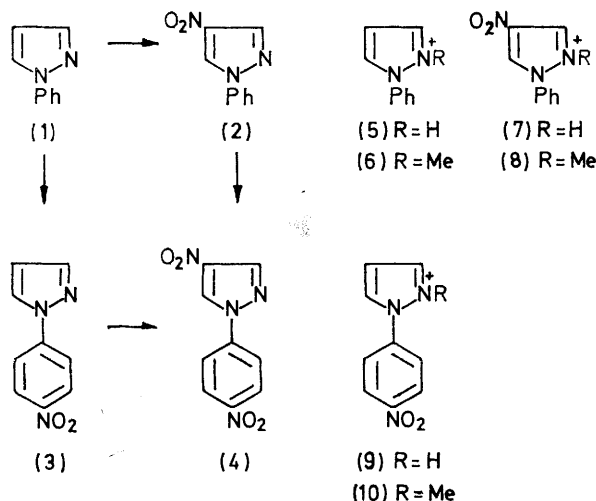# The Kinetics and Mechanism of the Electrophilic Substitution of Hetero-aromatic Compounds. Part XXXVI.[1] The Nitration of Some 1-Phenyl-pyrazoles

By **Alan G. Burton, Alan R. Katritzky,**[*] **Mustafa Konya,** and **H. Okan Tarhan,**[*] School of Chemical Sciences, University of East Anglia, Norwich, and the Department of Chemistry, Middle East Technical University, Ankara, Turkey

The kinetics of nitration of 1-phenylpyrazole and its 4- and 4'-nitro-derivatives, and the corresponding 2-methyl quaternary salts are used to elucidate the species which undergo nitration. The nitration rates are compared within the series and with those of other heteroaromatic compounds.

THE nitration of 1-phenylpyrazole (1) is reported to yield the 4-nitro-derivative (2) when the reaction is carried out in acetic anhydride,[2,3] but the *p*-nitro-compound (3) in sulphuric acid.[2,4] Lynch and his co-workers suggested[3] that nitration in the pyrazole ring was a reaction of the free base whereas if the compound underwent reaction as the conjugate acid substitution took place at the *para*-position. Following our work on pyrazolones[1] we have now studied the kinetics of the

under preparative conditions to test the positional selectivity of nitration. Conditions and results of these experiments (Table 1) indicate high selectivity in all the reactions studied. In particular the nitration of the 1-methyl-2-phenylpyrazolium cation (6) was shown to give selectively the 2-*p*-nitrophenyl cation (10): this has been previously[5] assumed but not proven.

nitration of 1-phenylpyrazole (1), and the further nitration of the 4- (2) and 4'-nitro-derivatives (3). The nitration of the corresponding 2-methyl cations (6), (8), and (10) has also been studied, as models for the proton-ated species (5), (7), and (9).

When this paper was in preparation, Schofield and his co-workers[5] reported the kinetics of the mononitration of 1-phenylpyrazole: this work, which is in good agreement with our results but was extended in directions other than those followed in the present project, is considered below.

Compounds and Preparative Nitrations.—1-Phenyl-pyrazole (1) and nitro-derivatives (2)—(4) were prepared by literature methods and converted successively into methotoluene-*p*-sulphonates and methoperchlorates [*cf.* (6), (8), (10), and (11)]. All substrates were nitrated

EXPERIMENTAL

Preparation of Compounds.—The following were prepared by the literature methods quoted: 1-phenylpyrazole[4] (90%), b.p. 99° at 3·5 mmHg (lit.,[4] 74° at 0·05 mmHg, 246° at 760 mmHg); 4-nitro-1-phenylpyrazole[4] (92%), m.p. 130—131° (lit., 129—130°); 1-*p*-nitrophenylpyrazole[4] (88%), m.p. 170—171° (lit.,[4] 169—170°); 4-nitro-1-*p*-nitro-phenylpyrazole[4] (85%), m.p. 152—153° (lit.,[4] 149—150°).

1-*Methyl-2-phenylpyrazolium Toluene-p-sulphonate.*—1-Phenylpyrazole (3·12 g) and methyl toluene-*p*-sulphonate (3·94 g) were heated for 24 h at 130°. The *sulphonate* crystallised from EtOH–Et$_2$O as plates (4·64 g, 65%), m.p. 110—112° (Found: C, 61·0; H, 5·5; N, 8·6. C$_{17}$H$_{18}$N$_2$O$_3$S requires C, 61·8; H, 5·5; N, 8·5%).

The following *toluene-p-sulphonates* were similarly prepared: 1-*methyl-4-nitro-2-phenylpyrazolium* (48%), needles from EtOH, m.p. 198—200° (Found: C, 54·5; H, 4·6; N, 11·3. C$_{17}$H$_{17}$N$_3$O$_5$S requires C, 54·4; H, 4·5; N, 11·2%); 1-*methyl-2-p-nitrophenylpyrazolium* (heating at 150°) (51%), needles from EtOH, m.p. 167—169° (Found: C, 54·5; H, 4·7; N, 11·2. C$_{17}$H$_{17}$N$_3$O$_5$S requires C, 54·4; H, 4·5; N, 11·2%); 1-*methyl-4-nitro-2-p-nitrophenylpyrazolium* (heating at 150°) (44%), plates from EtOH–Et$_2$O, m.p. 202—204° (Found: C, 47·3; H, 3·8; N, 13·1. C$_{17}$H$_{16}$N$_4$O$_7$S requires C, 48·6; H, 3·8; N, 13·3%).

1-*Methyl-2-phenylpyrazolium Perchlorate.*—The corresponding toluene-*p*-sulphonate (2·3 g) in deionized water (25 ml) was passed down a column of Amberlite resin

[1] Part XXXV, A. G. Burton, M. Dereli, A. R. Katritzky, and H. O. Tarhan, preceding paper.

[2] D. Dal Monte, A. Mangini, and R. Passerini, *Gazzetta*, 1956, **86**, 797.

[3] M. A. Khan, B. M. Lynch, and Y.-Y. Hung, *Canad. J. Chem.*, 1963, **41**, 1540.

[4] I. L. Finar and R. J. Hurlock, *J. Chem. Soc.*, 1957, 3024.

[5] M. R. Grimmett, S. R. Hartshorn, K. Schofield, and J. B. Weston, *J.C.S. Perkin II*, 1972, 1654.

IRA-400 in the perchlorate form. The eluate was evaporated to give the *perchlorate* (1·54 g, 86%) which recrystallized from EtOH as needles, m.p. 147—149° (Found: C, 46·0; H, 4·3; N, 11·1. $C_{10}H_{11}ClN_2O_4$ requires C, 46·5; H, 4·3; N, 10·8%).

1-*Methyl*-2-p-*nitrophenylpyrazolium perchlorate* was similarly prepared (85%) as prisms from EtOH–Et₂O, m.p. 131—133° (Found: C, 38·9; H, 3·8; N, 13·6. $C_{10}H_{10}ClN_3O_6$ requires C, 39·6; H, 3·3; N, 13·8%).

(from EtOH–Et₂O) (Found: C, 34·1; H, 2·7; N, 15·8. $C_{10}H_9ClN_4O_8$ requires C, 34·4; H, 2·6; N, 16·1%).

Spectroscopy.—N.m.r. spectra (Table 2) were recorded at 100 MHz (Varian HA 100), or at 60 MHz (Perkin-Elmer R12) (permanent magnet instrument) with sample spinning. Solutions in D₂SO₄ used tetramethylammonium sulphate (τ 6·81) as internal standard, otherwise tetramethylsilane (τ 10·00). U.v. spectra (Table 3) were determined on a Unicam SP 800 self-recording instrument; individual

TABLE 1

Preparative nitrations of 1-phenylpyrazoles

Starting material	Weight (g)	H_2SO_4 [a]–HNO_3 [b] (ml)	Reaction time (h)	$T/°C$	Product (substituents)	% Yield (crude)	% Purity (crude)
(1)	0·5	6 : 1·5	1	12	1-p-Nitro-(3)	90	95
(1) via (3)	1·0	10 : 3	18	20	4-Nitro-1-p-nitro-(4)	86	95
(1)	1·5	d	1·5	20	4-Nitro-(2)	55	95
(6)	0·5	2 : 1	3	20	1-Methyl-2-p-nitro-(10)	≥90 [e]	90 [e]

[a] d 1·84. [b] d 1·42. [c] By n.m.r. criteria, on isolated compound. [d] Mixture of HNO_3 (d 1·42; 1·50 ml) and Ac_2O (2 ml). Reaction followed by n.m.r. which indicated virtually complete conversion to the *para*-nitro-compound.

TABLE 2

¹H N.m.r. chemical shifts (τ [a]) and coupling constants (Hz) of substituted pyrazoles and pyrazolium salts [b]

	Pyrazole ring position									
Compound	1		J [c]	2		3		4		5	
(1) [d]	Ph	2·10—2·90				H	2·41	H	3·69	H	2·28
(2) [d]	Ph	2·15—2·65				H	1·76	(NO₂)		H	1·38
(3) [d]	p-$C_6H_4NO_2$	1·65, 2·10	9			H	1·96	H	3·41	H	1·91
(4) [d]	p-$C_6H_4NO_2$	1·58, 2·07	9			H	1·69	(NO₂)		H	1·25
(6) [e]	Ph	2·10—2·55		Me	6·07	H	1·86	H	3·00	H	1·80
(8) [e]	Ph	2·01—2·45		Me	5·95	H	0·96	(NO₂)		H	0·91
(10) [e]	p-$C_6H_4NO_2$	1·27, 2·07	9	Me	5·96	H	1·71	H	2·87	H	1·63
(11) [e]	p-$C_6H_4NO_2$	1·29, 2·01	9	Me	5·91	H	0·95	(NO₂)		H	0·90

[a] Relative to internal Me₄Si (τ 10) for solutions in CDCl₃, for D₂SO₄ tetramethylammonium sulphate (τ 6·81). [b] As perchlorate salts. [c] Coupling constants (Hz) for *p*-nitrophenyl substituents. [d] CDCl₃ as solvent. [e] D₂SO₄ as solvent.

TABLE 3

Absorption maxima (nm) and pK_a data for substituted pyrazoles and pyrazolium salts [a]

	Substituent at position					$\lambda_{max.}$ (log ε)			Basicity				
Compound	1	2	3	4	5	Neutral species [b]	Cationic species [c]	λ [e]	λ [f]	H_0 [k]	m	pK_a
(1)	Ph		H	H	H	203 (4·21), 248 (4·06)	245 (3·95)	283				0·44 [g]
(2)	Ph		H	NO₂	H	227 (4·05), 296 (3·99)	224 (4·03)	311	298	−3·62	0·73	−2·65
(3)	p-$C_6H_4NO_2$		H	H	H	224 (3·96), 317 (4·14)	283 (4·15)	311	325	−0·84	1·0	−0·84, −0·65 [g]
(4)	p-$C_6H_4NO_2$		H	NO₂	H	216 (4·18) 311 (4·32)	273 (4·23)		319	−5·10	0·87	−4·43
(6)	Ph	Me	H	H	H		228 (3·85), 230 (3·85) [d]	264				
(8)	Ph	Me	H	NO₂	H		238 (4·00), 242 (4·03) [d]	253				
(10)	p-$C_6H_4NO_2$	Me	H	H	H		264 (4·04), 259 (4·06) [d]	253				
(11)	p-$C_6H_4NO_2$	Me	H	NO₂	H		256 (4·22), 253 (4·23) [d]					

[a] As perchlorate salts. [b] Measured in acetate buffer at pH = 5. [c] Measured in 98% H_2SO_4 (H_0 *ca.* −10·5). [d] Measured in 5M-H_2SO_4 (H_0 *ca.* 0·05). [e] λ for study of nitration kinetics. [f] λ for pK_a. [g] From ref. 6.

1-*Methyl*-4-*nitro*-2-*phenylpyrazolium Perchlorate.*—73% Perchloric acid (1 ml) was added to the corresponding toluene-*p*-sulphonate (0·4 g) in deionized water (30 ml). The *product* recrystallized from EtOH–Et₂O as plates (0·25 g, 76%), m.p. 243—244° (Found: C, 38·9; H, 3·4; N, 13·7. $C_{10}H_{10}ClN_3O_6$ requires C, 39·6; H, 3·3; N, 13·8%).

1-*Methyl*-4-*nitro*-2-p-*nitrophenylpyrazolium perchlorate* was prepared similarly as plates (73%), m.p. 184—185°

optical densities were recorded in ' Spectrosil ' 10 mm silica cells using a Unicam SP 500 instrument.

Kinetic Determinations.—Nitric and sulphuric acids were AnalaR grade. H_0 and H_R values were interpolated from the data recently established [7,8] and each value was corrected for the reaction temperature. The log a_{H_2O} values were computed in a similar manner.[9,10]

[6] J. Elguero, E. Gonzalez, and R. Jacquier, *Bull. Soc. chim. France*, 1968, 5009.

[7] C. D. Johnson, A. R. Katritzky, and S. A. Shapiro, *J. Amer. Chem. Soc.*, 1969, **91**, 6654.

[8] N. L. Dassanayake, C. D. Johnson, A. R. Katritzky, and T. W. Toone, unpublished work.

[9] W. F. Giauque, E. W. Hornung, J. E. Kunzler, and T. R. Rubin, *J. Amer. Chem. Soc.*, 1960, **82**, 62.

[10] A. G. Burton, Ph.D. Thesis, University of East Anglia, 1971.

The 'aliquot method' for kinetic runs at elevated temperatures was used for the kinetic nitrations of compounds (2), (3), (8), and (10) by measuring the increased absorption of the dinitro-compound. The kinetic nitrations of compounds (8) and (10) were followed throughout the acidity range under pseudo-first-order conditions with a molar ratio of nitric acid : substrates ca. 50 : 1 in sealed tubes. Compounds (2) and (3) were followed at lower and higher acidities under pseudo-first-order conditions in stoppered volumetric flasks. Compounds (1) and (6) were followed at lower acidities under pseudo-first-order conditions by the 'aliquot method'; but in the range 84—98% H_2SO_4, compound (1) was followed under second-order conditions and compound (6) was followed under pseudo-first-order conditions by measuring the increased absorption of the mononitro-compound (as cation). The stabilities of the compounds studied were checked in sulphuric acid under conditions as for nitration except for the absence of nitric acid: all showed unchanged u.v. spectra.

The infinity optical densities observed and those calculated from the known extinction coefficient of the pure nitro-derivative agreed to within 5% in each case. Therefore, all rate constants were calculated using calculated optical densities. Rate constants are defined by equations (1)—(3), and are expressed throughout in 1 mol^{-1} s^{-1}.

$$-d[substr.]/dt = k_2(obs)[substr.][HNO_3]_{stoich} \quad (1)$$

$$\log k_2(fb) = \log k_2(obs) + m(H_0^{\ddagger} - H_0)_T \quad (2)$$

$$\log k_2^* = \log k_2(obs) - \log \{[NO_2^+]/[HNO_3]_{stoich}\} \quad (3)$$

In these equations $k_2(obs)$ is the observed second-order rate constant, $k_2(fb)$ is the second-order rate constant corrected for the concentration of free base, and k_2^* is the second-order rate constant corrected for the concentration of NO_2^+.

The H_0 value of half protonation, $H_0^{\ddagger}$, was measured using the spectrophotometric method, as previously described.[11] The slopes $-d(\log I)/dH_0$ are denoted by m (see ref. 11), and were used to measure pK_a values (see ref. 11) recorded in Table 3.

Comparison with Previous Kinetic Results.—k_2 Values at 75% H_2SO_4 and 25° were obtained from literature data [5] at higher acidities by extrapolation, 2·81 × 10^{-4} for (1) and 3·54 × 10^{-6} for (6). For comparison, values were obtained for (1) and (6) from the present results, using the procedure described later in this paper and $\Delta H^{\ddagger} = 11$ kcal mol^{-1}, as 5·36 × 10^{-4} for (1) and 7·06 × 10^{-6} for (6).

RESULTS AND DISCUSSION

Identification of Species undergoing Nitration.—The kinetic results for nitration at lower acidities are collected in Table 4. Plots of log $k_2(obs)$ against $(H_R + \log a_{H_2O})$ yield good straight lines (Figure 1). For all the metho-salts, and for the nitration of 1-phenylpyrazole itself, the slopes are in each case close to unity (Table 5) indicating that nitration is proceeding on the majority species. The second nitration of *both* the mononitro-derivatives (2) and (3) gave slopes considerably less than unity; however, correction for the free base concentration (using the pK_a and the values of Table 3) also brought these slopes close to unity (Figure

2). This is evidence for the nitration of (2) and (3) as the neutral free base forms.

TABLE 4

Nitration of substituted pyrazoles and pyrazolium salts in the low acidity region

%H_2SO_4	$-H_0$ [a]	$-(H_R + \log a_{H_2O})$ [b]	$-\log k_2$ (obs)	$\log k_2$ (fb) [c]	$\log k_2^*$
1-Phenylpyrazole (40°)					
69·95	5·52	12·52	3·943		3·317
71·90	5·86	12·92	3·425		3·135
73·58	6·12	13·43	2·854		3·166
75·12	6·37	13·84	2·468		3·092
77·48	6·74	14·54	1·595		3·145
80·44	7·15	15·48	0·751		3·149
81·72	7·35	15·88	0·276		3·174
4-Nitro-1-phenylpyrazole (40°)					
67·55	5·15	11·62	4·841	−3·716	3·039
71·96	5·87	13·03	4·161	−2·516	2·389
73·56	6·11	13·43	3·758	−1·952	2·282
76·35	6·55	14·20	3·337	−1·263	1·803
78·73	6·90	14·90	2·852	−0·459	1·588
1-*p*-Nitrophenylpyrazole (75°)					
75·61	5·79	11·63	4·662	0·297	1·998
77·51	6·08	12·11	4·291	0·928	1·869
78·41	6·21	12·42	4·178	1·201	1·682
79·21	6·32	12·67	3·965	1·514	1·655
1-Methyl-2-phenylpyrazolium perchlorate (50°)					
75·21	6·16	12·97	4·442		1·498
77·90	6·58	13·68	3·677		1·403
79·20	6·76	14·13	3·146		1·514
81·49	7·15	14·94	2·501		1·399
1-Methyl-4-nitro-2-phenylpyrazolium perchlorate (80°)					
74·59	5·67	11·41	5·432		1·488
77·98	6·16	12·06	4·711		1·329
79·01	6·30	12·63	4·104		1·556
80·18	6·47	12·95	3·857		1·483
81·49	6·70	13·44	3·168		1·632
1-Methyl-2-*p*-nitrophenylpyrazolium perchlorate (140°)					
76·74	5·11	9·02	4·717		3·263
78·43	5·33	9·46	4·357		3·213
79·36	5·43	9·69	3·997		3·313
81·02	5·64	10·10	3·646		3·354
81·55	5·73	10·26	3·402		3·398

[a] H_0 Values are corrected [7] for temperature. [b] H_R and log a_{H_2O} values are corrected [8-10] for temperature. [c] Calculated using pK_a values.
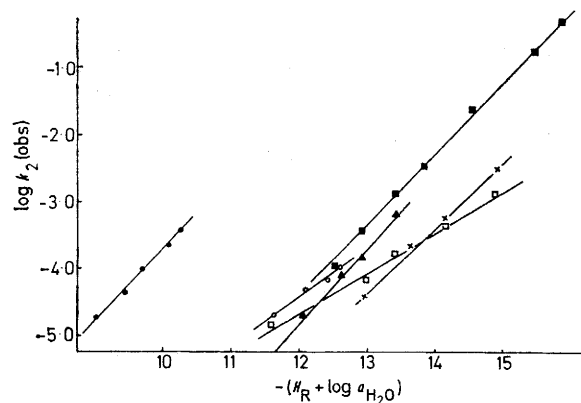

FIGURE 1 Moodie–Schofield plots for nitration of: (■) 1-phenylpyrazole at 40°; (×) 1-methyl-2-phenylpyrazolium perchlorate at 50°; (□) 4-nitro-1-phenylpyrazole at 40°; (▲) 1-methyl-4-nitro-2-phenylpyrazolium perchlorate at 80°; (○) 1-*p*-nitrophenylpyrazole at 75°; and (●) 1-methyl-2-*p*-nitrophenylpyrazolium perchlorate at 140°

[11] C. D. Johnson, A. R. Katritzky, B. J. Ridgewell, N. Shakir, and A. M. White, *Tetrahedron*, 1965, **21**, 1055.

TABLE 5

Rate profile slopes

Compound	Position of nitration	Low acidity					High acidity region (91—98% H_2SO_4)		
		$T/°C$	Slope [a]	Correlation coefficient	Slope [b]	Reaction species [c]	$T/°C$	Slope [d]	Reaction species
(1)	4'	40	1·07	0·999		C.A.	25	0·19	C.A.
(2)	4'	40	0·61	0·995	0·99	F.B.	25	0·88	F.B.
(3)	4	75	0·65	0·993	1·15	F.B.	60	1·04	F.B.
(6)	4'	50	0·99	0·996		Cation	40	0·33	Cation
(8)	4 '	80	1·09	0·998		Cation	60	0·35	Cation
(10)	4	140	1·06	0·995		Cation	115	0·10	Cation

[a] Moodie–Schofield plots. [b] Corrected for free base concentration (corrected Moodie–Schofield plot). [c] C.A. = Conjugate acid and F.B. = free base. [d] d[log k_2(obs)]/dH_0.

TABLE 6

Nitration of substituted pyrazoles and pyrazolium salts in the high acidity region

% H_2SO_4	$-H_0$ [a]	$-\log k_2$ (obs)
1-Phenylpyrazole (25°)		
77·70 [b]	7·06	2·413
80·20 [b]	7·46	1·632
82·10 [b]	7·78	0·767
84·80	8·24	0·452
85·36	8·32	0·351
87·56	8·65	−0·281
90·35	9·06	−0·734
91·39	9·24	−0·681
93·03	9·48	−0·612
97·21	10·26	−0·496
4-Nitro-1-phenylpyrazole (25°)		
80·30	7·51	2·684
81·77	7·77	2·217
83·94	8·11	1·884
84·23	8·15	1·694
85·40	8·32	1·348
86·92	8·57	0·952
88·44	8·78	0·800
91·17	9·20	0·739
93·07	9·50	1·194
95·86	9·95	1·504
98·08	10·42	1·864
1-p-Nitrophenylpyrazole (60°)		
81·14	6·84	4·584
81·74	6·96	4·280
83·94	7·31	4·014
85·98	7·58	3·707
87·42	7·79	3·394
89·19	8·06	3·250
91·17	8·36	3·155
91·69	8·44	3·274
93·21	8·68	3·601
95·12	8·96	3·689
98·08	9·58	4·480
1-Methyl-2-phenylpyrazolium perchlorate (40°)		
84·48	7·87	1·277
85·65	8·06	0·914
88·78	8·50	0·301
90·10	8·70	0·251
92·12	9·01	0·341
93·97	9·31	0·379
96·40	9·74	0·529
97·83	10·07	0·692
1-Methyl-4-nitro-2-phenylpyrazolium perchlorate (60°)		
83·36	7·21	3·465
84·61	7·41	2·997
88·01	7·88	2·156
89·44	8·06	2·003
92·05	8·45	1·929
93·66	8·70	2·006
96·27	9·17	2·134
97·80	9·52	2·318

TABLE 6 (Continued)

1-Methyl-2-p-nitrophenylpyrazolium perchlorate (115°)		
83·21	6·24	3·621
84·44	6·39	3·369
87·84	6·81	2·755
89·32	6·97	2·695
91·88	7·27	2·538
93·48	7·54	2·582
96·08	7·97	2·608
97·49	8·35	2·652

[a] H_0 Values are corrected [7] for temperature. [b] From ref. 5.

The kinetic results for nitration at high acidities (Table 6) disclose a similar pattern: d[log k_2(obs)]/dH_0 slopes were in the range 0·10—0·35, typical [10] for majority
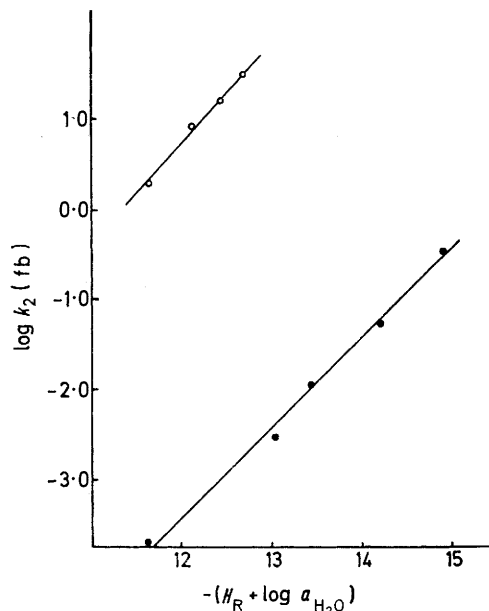
FIGURE 2 Corrected Moodie–Schofield plots for nitration of: (●) 4-nitro-1-phenylpyrazole at 40°; and (○) 1-p-nitrophenylpyrazole at 75°

species reaction for the metho-salts (6), (8), and (10) and for (1). However for (2) and (3) these slopes were much greater i.e. 0·88—1·04 which indicates nitration as a minority species (see Table 5 and Figure 3). These results indicate that no mechanistic ' change-over ' is occurring for any of the compounds investigated.

Kinetic results at different temperatures (Table 7) were used to calculate the Arrhenius parameters in Table 8. The high apparent $\Delta H^{\ddagger}$ values found for (2)

and (3) afford further evidence that the compounds are nitrated as the free base species.[12]

TABLE 7

Dependence of rate of nitration on temperature

1-*p*-Nitrophenylpyrazole

| In 81·0% H_2SO_4 | | | In 87·1% H_2SO_4 | | |
$T/°C$	$-\log k_2$ (obs)	$\log k_2$ (fb) [a]	$T/°C$	$-\log k_2$ (obs)	$\log k_2$ (fb) [a]
49·9	4·525	1·705	40·0	4·296	3·074
55·0	4·258	1·872	50·0	3·91	3·22
60·0	3·951	2·079	60·0	3·524	3·386
69·5	3·593	2·267	70·0	3·114	3·586

1-*p*-Nitrophenylpyrazole In 91·17% H_2SO_4			4-Nitro-1-phenylpyrazole In 95·86% H_2SO_4		
38·2	4·014	3·956	25·0	1·504	3·11
49·4	3·704	3·986	29·8	1·345	3·173
60·0	3·155	4·175	34·9	1·141	3·267
69·0	2·971	4·259	39·8	0·94	3·38
			45·6	0·748	3·455

[a] Calculated using pK_a values.

Relative Rates and Partial Rate Factors.—Comparison of the electrophilic substitution rates for different compounds must be done by reference to some standard conditions. Definition of standard conditions is more difficult for nitration [12] than for hydrogen exchange.[13] We use here 25° and 75% H_2SO_4 ($H_0 = -6·6$). The
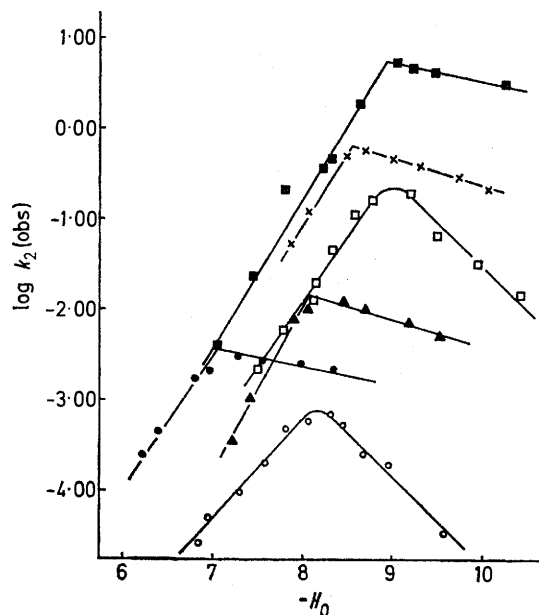

FIGURE 3   Rate profiles for nitration of: (■) 1-phenylpyrazole at 25°; (×) 1-methyl-2-phenylpyrazolium perchlorate at 40°; (□) 4-nitro-1-phenylpyrazole at 25°; (▲) 1-methyl-4-nitro-2-phenylpyrazolium perchlorate at 60°; (○) 1-*p*-nitrophenylpyrazole at 60°; and (●) 1-methyl-2-*p*-nitrophenylpyrazolium perchlorate at 115°

TABLE 8

Arrhenius parameters [a]

No.	Compound	% H_2SO_4	$\Delta H^{\ddagger}_{25}/$ kcal mol^{-1}	$\Delta S^{\ddagger}_{25}/$ cal mol^{-1} K^{-1}	$\Delta G^{\ddagger}_{25}/$ kcal mol^{-1}	$\log A$	$\Delta H^{\ddagger}_{25}$ (fb)/ kcal mol^{-1}[b]	$\Delta S^{\ddagger}_{25}$ (fb)/ cal mol^{-1} K^{-1}	$\Delta G^{\ddagger}_{25}$ (fb)/ kcal mol^{-1}	$\log A$ (fb)
(3)	1-*p*-Nitrophenyl-pyrazole	81·0	23·7	−6·1	25·5	11·9	14·1	−7·2	16·1	11·7
		87·1	18·7	−18·8	24·4	9·2	7·7	−20·0	13·6	8·9
		91·2	16·8	−23·0	23·7	8·2	4·5	−26·1	12·3	7·5
(2)	4-Nitro-1-phenyl-pyrazole	95·7	16·3	−12·6	20·1	10·4	7·0	−21·0	13·1	8·7

[a] Calculated from the equation $\log k_2(\text{obs}) = \log A - E_a/2·3RT$. Using a plot of $\log k_2(\text{obs})$ *vs.* $1/T$ we obtain $\Delta H^{\ddagger}_{25} = E_a - 0·593$ kcal mol^{-1}; $\Delta S^{\ddagger}_{25} = 4·57 \log A - 60·54$ cal mol^{-1} K^{-1}. [b] Calculated using $\log k_2(\text{fb})$ values in Table 7.

TABLE 9

Partial rate factors [a]

No.	Compound	Species	$T/°C$	$\log k_2(T)$	$\Delta H^{\ddagger}/$ kcal mol^{-1}	$\log k_2(25)$	P.r.f.[d]	$\log k_2$ 25(fb)	P.r.f.(fb) [d]
(1)	1-Phenylpyrazole	C.A.	40	−2·47	11 [b]	−3·27	$1·5 \times 10^{-4}$		
(2)	4-Nitro-1-phenylpyrazole	F.B.	40	−3·55	25 [c]	−4·45		−2·28	$1·5 \times 10^{-3}$
(3)	1-*p*-Nitrophenylpyrazole	F.B.	75	−4·80	25 [c]	−7·50		−1·74	$5·2 \times 10^{-3}$
(6)	1-Methyl-2-phenyl-pyrazolium perchlorate	Cation	50	−4·50	11 [b]	−5·15	$2·0 \times 10^{-6}$		
(8)	1-Methyl-4-nitro-2-phenylpyrazolium perchlorate	Cation	80	−5·20	11 [b]	−6·52	$8·6 \times 10^{-8}$		
(10)	1-Methyl-2-*p*-nitrophenyl-pyrazolium perchlorate	Cation	140	−5·07	11 [b]	−7·44	$1·0 \times 10^{-8}$		

[a] At standard conditions (*i.e.* 25° and 75% H_2SO_4). [b] Assumed as a typical value for conjugate acid nitrations.[10] [c] Assumed as appropriate value for free base nitration in 75% H_2SO_4. [d] Partial rate factor.

rate for a single position of benzene is given [14] by $k_2 = 3·5$ l mol^{-1} s^{-1}.

For nitrations carried out at temperatures other than 25°, the H_R value [8] and the $\log a_{H_2O}$ value [9,10] corresponding to 75% H_2SO_4 were used to read off the graphs in Figure 1, the $\log k_2$ corresponding to 75% H_2SO_4. A temperature conversion was now made using equation

(4) using $E_a = 11·6$ kcal mol^{-1} for conjugate acid nitrations.[12] Results are shown in Table 9.

$$\log k_{2(\text{obs, }25°)} - \log k_{2(\text{obs, }x°)}$$
$$= \frac{-E_a}{2·3R}\left(\frac{1}{298} - \frac{1}{273 + x}\right) \quad (4)$$

[12] A. G. Burton, S. Clementi, C. D. Johnson, A. R. Katritzky, and E. Scriven, in preparation; E. Scriven, Ph.D. Thesis, University of East Anglia, 1969.

[13] A. El-Anani, J. Banger, G. Bianchi, S. Clementi, C. D. Johnson, and A. R. Katritzky, *J.C.S. Perkin II*, 1973, 1065.

[14] R. G. Coombes, R. B. Moodie, and K. Schofield, *J. Chem. Soc. (B)*, 1968, 800.

The free base of 1-*p*-nitrophenylpyrazole (3) is nitrated about three times as fast at the 4-position as the 4-nitro-analogue (2) is nitrated at the *para*-position. This suggests that the free base of 1-phenylpyrazole itself might well undergo nitration at the 4-position, in accord with literature data for reaction in acetic anhydride.[2,3]

However, the 4-nitrometho-cation (8) undergoes nitration some eight times as fast at the *para*-position as the *p*-nitrometho-cation (10) at the 4-position. This suggests that the 1-phenylpyrazole cation will be nitrated preferentially at the *para*-position, as is found.

As Schofield and his co-workers have pointed out [for (5) and (6)] [5] the partial rate factors for cations (5), (6), and (8) show a remarkable deactivation of the benzene ring towards attack combined with a high selectivity for *para*-orientation. The steric effects of the 2-methyl groups in cations (6) and (8) were also discussed for (6); [5] our results are in good agreement. The partial rate factors will be compared in a later paper with data for other heterocyclic ring systems.