

09PH
H596



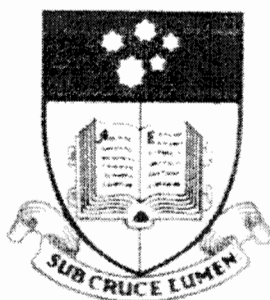
Migration and Cyclisation Reactions of Selected Organic Anions

A Thesis Submitted Towards the Degree of

Doctor of Philosophy

by

John Michael Hevko B.Sc. (Hons)



THE UNIVERSITY OF ADELAIDE

Department of Chemistry
The University of Adelaide
December 1998

Table of Contents

Abstract	xv
Statement	xvii
Acknowledgments	xviii
Chapter 1 - Introduction	
1.1 General Introduction	1
1.2 Formation of Negative Anions	2
1.2.1 Primary Ions	2
1.2.1.1 Resonance Capture (electron attachment)	3
1.2.1.2 Dissociative Resonance Capture (dissociative electron attachment)	5
1.2.1.3 Ion-Pair Formation	7
1.2.2 Secondary Ions Formed <i>via</i> Ion-Molecule Reactions	8
1.2.2.1 Proton Transfer	9
1.2.2.2 Charge Exchange	10
1.2.2.3 Nucleophilic Addition	10
1.2.2.4 Nucleophilic Displacement	11
1.3 The VG ZAB 2HF Mass Spectrometer	11

1.4	Mass Analysed Ion Kinetic Energy Mass Spectrum	14
1.5	Linked B^2/E Scanning	15
1.6	Structural Identification of Ions	16
1.6.1	Collisional Activation (CA)	17
1.6.2	Charge Reversal (CR) MIKE Scanning	17
1.6.3	Kinetic Energy Release (Peak Profiles)	19
1.7	Theoretical <i>Ab Initio</i> Molecular Orbital Calculations	22
1.8	Negative Ion Fragmentations	29
1.8.1	Simple Homolytic Cleavage	29
1.8.2	Formation of an Ion-Neutral Complex	30
1.8.3	Proton Transfer or Rearrangement Preceding Fragmentation	30
1.8.4	Remote Fragmentations	32
1.9	Migration of Anions	33

Chapter 2 - Cross-Ring Phenyl Anion Initiated Reactions as Fragmentations of (M-H)⁻ Species.

2.1	Introduction	35
2.2	Results and Discussion	37
2.2.1	N-(Methoxyphenyl) benzamide Series	37
2.2.2	N-(Ethoxyphenyl) benzamide Series	48
2.2.3	Methyl-benzoylaminobenzoate Series	51
2.3	Summary, Conclusions and Future Work	55

Chapter 3 - Ion Mobility in Keto Substituted Alkoxide Anions

3.1	Introduction	57
3.2	Results and Discussion	61
3.2.1	Migration of the Hydride Ion	62
3.2.1.1	Reactions of Deprotonated 6-Hydroxy-hexan-2-one	62
3.2.1.2	Reactions of Deprotonated 5-Hydroxy-pentan-2-one	74
3.2.1.3	Reactions of Deprotonated 7-Hydroxy-heptan-2-one	79
3.2.2	Possible Migration of the Methyl Ion	83
3.2.2.1	Reactions of Deprotonated 2-Dimethyl Substituted Keto-Alcohols	83
3.3	Summary and Conclusions	89

Chapter 4 - Competitive Cyclisations of Epoxy-Alkoxide Ions

4.1	Introduction	90
4.2	Results and Discussion	95
4.2.1	Competitive Cyclisations of the 3,4-Epoxybutoxide Anion	95
4.2.1.1	<i>Ab Initio</i> Calculations for Competing Cyclisations of the 3,4-Epoxybutoxide Anion	96
4.2.1.2	Gas Phase Reactions of 1, 2 and 3	98

4.2.1.3	Condensed Phase Reactions of 1 , 2 and 3	111
4.2.1.4	Summary	112
4.2.2	Competitive Cyclisations of 4,5-Epoxy pentoxide Anion	113
4.2.2.1	<i>Ab Initio</i> Calculations for Competing Cyclisations of the 4,5-Epoxy pentoxide Anion	114
4.2.2.2	Gas Phase Reactions of 7 , 8 and 9	115
4.2.2.3	Condensed Phase Reactions of 7 , 8 and 9	130
4.2.2.4	Summary	131
4.2.3	Competitive Cyclisations of 5,6-Epoxy hexoxide Anion	131
4.2.3.1	<i>Ab Initio</i> Calculations for Competing Cyclisations of 5,6-Epoxy hexoxide Anion	132
4.2.3.2	Gas Phase Reactions of 10 , 11 and 12	133
4.2.3.3	Condensed Phase Reactions of 10 , 11 and 12	144
4.2.3.4	Summary	145
4.3	Competing S_Ni Reactions - The Arrhenius Factor	146
4.4	Conclusions	161

Chapter 5 - Experimental

5.1	General Experimental	163
5.2	Compounds Described in Chapter 2	166
5.3	Compounds Described in Chapter 3	170

5.4	Compounds Described in Chapter 4	180
5.4.1	Compounds Described in Section 4.2.1	180
5.4.2	Compounds Described in Section 4.2.2	185
5.4.3	Compounds Described in Section 4.2.3	191
Appendices		200
References		228
Publications		246

Abstract

In this thesis the investigation of anionic migration reactions in the gas phase, and rearrangement reactions of selected organic anions in the gas and condensed phases were examined.

"Long-range" phenyl anion "cross-ring" reactions occur when $(M-H)^-$ ions of methoxy-, ethoxy-, and carbomethoxy- $C_6H_4^-NCOPh$ are subjected to collisional activation. These reactions are generally minor processes: a particular example is the "cross-ring" elimination $p-C_2H_5O-C_6H_4^-NCOPh \rightarrow [Ph^-(p-C_2H_5O-C_6H_4-NCO)] \rightarrow p-(^-\text{O})-C_6H_4-NCO + C_2H_4 + Ph$. Major processes of these $(M-H)^-$ ions involve losses of radicals to form stabilised radical anions, e.g. (a) loss of a ring H^\cdot or (b) CH_3^\cdot , (or $C_2H_5^\cdot$, or $\cdot CO_2CH_3$) from the alkoxy group.

Keto alcohols of the formula $MeCO(CH_2)_nOH$ ($n = 3 - 5$) are deprotonated by HO^- at both $-OH$ or α to the carbonyl group. The various deprotonated species interconvert under the conditions of collisional activation. The fragmentations of $(M-H)^-$ ions are varied and complex, with most fragmentations being directed from the alkoxide centre. These fragmentations have been investigated by product ion and deuterium labelling studies. An interesting hydride transfer reaction occurs when $n = 3$ and 4, i.e. H^- transfer occurs from the CH_2 group next to the alkoxide centre to the carbon of the carbonyl group to form $^-\text{CH}_2\text{CHO}$ as the product anion. This reaction does not occur when $n = 5$. The corresponding Me^- transfer from deprotonated $MeCO(CH_2)_nC(Me)_2OH$ ($n = 2$ and 3) is not observed.

Ab initio calculations [at the MP2(fc)/6-31+G(d) level] indicate that the 3,4-epoxybutoxide anion, the 4,5-epoxypentoxide anion, and the 5,6-

epoxyhexoxide anion should undergo competitive S_Ni cyclisations (through four- and five-, five- and six-, and six- and seven-membered transition states respectively) to yield the corresponding $(M-H)^-$ ions of the respective cyclic products. These systems have been studied experimentally in both the condensed and gas phases. A comparison is made of the reported competitive S_Ni reactions for the 2,3-epoxypropoxide anion, with those processes observed for 3,4-epoxybutoxide, 4,5-epoxypentoxide and 5,6-epoxyhexoxide anions. For all but the 3,4-epoxybutoxide system, the exclusive or major product is that which contains the smaller of the two ring systems for both gas phase and condensed phase reactions. In the case of the 3,4-epoxybutoxide system:- (i) in the gas phase, both four- and five-membered ring S_Ni products are formed in comparable yield, and (ii) in the condensed phase, the major product is that with the larger ring.