Kinetic Studies of the pH Dependence of the Decomposition of 3,7-Dinitro-1,3,5,7-tetra-azabicyclo[3.3.1]nonane (DPT) and Related Compounds

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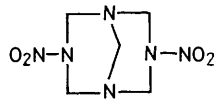
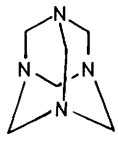
Kinetic studies are reported of the pH-dependence of the decomposition of 3,7-dinitro-1,3,5,7-tetra-azabicyclo[3.3.1]nonane (DPT) in aqueous media. For comparison, data were also obtained for reaction of methylenedinitroamine (MDNA) and nitramide (NH_2NO_2) which are potential intermediates on the reaction pathway of DPT. Our results, while not providing a complete description of the decomposition of DPT, show that at all acidities two stages are observed. The first stage, k_1, involves catalysis by protons and hydroxide ions and it is suggested that reaction occurs *via* a low-concentration, ring-opened structure which is in equilibrium with DPT. In acidic solution an intermediate, (**A**), is observed which is identified as nitramide while in basic solution a different intermediate (**B**) is formed. MDNA is shown not to be an intermediate in the DPT reaction since its rate of decomposition is too slow.

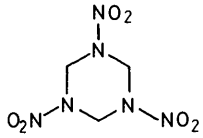
3,7-Dinitro-1,3,5,7-tetra-azabicyclo[3.3.1]nonane, DPT, (**1**) is one of the products of nitration of hexamethylenetetramine (**2**) with nitric acid[1-3] and is important because it has been postulated[4,5] as an intermediate in the Bachmann method[6] of synthesis of the commercial explosives RDX, (**3**), and HMX, (**4**). We report here on the stability of DPT in aqueous solutions over the range pH 0—13 and on mechanisms of its decomposition. Also reported are measurements of the kinetics of decomposition of methylenedinitroamine and nitramide which are potential intermediates in the reaction pathway of DPT. Our results for DPT are compared with those for the acid–base behaviour[7] of its diacetyl analogue DAPT (**5**).



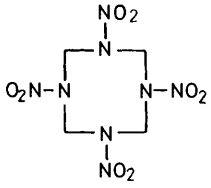
(**1**) DPT



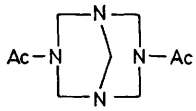
(**2**) Hexamethylenetetramine



(**3**) RDX



(**4**) HMX



(**5**) DAPT

Results and Discussion

DPT is stable for several days in solution in acetonitrile or in 1,4-dioxane, showing u.v. absorption at 241 nm, ε 11 000 l mol^{-1} cm^{-1}. In aqueous solutions decomposition occurs in stages with the observation of intermediates although our results will show that the nature of the decomposition and of the observable intermediates varies with pH. In acidic solution (0.1M-HCl) an intermediate (**A**) with $\lambda_{max.}$ 210 nm, ε 14 000 l mol^{-1} cm^{-1} is formed while in alkaline solutions (0.10M-NaOH) a species (**B**) with $\lambda_{max.}$ 230 nm, ε 16 000 l mol^{-1} cm^{-1}, is produced. Information as to the nature of the intermediates is provided by comparison with literature data[8] for the u.v. spectra of primary and secondary nitro amines. Thus reported values of $\varepsilon_{max.}$ for secondary nitro amines are *ca.* 5 500 l mol^{-1} cm^{-1} per nitroamino group while the corresponding values for primary nitro amines are *ca.* 7 000 in neutral solution and 8 500 in alkaline solution, the latter increase resulting from ionisation. Hence the extinction coefficients observed for each of the intermediates derived from DPT indicate the presence of two functionalities of the type $RNHNO_2$. That the difference in spectrum observed in acidic and alkaline media is not the result of simple deprotonation is shown by experiments in which the intermediate produced in alkaline solution was transferred to acidic solution and *vice versa*. Thus although transfer of (**B**) to a solution of pH = 1 gave a species the spectrum and rate of decomposition of which were identical to those of (**A**), the transfer of (**A**) to a solution of pH = 13 gave a species the spectrum, $\lambda_{max.}$ 225 nm, of which was different to that of (**B**) and the rate of decomposition of which was considerably faster.

Kinetics of Decomposition of DPT.—All kinetic measurements were made under first order conditions with concentration of acid, base, or buffer components in large excess of the concentration of DPT (2—5 × 10^{-5} mol l^{-1}). Solutions contained 1% (v/v) acetonitrile, the solvent used in preparation of stock solutions. Identical results were obtained when 1,4-dioxane was used to prepare stock solutions.

Two rate processes were observed at all acidities. The first process resulted in a hypsochromic shift and the decrease in absorbance at 240—250 nm was used to evaluate values for k_1. In the second process the u.v. absorbance faded to zero and measurements in the range 210—240 nm yielded values of k_2.

Data for k_1 in aqueous hydrochloric acid are given in Table 1 where they are related to the H_0 acidity function for protonation at nitrogen.[9] From a value of 0.002 s^{-1} in very dilute acid, values increase with acidity reaching a limiting value at an acid concentration of *ca.* 1 mol l^{-1}. This behaviour may be interpreted in terms of rate-determining decomposition of the protonated substrate, equation (1), which leads to equation (2). Here k_{1,H_2O} represents the spontaneous

Table 1. Rate coefficients for the initial stage of the decomposition[a] of DPT in aqueous hydrochloric acid at 25 °C

[HCl]/mol l^{-1}	h_0[b]	$10^3 k_1/s^{-1}$	$10^3 k_1$ (calc.)[c]/s^{-1}
0.0010	0.0010	2.0	2.2
0.0025	0.0025	2.6	2.6
0.0050	0.005	3.2	3.2
0.0075	0.0075	3.6	3.7
0.010	0.010	4.3	4.3
0.050	0.050	10	11
0.10	0.10	18	17
0.20	0.23	27	25
0.50	0.63	36	33
1.00	1.6	38	38

[a] First-order reaction followed by decrease in absorbance at 240 nm. [b] h_0 = antilog $(-H_0)$ from ref. (9). [c] Calculated from equation (2) with k_{1,H_2O} 2 × 10^{-3} s^{-1}, $k_{1,acid}$ 3.9 × 10^{-2} s^{-1}, and K_{H^+} 6.25 l mol^{-1}

Table 2. Rate coefficients for the initial stage of the decomposition of DPT in deuterium oxide containing deuterium chloride at 25 °C

[DCl]/mol l^{-1}	d_0[a]	$10^3 k_1/s^{-1}$	$10^3 k_1$ (calc.)[b]/s^{-1}
0.0025	0.0025	2.7	2.7
0.0050	0.0050	3.8	4.0
0.0075	0.0075	5.0	5.1
0.010	0.010	6.3	6.2
0.030	0.030	13	13
0.050	0.050	20	18
0.075	0.075	21	21
0.10	0.10	23	24
0.125	0.125	26	25
0.15	0.17	31	29
0.20	0.23	36	31
0.40	0.48	37	34

[a] d_0 = antilog $(-D_0)$ from ref. (9), (10). [b] Calculated from equation (3) with k_{1,D_2O} 1.4 × 10^{-3} s^{-1}, $k_{1,acid}$ 3.9 × 10^{-2} s^{-1}, and K_{D^+} 14 l mol^{-1}.

Table 3. Rate data for the initial stage of the decomposition of DPT in water containing sodium hydroxide at 25 °C

[NaOH]/mol l^{-1}	$10^3 k_1/s^{-1}$	$10^3 k_1$ (calc.)[a]/s^{-1}
0.0010	3.4	3.5
0.0025	5.2	5.5
0.0050	8.9	8.5
0.010	13.5	13.5
0.020	22.8	21
0.030	29.5	26
0.060	35	34
0.080	35	37
0.100	35	39

[a] Calculated from equation (5) with k_{1,H_2O} 2 × 10^{-3} s^{-1}, $k_{1,base}$ 0.05 s^{-1} and K_{OH^-} 30 l mol^{-1}.

$$DPT + H^+ \underset{}{\overset{K_{H^+}}{\rightleftharpoons}} DPTH^+ \xrightarrow{k_{1,acid}} (\mathbf{A}) \quad (1)$$

$$k_1 = k_{1,H_2O} + \frac{k_{1,acid} \cdot K_{H^+} \cdot h_0}{1 + K_{H^+} \cdot h_0} \quad (2)$$

$$k_1 = k_{1,D_2O} + \frac{k_{1,acid} \cdot K_{D^+} \cdot d_0}{1 + K_{D^+} \cdot d_0} \quad (3)$$

decomposition in water, and $k_{1,acid}$ the rate constant for decomposition of the protonated substrate. Measurements were also made in deuterium oxide containing deuterium chloride (Table 2) and are well correlated by equation (3). The main

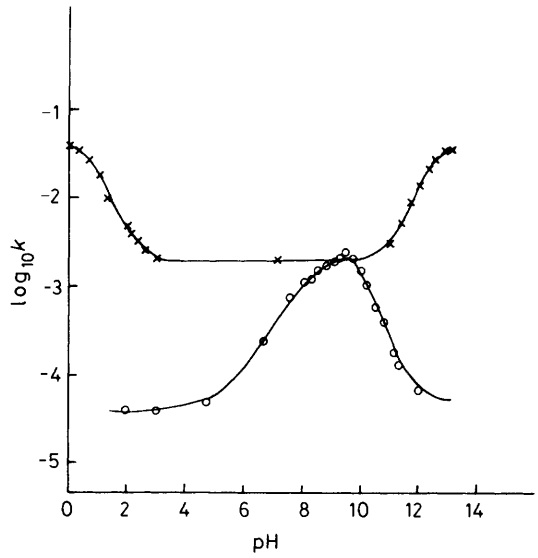


Figure 1. pH Profiles of the rate coefficients k_1 (x) and k_2 (○) for the decomposition of DPT in water at 25 °C. Values of k_2 refer to decomposition of intermediate (**B**)

change in transfer from water to deuterium oxide is the increase in the value of the equilibrium constant for hydronation, K_{D^+}/K_{H^+} = 2.24; the higher basicity observed for DPT in deuterium oxide being in accord with literature values for other weak bases.[11] The value of $k_{1,acid}$, 0.039 s^{-1}, is unchanged on transfer to D_2O, consistent with this step involving C–N bond cleavage, and little change is also observed in the value of the spontaneous rate.

In aqueous sodium hydroxide solution values of k_1 for the initial reaction increase with base concentration as shown in Table 3. The data are compatible with an initial fast equilibrium involving hydroxide before the rate-determining step, equation (4), leading to the dependence on hydroxide concentration given in equation (5). The value of 0.002 s^{-1} obtained for the spontaneous decomposition (k_{1,H_2O}) is

$$DPT + OH^- \underset{}{\overset{K_{OH^-}}{\rightleftharpoons}} DPT \cdot OH^- \xrightarrow{k_{1,base}} (\mathbf{B}) \quad (4)$$

$$k_1 = k_{1,H_2O} + \frac{k_{1,base} \cdot K_{OH^-}[OH^-]}{1 + K_{OH^-}[OH^-]} \quad (5)$$

identical with the value obtained from measurements made in acidic solutions. Measurements of the initial reaction in Tris buffer at pH 7.1 also yielded a value of 0.002 s^{-1} which was independent of buffer concentration in the range 0.01—0.05 mol l^{-1}. These results indicate that in the pH range 3—10 the spontaneous decomposition dominates and that strong buffer catalysis is not observed. The pH profile is shown in Figure 1.

In the range 4 > pH > 11 the second stage in the decomposition was considerably slower than the first stage. In these media, values of k_2 were determined after completion of the initial reaction. However, at intermediate pH, the absorbance *versus* time plots gave evidence that the two processes were of similar rate. In order to simplify the kinetic analysis we separated the two processes by preparing intermediate (**B**) in sodium hydroxide solution (0.05M) in which it was reasonably stable and then transferring portions to buffers of known composition. Thus the first stage producing (**B**) was allowed to go to completion before measurements of k_2 were made. The pH

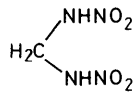
Table 4. Buffer catalysis of the second stage of the reaction, involving the intermediate (**B**)

Catalyst	Catalytic coefficient/ $l\ mol^{-1}\ s^{-1}$	pK_a
$CH_3CO_2^-$	0.048	4.75
Tris	0.17	8.1
$H_2PO_4^-$	2.4	7.2
Borax	0	9.1
HCO_3^-	0	10.2

profile obtained is in Figure 1 and shows values extrapolated to zero buffer concentration. Strong buffer catalysis of the second stage was observed using buffers with pH <9 and analysis indicated that catalysis was due primarily to the basic components of the buffer (Table 4). However in buffers with pH >9 no variation in rate coefficient with buffer concentration was observed.

Discussion of these data is deferred until we have considered the rate data for decomposition of potential intermediates.

Decomposition of Methylenedinitroamine.—Lamberton and co-workers [12] found that the addition of aqueous formaldehyde to a solution of methylenedinitroamine, MDNA, (**6**) containing ammonia resulted in the precipitation of DPT. This raised the possibility that MDNA might be an intermediate in the decomposition of DPT in aqueous solutions.



(**6**) MDNA

The u.v. spectrum of MDNA shows an absorption at 225 nm in acidic solution (0.1M-HCl) which shifts to 233 nm in alkaline solution (0.1M-NaOH) consistent with ionisation of the nitro amine functions. Kinetic measurements of the decomposition using the fading of this absorption indicated a single first-order process at all acidities. In agreement with previous qualitative results [12] the rate of decomposition was very slow in both acidic media, pH <3, and in alkaline media, pH >9, but showed a maximum at intermediate pH values. Measurements in buffer

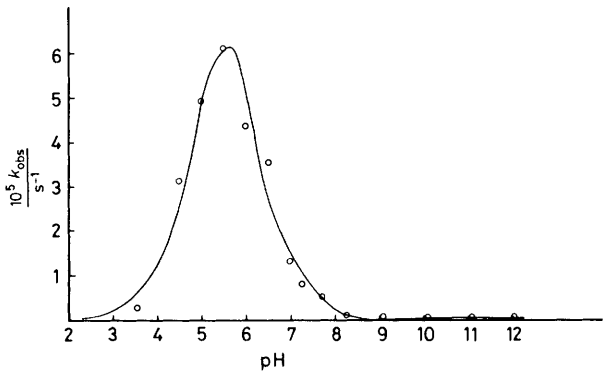


Figure 2. pH Dependence of k_{obs} for decomposition of MDNA in aqueous solution at 25 °C. The experimental points are shown as (○), and the solid line is calculated from equation (6) with $k = 8 \times 10^{-5}\ s^{-1}$, $pK_{a,1} = 4.77$, $pK_{a,2} = 6.39$

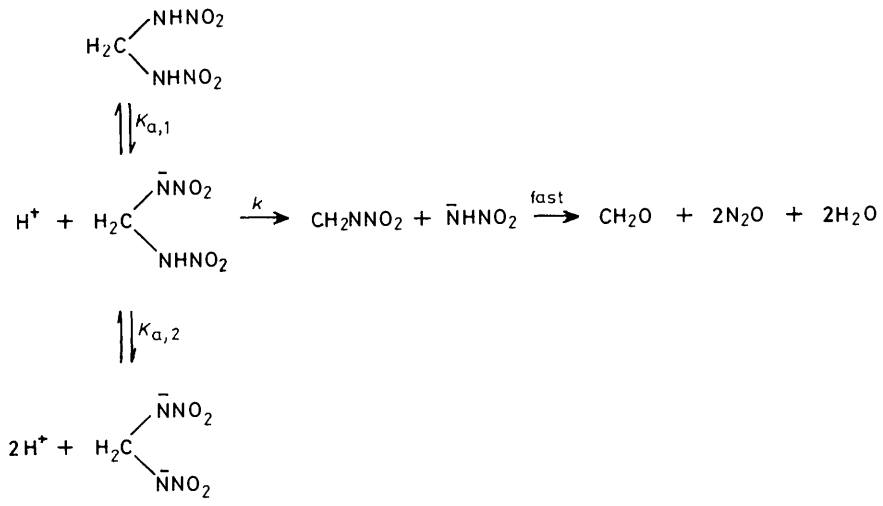
solutions containing acetate, phosphate, tris, or borax buffers showed the absence of catalysis by buffer components and yielded the data plotted in Figure 2. The value of k_{obs}, the first-order rate coefficient, is a maximum at pH *ca.* 5.5.

Values for the first- and second-dissociation constants of MDNA were determined by monitoring the pH during the addition of sodium hydroxide solution (0.05M) to an aqueous solution of MDNA (0.005M). Treatment of the data using the method of Noyes [13] gave values of $pK_{a,1}$ 4.77 ± 0.02 and $pK_{a,2}$ 6.39 ± 0.02. The rate data for the decomposition show a maximum at the pH value when the monoanion of MDNA is at maximum concentration and are best interpreted by Scheme 1.

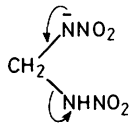
This scheme leads to equation (6) for the dependence of the decomposition on acidity, and values calculated using the known values for the dissociation constants and a value for k of $8 \times 10^{-5}\ s^{-1}$ were in good agreement with experimental data.

$$k_{obs} = \frac{k}{1 + \frac{[H^+]}{K_{a,1}} + \frac{K_{a,2}}{[H^+]}} \qquad (6)$$

Bond breaking will be easiest in the monoanion [as shown in (**7**)] with the un-ionised species and the dianion relatively stable.



Scheme 1.



(7)

In agreement with this formulation a test, using dimedone,[14] indicated the liberation of 1 mole of formaldehyde per mole of MDNA during the reaction.

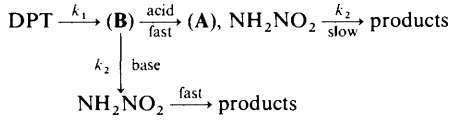
Our rate data show that at all acidities the decomposition of MDNA is slower than the decomposition of DPT or of the intermediates derived from DPT. Also the buffer catalysis observed in the second stage of the DPT decomposition is lacking in MDNA decomposition. Hence we can conclude that MDNA is not an intermediate in DPT decomposition. Lamberton's observation[12] of the formation of DPT from solutions containing MDNA can be rationalised[3] in terms of the prior decomposition of MDNA to fragments, probably nitramide, which then combine with the other reagents to form DPT.

Decomposition of Nitramide.—The decomposition of nitramide, equation (7), was one of the reactions used in classic studies of acid–base catalysis.[15] More recently, studies have been reported in both basic[16] and acidic solutions.[17] We measured the u.v. spectrum and rate of decomposition of

$$NH_2NO_2 \longrightarrow N_2O + H_2O \qquad (7)$$

nitramide under conditions identical with those used in the second stage of the DPT decomposition. The u.v. spectrum of nitramide at pH 2 shows an absorption at 210 nm, ε 7 500 l mol^{-1} cm^{-1}. In alkaline solution the band shifts to 225 nm. The value of the extinction coefficient is about half the value observed for the decomposition product of DPT in acidic solution but otherwise the behaviour is identical. This suggests that in acidic solution two equivalents of nitramide are formed from one equivalent of DPT. Confirmation that the intermediate (**A**) can be identified as nitramide comes from comparison of the rate coefficients in Table 5.

Mechanism of Decomposition of DPT.—Our results show that the decomposition of DPT involves the formation of two observable intermediates, (**A**) in acidic solution and (**B**) in basic solution, and we have identified (**A**) as nitramide. The least complicated pathway for the decomposition is shown in Scheme 2. Here the nature of the rate-determining step of the



Scheme 2.

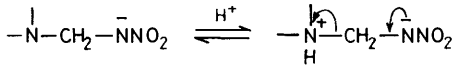
second stage of the reaction changes with pH. In basic solution decomposition of (**B**) to give nitramide, known to decompose rapidly at high pH (Table 5), is rate-determining. In acid solution nitramide decomposition becomes rate-determining. The pH at which the change occurs is probably *ca.* 8—9 as judged by the pH profile in Figure 1, and by the absence of buffer catalysis at high pH which is inconsistent with rate-determining nitramide decomposition. Scheme 2 is clearly a simplified description of the decomposition and there is no direct evidence that in acid solution the formation of nitramide involves the intermediacy of (**B**).

Table 5. Comparison of the u.v. spectra and rate coefficients for decomposition of nitramide and of intermediate (**A**)

	Nitramide		Intermediate (**A**)[a]	
Medium	$\lambda_{max.}$	k/s^{-1}	$\lambda_{max.}$	k_2/s^{-1}
HCl (0.01M)	210	6×10^{-5}	210	5×10^{-5}
HCl (0.001M)	210	4.6×10^{-5}	210	4.3×10^{-5}
Acetate,[b] pH = 5	220	1.8×10^{-3}	220	1.5×10^{-3}
Tris,[b] pH = 7	225	9×10^{-3}	225	8.6×10^{-3}
Tris,[b] pH = 9	225	1.4×10^{-2}	225	1.2×10^{-2}
NaOH (0.001M)	225	4×10^{-3}	225	4×10^{-3}
NaOH (0.01M)	225	5×10^{-2}	225	5×10^{-2}
NaOH (0.1M)	225	0.55	225	0.53

[a] Prepared by reaction of DPT with 0.01M-HCl. [b] Strong buffer catalysis is observed; values quoted for nitramide and for (**A**) refer to solutions with precisely the same buffer composition.

Regarding the structure of (**B**), we know from the u.v. data that two primary nitro amine functions are present and since the pK_a values are unlikely to be very different from that of nitramide (pK_a = 6.55[16]) these will be ionised in basic solution. It seems probable that (**B**) contains the structural feature shown in (**8**), and that the increase in the value of k_2 as the pH is decreased from 12 to 9 (Figure 1) reflects protonation to give (**9**) in which C–N bond cleavage is facilitated.



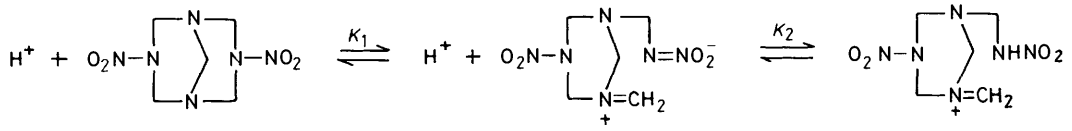
(**8**) (**9**)

We will briefly consider the first step, k_1, of the decomposition. The acid catalysis observed in aqueous hydrochloric acid is compatible with rate-determining decomposition of protonated DPT [equation (1)]. However, the value obtained for K_{H^+} of 6.25 l mol^{-1} is similar to the value (5 l mol^{-1}) found previously[5] for protonation of the diacetyl derivative, DAPT. The greater electron-withdrawing power of the nitro groups at the 3- and 7-position might have been expected to decrease the basicity of the nitrogens at the 1- and 5-position resulting in a lower value for K_{H^+}. A possible explanation is that K_{H^+} does not measure simple protonation, but also involves ring cleavage as indicated in Scheme 3. Compared with DAPT the greater electron-withdrawing power of the nitro groups in DPT will be expected to increase the value of K_1 reflecting ring-cleavage but will decrease the value of K_2 for protonation. Hence values of K_{H^+} ($= K_1K_2$) are similar. The acid-catalysed decomposition can then be interpreted in terms of inhibition of ring closure by protonation. The hydroxide-ion catalysis [equation (4)] might be interpreted in terms of stabilisation of the ring-opened form (**10**) by attack at the N=CH_2^+ group.

Other steps in the decomposition pathway are likely to involve hydrolysis of iminium ions and carbinolamine decomposition. However, further speculation on the details of the mechanism is not justified from our present results.

Experimental

DPT was prepared by a method adapted from that of Hale.[1] Hexamethylenetetramine (10 g) was added gradually with mixing to 95% nitric acid (35 g) at a temperature of 0—10 °C. On dilution of the solution with 100 cm^3 of iced water, RDX (**3**) separated out, was filtered off and was destroyed in aqueous sulphuric acid. The filtrate was neutralised with ammonia at



(10)

Scheme 3.

0 °C. DPT separated out as a white solid which was washed with water and recrystallised from acetone, m.p. 212 °C. The ^{1}H n.m.r. spectrum[18] in [$^2H_3$]acetonitrile showed a band at δ 4.14 (s, CH_2 bridge) and an AB quartet J 13 Hz, due to methylene protons with shifts of δ 4.9 and 5.65, respectively.

MDNA. Preparation by the method of Brian and Lamberton[19] yielded a white crystalline solid, m.p. 100 °C (lit.,[19] 98—101 °C). The ^{1}H n.m.r. spectrum in Me_2SO showed singlets at δ 4.8 due to methylene protons and at δ 13 due to amino protons.[20] The formation of formaldehyde during the decomposition of MDNA was quantified using the dimedone method.[14] MDNA (1.84 μmol) was dissolved in citrate buffer, pH 6.0, and allowed to stand for 24 h at 20 °C. Addition of an excess of saturated alcoholic dimedone precipitated the derivative which was recrystallised from 50% aqueous ethanol. The yield of the formaldehyde–dimedone derivative (m.p. 189 °C; lit.,[14] 189 °C) was 1.75 μmol indicating that, within experimental error, the methylene group of MDNA is wholly converted into formaldehyde during decomposition.

Nitramide was prepared by the method of Marlies *et al.*,[21] with the exception that isopropyl nitrate was used in place of ethyl nitrate in the nitration of urethane to form nitrourethane which is an intermediate and that the temperature during this stage was kept at −10 °C. The ^{1}H n.m.r. spectrum of the nitramide produced showed a single broad band at δ 11.5 in [$^2H_6$]Me_2SO.

The acetonitrile used for preparation of stock solutions was HPLC grade and the 1,4-dioxane was spectroscopic grade. U.v. measurements were made with Pye–Unicam SP-8-100 or Lambda 3 instruments. Kinetic measurements were made at 25 °C using freshly prepared solutions of reagents; kinetics were in all cases run under first-order conditions and rate coefficients were determined by standard methods. The following procedure was used to measure the values of the rate coefficient, k_2, for the second stage of the decomposition of DPT in the range $4 < pH < 10$. A stock solution of DPT in acetonitrile (5 cm^3) was added to aqueous 0.05M-sodium hydroxide (45 cm^3) and the reaction was left for 5 min to allow the first stage of the reaction, k_1, to go to completion. The resulting solution (5 cm^3) containing intermediate (**B**) was then transferred to the appropriate buffer (45 cm^3) and allowance was made for change in concentration of buffer components resulting from the hydroxide added. The second stage of the reaction was measured as a decrease in absorbance at 220 nm.

Acknowledgements

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