Organic Reactions in Melts and Solids. Part II.* Decomposition of Dissolved and Neat 4-Substituted 2-Nitrophenyl Azides

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The kinetics of the thermal decomposition of 4-substituted 2-nitrophenyl azides in solvents of widely differing dielectric constants, as well as in the molten or solid neat materials, have been investigated. The decomposition yields the corresponding benzofuroxans and follows first-order kinetics. The rate coefficients are remarkably independent of the nature of the reaction medium. The mechanism of the reaction is discussed.

THE classical definition of the molecularity of a chemical reaction [1a] is "the number of molecules necessarily undergoing covalency change." Solvent and other medium effects, owing to a variety of factors [1b] influence reaction rates profoundly, especially when the reaction involves charge separation. The requirements for solvation of the transition state may be satisfied within the reacting molecule itself.[2] It has been stated already [3] that the thermal decomposition of 2-nitrophenyl azide belongs to the latter category, and the behaviour of several substituted 2-nitrophenyl azides in dibutyl phthalate solvent has been studied.[4,5] The present Paper describes results obtained in solvents of very widely differing dielectric constants, as well as in the solid and in the molten state.

EXPERIMENTAL

Materials.—Commercially available pure solvents were dried and distilled before use. 2-Nitro-[6] (m. p. 51°), 2,4-dinitro-[7] (m. p. 65°), and 4-methoxy-2-nitrophenyl azide (m. p. 73°) were prepared either from the corresponding chloro-derivative and sodium azide [7] or by diazotisation of the corresponding substituted aniline and coupling with azide ions.[6,8]

The phenyl azides were rather unstable even at room temperature and were kept below 0°. They were difficult to analyse, but by thermal decomposition [9] gave quantitatively the corresponding stable benzofuroxans: *i.e.*, benzofuroxan, m. p. 71° (lit.,[9] 72°), 5-nitrobenzofuroxan, m. p. 72° (lit.,[9] 72°), and 5-methoxybenzofuroxan, m. p. 114·5° (lit.,[9] 118°).

Kinetic Runs.—These were performed by heating the solutions of the 4-substituted 2-nitrophenyl azides in a thermostat and quenching aliquot portions by diluting and cooling for the spectrophotometric measurements.

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If the concentrations permitted, runs were made in the thermostat-controlled spectrophotometer cells themselves. The spectral data which were used in the kinetic runs were determined using a Beckman model DU Spectrophotometer and are summarised in Table 1.

TABLE 1

Spectral data in various solvents ($\lambda_{max.}$ in mμ)

	Benzene		Xylene		95% EtOH		DMF		Formamide	
	$\lambda_{max.}$	ε	λ_{max}	ε	$\lambda_{max.}$	ε	$\lambda_{max.}$	ε	$\lambda_{max.}$	ε
2-Nitro-PA			359	780			359	1500		
BF			359	6730			359	7250		
2,4-Dinitro-PA					304	11,500				
	391	100			391	900	391	430	391	600
5-Nitro-BF	391	4510			304	2000				
					391	5000	391	4630	391	4700
2-Nitro-4-methoxy-PA			311	1400			310	1500		
5-Methoxy-BF			311	6250			310	6650		

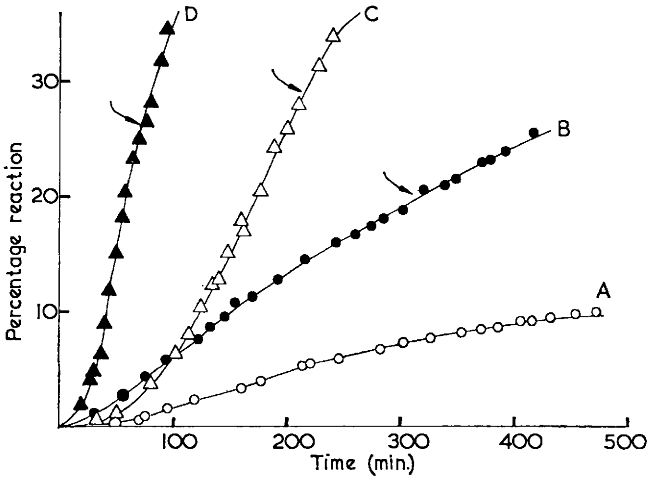
* PA = Phenyl azide, BF = Benzofuroxan.

The initial first-order rate coefficients (k_1) were calculated from the equation

$$k_1 = \frac{S}{(\varepsilon_{BF} - \varepsilon_{PA})[PA]}$$

where S is the slope of the experimental absorption *vs.* time line, ε_{BF} and ε_{PA} are the molar extinction coefficients of the product (5-X-benzofuroxan) and of the starting material (4-X-2-nitrophenyl azide), respectively, at the wavelength of the measurements and [PA] is the initial concentration of the 4-X-2-nitrophenyl azide.

Kinetic experiments with some neat materials were followed spectrophotometrically, by determining ten experimental points separately for each run. The reaction was quenched by adding cold benzene to the sample at predetermined reaction times. Other runs were followed gasometrically by continuously measuring the amount of nitrogen evolved. The two techniques gave very nearly identical results (See Figure). For the calculation of the rate coefficients in " neat " runs, the induction period of the run was neglected, and calculations using the standard first-order rate equations were made, taking a point in the vicinity of the inversion point of the sigmoid curves as zero.



Kinetic curves for the decomposition of 4-methoxy-2-nitrophenyl azide (curve A, at 57°; curve B, at 65°) and of 2,4-dinitrophenyl azide (curve C, at 40°; curve D, at 48°) in the neat state. The arrows show the point where total melting was observed. The experimental points for each curve are taken from three different runs, only a small number of the actually determined points are shown

RESULTS AND DISCUSSION

The first-order rate coefficients (k_1) for the thermal decomposition of the various 4-X-2-nitrophenyl azides are shown in Table 2, which also includes for comparison the relevant data published previously.[3-5]

It is obvious that the rate of cyclisation to 5-X-benzofuroxans is dependent on the concentration of the starting material only and is practically independent of the nature of the reaction medium. The range of solvents investigated by us and by others [3-5] includes non-polar solvents of very low dielectric constants (heptane, $D^{25} = 1{\cdot}9$; benzene, $D^{30} = 2{\cdot}27$; xylene, $D^{20} = 2{\cdot}27$—$2{\cdot}57$), some of intermediate polarity (dibutyl phthalate, $D^{25} = 6{\cdot}43$; cyclohexanol, $D^{25} = 16{\cdot}1$; 95% ethanol, $D^{30} = 26{\cdot}17$), and some of the most polar solvents (dimethylformamide, $D^{30} = 35{\cdot}87$; formamide, $D^{30} = 107{\cdot}5$). The results show the almost complete independence of the first-order rate coefficients of the nature of the solvent: a fifty-fold change in the dielectric constant (in the case of 2,4-dinitrophenyl azide at 40°) enlarges the rate coefficient from about $1{\cdot}2 \times 10^{-5}$ only to about 2×10^{-5} sec.$^{-1}$. It is, then, hardly surprising that the presence of 0·03 mole l.$^{-1}$ of lithium chloride or nitrate in 95% ethanol at 47° gives no change larger than the experimental error.

Furthermore, the same insensitivity towards the medium extends even to reactions of the neat material in both the solid and the molten state.

Comparison of the data in Table 3 with those in Table 2 shows that the decomposition of the material in the solid state, once the induction period characteristic of solid-state reactions is over, takes place at rates similar to those obtaining in solution. Since the neat material could not be observed very closely, the possibility that some sintering had already taken place in the vicinity of the inversion point of the kinetic curve could not be excluded.

On the other hand, at no portion of the kinetic curve, including the one where a rather fast and complete melting of the sample could be observed, was there any sudden change in the slope, indicating that the influence of the phase change, if any, cannot be very drastic.

Further indications of the similarity of the reactions in the dissolved, solid and molten states can be found in the data obtained from calculation of the Arrhenius activation energies and of the entropies of activation (Table 4). The activation parameters in Table 4 all fit one general picture, pointing to a reaction mechanism involving an ordered (probably cyclic) transition state and hence a negative entropy of activation. The only discrepancy is in the values for 2,4-dinitrophenyl azide in dibutyl phthalate, where Andersen, Birkhimer, and Bak[5] obtained an E_A value considerably higher than ours, and consequently calculated a positive activation entropy (+3·9 e.u.) in contrast with our negative values (−8 to −11 e.u. in different solvents). These authors themselves remarked on these inconsistent values, which give to the reaction with the highest rate (at identical temperatures) the highest activation energy, and stated that they do not believe that this means a change in the mechanism of the reaction. Actually our E_A aud $\Delta S^{\ddagger}$ values fit well into the linear $\Delta S^{\ddagger}$ *vs.* E_A plot in Figure 1 of ref. 5, supporting their argument in the rationality of a correlation between these two thermodynamical factors.

TABLE 2

Thermal decomposition of 4-X-2-nitrophenyl azides in various solvents at different temperatures

4-X	10^3 Concn. (mole l.$^{-1}$)	Solvent *	Temp.	Mean rate coeff. $10^5 k_1$ (sec.$^{-1}$)
CH_3O	1—13·0	Xylene	84·0°	4·29 ± 0·12
,,	0·8—1·4	,,	96·0	15·2 ± 0·5
,,	0·9—1·16	,,	105·5	37·6 ± 0·3
,,	[a]	DBP	80·36	5·0
,,	[a]	,,	90·57	13·43
,,	[a]	,,	100·11	34·36
,,	0·7—10·4	DMF	84·0	7·25 ± 0·04
,,	0·75—1·6	,,	96·0	26·0 ± 0·3
,,	0·86—1·2	,,	105·5	54·7 ± 2·2
H	5·0—15·5	Xylene	66·0	2·06 ± 0·06
H [b]		Heptane	65·18	2·201
,, [b]		,,	78·52	9·814
,, [b]		DBP	64·91	2·657
,, [b]		,,	74·54	7·842
,, [a]		,,	76·24	8·73
,, [a]		,,	81·20	14·88
,, [b]		,,	84·39	22·48
,, [a]		,,	90·57	37·32
,, [b]		Cyclohexanol	65·18	2·671
,, [b]		,,	70·21	4·71
,, [b]		,,	78·52	11·94
,, [b]		,,	87·74	29·76
,,	0·5—4·0	DMF	66·0	2·79 ± 0·04
,,	0·2—4·1	,,	80·0	13·9 ± 0·7
NO_2	1·5—10·3	Benzene	32·0	0·50 ± 0·03
,,	0·2—12·0	,,	40·0	1·26 ± 0·05
,,	0·1—3·1	,,	48·0	3·35 ± 0·15
,,	[a]	DBP	40·32	1·669
,,	[a]	,,	50·38	6·486
,,	0·7—5·9	95% EtOH	32·0	0·65 ± 0·02
,,	0·1—3·8	,,	40·0	1·73 ± 0·07
,,	0·9—1·9	,,	48·0	4·28 ± 0·16
,,	3·00	,,	47·0	3·54 ± 0·19
,,	3·00 [c]	,,	,,	3·72 ± 0·20
,,	3·00 [d]	,,	,,	3·62 ± 0·15
,,	2·5—5·5	DMP	32·0	0·74 ± 0·03
,,	0·9—7·3	,,	40·0	1·92 ± 0·03
,,	0·7—2·7	,,	48·0	4·96 ± 0·11
,,	0·4—24·7	Formamide	40·0	2·04 ± 0·03

* DBP = dibutyl phthalate, DMF = dimethylformamide.

[a] Values taken from ref. 4. [b] Values taken from ref. 3. [c] In the presence of 0·03 mole l.$^{-1}$ of lithium chloride. [d] In the presence of 0·03 mole l.$^{-1}$ of lithium nitrate.

TABLE 3

Thermal decomposition of neat 4-X-2-nitrophenyl azides

4-X	Temp.	State	$10^5 k_1$ (sec.$^{-1}$)
H	64·91° [a]	Melt	3·697
,,	74·21 [a]	,,	10·70
,,	75·6	,,	12·3—12·4
CH_3O	57·0	Solid [b]	0·56
,,	,,	Melt [c]	0·5
,,	65·0	Solid [b]	1·36
,,	,,	Melt	1·25
NO_2	40·0	Solid [b]	4·6
,,	,,	Melt [c]	4·1
,,	48·0	Solid [b]	11·5
,,	,,	Melt [c]	10·1

[a] Data from ref. 3. [b] Maximum rate at vicinity of inversion point of the kinetic curve, possibly somewhat sintered. [c] Rate at portion of the curve where complete melting was observed.

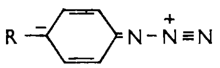
TABLE 4

Activation parameters for the decomposition of different 4-X-2-nitrophenyl azides in various solvents and in neat melts and solids

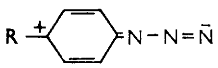
4-X	Solvent * or state	E_A (kcal.)	$\Delta S^{\ddagger}$ (e.u.)	Ref.
CH_3O	Xylene	26·5	−6·7	This work
,,	DBP	25·6	−8·1	5
,,	DMF	25·7	−7·7	This work
,,	Solid	24·7	−9·8	,,
,,	Melt	25·4	−8·1	,,
H	Heptane	26·6	−3·5	3
,,	DBP	25·7	−5·9	5
,,	,,	26·3	−3·8	3
,,	Cyclohexanol	26·3	−3·7	3
,,	DMF	25·9	−5·1	This work
,,	Melt	26·6	−2·2	3
,,	,,	—	−2·8	This work
NO_2	Benzene	22·7	−10·1	,,
,,	DBP	27·1	+3·9	5
,,	95% EtOH	22·2	−11·0	This work
,,	DMP	22·4	−10·2	,,
,,	Solid	22·8	−7·8	,,
,,	Melt	22·3	−9·4	,,

* DBP = dibutyl phthalate; DMP = dimethyl phthalate, DMF = dimethylformamide.

The transition state involved in the decomposition of phenyl azides has been discussed by Smith *et al.*,[10,11] who presented evidence that the conjugation between the benzene ring and the azido-group is better represented by structure (I) rather than by (II). The stability of (I)



(I)



(II)

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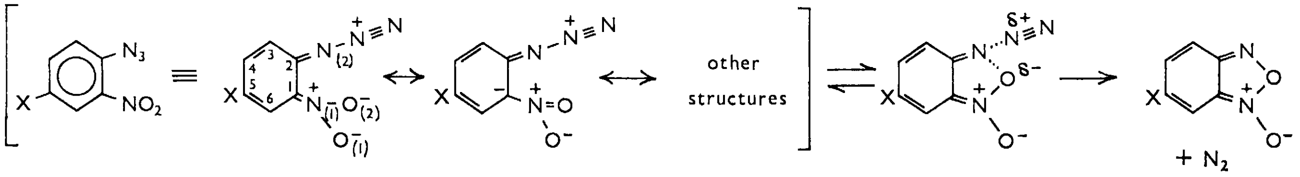
[10] P. A. S. Smith and J. H. Hall, *J. Amer. Chem. Soc.*, 1962, **84**, 480.

[11] P. A. S. Smith, J. H. Hall, and R. O. Kan, *J. Amer. Chem. Soc.*, 1962, **84**, 485.

should be enhanced by electron-attracting groups and lowered by electron-releasing ones.[10] Hence, the mechanism proposed[3,5] for the furoxan formation seems to be reasonable. In a somewhat modified version of the latter we formulate the reactions as shown in the annexed Scheme.



The negative values of the entropy of activation can be taken as a support for the hypothesis that the ("more ordered") transition state resembles the final cyclic product. The bond lengths and angles of 5-chlorobenzofuroxan have been determined[12,13] and the data should be applicable to the compounds studied by us. It is immediately obvious that the reaction involves a considerable change in both bond lengths and angles. The C(2)–C(1)–N(1) and the C(1)–C(2)–N(2) angles, for instance, in the 2-nitrophenyl azide must be at least 120° each (and probably more, owing to steric hindrance of the two groups), while these two angles in the product are of 106·3° and 108·6°, respectively. Also, the N(2)–O(2) distance in the starting material will not be significantly less than the sum of the Van der Waals radii (2·9 Å), while in the product the N(2)–O(2) distance is 1·23 Å. Therefore. all bonds and angles in the molecule, but especially those in which the atoms C(1), C(2), N(1), N(2), and O(2) are involved, have to undergo considerable changes to reach the cyclic transition state resembling the product. We believe that the sigmoid shape of the reaction curves in the solid state may be due to this. In the induction period, the reaction still takes place in a well-ordered crystal lattice where the neighbouring molecules will inhibit the movement of the azido- and nitro-groups which is necessary to reach the transition state. The more the reaction progresses, the less effective is this inhibition, the disorder in the crystalline lattice growing, allowing freer movement of the functional groups and leading to a rise in the reaction rate, until, at the inversion point of the curve, the maximum rate is reached, corresponding to the rate of the uninhibited unimolecular process. This happens at similar reaction percentages, even when working at different temperatures, with the same compound, but at different reaction percentages when comparing two different compounds, and we believe that this may also be taken as indicating that the induction period reflects the *physical* process of destruction of the crystal lattice rather than any kind of an autocatalytic (*i.e.*, chemical) process.

Once the maximum rate of the reaction is reached in the solid state, it is maintained at least up to the point when the whole material melts and in some cases much further. This rate is of the same order of magnitude as in the various solvents, but tends to be rather higher. While it is unusual that a solid-state decomposition should be faster than the same reaction at the same temperature in solution, it should be remembered that the reaction discussed seems to belong to a category which needs no assistance by solvent molecules. The maximum rate in the solid may correspond to the rate of the completely non-inhibited process. Molecules in the vicinity of the reacting entity cannot, it seems, aid this process, only interfere with it. In solution, the cage-effect of the solvent might well interfere with the necessary movement of the nitro- and the azido-groups, thus, the third nitrogen atom of the azido-group extends to *ca.* 4·5 Å from the ring carbon to which it is bound. Moreover, in addition to this external steric hindrance the presence of the solvent may also stabilise the initial state of the reaction, and favour the collapse of the transition state into the starting material.

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