Metal amide catalyzed amination of olefins

Guido P. Pez and James E. Galle (ref. 1)

Corporate Research & Development, Allied Corporation, Box 1021R, Morristown, NJ, 07960, USA

Abstract – The development of effective methods for promoting the addition of ammonia and amines to olefins to yield alkylamines has long been a challenge in catalysis. We have found that alkali metal amides (rather than transition metal complexes) can be surprisingly active homogeneous catalysts for the amination of olefins. The reaction of diethylamine with ethylene to yield triethylamine in the presence of lithium diethylamide and N,N,N',N'-tetramethylethylenediamine was studied as a model for the reaction of ammonia with ethylene. It proceeds at 70–90°C and 6–10 atm, with the rate limiting step being the addition of the diethylamide Et_2N^-, nucleophile to the olefin. Sodium and potassium diethylamides are initially even more active catalysts but degrade as the reaction proceeds. Solutions of cesium and rubidium amides are remarkably active catalysts for the reaction of ethylene with ammonia at ca. 100°C, and 110 atm pressure to yield a mixture of ethylamines with monoethylamine being the predominant product. Low melting mixtures of alkali metal amide salts also catalyze the amination of ethylene and propylene. Fundamental considerations regarding the effectiveness and limitations of these amide catalyzed olefin amination reactions are discussed.

INTRODUCTION

The hydration of olefins to alcohols proceeds readily over solid acid catalysts (ref. 2), yet the direct catalytic amination of simple olefins with ammonia to yield alkylamines e.g.,

$$NH_3 + C_2H_4 \longrightarrow C_2H_5NH_2 \tag{1}$$
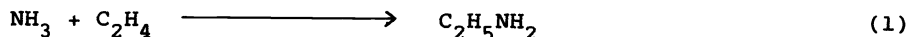
though thermodynamically feasible (at least for ethylene and propylene) (ref. 3, 4) has not been adequately realized. Alkylamines are produced commercially by reaction of ammonia and the corresponding alcohol (in the presence of hydrogen) over a metal supporting acidic oxide catalyst (ref. 5). Since simple alcohols are for the most part derived from olefins it is clear that there would be decided raw material and other economic advantages in the efficient direct synthesis of alkylamines from ammonia and olefins.

The general subject of amination of alkenes has been recently reviewed (ref. 6). While there is abundant literature covering this field, there are comparatively few accounts of the catalytic amination of mono-olefins. Howk et al, (ref. 7) reported in 1954 that ammonia and ethylene react in the presence of metallic sodium at 199–250°C and 380–1000 atmospheres (atm) pressure in an inert hydrocarbon medium to yield ethyl-, diethyl- and triethylamines. The high reaction pressures are apparently essential; at 205 atm for instance only a 0.7% conversion of ammonia was achieved. Ethylene and ammonia reportedly react over a molybdenum oxide on alumina catalyst at 175–300°C to yield ethylamine (ref. 3). The reaction is said to be relatively slow at 200°C while at the higher temperatures the

equilibrium becomes too unfavorable for achieving adequate conversions. In
view of the industrial importance of this synthesis it is surprising that
these results have not been confirmed by other investigators. We attempted
to repeat this reaction as described in ref. 3 using a commercial
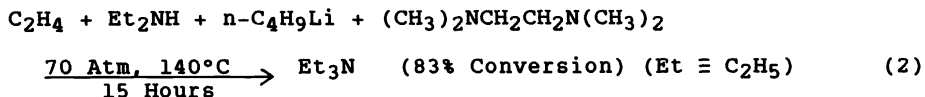MoO_3/alumina catalyst, but unfortunately we did not see any ethylamine.

According to a patent by McClain (ref. 8), alkylamines may be obtained by
passing NH_3 and olefins over a Pd/alumina catalyst at 120°C. However,
since no conversions or yields are reported it seems that only traces of
the alkylamines are actually formed. In another patent disclosure (ref. 9)
the amination of olefins using various iron and ruthenium compounds is
claimed. While reasonable conversions of diethylamine and ethylene to
triethylamine were apparently achieved, for the reaction of ethylene with
ammonia, the yield of alkylamines that are said to be formed was not
stated. Again, this suggests that the latter were produced in only very
small amounts.

An interesting synthesis of amines by reaction of ammonia with olefins in
the presence of various zeolite catalysts was recently (ref. 10,11)
reported. The reactions which are presumably acid catalyzed, proceed at
ca. 400°C, and because of the resultant thermodynamic limitations, only
very modest conversions of the olefin can be achieved. The non-catalytic
formation of alkylamines from olefins and ammonia in an electrical
discharge (ref. 12), ionizing radiation (ref. 13), or by irradiation with
U.V. light (ref. 14) in the presence of various sensitizers has been noted.

Despite the considerable prior attempts at the amination of simple olefins
we felt that the development of an effective low temperature (i.e. <150°C)
catalytic process was a feasible but nevertheless a very challenging
research goal. Our review of the literature had shown that the amination
of olefins with secondary amines is generally much more facile than with
ammonia. We accordingly decided to first investigate secondary amine and
olefin reaction systems, and then use the insight gained for devising new
catalysts for the reaction of ammonia with olefins. With this approach, we
have arrived at remarkably effective homogeneously catalyzed systems for
the synthesis of alkylamines from simple olefins and ammonia.

AMIDE CATALYZED CONVERSION OF DIETHYLAMINE AND ETHYLENE TO TRIETHYLAMINE

At the onset of this work, the most facile amination of a simple olefin
reported in the literature seemed to be the n-butyllithium catalyzed
reaction between diethylamine and ethylene to yield triethylamine
(ref. 15).

$$C_2H_4 + Et_2NH + n\text{-}C_4H_9Li + (CH_3)_2NCH_2CH_2N(CH_3)_2$$

$$\xrightarrow[\text{15 Hours}]{\text{70 Atm, 140°C}} Et_3N \quad (83\% \text{ Conversion}) \ (Et \equiv C_2H_5) \qquad (2)$$

The actual catalyst was presumed to be lithium diethylamide $Li(Et_2N)$,
promoted by N,N,N',N'-tetramethylethylenediamine (TMED). In preliminary
investigations we found that by using high concentrations of catalyst, this
reaction would proceed at even milder conditions. Thus, for example a
mixture of Et_2NH (3 ml), TMED (2 ml) and $Li(Et_2N)$ (200 mg) reacted with
C_2H_4 (initial pressure ~11 atm) at 80°C resulting after 18 hours, in
a total conversion of Et_2NH to triethylamine. This is a much more facile
and effective diethylamination of ethylene than with previously described
$RhCl_3$ (ref. 16), $RuCl_3 \cdot xH_2O$ (ref. 9) and Zr, Nb and Ta dialkylamide
catalysts (ref. 17). In view of this remarkably effective catalysis, we
decided to further study this transformation as a model for amide catalyzed
olefin amination reactions.

The kinetics of this reaction were investigated using a glass stirred
liquid reactor system operating at a constant total pressure. For each
kinetic run, the reactor was loaded (in a dry box) with the solid
$Li(Et_2N)$ catalyst and then with a measured aliquot taken from a stock
solution of diethylamine (66.4%), TMEN (28.69%) and n-octane (4.9%) (an
analytical standard). Once the reaction had reached operating temperature

under pressure of ethylene, small liquid samples were withdrawn periodically and analyzed for triethylamine. The kinetics of formation of Et_3N were thus determined for various controlling parameters namely the extent of reaction, total pressure, concentration of catalyst and reaction temperature. Results are presented in Table 1.

TABLE 1. Kinetics of Formation of Et_3N from Et_2NH and C_2H_4

Run #	Temp (°C)	Press[a] (atm)	[Catalyst][b] (m)	Initial Et_2NH (mmol)	Conv Et_2NH (%)	Rate x 10^2 (mmol Et_3N/min)
1	79	9.9	0.73	47.8	28	5.3
2	79	7.9	0.71	48.1	25	4.1
3	79	5.8	0.71	48.7	31	3.4
4	79	12.0	0.72	48.5	57	7.1
5	79	7.9	0.155	47.5	12	1.3
6	79	7.9	0.36	48.5	38	3.1
7	79	7.9	1.04	49.6	17	7.6
8	70	7.9	0.36	47.9	15	1.9
9	89	7.9	0.36	47.9	16	4.8

[a] Total system pressure, kept constant throughout each run
[b] Concentration (molal) based on $Li(Et_2N)$
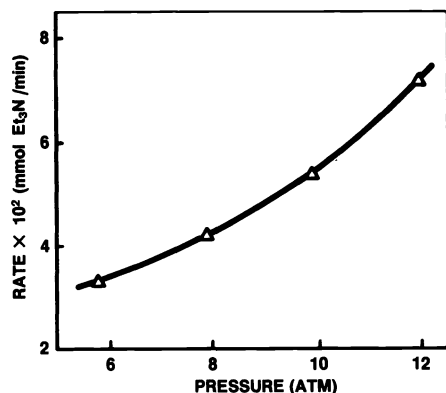[c] Maximum percent molar conversion of Et_2NH, at which data was taken

Fig. 1. Variation in the rate of formation of Et_3N with total system pressure (ethylene plus organic vapors)

It was found that under all the reaction conditions studied, at a constant total pressure,(Note a) the concentration of triethylamine was directly proportional to reaction time (see Experimental section). This surprising zero order dependence of the rate of formation of triethylamine on the concentration of Et_2NH was clearly seen up to at least a ca 50% conversion of the secondary amine.

On the other hand, the rate of formation of triethylamine is clearly enhanced by increasing the total applied pressure (see Fig. 1). The reaction rate increases smoothly with pressure at a mean overall rate for the data available, of about 0.6 mmol Et_3N/min.atm. The organic liquids in the reaction mixture are expected to contribute to the extent of about 1-1.4 atm to the total pressure. Since this contribution should be similar for each run, it seems reasonable to suppose that the reaction rate would also show a similar functional dependence on the partial pressure of ethylene and possibly also on the concentration of ethylene in the mixture.

The reaction kinetics were also determined for various concentrations of the lithium diethylamide catalyst, with the reaction mixtures always containing at least two molecules of TMED per lithium. As is evident from the data in Table 1, the rate shows a strong dependence on catalyst concentration. Unfortunately there is considerable scatter in the available experimental data, but it appears at least that with the more dilute solutions the reaction rate may be proportional to the catalyst concentration.

Note a: Note however, that the partial pressure of ethylene in the system should increase somewhat as the reaction proceeds to yield the less volatile triethylamine. At 30% conversion of Et_2NH this is expected to result in a rate increase of only about 0.1 to 0.2 mmoles Et_3N/min.
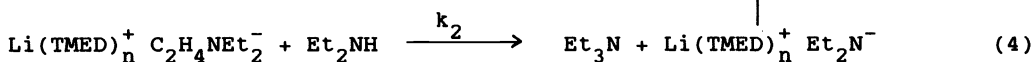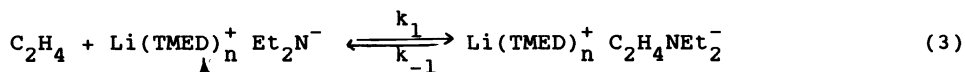
Kinetic data taken at 70-89°C were used to calculate an apparent Arrhenius activation energy of 12 Kcal/mole. This should be regarded as the lower limit for the activation energy of the rate controlling step since the concentrations of dissolved ethylene in the reaction mixture are expected to be less at the higher temperatures.

Thus, for the reaction of diethylamine with ethylene, within the range of conditions studied, the empirical rate law for the formation of triethylamine may be expressed as:

$$\frac{d[Et_3N]}{dt} = k[Et_2NH]^0 \cdot [C_2H_4]^{\sim 1} \cdot [Li(Et_2N)]^{\sim 1}$$

While the reaction is definitely zero order with respect to diethylamine, our experimental results should be taken as being only indicative of a probable first order dependence on the concentration of ethylene and catalyst.

As an initial hypothesis, this amination of ethylene may be viewed as taking place in a two step sequence, namely a reversible reaction of ethylene with the catalyst to form a TMED chelated lithium diethylamide which then reacts with diethylamine to yield the product triethylamine.

$$C_2H_4 + Li(TMED)_n^+ Et_2N^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Li(TMED)_n^+ C_2H_4NEt_2^- \qquad (3)$$

$$Li(TMED)_n^+ C_2H_4NEt_2^- + Et_2NH \xrightarrow{k_2} Et_3N + Li(TMED)_n^+ Et_2N^- \qquad (4)$$

The observed zero order dependence on diethylamine and the indicated probable first order dependence on ethylene and catalyst, strongly suggest that the rate determining step is the formation of the lithium(TMED)$_n$ ethylenediethylamide salt, (Equation 3). Once formed, this intermediate then presumably reacts very rapidly with (the comparatively "acidic") diethylamine (Equation 4), thus accounting for the zero order dependence in this reagent. The rate of formation of triethylamine is thus essentially determined by the overall rate of production of the TMED-chelated lithium ethylenediethylamide intermediate. (Note a)

A similar mechanism has been deduced for the amide catalyzed reaction of diethylamine with butadiene (ref. 18) except that in this case a diethylamine-lithium diethylamide complex (rather than a TMED chelated lithium diethylamide) was the active catalyst.

In our model reaction of diethylamine with ethylene the rate is thus essentially governed by the nucleophilicity of the chelated lithium diethylamide towards the olefin. This nucleophilicity is greater than can be achieved with only lithium diethylamide presumably because of the polarizing effect of TMED on the Li^+ Et_2N^- ion pair (or cluster) (Note b). Since in principle at least, the best nucleophile and catalyst should be a well separated A^+: Et_2N^- ion pair, we decided to investigate the catalytic activity of other alkali metal diethylamides for the reaction (see ref. 19 for related prior work). (For a review and discussions of ion-pairing phenomena see ref. 20, 21.)

Sodium and potassium diethylamides were prepared in a novel synthesis, by reaction of n-butyllithium, potassium t-butoxide and diethylamine (or potassium t-butoxide and lithium diethylamide in diethylamine).

$$t\text{-}C_4H_9O^-M^+ + Et_2NH + n\text{-}C_4H_9Li \xrightarrow{Et_2NH} M^+Et_2N^- \downarrow + t\text{-}C_4H_9O^-Li^+ + C_4H_{10}$$
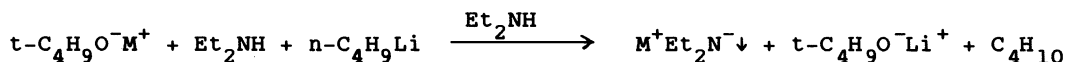
Note a: An alternative mechanism involving the rapid establishment of an equilibrium concentration of Li(TMED)$_n^+$C$_2$H$_4$NEt$_2^-$ is ruled out since this would require the rate of Et$_3$N synthesis to have a first order dependence on the concentrations of C$_2$H$_4$, catalyst, and also Et$_2$NH which is not what is observed.

Note b: In preliminary experiments where the reaction was followed by a decrease in total pressure, it was found that the rate was at least one order of magnitude less in the absence of TMED.

The compounds were found to be only sparingly soluble in diethylamine and could thus be easily isolated, as white, highly pyrophoric solids.

The kinetics of the diethylamine and ethylene reaction at 45°C, in the presence of dissolved potassium diethylamide as the catalyst, but with no added TMED, were examined. Details of reaction conditions, and the kinetic results in terms of Et_3N produced versus time are given in Fig. 2 (curve (a)). The curve (b) in the same Figure shows the results of a similar experiment where the potassium diethylamide catalyst was prepared in situ by the addition of potassium t-butoxide and lithium diethylamide. Both reactions display the same initial rate of formation of triethylamine of 0.36 mmol Et_3N/min.

This rate is some two orders of magnitude faster than that at which the $Li(TMED)_n^+$ Et_2N^- catalyzed reaction would proceed under the same conditions. However, with these potassium dialkylamide catalyzed reactions there is an obvious decrease in rate after about a 25% conversion of diethylamine. This decrease in reaction rate and its eventual levelling off with time is attributed to a decomposition or deactivation of the catalyst. For instance in the experiment corresponding to curve (b) in Fig. 2, the catalyst remaining after 19 hours of reaction time when contacted with fresh diethylamine and ethylene, was essentially inactive for the amination reaction. By using an in situ prepared sodium diethylamide the initial reaction rate was ca. 0.08 mmoles Et_3N/min (curve 2c), which is still about 20 times faster than with the lithium based catalyst. Unfortunately however, even with sodium diethylamide there is an eventual levelling off in rate indicative of catalyst decomposition.

The striking (at least initial), catalytic activity of potassium diethylamide for our model amination reaction, is very likely due to the presence of this catalyst as a well solvent separated ion pair in diethylamine. The evidently high nucleophilicity of the Et_2N^- ion with a potassium gegencation led us to carefully examine analogous amide salts for the desired ammonia and ethylene reaction.
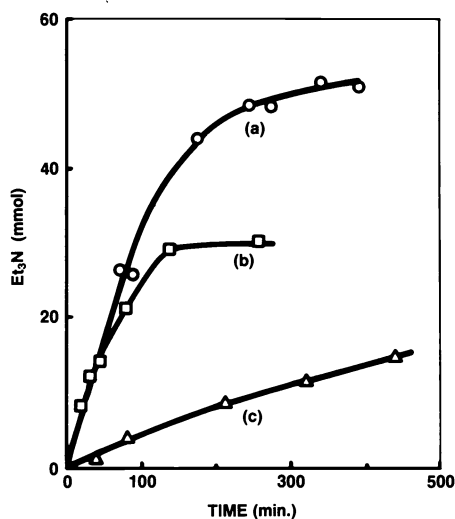
Curve (a): Et_3N formed starting from Et_2NH (89.2 mmole); n-octane (3.7 mmol) (analytical standard); catalyst $K(Et_2N)$ (1 mmol, 0.144m), at 45°C and 10 atm

Curve (b): Similar conditions, but using instead in situ prepared $K(Et_2N)$ catalyst from K-t-butoxide (2 mmole) + $LiNEt_2$ (1 mmole)

Curve (c): Et_3N formed starting from Et_2NH (88.9 mmol); n-octane (3.7 mmol); catalyst from Na t-butoxide (2 mmol) + $Li(Et_2N)$ (1 mmol); at 45°C and 10 atm

Fig. 2. Kinetics of formation of Et_3N from Et_2NH and C_2H_4 using sodium and potassium diethylamide catalysts

AMIDE CATALYZED CONVERSION OF AMMONIA AND ETHYLENE TO ALKYLAMINES

In view of the remarkable activity of potassium diethylamide for the diethylamine and ethylene reaction, we felt that under appropriate conditions potassium and other alkali metal amides might be effective ammonia and ethylene reaction catalysts. By analogy with the previously discussed mechanism for the diethylamination of ethylene, the rate determining step for the addition of ammonia to ethylene should be the formation of the alkali metal ethyleneamide intermediate. The latter

should then be rapidly quenched by ammonia to yield the product ethylamine, with regeneration of the amide catalyst.

$$C_2H_4 + M^+NH_2^- \rightleftharpoons M^+C_2H_4NH_2^-$$

$$M^+ C_2H_4NH_2^- + NH_3 \longrightarrow EtNH_2 + M^+NH_2^-$$
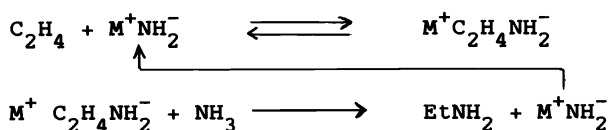
The best conditions for olefin amination should be those where (a) there is a high concentration of ethylene and metal amide and (b) where the metal amide and reaction solvent are chosen so as to maximize the nucleophilicity of the amide ion.

In view of the potentially favorable high r+/r- ionic radius ratios of rubidium and cesium amides and their relatively high solubility in liquid ammonia (ref. 22), it seemed reasonable to investigate these compounds in liquid NH_3, as possible ethylene and ammonia reaction catalysts.

We found that ethylamines are indeed produced in good yield by reaction of ethylene and ammonia in the presence of cesium or rubidium amides at ca. 80-110°C. Reaction parameters and product yields for a number of experiments are shown in Table 2. Further details are given in the Experimental section. Thus for the first example in the Table, reaction of NH_3 (237 mmol) with C_2H_4 (132 mmol) in the presence of $CsNH_2$ (10.1 mmol) at an initial pressure of 112 atm, reacted for 1 hour at 101°C to give 32 mmol of ethylamine together with smaller quantities of diethylamine and triethylamine. Under these conditions there was an overall 34% conversion of ethylene to alkylamines. Rubidium amide also proved to be an effective catalyst giving about the same conversion to ethylamines, but at a longer reaction time (Exp. 3, Table 2). In contrast, potassium and sodium amides gave very low conversions to ethylamines even at long reaction times (Exps. 8 and 9, Table 2). All the reactions were conducted in a pressure vessel of ca. 40cm³ total volume, which under the conditions stated, should contain some liquid ammonia. The catalytic reaction medium is thus expected to be liquid ammonia containing dissolved ethylene and metal amide, and we felt that perhaps this very low catalytic activity of KNH_2 and $NaNH_2$ might be due to their much lower solubility in ammonia.

To circumvent this difficulty we investigated the use of low melting metal amide mixtures as possible catalysts. A KNH_2-$2NaNH_2$ eutectic which reportedly melts at ~92°C (ref. 23) proved to be a reasonably effective

TABLE 2. Reaction of Ammonia with Ethylene in the Presence of Alkali Metal Amide Catalysts at 101°C[a]

Exp.	Catalyst (mmol)	Pressure[b] Start-Stop (atm)	Time (hours)	EtNH₂ (mmol)	Et₂NH (mmol)	Et₃N (mmol)	Conv. C₂H₄ (%)
1	CsNH₂(10.1)	112-92	1	32	3	2	34
2	CsNH₂ (6.7)	113-91	1.5	28	3	1	28
3	RbNH₂ (9.6)	111-89	3	34	3	0.7	32
4	CsNH₂ (5.1) KNH₂ (4.4)	118-105	1	21	2	1	21
5	Cat. from #4		6	59	9	4	67
6	CsNH₂ (5.1) KNH₂ (4.4)	111-84	3	32	3	2	33
7	KNH₂ (11.3) NaNH₂ (22.8)	119-96	19	26	1	--	21
8	KNH₂ (9.4)	113-113	20.5	1.6	0.1	--	1.4
9	NaNH₂(18.2)	113	19	2	--	--	1.4

a Reaction volume ~40cm³
b At operating temperature (101°C)

catalyst (Exp. 7, Table 2) and was certainly much more active than the sodium or potassium amides alone. We also investigated the $CsNH_2/KNH_2$ system and found that a liquid mixture containing 46 mole % KNH_2 solidified at 92-93°C which is considerably less than the melting points of the pure components ($CsNH_2$, m.p. 262°C; KNH_2, 338°C).

This $CsNH_2$-0.86 KNH_2 composition was predictably a more active catalyst than the KNH_2-2$NaNH_2$ eutectic, but on a weight basis it was less effective than cesium amide alone. With the use of molten mixed metal amide catalysts it should thus be possible in principle, to conduct reactions where temperature or other conditions preclude the use of liquid NH_3 as a reaction medium.

The ethylamines listed in Table 2 were the only organonitrogen reaction products that were detected by gas chromatography. However, in some instances ethane and a mixture of non-condensible gases (N_2, H_2 and possibly CH_4) were also formed. The use of prolonged reaction times usually led to the formation of these by-products. For instance, referring to Table 2 in experiments 5 and 7, 2 and 0.3 mmol of ethane and 0.4 and 1 mmol of non-condensibles, respectively, were detected. In experiments 2, 3, 4 and 6, with reaction times of <3 hours no ethane or non-condensibles were seen, with detection limits for these products being about 0.04 mmol and 0.1 mmol, respectively. However, for the most effective run using $CsNH_2$ alone as the catalyst (Exp. 1, Table 2), traces of non-condensibles (~0.04 mmol) were seen but there was no detectable ethane.

The formation of these by-products is indicative of chemical reactions occurring in the system that are outside the scope of those envisaged for the simple nucleophilic amination of ethylene (vide supra). Some insight on this was gained by an examination of the solid inorganic residue from $CsNH_2$ catalyzed NH_3/C_2H_4 reactions. Infrared spectra of this solid as a suspension in Nujol oil showed the presence of cesium amide and also a characteristic broad infrared absorption at 1940 cm^{-1}. By extraction of the solid with liquid ammonia at ca. -40°C a residue giving an intense 1940 cm^{-1} absorption was isolated. Elemental analyses gave its composition as approximately Cs_2CN_2H. It seems probable that the material is mainly cesium cyanamide Cs_2CN_2, the hydrogen arising from ammonia or contaminating cesium amide. For comparison, calcium cyanamide, $CaCN_2$ shows an intense infrared absorption at 2022 cm^{-1} (ref. 24). Considerable further work is clearly needed to elucidate the nature and mechanism of formation of this cesium amide reaction product.

The amination of ethylene is certainly catalytic with respect to cesium, rubidium, and the mixed cesium/potassium amides, although because of the necessarily large inventory of catalyst used in our experiments, its productivity (moles product per mole of catalyst) does not appear to be very high. Although some reactions were carried out with a used catalyst (Exp. 5, Table 2), we have not thus far carried out adequate catalyst lifetime studies. While there are evidently other chemical reactions occurring with the cesium amide, their effect on the activity of this catalyst has not been established. We have noted however, that there appears to be a one to one correspondence between the formation of the probable cesium cyanamide material (as shown by the intensity of the 1940 cm^{-1} infrared absorption) and that of the ethane and non-condensible gas by-products. Reaction conditions which we have noted minimize the formation of these by-products, such as the use of excess ammonia, short reaction times and low reaction temperatures are likely to also promote the lifetime of the catalyst.

Amination of propylene

The conversion of ammonia and propylene to isopropylamine and diisopropylamine was shown to take place over a sodium catalyst at ca. 250°C and 850-1000 atm pressure (ref. 7). In contrast, we have found that these reagents can react in the presence of cesium amide containing catalysts, under far milder reaction conditions to give mostly isopropylamine. In a specific example, NH_3 (112 mmol) and C_3H_6 (142 mmol) were reacted in a reactor of 40 cm^3 total capacity containing $CsNH_2$ (18.5 mmol) and $NaNH_2$ (6.4 mmol), for 17.5 hours at 139°C. Isopropylamine (13 mmol), n-propylamine (0.7 mmol), as well as propane (2 mmol) and non-condensible gases (0.8 mmol) were produced. However, when the reaction was conducted with $CsNH_2$ in liquid NH_3 as the catalyst and reaction medium lower conversions were seen but there were no by-products.

CONCLUSIONS

In contrast to prior findings, and in agreement with the thermodynamic predictions (ref. 3,4) we have shown that the amination of simple olefins can be effectively catalyzed under at least moderate conditions by solutions of alkali metal amides and alkylamides. The reaction of diethylamine with ethylene to yield triethylamine proceeds readily at 70-90°C and 6-10 atm in solutions containing TMED-chelated lithium diethylamide. Kinetic studies have shown that the reaction rate is dependent only on the concentrations of ethylene and catalyst, which suggests that the rate determining step is the nucleophilic addition of dialkylamide to the olefin. Sodium and potassium diethylamides are even more active catalysts presumably (at least in the initial stages of the reaction) by acting as even more effective sources of the diethylamide nucleophile.

Solutions of cesium and rubidium amides in liquid ammonia were shown to effectively catalyze the amination of ethylene to yield a mixture of ethylamines at ca. 110 atm and 100°C. These are much milder conditions than the 380-1000 atm and 200-250°C required for the previously reported sodium (or more likely $NaNH_2$) catalyzed amination of ethylene (ref. 7). Since the latter reaction was conducted in an n-heptane medium, well above the critical temperature of ammonia, the catalyst was almost certainly present as a solid. The remarkable catalytic activity that we have observed with $CsNH_2$, $RbNH_2$ and the mixed Cs-K and Na-K amides is ascribed in part, to the use of ammonia solutions or melts of the amide salts, wherein a high concentration of the NH_2^-, nucleophile can be realized.

Solutions of cesium amide and cesium amide-sodium amide melts also catalyze the reaction of ammonia with propylene to yield as expected for a nucleophilic addition mechanism, mostly isopropylamine, but under more severe conditions and with poorer yields than the reaction with ethylene. Nucleophilic addition reactions to propylene and other olefins are expected to be less facile than with ethylene.

We have found that in certain cases the metal amide promoted ammonia and olefin reactions yield small quantities of the corresponding alkanes as well as some non-condensible gases (H_2, N_2 and possibly CH_4), as by-products. Some chemical changes have been observed to occur with the catalysts. Further work is needed to characterize this chemistry and adequately establish the productivity and longevity of these metal amide catalysts for the amination of olefins.

EXPERIMENTAL NOTES

All the catalytic chemistry described in this paper involved the use of very reactive and sometimes pyrophoric alkali metal amides and alkylamides, and was thus conducted in the strict absence of air and moisture. A recirculating N_2 drybox with an atmosphere containing <5 ppm O_2 and H_2O was used for the transfer of solids, while volatile liquids and gases were transferred on a vacuum manifold. Commercial anhydrous ammonia was dried by contact with Na/K alloy and the corresponding amides. Diethylamine was purified by contact for a limited time, with Na/K followed by distillation at room temperature. n-Octane and N,N,N',N'-tetramethylethylenediamine (TMED) were dried by stirring over Na/K.

<u>Lithium(TMED)$_n$ diethylamide catalyzed conversion of Et$_2$NH and ethylene to Et$_3$N.</u> Lithium diethylamide (Alfa-Ventron) was purified by recrystallization from a mixture of diethylamine and isopentane. The resulting white solid was pumped extensively under a high vacuum at room temperature until no further volatiles were evolved, and was assumed to be free of any coordinating amine solvent. <u>Caution:</u> Li(Et$_2$N) is highly pyrophoric and will react violently upon even brief contact with ambient air.

The experimental conditions for studying the kinetics of the C_2H_4/Et$_2$NH reactions are typically illustrated by run #2 (Table 1) which was conducted as follows. A heavy wall glass reactor tube (ca. 15 cm x 2.5 cm O.D.) containing a glass covered magnetic stir bar, fitted with a rubber gasket sealed metal header and entry valve, was loaded in the drybox

with Li(Et$_2$N) (298 mg). The reactor was then transferred to a vacuum manifold and charged with 5.298g (ca. 7.3 ml) of a stock solution containing Et$_2$NH (66.40 w/w %), TMED (28.69%) and n-octane (4.91%). The latter was used as an internal analytical standard. Ethylene (Matheson Research Grade) was added to give a total system pressure of ca. 2 atm. The reactor was then placed in a preheated 79°C oil bath and when equilibration had been achieved, more C$_2$H$_4$ was added to achieve a total system pressure of 7.9 atm, which was kept constant throughout the experiment. The temperature was kept at 79 $\pm$ 1°C. Samples were periodically withdrawn from the reaction mixture and analyzed for all components by gas chromatography, using a 9-foot, 28% Pennwalt 223 with 4% KOH on 80/100 Gas Chrom R column, temperature programmed at 150-190°C. The amounts of Et$_3$N formed were calculated on the basis of ratio of concentrations of Et$_3$N to n-octane in the reaction mixture. For this run, nine significant sample points were taken to a ca. 25% conversion of Et$_2$NH after 324 mins. Plotting Et$_3$N (mmol) versus time (min) gave a straight line with a least-squares slope (including the 0,0 point) of 4.13 mmol Et$_3$N/min, with a y-intercept of -0.11 and a correlation coefficient of $R^2 = 0.9908$. Straight line plots for Et$_3$N (mmol) versus time (min) with $R^2 = 70.98$ were obtained for all the kinetic runs listed in Table 1 (at least up to ca 50% conversion of Et$_2$NH).

<u>Preparation of potassium diethylamide</u>. A solution of 10 ml of 2.5M n-butyllithium in hexane was added dropwise to a cooled (0°C) solution of potassium t-butoxide (25 mmol) in Et$_2$NH (25 ml). The solution was stirred with warming to room temperature (ca. 1 hour), it was then filtered and the solid residue washed with Et$_2$NH (20 ml). The latter was dried in vacuum at 50°C, affording 1.68g of a colorless product. Hydrolysis of a sample with n-hexanol and H$_2$O and analysis by glc gave Et$_2$NH as the only major product. No trace of t-butanol could be found. When a sample was hydrolyzed as above and the resulting Et$_2$NH removed in vacuo, titration of the resulting residue with standard HCl to a phenolphthalein endpoint required 91% of the theoretical amount. <u>Caution</u>: The solid sodium and potassium diethylamides are highly pyrophoric and will react violently upon even limited exposure to air.

<u>Preparation of alkali metal amides</u>. The Na, K, Rb and Cs amides were most conveniently (and safely) prepared by direct reaction of the alkali metals with NH$_3$ at ca. 8 atm pressure in a steel vessel at 150-250°C (ref. 23).

<u>Reaction of ethylene with ammonia (Exp. 1, Table 2)</u>. A stainless steel pressure vessel containing an uncovered metal alloy magnetic stir bar and equipped with a pressure gauge of minimum internal volume (to minimize any effects from the possible condensation of NH$_3$) was used for the reaction. The entire system had an internal volume of ca. 40cm^3. The reactor was loaded (in a drybox) with cesium amide (1.5g, 10.1 mmol), and using a vacuum/pressure manifold it was then charged with pure ammonia (vide supra) (237 mmol) and (Matheson Research Grade) ethylene (132 mmol). The entire reactor was heated with stirring at 101° for one hour, during which the pressure dropped from ca 112 to 92 atm. While still at this temperature, the volatile reactor contents were then slowly bled into a liquid N$_2$ trap (-196°C) and the pressure of non-condensible gases (if any) read on a mercury manometer. In Exp. 1, ca. 0.04 mmol of such gases were noted. The condensed product mixture was distilled at -111°C to separate the bulk of the unreacted ethylene. The distillate gas was analyzed for ethane by gas chromatography using an 8 foot, 1/8" Teflon® Carbosieve B® column, run isothermally at 150°C.

The distillation residue was transferred to a ~2 liter glass bulb, wherein it was allowed to evaporate to yield a homogeneous gas mixture of known pressure and volume. This gas was then analyzed by gas chromatography for mono-, di-, and triethylamine (vide infra) using calibrations prepared with known mixtures of NH$_3$, EtNH$_2$, Et$_2$NH and Et$_3$N. For the analyses a 9 foot, 1/8" Pennwalt 223 with 4% KOH column was used, temperature programmed at 4°C/min to 80°C then at 16°C/min to 160°C.

In Exp. 1, monoethylamine (32 mmol), diethylamine (3 mmol) and triethylamine (2 mmol) were produced, corresponding to a 34% conversion to alkylamines based on ethylene, which was the limiting reactant in this experiment.

The preparation of amine gas standards and all other gas transfers in the
course of the amine analyses were done using predominately apparatus made
from glass, teflon, or silicone rubber (for the injection septa). A glass
syringe equipped with a stainless steel needle was used for the injection
of gas samples into the gas chromatograph. We avoided as much as possible
the use of metal apparatus, which was found could give erroneous results
from the surface adsorption and competitive displacement of ammonia and
amines.

ACKNOWLEDGMENT

REFERENCES

1. G. P. Pez present address: Corporate Science Center, Air Products and
    Chemicals, Box 538, Allentown, Pa. 18105, USA.

2. P. D. Sherman, Jr., and P. R. Kavasmaneck in Encyclopedia of Chemistry
    and Technology, Kirk Othmer (Ed.) John Wiley & Sons New York Vol. 9
    (3rd Ed.) p. 344-350.

3. L. Uhlmann Wissenschaftliche Zeitschrift der Technischen Hochschule
    fur Chemie Leuna-Merseburg 5, 263-267 (1963).

4. D. R. Stull, E. F. Westrum, Jr., and G. C. Sinke The Chemical
    Thermodynamics of Organic Compounds, Wiley, New York p. 636-652 (1969).

5. A. E. Schweizer, R. L. Fowlkes, J. H. McMakin, T. E. Whyte, Jr., in
    "Encyclopedia of Chemistry and Technology" Kirk Othmer (Ed.), John
    Wiley Vol. 2 (3rd Ed.) p. 272-283.

6. M. B. Gasc, A. Lattes and J. J. Perie Tetrahedron 39, 703-731 (1983).

7. B. W. Howk, E. L. Little, S. L. Scott and G. M. Whitman, J. Amer.
    Chem. Soc. 76, 1899-1902 (1954).

8. D. M. McClain, U.S. Patent 3,412,158 (1968).

9. D. M. Gardner and R. T. Clark, Eur. Pat. Appl. EP 39061 Al (1981).

10. J. O. H. Peterson and H. S. Fales, U.S. Patents 4,307,250 (1981) and
    4,375,002A (1983).

11. M. Deeba and W. J. Ambs Eur. Pat. Appl. EP 77016 Al (1983).

12. J. C. Burleson, W. F. Yates U.S. Patent 3,518,173 (1970).

13. H. G. Schutze, A. Suttle, Jr., U.S. Patent 3,071,524 (1963).

14. D. M. Gardner and P. J. McElligott U.S. Patent 4,483,757 (1984).

15. H. Lehmkuhl and D. Reinehr J. Organomet. Chem 55, 215-220 (1973).

16. D. R. Coulson Tetrahedron Lett. (5), 429-30 (1971).

17. M. G. Clerici, F. Maspero Synthesis (4) 305-6 (1980).

18. T. Narita, N. Imai and T. Tsuruta Bull Chem Soc Japan 46 1242-1246
    (1973).

19. R. D. Closson, A. J. Kolka and W. B. Ligett U.S. Patents 2,750,417 and
    2,750,384 (1956).

20. M. Szwarc (Ed), Ions and Ion Pairs in Organic Reactions,
    Wiley-Interscience, New York, Vol 1 (1972), Vol 2 (1974).

21. B. J. Herold Catal. Rev. Sci. Eng. 17, 1-29 (1978).

22. P. W. Schenk and H. Tulkoff Berichte der Bunsen Physikalische Chemie
    71 210-214 (1967).

23. C. A. Kraus and E. J. Cuy J. Amer. Chem. Soc. 45 712-715 (1923).

24. B. I. Sukhorukov and A. I. Finkel'shtein Optika i Spektroskopiya 7
    653-8 (1959).