The Stabilities of Meisenheimer Complexes. Part 18.[1] Proton Transfer and σ-Complex Formation in the Reactions of *N*-Substituted 2,4,6-Trinitroanilines (Picramides) with Sodium Methoxide in Methanol

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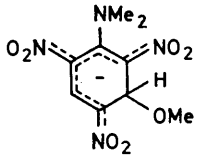
The 1 : 1 interactions of picramide, *N*-substituted picramides, and *NN*-dimethylpicramide with sodium methoxide in methanol have been investigated by stopped-flow and *T*-jump spectrophotometry. Picramide and its *N*-substituted derivatives give rise to a very rapid process which is attributed to proton transfer to give the conjugate base, and to a slower process (measurable by stopped-flow) attributed to methoxide addition at the unsubstituted 3-position. The variation of rate and equilibrium constants with substituent are discussed.

GOLD and ROCHESTER [2] in 1964 made a study by u.v.–visible spectroscopy of the interactions of picramide (2,4,6-trinitroaniline) and *NN*-dimethylpicramide with sodium methoxide in methanol. Measurements of



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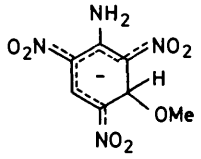

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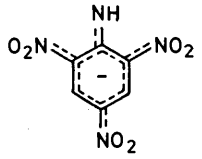

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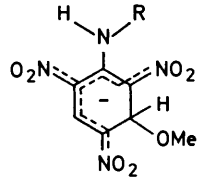

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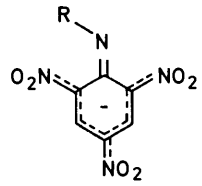

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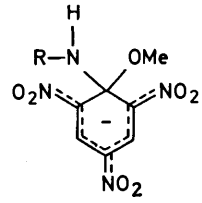

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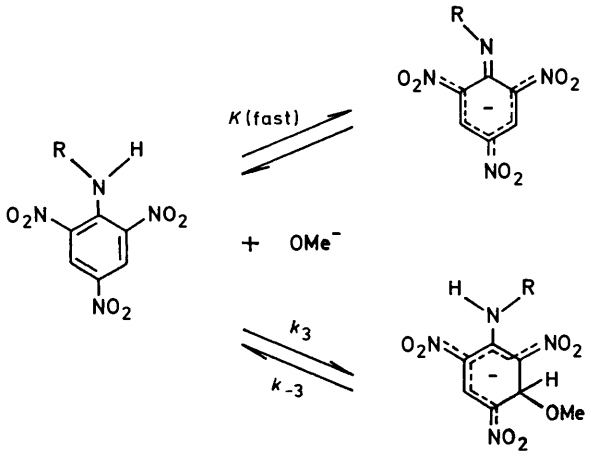
equilibrium optical densities and rates of substrate decomposition led them to conclude that for the *NN*-dialkyl compound the product of 1 : 1 interaction was the 3-methoxy-adduct (1) while for picramide the possibilities of base addition at the 3-position to give (2) and proton loss from the amino-group to give (3) were closely balanced. Confirmation of these structures was provided by ^{1}H n.m.r. measurements in methanol–dimethyl sulphoxide.[3,4] The changes in n.m.r. spectrum of *N*-methylpicramide in dimethyl sulphoxide brought about by the addition of alkoxide ions have similarly been interpreted as indicating competitive base addition at the 3-position and proton loss from the methylamino-group.[3,4] Thus spin-coupled bands at δ 6.16 and 8.48 were attributed to the 3-methoxy-adduct (4; R = Me) while the upfield shift in the remaining ring-proton resonance was attributed to proton loss from the amino-group. Magnetic non-equivalence of the ring-protons of (5; R = Me) in solutions containing a slight excess of base was attributed to slow rotation about the ring carbon–nitrogen bond.[3,4]

Nevertheless this interpretation has been questioned and it has been suggested [5] that the non-equivalence of the ring protons is due to the formation of the 1-methoxy-adduct (6) rather than to proton loss. This alternative explanation deserves consideration in view of the formation (from *N*-methyl-2,4,6-trinitroanilinopropionamide and methoxide ions [6]) of an adduct with structure (6; R = CHMeCONHMe) albeit that this structure depends for its stability on an intramolecular hydrogen bond between the amide N–H and an *o*-nitro-group. Also transient intermediates of type (6) have been observed in the reactions of picryl ethers with aliphatic amines.[7,8] In the naphthalene series adducts formed by alkoxide addition to the 1-position of 2,4-dinitro-1-piperidinonaphthalene have some stability.[9]

In this paper we report measurements by stopped-flow and *T*-jump spectrophotometry of the interactions of picramide, various *N*-substituted picramides, and *NN*-dimethylpicramide with sodium methoxide in methanol. The introduction of time as a variable allows a distinction



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to be made between proton transfer from an amino-group (fast) and base addition at ring-carbon atoms. Our results are in accord with the major 1 : 1 interactions shown in the Scheme and allow an analysis of the effects of the nature of the substituent R on rate and equilibrium constants.

RESULTS

N-Alkylpicramides.—The visible spectra obtained using a conventional recording spectrophotometer (SP 8000) of *N*-methylpicramide in methanolic sodium methoxide solutions are shown in Figure 1. Increasing the base concentration

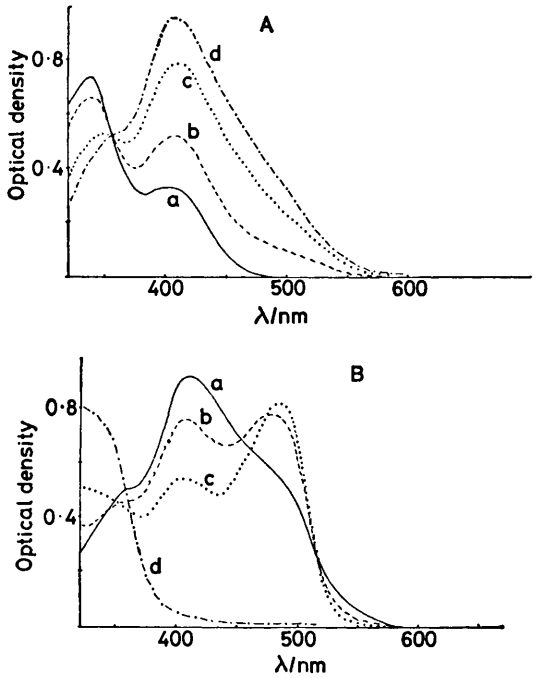


FIGURE 1 Visible spectra of *N*-methylpicramide (5×10^{-5}M) in methanol containing the following concentrations of sodium methoxide: A, a, 0; b, 0.01; c, 0.05; d, 0.18; B, a, 0.48; b, 0.90; c, 1.8; d, 4.5

in the range 0—0.2M causes an increase in intensity of a new band with $\lambda_{max.}$ 410 nm and an isosbestic point is present at 357 nm. These changes are consistent with 1 : 1 interaction between the substrate and base. In the range 0.4—2.0M base a band at 485 nm increases in intensity at the expense of the band at 410 nm; we interpret this change as 1 : 2 interaction between the substrate and base. Above 2.0M-base the visible absorption decreases and eventually solutions show little absorption above 350 nm; this change is consistent with 1 : 3 interaction. The behaviour of parent molecules containing *N*-n-butyl, *N*-isopropyl, and *N*-t-butyl substituents was qualitatively similar although the precise position of absorption maxima and ranges of base concentration over which spectral changes occurred varied somewhat.

We are concerned here primarily with the products of 1 : 1 interaction. Examination by stopped-flow spectrophotometry in dilute ($\leqslant$0.4M) sodium methoxide solutions indicated the presence of two processes associated with 1 : 1 complex formation. For each compound studied the faster process, which was colour-forming at wavelengths above 400 nm, is too rapid for kinetic study in our apparatus (mixing time 2 ms), and is identified with the proton transfer process. In terms of the Scheme, which will be justified later, the slower (measurable) process has a rate coefficient which, with base concentration in large excess of substrate concentration, is given by equation (1). This can be re-arranged to give the inversion plot of equation (2). If K[NaOMe] $\ll$ 1 then equation (1) simplifies to give (3).

$$k_{obs.} = k_{-3} + \frac{k_3[\text{NaOMe}]}{1 + K[\text{NaOMe}]} \quad (1)$$

$$\frac{1}{k_{obs.} - k_{-3}} = \frac{1}{k_3[\text{NaOMe}]} + \frac{K}{k_3} \quad (2)$$

$$k_{obs.} = k_{-3} + k_3[\text{NaOMe}] \quad (3)$$

In some cases optical densities at the completion of the very rapid process were measured by stopped-flow spectrophotometry. These measurements lead to values for K. Equilibrium optical densities at completion of the two 1 : 1 processes were measured either by stopped-flow spectrophotometry or by conventional u.v.–visible spectrophotometry and lead to values of K_T, the sum of K and K_3, as indicated in equation (4). Values of K_T were evaluated

$$K_T = K + K_3 \quad (4)$$

$$\frac{1}{\text{OD} - (\text{OD})_0} = \frac{1}{(\varepsilon_c - \varepsilon_p)} \cdot \frac{1}{K_T} \cdot \frac{1}{P_{stoich}[\text{NaOMe}]} + \frac{1}{(\varepsilon_c - \varepsilon_p)P_{stoich}} \quad (5)$$

using equation (5) where $(OD)_0$ is the optical density in the absence of base, ε_p and ε_c are respectively the extinction coefficient of the parent and the apparent extinction coefficient of the mixture of 1 : 1 complexes, and P_{stoich} is the stoicheiometric concentration of the substrate.

N-Methylpicramide.—Rate and equilibrium data for *N*-methylpicramide are in Table 1. Two rate processes were observed due to 1 : 1 interaction. The faster process was colour-forming at wavelengths >400 nm. At 410 nm the slower process was colour-forming at all base concentrations indicating that at this wavelength the extinction coefficient of (4; R = Me) is higher than that of (5; R = Me). At 500 nm the slower process was colour-forming in dilute base solutions (where a large proportion of

TABLE 1

Kinetic and equilibrium data for 1 : 1 reaction of *N*-methylpicramide (4×10^{-5}M) and sodium methoxide in methanol at 25°

[NaOMe]/M	$k_{obs.}$/s^{-1}	$k_{calc.}$/s^{-1} [a]	OD (480)$_i$ [b]	OD (480)$_e$ [c]	K/ l mol^{-1}	K_T/ l mol^{-1}
0			0.000	0.000		
0.004	22 ± 1	22	0.035	0.040	21	31
0.006	23	22.5	0.045	0.055	19	30
0.010	24	23.5	0.075	0.090	20	33
0.020	26	25	0.125	0.140	19	32
0.030	27	26.5	0.175	0.185	21	35
0.040	28	27	0.200	0.205	20	33
0.060	29	28.5	0.250	0.240	21	33
0.080	29.5	30	0.280	0.260	20	32
0.10	30	30.5	0.295	0.270	19	30
0.15	31	31.5	0.340	0.30	20	33
0.20	31.5	32	0.375	0.33	25	

[a] Calculated from equation (1) with k_{-3} 21 s^{-1}, k_3 280 l mol^{-1} s^{-1}, and K 20 l mol^{-1}. [b] Optical density after completion of the very fast colour forming reaction, measured by stopped-flow. A Benesi–Hildebrand [10] plot gives an optical density of 0.45 for complete conversion. [c] Equilibrium optical density measured by stopped-flow; value for complete conversion is 0.36.

the substrate is present as free *N*-methylpicramide) but resulted in fading at base concentrations >0.05M. This latter observation indicates that at this wavelength the extinction coefficient of (4; R = Me) is lower than that of (5; R = Me). Values of $k_{obs.}$ were independent of the wavelength of measurement. Extrapolation to zero base concentration gives k_{-3} 21 ± 1 s^{-1}. However in this case variation of $k_{obs.}$ with base concentration is small so that values of K and k_3 from the inversion plot [equation (2)] would have high uncertainties.

Optical densities at the completion of the very rapid process obtained at 480 nm lead to a value for K of 20 l mol^{-1}. Similar measurements, not shown, at 410 nm gave a value of 21 l mol^{-1}. Equilibrium optical densities measured at 480 nm lead to a value for K_T of 32 l mol^{-1} (Table 1). Similar measurements at 410 and 515 nm (not shown) give values of 35 and 31 l mol^{-1}, respectively. We obtain a value for K_3 of 13 ± 2 l mol^{-1} by difference [equation (4)]. Thus k_3 (= K_3k_{-3}) has the value of 280 ± 60 l mol^{-1} s^{-1}.

Temperature-jump measurements (ΔT *ca.* 7°) were made on solutions containing 10^{-4}M-*N*-methylpicramide and 0.03M- or 0.06M-sodium methoxide made up to *I* 0.2M with sodium perchlorate. In each case a very fast colour-forming reaction was observed whose rate was characteristic of the heating time of the apparatus (2 μs). This was followed by a slower process ($t_{\frac{1}{2}}$ *ca.* 30 ms) similar to that observed by stopped-flow spectrophotometry.

N-*n-Butylpicramide*.—In dilute base a band at 405 nm is attributed to 1 : 1 interaction. Stopped-flow measurements show the presence of a very fast colour-forming reaction and a slower isomerisation whose rate coefficients are in Table 2. A plot according to equation (2) taking k_{-3} 20 s^{-1} was linear and gave values for k_3, 440 l mol^{-1} s^{-1}, and K, 8.3 ± 1 l mol^{-1}. Combination of k_3 and k_{-3} gives a value for K_3 of 22 l mol^{-1}. Equilibrium optical densities measured at 405 nm with a conventional spectrophotometer give a value for K_T of 29 ± 2 l mol^{-1} in accord with the sum of the values for K and K_3 obtained kinetically.

N-*Isopropylpicramide*.—Rate data for the slower process associated with 1 : 1 interaction are in Table 3 and lead to values for k_{-3}, 16 ± 1 s^{-1}, k_3, 450 ± 30 l mol^{-1} s^{-1}, and K, 5.5 ± 0.5 l mol^{-1}. Hence K_3 (= k_3/k_{-3}) has the value of 28 ± 3 l mol^{-1}. Equilibrium optical densities measured at 474 nm using a conventional spectrophotometer yield a value for K_T of 31 ± 2 l mol^{-1} in satisfactory agreement with the sum of K and K_3. The stopped-flow spectrophotometer was used to determine point-by-point optical densities at various wavelengths after completion of the very fast 1 : 1 process but before significant isomerisation had occured. The spectral shapes of the two species produced from 1 : 1 interaction are in Figure 2.

TABLE 2

Kinetic and equilibrium data for 1 : 1 reaction of *N*-n-butylpicramide (2×10^{-5}M) with sodium methoxide in methanol at 25°

[NaOMe]/M	$k_{obs.}$/s^{-1}	$k_{calc.}$/s^{-1} [a]	OD (405)$_e$ [b]	K_T/l mol^{-1} [c]
0			0.120	
0.004	21.7 ± 0.6	21.7		
0.006	22.3	22.5		
0.010	24.9	24	0.217	30
0.020	27.4	27.5		
0.030	30.9	30.5	0.314	29
0.050	35.0	35.4	0.355	25
0.070	39.1	39.3	0.405	30
0.10	43	43.8	0.433	29
0.15			0.457	27
0.20			0.480	30

[a] Calculated from equation (1) with k_3 440 l mol^{-1} s^{-1}, k_{-3} 20 s^{-1}, and K 8.3 l mol^{-1}. [b] A plot using equation (5) leads to a value of 0.54 for complete conversion to 1 : 1 complex. [c] Defined as (O.D. − 0.120)/(0.54 − O.D.)[NaOMe].

TABLE 3

Equilibrium and kinetic data for 1 : 1 interaction of *N*-isopropylpicramide (4×10^{-5}M) and sodium methoxide in methanol at 25°

[NaOMe]/M	$k_{obs.}$/s^{-1}	$k_{calc.}$/s^{-1} [a]	OD (474 nm) [b]	K_T/l mol^{-1} [c]
0			0.009	
0.001			0.021	34
0.002	16.8 ± 1	16.9		
0.004	18.4	17.8	0.047	30
0.008	19.5	19.5	0.085	33
0.010	19.1	20.2	0.089	29
0.020	23.1	24.1	0.140	29
0.040	30.6	30.7	0.206	31
0.080	42.1	41	0.264	30
0.100	46.6	45	0.280	30
0.200	61	59	0.320	31
0.300	69.4	67		
0.400	70.6	72		

[a] Calculated from equation (1) with k_{-3} 16 s^{-1}, k_3 450 l mol^{-1} s^{-1}, and K 5.5 l mol^{-1}. [b] Value for complete conversion is 0.37, from equation (5). [c] Defined as

(O.D. − 0.009)/(0.37 − O.D.)[NaOMe].

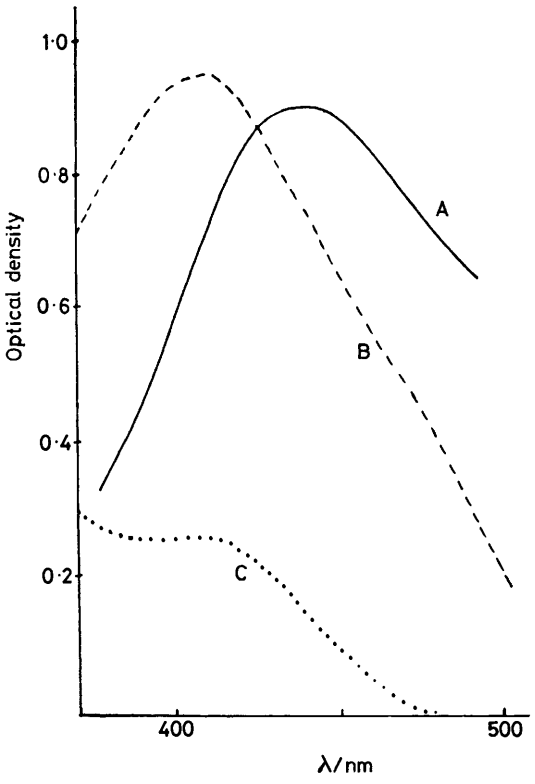


FIGURE 2 Spectral shapes, determined by stopped-flow of the 1 : 1 complexes produced from *N*-isopropylpicramide (5×10^{-5}M) in 0.5M sodium methoxide solution. The initial spectrum, A, is attributed to the anion (5); B is attributed to the adduct (4); and C is the spectrum of the parent

N-*t-Butylpicramide*.—A band at 405 nm attributed to 1 : 1 interaction is dominant in dilute (<0.5M) base solutions. Stopped-flow investigation showed that the very fast colour-forming reaction was present but of very low intensity

at all wavelengths. This is to be expected if the equilibrium constant K for production of the anion formed by proton loss has a low value.

Confirming this, a plot of $k_{obs.}$ *versus* base concentration showed no deviation from linearity and gave values [equation (3)] for k_{-3} of 10.5 s^{-1} and k_3 of 270 $\pm$ 30 l mol^{-1} s^{-1}. We estimate that a value of $K \geqslant 1$ l mol^{-1} would produce obvious curvature thus setting an upper limit on the value of K. Equilibrium optical densities at 400 nm yield a value for K_T of 24 l mol^{-1}. Optical densities after completion of the very fast process were measured by stopped-flow spectrophotometry at two base concentrations and give K 0.5 $\pm$ 0.5 l mol^{-1}.

Picramide.—A band at 400 nm is attributed to 1 : 1 interaction. Stopped-flow measurements were made at this wavelength and show that a very fast colour-forming process (faster than the mixing time) is followed by a slower reaction. Rate data are in Table 5 and analysis according to equation (2) yields values of k_{-3}, 60 s^{-1}, k_3, 1 900 l mol^{-1} s^{-1}, and K, 9 $\pm$ 2 l mol^{-1}. Hence K_3 has the value of 32 $\pm$ 2 l mol^{-1}. The sum of K and K_3 is in reasonable agreement with the value for K_T of 38 l mol^{-1} found previously [2] using optical densities.

A T-jump study of a solution containing 5×10^{-5}M-picramide, 0.05M sodium methoxide, and 0.15M-sodium perchlorate revealed two processes at 450 nm. The more rapid process has a relaxation time < 2 μs, while the slower process was of similar rate to that measured in the stopped-flow study.

NN-*Dimethylpicramide.*—Visible measurements [2] have been interpreted in terms of the formation of 1 : 1 and 1 : 2

TABLE 4

Kinetic and equilibrium data for 1 : 1 reaction of *N*-t-butylpicramide (4×10^{-5}M) and sodium methoxide in methanol at 25°

[NaOMe]/M	$k_{obs.}$/s^{-1}	OD $(400)_i$ [a]	OD $(400)_e$ [b]	K_T/ l mol^{-1} [c]	K/ l mol^{-1} [d]
0		0.190	0.190		
0.01	13.3 $\pm$ 1		0.350	25	
0.02	15.8		0.420	20	
0.04	21.1		0.580	23	
0.06	26.1		0.673	25	
0.08	29.2		0.730	25	
0.10	35.2		0.760	24	
0.15	54				
0.20	70.5	0.25	0.90		0.5
0.30	90.5	0.30			0.7

[a] Value after completion of very fast colour-forming reaction measured by stopped-flow. [b] Equilibrium optical density. A plot of equation (5) gives a value of 1.00 for complete conversion. [c] Defined as $(OD_e - 0.19)/(1.00 - OD_e)[NaOMe]$. [d] Calculated assuming a value for ε of 2×10^{-4} l mol^{-1} cm^{-1}.

TABLE 5

Rate data for 1 : 1 interaction of picramide and sodium methoxide in methanol at 25°

[NaOMe]/M	$k_{obs.}$/s^{-1}	$k_{calc.}$/s^{-1} [a]
0.002	63.7	63.8
0.004	66.7	67.2
0.008	74.8	74.2
0.010	77	77.4
0.020	92	92.2
0.03	108	105
0.04	117	116
0.05	128	126

[a] Calculated from equation (1) with k_{-3} 60 s^{-1}, k_3 1900 l mol^{-1} s^{-1}, and K 9 l mol^{-1}.

TABLE 6

Rate data for reaction of *NN*-dimethylpicramide with sodium methoxide in methanol at 25°

[NaOMe]/M	0.02	0.05	0.10	0.20	0.30	0.40
$k_{obs.}$/s^{-1}	38 $\pm$ 2	40	52	68	84	108

adducts. In this case no amino-proton is present and stopped-flow measurement in the range 0.02—0.4M-sodium methoxide showed the absence of a very rapid process. A fast colour-forming reaction interpreted as formation of the 3-methoxy-adduct (1) was present. Rate data in Table 6 show a linear dependence on base concentration [equation (3)] and lead to values of k_3 of 180 $\pm$ 20 l mol^{-1} s^{-1} and k_{-3} of 31 s^{-1}. The value of K_3 so obtained, 6 l mol^{-1}, is in agreement with the value of 7 l mol^{-1} obtained previously [2] from optical density measurements. A second much slower process whose rate coefficient was in the range 0.2—1 s^{-1} was observed and is attributed to formation of the 1 : 2 dimethoxy-adduct.

N-*Phenylpicramide.*—In dilute base solutions a single colour forming reaction is observed giving rise to a species with $\lambda_{max.}$ 435 nm. A T-jump experiment with 10^{-4}M-parent, 10^{-3}M-sodium methoxide, and 0.2M-sodium perchlorate in methanol showed that this process is faster than the heating time of the instrument, so that $k > 3 \times 10^5$ s^{-1}. Visible measurements showed that in a solution containing 10^{-3}M-sodium methoxide $\geqslant$90% of the parent is converted into its anion; hence $K \geqslant 10^4$ l mol^{-1}.

At base concentrations >2M a new band at 480 nm is observed and is attributed to 1 : 2 interaction and above 3M-base the spectrum shows absorption at 345 nm due to 1 : 3 interaction.

DISCUSSION

Substrates containing amino-protons give evidence of a very fast colour-forming reaction. Temperature-jump measurements on picramide, *N*-methylpicramide, and *N*-phenylpicramide show that this process is faster than the heating time of the instrument. This is to be expected if this fast process involves proton transfer from the amino-group to methoxide ions since with values of K near unity the rates of forward and reverse reactions will be close to that for diffusion control.[11] The observed rates are faster than would be expected for methoxide attack at ring carbon atoms.[12-14] Hence we ascribe the very fast process to proton transfer.

The slower, measurable process might be due to methoxide addition at the 1- or 3-position. Data in the literature indicate that addition at substituted positions is normally a comparatively slow process. For example in the formation of (6; R = CHMeCONHMe) the rate coefficients for forward and reverse reactions have values [6] of 6.5 l mol^{-1} s^{-1} and 5.2×10^{-5} s^{-1}, respectively, and the corresponding values for methoxide attack at the 1-position of 2,4,6-trinitroanisole [12] are 17 l mol^{-1} s^{-1} and 1×10^{-3} s^{-1}. The values obtained in the present work are closer to those expected for addition at unsubstituted ring positions. The ^1H n.m.r. spectral evidence also favours addition at the 3-position. We conclude that the major 1 : 1 interactions of picramide and *N*-alkylpicramides with methoxide are as depicted in the Scheme.

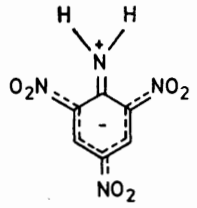
TABLE 7

Summary of rate and equilibrium data for 1 : 1 reaction of picramide and *N*-substituted picramides with sodium methoxide in methanol at 25°

Substituent [a]	k_3/ l mol^{-1} s^{-1}	k_{-3}/s^{-1}	K_3/ l mol^{-1}	K/ l mol^{-1}	$K/(K + K_3)$
NH_2	1 900	60	32	9	0.22
NHMe	280	21	13	20	0.60
NHBu^n	440	20	22	8.3	0.27
NHPr^i	450	16	28	5.5	0.16
NHBu^t	270	10.5	26	0.5	0.02
NHPh				$>10^4$	~1.0
NMe_2	180	31	6		
H [b]	7 050	305	23		

[a] The parent is 1,3,5-trinitrobenzene. [b] Ref. 14.

The data in Table 7 show that for the *N*-alkylpicramides the values of K, reflecting the acidities of the substrates, decrease as the substituent changes along the series Me, Bu^n, Pr^i, Bu^t. These changes are in the direction expected from inductive effects. However another important factor may be steric interaction between the substituent and the *o*-nitro groups. To obtain maximum charge delocalisation in anions of structure (5), the =NR group should be coplanar with the ring. The decrease in value of K with the size of the *N*-substituent may reflect the increasing difficulty of achieving this result. The high value of K for *N*-phenylpicramide reflects the good ability of the phenyl group to delocalise the negative charge on the anion. That the value of K for picramide is lower than that for *N*-methylpicramide is perhaps surprising. This may reflect ground-state stabilisation of picramide through resonance interaction of type (7) which is lost or partially lost on formation of the anion. Because of the steric factors the ground-state stabilisation of *N*-alkylpicramides may be smaller.



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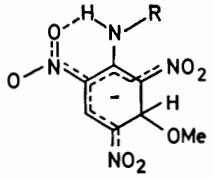


(8)

The values of K_3, for methoxide addition at the 3-position, for picramide and its derivatives are similar to that for addition to 1,3,5-trinitrobenzene. The electronic effects of the amino-substituents will not be large, but increasing size which inhibits the planarity of the nitro-groups would be expected to limit their ability to delocalise charge and hence reduce values of K_3. Such an effect may operate in the case of *NN*-dimethylpicramide. In the *N*-alkylpicramides hydrogen-bonding, as shown in (8), may be more effective in the negatively charged complexes than in the parent molecules and hence increase complex stability. Value of k_3 and k_{-3} are about an order of magnitude smaller for picramide and its derivatives than for 1,3,5-trinitrobenzene.

The values of the ratio $K/(K + K_3)$ give the fraction of substrate ionising by proton loss and show that the two ionisation processes are closely balanced. N.m.r. measurements have been used previously [3] to obtain the corresponding ratios in methanol–dimethyl sulphoxide solvent; they give values of 0.20 for picramide and 0.80 for *N*-methylpicramide. The ratio will be expected to increase with decreasing proportion of methanol in the solvent since the two products of 1 : 1 interaction differ by a molecule of methanol.

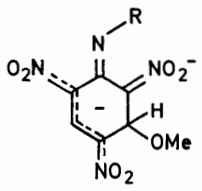
It is of interest to compare the spectral shapes of the products of 1 : 1 interaction. The spectra (Figure 2) obtained by stopped-flow measurements show that base addition to *N*-isopropylpicramide results in a species with $\lambda_{max.}$ 400 nm while the anion formed by proton loss has $\lambda_{max.}$ 440 nm and absorbs at slightly longer wavelengths. The spectra obtained at equilibrium will consist of the sum of the spectra for the species present. The data in Table 8 show that there is a rough correlation

TABLE 8

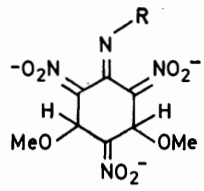
Substituent	NH_2	NHBu^t	NHPr^i	NHBu^n	NHMe	NHPh
$\lambda_{max.}$	400	405	405	405	410	435
$K/(K + K_3)$	0.22	0.02	0.16	0.27	0.60	1.0

between the extent of proton loss and the position of the absorption maximum.

In the case of the *N*-substituted picramides, increasing the base concentration above 0.5M causes the gradual replacement of the absorption due to 1 : 1 interaction with a band at 480 nm. In the light of ^{1}H n.m.r. data [3] this change is likely to indicate formation of the 1 : 2 adducts (9). At base concentration above 2M the band



(9)



(10)

at 480 nm decreases in intensity and at sufficiently high base concentration, solutions show little absorption above 350 nm. This further change is reasonably attributed [15] to 1 : 3 interaction to give (10).

EXPERIMENTAL

Picramide and its derivatives were prepared by reaction of 1-chloro-2,4,6-trinitrobenzene with the appropriate amine in methanol or aqueous methanol. Recrystallisation from methanol yielded products with the following m.p.s: picramide, 195° (lit.,[16] 192—195°); *N*-methyl, 116° (lit.,[16] 115°); *N*-butyl, 82° (lit.,[16] 81°); *N*-isopropyl, 108° (lit.,[16] 107°); *N*-t-butyl, 95° (lit.,[17] 95°); *N*-phenyl, 183° (lit.,[16] 183°); *NN*-dimethyl, 139° (lit.,[16] 138°). Sodium methoxide solutions were prepared by dissolving clean sodium in AnalaR methanol under nitrogen and were titrated with standard acid.

U.v.–visible spectral shapes were determined with a Unicam SP 8000 instrument. Optical densities at 25° were measured with an SP 500 instrument or with a Canterbury stopped-flow spectrophotometer. The latter instrument

was used to measure rate coefficients. *T*-Jump spectrophotometric measurements were made with an instrument supplied by Hartley Measurements Ltd. consisting of a delay line energy-storage system at 30 kV with a square heating pulse and including variable charging rate, automatic triggering on auto zero circuit, and delay unit. *T*-Jumps of *ca.* 7° were obtained by discharging a 0.05 μF capacitor through a heated volume of 0.5 cm^3. Tests with alkaline glycine containing phenolphthalein indicated a heating time of *ca.* 2 μs.

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