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REACTIVITIES OF ANIONIC SPECIES FOR THE RING OPENING OF ETHYLENE OXIDE

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Anionic polymerisation of ethylene oxide has been studied for a long time by several authors. However the dependence of the rate of polymerization on the concentration of active centers is complex due to associations of ion pairs which persist down to low living ends concentrations, and occur even in high polarity solvents such as HMPA.

As models of the nucleophilic ring opening of ethylene oxide, we have investigated the reactivity of this monomer with various nucleophilic initiators for which the concentrations of the different ionic species could be measured and varied according to solvent, concentration and temperature (1). Similar studies have been done by Hogen-Esch et al. (2) and by Kazanskii et al. (3).

More recently we have examined the effects of the addition of some macrobicyclic ligands discovered by Lehn (4) on both kinetics of initiation and propagation reactions of the anionic polymerization of ethylene oxide. These ligands form extremely stable cation inclusion complexes, called cryptates, in which the cation is completely surrounded by the ligand. This leads to a considerable increase of the interionic distance in the corresponding ion pair and of the dissociation constant K_D. Moreover the aggregates are destroyed making possible the determination of ion pairs and free ions reactivities for the propagation reaction, in THF at 20°C, since cryptated living ends are stable.

We wish to report our recent results in this field and we will discuss the relative reactivities of free ions and of various types of ion pairs for the ring opening of ethylene oxide.

Initiation Reaction

Such reactions are conveniently studied by UV and visible spectrophotometric monitoring of the anion absorption in the presence of excess epoxide in different media, in and without the presence of an equimolar amount of cryptand |222|. Our results are shown in Table 1.

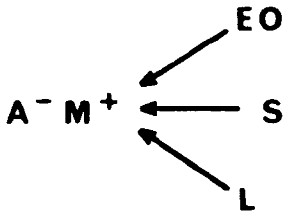
Table 1. Reactivities of Ion Pairs and Free Ions in the Cleavage of Ethylene oxide by Several Organometallic Compounds.

A^-M^+ /Solvent	t°C	k± l. mole^{-1}.min^{-1}.	k- l. mole^{-1}.min^{-1}.
NNa/THF	20	$8.5\ 10^{-3}$	-
NK/THF	20	$21 \pm 3\ 10^{-3}$	-
NK+|222|/THF	20	$78 \pm 8\ 10^{-3}$	$78 \pm 8\ 10^{-3}$
NK/HMPA	20	-	$82 \pm 8\ 10^{-3}$
DBNK/THF	20	$5.7 \pm 0.3\ 10^{-3}$	-
DBNK+|222|/THF	20	$2.4 \pm 0.6\ 10^{-3}$	$2.4 \pm 0.6\ 10^{-3}$
9MeFlNa/THP	-30	$8.5\ 10^{-1}$	-
9MeFlK/THP	-30	$9\ 10^{-3}$	-
9MeFlNa+|222|/THP	-30	$3\ 10^{-5}$	-
9MeFlNa/THF	-30	$2.5\ 10^{-1}$	-
9MeFlNa+|222|/THF	-30	$3\ 10^{-5}$	$3\ 10^{-5}$

N : Carbazyl ; DBN : Dibenzocarbazyl ; 9 MeFl : 9-methylfluorenylanions.

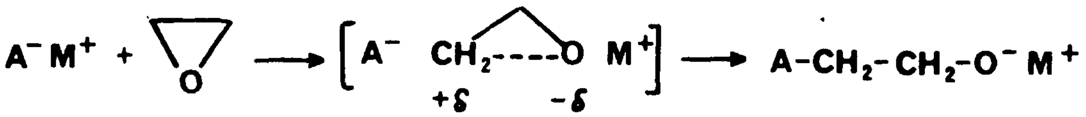
In some systems such as carbazyl and poly(styryl) salts (3), the ion pair reactivity increases with the size of the counterion whereas the results are opposite for 9-methylfluorenyl, fluoradenyl (2) and dibenzocarbazylsalts.

These results can be explained if we consider that ethylene oxide may strongly interact with alkali cations M^+. In his studies on cation effects in ethylene oxide cleavage reactions initiated by fluoradenylsalts Hogen-Esch (2) has shown that EO is a substantially stronger coordinating solvent than THF and THP. According to the following scheme :



M^+ is, of course, attracted by A^- but it can interact also with solvent (S), EO or with a ligand (L) such as crown ethers (CE) or cryptands; the strength of this interaction following the sequence : THP < THF < EO << CE < |222|. This coordination will be stronger if the negative charge on the anion is more delocalized. It will be also stronger for smaller cations of high field strength such as Li^+ for a given anion.

Thus when EO can act as a coordinating agent (delocalization of the anion, absence of ligand) a "push-pull" mechanism may be written :



In this scheme the transition state is stabilized by the interaction of the metal ion and the incipient negative charge on oxygen. In other words, electrophilic activation of EO by cation plays a predominant role in the reaction.

For more localized anions, interaction between M^+ and EO is largely weakened and the predominant factor is the interaction between A^- and M^+ leading to a decrease of nucleophilicity and thus of reactivity of A^- on decreasing the size of the cation.

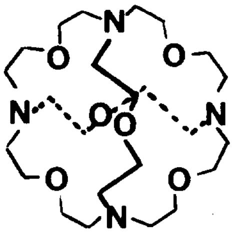
Propagation reaction

Kinetic measurements were made by dilatometry, in THF at 20°C, at concentrations lower than 2 10^{-4} mole. l^{-1} since associations of ion pairs become too important and cannot be neglected at higher concentrations. Use of cryptates leads to the formation of a simple equilibrium between cryptated alkoxide ion pairs and free ions, and allows the determination of k_- (5). The results obtained with different counterions are shown in Table 2.

Free alkoxide ions are more reactive than ion pairs. Cryptated ion pairs are surprisingly slightly less or as reactive as the corresponding non complexed ion pairs within the experimental errors though the charges are more separated. K_D is equal to 3 10^{-7} for $\sim\!\sim O^- K^+|222|$ in THF at 20°C (5) instead of 1.8 10^{-10} for $\sim\!\sim O^- K^+$ (7). The former value leads to an interionic distance a_K^F equal to 4.6 Å according to the Fuoss equation :

$$K_D = 3000/4\pi N(a_K^F)^3 \quad \exp \quad (-e^2/a_K^F DkT)$$

Table 2. Propagation Constants of Ion Pairs and Free Ions for the Anionic Polymerization of Ethylene Oxide in THF at 20°C.

Counterion	$k_{\pm}$ l. $mole^{-1}.min^{-1}$.	k_{-} l. $mole^{-1}.min^{-1}$.
Na^+	∿0	-
Na^+ + |222|	∿0	-
K^+	∿2.9	-
K^+ + |222|	1.5	100
Cs^+	7.3	-
Cs^+ + |TC|	5.6	-
[TC] =	 (6)	

This value is too small with respect to the results obtained for cryptated living poly (propylene) sulphide (8) and for cryptated tetraphenylborides in THF (9). This might mean that the oxanion could penetrate into the cavity of the ligand because it is a small anion of high field strength. The unexpected low reactivity of cryptated alkoxide ion pairs might be explained by a steric hindrance phenomenon.

In conclusion, it was shown that the ability of ethylene oxide to strongly interact with alkali cations can explain the differences in epoxide cleavage rate by several organo-alkali salts.

References

1. D. Lassalle, S. Boileau, and P. Sigwalt, Europ. Polym. J. 13, 599 (1977).
2. C.J. Chang, R.F. Kiesel, and T.E. Hogen-Esch, J. Amer. Chem. Soc. 95, 8446 (1973).
3. A.A. Solovyanov, and K.S. Kazanskii, Vysokomol. Soedin. A 16, 595 (1974).
4. J.M. Lehn, Structure and Bonding, 16, 1 (1973).
5. A. Deffieux, and S. Boileau, Polymer, 18, 1047 (1977).
6. E. Graf, and J.M. Lehn, J. Amer. Chem. Soc. 97, 5022 (1975).
7. A.A. Solovyanov, and K.S. Kazanskii, Vysokomol. Soedin. A 14, 1063 (1972).
8. P. Hemery, S. Boileau, and P. Sigwalt, J. Polym. Sci. Symp. 52, 189 (1975).
9. S. Boileau, P. Hemery, and J.C. Justice, J. Solut. Chem. 4, 873 (1975).