AZO-COMPOUNDS. IV.*

THE KINETICS OF THERMAL DECOMPOSITION OF SOME ASYMMETRIC AZO COMPOUNDS WITH A CONJUGATED AZO GROUP

M.Procházka, O.Ryba and D.Lím

Institute of Macromolecular Chemistry,
Czechoslovak Academy of Sciences, Prague 6

A number of asymmetric azo compounds were prepared, in which the azo group is conjugated with the phenyl or carbonyl group. The compounds were subjected to thermal decomposition; the effect of substituents and conjugation on their stability was followed, and the results were used to suggest the mechanism of splitting.

In the preceding paper, the effect of asymmetry on the decomposition of aliphatic azo compounds was investigated[1]. The results showed that the conditions of decomposition are prevailingly determined by the nature of that substituent at the azo group which yields a more labile symmetric azo compound. For azo compounds whose azo bond forms a conjugated system with further groups capable of conjugation, a pronounced effect of conjugation on thermal decomposition may be expected. In the present work, decomposition of the azo compounds of the following type has been studied.

$$R^1-N=N-\underset{\underset{CN}{|}}{\overset{\overset{CH_3}{|}}{C}}-R^2$$
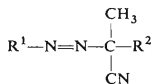
I, $R^1 = COOCH_2CH_3$, $R^2 = CH_3$ *V,* $R^1 = 2\text{-}CH_3C_6H_4$, $R^2 = CH_3$
II, $R^1 = C_6H_5$, $R^2 = CH_3$ *VI,* $R^1 = 2,4,6\text{-}(CH_3)_3C_6H_2$, $R^2 = CH_3$
III, $R^1 = 4\text{-}NO_2C_6H_4$, $R^2 = CH_3$ *VII,* $R^1 = C_6H_5$, $R^2 = C_6H_5$
IV, $R^1 = 4\text{-}CH_3OC_6H_4$, $R^2 = CH_3$ *VIII,* $R^1 = 2\text{-}CH_3C_6H_4$, $R^2 = CH_2C(CH_3)_2C_6H_5$
   IX, $R^1 = C_6H_5$, $R^2 = CH_2C(CH_3)_2C_6H_5$

The decomposition of all the above azo compounds proceeds *via* a first order reaction;

the time dependences of the logarithms of concentration of the azo compound are linear, and the dependences of the logarithms of the rate constants on the reciprocal value of the absolute temperature of decomposition are also linear (Table 1).

The decomposition of 2-(ethoxycarbonylazo)isobutyronitrile (I) corresponds to a first order reaction in accordance with the behaviour of symmetric aliphatic azo compounds without conjugation. The effect of the solvent on the rate of decomposition is small and varies within the limits of the symmetric azo compounds under investigation[2]. The kinetic constants of decomposition are close to those of azo-2,2'-bis(isobutyronitrile) (Table II), whose azo group absorbs in the region of 346 nm; the absorption of the azo group of compound I exhibits red shift, but its molar

TABLE I

Decomposition Kinetics of Azo Compounds
  Solvent decalin.

Compound	Temperature, °C	$k_d \cdot 10^5$ s^{-1}	E_a kcal/mol	A s^{-1}	Compound	Temperature, °C	$k_d \cdot 10^5$ s^{-1}	E_a kcal/mol	A s^{-1}
I	120	5·4	32·5	$7·3 \cdot 10^{13}$	V	160	6·7	42·9	$3·2 \cdot 10^{17}$
	130	18.1				170	21·1		
	140	44·1				180	63·9		
	150	111				190	156·0		
II^a	150	1·5	43·9	$9·4 \cdot 10^{17}$	VI	130	2·1	36·3	$2·4 \cdot 10^{15}$
	160	5·3				140	6·0		
	170	14·2				150	14·6		
	180	46·8				160	37·0		
III^b	180	33·9	41·3	$3·0 \cdot 10^{16}$		170	114		
	190	100			VII	70	3·6	32·7	$2·5 \cdot 10^{16}$
	200	246				80	14·7		
	210	614				90	51·0		
IV	160	3·0	42·4	$7·1 \cdot 10^{16}$		100	166·0		
	170	8·6			$VIII$	130	5·8	41·1	$1·2 \cdot 10^{18}$
	180	26·4				140	20·0		
	190	72·9				150	67·4		
						160	204		
					IX	140	14·9	36·8	$4·5 \cdot 10^{15}$
						150	44·4		
						160	114		
						170	320		

[a] Solvent cetane, [b] solvent benzene.

Table II

Effect of the Structure of Azo Compounds on Their Decomposition and Spectral Properties

Compound	λ_{max} nm	ε	E_a kcal/mol	A s^{-1}
I	372	29	32·5	$7·3 . 10^{13}$
II	397	158	43·9	$9·4 . 10^{17}$
IX	397	144	36·8	$4·5 . 10^{15}$
X^a	346	21·4	31·1	$2·7 . 10^{15}$
XI^b	345	29·1	22·8	$1·9 . 10^{12}$
XII^c	440	537	—	—

[a] Azo-2,2'-bis(isobutyronitrile)[9].   [b] Azo-2,2'-bis(2,4-dimethyl-4-phenylvaleronitrile)[2], measured in toluene.   [c] Azobenzene, spectral measurements in ethanol as solvent.

extinction coefficient indicates a comparatively weak conjugation effect of the alkoxy-carbonyl groups.

The activation energy of decomposition (E_a) of 2-(phenylazo)-isobutyronitrile (II) is much higher than E_a of the 2-(ethoxycarbonylazo) derivative, which along with the optical properties demonstrates a considerable effect of conjugation of the azo group with the phenyl group on stability. The cause of decomposition, typical of the aliphatic azo compounds, has again to be attributed to the behaviour of the isobutyro-nitrile part of the molecule. Similarly, the activation energy of decomposition of 2-phenylazo-2,4,4-trimethylvaleronitrile[3] is higher (37·7 kcal/mol) than E_a of the decomposition of azo-2,2'-bis(2,4,4-trimethylvaleronitrile) (29·7 kcal/mol)[2,4]; the same is true for 2-phenylazo-2,4-dimethyl-4-phenylvaleronitrile (IX) and 2,2'-azo-bis(2,4-dimethyl-4-phenylvaleronitrile) (XI) (Table II). The optical properties of these aromatic–aliphatic compounds are identical. Another analogy may be quoted for phenylazodiphenylmethane and azobis(diphenylmethane)[5,6], whose E_a of decompo-sition is 34·0 and 26·6 kcal/mol, respectively. Consequently, the conjugation of the azo bond with the phenyl group in the case of asymmetric aromatic–aliphatic azo compounds manifests itself by the fact that it makes the decomposition substantially more difficult. A pronounced stabilization effect of the conjugation of aromatic rings with the azo group may be observed with azobenzene, where decomposition and formation of the phenyl radicals occur at a temperature above 600°C (ref.[7]). The rate of decomposition of compound II in comparison with azo-2,2'-bis(iso-butyronitrile) or 2-(tert-butylazo)isobutyronitrile[1] is much lower, whereas the activa-tion energy is higher by approximately 10 kcal/mol. Although the bond between the carbon atom of the aromatic ring and the nitrogen atom of the azo group is stronger

than the bond between the carbon and the nitrogen atom of the other half of the molecule, both the C—N bonds probably split simultaneously. In the transition state, a greater loosening of the bond between the nitrogen atom and the isobutyronitrile part may be assumed. On the assumption that the bond on the side of the isobutyro-nitrile residue would be interrupted in the first place, the azo radical thus obtained might be more stabilized by resonance[8] in comparison with the aliphatic radicals; consequently, the activation energy of decomposition of arylazonitriles in the absence of further complicating agents should be lower in comparison with alkylazonitriles, in which the bond between the carbon atom of the alkyl group and the nitrogen atom of the azo group is not strengthened by conjugation. What actually happens, however, is that the decomposition of alkylazonitriles occurs more readily than that of arylazo-nitriles, which may indicate that during thermolysis of arylazonitriles the C—N bonds are broken simultaneously on both sides of the azo group with the cooperation of both substituents according to their nature.

The rate of decomposition and the activation energy of arylazonitriles may be affected by substituents on the aromatic ring. 2-(4-Nitrophenylazo)isobutyronitri-le *(III)* and 2-(4-methoxyphenylazo)isobutyronitrile *(IV)* exhibit a slight decrease in the rate of decomposition in comparison with the unsubstituted compound. This decrease in the rate may in both cases be explained by an increased resonance stabiliza-tion of the basic state due to the $+M$ effect of the methoxy group and the -M effect of the nitro group, which in its turn strengthens the bond between the phenyl group and the nitrogen atom. In the case of the *o*-tolylazo derivative *(V)*, a slight increase in the rate of decomposition with respect to the phenylazo derivative was observed. The decomposition might be affected by the $+M$ effect of the methyl group, which would have as its consequence an increase in the stabilization of the phenyl radical and thus a decrease in the strength of the bond between the phenyl group and the nitrogen atom; a greater importance, however, may be attributed to the steric effect of the methyl group at the position *ortho*. The presence of three methyl groups on the benzene ring in the case of 2-(mesitylazo)isobutyronitrile *(VI)* causes a considerable increase in the rate of decomposition and a decrease in the activation energy by 8 kcal/mol. This is probably due to a greater contribution of the $+M$ effect of the methyl groups and a greater strain of the bond between the phenyl group and the nitrogen atom owing to the steric effect. The greatest decrease in stability in the series mentioned above was observed with 2-phenylazo-2-phenyl-propionitrile *(VII)*. The rate of decomposition rises by four orders of magnitude and the activation energy falls by 11 kcal/mol. The presence of the phenyl and nitrile groups at the α-position to the carbon atom with an odd electron stabilizes the forming 2-phenylpropionitrile radical by enabling a considerable delocalization of the free electron, thus facilitating the decomposition. Moreover, the steric influence of this part of the molecule on the strength of the C—N bond also plays an important part.

It may be seen from the above results found for the decomposition of substituted

2-phenylazoisobutyronitrile that the substituents at the aromatic ring, as long as they manifest themselves by polar effects only, have but little effect upon the stability of these compounds. A more pronounced increase in the rate of decomposition is observed with 2-(2-tolylazo)-2,4-dimethyl-4-phenylvaleronitrile (*VIII*) and 2-phenyl-azo-2,4-dimethyl-4-phenylvaleronitrile (*IX*), which may theoretically be derived from *V* or *II* by substitution of the cumyl group for one hydrogen atom of the isobutyro-nitrile part. The introduction of the bulky cumyl group into the molecule considerably increases the rate of decomposition in comparison with azo compounds *V* and *II*. The rise in the rate of decomposition may be attributed to a decrease in the strength of the bond between the carbon and nitrogen atoms of the azo group, due to the steric interaction of the 2,4-dimethyl-4-phenylvaleronitrile residue with the substituent at the other nitrogen atom of the azo group. This confirms once again the great influence of the branching of the alkyl group at the β-position on the rate of decom-position of the azo compounds.

Similarly to the aliphatic asymmetric azo compounds, the presence of a more active substituent at one of the nitrogen atoms of the azo group (*e.g.*, a substituent allowing the delocalization of the unpaired electron and occasionally playing a steric part) facilitates the decomposition; in this manner, similar types of the aromatic–aliphatic azo compounds may serve as a source of the aryl radicals under comparati-vely mild conditions.

EXPERIMENTAL

Preparation of the Azo Compounds

Measurements in the visible region of the spectrum were made in decalin as solvent.

2-(*Ethoxycarbonylazo*)*isobutyronitrile* (I) was obtained by the oxidation of 2-(ethoxycarbonyl-hydrazo)isobutyronitrile[10,11] with chromium trioxide in dilute sulphuric acid, b.p. 73°C/0·01 Torr; λ_{max} 372 nm (ε 29). 2-(*Phenylazo*)*isobutyronitrile* (II) was prepared according to ref.[3,12,13]; λ_{max} (cetane) 397 (ε 158). 2-(4-*Nitrophenylazo*)isobutyronitrile (III) was obtained by the oxidation of 2-(4-nitrophenylhydrazo)isobutyronitrile[14] with potassium permanganate in acetone, m.p. 129°C; λ_{max} 397 (ε 355).

2-(4-*Methoxyphenylazo*)*isobutyronitrile* (IV) was obtained by the condensation of 4-methoxy-phenylhydrazine with acetonecyanohydrin, followed by the oxidation of the hydrazo compound thus obtained with potassium permanganate in acetone; yield 44% (related to 4-methoxyphenyl-hydrazine), m.p. 55°C; λ_{max} 387 nm, ε 315 (*cf.*[15]). For $C_{11}H_{13}N_3O$ (203·2) calculated: 65·20% C, 6·45% H, 20·67% N; found: 65·32% C, 6·64% H, 20·64% N. Another two azo com-pounds were prepared in a similar way.

2-(2-*Tolylazo*)*isobutyronitrile* (V) (yield 48%), m.p. 22°C; λ_{max} 403 nm, ε 187 (*cf.*[13]). For $C_{11}H_{13}N_3$ (187·2) calculated: 70·56% C, 7·00% H, 22·44% N; found: 70·60% C 7·25% H, 22·51% N. 2-(*Mesitylazo*)*isobutyronitrile* (VI), yield 24%, m.p. 19°C; λ_{max} 407 nm, (ε 353). For $C_{13}H_{17}N_3$ (215·3), calculated: 72·52% C, 7·96% H, 19·52% N; found: 72·33% C, 8·15% H, 19·22% N.

2-(*Phenylhydrazo*)-2-*phenylpropionitrile*. A mixture of 17 g of acetophenone phenylhydrazone[16] and 10 ml of hydrogen cyanide was sealed in an ampoule and left two months at room temperature. After evaporation of the excess of hydrogen cyanide, the crystalline residue was dissolved in 400 ml of ether, the solution was filtered with active carbon and concentrated to 50 ml under reduced pressure. The precipitate was filtered off and washed with 30 ml of ether. Crystallization from ether gave 4·1 g (21%) of 2-(phenylhydrazo)-2-phenylpropionitrile, m.p. 126°C. For $C_{15}H_{15}N_3$ (237·3) calculated: 75·92% C, 6·37% H, 17·71% N; found: 75·70% C, 6·25% H, 17·87% N.

2-*Phenylazo*-2-*phenylpropionitrile* (VII). A solution of 8·2 g (0·345 mol) of phenylhydrazo-2-phenylpropionitrile in 150 ml of acetone was oxidized with potassium permanganate (suspension of 8 g of finely ground substance in 200 ml of acetone) while stirring and cooling until the reaction mixture became purple. The temperature was maintained around 5°C. After filtration a few drops of hydrazine hydrate were added in order to remove the excess of permanganate. The mixture was filtered once again, acetone was evaporated under reduced pressure, the remaining yellow oil was dissolved in light petroleum and dried with anhydrous magnesium sulphate. On cooling, yellow crystals were obtained. Crystallization from light petroleum yielded 7·5 g (93%) of 2-phenylazo-2-phenylpropionitrile, m.p.'46— 47°C; λ_{max} 397 nm (ε 136). For $C_{15}H_{13}N_3$ (235·3) calculated: 76·57% C, 5·57% H, 17·86% N; found: 76·27% C, 5·69% H, 17·70% N.

2-(2-*Tolylazo*)-2,4--*dimethyl*-4-*phenylvaleronitrile* (VIII). A mixture of 6·1 g (0·057 mol) of *o*-tolylhydrazine and 10·1 g (0·057 mol) of 4-methyl-4-phenylpentane-2-one was heated in a sealed ampoule to 80°C for 9 hours. By cooling and sucking off, 4·2 g of crude 4-methyl-4-phenylpentane-2-one *o*-tolylhydrazone was obtained; this product was sealed with 4 ml of hydrogen cyanide in an ampoule, and the mixture was left at room temperature for three days. Evaporation of the excess of hydrogen cyanide under reduced pressure yielded 5 g of crude *o*-tolylhydrazone-2,4-dimethyl-4-phenylvaleronitrile in the form of red oil. The latter was oxidized with potassium permanganate on dissolving in acetone (*cf.* preparation of compound *VII*). Crystallization from light petroleum gave 1·5 g (10%) of yellow crystalline compound, m.p. 85°C; λ_{max} 403 nm (ε 166). For $C_{20}H_{23}N_3$ (305·4), calculated: 78·65% C, 7·59% H, 13·76% N; found: 78·71% C, 7·73% H, 14·06% N.

2-*Phenylazo*-2,4-*dimethyl*-4-*phenylvaleronitrile* (IX) was obtained from phenylhydrazine by a procedure similar to *VIII* in a yield 25%, m.p. 85·5°C; λ_{max} 397 nm (ε 144). For $C_{19}H_{21}N_3$ (291·4) calculated: 78·31% C, 7·27% H, 14·42% N; found: 78·25% C, 7·43% H, 14·83% N.

Decomposition of the Azo Compounds in Solution

The kinetics of decomposition of 2-(ethoxycarbonylazo)isobutyronitrile was followed volumetrically. The variation in concentration of the remaining azo compounds with time was determined spectrometrically. The measurements were carried out in decalin and cetane in the same way as described earlier[17]. For an investigation of the decomposition of 2-(4-nitrophenylazo)isobutyronitrile, when spectral measurements were made impossible by overlapping of the absorption maximum of the azo group due to the products of decomposition, the polarographic method was used[17].

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