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KINETICS AND MECHANISM OF THE REACTION BETWEEN DIBENZYL TRISELENOCARBONATE AND OXYGEN-BASES

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Abstract—The base-induced solvolysis of dibenzyl triselenocarbonate in DMSO/water (4:1) has been studied by UV spectrophotometric measurements under *pseudo*-first order conditions, using KOH, Me_4NOH, Bu_4^nNOH and $Bu_4^nNHCO_3$ as bases. The reaction is first order with respect to the substrate as well as to the base. Rate constants and activation parameters for the four bases indicate that the rate determining step is the nucleophilic attack by the base, as an ionic couple, on the substrate. Fast reactions, due to strong nucleophilic selenolate species, may follow this slow step; a tentative mechanism is proposed on the basis of experimental evidence.

Dialkyl triselenocarbonates are prepared in good yields by the reaction of carbon diselenide with the appropriate alkyl halide in dimethyl sulfoxide/water (10–20% of water) in the presence of various oxygen-bases, according to the following scheme:[1,2]

$$3CSe_2 + 5B^- + 3H_2O + 4RX \xrightarrow{DMSO/H_2O} 2R_2CSe_3 + 5HB + 4X^- + HCO_3^- \quad (1)$$

where B^- may be HCO_3^-, CO_3^{2-} or OH^- and HB is its conjugate acid. During attempts to optimize the reaction conditions it was observed that the triselenocarbonate, thus obtained, was sometimes destroyed very rapidly in the reaction mixture. In order to clarify the decomposition mechanism we started a kinetic investigation. Dibenzyl triselenocarbonate (1) was choosen as the model substrate as a matter of convenience; compound 1, and its decomposition products are more readily purified and at the same time less obnoxious to handle than the corresponding products from the lower, aliphatic triselenocarbonates.

RESULTS AND DISCUSSION

Dibenzyl triselenocarbonate decomposes in the presence of an oxygen-base according to the reaction:

$$\underset{1}{2Bz_2CSe_3} + 4B^- + 3H_2O \xrightarrow{DMSO/H_2O} BzCSe_3^- + 3BzSe^- + 4HB + H_2CO_3 \quad (2)$$

(For detection of reaction products, see Experimental). The disappearance of 1 could be followed by measuring the decrease in optical density at either of the two absorption bands in the UV-visible spectrum ($\lambda_{max} = 360$ nm, $\log \epsilon = 4.15$ and $\lambda_{max} = 546$ nm, $\log \epsilon = 2.29$) since the absorption caused by the product mixture differs considerably in both regions. The spectra of 1 and its decomposition products are shown in Fig. 1. The latter spectrum was independent of the base employed and it was unchanged for a considerable period after the end of the reaction.

The 546 nm band might look the most promising for measurements because of the absence of absorption from the products in this region. However, the low extinction coefficient calls for substrate concentrations $> 2 \times 10^{-3}$ mol l^{-1} and preliminary experiments in this concentration range indicated a complicated kinetics resembling an autocatalytic reaction. This result is understandable in terms of the product, $BzCSe_3^-$ (3), being a powerful nucleophile, *cf* the subsequent discussion of the reaction mechanism. Instead, the measurements were performed on the 360 nm band so that a low concentration of 1 ($5 \times 10^{-5} - 1 \times 10^{-4}$ mol l^{-1}) could be used. This allowed us to employ a large excess of base in the kinetic experiments and in this way keep disturbing by-reactions caused by nucleophilic reaction products to an insignificant level.

Kinetic measurements were performed under *pseudo*-order conditions with respect to the substrate, following in time-drive the decrease of the absorbance at 370 nm corresponding to the wavelength of maximum difference between substrate and product absorptions. *Pseudo*-first

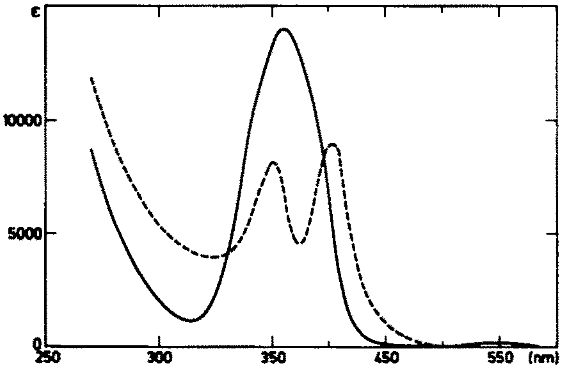


Fig. 1. UV-vis spectra of Bz_2CSe_3 (solid line) and its decomposition products (dotted lines) after treatment with KOH 0.1 M in $DMSO/H_2O$ (4:1 vol).

Table 1. *Pseudo*-first order k_{obsd}'s for the Bz_2CSe_3 basic decomposition in DMSO/H_2O (4:1 vol)

[Base] x 10^2	KOH$^{a)}$	$Me_4NOH^{a)}$	$Bu^n_4NOH^{a)}$	$Bu^n_4NHCO_3{}^{b)}$
10	-	-	-	4.58 ± .09
8	-	-	-	3.65 ± .07
6	-	-	-	2.80 ± .08
4	4.30 ± .08	-	-	1.80 ± .05
2	2.15 ± .06	-	-	0.89 ± .05
1	1.10 ± .06	2.70 ± .1	4.60 ± .1	-
0.8	0.90 ± .05	2.13 ± .09	3.65 ± .09	-
0.6	0.65 ± .05	1.60 ± .08	2.83 ± .05	-
0.5	0.58 ± .06	1.33 ± .07	2.23 ± .07	-
0.4	-	1.11 ± .05	1.82 ± .04	-

a) k_{obsd} x 10^2 at 25 °C

b) k_{obsd} x 10^3 at 86.1 °C

order rate constants, k_{obsd} were evaluated from the straight lines obtained by plotting $\ln(A_t - A_\infty)$ vs time. The values obtained at different base concentrations are reported in Table 1. The plot of k_{obsd} vs the base concentrations are straight lines, showing that the reaction in each case is first order in the base. The first order dependency upon both **1** and the base indicates a rate determining nucleophilic attack of the base on **1**. This view was supported by experiments at varying ionic strength. The variations of k_{obsd} were inside the limits of experimental error when μ was varied between 0.03 and 0.10 mol l^{-1} by addition of n-tetrabutylammonium perchlorate, as expected for reactions in whch one or both the reactants are neutral species.[3] The dependency of the rate constant on the identity of the cation (A^+) is likewise in accord with this hypothesis. The influence of the cation on the second order rate constants (Table 2) suggests that the hydroxides are mainly present as ion-pairs in the solvent employed. This view was supported by conductance measurements on KOH and Bu_4NOH in DMSO-water (4:1). With increasing dilution the molar conductivities at 20° of both salts remained roughly constant, 22.8 ± 1.5 and 23.9 ± 1.0 Ω^{-1} cm^2 mol^{-1}, respectively, down to *ca* 2×10^{-3} mol l^{-1}. Below this concentration both conductivities showed minima, at 2×10^{-5} and 8×10^{-4} mol l^{-1}, respectively, to rise steeply at still lower concentrations. This pattern shows[4] that ion-pairing in the concentration range ($4 \times 10^{-3} - 4 \times 10^{-2}$ mol l^{-1}) used in the kinetic experiments is virtually complete and the observed conductivity is caused by ion-triplets or higher aggregates.

In order to evaluate the activation parameters the temperature dependence of the rate constants was determined. From the straight lines obtained by plotting $\ln k_{obsd}$ vs $1/T$ (Fig. 2) the activation energies could be evaluated. $\Delta H^{\neq}$ and $\Delta S^{\neq}$'s, obtained from the Eyring's plots,[5] are reported in Table 2, together with the corresponding correlation coefficients. For the hydroxide bases both $\Delta H^{\neq}$ and $\Delta S^{\neq}$ decrease with increasing size of the cation. Both trends are in accord with the assumption that the hydroxides mainly exist as ion-pairs.

It is suggested that the transition state contains one

Table 2. Activation parameters for Bz_2CSe_3 decomposition with the different bases

Base	$\Delta H^{\ddagger}$ a)	$S^{\ddagger}$ b)	ρ c)
KOH	11.0 ± .2	-21.3 ± .8	.998
Me_4NOH	10.7 ± .2	-20.8 ± .7	1.000
Bu^n_4NOH	8.3 ± .2	-27.6 ± .7	.998
$Bu^n_4NHCO_3$	11.6 ± .1	-32.7 ± .2	1.000

a) $Kcal \cdot mol^{-1}$

b) $cal \cdot mol^{-1} \cdot K^{-1}$

c) Correlation coefficient of the Eyring's plot, evaluated on the second order rate constants.

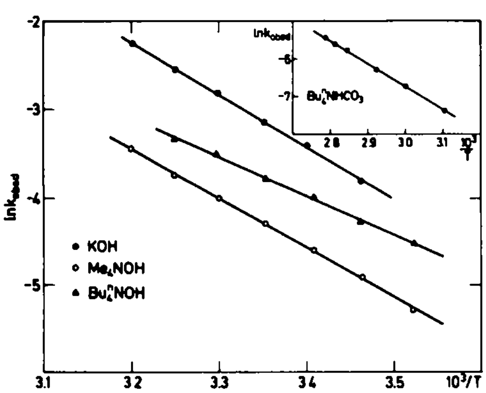
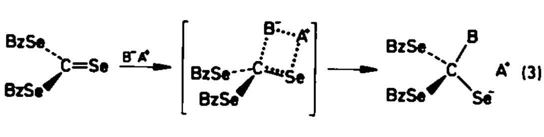


Fig. 2. Arrhenius' plots for Bz_2CSe_3 decomposition with potassium hydroxide $[KOH] = 4.0 \times 10^{-2}$, tetramethylammonium and n-tetrabutylammonium hydroxides $[Me_4NOH] = [Bu_4{}^nNOH] = 5.0 \times 10^{-3}$ in $DMSO/H_2O$ (4:1 vol). On the right top the analogous plot for n-tetrabutylammonium bicarbonate ($[Bu_4{}^nNHCO_3] = 0.1$) is given.

molecule of 1 and one cation-base ion-pair. Such a model would explain the observed variations of $\Delta H^{\neq}$ and $\Delta S^{\neq}$. The decrease of $\Delta H^{\neq}$ with increasing size of the cation reflects the action of a looser, i.e. more energetic ion-pair. The simultaneous lowering of $\Delta S^{\neq}$ is in accord with a transition state where dispersal of the negative charge partially has released the ion-pairing.

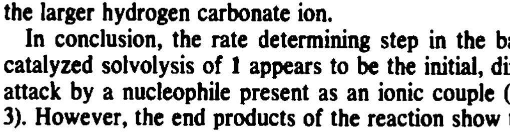


(3)

A strong decrease of the reaction rate is observed on passing from the hydroxides to tetrabutylammonium hydrogencarbonate. Indeed, it was necessary to raise the temperature to *ca* 350°K in order to obtain reasonable rates. However, also in this case the reaction is first order in both the substrate and the base. This shows that in the solvolysis process of 1 each nucleophile present attacks it at its own rate, since the lyate (hydroxide) ion concentration is approximatively independent of the concentration of the amphoteric species $HCO_3{}^-$.

Table 2 shows that an enhanced activation enthalpy as well as a lower activation entropy contributes to the decrease in reaction rate in going from the tetrabutylammonium hydroxide to the hydrogencarbonate. This is in agreement with the model given above for the rate-determining step. Thus the enthalpy difference reflects the difference in intrinsic basicity while, in this model, a major contribution to the entropy change could be caused by diminished ion-pairing in the ground state for the larger hydrogen carbonate ion.

In conclusion, the rate determining step in the base-catalyzed solvolysis of 1 appears to be the initial, direct attack by a nucleophile present as an ionic couple (eqn 3). However, the end products of the reaction show that this step is followed by additional, fast reactions. The major paths indicated by experiments are shown as eqns (4) and (5).



(4)

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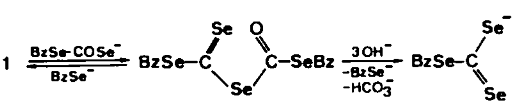

(5)

The intermediacy of the Se-benzyldiselenocarbonate ion (2) was indicated by trapping experiments. Se, Se'-dibenzyl diselenocarbonate (1–2%) was isolated when benzyl bromide was added as a trap for nucleophilic species at the start of the solvolysis but not observed at all when the addition took place at the end. Benzyl triselenocarbonate ion (3), produced in (5), was identified as a major reaction product when the solvolysis was carried out according to the stoichiometry of (2).

This species can enter as B^- in steps (3) and (4) and thus acts as a catalyst for the solvolysis. While the straight 2 order kinetics shows that this pathway is not an important contributor in the kinetic experiments, qualitative experiments at concentrations $> 10^{-2}$ mol l^{-1} of 1 corresponding to preparative conditions showed that the addition of 3 accelerated the hydrogen carbonate assisted solvolysis of 1.

EXPERIMENTAL

Materials. Benzyl triselenocarbonate was prepared according to literature[1] and recrystallized from acetone, before the kinetic experiments.

Tetramethyl- and n-tetrabutylammonium hydroxides and n-tetrabutylammonium perchlorate were supplied by Fluka.

n-Tetrabutylammonium bicarbonate was prepared by bubbling CO_2 in the base soln until a clear soln was obtained. All the base solns were tested by conductometric titrations with HCl. *Potassium benzyl triselenocarbonate*: A soln of KOH (20 mmol) in water (10 ml) and 2-propanol (75 ml) was flushed with argon and kept under a cover of this gas. Phenylmethaneselenol (20 mmol) followed by carbon diselenide (20 mmol) were added. The mixture was stirred for 10 min and then evaporated to dryness. The residue was extracted with EtOAc–toluene (1:2) (50 ml) and the product (15 mmol) was precipitated by addition of hexane to the filtered extract. (Found: C, 25.03; H, 1.97; Se, 62.65; Calc. for $C_8H_7Se_3K$: C, 25.33; H, 1.85; Se, 62.53%). UV-vis spectrum in $DMSO–H_2O$ (4:1) (λ_{max}, nm, log ϵ): 353, 3.77; 404 3.87; 558, 2.30.

Se-Se'-*Dibenzyl diselenocarbonate*. Compund 1 (1 mmol) was dissolved in 80% aqueous acetone (50 ml) at reflux temp. $KHCO_3$ (2 mmol) followed by mercuric chloride (2 mmol) were added and the reflux was continued for 5 min. Filtration from a light colored ppt (presumably Hg_2Cl_2Se) and evaporation of solvent left a colorless solid which was recrystallized from hexane, yield 59% (Found: C, 48.90; H, 3.84; Se, 43.10; Calc. for $C_{15}H_{14}OSe_2$: C, 48.94; H, 3.83; Se, 42.88%), m.p. 70–72°, IR 1680 cm^{-1} ($\nu_{C=O}$).

Detection of reaction products

$BzSe^-$ *and* $BzCSe_3{}^-$. Benzyl triselenocarbonate (2.0 mmol) and K_2CO_3 (3.0 mmol) in 40 ml $DMSO/H_2O$ (4:1 vol) were heated to 70° for 5 min when the reaction was complete. Ice (10 g) was added and the mixture left at 0° overnight. Dibenzyldiselenide, obtained from oxidation of the benzylselenide ion, was filtered off, washed with 70% MeOH and dried, yield 2.15 mmol (95%). Its identity was confirmed by comparison (m.p., mixed m.p., IR spectrum) with an authentic sample.

The UV-vis spectrum of the filtered reaction mixture was identical with that of a soln of potassium benzyltriselenocarbonate in DMSO. To confirm the presence of $BzCSe_3{}^-$ in the mixture, benzenyl bromide (3 mmol) in 30 ml DMSO was added to the filtrate. Addition of water and cooling yielded dibenzyl triselenocarbonate (1.19 mmol, 80%) which was isolated by filtration, washed with 70% MeOH and dried. Similar treatment with *p*-nitrobenzylbromide gave Se-benzyl Se'-*p*-nitrobenzyl triselenocarbonate, yield 82%. (Found: C, 38.10; H, 2.78; N, 2.78. Calc. for $C_{15}H_{13}NO_2Se_3$: C, 37.83; H, 2.75; N, 2.95%). ^1H NMR spectrum showed one benzyl and one *p*-substituted benzyl group.

BzSeCOSe$^-$. The solvolysis of 1 with KOH was carried out as in the kinetic runs, but with benzyl bromide (2×10^{-2} M) added. At the end of the reaction the mixture was diluted with water and extracted with toluene. The residue from evaporation of the toluene was separated on Al_2O_3 with hexane–CH_2Cl_2 as eluent. In addition to dibenzyl diselenide as the major product was obtained one fraction which was identical (mixed m.p., IR and ^{1}H NMR spectrum) with an authentic sample of Se, Se'-dibenzyl diselenocarbonate.

Spectrophotometric and conductivity measurements. The UV-vis spectrum of Bz_2CSe_3 (Fig. 1) was recorded in freshly prepared DMSO solns, using a Perkin–Elmer Model 402 spectrophotometer. The spectra of the decomposition products were recorded after the completion of the reactions, i.e. when reaching the stability of the spectra.

Conductivity measurements were carried out with a WTW bridged at 20°.

Kinetic measurements. These measurements were carried out with a Perkin–Elmer Model 402 spectrophotometer connected with a Lauda K2RD thermostat (±0.02°). Each run was carried out in pseudo-first order conditions, i.e. with a large excess of base, by adding, all at once, the proper amount of Bz_2CSe_3 ($5 \times 10^{-5} - 1 \times 10^{-4}$ mol l^{-1}) dissolved in DMSO to a prethermostated solution of the base and following in time-drive the decrease of the absorbance at 370 nm.

Data processing. Kinetic experimental data were processed by an H.P. 9100B calculator, connected with a 9125A plotter. The straight lines, obtained by plotting $\ln(A_t - A_\infty)$ vs time, were calculated by the least square method.

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