N-C BOND CLEAVAGE IN THE ACID-CATALYZED DECOMPOSITION OF SOME DITHIO- AND DISELENOCARBAMATES

A KINETIC INVESTIGATION OF DITHIOCARBAMATE DECOMPOSITION IN BENZENE AND METHANOL

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Abstract—The acidic decomposition of some dithiocarbamic internal salts in MeOH and in benzene has been carried out by UV spectrophotometric measurements under *pseudo*-first order conditions. In both solvents the reaction is a first order with respect to the substrate and the HCl concentration. A mechanism with two consecutive irreversible steps is proposed in benzene and the results are compared with the diselenocarbamates under the same conditions. In methanol a reversible first stage has been proposed. A general conclusion on the kinetic behaviour of dithio- and diselenocarbamates in solvents at different dielectric constants has been suggested.

In recent years we started a kinetic investigation¹⁻⁴ of dichalcogen carbamic ion decomposition, according to the following reaction scheme:

$$X \longrightarrow C_{Y}^{Y} (-) + H^{(*)} \longrightarrow X \longrightarrow NH + CY,$$
(1)

where $X = CH_2$, O, S, HN and CH_3N and Y = O, S and Se. In water the carbamates decompose with hydrolytic and acid-catalyzed mechanisms, while dithio- and diselenocarbamates react only with an acid catalyst, thus confirming the strong similarity[†] between S and Se and their separation from oxygen.

As far as the X influence on the rate of the diselenocarbamate decomposition is concerned, it is coherent with an inductive effect both in polar and in non polar solvents,^{3,4} while, in the dithiocarbamates, we observed an exchange in the reactivity of the unsubstituted derivative, which is slowest in water and fastest in non polar solvents. This fact diversifies the dithio from the diselenocarbamates; and consequently we made further investigations.

RESULTS AND DISCUSSION

Decomposition in acidic benzene.[‡] As in the diselenocarbamates,⁴ the dithiocarbamate kinetic decompositions were carried out on sulphur, oxygen and unsubstituted derivatives, NH and NMe not being soluble in acidified benzene.

Kinetic measurements were performed under *pseudo*first order conditions (|HCl| = constant) with respect to the substrate. From the straight lines obtained by plotting $\ln (A_t - A_s)$ vs time, the *pseudo*-first order k_{obsd} 's were evaluated. The straight lines obtained from the plot $k_{obsd}/|HCl|$ prove a first order with respect to |HCl| (Fig. 1). On the contrary, the diselenocarbamate decomposition⁴ did not depend on |HCl| and it was found that in almost all the acid range examinated, the k_{obsd} 's were practically constant, changing only in a first very narrow range. For the aqueous decomposition we suggested⁴ the

following mechanism

$$B \xrightarrow[k_1, H^{-1}]{k_2} C \xrightarrow{k_2} Products \qquad (2)$$

where B is the dithiocarbamate ion, C is its conjugated acid in steady state condition^{*} and $k_{obsd} = k_1 \cdot k_2 \cdot |H^+|/(k_1 + k_2)$ depending on the acid concentration in the whole range.

On the basis of the exterimental data in benzene we could propose a similar mechanism, but, since the solvent has low dissociative properties,⁹ we think that the reverse reaction is highly unlikely and hence $k_{-1} \ll k_2$. Then the mechanism should be

$$B \xrightarrow{k_1 \mid HC \mid l} C \xrightarrow{k_2} Products \qquad (3)$$

with two subsequent steps, where the former is rate determining and $k_{obsd} = k_1 \cdot |HCl|$. In (3) B is the dithiocarbamate internal salt and C is an intermediate species with a very low stability. A proof of eqn (3) is obtained by carrying out the kinetic decomposition on N-d₂ piperidinium piperidine dithiocarbamate in benzene/DCl. The ratio k_H/k_D would¹² be lower than the unity for the scheme in eqn (2); viceversa the experimental ratio (>1) supports the mechanism (3) ($k_D = 0.13 \pm 0.01 \text{ sec}^{-1}$ at 10° and $|DCl| = 5 \times 10^{-3} \text{ moles/}|$).

On the other hand the proposed mechanism is proved by the diselenocarbamate decomposition,⁴ where B immediately gives C[§] and the decomposition of the acid is

[†]The great similarity in chemical properties between S and Se is particularly shown by IR spectra. In fact the substitution of S by Se, named "selenation", works like an isotopic substitution, leaving the remainder of the spectrum virtually unchanged.⁵

[‡]The internal salt decomposition takes place with a first order kinetic even in non acidified benzene, giving the same products. However its decomposition rate is very slow with respect to the acid one (e.g. for $CH_2 \ k = (3.05 \pm 0.04) \times 10^{-3} \text{ sec}^{-1}$ at $t = 23.3^\circ$) so much so that all the lines of Fig. 1 have intercepts close to the origin.

^{\$}Conductivity measurements and IR and PMR evidences¹¹ proved that the piperidinium piperidine diselenocarbamate prevalently exists in benzene or CCL solutions as piperidine and N-protonated piperidine diselenocarbamic acid C.





Fig. 1. Dependence of the k_{obsd} on the HCl concentration in benzene.

observed; consequently the k_{obvd} is equal to k_2 and the rate does not depend on the HCl concentration. Then the different kinetic behaviour between dithio- and diselenocarbamates must be attributed to a different stability of the intermediate species C, more stable in the diseleno than in the dithiocarbamates.

Decomposition in acidic methanol. The decomposition was also carried out in MeOH, since it has dielectric constant intermediate between water and benzene. Analogous experiments on the diselenocarbamate series were not possible, in consequence of the stronger nucleofilic properties of Se,¹⁰ which soon reacts with the solvent.

The k_{obsd} 's, evaluated from the straight lines $\ln (A_t - A_{\infty})$ + *versus* time, at various temperatures and different HCl concentrations are shown in Figs. 2 and 3. The decomposition is a first order with respect to the substrate and the hydrochloric acid; further, all the lines do not pass through the origin and they have positive intercepts.

Hence the observed rate constant must be written as:

$$\mathbf{k}_{obsd} = \mathbf{k}_{HCl} \cdot |HCl| + \sum_{i} \mathbf{k}'_{i}$$
 (4)

where k_{HCI} is the observed rate constant for the acid catalyzed decomposition and $\Sigma k'_i$ is a set of *pseudo*-first

order constants of the by-reactions, where the most important could be the oxidation and the esterification as

Fig. 2. Dependence of the k_{obsd} on the HCl concentration at various temperatures for piperidinium piperidine dithiocarbamate in CH₃OH.



Fig. 3. Dependence of the k_{obsd} on the HCl concentration at various temperatures for thio-morpholinium thio-morpholine dithiocarbamate in CH₃OH.

[†] In contrast with the A_{∞} values (~0) observed in benzene, here the A_{∞} 's are far from zero value, thus indicating by-reactions with different products than CS_2 and amine hydrochloride.

shown:



It is possible to exclude in the $\Sigma \mathbf{k}'_i$ term a considerable

contribution of the uncatalysed reaction, because in deoxygenated methanol the reaction proceeds with very slow

rates $(CH_2: k = (2.8 \pm 0.2) \times 10^{-4} \text{ sec}^{-1}; O: k = (2.2 \pm 0.1) \times 10^{-4} \text{ sec}^{-1}; S: k = (2.5 \pm 0.1) \times 10^{-4}; t =$

20°C) and the absorbance at $t = \infty$ is close to zero.

Then the positive intercept of the plot $k_{obsd}/|HCl|$ gives $\sum k'_{i}$, while its slope is k_{HCl} . Table 1 summarizes the results at 10, 15, 20, 25 and 30°C.

From these we think that in methanol the acid decomposition mechanism occurs as in water, according to the scheme (2) with C in steady-state and

$$\mathbf{k}_{\mathrm{HC1}} = \frac{\mathbf{k}_1 \cdot \mathbf{k}_2}{\mathbf{k}_2 + \mathbf{k}_1}.$$

In Table 1 the activation parameters ΔH^{*} and ΔS^{*} for the acid catalysed reaction are reported. Their comparison with those obtained in water¹ ($\sum CH_2$: $\Delta H^{*} = 18.1 \pm$ 0.2 kcal/moles, $\Delta S^{*} = -17.1 \pm 0.6$ e.u.; $\sum S$: $\Delta H^{*} =$ 16.6 ± 0.2 kcal/moles, $\Delta S^{*} = -19.9 \pm 0.7$ e.u.) shows very close ΔS^{*} values and different ΔH^{*} 's lower in Me₃OH than in H₂O. Consequently the high rate of decomposition in MeOH is not attributable to entropic but enthalpic factors, produced by the higher solvating power of water.

GENERAL CONCLUSIONS

When we started to investigate the acid decomposition of dichalcogen carbamic ions, we wished to compare the kinetic properties of the family as the whole; but, as shown in previous papers, carbamates substantially differ from dithio and diseleno-carbamates. Hence the meaningful conclusions are a direct comparison between S- and Se-compounds.

On passing from water to benzene a noteworthy increase in the rate occurs for both series, but in any case a lower decomposition rate of the diselenocarbamates with respect to the sulphur ones is observed, in contrast with the well known reactivity of Se-compounds.

The decomposition mechanisms are solvent-dependent; in fact the dithio and diselenocarbamates decompose according to the scheme (2) in water and to the scheme (3) in benzene. In water the lower reactivity of the diselenocarbamates must be due to a higher contribution of the resonance structure¹¹ which hinders the transition



state formation with the H-bonded to the N atom. On the other hand the enlarged weight of the above resonance form on going from the carbamates to the diselenocarbamates is also exhibited by the influence of X substituent, which affects carbamates more than dithio- and diselenocarbamates, as a direct consequence of the different π bond order. However in dithio- and diselenocarbamates the X-influence is coherent with an inductive effect with the reactivity sequences as shown in Table 2.

In benzene the same sequence of reactivity was found in the diselenocarbamates, while in the dithio series the unsubstituted becomes the fastest (see Table 2). The decomposition occurs according to the scheme (3) and the rate-determining step is the protonated intermediate formation (1st step) in dithio-series, while it is the intermediate decomposition (2nd step) in diselenocarbamates, since its formation is very fast. Then, in dithiocarbamates,

the nitrogen of the CH_2 derivative is the most basic, and

its protonation, followed by an immediate decomposition, occurs more rapidly. Whereas in the diselenocarbamates, since the intermediate decomposition is rate-determining,

the CH_2 is the least reactive.

CH ₂				>s		
t°C	k _{FIC1}	$\sum_{k} \mathbf{k}'_{i} \times 10$	r*	k _{HC1}	$\sum_{i} \mathbf{k}'_i \times 10$	r"
10	1.46 ± 0.05	0.875 ± 0.02	0.998	0.85 ± 0.01	0.88 ± 0.01	1.000
15	2.02 ± 0.16	1.15 ± 0.07	0.991	1.33 ± 0.06	1.15 ± 0.02	0.998
20	3.34 ± 0.12	1.62 ± 0.05	0.996	1.79 ± 0.03	1.57 ± 0.01	1.000
25	3.77 ± 0.16	2.30 ± 0.07	0.997	2.26 ± 0.17	2.04 ± 0.07	0.992
30	6.17 ± 0.11	2.89 ± 0.04	0.999	3.34 ± 0.15	2.39 ± 0.05	0.995
۲ ^۳	0.988			0.995		
∆H۲۰	11.4 ± 0.7			10.6 ± 0.4		
4S***	-17.5 ± 2.4			-21.3 ± 1.5		

Table 1. k_{HCI} (*l* moles ' sec ') and $\sum k_i \times 10(sec ')$ obtained from the plots $k_{obsd}/|HC|^2$

"Correlation coefficient for the plot kobsd/[HCI].

^bCorrelation coefficient for the Eyring's plot.

°kcal moles⁻¹

dcal moles" ' K

 Table 2. Reactivity sequences in the decomposition of dithio and diseleno-carbamate internal salts in different solvents

<u></u>	Dithio	Diseleno	
H₂O	$S > NH > O > CH_3N > CH_2$	$H_2 \overset{(\cdot)}{N} > CH_3 \overset{(-)}{N} H > S > O > CH_2$	
CH ₃ OH Benzene	$CH_2 > O^+ > S$ $CH_2 > O > S$	$S > O > CH_2$	

†Although the experimental data obtained for this derivative are not reported in consequence of its

low solubility, they show intermediate values between S and CH2.

As far as the decomposition in MeOH is concerned, it is impossible to make a direct comparison between dithio and diselenocarbamates. However Table 2 shows the same sequence of reactivity as in benzene. Since the two proposed mechanisms differ in the k_{-1} values, very high in water and close to zero in benzene, it is k_{-1} that determines this change in the sequence. Naturally, in CH₃OH, which is a solvent less dissociative than water, k_{-1} should be lower than in water but less enough to verify the inversion.

EXPERIMENTAL

Preparation of compounds and acidic solutions. Internal salts of dithiocarbamates were prepared at 5°, by adding stepwise under vigorous stirring CS₂(10⁻³ moles) to a dilute solution of amines $(2 \times 10^{-3} \text{ moles})$ in cyclohexane. The white crystalline products were filtered off and washed with ligroin. The analytical data are: piperidinium piperidine dithiocarbamate (Found: C, 53.45; H 9.07; C₁₁H₂S₂S₂ Requires: C, 53.61, H, 9.00%), oxygen derivative (Found: C, 43.27, H, 7.40; C₉H₁₈N₂O₂S₂ Requires: C, 43.17, H, 7.24%), sulphur derivative (Found: C, 38.21; H, 6.38; C₉H₁₈N₂S₄ Requires: (38.26; H, 6.42%), HN derivative (Found: C, 43.39, H, 8.30; C₉H₂₀N₄S₂ Requires: C, 43.51; H, 8.12%). CH₃N derivative (Found: C, 47.69; H, 8.68; C₁₁H₂₄N₄S₂ Requires: C, 47.78; H. 8.75%). N-d₂ piperidinium piperidine dithiocarbamate was obtained as above starting from N-d piperidine.

The acid solns were prepared by bubbling HCl in benzene or MeOH and tested by alkalimetric titrations before and after every kinetic experiment. DCl was obtained by treating KCl with D_2SO_4 (Merck supplied).

Spectrophotometric measurements. The kinetic experiments in benzene and MeOH were performed by UV spectrophotometric measurements by adding the proper amount of internal salt to a prethermostated acid solution and following in time drive the

decrease of the absorption at the maxima wavelengths (in benzene:

CH₂
$$\lambda_{max} = 292 \text{ nm}$$
; O $\lambda_{max} = 295 \text{ nm}$ and S $\lambda_{max} = 294 \text{ nm}$;

in MeOH,
$$\sum CH_2 \lambda_{max} = 289 \text{ nm}$$
; $\sum 0 \lambda_{max} = 293 \text{ nm}$ and $\sum S \lambda_{max} = 292 \text{ nm}$).

The equipment employed was a Perkin Elmer 402 spectrophotometer connected to a Lauda K2RD thermostat.

Data processing. The kinetic experimental data were processed by a Hewlett Packard 9100B calculator connected with a 9125A plotter. The straight lines were calculated by the least square method.

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