

THE KINETICS OF THERMAL DECOMPOSITION OF ASYMMETRICAL ALIPHATIC AZO COMPOUNDS

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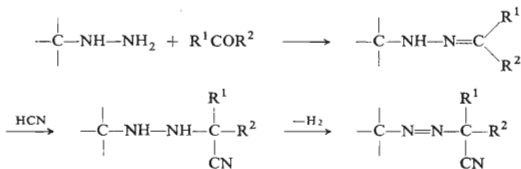
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Azo compounds of type $\begin{array}{c} | \\ \text{—C—N=N—C—CN} \\ | \end{array}$ were prepared, and the effect of the structural asymmetry upon their thermal decomposition in solution was studied. The decomposition kinetics was investigated by means of UV spectrometry and polarography; the kinetic data thus obtained were compared with the values established in the decomposition of the corresponding symmetrical azo alkanes and azo nitriles.

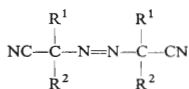
In the investigations of aliphatic azo compounds, attention has been concentrated mainly on those exhibiting structural symmetry. In the preceding papers we have investigated the decomposition of some symmetrical azo nitriles (*I*) (ref.¹) and azo hydrocarbons (*II*) (ref.²), having a tertiary alkyl group in the vicinity of the azo bond. To extend the knowledge of the mechanism of splitting and reactions of the released radicals, it was necessary to study the structurally asymmetrical aliphatic azo compounds and to compare their behaviour with the corresponding symmetrical compounds.

The investigations were carried out using compounds of the general type of alkyl azo nitrile, which are comparatively easy to prepare, *cf.* Scheme 1.



SCHEME 1

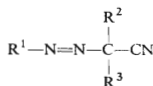
The decomposition kinetics was measured in the case of 2-tert-butylazoisobutyronitrile (*IIIa*), 2,4,4-trimethyl-2-(tert-butylazo)valeronitrile (*IIIb*), and 2-(1-adamantylazo)isobutyronitrile (*IIIc*).

*I*

- a*, R¹ = R² = methyl
b, R¹ = methyl, R² =
 = neopentyl

*II*

- a*, R = tert-butyl
c, R = 1-adamantyl

*III*

- a*, R¹ = tert-butyl, R² =
 = R³ = methyl
b, R¹ = tert-butyl, R² =
 = methyl, R³ = neopentyl
c, R¹ = 1-adamantyl, R² =
 = R³ = methyl

EXPERIMENTAL

N-Nitroso-N-tert-butylglycine

To a solution of 68 g (0.93 mol) of tert-butylamine in 75 ml water, 25 g (0.93 mol) hydrogen cyanide and 80 g aqueous solution of formaldehyde (38%) were added under stirring. The mixture was stirred one hour at room temperature, then 125 ml 50% solution of potassium hydroxide were added dropwise. The mixture was heated to boil for two hours and diluted with 400 ml water, which was then distilled off in order to remove the excess of ammonia. On cooling, the solution was acidified with 125 ml hydrochloric acid, cooled to 0°C, and a solution of 65 g (0.94 mol) sodium nitrite in 150 ml water was added dropwise; the mixture was stirred at 0°C for two hours. On adding another 125 ml hydrochloric acid, an oily layer was formed on the surface, which solidified by cooling. On sucking off and recrystallizing from water (90 ml), 75 g of the product (50%) were obtained, m.p. 108–110°C. For C₆H₁₂N₂O₃ (160.2) calculated: 44.99% C, 7.55% H, 17.49% N; found: 44.95% C, 7.54% H, 17.75% N.

N-tert-Butylsydnone

A mixture of 40 g (0.25 mol) N-nitroso-N-tert-butylglycine and 240 ml (2.5 mol) acetic anhydride was heated for three hours on a water bath. On cooling, the product was sucked off and recrystallized from 90% methanol; the yield was 26 g (73%), m.p. 178°C. For C₆H₁₀N₂O₂ (142.2) calculated: 50.69% C, 7.09% H, 19.71% N; found: 50.61% C, 6.91% H, 19.90% N.

N-tert-Butylacetaldimine

To 36.5 g (0.5 mol) tert-butylamine, 22 g (0.5 mol) acetic aldehyde were added dropwise for two hours; 25 g potassium hydroxide were then added, and the mixture was stirred for ten minutes. The oily layer thus obtained was separated, dried, and distilled in the presence of potassium hydroxide. Redistillation (Vigreux column, 10 cm) yielded 28 g (56.5%) of the compound having b.p. 81–82°C, n_D²⁰ 1.4029. For C₆H₃N (99.2) calculated: 72.66% C, 13.21% H, 14.13% N; found: 72.74% C, 13.52% H, 14.18% N.

1-tert-Butyl-3-methyldiaziridine

To a mixture of 17 g (0.172 mol) N-tert-butylacetaldimine and 12.5 g (0.172 mol) tert-butylamine in 100 ml ether, an ether solution of monochloramine (0.174 mol) was added, and the solution was left to stand at room temperature for ten hours. The precipitated salt was filtered off, the ether was evaporated, and the residue was distilled through the Vigreux column (b.p. 58–72°C/116 Torr). The product was diluted with ether and extracted into 1M-H₂SO₄. The aqueous solution was adjusted by a soda solution to pH 9, and diaziridine was extracted with ether. On drying the ether solution with anhydrous potassium carbonate and removing the ether, 3.5 g (17.9%) 1-tert-butyl-3-methyldiaziridine was obtained by distillation, b.p. 65–66°C/105 Torr, n_D^{20} 1.4269. For C₆H₁₄N₂ (114.2) calculated: 63.11% C, 12.36% H, 24.53% N; found: 63.10% C, 12.44% H, 24.43% N.

tert-Butylhydrazinium Chloride

a) *Hydrolysis of N-tert-butylsydnone*. A mixture of 26 g N-tert-butylsydnone with 140 ml of 5M methanol solution of hydrogen chloride and 10 ml water was heated four hours on a water bath. Evaporation under reduced pressure and crystallization of the compound from ethanol yielded 8 g of tert-butylhydrazinium chloride (35%), m.p. 195°C. For C₄H₁₃ClN₂ (124.6) calculated: 38.55% C, 10.52% H, 22.48% N; found: 38.59% C, 10.58% H, 22.53% N.

b) *Hydrolysis of 1-tert-butyl-3-methyldiaziridine*. A mixture of 1.5 g tert-butylmethyldiaziridine and 8 ml 10% hydrochloric acid was heated to boil for twenty minutes. On diluting with 10 ml water the remaining acetic aldehyde was distilled off with water vapour. The solution after filtration was evaporated, and the precipitated tert-butylhydrazinium chloride was recrystallized from ethanol, m.p. 195°C, yield 0.82 g (50%).

c) *Reaction of tert-butylamine with hydroxylamine-O-sulphonic acid*. To a solution of 36.5 g potassium hydroxide (0.65 mol) in 250 ml water, 73 g (1 mol) tert-butylamine was added, and a solution of 36.4 g (0.32 mol) hydroxylamine-O-sulphonic acid³ in water was added dropwise under stirring. The temperature of the reaction mixture was maintained within the range 50–60°C, and at the end the mixture was boiled for ten minutes. On cooling and acidifying with acetic acid to pH 6 the salt was filtered off, 36 ml (0.34 mol) benzaldehyde was added to the filtrate, and the mixture was heated to 50–60°C for twenty minutes. The hydrazone thus obtained was extracted with ether. The ether fractions were acidified with diluted hydrochloric acid (1 : 2), the ether was distilled off, and benzaldehyde was removed by steam distillation. The residue after filtration (active carbon) was evaporated to dryness under reduced pressure, and the dry residue was recrystallized twice from ethanol, m.p. 195°C. The yield was 14.5 g tert-butylhydrazinium chloride (11.7%, referred to tert-butylamine). For C₄H₁₃ClN₂ (124.6) calculated: 38.55% C, 10.52% H, 22.48% N; found: 38.74% C, 10.63% H, 22.60% N.

tert-Butylhydrazine. To 13 g of tert-butylhydrazine hydrochloride, a solution of 13 g potassium hydroxide in 15 ml water was added in the absence of air. On cooling, the released base was extracted with ether, and the ether solution was dried with potassium hydroxide. The ether was then distilled off, the tert-butylhydrazine thus obtained was heated four hours with barium oxide under reflux and then redistilled. The yield was 4.1 g (45%), b.p. 114–115°C, n_D^{20} 1.4290.

2-tert-Butylazoisobutyronitrile (IIIa)

tert-Butylhydrazine (8 g, 0.09 mol) was mixed in the absence of air with 8.6 g (0.1 mol) acetone-cyanhydrin. The reaction mixture was left to stand overnight. The crude hydrazo compound thus obtained was dissolved in 10 parts by weight of diluted hydrochloric acid (1 : 2) and oxidized

at -10° to 0°C by adding bromine dropwise to achieve a lasting orange colour. The mixture was then diluted with water, and the product was extracted with ether. The ether solution was washed with water several times, dried and partly evaporated; on cooling, crystals were formed. A two-fold recrystallization from ether yielded 9.5 g of compound *III a* (65.5%), m.p. 8°C ; λ_{max} 360 nm (ϵ 18.7). For $\text{C}_8\text{H}_{15}\text{N}_3$ (153.2), calculated: 62.70% C, 9.87% H, 27.43% N; found: 62.89% C, 10.15% H, 27.59% N.

2,4,4-Trimethyl-2-(tert-butylazo)-valeronitrile (*IIIb*)

tert-Butylhydrazine (8 g; 0.09 mol) was mixed with 11.4 g (0.1 mol) methyl neopentyl ketone (b.p. 128°C) (ref.⁴). When the main reaction was completed, 8 ml (0.2 mol) liquid hydrogen cyanide was added to the reaction product. The mixture was left to stand at room temperature for two days. After this time the excess of hydrogen cyanide was removed, the crude hydrazo compound was dissolved in a mixture of the same volumes of ethanol and diluted hydrochloric acid (1 : 3) and oxidized with bromine at -20 to -10°C to a lasting orange colour. The product was isolated similarly to the preceding case, m.p. 38.4°C ; λ_{max} 359 nm (ϵ 17.7); the yield 9.1 g (51.5%). For $\text{C}_{12}\text{H}_{23}\text{N}_3$ (209.3) calculated: 68.85% C, 11.08% H, 20.07% N; found: 69.00% C, 11.28% H, 20.08% N.

N-Nitroso-N-(1-adamantyl)glycine

Crude N-(1-adamantyl)aminoacetonitrile⁵ (80 ml) was heated with a solution of potassium hydroxide (10 g in 40 ml of water) for 30 minutes, the mixture was diluted with 50 ml of water and heated to boil for two hours. On cooling, a precipitate of N-(1-adamantyl)glycine was formed. The suspension was acidified with 90 ml conc. hydrochloric acid, a solution of sodium nitrite (40 g in 150 ml water) was added dropwise to the solution, and the mixture was stirred at room temperature for four hours. The mixture was then cooled, the precipitate was sucked off, washed with water and dried. M.p. $150-152^{\circ}\text{C}$; yield 37 g (37%). For $\text{C}_{12}\text{H}_{18}\text{N}_2\text{O}_3$ (238.3) calculated: 60.49% C, 7.61% H, 11.76% N; found: 60.23% C, 7.81% H, 11.78% N.

3-(1-Adamantyl)sydnone

A mixture of 37 g (0.15 mol) N-nitroso-N-(1-adamantyl)glycine with 300 ml acetic anhydride was heated to 100°C five hours under stirring. On concentrating at reduced pressure the product was recrystallized from methanol; m.p. $223-224^{\circ}\text{C}$; yield 21 g (62%). For $\text{C}_{12}\text{H}_{16}\text{N}_2\text{O}_2$ (220.3) calculated: 65.43% C, 7.32% H, 12.72% N; found: 65.39% C, 7.46% H, 12.60% N.

(1-Adamantyl)hydrazinium Chloride

21 g 3-(1-adamantyl)sydnone was introduced into aqueous methanol (93.6% by vol.), saturated with hydrogen chloride under cooling; the mixture was heated four hours on a water bath. The solution was then concentrated under reduced pressure, and the salt was twice recrystallized from ethanol; the yield, 12.6 g (66%); m.p. $258-68$ (in a sealed capillary). For $\text{C}_{10}\text{H}_{19}\text{ClN}_2$ (202.7), calculated: 59.24% C, 9.44% H, 17.49% Cl, 13.82% N; found: 59.44% C, 9.71% H, 17.64% Cl, 14.16% N.

2-(1-Adamantylazo)isobutyronitrile (*IIIc*)

To a solution of 5 g (0.025 mol) (1-adamantyl)hydrazinium chloride in 75 ml hot water, 50 ml saturated soda solution was added under stirring. The precipitated 1-adamantylhydrazine was

extracted with dichloromethane. After evaporation of the solvent, 4 g base were obtained, which was then dissolved in 12 ml (0.13 mol) acetonecyanhydrin, and the solution was left at room temperature for two days. The product was washed with water (3×100 ml), dissolved in 30 ml dichloromethane and oxidized with mercuric oxide (10 g) for twelve hours. The solvent was distilled off, and the remaining yellow oil was dissolved in 10 ml methanol; from the undercooled solution, white crystals of 2-(1-adamantylazo)-isobutyronitrile were formed in a yield 1.8 g (31%); m.p. 55-56°C; λ_{\max} 358 nm (ϵ 17.5). For $C_{14}H_{21}N_3$ (231.3) calculated: 72.69% C, 9.15% H, 18.17% N; found: 72.66% C, 9.35 H, 18.17% N.

Decomposition Kinetics of Azo Compounds

The course of decomposition of 2-tert-butylazoisobutyronitrile (*IIIa*) and 2,4,4-trimethyl-2-(tert-butylazo)valeronitrile (*IIIb*) was followed spectrometrically, as described in the preceding paper².

To investigate the decomposition kinetics of 2-(1-adamantylazo)-isobutyronitrile (*IIIc*), its polarographic activity was made use of. The decomposition was carried out in benzene by a technique similar to that employed in the case of 1,1'-azoadamantane² (*IIC*). The content of non-decomposed *IIIc* was determined in 5 ml 0.1M solution (C_4H_9)₄.NClO₄ in acetonitrile. *IIIc* in this solution gives a cathodic wave ($E_{1/2} = -2.3$ V against aqueous saturated calomel electrode), whose height is a linear function of the concentration of the azo compounds, and is not affected by the presence of the decomposition products.

The decomposition of the above asymmetrical azo compounds proceeds in all cases according to the equation for a first order reaction. The dependence of the logarithm of the concentration of the compound on time is a linear one.

RESULTS AND DISCUSSION

The investigation of the effects of the medium upon the decomposition of tert-butylazonitriles has shown that these effects are not pronounced, and that they are not qualitatively different from the effects of the solvents upon the decomposition of symmetrically substituted azo compounds¹. The results of the decomposition of azo compounds in hydrocarbons are summarized in Table I. As expected, all the compounds mentioned above are decomposed slower than the corresponding symmetrical azo nitrile, but much easier than the corresponding symmetrical azo alkanes. The decomposition of 2-tert-butylazoisobutyronitrile (*IIIa*) occurs by four orders faster than that of the symmetrical 2,2'-azoisobutane (*IIa*), and by more than one order slower than that of 2,2'-azoisobutyronitrile (*Ia*). The activation energy of *IIIa* was decreased in comparison with the symmetrical 2,2'-azoisobutane (*IIa*), and approached the value of azoisobutyronitrile (*Ia*). An even more important drop in stability in comparison with 2,2'-azoisobutane (*IIa*) was observed with 2,4,4-trimethyl-2-(tert-butylazo)-valeronitrile (*IIIb*). In this case, the cleavage is made easier by the steric influence, due to the branching of trimethylvaleronitrile residue at the position beta. The activation energy decreased by more than 13 kcal/mol and approached the activation energy of a symmetrical 2,2'-azobis(2,4,4-trimethylvaleronitrile) (*Ib*). The rate of decomposition increased by six orders. The effect

TABLE I
Kinetic Decomposition Constants of Asymmetrical Alkyl Azo Nitriles

Azo Compound	Solvent	Temperature °C	$k_d \cdot 10^5$ s^{-1}	E kcal/mol	A s^{-1}
<i>IIIa</i>	cetane	90	4.11	34.9	$4.0 \cdot 10^{16}$
		95	7.47		
		100	14.57		
		105	27.15		
		110	50.06		
<i>IIIb</i>	decalin	60	3.26	30.2	$2.1 \cdot 10^{15}$
		70	12.1		
		80	43.0		
<i>IIIc</i>	benzene	120	18.2	34.3	$2.2 \cdot 10^{15}$
		130	56.6		
		140	145.0		
		150	417.0		

TABLE II
Kinetic Constants of the Thermal Decomposition of Azo Compounds

Compound	Solvent	Temperature °C	$k_d \cdot 10^4$ s^{-1}	E_a kcal/mol	A s^{-1}
<i>IIa</i>	cetane	180	0.9	43.9	$3.0 \cdot 10^{17}$
<i>IIIa</i>	cetane	100	1.4	34.9	$4.0 \cdot 10^{16}$
<i>Ia</i>	decalin	80	1.5	33.4	$6.9 \cdot 10^{16}$
<i>IIIb</i>	decalin	80	4.3	30.2	$2.1 \cdot 10^{15}$
<i>Ib</i>	cetane	70	54.8	29.7	$4.6 \cdot 10^{16}$
<i>IIc</i>	benzene	280	1.0	63.0	$7.4 \cdot 10^{20}$
<i>IIIc</i>	benzene	130	5.6	34.3	$2.2 \cdot 10^{15}$

of the more active part of the molecule is best seen from comparison of the kinetic parameters of 1,1'-azoadamantane (*IIc*) and 2-(1-adamantylazo)isobutyronitrile (*IIIc*). The comparatively very high stability of azoadamantane (*IIc*) is considerably reduced by the introduction of the isobutyronitrile residue into the molecule, instead of one

adamantyl group. The activation energy decreases by 29 kcal/mol; the decomposition rate increases by nine orders.

The kinetic decomposition constants of asymmetrical azo compounds are affected by the nitrile group containing substituents to such a degree that they are close to the decomposition constants of symmetrical azo nitriles (Table II). The motive force of decomposition of the azo compounds $R-N=N-R$ is a strongly exothermal reaction phase of the transition of the azo bond to the nitrogen molecule. However, in the process of cleavage a nitrogen molecule can be formed already in the transition state, while the electron density of the unpaired electron is partly transferred on the R-groups. The structure of these R-groups affects their ability of carrying a free electron, which manifests itself in a more or less stable nature of the radical formed, and consequently also in the bond strength between the carbon atom of the group R and the nitrogen atom of the azo group.

The cleavage of asymmetrical compounds probably leads to the formation of such a transient state when both the different groups on both sides of the azo bond contribute to the interruption of the carbon-nitrogen bonds according to their structures. The energy of the tert-butyl part of the molecule is low, owing to the low rate of decomposition of azoisobutane at the decomposition temperature of the asymmetrical azo compounds under study, so that it alone cannot be the cause of decomposition. On the other hand, the nitrile part of the molecule has enough energy for a fast decomposition, if it is estimated by the behaviour of the corresponding symmetrical azo nitriles. Therefore, the attaining of critical vibrations needed for the decomposition of asymmetrical azo compounds is made more difficult, in comparison with the symmetrical azo nitriles, by a smaller contribution of the tert-butyl or 1-adamantyl residue. A larger loosening of the bond between the nitrogen atom of the azo group and the carbon atom of the nitrile group containing alkyl group can therefore be assumed in the transient state. The participation of the polar factor in the decomposition of symmetrical azo compounds does not essentially differ from the asymmetrical ones. Similarly, it can be assumed that the contribution of the stabilization energy of the nitrile radicals in asymmetrical or symmetrical azo compounds is the same. It can be concluded, therefore, that the decrease in stability of the azo compound will most affect the more active substituent. With respect to the high stability of the symmetrical 1,1'-azoadamantane (*Iic*), high value of the activation energy needed for the interruption of the bond between the adamantyl group and the nitrogen atom of the azo compound, and on the other hand, owing to the much lower bond strength between the nitrogen and carbon atoms of the isobutyronitrile residue, it cannot be precluded that the cleavage occurs under the primary formation of 2-isobutyronitrile radical and 1-adamantyl azo radical, which is later decomposed into nitrogen atom and 1-adamantyl radical.

An important conclusion can be drawn from the knowledge acquired about the behaviour of the asymmetrical azo compounds in the thermal decomposition,

namely, that to decrease the stability of a symmetrical azo compound it is sufficient that only one substituent of the azo group contributes effectively to the decrease in stability. The above finding can be made use of in the preparation of such asymmetrical compounds, the decomposition of which would yield suitable reactive radicals under milder decomposition conditions than those needed for a more stable symmetrical azo compound.

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