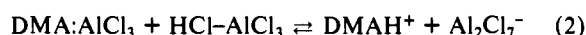


**Figure 2.** The  $^1\text{H}$  NMR spectra of DMA in acidic melts at  $20\text{ }^\circ\text{C}$ : (a and b) the  $^1\text{H}$  resonance of the dimethylanilinium N-H proton and  $\text{N}(\text{CH}_3)_2$  protons, respectively, in the presence of excess  $\text{ImHCl}_2$ ; (c) the  $^1\text{H}$  resonance of the  $\text{N}(\text{CH}_3)_2$  protons for a mixture of  $\text{DMAH}^+$  and  $\text{DMA}:\text{AlCl}_3$ . (The chemical shifts are in ppm referenced to TMS in a coaxial tube.)

DMA to produce a protonated species,  $\text{DMAH}^+$ .

It has been proposed that the proton in acidic chloroaluminate molten salts exists as  $\text{HCl}$ .<sup>4a</sup> Recent results indicate, however, that while small amounts of "free"  $\text{HCl}$  are present in acidic melts, the proton appears to exist primarily in an as yet unidentified "acidic" form.<sup>7</sup> Thus, for the sake of the following discussion we choose to write the "acidic" form of the proton as  $\text{HCl}:\text{AlCl}_3$ . (Mixtures of  $\text{HCl}$  and  $\text{AlCl}_3$  appear to have acidities in the range of what is considered a Brønsted superacid.<sup>8,9</sup>) Consequently, the reaction of the proton with  $\text{DMA}:\text{AlCl}_3$  is



When the added proton concentration is less than the DMA concentration, the observed NMR spectrum is simply the superposition of the spectra of  $\text{DMAH}^+$  and  $\text{DMA}:\text{AlCl}_3$  (Figure 2c), indicating the exchange between  $\text{DMAH}^+$  and  $\text{DMA}:\text{AlCl}_3$  is slow on the NMR time scale. Our preliminary results indicate that while  $\text{HCl}:\text{AlCl}_3$  is a much stronger acid than  $\text{Al}_2\text{Cl}_7^-$ , acidic melts contain an equilibrium mixture of  $\text{DMAH}^+$  and  $\text{DMA}:\text{AlCl}_3$  (reaction 2).

Previous studies of proton transfer to DMA have shown that, even in strong aqueous acids, the process is diffusion controlled.<sup>10</sup> However, in acidic chloroaluminate molten salts, when excess proton is added, the dimethylanilinium  $\text{N}(\text{CH}_3)_2$  protons (figure 2b) exhibit a doublet, demonstrating proton transfer on  $\text{DMAH}^+$  is slow. The apparent slow proton transfer could result from the highly acidic, and as yet unknown, nature of protons in this solvent, the presence of a complexing Lewis acid, or a combination of both. We are currently studying proton transfer reactions of DMA and other bases in this new superacid medium in an attempt to gain further understanding of the problem.

**Acknowledgment.** We acknowledge helpful discussions about this work with Prof. Calvin D. Ritchie. This work was supported in part by the Air Force Office of Scientific Research. Portions of the electrochemical experiments cited here were carried out by Dr. S.-G. Park.

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## High Turnover Rates in pH-Dependent Alkene Epoxidation Using $\text{NaOCl}$ and Square-Planar Nickel(II) Catalysts

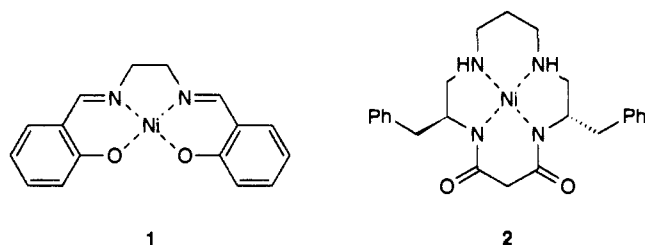
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Received August 8, 1989

Revised Manuscript Received February 9, 1990

Transition-metal-catalyzed transfer of oxygen atoms to organic substrates is of interest in the study of bioinorganic mechanisms and the development of efficient catalysts for laboratory and industrial organic synthesis.<sup>1</sup> Certain nickel(II) catalysts have recently joined the plethora of metalloporphyrin complexes capable of facilitating this reaction using  $\text{OCl}^-$ ,  $\text{PhIO}$ , or  $\text{KHSO}_5$  as terminal oxidant.<sup>2,3</sup> These studies were undertaken because of the intriguing possibility that a heretofore unprecedented high-valent nickel-oxo species may be responsible for substrate oxidation.<sup>4</sup> The only known high-valent oxide of nickel is the poorly characterized nickel(III) peroxide formed from  $\text{Ni}^{2+}$  salts and basic hypochlorite.<sup>5</sup> Here, we report an unusual pH dependence of the  $\text{OCl}^-$ -based reactions which leads to dramatic rate accelerations in olefin epoxidation at reduced pH.



We previously described the use of  $\text{NaOCl}$  under phase-transfer conditions in the presence of  $\text{Ni}^{\text{II}}(\text{salen})$  (1)<sup>2c</sup> or  $\text{Ni}^{\text{II}}(\text{dibenzyl-dioxocyclam})$  (2)<sup>2d,e</sup> as an alkene epoxidation system. At pH 12.5, epoxidation is slow, requiring 4-5 h for 20-40 turnovers of catalyst. As indicated in Figure 1, the epoxidation of styrene is dramatically accelerated by lowering the pH of the aqueous phase to 9.3 (curve C). Using 2.5 mol % catalyst, >20 turnovers to give epoxide occur in 15 min. A pH-rate profile of the reaction showed an inverted bell-shaped curve with a maximum at 9.3. Similarly, addition of certain  $\text{CH}_2\text{Cl}_2$ -soluble weak acids also increased the reaction rate. For example, the use of a 2:1 ratio of  $\text{salen}:\text{Ni}(\text{salen})$  provided nearly the same rate enhancement as lowering the pH (curve B). In addition to  $\text{salen}$ , both *o*- and *p*-salicylaldehydes ( $\text{p}K_a$  6.8 and 7.7, respectively) were effective as additives, while catalytic amounts of simple phenols, electron-rich phenols (2,6-di-*tert*-butyl-*p*-cresol), and water-soluble phenols (*p*-nitrophenolate) were ineffective. A combination of both lowering the pH and addition of  $\text{salen}$  led to the highest reaction rate (curve D).

Reaction conditions were optimized for one of the more reactive substrates, *trans*- $\beta$ -methylstyrene (see Table I).<sup>6</sup> Under the best

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Table I. Turnover Numbers and Selectivity of Alkene Epoxidation Using NaOCl and Ni<sup>II</sup> Catalysts

entry	catalyst (mol %) <sup>a</sup>	pH	salen mol % <sup>b</sup>	substrate	conversn, <sup>c</sup> %	epoxide	
						select., <sup>d</sup> %	turnover no., min <sup>-1</sup>
1	1 (2.5)	12.5	0	norbornene	94	32	0.040
2	1 (2.5)	9.3	7.5	norbornene	100	23	1.8
3	1 (2.5)	12.5	0	( <i>E</i> )-PhCH=CHCH <sub>3</sub>	100	89	0.15
4	1 (0.063)	9.3	1.5	( <i>E</i> )-PhCH=CHCH <sub>3</sub>	100	69	221
5	1 (0.013)	9.3	0.3	( <i>E</i> )-PhCH=CHCH <sub>3</sub>	100	27	432
6	1 (0.013) <sup>e,f</sup>	9.3	0.3	( <i>E</i> )-PhCH=CHCH <sub>3</sub>	63	76	640
7	2 (1.0)	12.5	g	( <i>E</i> )-PhCH=CHCH <sub>3</sub>	30	53	0.047
8	2 (1.0)	9.3	g	( <i>E</i> )-PhCH=CHCH <sub>3</sub>	100	45	9.0
9	2 (2.5)	12.5	g	cyclohexene	100	13	0.17
10	2 (2.5)	9.3	g	cyclohexene	100	16	0.21
11	Fe(TDCPP)Cl (0.063) <sup>g</sup>	9.3	0	( <i>Z</i> )-PhCH=CHCH <sub>3</sub>	78	87 <sup>h</sup>	218

<sup>a</sup> (Moles of catalyst/moles of alkene) × 100. <sup>b</sup> (Moles of additional salen/moles of alkene) × 100. <sup>c</sup> Disappearance of alkene. <sup>d</sup> Epoxide/total products. <sup>e</sup> Slow addition of NaOCl at a rate of 1 equiv of NaOCl per alkene per minute. <sup>f</sup> Results after 5 min of reaction time. <sup>g</sup> Additives such as salicylaldehyde had little effect on the reaction. <sup>h</sup> Greater than 99% *Z* epoxide.

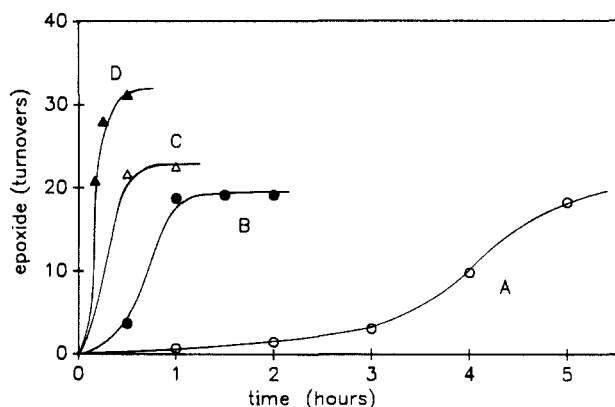


Figure 1. Effect of pH and additives on activity of Ni<sup>II</sup>(salen)-catalyzed epoxidation of styrene using 2.5 mol % 1: curve A, pH 12.5, no additives; curve B, pH 12.5, 7.5 mol % salen added; curve C, pH 9.3 (borate buffer), no additives; curve D, pH 9.3 (borate buffer), 7.5 mol % salen added.

conditions, pH 9.3, addition of salen, and slow addition of OCl<sup>-</sup> (entry 6), this substrate could be epoxidized at a rate of 3840 turnovers of 1 in 6 min. This rate is similar to that observed for epoxidation catalyzed by Mn<sup>III</sup> tetraarylporphyrins using OCl<sup>-</sup><sup>7</sup> although still somewhat slower than the best ferric porphyrin/iodosylarene systems.<sup>8</sup> Comparison with the Fe<sup>III</sup> complex of tetra(2,6-dichlorophenyl)porphyrin (TDCPP) is given by entries 4 and 11 in Table I. Epoxidation of aliphatic alkenes also displayed a high pH dependence on rate; however, the selectivity for epoxidation compared to other products was much lower than with the arylalkanes. The major side product was the product of chlorination of the alkene in a nickel-independent reaction. In fact, chlorination eventually overwhelms epoxidation for all substrates if the pH is lowered below 8.

Control studies were carried out to ensure that the epoxidation reaction is metal-dependent, independent of other oxidants such as O<sub>2</sub>, and that the reaction occurs only in the organic phase.<sup>9</sup> In another experiment, alkene and 1 were added to a solution of

(6) In typical reaction conditions, a solution of 4 mmol of alkene, 0.15 mmol of benzyltributylammonium bromide, and 0.001–0.1 mmol of nickel catalyst in 10 mL of CH<sub>2</sub>Cl<sub>2</sub> was stirred at room temperature with 20 mL of 0.77 M NaOCl at pH 9.3 (borate buffer). GC analysis using *o*-dichlorobenzene as internal standard gave the results listed in Table I.

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(9) In a transport-type experiment, two CH<sub>2</sub>Cl<sub>2</sub> solutions containing alkene and phase-transfer catalyst were connected by an aqueous NaOCl solution. Epoxidation occurred only in one CH<sub>2</sub>Cl<sub>2</sub> solution which also contained Ni<sup>II</sup>(salen).

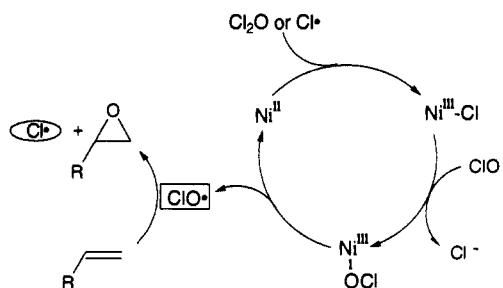
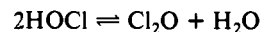


Figure 2. Possible mechanism for generation of ClO•, an epoxidizing agent, and Cl•, a chlorinating agent, from square-planar Ni<sup>II</sup> complexes. Ligands around Ni are omitted for clarity.

anhydrous Bu<sub>4</sub>N<sup>+</sup>OCl<sup>-</sup> in CH<sub>2</sub>Cl<sub>2</sub>. No epoxide was formed after 30 min; however, upon addition of excess benzoic acid, 26 turnovers yielding epoxide were observed. We conclude that HOCl is required for efficient catalysis with Ni<sup>II</sup> complexes. Either R<sub>4</sub>N<sup>+</sup>-assisted phase transfer of OCl<sup>-</sup> in conjunction with protonation by a CH<sub>2</sub>Cl<sub>2</sub>-soluble acid (e.g., salen) or formation of HOCl in a pH 9.3 aqueous solution and transfer of neutral HOCl to CH<sub>2</sub>Cl<sub>2</sub> could operate to provide a sufficient concentration of HOCl in the organic phase for efficient oxidation. Thus, the optimal conditions involve both a lowered pH and the addition of a CH<sub>2</sub>Cl<sub>2</sub>-soluble weak acid (salen).

Loss of *E,Z* stereochemistry and formation of small amounts of C=C bond cleavage products<sup>10</sup> are evidence for a stepwise epoxidation mechanism involving attack of a radical species at the alkene. Two possible mechanisms are suggested. At pH 9.3 sufficient quantities of chlorine monoxide may be formed according to the reaction



Rapid reactions of Cl<sub>2</sub>O with Mn(TPP)Cl<sup>11</sup> and the square-planar complex [Ni(CN)<sub>4</sub>]<sup>2-</sup> have been described.<sup>12</sup> Reaction of 1 or 2 with Cl<sub>2</sub>O would likely generate the corresponding Ni<sup>III</sup>-Cl complex, which may exchange Cl<sup>-</sup> for OCl<sup>-</sup> according to the scheme in Figure 2. Homolytic cleavage of a Ni<sup>III</sup>-OCl bond would generate ClO•, a known epoxidizing agent.<sup>13</sup> Some support for this pathway is gained by comparison of the yield of epoxide formed by treatment of (*E*)-β-methylstyrene with 3 equiv of Cl<sub>2</sub>O in anhydrous CCl<sub>4</sub> in the presence and absence of 0.063 mol % 1. A 2-fold enhancement in epoxidation observed in the presence

(10) In the epoxidation of (*Z*)-stilbene, loss of stereochemistry in the alkene and the epoxide in addition to the formation of PhCHO in the presence of O<sub>2</sub> is observed.

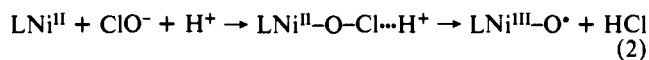
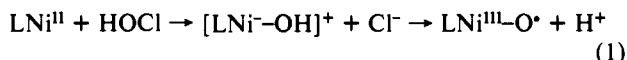
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(12) The reaction of [Ni(CN)<sub>4</sub>]<sup>2-</sup> with Cl<sub>2</sub>O is 10<sup>7</sup> faster than with HOCl. A 2e<sup>-</sup> oxidation to form Ni<sup>IV</sup>(CN)<sub>4</sub>(Cl)(H<sub>2</sub>O)<sup>-</sup> is proposed: Beach, M. W.; Margerum, D. W. *Inorg. Chem.* **1990**, *29*, 1225–1232.

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of catalyst (10.3% compared with 4.2%) is consistent with Ni<sup>II</sup> playing a role in activation of Cl<sub>2</sub>O. However, the inefficiency of this pathway for epoxidation must be attributed to rapid competing chlorination of the alkene and the lack of ClO<sup>-</sup> for a ligand-exchange reaction (Figure 2).

A second mechanistic possibility would involve formation of a Ni<sup>III</sup>-oxo radical through either direct reaction with HOCl (eq 1) or proton-assisted cleavage of the O-Cl bond in an association complex (eq 2).<sup>14</sup> The species LNi<sup>III</sup>-O<sup>•</sup> could be responsible



for both H atom abstraction pathways and epoxidation. Experiments are in progress to distinguish between these pathways.

These findings are significant for two reasons. First, they demonstrate that very high turnover rates can be achieved for alkene epoxidation without resorting to elaborate catalysts<sup>15</sup> and exotic terminal oxidants. Second, they suggest the intermediacy of a high-valent nickel-oxygen species, either Ni<sup>III</sup>-OCl or Ni<sup>III</sup>-O<sup>•</sup>, whose formation is dependent upon the nature of the ligand field<sup>16</sup> and lability of the oxygen atom donor. Alkene epoxidation occurs under conditions implicating radical character at an alkene carbon whose properties may be harnessed for reaction with other inter- or intramolecular trapping agents.

**Acknowledgment.** We thank Professor D. W. Margerum for helpful discussions and communication of results prior to publication, Professor T. C. Bruice for a sample of Fe(TDCPP)Cl, and a referee for helpful suggestions. A grant from the National Science Foundation (CHE-8706616) in support of this research is gratefully acknowledged.

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(15) Furthermore, more than 50% of the Ni(salen) survives the reaction if NaOCl is not used in large excess.

(16) For example, Ni<sup>II</sup>(TPP) shows low turnover as an epoxidation catalyst, while 13- to 14-membered-ring square-planar complexes are generally active.<sup>4</sup>

### Effect of 2,2-Dimethyl Substitution on the Lifetimes of Cyclic Hydrocarbon Triplet 1,3-Biradicals

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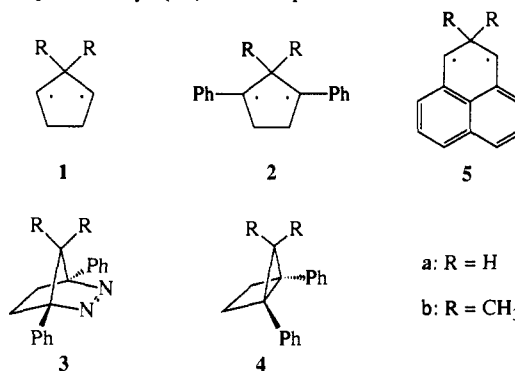
Oxygen trapping experiments have indicated that the lifetime of triplet 1,3-cyclopentadienyl (**1a**) is reduced by at least 2 orders of magnitude upon 2,2-dimethyl substitution (**1b**).<sup>1,2</sup> However, a question has been raised concerning the validity of the upper limit for the lifetime of biradical **1b** obtained by this method.<sup>3</sup> We now present direct kinetic evidence for a marked reduction of 1,3-biradical lifetimes arising from 2,2-dimethyl substitution. The presence of the benzyl chromophore in 1,3-diphenyl-1,3-

**Table I.** Zero-Field Parameters (EPA, 77 K), Lifetimes, and Activation Parameters of the Triplet Biradicals **2** and **5**

	ESR		decay kinetics in acetonitrile <sup>a</sup>		
	$ D/hc $ , cm <sup>-1</sup>	$ E/hc $ , cm <sup>-1</sup>	<sup>3</sup> $\tau$ (ca. 20 °C), $\mu$ s	$E_a$ , kcal/mol	log (A/s <sup>-1</sup> )
<b>2a</b>	0.047	≤0.001	16 ± 2 <sup>b</sup>	2.6 ± 0.2 <sup>c</sup>	6.7 ± 0.1 <sup>c</sup>
<b>2b</b>	0.049	≤0.001	1.3 ± 0.1	1.2 ± 0.1 <sup>d</sup>	6.9 ± 0.1 <sup>d</sup>
<b>5a</b>	0.026 <sup>e</sup>	≤0.002 <sup>e</sup>	>20 000	5.3 ± 1.0 <sup>e</sup>	5.1 ± 1.0 <sup>e</sup>
<b>5b</b>	0.033 <sup>f</sup>	≤0.002 <sup>f</sup>	400 <sup>f</sup>	6.8 ± 1.6 <sup>f</sup>	8.4 ± 0.2 <sup>f</sup>

<sup>a</sup> Errors are standard deviations (30 data points). <sup>b</sup> Instrumental settings were carefully optimized; the value of 27  $\mu$ s reported previously<sup>4</sup> appears to contain systematic error arising from instability of the pulsed monitoring light source. <sup>c</sup> Temperature range 0-50 °C. <sup>d</sup> Temperature range -45 to 21 °C. <sup>e</sup> Temperature range 120-140 K, ref 11. <sup>f</sup> Temperature range 240-273 K, ref 12.

cyclopentadienyl (**2a**) allowed a direct determination of its triplet lifetime by means of time-resolved flash photolysis.<sup>4</sup> Therefore, we chose to investigate the biradical 2,2-dimethyl-1,3-diphenyl-1,3-cyclopentadienyl (**2b**) for comparison.



7,7-Dimethyl-1,4-diphenyl-2,3-diazabicyclo[2.2.1]hept-2-ene (**3b**) was prepared by the usual triazoline route<sup>5</sup> starting from 5,5-dimethyl-1,4-diphenylcyclopentadiene. The latter was conveniently obtained<sup>6,7</sup> via pyrolysis of the mixture of isomeric azoalkanes resulting from the cycloaddition of norbornadiene and 4,4-dimethyl-3,5-diphenylisopyrazole. In contrast to **3a**,<sup>4,8</sup> the azoalkane **3b** was thermally stable for at least several days at room temperature. Direct laser photolysis of **3b** at 351 nm gave 5,5-dimethyl-1,4-diphenylbicyclo[2.1.0]pentane (**4b**) as the only product. The housane **4b** was much more stable against auto-oxidation than parent **4a**.<sup>9</sup>

Direct photolysis of **3a** and **3b** in an EPA glass (5 parts ether, 5 parts isopentane, 2 parts alcohol) at 77 K gave the triplet biradicals **2a**<sup>8</sup> and **2b**, respectively, which were characterized by their ESR (Table I) and fluorescence excitation and emission spectra. Both **2a** and **2b** exhibited weak, structured absorption in the visible region (ca. 460 nm) and medium-intensity absorption at ca. 320 nm (relative intensity ca. 1:40). The structured fluorescence emission showed two prominent peaks at 470 and 505 nm. The fluorescence lifetimes were determined as 217 ± 8 ns (**2a**) and 168 ± 2 ns (**2b**) by excitation with 20-ns pulses from a Nd (265 nm) or a XeF excimer laser (351 nm). The fluorescence spectra and lifetimes of both biradicals are thus similar to those of related benzyl monoradicals.<sup>10</sup>

The lifetime of triplet **2b** in degassed solution at ambient temperature was measured by flash photolysis using a XeF excimer laser (351 nm, 75 mJ, 20 ns) for excitation. As with **3a**,<sup>4</sup> no

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