Rates of thermolysis of azidobenzenes in solution: large stabilizations of transition states by charge transfer from electron-donor substituents

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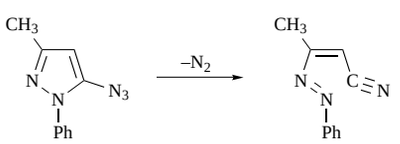
Introduction of +R type *para* substituents into azidobenzenes causes very large increases in rate of thermolysis, up to 225-fold. The rates of nitrobenzene solutions at 120 °C follow a Hammett-type linear free energy relationship log $k = -5.44 - 2.33\sigma_I - 1.48R^+$ which indicates conjugative stabilization of a nitrene-like transition state. *ortho*-Substituents of the +R type causes still larger rate enhancements, up to 456-fold for 2-amino, which identify a special resonance proximity effect. It is suggested that the very high rates reported for such α-azidoheterocycles as 2-azidothiophene are due to similar resonance stabilizations and not to ring-opening concerted with nitrogen loss.

Both azidobenzenes and the α-azides of the five-membered heteroaromatics lose nitrogen when heated in solution, but there are considerable differences in both reaction products and rates. Whereas the azidobenzenes yield such products as azo-compounds and amines[1,2] in which the aromatic ring is intact, the α-azido-heterocycles usually ring-open[3,4] (Scheme 1).



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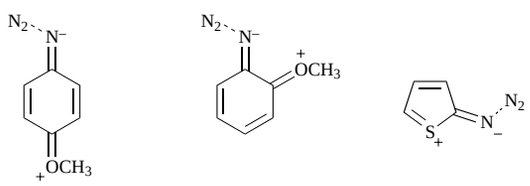
Scheme 1

The differences in rate constants for the unimolecular decompositions are very large indeed. One can calculate from published rate constants that, at 80 °C, the relative rates for azidobenzene,[5] the azidopyrazole **1**[6] and 2-azidothiophene[7] are 1, 3600 and 69 000, respectively. (There is unfortunately no common solvent for these rate measurements, which were made in decalin, *p*-xylene and *p*-chlorotoluene respectively, but data already published[8,9] indicate that solvent change would cause only about a two-fold alteration in the figures). Whereas simple azidobenzenes are believed to thermolyse to a singlet nitrene in the rate-determining step,[1,2] the very high reaction rates observed for the azidoheterocycles have suggested[3,4,7,10] that the ring-opening shown in Scheme 1 is concerted with nitrogen loss. In such a pathway, there would be no nitrene intermediate and the transition state would not therefore resemble a nitrene.

Although this concerted ring-opening provides an attractive explanation of both the high thermolysis rate and the observed products, we have recently suggested[6] that the rates might be explained in terms of a highly stabilized nitrene, which could ring-open subsequent to the rate-determining step. The basis for the suggestion was our observation that the small increase in rate for azidobenzene from introduction of a 4-methoxy group (4.5-fold) is enhanced to 16-fold by a 2-methoxy group. These rate increases are consistent with conjugative stabilization of the nitrene-like transition states **2** and **3**. The rates indicate a favourable *ortho* effect in **3**, which we suggested to be electrostatic attraction but perhaps is best described as a direct through-space transfer of charge. The heteroaromatic rings such as thiophene and pyrazole are believed[11] to be very good transmitters of π-electron effects so that the stabilization implied by **4** will be much larger than in **3**. This stabilization of a nitrene through conjugation with the ring heteroatom has previously been proposed for α-azidofurans by Barnes *et al.*[12]



2 **3** **4**

This postulate of considerable charge transfer from the ring heteroatom to the incipent nitrene is supported by recent *ab initio* calculations[13] at the 6-31G(p,d)MP2 = Full level. For a series of five-membered heteroaromatic compounds, these calculations located a transition state in which the inner N–N bond of the azido group has stretched 34–42%, whereas the α-bond of the heterocyclic ring has stretched only 2–5% and is clearly not breaking in concert.

Unfortunately, the *ab initio* calculations could not identify the transition state structure in the case of azidobenzene, and the methoxy-substituted compounds were too large for high-level calculations. Thus, it is not clear that the azidobenzenes and the α-azidoheterocycles do all thermolyse through similar nitrenoid transition states which vary only in the degree of stabilization provided by charge transfer. The small rate enhancement (16-fold) from a 2-methoxy group in azidobenzene is a far cry from the enhancements of 3660 and 69 000 mentioned above for the α-azidoheterocycles.

The present paper describes experiments with azidobenzenes which have amino-substituents to provide substantial electron-donation but which are not going to undergo a concerted ring-opening. The sizeable rate enhancements produced by these and other electron-donating substituents are correlated by means of the Hammett $\rho\sigma$ equation to demonstrate the nature of the transition state stabilization.

Results and discussion

Kinetic behaviour

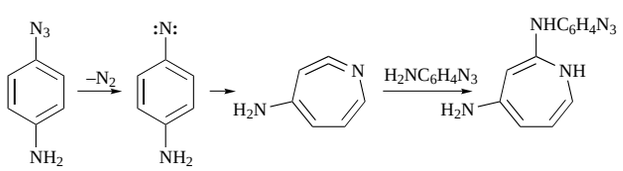
The purpose of the present work is to compare rates of unimolecular decomposition of azidobenzenes whose ring substituents can stabilize the transition states to various degrees. First, one must eliminate decomposition pathways which are not unimolecular, a task which is not always straightforward.

The susceptibility of simple aryl azides to radical-induced decomposition is well known[5] and leads to observation of kinetic orders somewhat greater than unity.[14] We have previously reported that the presence of a higher-order reaction occurring alongside the unimolecular decomposition does not necessarily produce detectable curvature in the ln(absorbance) *vs.* time plots, but does increase the measured first-order rate constant. In that work, we were able to suppress the radical-induced pathway either by addition of a radical chain inhibitor (2,6-di-*tert*-butyl-4-methylphenol) or by using nitrobenzene as a solvent to provide similar inhibition.[5]

The kinetic behaviour of 2-aminoazidobenzene is reported in Table 1. In decalin or *p*-xylene solvents, with no added inhibitor, the reactions appeared to be smoothly first-order, at least as far as the three half-lives for which they were followed. When one run at a given temperature included the inhibitor and one did not, the rate constants agreed within a few percent. Nevertheless, the runs with the added inhibitor generally gave the lower rate constant, and one can speculate whether that is due to suppression of a very minor pathway of radical-induced decomposition or to a solvation effect from the added inhibitor. In any event, the effects are so minor that we believe we are obtaining the rate constant for the unimolecular decomposition, even in the absence of the inhibitor. The kinetic behaviour in nitrobenzene solvent was, as expected, cleanly first-order across the three half-lives covered.

4-Aminoazidobenzene exhibited quite different behaviour. In decalin solvent, with no added inhibitor, the plot of ln(absorbance) *vs.* time was markedly curved, in the concave-up sense. Addition of the inhibitor (3.3 mol/mol azide) had a dramatic effect on the rate, the reaction now taking 25 times as long to reach the half-life, but the curvature of the first-order kinetic plot remained substantial. Switching to nitrobenzene solvent reduced the curvature to a low level, but neither reducing the initial azide concentration (from 0.01 to 0.004 M), nor adding 2,6-di-*tert*-butyl-4-methylphenol in ratios up to 17 mol/mol azide, reduced the curvature any further. A more effective radical chain inhibitor [4,4′-thiobis(2-*tert*-butyl-5-methylphenol)] was likewise ineffective.

A possible explanation of this curvature is that the original azide is reacting, at least to some extent, with one of its reaction products to produce a second thermolysable azide in the system. Nucleophilic addition to a 1-azacyclohepta-1,2,4,6-tetraene intermediate[2] provides such a pathway (Scheme 2), and the



Scheme 2

azido-azepine product would doubtless thermolyse at a different rate.

We presumed that this undesirable reaction could be suppressed by addition of a competing nucleophile, and benzylamine proved to be successful. When this amine was added in ratios of at least 5:1 to 0.01 M solutions of the azide in nitrobenzene, the ln(absorbance) *vs.* time plots became linear across the 2.2 half-lives for which we followed these reactions.

Table 1 Rate constants and activation parameters for thermolysis of 2-aminoazidobenzene in various solvents

Solvent	*T*/°C	Inhibitor[a] mol/mol azide	$k_1/10^{-5}$ s^{-1}	Activation parameters[b]
Decalin	90.0	0, 2.3	2.72, 2.63	ln(*A*/s^{-1}) 34.1 ± 2.3
	100.0	0, 1.1	8.99, 8.70	E_a/kJ mol^{-1} 134.6 ± 0.7
	110.0	0, 2.0	27.1, 26.3	S_a/J K^{-1} mol^{-1} 28.0 ± 2.0
	120.0	0, 1.7	83.0, 79.3	k_{rel} 215[c]
p-Xylene	90.0	2.2, 2.1	3.65, 3.88	ln(*A*/s^{-1}) 33.0 ± 3.1
	100.0	0, 1.3	12.7, 12.2	E_a/kJ mol^{-1} 130.3 ± 1.0
	110.0	1.2, 2.7	35.6, 34.5	S_a/J K^{-1} mol^{-1} 19.2 ± 2.7
	120.0	0, 2.2	104, 103	
Nitro-benzene	90.0	0, 3.3	6.57, 6.36	ln(*A*/s^{-1}) 32.1 ± 2.3
	100.0	2.2, 0	19.2, 19.7	E_a/kJ mol^{-1} 126.0 ± 0.7
	110.0	0, 0	58.5, 56.0	S_a/J K^{-1} mol^{-1} 11.8 ± 2.0
	120.0[d]	3.0, 2.8	160, 151	k_{rel} 456[e]

[a] The radical chain inhibitor was 2,6-di-*tert*-butyl-4-methylphenol. [b] The linear plots of ln(k_1/s^{-1}) *vs.* K/*T* have correlation coefficients in the range 0.9995–0.9999. Errors are expressed as 90% confidence levels. [c] Relative to the published value of $k_1 = 3.78 \times 10^{-6}$ s^{-1} for azidobenzene (ref. 5). [d] In a further run at 120.0 °C, with no inhibitor present but with benzylamine added in the ratio 3.2 mol/mol azide, the 10^5 k_1 value was 161 s^{-1}. [e] Relative to the value of $k_1 = 3.42 \times 10^{-6}$ s^{-1} for azidobenzene (see Table 3).

Table 2 Rates constants and activation parameters for thermolysis of 4-aminoazidobenzene in nitrobenzene solution

T/°C	Benzylamine mol/mol azide	$k_1/10^{-5}$ s^{-1}	Activation parameters[a]
100.0	10.6, 9	3.68, 3.59	ln(*A*/s^{-1}) 32.0 ± 1.6
110.0	12, 7	10.8, 11.2	E_a/kJ mol^{-1} 130.9 ± 0.5
120.0	5, 11	31.2, 30.3	S_a/J K^{-1} mol^{-1} 10.6 ± 1.3
130.0	11, 15	84.6, 84.4	k_{rel}(120 °C) 90.1

[a] The plot of ln(k_1/s^{-1}) *vs.* K/*T* has a correlation coefficient of 0.9999. Errors are expressed as 90% confidence limits. The k_{rel} value is calculated from $k_1 = 3.42 \times 10^{-6}$ s^{-1} for azidobenzene at 120 °C (see Table 3).

We also noted that the reaction took twice as long to reach the first half-life when the benzylamine was present. The kinetic behaviour of this amino-azide was now excellent (see Table 2). However, the first-order plots remained curved for thermolyses in decalin solution even when the radical chain inhibitor (3.3 mol/mol azide) and benzylamine (11 mol/mol) were both present. We therefore elected to use nitrobenzene as solvent for all the azides involved in this study. The decompositions of all the azides shown in Table 3 were followed for at least two half-lives, and often for three, and yielded strictly linear first-order plots with correlation coefficients better than 0.999.

The rate constants for 2-aminoazidobenzene in nitrobenzene solution are apparently not affected by the side-reaction shown in Scheme 2, the addition of benzylamine making no difference (see footnote *d*, Table 1). If our explanation of the behaviour of the 4-amino compound is correct, then 4-dimethylamino-azidobenzene should not enter into such a side-reaction. In practice, its first-order plots for nitrobenzene solutions were linear and addition of benzylamine made no difference to the rate constant (see footnote *d*, Table 3). This last result indicates that addition of benzylamine has not introduced a significant solvent effect on the measured rates.

Although this addition of benzylamine provided a solution to the aberrant behaviour of 4-aminoazidobenzene, we are not able to provide direct evidence for a second azide (as in Scheme 2) being formed. Close examination of the azido band profile in the IR spectrum as a function of time revealed only a minor degree of band broadening (from 15.9 to 17.0 cm^{-1} width at half peak height) as the reaction progressed from 0 to 80% completion in nitrobenzene solution at 120 °C. Whether this

Table 3 Rate constants and activation parameters for thermolysis of 2- and 4-substituted azidobenzenes in nitrobenzene solution

Substituent	T/°C	$k_1/10^{-5}$ s^{-1}	Activation parameters[a]
H	120.0	0.347,[b] 0.337	k_{rel} 1
2-NMe_2	90.0	4.47, 4.47	ln(A/s^{-1}) 31.1 ± 1.3
	100.0	13.2,[d] 12.9[d]	E_a/kJ mol^{-1} 124.2 ± 0.4
	110.0	37.9, 38.0	S_a/J K^{-1} mol^{-1} 3.6 ± 1.2
	120.0	103, 102	k_{rel}(120 °C) 300
4-NHAc	120.0	1.57, 1.55	ln(A/s^{-1}) 33.8 ± 1.9
	130.0	4.92, 4.94	E_a/kJ mol^{-1} 146.6 ± 0.6
	140.0	14.1, 13.9	S_a/J K^{-1} mol^{-1} 25.4 ± 1.4
	150.0	37.6, 37.8	k_{rel}(120 °C) 4.56
4-OMe	120.0	2.89, 2.89	ln(A/s^{-1}) 33.5 ± 1.1
	130.0	8.55, 8.53	E_a/kJ mol^{-1} 143.7 ± 0.3
	140.0	23.7, 14.1[b]	S_a/J K^{-1} mol^{-1} 22.9 ± 0.8
	150.0	64.9, 66.1	k_{rel}(120 °C) 8.45
4-NMe_2	100.0	9.15, 9.25	ln(A/s^{-1}) 32.1 ± 1.8
	110.0	28.3, 28.4	E_a/kJ mol^{-1} 128.3 ± 0.6
	120.0	76.9, 75.7,[c] 77.5	S_a/J K^{-1} mol^{-1} 11.4 ± 1.5
	130.0	202, 203	k_{rel}(120 °C) 225

[a] The plots of ln(k_1/s^{-1}) *vs.* K/T were linear, with correlation coefficients in the range 0.9998–1.0000. Errors are expressed as 90% confidence limits. [b] The radical chain inhibitor, 2,6-di-*tert*-butyl-4-methylphenol, was added to these runs in the ratio of 2.6 mol/mol azide. [c] Benzylamine was added to this run in the ratio of 8.7 mol/mol azide. [d] Measurement on the decay on the weaker of the two azido bands gave $10^{-5}k_1$ values of 13.2 and 12.4 s^{-1}.

broadening is due to overlapping absorbance by another azide, or to interactions such as hydrogen-bonding with reaction products, is not clear.

We were unable to achieve unimolecular decomposition of 2-hydroxyazidobenzene. In decalin solution (0.025 M) at 100 °C, the first-order plot [ln(absorbance) *vs.* time] had pronounced curvature which was not reduced by adding 2,6-di-*tert*-butyl-4-methylphenol (1.4 mol/mol azide) as a radical chain inhibitor; the only effect of the addition was to defer the appearance of a brown precipitate from 5% reaction until 50%. In nitrobenzene solvent, the curvature of the first-order plots was not reduced either by adding the inhibitor (5 mol/mol azide), or by adding benzylamine (5.7 or 17 mol/mol azide). None of these additions had an appreciable effect on the half-life, which in nitrobenzene at 110 °C was quite short (approximately 12 min).

In the case of azidobenzene, Prokudin[14] has recently reported that there is a bimolecular reaction running parallel to the unimolecular decomposition in nitrobenzene solution. His initial concentrations were however very high (0.2–0.6 M) and at our much lower concentrations (0.01 M) we would not expect to detect this bimolecular reaction.

Correlations of rate constants for *para*-substituted azidobenzenes

Previous measurements of substituent effects on the thermolysis of *meta*- or *para*-substituted azidobenzenes have discovered only quite small variation (up to 8.4-fold) in reaction rates.[14,16] We have chosen a variety of π-electron donors as *para*-substituents, and in marked contrast to these earlier studies we find a range of relative rates (nitrobenzene solutions, 120 °C) from 1 for the unsubstituted compound to 225 for the 4-dimethylamino compound (Tables 2 and 3). Correlations of these rates with the various types of Hammett substituent constant (see Table 4) have yielded important information about the way in which these substituents have stabilized the transition state. The correlations have been made with the MINITAB statistical program, which adjusts the correlation coefficient to compensate for the inbuilt advantage of using more parameters.

The simplest correlation, of log k_1 with the Hammett σ-constant, has the datum point for the acetylamino substituent fitting badly, and the correlation coefficient r is only 0.970. Dissection of the σ value into inductive (σ_I) and resonance (σ_R) components yields eqn. (1) whose fit of the data is rather worse

Table 4 Log(rate constant) and Hammett substituent constants[a] for *para*-substituted azidobenzenes. The rate data are for nitrobenzene solutions at 120 °C

p-Substituent	log(k_1/s^{-1})	σ	σ^+	σ_I(F)	σ_R	R^+
H	−5.469	0	0	0	0	0
NHAc	−4.807	0	−0.60	0.31	−0.21	−0.91
OMe	−4.539	−0.27	−0.78	0.29	−0.43	−1.07
NH_2	−3.511	−0.66	−1.30	0.08	−0.48	−1.38
NMe_2	−3.115	−0.83	−1.70	0.15	−0.56	−1.85

[a] Values of the Hammett constants are taken from the compilation by C. Hansch, A. Leo and R. W. Taft, *Chem. Rev.*, 1991, **91**, 165

$$\log k = -5.39 - 1.90\sigma_I - 4.20\sigma_R \quad (1)$$

(r = 0.917). These rather poor correlations suggest that the special resonance donation effect (measured by σ^+) is being called into play. Eqn. (2) gives a quite satisfactory fit of the data

$$\log k = -5.57 - 1.46\sigma^+ \quad (2)$$

(r = 0.989) while dissection of σ^+ into inductive and resonance terms [eqn. (3)] gives an excellent fit (r = 0.997).

$$\log k = -5.44 - 2.33\sigma_I - 1.48R^+ \quad (3)$$

The requirement to use σ^+ (or its variant R^+) to obtain good correlations indicates that the reaction centre makes a demand for π-electron release in the transition state, and explains the very high rates we have measured for the two *para*-amino substituents. This result is consistent with the electron-deficient nitrene-like transition state generally assumed in these thermal decompositions[1,2] and demonstrates that the stabilization represented by structure **2** (see Introduction) is realistic. It is to be noted that the nitrene centre is electron-deficient but does not carry a formal charge: thus the reaction constant [−1.48 in eqn. (3)] is smaller than those reported by Brown and Okamoto[17] for carbocation reactions in aromatic side-chains (−2.69 to −4.67).

Effects of *ortho*-substituents on rate

While the effects of electron-releasing *para*-substituents on the reaction rate are large, the effects of *ortho*-substituents are still larger: 456-fold for 2-amino and 300-fold for 2-dimethylamino. These high rates do much to bridge the gap between azidobenzenes and azidoheterocycles (see Introduction), and make it a reasonable supposition that both families of azides thermolyse *via* a transition state resembling a nitrene.

The question of why these *ortho*-substituents are so effective has direct relevance to the observation that 2-azidothophene is reported to react 707 times as fast as 3-azidothiophene (*p*-chlorotoluene solvent, data recalculated to 120 °C).[7] Because appropriate *ortho*-substituent constants do not exist,[18] the rates for *ortho*-substituted azidobenzenes cannot be correlated by eqn. (3) or some equivalent. However, Charton,[18] in a review of a large volume of data, has observed that resonance stabilization of transition states is often especially effective from *ortho*-substituents. The exact nature of this special effect is unknown, but Charton has coined the term 'resonance proximity effect'.

Our thermolysis data exhibit quite large proximity effects: the *ortho*-amino group increases the rate 5.1 times more than the *para*-amino group, while the dimethylamino group (which doubtless suffers some degree of steric inhibition of conjugation) is 1.33 times more effective than the corresponding *para*-group. We have already reported[6] that *ortho*-methoxy increases the rate of azidobenzene thermolysis (decalin solvent, 120 °C) 3.56 times more than the *para*-group. Viewed in this context, it is possible that the 707-fold rate advantage for 2-azidothiophene over 3-azidothiophene is another example of the special resonance proximity effect and not to ring-opening concerted with nitrogen loss.

Experimental

Mp values were determined using a Reichert Thermovar apparatus. IR spectra were recorded on a Perkin-Elmer 1720 FT spectrometer and NMR spectra on a Bruker AMX-400 instrument. The NMR spectra are all measured with deuteriochloroform solutions and *J* values are recorded in Hz. Low resolution mass spectra (EI, 70 eV) were measured with a Hewlett Packard 5989 A instrument and high resolution mass spectra with a Kratos MS50 TC machine.

Synthesis of azides

Azidobenzene and 4-methoxyazidobenzene were each synthesized by diazotizing the corresponding amine and adding the diazonium solution to sodium azide in a sodium acetate buffer, following our published method.[9] The crude azides were purified by chromatography over silica gel with dichloromethane or chloroform elution.

2-Dimethylaminoazidobenzene was synthesized from 2-nitro-*N*,*N*-dimethylaniline.[19] Reduction to *N*,*N*-dimethyl-*o*-phenylenediamine[20] with iron dust–aqueous acetic acid[21] was followed by conversion to the azide as follows. The amine (952 mg, 7.0 mmol) was dissolved in 2 M HCl (10 cm^3) and chilled with stirring in an ice–salt mixture. An ice-cold solution of sodium nitrite (580 mg, 8.4 mmol) in water (2 cm^3) was added dropwise during 5 min, the reaction mixture being at −3 to −4 °C. After a further 5 min, urea (50 mg) was added to destroy the excess of nitrous acid. This diazonium salt solution was then added during 5 min to a stirred ice-cold solution of sodium azide (910 mg, 14 mmol) and sodium acetate (1.65 g) in water (10 cm^3). The mixture was stirred 2 h in the cold, and the black oily product was then extracted into diethyl ether (2 × 25 cm^3). The combined ethereal extracts were washed with sodium hydroxide solution (5%, 2 × 25 cm^3) and then water (2 × 25 cm^3). Evaporation of the dried solution gave the crude oily product which was chromatographed on silica gel with chloroform elution to obtain the pure azide as a pale-yellow oil (875 mg, 77%); ν_{max}/cm^{-1} ($CHCl_3$) 2127s and 2105m (N_3), 1593m, 1498s; δ_H 2.77 (6 H, s, NMe_2), 6.99–7.03 (2 H, m, ArH), 7.06–7.10 (2 H, m, ArH); δ_C 43.67 (Me), 119.34, 119.50, 122.92, 125.30 (tertiary ring carbons), 132.55 (C–N_3), 145.17 (C–NMe_2); *m*/*z* 162 ($M^{\bullet+}$, 28%), 134 ($M^{\bullet+} - N_2$, 22), 133 ($M^{\bullet+} - N_2 - H$, 100) (Found: $M^{\bullet+}$, 162.0909. $C_8H_{10}N_4$ requires M, 162.0905).

2-Hydroxyazidobenzene was likewise synthesized, by diazotization of 2-aminophenol. The crude product was chromatographed over silica gel with chloroform elution to obtain the pure azide as a pale-yellow oil which later crystallized. Yield 88%; mp 33.2–34.5 °C; ν_{max}/cm^{-1} ($CHCl_3$) 3536m and 3252w (OH), 2137s, 2119s and 2092m (N_3), 1596m, 1494s; *m*/*z* 135 ($M^{\bullet+}$, 10%), 107 ($M^{\bullet+} - N_2$, 12), 79 (51), 52 (100).

4-Aminoazidobenzene was obtained from *p*-phenylenediamine by the same diazotization procedure. The crude product was extracted into diethyl ether and then freed of a minor amount of bis-azide by treatment with 2 M HCl, which precipitated the amine salt. Both the precipitate and the aqueous mother liquor were basified (KOH) to obtain the crude solid amino-azide. Chromatography over silica gel, with chloroform elution, gave the mono-azide, which crystallized from chloroform–hexane as pale-yellow needles (yield, 56%); mp 63.5–65.2 °C lit.,[22] 66 °C; ν_{max}/cm^{-1} (CCl_4) 3481w and 3395w (NH_2), 2144w, 2112s and 2075m (N_3), 1623m, 1509m, 1272m; *m*/*z* 134 ($M^{\bullet+}$, 9%), 106 ($M^{\bullet+} - N_2$, 100), 105 (48), 79 (68).

This azide (370 mg) was dissolved by gentle warming in 2 M HCl (15 cm^3). The stirred solution was then chilled in ice, and treated with sodium acetate (3.7 g in 18 cm^3 water) followed by acetic anhydride (3.7 cm^3). After a further 15 min, the precipitated *N*-acetyl derivative was collected and recrystallized from water–methanol to obtain pale-yellow crystals (240 mg, 49%); mp 123.4–125.4 °C (lit.,[23] 122–123 °C); ν_{max}/cm^{-1} ($CHCl_3$) 3436m (NH), 2120s and 2084m (N_3), 1688m (CO), 1511s, 1290m, 1233m, 1200m; *m*/*z* 176 ($M^{\bullet+}$, 17%), 148 ($M^{\bullet+} - N_2$, 38), 106 ($M^{\bullet+}$ − ketene, 100), 43 (Ac^+, 90).

4-Dimethylaminoazidobenzene was obtained by diazotization of *N*,*N*-dimethyl-*p*-phenylenediamine dihydrochloride in water at 0 °C, and treatment with aqueous sodium azide (2 mol/mol). Basification (KOH) then diethyl ether extraction recovered the crude product, and the pure azide was obtained in 75% yield after chromatography on silica gel with chloroform elution; mp 41.4–42.4 °C (lit.,[24] 43–44 °C); ν_{max}/cm^{-1} ($CHCl_3$) 2124s and 2094vs (N_3), 1611m, 1514s, 1291m; *m*/*z* 162 ($M^{\bullet+}$, 19%), 134 ($M^{\bullet+} - N_2$, 100), 133 (51).

2-Aminoazidobenzene was synthesized from 2-nitroaniline following the procedure of Smith *et al.*[25] The azide crystallized from water–methanol as needles; mp 62.6–62.9 °C (lit.,[25] 63–63.5 °C); ν_{max}/cm^{-1} (CCl_4) 3489w and 3395w (NH_2), 2124vs and 2092sh (N_3), 1614m, 1499m, 1303m, 1263m; *m*/*z* 134 ($M^{\bullet+}$, 17%), 106 ($M^{\bullet+} - N_2$, 100), 105 (58), 79 (85).

Products of thermolysis

2-Aminoazidobenzene (400 mg) was heated in boiling toluene (50 cm^3) during 4.5 h, by which time the azide band in the IR spectrum had disappeared. Filtration removed a black amorphous solid (51 mg), and the solvent was then removed. The residue was chromatographed over silica gel with chloroform elution to obtain first the red–orange azo compound and then 1,2-diaminobenzene. 2,2′-Diaminoazobenzene (95 mg, 30%) had mp 136–137 °C (lit.,[26] 135 °C) after crystallization from ethanol or chloroform–petrol; ν_{max}/cm^{-1} ($CHCl_3$) 3484m, 3400w, 3317w (NH_2), 1612s, 1574m, 1481m; *m*/*z* 212 ($M^{\bullet+}$, 70), 92 (100), 65 (61). 1,2-Diaminobenzene (152 mg, 47%) was identified by comparison of the IR spectrum with that of an authentic sample.

4-Aminoazidobenzene (400 mg) was heated in boiling toluene (50 cm^3) till the azide band in the IR spectrum had decayed completely (8 h). A black tar separated early in the reaction. After removal of the toluene, the residue was extracted with boiling chloroform (2 × 25 cm^3), and the extracts were chromatographed over silica gel with chloroform elution to obtain two red bands. The first band yielded a red solid (28 mg) and the second, 13 mg of a dark-red solid. Both the fractions from the column gave two closely spaced spots on TLC, and had identical IR and mass spectra. We believe them to be the *E*,*Z*-isomers of 4,4′-diaminoazobenzene, apparently undergoing photochemical and/or thermal interconversion to an equilibrium mixture. ν_{max}/cm^{-1} ($CHCl_3$) 3500w, 3408m, 3382w, (NH_2), 1620s, 1598s, 1506m, 1291m, 1149m; *m*/*z* 212 ($M^{\bullet+}$, 69%), 120 (ArN_2^+, 30), 92 (Ar^+, 100), 65 (77). Total yield, 41 mg (13%). Recrystallization from aqueous ethanol gave orange rods, mp 249.0–250.5 °C (lit.,[27] 249–250 °C) which also exhibited two TLC spots. Further elution of the column with methanol afforded 1,4-diaminobenzene (122 mg, 38%) which was identified by comparison of the IR spectrum with that of an authentic sample.

Measurement of reaction rates

All rates were measured by monitoring the decay of the azido band near 2120 cm^{-1} in the IR spectrum. Initial azide concentrations were approximately 0.01 M. Reactions were started by adding the azide to solvent which had been preheated in a flask immersed in an oil bath at constant temperature. The temperature was monitored in a corresponding flask of solvent immersed alongside the reaction vessel. Samples were withdrawn from the reaction at suitable intervals and quenched in ice-cold tubes. Runs were generally followed to approximately two half-lives, and sometimes as far as three; at least one run for each azide was checked after eight to ten half-lives to demonstrate that the absorbance had decayed to zero. All the reactions showed strictly first-order behaviour, the correlation coefficients for the ln(absorbance) *vs.* time plots being better than 0.999. All

runs were duplicated. The Arrhenius plots of ln k *vs.* 1/T also showed high correlation coefficients (0.9995 or better). Errors in E_{act}, ln A and S_{act} are expressed as 90% confidence limits.

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