

INFLUENCE OF SOLVENT AND TEMPERATURE ON DECOMPOSITION AND ISOMERISATION OF Z- ALKYLARYLDIAZO SULPHIDES

J. BROKKEN-ZIIP* and H. v.d. BOGAERT

Philips Research Laboratories Eindhoven-The Netherlands

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Abstract—Z-benzenediazo t-butyl sulphides isomerise to the E-modification and at the same time decompose into t-butyl aryl sulphides, substituted benzenes, t-butyl disulphides and t-butyl thiol. These are first-order reactions.

In decomposition, the enthalpies, ΔH^\ddagger , and the entropies, ΔS^\ddagger , of activation decrease as the solvent becomes more polar and as the substituent becomes less electron-accepting, indicating a polar reaction mechanism for the rate-determining step.

The rate of isomerisation appears to be almost independent of the solvent, thus suggesting to an apolar reaction mechanism. In the case of isomerisation there is a linear relationship between ΔH^\ddagger and ΔS^\ddagger with all the solvents and substituents studied.

INTRODUCTION

The literature concerning the preparation and properties of Z-benzenediazoalkyl sulphides is not very abundant^{1,4}. Van Zwet² isolated two kinds of isomers the more stable modification being called the E-isomer, the other the Z-isomer. The Z-isomers of these sulphides have been studied in solution, but only in the presence of the E-form and/or other compounds. The workers^{1,4} in this field assumed that, on heating, the Z-form was completely converted to the E-isomer, the latter decomposing by a radical mechanism on further heating,² so that the following reaction scheme² was proposed (Fig 1).

In our examination of the pure Z-isomer we discovered that both decomposition and isomerisation occurred on heating. In more polar solvents decomposition was found to dominate.

The UV spectra of the E- and Z-isomers of the diazosulphides differ quite appreciably, whereas the spectra of the decomposition products almost coincide with that of the Z-isomer, the disappearance of which during either reaction could therefore be monitored more easily by means of NMR.

RESULTS AND DISCUSSION

We were able to isolate and obtain in a pure state

the following two Z-isomers: Z-3,5-dichloro-4-N,N-dimethylaminobenzenediazo t-butyl sulphide (Z-1) and Z-4-nitro-benzenediazo t-butyl sulphide (Z-2).

By means of NMR we were able to observe the disappearance of these Z-isomers and the appearance of the E-isomers as well as of other products. These products were identified as t-butyl-3,5-dichloro 4-N,N-dimethylaminophenyl sulphide and 3,5-dichloro-N,N-dimethylaniline if the starting compound was Z-1, and t-butyl-4-nitrophenyl sulphide and nitrobenzene if Z-2 was the starting compound; t-butyl disulphide and a small quantity of t-butyl thiol always accompanied the reaction products, irrespective of the starting material. Under the same reaction conditions, and in the time needed for complete disappearance of the Z-isomers, no decomposition of the E-compounds could be detected, hence thermal decomposition of the E-form cannot here explain the formation of these products. The disappearance of the Z-isomers as well as the appearance of the E-isomers and of the other products accorded with simultaneous first-order reactions. To explain these facts we would suggest the following new scheme (Fig 2).

The nature of the reaction products did not de-

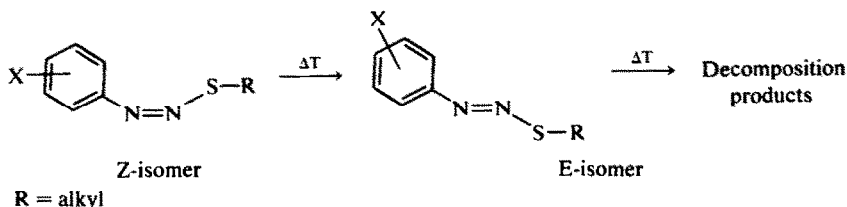


Fig 1.

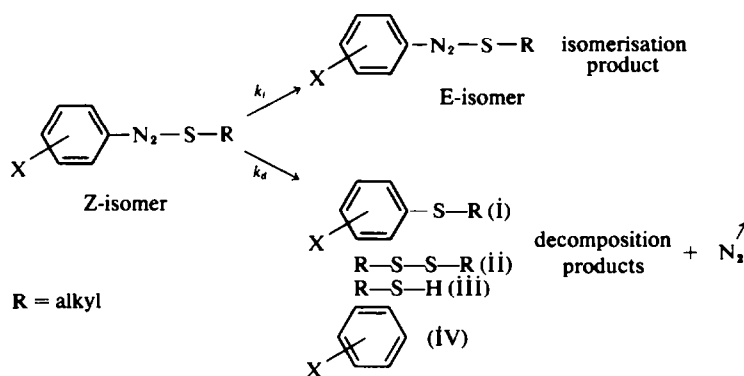


Fig 2.

Table 1a. The products formed from Z-3,5-Cl₂-4-N,N-dimethylaminobenzenediazo t-butyl sulphide in different solvents at 20°

Solvent	E	3,5-Cl ₂ -4-N(CH ₃) ₂ -benzene t-butyl sulphide	2,6-Cl ₂ dimethyl- aniline	t-butyl disulphide t-butyl thiol
Decaline*	100%			
Benzene*	100%			
Dioxane	100%			
Acetone	6%	66%	27%	27%
Dimethyl formamide	70%	14%	14%	14%
Dimethyl sulphoxide	30%	63%	7%	7%
Acetonitrile	3%	68%	28%	28%
Nitromethane	15%	68%	16%	16%

*At higher temps decomposition products are formed to a greater extent.

Table 1b. The products formed from Z-4-NO₂-benzenediazo t-butyl sulphide in different solvents at 20°

Solvent	E	4-NO ₂ -benzene t-butyl sulphide	Nitrobenzene	t-butyl disulphide t-butyl thiol
Decaline*	100%			
Benzene*	100%			
Acetone	28%	47%	25%	25%
Dimethyl formamide	90%	4%	5%	5%
Dimethyl sulphoxide	95%	5%		
Acetonitrile	10%	63%	27%	27%
Nitromethane	52%	36%	12%	12%

*See Table 1a.

pend on the solvent used,* but the ratio of the products did (Table 1a, 1b). However, the rate of decomposition was influenced greatly by the polarity of the solvent used (Table 2). With increasing polarity of the solvent the reaction rate increased drastically. When we used the experimental E_T scale⁵ as a measure of the polarity of the solvent we found a more or less quantitative correlation, so that the

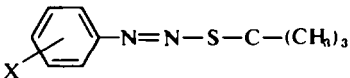
rate determining reaction would appear to be mediated by a polar transition state both with apolar and with polar solvents.

The sterically hindered Z-compound has a weak N-S bond.² In the transition state this bond may in part have broken heterogeneously, resulting in the formation of diazonium ions or ion pairs.

The presence of these ions or ion pairs in solutions of Z-diazo compounds has been observed by several authors,^{1,6} in consequence of the ability of these ions to couple with β-naphthol to yield an azo-dye. With Z-diazosulphides a coupling reaction with β-naphthol was observed by van Zwet² and

*An exception to this was found with benzene as solvent. Of the above decomposition products, the 2,6-dichloro-dimethylaniline was not found, instead, 3,5-dichloro-4-dimethylaminobiphenyl was probably formed.

Table 2. Influence of solvent on the first-order reaction constants of isomerisation and decomposition of Z-diazosulphides^a

					
X = 3,5-Cl ₂ -4-N(CH ₃) ₂ -			X = 4-NO ₂ -		
Solvent ^b	E _T ^c	k _i (s ⁻¹) ^e	k _d (s ⁻¹) ^f	k _i (s ⁻¹) ^e	k _d (s ⁻¹) ^f
Decaline ^a	31.1 ^d	2.1 × 10 ⁻⁷	± 10 ⁻¹²	2.5 × 10 ⁻⁷	> 10 ⁻¹²
Benzene ^a	34.5	1.4 × 10 ⁻⁷	2.0 × 10 ⁻⁹	2.0 × 10 ⁻⁷	> 10 ⁻¹⁰
Dioxane ^a	36.0	1.0 × 10 ⁻⁷	2.5 × 10 ⁻⁹		
Acetone	42.2	1.6 × 10 ⁻⁷	3.4 × 10 ⁻⁶	0.8 × 10 ⁻⁷	2.0 × 10 ⁻⁷
Dimethyl formamide	43.8	2.0 × 10 ⁻⁷	5.6 × 10 ⁻⁸	1.6 × 10 ⁻⁷	1.8 × 10 ⁻⁸
Dimethyl sulphoxide	45.0	1.3 × 10 ⁻⁷	2.9 × 10 ⁻⁷	0.1 × 10 ⁻⁷	9.8 × 10 ⁻⁸
Acetonitrile	46.0	5.0 × 10 ⁻⁷	1.7 × 10 ⁻⁵	0.4 × 10 ⁻⁷	3.9 × 10 ⁻⁷
Nitromethane	46.3	7.1 × 10 ⁻⁶	2.2 × 10 ⁻⁵	4.5 × 10 ⁻⁷	4.1 × 10 ⁻⁷

^a Measurements were carried out at 20° in the dark to prevent isomerisation by light.

^b Deuterated solvents were used.

^c Experimental scale for polarity of solvent¹.

^d E_T-value of cyclohexane.

^e First-order reaction constant of isomerisation.

^f First-order reaction constant of decomposition.

^g k-values extrapolated from measurements at higher temperatures.

Yamada.⁴ We discovered that Z-1 and Z-2 coupled with β-naphthol also in nitromethane. Furthermore it is known that the thiolate ion couples with the diazonium ion to form the Z-isomer in solution.² In some cases, at least, Z-isomers are therefore in equilibrium with ions or ion pairs of diazonium thiolate. However, they seem to be present in very low concentrations, since they cannot be detected by NMR.

Part of the products formed, viz. (ii,* iii and iv), suggest a radical mechanism for the product determining reaction. However, the dependence of the values of ΔH‡ and ΔS‡ on the polarity of the solvent (Table 3) is such that a homolytic dissociation seems improbable as the rate determining step, in contrast, for instance, to the dependence of ΔH‡ and ΔS‡ in the homolytic decomposition of phenylazotriphenylmethane on the nature of the solvent.⁷

From the literature some results are known of the decomposition of diazonium salts by a radical mechanism,⁸ or by an ionic mechanism,⁹ in either case with the evolution of nitrogen. The products formed depend on the solvent and the diazonium salt used. The diazonium ion is known to be suscep-

tible to reduction^{8c,d,e} while the t-butylthiol anion becomes oxidized rather easily, so that it is perhaps able to cause an electron to be transferred to the diazonium ion within the ion pair. Facts have furthermore been described in the literature,^{8a,b} which make it probable that the role played by the free radical mechanism of the decomposition of diazonium salts becomes greater, the greater the stability of the radical formed under the conditions of the experiments.^{8a,b} Diazonium borofluoride decomposes in an ionic way in several of the solvents⁹ mentioned in Table 3, because the fluorine radical is most unstable. However, the t-butyl-thiyl radical is rather stable²; hence, radical decomposition of diazonium thiolate as the product determining reaction step seems to be possible, so that products (ii, iii, and iv) may be formed by a radical mechanism. The sulphide may be formed by a radical mechanism as well as by an ionic mechanism.

On the basis of our results we would propose the following reaction scheme for the decomposition of Z-benzenediazoalkyl sulphides (Fig. 3).

The rate of the reaction decreases if the substituents of the benzene ring of Z-1 are replaced by that of Z-2. The same influence of the 4-nitro-substituent is observed on the reaction rate of the coupling of β-naphthol with Z-4-nitrobenzenediazo-triphenylmethyl sulphides.⁴ Yamada⁴ found a negative ρ-value for this reaction and explained this by a lower concentration of the 4-nitrobenzenediazonium ions in solution than in the case of the less electron-attracting substituents because the 4-nitro-substituent destabilises the diazonium ion to a greater extent.

*Neither the sum nor the ratio of disulphide and thiol changed when these experiments were repeated in a nitrogen atmosphere, so that oxidation of thiol to disulphide by the oxygen present in the solution is excluded as the only reaction leading to disulphide formation.

[†]Recent experiments disclosing CIDNP effects, support this interpretation of the reaction mechanism. These experiments will be described later¹⁷.

Table 3. Influence of the solvent on the thermodynamic parameters of isomerisation and decomposition of Z-benzenediazo t-butyl sulphides.

Solvent	X = 3,5-Cl ₂ -4-N(CH ₃) ₂ -					X = 4-NO ₂ -				
	ΔE	log A	ΔH [‡]	ΔS [‡] ^b	ΔG [‡]	ΔE	log A	ΔH [‡]	ΔS [‡] ^b	ΔG [‡]
Decaline	>38	>20								
Benzene	37.0	19.0	36.5	+27.0	29	>38	>20			
Dioxane	32.0	15.0	31.0	+13.5	27					
Acetone	25.0	13.0	24.0	0.0	24					
Dimethyl formamide	26.5	12.5	26.0	-3.5	27	27.0	12.5	26.0	-4.0	27
Acetonitrile	21.0	11.0	20.0	-12.0	24					
Nitromethane	11.0	3.5	10.5	-44.0	23	22.5	10.5	22.0	-13.0	26

Solvent	X = 3,5-Cl ₂ -4-N(CH ₃) ₂ -					X = 4-NO ₂ -				
	ΔE	log A	ΔH [‡]	ΔS [‡] ^b	ΔG [‡]	ΔE	log A	ΔH [‡]	ΔS [‡] ^b	ΔG [‡]
Decaline	27.0	13.5	26.5	+1.5	26	27.5	14.0	27.0	+3.5	26
Benzene	27.0	13.5	26.5	+1.0	26	27.0	13.5	26.5	+1.0	26
Dioxane	28.0	14.0	27.0	+3.0	26					
Acetone	28.5	14.5	27.5	+5.0	26					
Dimethyl formamide	28.0	14.0	27.0	+3.1	26	28.0	14.0	27.5	+4.0	26
Acetonitrile	20.0	8.5	19.0	-21.5	25					
Nitromethane	10.0	2.5	9.5	-50.0	24	22.5	10.5	21.5	-13.5	26

^ak-values were calculated from measurements at several temperatures (at least three temperatures for each solvent). The deviations from ΔE and log A are ±2%, ΔG[‡], ΔS[‡] have been calculated for 20[°]¹⁶

^bΔS[‡] = entropy of activation (cal/mol[°]K)

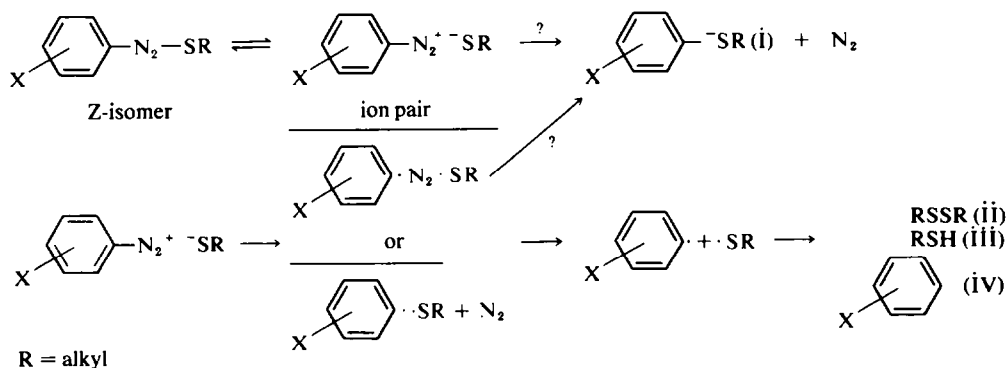


Fig 3.

Qualitatively the variation of ΔH[‡] in the different solvents is in agreement with our proposed mechanism, but the value of ΔH[‡] found in nitromethane is rather low. Presumably this can be ascribed to the acidic character of the solvent.^{5a} We observed that small quantities of acid greatly accelerated the decomposition as well as the isomerisation

reaction. The rather low value of ΔS[‡] indicates also a strong solvation of the transition state and can be interpreted as loss of freedom of movement of the solvent.

The rate of isomerisation is only slightly influenced by the polarity of the solvent (Table 2), so that an apolar reaction mechanism seems plausible.

The values of ΔE_{isom} in the different solvents (Table 3) suggest the same, except those measured in nitromethane and acetonitrile. Perhaps the acidic character of nitromethane plays a role here, too, as mentioned in the discussion of the decomposition of the Z-isomers.

Both with Z-1 and with Z-2 a linear correlation* between ΔS^\ddagger and ΔH^\ddagger for isomerisation is found in all the solvents used. If this "isokinetic relation"¹⁰ holds, then it may be assumed that the mechanism of the reaction will not change if the solvent and the substituent are changed. Hence, the same mechanism may be operating in the polar as well as in the apolar solvents with which we experimented. Three mechanisms have always been proposed to explain the differences in isomerisation rates of diazo and azo compounds.^{2,3,11} The first is an inversion mechanism, i.e. hybridisation takes place around one or both N-atoms, so that in the transition state the sp_2 -orbitals change into sp -orbitals (the molecule becomes linear) and then become sp_2 -orbitals again on formation of the E-isomer. The second mechanism involves an uncoupling of the II-orbitals; these orbitals rotate around the sp_2 N-N bond, taking with them the N-S bond. After rotation, the π -bond is formed again. According to the third mechanism, the Z-isomer decomposes to a completely free positive diazonium ion and a negative thiolate ion.[†] These ions couple again to form the E-isomer. Because the difference of ΔE_{isom} to both Z-isomers is rather small, rotation or inversion mechanisms are more likely. The only mechanism which operates in the isomerisation of stilbenes is the rotation mechanism. However, the ΔE_{isom} values found with stilbenes (34–37 kcal)¹² are much higher than those found with azobenzenes (21–24 kcal). There is no indication that the breakdown of the π -bond is much easier in azo compounds. On the contrary, calculations show that π -bond breaking requires more energy when there is a N=N double bond,¹¹ so that a rotating mechanism is unlikely.

In our case the values of ΔE_{isom} are close to those found with azobenzenes. Hence, an inversion mechanism is presumably operating here, too, the transition state becoming polar in strongly polar solvents such as acetonitrile and nitromethane.

* $\Delta H^\ddagger = 0.33 \Delta S^\ddagger + 26.02$. Correlation factor = 0.99.

†From the values of ΔE_{isom} and ΔE_{dec} in polar solvents the impression may be created that isomerisation also proceeds via a pair of diazonium and thiolate ion. This would imply, however, that the E-isomers would be formed directly from a diazonium and a thiolate ion. In the synthesis of diazosulphides in acetone³ the starting materials are a thiol or a thiolate and a diazonium ion. But if these experiments are performed at sufficiently low temperatures, only the Z-isomer can be detected in the reaction mixture. For this reason we do not think the intermediacy of paired diazonium and thiolate ions to be probable in isomerisation.

CONCLUSION

The thermal reaction of Z-benzenediazoalkyl sulphides leads to isomerisation as well as to simultaneous decomposition, both in accordance with first-order kinetics.

In a more polar solvent the decomposition becomes dominating: the degree of solvent polarity determines the accelerating effect on the rate of decomposition to a great extent. This effect is caused by a lowering of ΔH^\ddagger in more polar solvents, but is compensated partly by a lowering of ΔS^\ddagger . This points to a polar transition state in the decomposition reaction. Hence, we propose as the major rate-determining step the formation of diazonium thiolate ions or ion pairs, which react to give further decomposition products. Some of these decomposition products are probably formed by a radical mechanism. Therefore decomposition of diazonium thiolate ions or ion pairs is likely to proceed via radicals. In agreement with this mechanism is the decrease of the rate of decomposition of Z-2 as compared to that of Z-1.

An examination of the influence on ΔE_{isom} of the solvent and substituents in the benzene ring indicates an apolar transition state for Z-to-E isomerisation in most solvents. The linear correlation found between ΔS^\ddagger and ΔH^\ddagger indicates the applicability of an "isokinetic temperature concept" in respect of isomerisation.

A comparison of our results with those obtained with azobenzenes¹¹ suggest that an inversion mechanism may be operating here too.

EXPERIMENTAL

The Z- and E-compounds were synthesised by the method described by van Beek *et al.*³ The two Z-compounds were recrystallised at least four times at low temperatures from *n*-pentane as solvent for the 4-nitro compound and diethyl ether and methanol for the 3,5-dichloro-4-N,N-dimethylamino compound. The crystalline compounds were kept at -60° .

Z-3,5-Cl₂-4-N(CH₃)₂-benzenediazo *t*-butyl sulphide: m.p. 31.5–32.5°; UV $\nu_{\text{max}} = 32400 \text{ cm}^{-1}$, $\epsilon_{\text{max}} = 4680$ (EtOH); IR 1472(s)-1418-1360-1160-950-878-803-575 cm^{-1} (KBr); NMR δ 1.61 (-C(CH₃)₃), δ 2.93 (-N(CH₃)₂), δ 7.03 (aromatic protons) (CCl₄).

Z-4-NO₂-benzenediazo *t*-butyl sulphide: m.p. 56.5–57.5°; UV $\nu_{\text{max}} = 33100 \text{ cm}^{-1}$, $\epsilon_{\text{max}} = 8040$ (EtOH); IR 1600-1585-1515 (s)-1480 (s)-1345 (s)-1165-1108-880-858-720-674-580-550 cm^{-1} (KBr); NMR δ 1.61 (-C(CH₃)₃), δ 7.04-7.19-8.26-8.41 (aromatic protons) (CCl₄). The sulphides were isolated from the reaction mixtures by TLC or by evaporation and recrystallisation (EtOH).

3,5-Cl₂-4-N(CH₃)₂-benzene *t*-butyl sulphide: m.p. 94–95°; UV $\nu_{\text{max}} = 33750 \text{ cm}^{-1}$, $\epsilon_{\text{max}} = 5640$ (EtOH); IR 1480-1440-1420-1368-1168-950-896-790-619 cm^{-1} (KBr); NMR δ 1.30 (-C(CH₃)₃), δ 2.90 (-N(CH₃)₂), δ 7.42 (aromatic protons) (CCl₄), new compound.

4-NO₂-benzene *t*-butyl sulphide: IR 1590-1570-1508-1418-1345-1154-850-742-687 cm^{-1} (between KBr windows); NMR δ 1.34 (-C(CH₃)₃), δ 7.55-7.70-8.07-8.22(q) aromatic protons) (CCl₄).

2,6-Cl₂-dimethylaniline was prepared by reduction of the corresponding diazonium salt with an alkali stannite solution.¹³

t-Butyl disulphide was prepared by reaction of the *t*-butyl alcohol with *t*-butylthiol in a solution of H₂SO₄, bp 148–149°¹⁴. Nitrobenzene and other solvents were of analytical quality (Merck) and dried on molecular sieves before use.

Kinetic measurements. The reactions were followed as a function of time on an A60 Varian NMR spectrometer, mostly with deuterated solvents.

The temp, chosen so that the E-isomer was completely stable in the time required for measurement, was checked for constancy before and after the experiment ($\pm 0.5^\circ$). The starting concentrations of the Z-isomers varied between 0.05 N and 0.2 N. No dependence of the rate of the reaction on the concentration could be detected. Neither the sum nor the ratio of the products formed in the reaction changed when these experiments were performed in a N₂ atmosphere. Comparison of the reaction in deuterated and undeuterated nitromethane revealed no differences either in the kinds of products or in the rates of reaction.*

The concentrations of the compounds were determined at different times by integration.

For each experiment some ten measurements were performed to cover a conversion of up to about 80% of the Z-isomer. The disappearance of the Z-isomer as well as the formation of the E-isomer and decomposition products were first-order reactions. The *k*-values were obtained by the method of least squares (correlation factors 0.99 or higher), being calculated for at least three temps (between 20° and 90°). The errors in the values of ΔE and log *A* did not exceed 2%.

The presence of acid or water accelerated the rate of decomposition. We checked that influence of traces of acid or water on the rates of reaction in the carefully cleaned vessels and purified solvents is highly improbable.

Product identification. The products were identified by comparison with authentic compounds by means of the NMR peak produced in the mixture and by TLC. It is possible to identify the different products as single spots with, as eluent, cyclohexane containing varying concentrations of chloroform or acetone. Silica gel or aluminium oxide was used as carrier material. The most sensitive col-

our reagent for sulphur compounds appeared to be a PdCl₂ solution in 6N HCl.¹⁵

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*In dueterated solvents, deuterium substitutes in position four of the benzene ring.