891. *The Reaction of Tetra-alkylammonium Halides with Potassium in Liquid Ammonia.*

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The cation of a tetra-alkylammonium salt NR_4X undergoes N–C bond fission with potassium in liquid ammonia, giving a hydrocarbon RH and an amine NR_3. With a tetramethylammonium salt the yield of methane decreases in the order X = Cl, Br, I, and C–H fission may occur to yield hydrogen and ethylene. The rate of reaction at $-78°$ is $R = Pr^n > Me > Et$; unsymmetrical ions R_3NMe^+ react very rapidly, yielding methane. Amide ion resulting from N–C fission or solvolysis gives olefin if R contains a β-carbon atom.

THE reaction of tetramethylammonium iodide with a solution of potassium in liquid ammonia was first investigated by Thompson and Cundall;[1] the products at room temperatures were trimethylamine, ethane, and potassium iodide. Schlubach and Ballauf[2] found that tetraethylammonium chloride and potassium yielded more gas than that expected from the equation $2K + 2NEt_4Cl = 2KCl + 2NEt_3 + C_4H_{10}$. Recently, Jolly[3] has found that tetraethylammonium bromide and potassium in liquid ammonia at $-36°$ yield triethylamine and variable amounts of ethylene, ethane, and hydrogen. In some of Jolly's experiments, ferric nitrate was added to catalyse the reaction between the ammoniated electron (written as e^- here) and solvent, *i.e.*, $2e^- + 2NH_3 = 2NH_2^- + H_2$. It is known that the reaction of the ions NEt_4^+ and NH_2^- yields ethylene, and it is not clear how much of Jolly's ethylene was formed in this way.

One object of all the above investigations was to find evidence for the existence of the tetra-alkylammonium radical NR_4. In the reaction $NR_4X + K$ (X = halogen), in liquid ammonia, KX is precipitated; hence there are in solution NR_4^+ ions and solvated electrons, e^-. The latter may undergo solvolysis to give amide ion and hydrogen; or they may unite with the NR_4^+ ions to give radicals NR_4; or they may attack NR_4^+ ions and break bonds.

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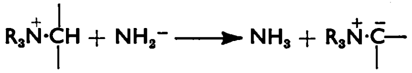
[1] Thompson and Cundall, *J.*, 1888, **53**, 761.
[2] Schlubach and Ballauf, *Ber.*, 1921, **54**, 2811.
[3] Jolly, *J. Amer. Chem. Soc.*, 1955, **77**, 4958.

Valency considerations make the existence of the radical NR_4 seem improbable, and hence breakdown of the ion NR_4^+ is likely; Birch[4] has shown that electrons of metal–ammonia solutions can produce fission of the N–C bonds in quaternary ammonium ions (*e.g.*, $Ph{\cdot}NMe_3^+ \longrightarrow PhH + NMe_3$). Kantor and Hauser[5] have shown that fission of a C–H bond can occur by reaction of a base B^- (*e.g.*, NH_2^-) in liquid ammonia, *e.g.*,



$$R_3\overset{+}{N}{\cdot}CH + NH_2^- \longrightarrow NH_3 + R_3\overset{+}{N}{\cdot}\overset{-}{C}— \quad (I)$$

The carbanion (I) may then re-arrange to give a tertiary amine, or undergo alkylation. If a β-carbon atom with attached hydrogen is present, then β-elimination is preferred, giving an olefin, *e.g.*,

$$R_3\overset{+}{N}{\cdot}CH_2{\cdot}CH_3 + NH_2^- \longrightarrow R_3N + C_2H_4 + NH_3$$

In the present work, the reaction of NR_4^+ ions and ammoniated electrons has been investigated *in vacuo* at −78°, and as many reaction products as possible have been analysed quantitatively so that the reaction mechanism might be understood.

EXPERIMENTAL

All manipulations involving liquid ammonia were made in a vacuum apparatus. The ammonia was dried over sodium and stored as gas. Quaternary ammonium halides were either obtained from B.D.H. or made by usual methods; they were dried *in vacuo* and analysed for purity before use. The dry salt was introduced into the reaction tube, followed by the potassium (weighed under light petroleum), and the tube was then attached to the vacuum system and pumped for some hours. About 10 c.c. of liquid ammonia were condensed into the tube, and the latter was sealed off and left at −78°, with occasional shaking, until the blue colour disappeared. The tube was then placed in liquid nitrogen and opened to the vacuum system; non-condensable gases were removed with the Töpler pump and analysed by combustion. The ammonia was carefully removed from the reaction tube, and condensable hydrocarbon products were then separated by fractionation through U-traps; absorption of the large amount of ammonia on calcium chloride assisted separation of hydrocarbons of similar vapour pressure to ammonia. Condensable and non-condensable hydrocarbon products were analysed by combustion, by absorption in bromine water, and by infrared absorption spectra; vapour-density measurements were also made in some cases. Identification of the small amount of amine formed ($<0{\cdot}1$ g.) in presence of much ammonia was carried out by one or more of the following methods: (*a*) allowing amine to accumulate in the solvent ammonia from successive experiments and then extracting the hydrochloride with chloroform (Watt and Otto's method[6]); (*b*) using larger quantities of reactants, and then separating the amines by fractional distillation, using the micro-still described by Craig;[7] (*c*) separating the hydrochlorides by paper chromatography.[8]

After removal of all volatile material from the reaction tube, the solid residue was dissolved in water, warmed to remove any traces of ammonia and amine, and analysed for (i) alkalinity (corresponding to amide ion content of the residue), (ii) potassium and quaternary ammonium ion concentration, by use of sodium tetraphenylboron, and (iii) halide content, as a check on the amount of salt added initially. From (ii) and (iii) the amount of quaternary salt used in the reaction could be estimated. Determinations in the residues were occasionally precluded by loss of solid on removal of solvent ammonia.

Results.—These are given in Tables 1, 2, and 3; units are mmoles unless otherwise stated. Expts. 1—7, Table 1, were with potassium and tetraethylammonium chloride. The results of expts. 1 and 2 show that very variable ethane : ethylene ratios were obtained under apparently similar conditions, and that the time of reaction (*i.e.*, the time to become colourless) also varied. It may be noted that solutions of potassium with no quaternary salt present became colourless after very variable periods of time, and that these times were of the same order as those obtained

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[4] Birch, *Quart. Reviews*, 1950, **4**, 69.

[5] Kantor and Hauser, *J. Amer. Chem. Soc.*, 1951, **73**, 4122.

[6] Watt and Otto, *ibid.*, 1947, **69**, 836.

[7] Craig, *Ind. Eng. Chem. Anal.*, 1936, **8**, 219.

[8] Schwyzer, *Acta Chem. Scand.*, 1952, **6**, 219.

when tetraethylammonium chloride was present. In expts. 3 and 4 excess of potassium was used but similar variations occurred; the use of excess of quaternary salt (expt. 5) or of a higher reaction temperature (expt. 6) did not produce any significant changes except that the reaction time was much shorter at the higher temperature. In expt. 7, the reaction tube was opened after a short period of reaction to find the relative rates of production of ethane and ethylene. In expts. 8 and 9, the reaction was between potassium amide and tetraethylammonium chloride, and the reaction times were arbitrary. Ethylene was the only hydrocarbon product of these amide reactions.

TABLE 1.

Experiment	1	2	3	4	5	6	7	8 †	9 †
Temp.	−78°	−78°	−78°	−78°	−78°	−33°	−78°	−78°	−78°
NEt_4Cl added	1·00	1·06	1·06	0·55	2·15	1·03	1·05	1·10	1·28
NEt_4Cl used	—	—	1·06	0·55	1·00	—	—	0·75	1·19
K added	0·92	0·99	3·96	1·45	1·08	0·92	0·94	0·91	1·16
Products : H_2	0·03	0·27	1·38	0·60	0·05	—	0·01	0·00	0·00
C_2H_6	0·45	0·22	0·48	0·12	0·54	0·42	0·08	0·00	0·00
C_2H_4	0·45	0·66	0·55	0·39	0·55	0·46	0·06	0·29	1·04
NH_2^-	—	0·08	—	0·87	0·05	—	—	0·61	0·08
Time (hr.)	120	186	230	160	160 ‡	20	6 *	24	168

* Reaction incomplete.
† Potassium–ammonia solution colourless before addition of NEt_4Cl.
‡ Left at −78° for a further 384 hours.

TABLE 2.

Experiment	10	11	12	13	14 †	15 †
Halide (X)	Cl	Cl	Br	I	Cl	Cl
NMe_4X added	1·32	6·26	1·48	1·17	2·62	1·92
,, used	0·56	0·70	—	0·27	0·03	0·51
K added	1·14	1·35	1·31	1·15	1·94	1·10
Products : H_2	0·06	0·23	0·34	0·35	0·00	0·00
CH_4	0·49	0·44	0·03	0·20	0·00	0·00
C_2H_6/C_2H_4	trace	trace	trace	trace	0·06 *	0·00
NH_2^-	0·54	0·78	—	0·79	1·81	0·54
Time (hr.)	45	41	168	140	44	312

* Ethylene only.
† Potassium–ammonia solution colourless before addition of NMe_4Cl.

TABLE 3.

Experiment	16	17	18	19	20	21
Cation	$Pr^n_4\overset{+}{N}$	$Et_3\overset{+}{N}H$	$Et_3\overset{+}{N}Me$	$Et_3\overset{+}{N}Me$	$Pr^n_3\overset{+}{N}Me$	$Pr^n_3\overset{+}{N}Me$
added	1·56	1·37	1·36	1·32	1·43	1·32
used	0·98	—	1·07	0·94	1·43	1·00
K added	1·07	1·17	1·07	0·96	1·16	1·12
Products : H_2	0·02	0·54	0·00	0·02	0·00	0·00
CH_4	0·00	0·00	0·45	0·38	0·34	0·52
C_2H_6	0·00	0·00	trace	trace	trace	trace
C_2H_4	0·00	0·00	0·42	0·40	0·00	0·00
C_3H_8	0·48	0·00	0·00	0·00	0·00	0·00
C_3H_6	0·52	0·00	0·00	0·00	0·45	0·47
NH_2^-	0·15	0·07	0·11	0·10	0·28	0·10
Amines	Pr^n_3N	Et_3N	Et_3N	Et_3N	Pr^n_3N	Pr^n_3N
Found	—	—	Et_2NMe	Et_2NMe	Pr^n_2NMe	Pr^n_2NMe
Time (hr.)	<20	<0·01	4	4	0·6	1·6

In the above experiments, triethylamine was the only amine product identified, and no higher hydrocarbons or methane was found.

The results of potassium–tetramethylammonium halide reactions are given in Table 2, expts. 10—13. Methane was the major hydrocarbon product, and trimethylamine was the only amine identified. The trace of noncondensable hydrocarbon was found (in expt. 10) to be mainly ethane, containing a little olefin, probably ethylene. In expts. 10 and 11, with the chloride, the effect of increasing the concentration of the latter was to increase the hydrogen yield, but there was little change in reaction time. Expts. 12 and 13 show that the hydrocarbon yield was reduced when the bromide and iodide were used. In expts. 14 and 15, potassium amide was used and the reaction times were arbitrary. Expt. 14 (where a little ethylene was found) was a single experiment, whereas 15 is typical of several similar experiments in which no ethylene was found.

The reaction of tetra-*n*-propylammonium chloride and potassium is given as expt. 16, Table 3. The other results in this table are for unsymmetrical quaternary salts. The reaction with trimethylammonium chloride was very rapid and hydrogen was the only gaseous product. Triethylmethylammonium chloride also reacted fairly rapidly, and reproducible results were obtained; little or no hydrogen was formed and there were two amine products as well as methane, ethylene, and a trace of ethane. Expts. 20 and 21, by use of methyltri-*n*-propylammonium chloride gave similar results, and propylene instead of ethylene.

DISCUSSION

From a quaternary ion NR_4^+, the hydrocarbon RH and the amine NR_3 are always obtained. This clearly indicates N–C bond fission as postulated by Birch,[4] and suggests the scheme

$$NR_4^+ + e^- \longrightarrow NR_3 + R \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$R + e^- \longrightarrow R^- \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$R^- + NH_3 \longrightarrow RH + NH_2^- \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Amide ion is also produced by electron solvolysis, *i.e.*,

$$NH_3 + e^- \longrightarrow NH_2^- + \tfrac{1}{2}H_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

The tetraethylammonium ion reacts slowly, and the variation in ethane : ethylene ratio does not appear to be determined by reactant ratio or temperature. The absence of butane suggests that ethyl radicals formed by reaction (1) immediately undergo reaction (2), so that disproportionation of ethyl radicals is unlikely as a source of ethylene. The latter must be formed by the reaction

$$NEt_4^+ + NH_2^- \longrightarrow NEt_3 + C_2H_4 + NH_3 \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

If amide ion were formed only by (3), then equal amounts of ethane and ethylene would be expected—provided that reaction (5) is complete when the solution becomes colourless. The results of expts. 8 and 9 verify reaction (5), but show that the reaction is slow at —78°. Expt. 7 shows that formation of ethylene is somewhat less than that of ethane at an early stage in the reaction, and expt. 5 shows that while a $C_2H_6 : C_2H_4$ ratio may exceed 1 after 160 hr. or so, the ultimate ratio is 1 after long storage, *i.e.*, when reaction (5) is complete. But there are experiments in which the $C_2H_6 : C_2H_4$ ratio is much less than 1, and here more ethylene must be formed by amide from the solvolysis reaction (4). The solvolysis reaction can proceed at a rate comparable with that of the ethane-forming reaction; but this rate is subject to considerable variation because of the possible presence of a trace of catalyst. Hence, if the solvolysis reaction happens to be catalysed, then extra ethylene and hydrogen are produced at the expense of ethane. The stoicheiometric basis for this reasoning can be understood by reference to expt. 2. Here, 0·22 mmole of C_2H_4 was produced by amide from reaction (3); hence 0·44 mmole must have been produced by amide from the solvolysis reaction. This corresponds to 0·22 mmole of hydrogen, but the amount actually found was 0·27 mmole. Hence $0{\cdot}05 \times 2 = 0{\cdot}10$ mmole of amide was produced, by solvolysis, in excess of that used to produce ethylene, and should have remained as such. In fact 0·08 mmole was found in the residue. A similar check can be applied in the other cases where the data are available. In expt. 2, the potassium required to produce ethane and ethylene was 0·44 mmole, for the " excess " of ethylene 0·44 mmole, and as residual amide 0·08 mmole, a total of 0·96 mmole compared with 0·99 mmole actually added.

Tetramethylammonium chloride (Table 2) reacts more rapidly than the tetraethylammonium salt, and any effect of solvolysis is therefore reduced. However, the results show that the yield of methane is reduced and that of hydrogen increased by using the bromide or iodide, or by using a large excess of the chloride (expt. 11). Now the amount of quaternary salt added in these experiments exceeds that required to saturate the liquid ammonia at −78°. The effective concentration of quaternary ion is therefore determined primarily by the extent to which the anion X^- is removed as insoluble KX; and as the solubilities of KX are in the order $KI > KBr > KCl$, the quaternary-ion concentration (and yield of methane) will be low in the case of the bromide and iodide. The unused electrons in these cases take part in slow solvolysis and the hydrogen yield therefore increases. The amount of methane and hydrogen is satisfactorily accounted for by the equations (1)—(4). Thus, in expt. 10, 0·98 mmole of potassium is required for the methane and 0·12 mmole for the hydrogen, *i.e.*, 1·10 mmoles. The remainder of the potassium added (0·04 mmole) can be accounted for in terms of the trace of condensable hydrocarbon, mainly ethane. The latter may originate by combination of two methyl radicals, from reaction (1), or by a reaction

$$NMe_4^+ + Me^- \longrightarrow NMe_3 + C_2H_6 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (6)$$

Porter [9] has shown that methyl radicals are produced from tetramethylammonium amalgam on heating, and the recovery of ethane from Thompson and Cundall's tetramethylammonium iodide–potassium reaction at ordinary temperature [1] suggests that radical combination may have occurred in their experiments. But reaction (6) is also a possible source of ethane, since the CH_3^- ion acts as a base in liquid ammonia and so can attack the quaternary ion. In the case of tetraethylammonium salts no corresponding reaction to give butane occurred, probably because of preferential attack on the NEt_4^+ ion by NH_2^- rather than by $C_2H_5^-$ ions.

The results of Table 2 show that some amide and quaternary ions have reacted, but without giving hydrocarbon products. Franklin [10] refers to a reaction

$$NMe_4^+ + NH_2^- \longrightarrow [NMe_4{\cdot}NH_2] \longrightarrow NMe_3 + Me{\cdot}NH_2$$

and the results of expt. 15 show that this reaction occurs slowly at −78°. There remains the single experiment 14, where a small amount of ethylene was produced from the NMe_4^+–NH_2^- reaction, and the probability that a trace of ethylene was formed in the NMe_4^+–K reactions also. Formation of ethylene would require, first, fission of a C–H bond by a base B^-, thus : [5]

$$Me_3\overset{+}{N}{\cdot}Me + B^- \longrightarrow Me_3\overset{+}{N}{\cdot}\overset{-}{C}H_2 + BH \quad . \; . \; . \; . \; . \; . \; . \; . \quad (7)$$

The carbanion formed by this reaction has been prepared in ether solution by Wittig and Wetterling.[11] They found it to be stable; it did not rearrange to give ethyldimethylamine, nor did it decompose directly to give ethylene. Reaction with water gave tetramethylammonium hydroxide. Hence, if ethylene is to be formed from this carbanion, it must be by alkylation to $Me_3N^+{\cdot}CH_2Me$ followed by β-elimination. Now if the base B^- in reaction (7) is NH_2^-, then the reaction produces ammonia. In liquid ammonia as solvent, the reverse of reaction (7) seems probable, by analogy with the reaction with water. Hence little or no ethylene would be expected from a NMe_4^+–NH_2^- reaction. But if B^- is identified as e^-, then reaction (7) becomes

$$\overset{+}{N}Me_4 + e^- \longrightarrow Me_3\overset{+}{N}{\cdot}\overset{-}{C}H_2 + \tfrac{1}{2}H_2 \quad . \; . \; . \; . \; . \; . \; . \; . \quad (8)$$

and hydrogen is produced : and if the carbanion is then destroyed by ammonia, the other reaction product is amide, so that the overall result is

$$e^- + NH_3 \longrightarrow NH_2^- + \tfrac{1}{2}H_2$$

i.e., the same as the solvolysis reaction. It is therefore possible that carbanion formation by reaction (8) can yield a trace of ethylene by alkylation, but the greater amount of carbanion must undergo solvolysis and produce amide. In expt. 11, a large excess of

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[9] Porter, *J.*, 1954, 760.

[10] Franklin, " The Nitrogen System of Compounds," Reinhold, New York, 1935, p. 63.

[11] Wittig and Wetterling, *Annalen*, 1947, **557**, 193.

tetramethylammonium chloride produced more hydrogen and amide, and less hydrocarbon, than the normal amount. It may be that the production of amide and hydrogen was here catalysed by the carbanion mechanism; equally, the effect may have been a heterogeneous catalysis of the solvolysis reaction by the large amount of undissolved quaternary salt.

The reaction of tetra-*n*-propylammonium chloride and potassium (expt. 16, Table 3) proceeds rapidly and little solvolysis occurs. Propane and propene are found in approximately equal amounts as would be expected if amide ion formed by reaction (3) reacts completely with the $Pr^n_4N^+$ ion to yield propene. However, the latter reaction is not complete, since some amide and unchanged quaternary ion are found in the residues. It is therefore possible that all the propane formed was not recovered from the ammonia, *i.e.*, the ratio propane : propene is too low.

The rate of reaction of tetra-alkylammonium ions and potassium is in the order $R = Pr^n > Me > Et$. The rapid reaction of the tetrapropylammonium ion may be attributed to two factors—the greater solubility of the quaternary salt, and the greater ease of fission of the N–Pr bond compared with that of N–Et or N–Me. The more rapid reaction of tetramethyl- than of tetraethyl-ammonium ion cannot be attributed to these factors; but it may well be that reactions (2) and (3) occur more readily with methyl than with ethyl radicals.

With the unsymmetrical quaternary ions of Table 3, N–H or N–C fission occurred to give the tertiary amine, *i.e.*, hydrogen was obtained from trimethylammonium ions and methane from triethyl- or tri-*n*-propyl-methylammonium ions. The amide produced attacks the group with a β-carbon atom if available, *i.e.*,

$$Et_3NMe^+ + NH_2^- \longrightarrow Et_2NMe + C_2H_4 + NH_3$$
$$Pr^n_3NMe^+ + NH_2^- \longrightarrow Pr^n_2NMe + C_3H_6 + NH_3$$

so that two amines are formed in the products. The order of ease of fission here is H > Me > larger alkyl, and the rapidity of reaction of the unsymmetrical ions may be due to a combination of steric effects, the presence of an easily removed hydrogen atom or methyl group, and the ready occurrence of reactions (2) and (3). The appearance of a trace of ethane from the ions Et_3NMe^+ and $Pr^n_3NMe^+$ is of interest. Formation by a reaction

$$R_3NMe^+ + Me^- \longrightarrow R_3N + C_2H_6$$

is unlikely, since methyl ions undergo rapid solvolysis; and in any case, the Me^- ion is a base and the reaction would therefore be (for Et_3NMe^+)

$$Et_3NMe^+ + Me^- \longrightarrow Et_2NMe + MeH + C_2H_4$$

It is more likely that ethane is formed here by union of methyl radicals since these will be released more readily from triethyl- or tripropyl-methylammonium than from tetramethylammonium ions.

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