

THERMAL DECOMPOSITION OF ARYLAZO(METHYL)MALONONITRILES*

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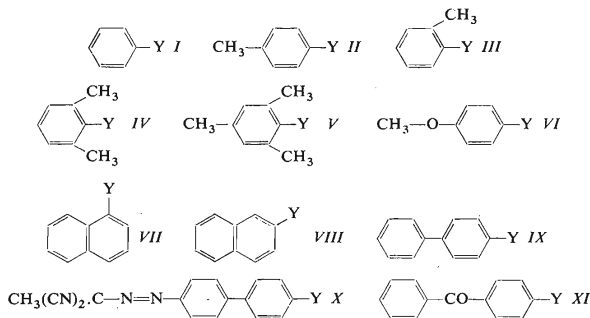
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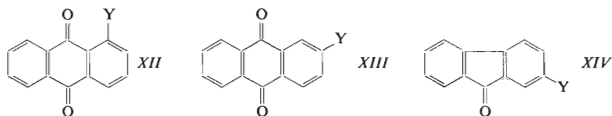
A number of arylazo(methyl)malononitriles were prepared, kinetics of their thermal decomposition in benzene solution was measured, and the effect of structure on the kinetic decomposition parameters was investigated.

In our preceding paper we reported on the properties of asymmetric variously substituted phenylazonitriles¹. Several examples were used to elucidate the effect of substituents in the benzene ring and the effect of the structure of the nitrile residue on thermal decomposition of the above compounds.

To obtain a better insight into the effects exerted upon thermal decomposition of azo compounds, especially the resonance and steric effects, arylazo(methyl)malononitriles (I–XIV) of the general formula $R-N=N-C(CN)_2CH_3$ were prepared, and the kinetic quantities of thermal decomposition were determined ($Y = -N=N-C(CN)_2CH_3$):



* Part V in the series Azo-Compounds; Part IV: This Journal 36, 3650 (1971).



The rate of thermal decomposition was investigated for all the above compounds within a temperature range of 60 to 120°C. The results of kinetic measurements are summarized in Table I.

Phenylazo(methyl)malononitrile (*I*) was chosen as the basic compound for the characterization of steric, induction and resonance effects of aromatic substituents. The effect of the position and number of the methyl groups in the benzene ring on the kinetics of thermal decomposition can be observed for compounds *II*–*V*. The methyl group at the position *para* in *II* compared with *I* slightly reduces the rate of decomposition, which may be assigned to the hyperconjugation effect. On the other hand, the methyl group at the position *ortho* (*III*) leads to an increase in the rate of decomposition. By introducing two methyl groups into positions 2,6 (*IV*), an almost eightfold acceleration compared to *I* is achieved. In the two latter cases the increase in the rate of decomposition is due predominantly to steric effects, as may be verified on Courtauld's atomic models. The methyl group at the position *ortho* prevents free rotation about the C—N bond; two methyl groups in positions 2,6 hinder the coplanarity of the benzene ring and the azo group. In this way the whole conjugated system is disturbed, the C—N bond strength between the benzene ring and the azo group is reduced, and the rate of decomposition increases. The presence of a third methyl group in position 4 (*V*) is again reflected in a slight decrease in the rate of decomposition compared to *IV*, which similarly to *II* may be explained by hyperconjugation. Despite the restriction of the coplanar arrangement of the aromatic system with the azo group by steric effect of the methyl groups in positions 2 and 6 there also is a shift of light absorption to longer wavelengths².

Some other compounds were investigated with respect to the influence of increased conjugation between the aromatic substituents and the azo group on thermal decomposition. The results show the overall effect of resonance of the individual aromatic substituents on the rate of decomposition. Data summarized in Table I indicate that the rate of decomposition gradually decreases in the order of derivatives phenyl-, 4-methoxyphenyl-, 2-naphthyl-, biphenyl-, that is, accordingly to the increase in the resonance energies of the substituents³ (benzene 36, anisol 52, naphthalene 61, diphenyl 71 kcal/mol). The increasing conjugation leads again to strengthening of the C—N bond between the aromatic substituent and the azo group, which prevents homolytic decomposition.

Another important factor affecting the decomposition, which can be observed for the naphthalene (*VII*, *VIII*) and anthraquinone (*XII*, *XIII*) derivatives, con-

TABLE I
Kinetic Constants of Thermal Decomposition of Arylazo(methyl)malononitriles

Compound	Temperature °C	$k_d \cdot 10^5$ s^{-1}	E_a kcal/mol	A s^{-1}	ΔS^\ddagger e.u.
<i>I</i>	80	9.9	31.8	$4.8 \cdot 10^{15}$	10.8
	90	30.5			
	100	114.0			
	110	341.0			
<i>II</i>	80	6.7	33.5	$4.0 \cdot 10^{16}$	15.0
	90	26.1			
	100	95.2			
	110	274.0			
<i>III</i>	70	2.8	33.1	$3.4 \cdot 10^{16}$	14.7
	80	10.3			
	90	36.7			
	100	133.5			
	110	450			
<i>IV</i>	60	4.7	32.6	$1.1 \cdot 10^{17}$	17.0
	70	19.2			
	80	76.8			
	90	270			
<i>V</i>	60	3.5	32.1	$3.7 \cdot 10^{16}$	14.9
	70	14.8			
	80	54.0			
	90	193			
<i>VI</i>	80	5.6	33.1	$2.5 \cdot 10^{16}$	13.6
	90	23.2			
	100	71.1			
	110	245.0			
<i>VII</i>	80	13.7	33.6	$4.6 \cdot 10^{16}$	15.3
	90	48.7			
	100	179.1			
	110	552.0			
<i>VIII</i>	80	5.2	33.3	$2.1 \cdot 10^{16}$	13.7
	90	18.3			
	100	66.7			
	110	209.0			
<i>IX</i>	90	17.0	36.1	$8.3 \cdot 10^{17}$	21
	100	63.3			
	110	204			
	120	768			

TABLE I
(Continued)

Compound	Temperature °C	$k_d \cdot 10^5$ s^{-1}	E_a kcal/mol	A s^{-1}	ΔS^\ddagger e.u.
X	90	15.6	35.4	$3.4 \cdot 10^{17}$	19.3
	100	61.2			
	110	206			
	120	702			
XI	80	7.1	34.0	$2.8 \cdot 10^{16}$	14.3
	90	28.3			
	100	98.0			
	110	315			
XII	70	3.7	33.1	$4.7 \cdot 10^{16}$	15.4
	80	14.3			
	90	55.2			
	100	188			
XIII	80	6.5	33.3	$2.7 \cdot 10^{16}$	14.3
	90	23.6			
	100	83.2			
	110	270			
XIV	80	3.6	33.5	$2.0 \cdot 10^{16}$	13.7
	90	13.1			
	100	44.8			
	110	153.5			

sists in the attachment of the azo group to the aromatic substituents in position 1 or 2. One may notice the steric effect of the α -isomers of condensed aromatic rings in the atomic models of these compounds. Free rotation about the C—N bond is again restricted, the aromatic system is in an out-of-plane position with respect to the plane of the azo bond. As a result, the rate of decomposition of α -isomers compared to β -isomers is increased two to three times. The benzophenone and anthraquinone derivatives do not exhibit such considerable decrease in the rate with respect to *I*, even though the resonance energies of the substituents alone are comparatively high (benzophenone⁴ 69 kcal, anthraquinone⁵ 83 kcal/mol). This is probably due to the fact that the resonance of the substituents with the azo group is used up only partly because of the cross conjugation. The rate of decomposition of the fluorenone derivative is the lowest. Although we do not know the resonance energy of fluorenone to use it for the sake of comparison, we still may assume that the conjugation effects of its planar and rigid structure will considerably strengthen the C—N bond in the fluorenone-azo group system.

The activation energies of thermal decomposition of arylazomethylmalononitriles are comparatively low, if it is borne in mind that the compounds contain aromatic substituents directly bonded to the azo group and vary around 33 kcal, or exceptionally around 36 kcal for the derivatives of IX and X. The pre-exponential factors have values common for the azo compounds, that is, $10^{15} - 10^{17} \text{ s}^{-1}$. The activation entropies vary within the range from +10 to +20 eu. The high values of ΔS^\ddagger may be assigned to the greater freedom of torsional movement in the activated state in the C—N bond between the aromatic part of the molecule and the azo group compared to the ground state.

Generally, the arylazo(methyl)malononitriles described above can be characterized as compounds which are stabilized by resonance strongly counteracted in some cases by steric effects. On the other hand, the presence of the methylmalononitrile part makes possible delocalization of the charge of the radical originated in this part of the molecule, thus facilitating decomposition, which is reflected in the comparatively low temperature range of decomposition of arylazonitriles. Taking into account the different bond strength between the carbon atom of the substituents and the nitrogen atom on both sides of the azo group, one may assume for the transition state a much lengthened bond between C and N for the nitrile part of the molecule, or asynchronous splitting of the C—N bonds with formation of the transition arylazo radical⁶⁻⁸.

EXPERIMENTAL

Preparation of Azo Compounds

2,6-Xylylazo(methyl)malononitrile (IV). A mixture of 10 ml (0.05 mol) of dilute hydrochloric acid (1 : 1), and 2.42 g (0.02 mol) of 2,6-xylylidine was cooled to -5°C , and a solution of 1.4 g (0.02 mol) of sodium nitrite in 5 ml of water was added dropwise. The temperature was maintained at -4°C . Finally, a solution of 1.6 g (0.02 mol) of methylmalononitrile in 80 ml of ethanol and a solution of 8 g (0.1 mol) of sodium acetate in 10 ml of water were added, the mixture was stirred at 0°C for 30 min and poured into 500 ml of water. The product was extracted with hexane. On cooling, crystals were obtained, which were recrystallized from a mixture of 50 ml of petroleum ether and 10 ml of ether. The yield was 2.8 g (66%) of yellow crystalline compound, m.p. $48-9^\circ\text{C}$, λ_{max} 403 nm, $\epsilon = 517$. For $\text{C}_{12}\text{H}_{12}\text{N}_4$ (212.3) calculated: 67.91% C, 5.70% H, 26.40% N; found: 67.93% C, 5.75% H, 26.39% N. The other azo compounds were prepared in a similar way. Phenylazo(methyl)malononitrile (I), yellow crystalline compound, m.p. 23°C (cf.^{6,9}), λ_{max} 380 nm, ϵ 279. For $\text{C}_{10}\text{H}_8\text{N}_4$ (184.2) calculated: 65.21% C, 4.38% H, 30.42% N; found: 65.20% C, 4.39% H, 30.74% N. 4-Tolylazo(methyl)malononitrile (II), m.p. $62-3^\circ\text{C}$ (cf.^{6,9}), λ_{max} 383 nm, $\epsilon = 361$. 2-Tolylazo(methyl)malononitrile (III), m.p. $56-7^\circ\text{C}$ (cf.⁹), λ_{max} 393 nm, ϵ 353. For $\text{C}_{11}\text{H}_{10}\text{N}_4$ (198.2), calculated: 66.65% C, 5.08% H, 28.26% N; found: 66.76% C, 5.24% H, 28.13% N. Mesitylazo(methyl)malononitrile (V), m.p. 32°C , λ_{max} 404 nm, $\epsilon = 681$. For $\text{C}_{13}\text{H}_{14}\text{N}_4$ (226.3) calculated: 69.00% C, 6.24% H, 24.76% N; found: 69.12% C, 6.23% H, 24.93% N. 4-Methoxyphenylazo(methyl)malononitrile (VI), m.p. 90°C (cf.⁶), λ_{max} 390 nm, (inflexion). For $\text{C}_{11}\text{H}_{10}\text{N}_4\text{O}$ (214.2) calculated: 61.67% C, 4.71% H, 26.15% N; found: 61.96% C,

4.80% H, 26.56% N. 1-Naphthylazo(methyl)malononitrile (VII), m.p. 97°C. For $C_{14}H_{10}N_4$ (234.3) calculated: 71.78% C, 4.30% H, 23.92% N; found: 79.79% C, 4.28% H, 23.40% N. 2-Naphthylazo(methyl)malononitrile (VIII), m.p. 68–9°C. Calculated values for C, H, N *cf.* (VII). Found: 71.73% C, 4.53% H, 23.78% N. 4-Biphenylazo(methyl)malononitrile (IX), m.p. 77–8°C. For $C_{16}H_{12}N_4$ (260.3), calculated: 73.83% C, 4.65% H, 21.52% N; found: 74.00% C, 4.79% H, 21.39% N. 4,4'-Bis(methylmalononitrilazo)biphenyl (X), m.p. 155°C. For $C_{20}H_{14}N_8$ (366.4) calculated: 65.56% C, 3.85% H, 30.59% N; found: 65.26% C, 3.99% H, 30.60% N. 4-(Methylmalononitrilazo)benzophenone (XI), m.p. 102°C. For $C_{17}H_{12}N_4O$ (288.3) calculated: 70.82% C, 4.20% H, 19.43% N; found: 70.69% C, 4.31% H, 20.15% N. 1-(Methylmalononitrilazo)anthraquinone (XII), m.p. 147°C. For $C_{13}H_{10}N_4O_2$ (314.3) calculated: 68.79% C, 3.21% H, 17.83% N; found: 68.83% C, 3.46% H, 18.00% N. 2-(Methylmalononitrilazo)anthraquinone (XIII), m.p. 159°C. The calculated values for C, H, N *cf.* (XII). Found: 69.16% C, 3.38% H, 17.97% N. 2-(Methylmalononitrilazo)fluorene-9-one (XIV), m.p. 157°C. For $C_{17}H_{10}N_4O$ (286.3) calculated: 71.32% C, 3.52% H, 19.57% N; found: 71.68% C, 3.62% H, 19.31% N.

Thermal Decomposition of Azo Compounds

Decomposition in benzene solution was carried out each time in sealed ampoules¹⁰. Concentration changes were measured for *I–V* spectroscopically with a Carry 14 spectrometer, for the other compounds polarographically, similarly to an earlier paper¹⁰. The time dependences of the logarithms of concentrations of the azo compounds were linear in all cases.

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REFERENCES

1. Procházka M., Ryba O., Lím D.: This Journal 36, 3650 (1971).
2. Wheland G. W.: *Resonance in Organic Chemistry*, p. 314. Wiley, New York 1955.
3. Ferguson L. N.: *The Modern Structural Theory of Organic Chemistry*, p. 319. Prentice-Hall, New Jersey 1963.
4. Klages F.: Chem. Ber. 82, 372 (1949).
5. Magnus A.: Z. Physik. Chem. N.F. 9, 159 (1956).
6. Kerber R., Nuyken O.: Makromol. Chem. 164, 183 (1973).
7. Hinz J., Oberlinner A., Rüdhardt C.: Tetrahedron Letters 1973, 1975.
8. Kerber R., Nuyken O., Pasupathy V.: Makromol. Chem. 170, 155 (1973).
9. Zsolnai T.: Biochem. Pharm. 14, 1337 (1965); 13, 285 (1964).
10. Procházka M., Ryba O., Lím D.: This Journal 33, 3387 (1968).

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