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KINETIC STUDIES OF THE THERMAL DECOMPOSITION OF FERROCENYL AZIDE AND FERROCENYLSULPHONYL AZIDE IN 1-CHLORONAPHTHALENE

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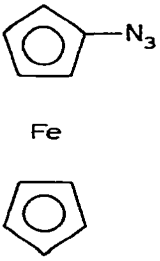
Summary

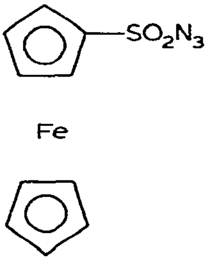
The kinetics of the thermal decomposition of ferrocenyl azide and ferrocenylsulphonyl azide in 1-chloronaphthalene indicate that there is neighbouring group participation by the lone pair e_{2g} electrons of the iron atom in the elimination of nitrogen from ferrocenyl azide, while ferrocenylsulphonyl azide undergoes unassisted decomposition to give a discrete metal-nitrene intermediate.

Introduction

For the thermolyses of ferrocenyl azide (I) and ferrocenylsulphonyl azide (II) it has been suggested [1,2] that with I the iron atom participates in the elimination of nitrogen to form the nitrene (or nitrenoid), either by utilizing its non-bonding e_{2g} electron pair or by a σ—π carbon—metal hyperconjugation mechanism as suggested for metal participation in α-metallocenyl carbonium ions [3,4]. In the case of II, the intermediacy of both free and complexed



(I)



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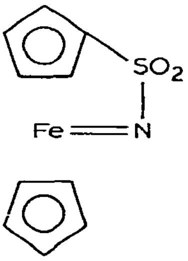

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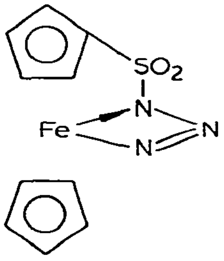


(IV)

nitrenes (III) was proposed on the basis of the temperature required for reaction, the nature of products isolated, and the results of reaction in dimethylsulphoxide. It was not certain, however, whether the complexed nitrenes arose from an initially-formed metal-azide complex such as IV as in the copper-catalysed decomposition of benzenesulphonyl azide [5,6]. We have carried out a kinetic investigation of these reactions in an attempt to throw more light on the mechanisms.

Results and discussion

In order to establish metal participation in the decomposition of I and II, it was considered necessary to show that the iron atom in ferrocene is capable of catalysing the decomposition of aryl and arylsulphonyl azides. Results obtained from experiments in which various transition metals and their salts were employed as catalysts indicated that ferrocene was more effective than copper powder in catalysing the decomposition of sulphonyl azides. Activation parameters obtained from kinetic studies offered conclusive evidence for the formation of a metal-azide complex in such ferrocene-catalysed reactions [7]. Such a participation by the iron atoms would be expected to be more facile in the decomposition of I and II in which the reactions are intramolecular.

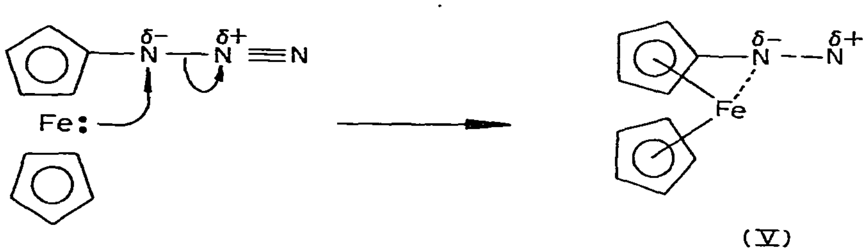
The kinetics of the thermal decomposition of I and II have been studied in 1-chloronaphthalene. Phenyl and benzenesulphonyl azides were also studied and their activation parameters used for comparison. The data are presented in Table 1.

Comparison of the activation parameters obtained for ferrocenyl azide with those for phenyl azide indicate that there is anchimeric assistance by the iron atom to the loss of nitrogen. The low $\Delta S^{\neq}$ value favours nucleophilic participation by the lone pair e_{2g} electrons of the iron atom. For effective participation by the e_{2g} electrons, a transition state structure such as V could be envisaged in which the cyclopentadienyl rings are splayed to allow for more effective overlap between the filled e_{2g} orbital of the iron atom and the developing vacant p-orbital on the α-nitrogen. Molecular orbital calculations [8] have previously shown that splaying of the rings could occur without any significant loss in bond energy since the bonding of the rings to the metal atom is relatively insen-

TABLE 1

FIRST ORDER RATE CONSTANTS AND THE ACTIVATION PARAMETERS FOR THE THERMOLYSIS OF FERROCENYL AZIDE AND FERROCENESULPHONYL AZIDE

Azide	K (sec)	$\Delta H^{\neq}$ (kcal mol^{-1})	$\Delta S^{\neq}$ (e.u.)	ΔG (kcal mol^{-1})
Ferrocenyl	K(135°C) $4.4 \pm 1.1 \times 10^3$ K(100°C) $9.64 \pm 0.65 \times 10^4$	12.35	—39.68	29.1
Ferrocenylsulphonyl	K(162°C) $2.805 \pm 0.0 \times 10^4$ K(135°C) $0.144 \pm 0.0 \times 10^5$	44.27	30.80	31.2
Phenyl	K(165°C) $2.13 \pm 0.04 \times 10^4$ K(135°C) $0.39 \pm 0.0 \times 10^5$	47.34	30.25	34.5
Benzenesulphonyl	K(165°C) $9.85 \pm 0.57 \times 10^4$ K(135°C) $4.98 \pm 0.37 \times 10^5$	34.51	5.70	32.1



(V)

sitive to the value of the angle between the radius vectors from the metal to the centres of the rings.

The high $\Delta H^{\ddagger}$ and high positive $\Delta S^{\ddagger}$ obtained for II as compared to those for benzenesulphonyl azide indicate absence of participation by the iron atom in the decomposition of the azide. This absence of participation may arise from steric interference by the sulphonyl (-SO$_2$-) group which prevents the e_{2g} electrons from readily participating in a backside displacement of nitrogen. Secondly, the -SO$_2$- group, being electron-withdrawing, would make such a participation more difficult since the electrons would be held more tightly to the iron atom. The kinetic data thus suggest that thermolysis of II, which has been postulated [2] to proceed via III, does not involve an initial formation of a metal-azide complex. The azide decomposes by an unassisted loss of nitrogen to give a discrete nitrene intermediate. The intermediate is then stabilized by complexation with the iron atom in a fast step to form III, which reacts in a manner characteristic of metal-nitrene complexes [9] to give the observed high yields of sulphonamide [2].

Experimental

Ferrocenyl azide (I)

Ferrocenyl azide was prepared from ferrocene by literature procedures [10,11].

Ferrocenylsulphonyl azide (II)

An ice-cooled solution of sodium azide (4 g, 0.062 mol) in water (8 ml) was added dropwise to a vigorously stirred ice-cooled solution of ferrocenesulphonyl chloride [12] (7.9 g, 0.028 mol) in acetone (35 ml). Some solid precipitated out within a few minutes but redissolved upon careful addition of more water. The orange-brown solution was stirred at room temperature overnight and poured into ice water (1 l) whereupon II separated as an oil, which solidified on vigorous stirring in an ice bath. The yellowish-brown mass was filtered off and washed several times with water until tests with silver nitrate solution gave no precipitate. Chromatography of the solid on alumina (2 × 50 cm) and elution with n-hexane/benzene (1/1) gave II (6.2 g, 76%) as golden platelets, m.p. 43°C (from n-pentane). Mol. wt. = 291 (mass spec.). IR spectrum (KBr disc): 2100s [-N$_3$], 1360s [-SO$_2$-], 1200s, 1135s [-SO$_2$-], 1015w, 815m, and 725m cm^{-1}. UV spectrum (absolute ethanol): λ_{max} 428 (ϵ = 294.8), 308 (ϵ = 1626), 257 (ϵ = 5781). NMR spectrum (CDCl$_3$): δ values: 4.80 (t, 2 H, H(2, 5) of substituted ring), 4.57 (t, 2 H, H(3, 4) of substituted ring) and 4.45 ppm (s, 5 H, unsubstituted cyclopentadienyl ring). Elemental analysis: Found: C, 41.46; H, 3.21. Calcd. for $C_{10}H_9FeN_3O_2S$: C, 41.25; H, 3.12%.

Kinetics

The azides (1.37—1.76 mmol) in 1-chloronaphthalene (15 ml) were thermolysed at two temperatures (100 and 135°C for I and 135 and 162°C for II) in oval-shaped 50 ml flasks fitted with magnetic stirrer and connected to gas burettes. The flasks were immersed in a thermostated oil bath maintained at the desired temperature to ±0.1°C. The disappearance of the azides was monitored by measuring the volume of nitrogen evolved at various times. The initial rate constant k was obtained from a plot of $\log(V_\alpha - V_0)/(V_\alpha - V_t)$ versus t, where $V_\alpha - V_0$ represented the initial concentration of the substrate and $V_\alpha - V_t$ the concentration at time t.

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