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ELECTRON TRANSFER AND NUCLEOPHILIC ADDITION REACTIONS OF ω,ω′-DICARBANIONIC OLIGOMERS WITH ELEMENTAL SULPHUR

J.M. CATALA, J.F. BOSCATO and J. BROSSAS

Centre de Recherches sur les Macromolécules (CNRS), 6, rue Boussingault – 67083 STRASBOURG Cédex (France)

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Summary

The reactions of dicarbanionic species with elemental sulphur have been studied by analysis of the products. This has shown that the reaction can be either an electron transfer or a nucleophilic addition, depending on the structure of the carbanion and on the number of carbon atoms separating the two anionic centres.

Introduction

The reaction of organolithiated compounds with sulphur is reported to give thiols and dialkylpolysulfides [1–3]. Our studies [4,5] of the reaction of organolithium species with sulphur led to the conclusion that the formation of coupled compounds and thiolates depends essentially on the ratio (K) of the concentration of carbanion to that of the elemental sulphur. For low values of K ($K < 2$) the formation of alkylpolysulfide is quantitative, whereas for high values of K ($K > 2$) thiolate formation predominates. Consequently we thought that the addition of dicarbanionic oligomers to sulphur would give polysulfide polymers, but the reaction was found in fact, to take a completely different course.

Definitions

D	1,1-diphenylethylene monomer
$^-$D–D$^-$	dicarbanionic dimer of the 1,1-diphenylethylene monomer
α	α-methylstyrene monomer
$^-\alpha-\alpha^-$	dicarbanionic dimer of α-methylstyrene monomer
$^-\alpha-\alpha-\alpha-\alpha^-$	dicarbanionic tetramer of α-methylstyrene monomer
M (%)	percentage of monomer recovered relative to that used up to form dicarbanionic oligomers
S_8 (%)	percentage of elemental sulphur consumed in the reaction
$\overline{(\mathrm{M})_y-\mathrm{S}_x}$ %	percentage of monomer involved in the formation of cyclic sulfide
$[-\mathrm{M}-\mathrm{M}-\mathrm{S}_x-]_n$	percentage of monomer engaged in the formation of linear polymer polysulfide
$K = [M^-]/[\mathrm{S}_8]$	anion concentration divided by sulphur concentration

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Experimental

Purification

Tetrahydrofuran (THF) was purified by refluxing over and distillating from sodium wire. Immediately before use it was distilled from benzophenone sodium. 1,1-Diphenylethylene was distilled twice over sodium wire under reduced pressure. α-Methylstyrene was purified similarly.

Synthesis

1,1-Diphenylethylene dilithiated dimer. Lithium (1.4 g, 0.20 mol), as fine beads, and THF (200 ml) were placed in a three-necked flask (250 ml), equipped with an argon inlet tube and 1,1-diphenylethylene (36 g, 0.2 mol) was added with stirring. The solution rapidly turned deep red due to the formation of the dicarbanionic species. After 12 h the solution was titrated.

1,1-Diphenylethylene monolithiated species. s-Butyllithium (1 *N*) (200 ml of a 1 *M* solution in benzene) was placed in a dry three-necked flask and 1,1-diphenylethylene (35 g, 0.2 mol) was added with stirring. The reaction was allowed to proceed for 24 h.

Dicarbanionic dimer of α-methylstyrene [6]. Sodium (4.2 g, 0.20 mol), potassium (8 g, 0.20 mol), and THF (500 ml) were placed in a three-necked flask (1 l) equipped with an argon inlet tube, stirring gave a liquid sodium-potassium alloy, and 6.49 ml (0.05 mol) of α-methylstyrene were then added dropwise. The reaction was allowed to proceed for 5 h.

Dicarbanionic tetramer of α-methylstyrene. α-Methylstyrene (14 ml, 0.10 mol) was introduced into a dry three-necked flask (250 ml) equipped with an argon inlet tube, containing 150 ml of purified THF and 2.3 g (0.1 mol) of sodium. The solution was stirred for 12 h before titration.

All the reactions were carried out under argon and in rigorously dry apparatus. The various anionic solutions were diluted by addition of THF before the reaction of carbanions with sulphur: s-BuD$^-$, $^-$D–D$^-$ and $^-\alpha$–α^- [M$^-$] 10^{-2} *M*; $^-\alpha$–α–α–α^- [M$^-$] 0.35 *M*.

All the carbanionic solutions were added to THF containing sulphur ([S_8], 4×10^{-2} *M*) and an appropriate amount of benzene to provide an internal standard for estimation of the yields. The resulting compounds for each value of *K* were analyzed by Gel Permeation Chromatography (GPC Waters) and characterized by their NMR (Bruker 90 MHz) and Mass Spectra (Ribermag R 10).

Results and discussion

I. 1,1-Diphenylethylene dicarbanionic dimer: $^-$D–D$^-$

After the addition of $^-$D–D$^-$ to S_8 a sample of the solution was injected into a GPC column. The chromatogram showed five peaks, which were characterized as follows: peak 1: elemental sulphur; peak 2: benzene present as standard; peak 3: the 1,1-diphenylethylene monomer; peak 4: the cyclic monosulphide 2,2,5,5-tetraphenylthiacyclopentane, as characterized by NMR and mass spectroscopy; peak 5: a polysulphide [–D–D–S_x–]$_n$ of low molecular weight.

The most significant from this reaction is the high yield of 1,1-diphenylethylene monomer. Table 1 shows the results of a study of the product composition as a function of the ratio K.

Examination of the results reveals that 70% of monomer used in the synthesis of $^{-}$D–D^{-} was recovered after the reaction of $^{-}$D–D^{-} with S_8. The yield was constant and independent of the ratio K. To explain the monomer formation we propose the following mechanism:

$$^{-}\text{D–D}^{-} + S_8 \rightarrow S_8{}^{-} + {}^{-}\text{D–D}$$

$$^{\cdot}\text{D–D}^{-} \rightleftarrows \text{D}^{\dot{-}} + \text{D}$$

$$\text{D}^{\dot{-}} + S_8 \rightarrow \text{D} + S_8{}^{\dot{-}}$$

$$\text{D}^{\dot{-}} + S_8{}^{\dot{-}} \rightarrow \text{D} + S_8{}^{2-}$$

The electron transfer reaction was observed previously between $^{-}$D–D^{-} and anthracene [7,8] or oxygen [9]. However in our case the electron transfer reaction occurs simultaneously with elemental sulphur and with lithium polysulphide: as can be seen from the plot (Fig. 1), S_8 was still present for $K = 1$ (one carbanion for one S_8) but not for $K = 8$. The average consumption of sulphur corresponds to one sulphur atom per monomer molecule. Consequently we suggest an electron transfer reaction from $^{-}$D–D^{-} to lithium polysulphides:

$$^{-}\text{D–D}^{-} + S_x^{2-} \rightarrow 2\ \text{D} + 2\ S_y^{2-} \quad (y = x/2)$$

The electron transfer reaction from the 1,1-diphenylethylene carbanion to S_8 was observed only in the case of the dicarbanionic diphenylethylene dimer. An experiment with the monocarbanionic species gave coupled products and thiolate without formation of monomer:

$$3\ \text{s-Bu–D}^{-} + S_8 \rightarrow \text{s-Bu–D–S}^{-} + (\text{s-Bu–D–S}_x)_2$$

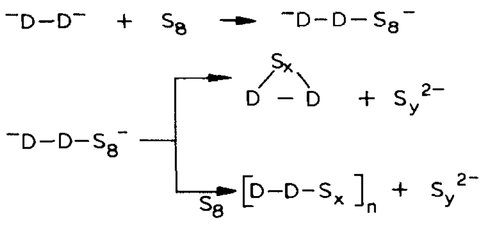
This result means that the electron transfer occurs only when the two carbanions are sufficiently close to interact. Thus when one of the two carbanions of $^{-}$D–D^{-} reacts by a nucleophilic addition to sulphur there is no interaction between the two centres of electronic density and the second carbanion reacts as a monocarbanion by

TABLE 1

PERCENTAGES OF MONOMER AND OTHER PRODUCTS FORMED IN THE REACTION OF $^{-}$D–D^{-} WITH ELEMENTAL SULPHUR

K	D (%)	S_8 (%)	$\overline{\text{D–D–S}}$ (%)	[–D–D–S_x–]$_n$ (%)
0.5	75	5	5	20
1	64	11	9	27
1.5	68	23	8	24
2	72	31	7	21
2.5	69	36	9	22
3	70	46	8	22
4	69	56	12	19

nucleophilic addition:



II. α-Methylstyrene dicarbanionic dimer: $^{-}\alpha-\alpha^{-}$

As previously, the α-methylstyrene dicarbanionic dimer was deactivated by sulphur and was analyzed by GPC. The chromatogram shows three main products identified as follows: peak 1: elemental sulphur; peak 2: GLC-MS showed the presence of four products, two isomers of the 2,5-diphenyl-2,5 dimethylthiacyclopentane, and two isomers of the 2,5-diphenyl-2,5 dimethyldithiacyclohexane; peak 3: polysulphide polymers of low molecular weight $[\alpha-\alpha-S_x]_n$. The yields of these products are listed in Table 2.

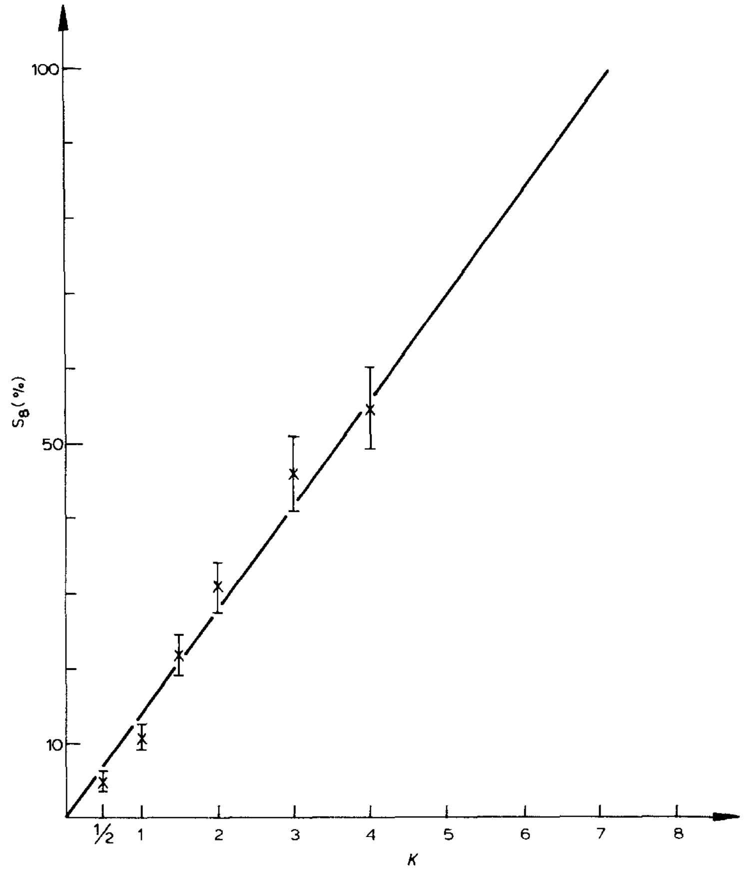


Fig. 1. Variation of the percentage of S_8 consumed with the ratio K.

No α-methylstyrene monomer was recovered after the reaction with sulphur. The main products were the cyclic sulphides formed by nucleophilic attack of the anions on the elemental sulphur for $K < 2$, or on the sodium sulphides and polysulphide oligomers for $K > 2$.

$$^{-}\alpha{-}\alpha{-}S_8^{-} \rightarrow \overline{\alpha{-}\alpha{-}S}_x + S_y^{2-} \quad (x + y = 8)$$

This reaction is favoured by the absence of steric hindrance in the molecule, as can be seen from Dreiding models.

III. α-Methylstyrene dicarbanionic tetramer: $^{-}\alpha{-}\alpha{-}\alpha{-}\alpha^{-}$

The GPC chromatogram of the deactivated solution shows the presence of elemental sulphur (peak 1) and polysulphide polymers (peak 2) but no monomer and thiacycloalkane. The main product consists of polysulphide polymers in which the number (x) of sulphur atoms varies with the ratio K. The molecular weight of the polymer similarly decreases with K (Table 3).

To understand the difference between the reaction of the dicarbanionic dimer and tetramer of α-methylstyrene it is necessary to look at the structure of the molecules with the aid of Dreiding models. In the case of the tetrametric species a steric hindrance prevent the carbons of the end chains from getting close to one another as they can in the case of the dimeric species. Consequently the formation of thiacycloalkane is disfavoured relative to that of linear polysulphide polymers.

The results in Table 3 show that the disappearance of S_8 from the mixture results in nucleophilic attack of the sulphur bridges of the polysulphide polymers. These

TABLE 2

CONSUMPTION OF S_8 AND YIELD OF SULPHIDE COMPOUNDS IN THE REACTION OF $^{-}\alpha{-}\alpha^{-}$ WITH ELEMENTAL SULPHUR

K	S_8 %	$\overline{\alpha{-}\alpha{-}S}_x$ %	$[-\alpha{-}\alpha{-}S_x]_n$
1	50	71	29
2	0	70	30
4	0	82	18
8	0	82	18

TABLE 3

VARIATION OF CONSUMPTION OF S_8 AND OF THE NUMBER OF SULPHUR ATOMS IN THE POLYSULPHIDE POLYMER FORMED IN THE REACTION OF $^{-}\alpha{-}\alpha{-}\alpha{-}\alpha^{-}$ WITH ELEMENTAL SULPHUR

K	S_8 %	$\overline{M}_n$	$\bar{x}$
1	46	7000	3,2
2	0	7300	3,2
4	0	5100	2
8	0	2800	1

reactions lower the number of sulphur atoms in the polymer and so the molecular weight.

Conclusion

The reactions of carbanionic oligomers with elemental sulphur proceed by electron transfer processes when the following three conditions are met: (a) the oligomer is a dianionic species, (b) the two carbanions are separated by only two carbon atoms, and (c) the carbanion is shielded by bulky groups.

In other cases the reactions of the dicarbanionic species proceed by a nucleophilic addition, to give thiacycloalkanes or polymers depending on the extent of steric hindrance which prevent the carbanionic centres from coming close together.

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