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An Unusual Reduction of Ethylene Occurring during the Thermal Decomposition of Alkalides and Electrides.

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Abstract: Alkalides and electrides thermally decompose by a reductive elimination process leading to the formation of ethylene and a ring opened complexant which has lost an ethylenic unit. Surprisingly, gas phase nmr also shows the formation of ethane and butane. We postulate that these compounds arise from a reduction of the first-formed ethylene by the alkalide or electride.

Alkalides are ionic salts consisting of an alkali metal cation encapsulated in an organic complexant (crown ether, cryptand, aza crown ether...) and of an alkali metal anion. Since the 1974 preparation and characterization of $Na^+C222Na^-$,[1] the first crystalline alkalide, many other alkalide salts have been prepared. Analogous species in which the anion is an electron are called electrides. To date, crystal structures have been obtained for more than 25 alkalides and four electrides.

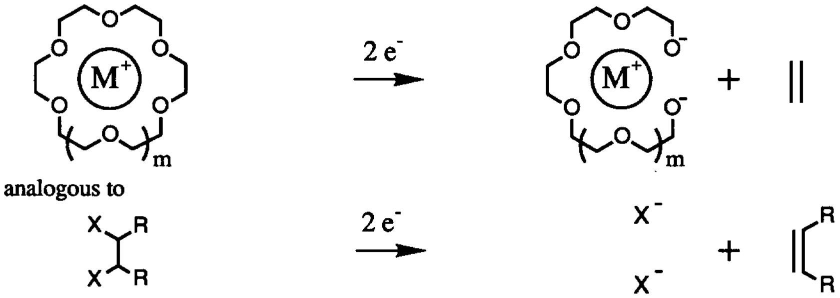
Alkalides and electrides are potent reducing agents. They should be 2 and 1 electron reductants, respectively. Their application for organic reductions has been limited to only a few examples, in which the alkalide is prepared *in situ* by reaction of a solution of a crown ether (or cryptand) with a metal mirror in an inert solvent.[2,3] Recently, they have been used to prepare nanoscale metal particles by homogeneous reduction of metal salts.[4]

In addition to their high reactivity as reductants, alkalides and electrides are thermally sensitive. They can be prepared and studied in pure crystalline form only at low temperatures. They are stable for long periods of time below about - 60 °C, but when warmed to ambient temperatures, they decompose irreversibly in periods that range from a few seconds to several days. Decomposition processes have been studied only in solution, where cleavage of the solvent by the strongly reducing alkalide or electride occurs.[5] Because of our interest in the stability of crystalline alkalides and electrides, we have investigated the products and possible mechanisms of their solvent-free degradation.

We first examined the decomposition products of the compounds $(MC_n)^+M'^-$ and $(MC_n)^+e^-$ (where M and M' are alkali metals, C is a crown ether and n is 1 or 2). Crystalline samples of active compounds were thermally decomposed at room temperature under an inert atmosphere. Depending on the alkalide or electride studied, this process took from a few minutes for the more sensitive compounds to several days for the more stable species. Complete decomposition was indicated by fading of the color, after which the sample was quenched with D_2O.

^1H and ^{13}C NMR showed that a substantial amount of crown ether remained unchanged. The main dissolved organic product (after the quench) was the polyethylene glycol resulting from loss of an ethylenic unit from the crown ether. These results suggest that the main pathway is a "classical" reduction of the crown ether, analogous to the reduction of vicinal dihalides,[6] leading to olefins (Scheme 1). The alkali metal cation in the crown ether may assist the cleavage by polarizing the C-O bonds which are broken.

Scheme 1



In order to probe this pathway more completely, the alkalide or electride was thermally decomposed in a sealed NMR tube, and the gaseous products in the headspace were examined by ^1H NMR. In addition to the expected ethylene, these experiments surprisingly revealed significant quantities of ethane and butane among the decomposition products.[7] Despite substantial effort, we have been unable to establish the source of the extra protons in these saturated products.

Quantitative analysis was accomplished using NMR and a gas evolution apparatus which has been previously described in detail.[8] Cold alkalide samples were placed in a weighed vessel which was then connected to the apparatus and evacuated before decomposition. A calibrated pipet was used to measure the gas volume and a mercury leveling bulb was used to measure its pressure. The gases were then condensed in an NMR tube and the composition of this mixture was determined by gas phase NMR. Relaxation times for all the gases studied were determined, and sufficient delay times were used to yield reliable integrations. The non-volatile residue was weighed, dissolved in D_2O and its composition determined by ^1H and ^{13}C NMR.

Examples of the results obtained for an alkalide $[Cs^+(18C6)_2Cs^-]$ and an electride $[K^+(15C5)_2e^-]$ are presented in Table 1. In both cases the quantities of ethylene, ethane and butane found account quite well for the amount of crown ether converted. Thus, we obtain rather good carbon balances for the decomposition. We may also examine the "electron balance" by counting the reducing equivalents consumed. Reduction of the crown ether to polyethylene glycol is expected to need 2 electrons per crown ether. Similarly, formation of ethane and butane from ethylene requires 2 additional electrons in each case. Since the alkalide is expected to give 1 electron per crown ether, while for the electride it is only 1/2 electron per crown ether, we can estimate "electron yields" by dividing the number of electrons used to produce the reduced species by the number of electrons available. These "yields" are respectively ca. 76 % and ca. 93 %. While the second is quantitative within experimental error, it is not clear why the first one is too small. Some possible explanations are as follows: i) decomplexation occurred during the decomposition yielding alkali metal that might not be a strong enough reductant to react with the crown ether or with ethylene; ii) sample was partially decomposed before the decomposition study;

iii) sample was contaminated by an excess of crown ether; iv) reaction was not completed (our only criterion to determine the end of the decomposition is the color of the alkalide).

Table 1 : Products Obtained by Decomposition of an Alkalide and an Electride.

Compound	Crown Ether Derivatives (%)		Gases (mol % relative to Starting Material)			
	Unreacted Crown Ether	Polyethylene Glycol	Ethylene	Ethane	Butane	Total Yield of Gases*
$Cs^+(18C6)_2Cs^-$	74.4	25.6	10.9	7.9	4.4	27.6
$K^+(15C5)_2e^-$	79.9	20.1	12.4	0.6	2.5	18.0

*This mol percent is given in terms of C2 units (the butane percentage is multiplied by 2, the number of C2 units incorporated)

In search of the origins of the reduction products, we used fully deuterated ethylene to demonstrate that gaseous ethylene can be reduced by a crystalline alkalide at low temperature. In a typical procedure, a cold active alkalide was quickly loaded, under an inert atmosphere of nitrogen, in the reaction vessel. After evacuation to ca. 10^{-5} Torr, the vessel was connected to another vessel that contained the desired amount of ethylene-d_4, and the latter was condensed into the reaction vessel. The temperature was maintained at - 40 °C (a temperature at which the alkalide is relatively stable) until the alkalide was completely decolorized (roughly a week in the case of $Cs^+(18C6)_2Cs^-$). The gases were then condensed into an NMR tube which was then sealed and examined by ^1H and ^2H gas phase NMR. Three deuterated gases were observed in these experiments: unreacted ethylene-d_4, ethane-d_4 and butane-d_8 (Scheme 2). Typical yields obtained (based on ethylene-d_4) were ca. 5 % of ethane-d_4 and ca. 70 % of butane-d_8.

Scheme 2

It appears from the labeling studies above that ethane and butane are produced during normal decomposition by further reaction of the initially formed ethylene with undecomposed crystalline alkalides or electrides. This sequential pathway was confirmed by an experiment in which the gaseous products were continuously removed from the decomposition mixture by trapping them in a side arm at liquid nitrogen temperature. Ethylene was then the only gas observable by ^1H gas phase NMR, implying its intermediacy in the paths to alkanes.

The observation of alkene reduction by alkalides in solution has been reported.[3] However, the strongly negative electron affinity of ethylene in the gas phase[9] makes the present observation particularly intriguing. In the light of recent matrix isolation studies,[10] where an electron was trapped by an alkene in alkane matrices, we think it likely that ethylene in the polar environment of the solid alkalide may similarly trap an electron. The resulting radical anion would then produce ethane and butane by various sequences of protonation or hydrogen atom abstraction, further electron transfer and dimerization, in unknown order.[11]

An unresolved problem about our suggested mechanism is the nature of the proton source. Despite careful examination of the reaction mixtures, we have not been able to identify any other products than the ones reported above. Specifically ^{1}H and ^{13}C NMR of the quenched solutions do not show any olefinic or aldehydic products. Such compounds would be expected if a proton were abstracted from the crown ether. When methyl iodide was used as a quencher, polyglymes were obtained instead of the polyethylene glycols, but no other methylated products were observed. This rules out the presence of carbanions in the reaction mixture. Further experiments to identify the proton source are in progress.

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References and Notes

1. Dye, J. L.; Ceraso, J. M.; Lok, M. T.; Barnett, B. L.; Tehan, F. J. *J. Amer. Chem. Soc.* **1974,** *96*, 608.
2. see for example: (a) Jedlinski, Z.; Misiolek, A.; Glowkowski, W.; Janeczek, H.; Wolinska, A. *Tetrahedron* **1990,** *46*, 3547-3558. (b) Barrett, A. G. M.; Godfrey, C. R. A.; Hollinshead, D. M.; Prokopiou, P. A.; Barton, D. H. R.; Boar, R. B.; Joukhadar, L. J.; McGhie, J. F.; Misra, S. C. *J. Chem. Soc. Perkin Trans. I*, **1981**, 1501-1509. (c) Ohsawa, T.; Mitsuda, N.; Nezu, J.; Oishi, T. *Tetrahedron Lett.*, **1989,** *30*, 845-846 and references cited therein.
3. Mathre, D. J.; Guida, W. C. *Tetrahedron Lett.* **1980,** *21*, 4773-4776.
4. Tsai, K.-L.; Dye, J. L. *J. Amer. Chem. Soc.* **1991,** *113*, 1650.
5. Jedlinski, Z.; Stolarzewicz, A.; Grobelny, Z. *Makromol. Chem.* **1986,** *187*, 795.
6. for a review, see Baciocchi, E. 1,2-dehalogenations and related reactions. In *The Chemistry of Functional groups, Supplement D;* Patai, S.; Rappoport, Z. Eds; John Wiley and Sons Ltd.: New York, 1983; pp. 161-201.
7. The formation of all gases was confirmed by gas chromatography. The headspace gas phase NMR technique has recently been applied to the study of polyphosphoric acid catalyzed hydrocarbon formation from methanol: Jackson, J. E.; Bertsch, F. M. *J. Amer. Chem. Soc.* **1990,** *112*, 9085.
8. Dewald, R. R.; Dye, J. L. *J. Phys. Chem.* **1964,** *68*, 128.
9. Jordan, K. D.; Burrow, P. D. *Chem. Rev.* **1987,** *87*, 557-588 and references cited therein.
10. Muto. H.; Nunome, K.; Matsura, K. *J. Amer. Chem. Soc.* **1991,** *113*, 1840-1841.
11. A similar mechanism has recently been proposed for the reaction of lithium with ethylene at low temperature: Van Eikema Hommes, N. J. R.; Bickelhaupt, F.; Klumpp, G. W. *Angew. Chem., Int. Ed. Engl.* **1988,** *27*, 1083.

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