub>5</sub> Cl
N <sub>3</sub> <sup>-</sup>	2.9	11.6	11.7
Cl <sup>-</sup>	0.26	3.4	3.4
Br <sup>-</sup>	0.42	1.1	1.1
I <sup>-</sup>	0.29	0.42	0.45

<sup>a</sup> From Octyl<sub>4</sub>N<sup>+</sup>Y<sup>-</sup>.

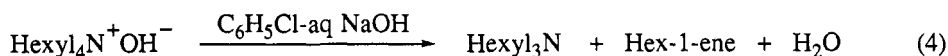
TABLE 7. Effect of the specific hydration on the basicity of OH<sup>-</sup> in the Hofmann elimination reaction of Hexyl<sub>4</sub>N<sup>+</sup>OH<sup>-</sup>·*n*H<sub>2</sub>O, at 25 °C.

NaOH%	Hydration state <i>n</i> , of Q <sup>+</sup> OH <sup>-</sup> · <i>n</i> H <sub>2</sub> O	k <sub>rel</sub>
15	11.0	(1)
30	5.0	(39)
40	4.0	(1.4 x 10 <sup>3</sup> )
50	3.5	(1.1 x 10 <sup>4</sup> )
solid	3.0	(5 x 10 <sup>4</sup> )
	0.0	(4 x 10 <sup>9</sup> ) <sup>a</sup>

<sup>a</sup> Extrapolated value.

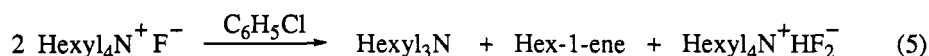
### SPECIFIC SOLVATION AND REACTIVITY OF VERY HYDROPHILIC ANIONS (OH<sup>-</sup>, F<sup>-</sup>)

The reactivity of anions with high charge density, like OH<sup>-</sup> and F<sup>-</sup>, is dramatically affected by the specific interaction with protic species like water.



Basicity of OH<sup>-</sup> in the Hofmann elimination reaction of Hexyl<sub>4</sub>N<sup>+</sup>OH<sup>-</sup>·*n*H<sub>2</sub>O [reaction 4], carried out in the chlorobenzene-aqueous NaOH two-phase system, increases 50,000 times by reducing the hydration number *n* of the anion from 11 to 3 (Table 7). The enhancement is extrapolated to be more than nine powers of ten in the hypothetical case of anhydrous hydroxide (15). Interestingly the reactivity differences found are comparable with those obtained by Bohme (16) in reactions promoted by clusters OH<sup>-</sup>·*n*H<sub>2</sub>O, in the range *n* = 0-3 (5,000 times) in the gas phase. In a low polarity medium, the largely dehydrated OH<sup>-</sup> extracted from concentrated alkaline solutions is therefore an extremely powerful base. Our results account for the dramatic effect produced by an increase of base on the rate of reactions promoted by alkali hydroxides under LL-PTC conditions, such as carbanion formation and alkylation, alkene isomerization, H/D exchanges in carbon acids, and acid-base equilibria.

The reactivity of fluoride is also noticeably affected by the specific hydration both as a base and as a nucleophile. By reducing the hydration number *n* of Hexyl<sub>4</sub>N<sup>+</sup>F<sup>-</sup>·*n*H<sub>2</sub>O (from 4.6 to 0) the rate of the Hofmann-like elimination 5 increases by more than seven orders of magnitude (Table 8) (17). Analogously, nucleophilicity of Hexyl<sub>4</sub>N<sup>+</sup>F<sup>-</sup>·*n*H<sub>2</sub>O increases of about 3 powers of ten (Table 9) by completely removing the hydration sphere *n* of the fluoride [reaction 3].



Results show that, in the same hydration range (*n* = 0-3) basicity of the F<sup>-</sup> ion (Table 8) is much more affected by specific hydration than its nucleophilicity is (Table 9) (Δk<sub>basicity</sub>/Δk<sub>nucleophilicity</sub> ~ 10<sup>4</sup>). This clearly indicates the virtual impossibility to obtain "naked" tetraalkylammonium fluorides due to their instability both as pure products and in solutions of anhydrous aprotic solvents (17). Comparison with quaternary ammonium poly(hydrogenfluorides) Hexyl<sub>4</sub>N<sup>+</sup>HF<sub>2</sub><sup>-</sup> and Hexyl<sub>4</sub>N<sup>+</sup>H<sub>2</sub>F<sub>3</sub><sup>-</sup>, considered alternative sources of F<sup>-</sup> (18) and HF (19), gave the following nucleophilicity sequence: F<sup>-</sup> >> F<sup>-</sup>·*n*H<sub>2</sub>O > HF<sub>2</sub><sup>-</sup> > H<sub>2</sub>F<sub>3</sub><sup>-</sup> (17). Reactivity of the tetrahydrated Hexyl<sub>4</sub>N<sup>+</sup>F<sup>-</sup>·4H<sub>2</sub>O is, in particular, 17 and 2,000 times higher than that of the anhydrous HF<sub>2</sub><sup>-</sup> and H<sub>2</sub>F<sub>3</sub><sup>-</sup> respectively (17). According to

TABLE 8. Influence of the specific hydration of the F<sup>-</sup> anion on its basicity in the Hofmann-like elimination reaction of Hexyl<sub>4</sub>N<sup>+</sup>F<sup>-</sup>·nH<sub>2</sub>O, at 60 °C.

Hydration state <i>n</i> , of Q <sup>+</sup> F <sup>-</sup> ·nH <sub>2</sub> O	<i>k</i> × 10 <sup>5</sup> /s <sup>-1</sup>	<i>k</i> <sub>rel</sub>
4.6	0.005	(1)
3.2	0.035	(7)
2.0	9.5	(1.9 × 10 <sup>3</sup> )
1.7	38	(7.6 × 10 <sup>3</sup> )
0	1.2 × 10 <sup>5</sup> <sup>a</sup>	(2.3 × 10 <sup>7</sup> )

<sup>a</sup> Extrapolated value.

TABLE 9. Effect of specific hydration of F<sup>-</sup> anion on its nucleophilicity in the substitution reaction 3, at 60 °C.

Hydration state <i>n</i> , of Q <sup>+</sup> F <sup>-</sup> ·nH <sub>2</sub> O	<i>k</i> × 10 <sup>3</sup> /M <sup>-1</sup> s <sup>-1</sup>	<i>k</i> <sub>rel</sub>
8.5	2.3	(1)
4.0	4.3	(2)
2.6	46	(20)
1.5	220	(96)
0.0	1890 <sup>b</sup>	(822)

<sup>a</sup> From Hexyl<sub>4</sub>N<sup>+</sup>F<sup>-</sup>·nH<sub>2</sub>O. <sup>b</sup> Extrapolated value.

these data the partially hydrated Q<sup>+</sup>F<sup>-</sup>·nH<sub>2</sub>O (*n* = 3, 4) can always be considered the fluorinating agent of choice in low polarity solvents, whereas the slightly less reactive quaternary hydrogen difluoride Q<sup>+</sup>HF<sub>2</sub><sup>-</sup> can be alternatively used in rigorously anhydrous media.

### CONCLUSION

Quaternary onium salts and lipophilic polyether ligands, like crown ethers or cryptands, give rise to extremely reactive ion pairs in solvents of low polarity. Due to the scarce stabilization by the medium and the low interaction with the bulky cation the reactivity of these ion pairs is even higher than that observed in dipolar aprotic solvents where mostly free ions are present.

Analogously, phase-transfer catalysis has proved to be a simple and powerful anion-activating system. In this case, however, the specific solvation of the anions by a limited number of water molecules remarkably reduces their reactivity. Anion activation of the anhydrous homogeneous phase can be realized under liquid-liquid PTC conditions with concentrated aqueous alkaline solutions where the anions are transferred into the organic medium largely or completely dehydrated.

The reactivity observed is probably the highest attainable in solution, approaching that of the gas phase.

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