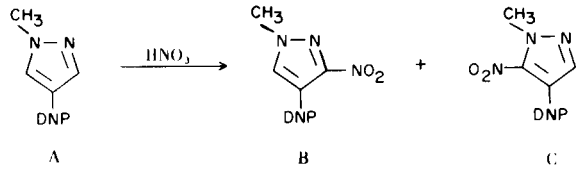
Kinetics of the Nitration of 4-(2,4-Dinitrophenyl)-1-methylpyrazole

Michael D. Coburn

University of California, Los Alamos Scientific Laboratory, Los Alamos, New Mexico 87544

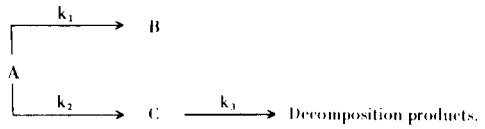
Received September 26, 1970

The nitration of 4-(2,4-dinitrophenyl)-1-methylpyrazole (A) to a mixture of 4-(2,4-dinitrophenyl)-1-methyl-3-nitropyrazole (B) and 4-(2,4-dinitrophenyl)-1-methyl-5-nitropyrazole (C) was reported in a previous communication from this laboratory (2). Subsequently, pure samples



DNP = 2,4-Dinitrophenyl

of B and C were isolated and the kinetics of the nitration of A were studied. It was observed that the ratio of B to C increased with time. This observation indicated that either C was slowly decomposing under the conditions of the nitration or the nitration of A to C was reversible. The latter possibility was eliminated when we were unable to convert C to B under the conditions of the nitration of A. The results of the kinetic study are in good agreement with the following kinetic interpretation:



The rate equations corresponding to these reactions are

$$-\frac{dA}{dt} = (k_1 + k_2)A \quad (1)$$

$$\frac{dB}{dt} = k_1 A \quad (2)$$

$$\frac{dC}{dt} = k_2 A - k_3 C. \quad (3)$$

Integration of equation 1 gives equation 4.

$$A = A_0 e^{-(k_1 + k_2)t} \quad (4)$$

Substitution of equation 4 into equations 2 and 3, followed by integration, yields equations 5 and 6. Thus the value $k_1 + k_2$, readily obtained from

$$B = \frac{k_1 A_0}{k_1 + k_2}\left[e^{-(k_1 + k_2)t} - 1\right] \quad (5)$$

$$C = \frac{k_2 A_0}{k_3 - k_1 - k_2}\left[e^{-(k_1 + k_2)t} - e^{-k_3 t}\right] \quad (6)$$

equation 4, can be substituted into equation 5 to obtain k_1. Once k_1 and k_2 are known, k_3 can be obtained from equation 6 with the aid of a programmable desk calculator.

The ratios A/A_0, B/A_0, and C/A_0 required for the calculations were determined by nmr as described in the Experimental section. The results are summarized in Table I.

In the mononitration of 1-methyl-4-picrylpyrazole we obtained only the 3-nitro derivative (2). In view of the results of the present study we propose that the 5-nitro derivative was formed but that its rate of decomposition was greater than its rate of formation. This proposal is supported by the fact that the yield of the 3-nitro derivative was only 55%.

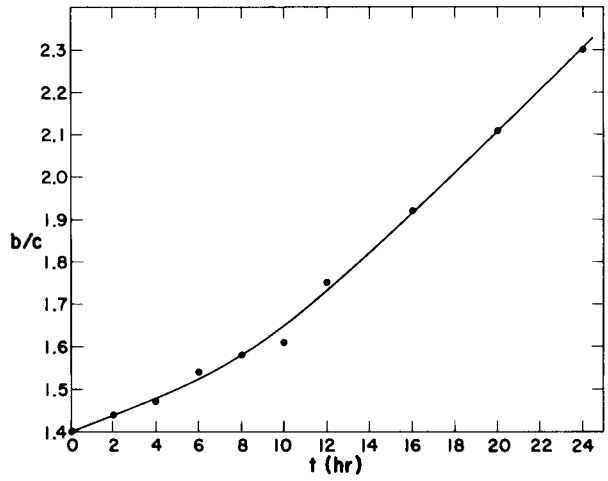


Figure 1.

TABLE I

The Nitration of 4-(2,4-Dinitrophenyl)-1-methylpyrazole with 70% Nitric Acid at 114.5° (a)

t (hours)	Relative Concentration A	B	C	$k_1 + k_2$ (hr^{-1})	k_1 (hr^{-1})	k_2 (hr^{-1})	k_3 (hr^{-1})
2	79	12	9	0.118	0.067	0.049	---
4	62	22	15	0.119	0.069	0.047	---
6	49	30	19	0.119	0.069	0.047	0.027
8	39	35	22	0.118	0.067	0.049	0.028
10	33	39	24	0.111	0.066	0.050	0.029
12	25	44	25	0.115	0.068	0.048	0.030
16	16	49	25	0.115	0.067	0.049	0.033
20	10	53	25	0.115	0.068	0.048	0.030
24	7	54	23	---	0.067	0.049	0.032
48	0	58	7	---	0.068	0.048	---
			Average	0.116	0.068	0.048	0.030

(a) The concentrations of A, B, and C are given as percentages of A_0; i.e., $A_0 = 100$.

TABLE II

NMR Spectra

Pyrazole	δ (C–H) (ppm) Pyrazole C-3	C-5	Methyl
4-(2,4-Dinitrophenyl)-1-methyl-	8.10	8.00	3.97
4-(2,4-Dinitrophenyl)-1-methyl-3-nitro-		8.37	4.12
4-(2,4-Dinitrophenyl)-1-methyl-5-nitro-	7.90		4.27

EXPERIMENTAL (3)

Nitration of 4-(2,4-Dinitrophenyl)-1-methylpyrazole (A).

4-(2,4-Dinitrophenyl)-1-methylpyrazole (0.20 g., 0.0008 mole) was added to 20 ml. of concentrated nitric acid (70% nitric acid) at reflux (114.5°/580 mm). The solution was heated under reflux for the appropriate period of time, then poured over crushed ice (200 g.). The product mixture was extracted with dichloromethane (3 x 50 ml.), the combined extracts were washed with water and dried, and the solvent was removed under reduced pressure. The residue was dissolved in DMSO-d_6 (1 ml.) and the solution was analyzed by nmr spectroscopy (see Table II). The methyl protons were integrated to obtain the integrals a, b, and c, which are proportional to the concentrations of A, B, and C, respectively. The b/c ratio was plotted against time (see Figure 1) and extrapolated to t = 0. At t = 0, b/c = 1.40; therefore, at time t

$$\frac{b}{c + s} = 1.40 \text{ or } x = \frac{b - 1.40\,c}{1.40}$$

where x corresponds to the amount of C that has decomposed. The value of a at t = 0, a_0, was then obtained from the equation $a_0 = a + b + c + x$, and this in turn was used to compute the ratios $A/A_0 = a/a_0$, $B/A_0 = b/a_0$, and $C/A_0 = c/a_0$.

4-(2,4-Dinitrophenyl)-1-methyl-3-nitropyrazole (B).

4-(2,4-Dinitrophenyl)-1-methylpyrazole (1.0 g., 0.004 mole) was refluxed with 100 ml. of concentrated nitric acid for 3 days. The solution was poured over ice and the product was extracted with dichloromethane (3 x 100 ml.). The combined extracts were washed with water, dried (magnesium sulfate), and evaporated to dryness under reduced pressure. The residue was recrystallized from ethanol to yield 0.48 g. (41%) of B, m.p. 147°, which was pure according to TLC and nmr analysis.

Anal. Calcd. for $C_{10}H_7N_5O_6$: C, 40.96; H, 2.39; N, 23.89. Found: C, 40.72; H, 2.13; N, 24.01.

4-(2,4-Dinitrophenyl)-1-methyl-5-nitropyrazole (C).

4-(2,4-Dinitrophenyl)-1-methylpyrazole (3.0 g., 0.012 mole) was refluxed with 200 ml. of concentrated nitric acid (70% nitric acid) for 16 hours. The solution was poured over ice and the product was extracted with dichloromethane (3 x 100 ml.). The combined extracts were washed with water, dried (magnesium sulfate, and evaporated to dryness under reduced pressure. The residue was chromatographed over silica gel with a 1:1 mixture of 1,2-dichloroethane and isopropyl ether. The column dimensions were 40 x 4 cm. The first 50 ml. of yellow eluate contained pure

C according to TLC analysis. The solvent was removed under reduced pressure and the residue was recrystallized from ethanol to give 0.46 g. (13%) of C, m.p. 100°. Subsequent fractions contained mixtures of B and C.

Anal. Calcd. for $C_{10}H_7N_5O_6$: C, 40.96; H, 2.39; N, 23.89. Found: C, 40.72; H, 2.22; N, 23.91.

Acknowledgment.

The author is grateful to Dr. L. C. Smith for many helpful suggestions and for helpful criticism of the manuscript. The author is also grateful to Dr. S. K. Yasuda for resolving the reaction mixture by thin layer chromatography and suggesting the solvent system used in the column chromatographic isolation of 4-(2,4-dinitrophenyl)-1-methyl-5-nitropyrazole.

REFERENCES

(1) This work was performed under the auspices of the U. S. Atomic Energy Commission.

(2) M. D. Coburn, *J. Heterocyclic Chem.*, 7, 707 (1970).

(3) Microanalyses by M. J. Naranjo. All melting points are corrected.