Kinetics of ring opening of propylene sulphide: 1. Alkali metal and cryptated alkali metal carbazyl salts

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(Received 5 May 1979; revised 4 July 1979)

The reactivities of free ions and ion pairs have been determined for the ring opening of propylene sulphide with carbazyl salts, in THF at −30°C. A large increase of the ion pair reactivity is observed on increasing the size of the counterion ($Na^+ < Cs^+ < Na^+ +$ [222]). Moreover, cryptated carbazyl ion pairs are three times more reactive than free ions in the same manner as thiolate species for the propagation of propylene sulphide in similar conditions.

INTRODUCTION

Some very powerful cation binding reagents called cryptands recently discovered by Lehn *et al.*[1] have been used for the anionic polymerization of propylene sulphide, in tetrahydrofuran (THF)[2,3]. The propagation rate is greatly enhanced. This is due not only to a large increase of the propagation of free ions which are very reactive, but also to the fact that cryptated thiolate ion pairs are more reactive than free ions.

The initiation reaction of anionic polymerization of propylene sulphide has been studied by u.v. and visible spectrophotometry, using alkaline salts of carbazole with and without cryptands, in THF at −30°C. The reactivities of different types of ionic species with propylene sulphide could be obtained since we were able to determine the extent and the structure of ion pairing in the systems investigated from spectrophotometry and conductivity measurements.

EXPERIMENTAL

All the experiments occurred in glass apparatus sealed under high vacuum as usual. THF and propylene sulphide were dried over calcium hydride and several sodium mirrors as described elsewhere[3]. Alkaline salts of carbazole were prepared by adding solutions of carbazole to solutions of alkaline dianions of 1,1-diphenylethylene, in stoichiometric proportions. The macroheterobicyclic compound. $N[CH_2CH_2(OCH_2CH_2)_2]_3N$, ([222]), was purified by freeze-drying in benzene and sealed under high vacuum in ampoules fitted with break-seals as described previously[4]. The [222] compound was added to the carbazyl salt solution in a ratio $[222]/[M^+]$ slightly higher than 1 in order to insure a complete complexation of the cation.

A full description of the conductance apparatus and of the procedure used in obtaining the conductance data have been reported elsewhere[4,5] as well as the spectrophotometric method used for kinetic measurements of the initiation reaction in the case of ethylene oxide[6].

RESULTS AND DISCUSSION

The initiation reaction of anionic polymerization of propylene sulphide has been studied using carbazyl salts, in THF at −30°C, with Na^+, Cs^+ and $Na^+ +$ [222] as counterions. These initiators lead to living monofunctional polymers, the molecular weight of which can be predicted from the monomer and initiator concentrations[7,8].

Table 1 gives the results of physicochemical studies made on carbazyl salt solutions. In THF, carbazylsodium and carbazylcaesium are predominantly of the tight ion pair variety. The dissociation constants K_D are very low for these salts whereas K_D markedly increases when the sodium cation is cryptated. In this case, all the ion pairs are loose and the fraction of free ions may vary from 0.1 to 0.4 in the concentration range examined in the present work (that is from 4×10^{-4} to 8×10^{-5} mol l^{-1}).

Propylene sulphide ring opening was followed by monitoring the decrease of the highest maximum of absorption of the carbazyl salt for which the Beer–Lambert relation has been verified. The rate of disappearance of initiator is given by:

$$R_i = -\frac{dC}{dt} = k_i C^x M^y \qquad (1)$$

Table 1 Physicochemical studies on carbazyl salts solutions in THF

	Spectrophotometry		Conductivity
Counterion	Ion pairs λ max. (nm)	Free ions λ max. (nm)	K_D (−30°C)
Na^+	380; 399	–	1.3×10^{-9}
Cs^+	387; 407.5	–	4.1×10^{-8}
$Na^+ +$ [222]	398.5; 420	398.5; 420	1.45×10^{-5}

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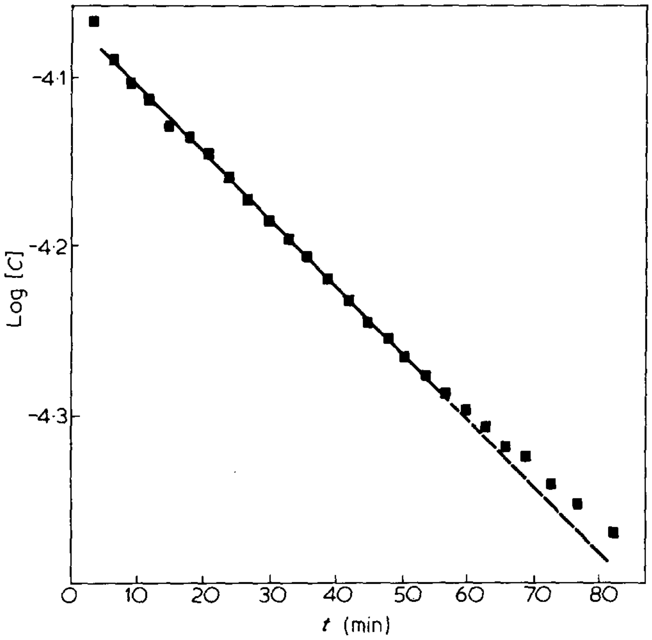

Figure 1 Plot of log C vs time for the reaction of carbazylcaesium with propylene sulphide, in THF at –30°C (C_0 = 1.13 x 10^{-4} mol l^{-1}) λ = 387 nm

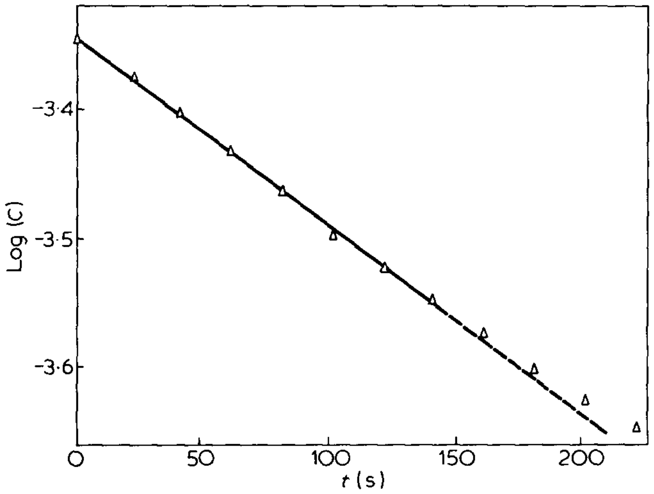

Figure 2 Plot of log C vs time for the reaction of carbazylsodium + |222| with propylene sulphide, in THF at –30°C (C_0 = 4.49 x 10^{-4} mol l^{-1}) λ = 398.5 nm

where C, C_0, M, M_0 are the initiator and monomer concentrations at a given time t and for $t = 0$ respectively, k_i is the apparent rate constant of initiation, x and y are the orders of the reaction for initiator and for monomer. All the initiation reactions were made with a large excess of monomer over initiator ($M_0 \gg C_0$); thus $M \approx M_0$. We have assumed that x and y are equal to 1. This is verified at the beginning of the reaction of carbazylcaesium and of carbazylsodium + |222| with propylene sulphide since plots of log C vs time are straight lines as shown in *Figures 1* and *2*. Thus k_i can be deduced from the slope of these lines. Several experiments were carried out with different values of C_0 in the case of Na^+, Cs^+ and Na^+ + |222| as counterions. The results are given in *Table 2*.

For cryptated carbazylsodium, both free ions and ion pairs contribute to the reaction:

$$k_i = (1-\alpha)k_{\pm} + \alpha k_{-} \qquad (2)$$

$k_{\pm}$ and k_{-} are the initiation constants on the ion pairs and on the free ions, and α is the fraction of free ions which is known from the value of K_D, at different initiator concentrations. When k_i is plotted vs α, a straight line is obtained which leads to the values of $k_{\pm}$ and k_{-}, in the case of cryptated carbazylsodium (*Figure 3*).

When α is very low and $k_{-} \gg k_{\pm}$, equation (2) can be simplified:

$$k_i \cong k_{\pm} + k_{-} K_D^{1/2} C^{-1/2} \qquad (3)$$

Such a relationship is verified in the case of carbazylcaesium since the plot of k_i vs $C^{-1/2}$ is a straight line from which $k_{\pm}$ and k_{-} can be determined (*Figure 4*).

It might be noticed that k_i is determined from the slope of log C vs time, however it depends on α which varies with time since C is decreasing. We have verified that after 40% of conversion of the initiator, there is an increase of 2% for k_i in the case of Na^+ + |222| whereas there is a decrease of 7% for k_i in the case of Cs^+. These variations are negligible with respect to the experimental errors.

Two experiments have been performed with carbazylsodium. In this case, $k_{\pm}$ was determined from equation (2) in which k_{-} was equal to 0.31 mol^{-1} min^{-1} (average value found in the case of Cs^+ and of Na^+ + |222|, see *Table 3*).

Table 2 Kinetic results for the ring opening of propylene sulphide with carbazyl salts, in THF at –30°C

Run	Counterion	C_0 x 10^4 (mol l^{-1})	M_0 (mol l^{-1})	k_i (l mol^{-1} min^{-1})	α[a]
1	Na^+	5.15	0.752	0.00052	0.0016
2		13.00	1.610	0.00034	0.0010
3	Cs^+	1.13	0.908	0.0094	0.019
4		1.84	1.165	0.0078	0.015
5		3.22	0.818	0.0065	0.011
6		6.31	1.256	0.0055	0.008
7	Na^+ + |222|	0.78	0.165	0.612	0.365
8		1.69	0.351	0.674	0.272
9		2.53	0.507	0.703	0.235
10		4.49	0.279	0.721	0.176

[a] calculated taking into account the small increase of the dielectric constant of the solution due to propylene sulphide (D_{PS} = 13.6 whereas D_{THF} = 9.3 at –30°C)[3]

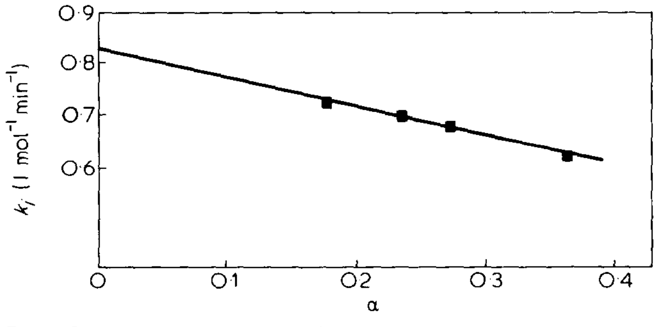

Figure 3 Linear dependence of the apparent bimolecular rate constant of the ring opening of propylene sulphide by carbazylsodium + |222| on the fraction of free ions α, in THF at –30°C

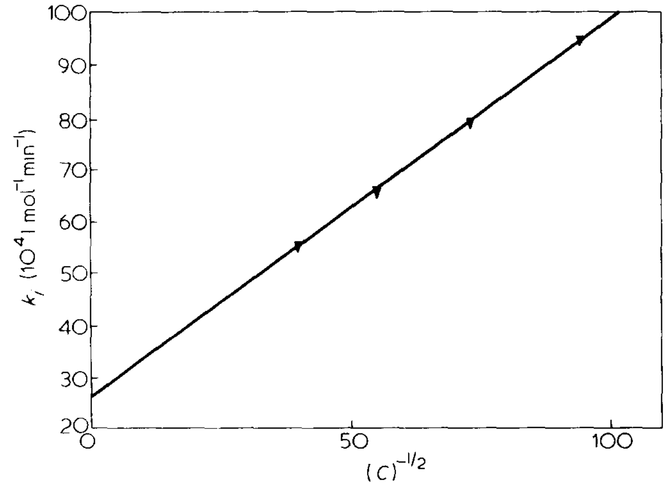

Figure 4 Linear dependence of the apparent bimolecular rate constant of the ring opening of propylene sulphide by carbazylcaesium on the reciprocal of the square root of initiator concentration, in THF at –30°C

Table 3 Reaction of propylene sulphide with carbazyl salts in THF at –30°C

Counterion	$k_{\pm}$ l mol^{-1} min^{-1}	k_{-} l mol^{-1} min^{-1}
Na^+	4×10^{-5}	–
Cs^+	2.6×10^{-3}	0.35
Na^+ + I222I	0.825	0.28

The values of $k_{\pm}$ and of k_{-} are collected in *Table 3* for different counterions. The values obtained for k_{-} are nearly the same within experimental errors. A large increase of $k_{\pm}$ is observed on increasing the size of the counterion. Moreover, for Na^+ + I222I, cryptated ion pair reactivity is three times that of free ions.

The initiation of anionic polymerization of propylene sulphide by carbazyl salts, in THF at –30°C, exhibits the same behaviour as that observed for the propagation reaction of this monomer in the same conditions[3]. If we compare the reactivity of carbazyl salts to that of thiolates, we can see that the ratio k_{-} (thiolate)/k_{-} (carbazyl) is nearly the same as the corresponding ratio of $k_{\pm}$ for cryptated ion pairs. Thiolate free ions are about 800 times more reactive than carbazyl free ions for the ring opening of propylene sulphide. This large difference in reactivity between these two types of nucleophiles may be partly explained by the high polarizability of thiolate anions.

On the other hand, it may be asked whether the monomer concentration remains constant during the initiation reaction since k_p/k_i is high. The rate of disappearance of monomer is given by:

$$-\frac{dM}{dt} = k_p M(C_0 - C) + k_i MC \tag{4}$$

where k_p is the apparent rate constant of propagation.

$$-\frac{dC}{dt} = k_i MC \tag{5}$$

thus:

$$\frac{dM}{dC} = 1 + \frac{k_p}{k_i}\,\frac{(C_0 - C)}{C} \tag{6}$$

$$M - M_0 = C - C_0 + \frac{k_p}{k_i} C_0 L_n \frac{C}{C_0} - \frac{k_p}{k_i}(C - C_0) \tag{7}$$

If we call

$$X_i = \frac{C_0 - C}{C_0}$$

and

$$X_p = \frac{M_0 - M}{M_0}$$

equation (7) becomes:

$$X_p = X_i \frac{C_0}{M_0} - \frac{k_p}{k_i}\,\frac{C_0}{M_0}\,|L_n(1 - X_i) + X_i| \tag{8}$$

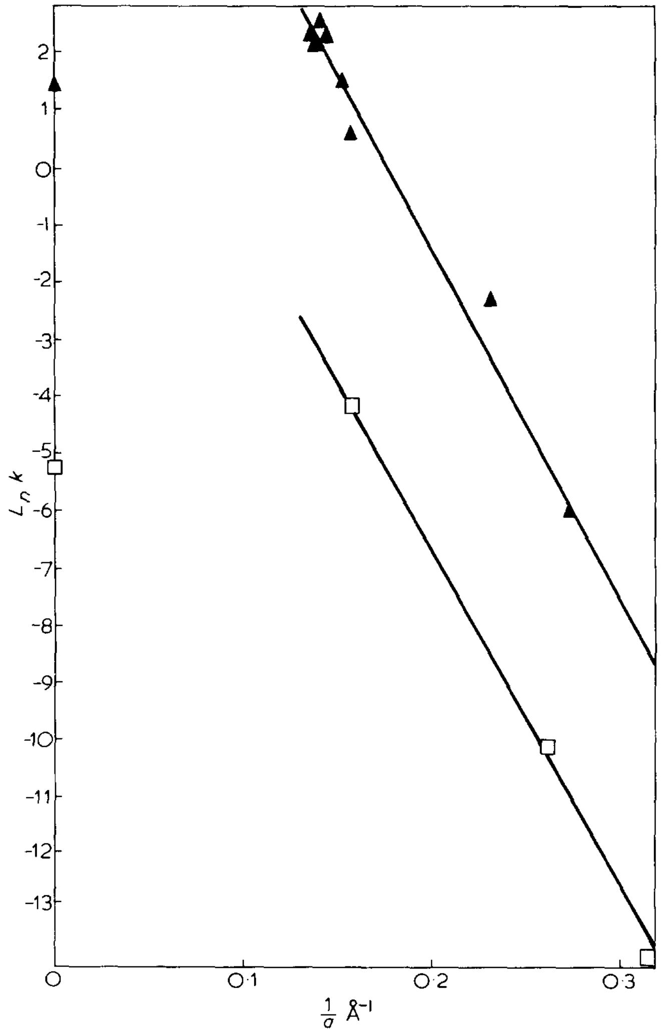

Figure 5 Variations of the thiolate and carbazyl ion pairs reactivities with the reciprocal of the interionic distance parameter of ion pairs for the ring opening of propylene sulphide, in THF at –30°C. ▲ – thiolate ion pairs (ref 3); □ – carbazyl ion pairs

All our experiments have been made with a large excess of monomer over initiator ($C_0/M_0 \leqslant 1.6 \times 10^{-3}$). In the case of Na^+ + |222| as counterion, we have calculated X_p for different values of X_i. For instance, in the case of run 10 (*Table 2*), $C_0/M_0 = 1.6 \times 10^{-3}$, $k_i = 0.7$ l mol^{-1} min^{-1} and $k_p = 650$ l mol^{-1} min^{1} (ref 3), we found a decrease of 9% of the monomer concentration when 30% of the initiator was consumed. The decrease of the monomer concentration is less important for the other experiments.

In *Figure 5*, we have plotted $L_n k_\pm$ vs the inverse of the interionic distance a in the ion pair for thiolates and carbazyl salts. The results lie approximately on parallel straight lines. The experimental values for k_-, in both cases, are quite far from the extrapolated values for $a = \infty$. One can conclude that, for the ring opening of propylene sulphide by nucleophiles having a localized negative charge, ion pairs and free ions react with the monomer according to different mechanisms. It may be imagined that a polarization of the CH_2–S bond in the monomer occurs before the ring cleavage and is induced by the ion pair dipole of the thiolate or carbazyl ion pair. Such a modification should increase with the magnitude of the ion pair dipole and then with the interionic distance a. This leads to an increase of the interaction with the monomer, together with the reaction rate. It is understandable that the modification of the polarization of the CH_2–S bond may be quite different when the interaction occurs with free ions.

ACKNOWLEDGEMENTS

V.W. is indebted to the Centre National de la Recherche Scientifique for the financial support through grant ATP Internationale No. 651 2553.

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