

The Stabilities of Meisenheimer Complexes. Part 31.¹ The Reactions of 2,2',4,4',6,6'-Hexanitrostilbene with Alkoxides

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¹H N.m.r. and visible spectral measurements indicate three types of 1:1 interaction of 2,2',4,4',6,6'-hexanitrostilbene with alkoxides. σ -Adducts are formed by attack at the 3- or 1-ring position, while the third interaction may involve attack at the olefinic double bond. A 1:2 adduct is produced by attack at the 1- and 1'-ring position. Kinetic and equilibrium results for reactions with methoxide ions in methanol and ethoxide ions in ethanol have been obtained and are compared with those for related compounds.

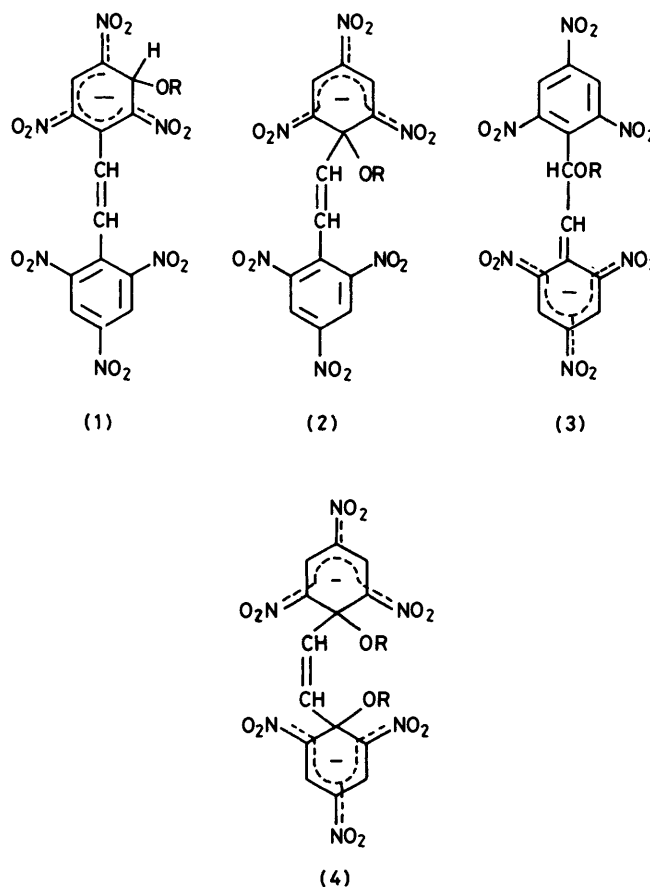
2,2',4,4',6,6'-Hexanitrostilbene (HNS) has found commercial use as a thermally stable explosive.² One important method of its preparation involves the reaction of 2,4,6-trinitrotoluene with aqueous sodium hypochlorite in mixed solvents.³ During this reaction intense colours are produced and we have sought to identify the species responsible and to show whether or not they are intermediates on the reaction pathway.^{4,5} In this paper we consider the colour-forming reactions of the product, HNS, with alkoxide ions.

Likely products of 1:1 interaction of HNS with base are the σ -adducts (1) and (2) formed by attack at the 3- or 1-position, respectively.⁴⁻⁶ Further possibilities involve attack at the olefinic part of the molecule either by base addition to give (3) or by proton abstraction.^{7,8} Thus Fyfe⁹ has shown that α -cyano-4-nitro-4'-X-stilbenes undergo base addition at the β -carbon atom of the double bond.

¹H N.m.r. Measurements.—Spectra were recorded with 0.02M-HNS in 80:20 (v/v) fully deuteriated dimethyl sulphoxide-methanol. The parent, being the *trans*-isomer, shows two sharp bands at δ 9.10 and 7.12 with intensity ratio 2:1 due respectively to ring and olefinic protons. The spectrum obtained in the presence of 1 mol. equiv. of sodium tri-deuteriomethoxide showed clear evidence for the formation of the adduct (2; R = CD₃); two singlets, δ 8.9 and 8.65, are attributed to the ring protons while the olefinic protons give an AB quartet with δ 6.45 and 6.8 and *J* 17 Hz, this coupling constant being typical of a *trans*-orientation.¹⁰ Interestingly transient bands were observed at δ 9.0, 8.5, and 6.2 which are attributed⁶ to the ring protons of (1; R = CD₃). This observation indicates that as with related compounds⁵ attack at the 3-position is kinetically favoured while attack at the 1-position leads to the thermodynamically more stable product. In the presence of 2 mol. equiv. of base the spectrum consisted of two singlets, δ 8.53 and 6.05, with intensity ratio 2:1 consistent with the formation of the symmetrical diadduct (4; R = CD₃). Similar spectra were obtained in a 50:50 methanol-DMSO solvent system. In these solutions the visible spectra showed double absorption maxima, λ_{\max} ca. 430 and 480 nm, characteristic of σ -adducts.⁶

N.m.r. measurements in methanol were also attempted, where visible spectra indicate formation of a different species, λ_{\max} 470 nm, and in 80:20 (v/v) methanol-dimethyl sulphoxide. However because of the extreme insolubility of HNS in these media no clear spectra could be obtained even after many accumulations.

Reactions with Sodium Methoxide in Methanol.—Sodium methoxide in methanol is a much less basic medium than methoxide in dimethyl sulphoxide so that the reaction with a

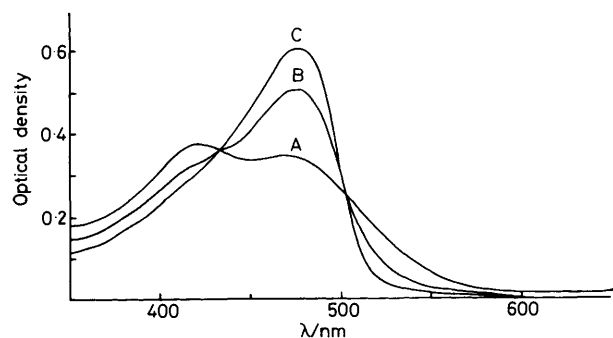


stoichiometry of 1 HNS: 2 methoxide observed by n.m.r. is not important in dilute solutions ($[NaOMe] \leq 0.1M$). However in these solutions there is evidence for three types of reversible reaction resulting from 1:1 interaction. Examination by stopped-flow spectrophotometry indicates the presence of a very rapid colour-forming reaction, whose rate is too fast for the technique, and a fast measurable process giving an orange species with λ_{\max} 420 and 480 nm. We take these processes to involve respectively attack at the 3-position to give (1; R = Me) and at the 1-position to give (2; R = Me). There is also a very much slower reaction, measurable by conventional spectrophotometry, giving a yellow species with λ_{\max} 470 nm (ϵ 3.0×10^4 l mol⁻¹ cm⁻¹). Visible spectra are in the Figure. N.m.r. measurements did not allow the determination of the structure of the final product but as indicated

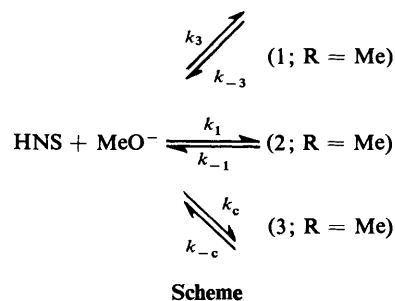
Table 1. Kinetic results for reaction of HNS with methoxide ions in methanol at 25°

$10^5[\text{MeO}^-]/\text{M}$	Conditions	$k_{\text{med}}/\text{s}^{-1}$	k_{calc}^d	$10^4 k_{\text{slow}}/\text{s}^{-1}$	$10^4 k_{\text{calc}}^e$	O.D. (470 nm) ^f
3.2	a			0.63 ± 0.03	0.66	0.48
6.9	a			1.25	1.20	0.55
16	a			2.5	2.45	0.57
23	b			3.3	3.4	
31	b			4.3	4.4	0.57
48	b			6.3	6.5	0.56
100	c	0.88 ± 0.08	0.89	12.3	12.2	0.56
200	c			20	20	
400	c	1.19	1.30	32	32	
500	c	1.43	1.44			
600	c			43	39	
700	c	1.72	1.70			
800	c			45	44	
1 000	c	2.10	2.07	49	47	
2 000	c			55	56	
4 000	c	4.50	4.90			
7 000	c	6.9	6.7			
10 000	c	8.1	8.0			

^a 4-Bromophenol-4-bromophenoxide buffers. ^b Phenol-phenoxide buffers prepared according to ref. 11. ^c Sodium methoxide in methanol. ^d Calculated from equation (2) with k_1 145 l mol⁻¹ s⁻¹, k_{-1} 0.75 s⁻¹, and K_3 10 l mol⁻¹. ^e Calculated from equation (3) with k_c 1.45 l mol⁻¹ s⁻¹, k_{-c} 2×10^{-5} s⁻¹, K_1 200 l mol⁻¹, and K_3 10 l mol⁻¹. ^f At the completion of the slow reactions with $2 \times 10^{-5}\text{M}$ -HNS.



Visible spectra of HNS ($2 \times 10^{-5}\text{M}$) and sodium methoxide (0.04M) in methanol after A, 1 min; B, 3 min; and C, 20 min. These spectra show the conversion of (2; R = Me) to another species, probably (3; R = Me)



imprecise and we prefer to quote a value of $\geq 10^5$ l mol⁻¹. Additional evidence for the high value of K_c comes from the optical density measurements at the completion of reaction which show extensive conversion even at very low methoxide concentrations.

Reaction with Sodium Ethoxide in Ethanol.—Ethoxide in ethanol is a more basic medium than methoxide in methanol so that formation of the 1:2 adduct (4; R = Et) occurs in fairly dilute solutions.

Visible spectra were recorded on a conventional spectrophotometer for solutions containing $2 \times 10^{-5}\text{M}$ -HNS and 0.0004–0.2M-sodium ethoxide. The spectra recorded within one minute of mixing the reactants showed the double absorption maxima characteristic of σ -adduct formation.⁶ In the most dilute base concentrations the maxima were at 425 and 490 nm while in the more concentrated solutions small shifts to 435 and 480 nm were observed. With time these bands slowly faded with the appearance of a new band at 475 nm. Values of optical density after completion of the reaction giving σ -adducts but before decomposition had occurred are in Table 2. A Benesi-Hildebrand plot¹³ of reciprocal of optical density versus reciprocal of base concentration was curved indicating the presence of more than one equilibrium. However a short extrapolation gave a value of 0.543 at 480 nm corresponding to complete conversion. From this we are able to calculate values of extinction coefficients for the species formed at the higher base concentrations. These values, ϵ 4.6×10^4 (435 nm) and 2.7×10^4 l mol⁻¹ cm⁻¹ (480 nm), are considerably higher than those found for adducts

later it seems highly probable that it has structure (3; R = Me). We analyse our results according to the Scheme. All measurements were made with methoxide concentration buffered. Since the rates of the three processes designated k_{fast} , k_{med} , and k_{slow} are well separated, it is readily shown by standard methods¹² that equations (1)–(3) will apply.

$$k_{\text{fast}} = k_3[\text{MeO}^-] + k_{-3} \quad (1)$$

$$k_{\text{med}} = k_{-1} + \frac{k_1[\text{MeO}^-]}{1 + K_3[\text{MeO}^-]} \quad (2)$$

$$k_{\text{slow}} = k_{-c} + \frac{k_c[\text{MeO}^-]}{1 + K_1[\text{MeO}^-] + K_3[\text{MeO}^-]} \quad (3)$$

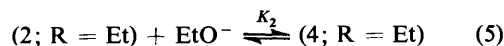
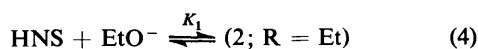
The values of k_{med} are fitted well by equation (2) with K_3 10 l mol⁻¹, k_1 145 l mol⁻¹ s⁻¹, and k_{-1} 0.75 s⁻¹. Combination of the two latter values gives K_1 200 ± 10 l mol⁻¹. The variation with base concentration of values of k_{slow} is accommodated by equation (3) using the known values of K_1 and K_3 and with k_c 1.45 ± 0.05 l mol⁻¹ s⁻¹ and k_{-c} $(2 \pm 2) \times 10^{-5}$ s⁻¹. The high uncertainty in the value of k_{-c} makes the value of K_c ($= k_c/k_{-c}$)

Table 2. Equilibrium optical densities for reaction of HNS (2×10^{-5} M) with sodium ethoxide in ethanol at 25°

No.	[NaOEt] ^a /M	O.D. (480 nm) observed	O.D. (480 nm) ^b calculated
1	0.000 42	0.175	0.175
2	0.000 63	0.194	0.202
3	0.000 84	0.218	0.219
4	0.001 04	0.236	0.232
5	0.002 10	0.260	0.269
6	0.004 18	0.301	0.304
7	0.006 25	0.320	0.326
8	0.008 30	0.340	0.344
9	0.0106	0.362	0.360
10	0.0212	0.415	0.409
11	0.0424	0.452	0.455
12	0.0636	0.478	0.478
13	0.0848	0.489	0.491
14	0.106	0.501	0.500
15	0.212	0.523	0.520

^a In solutions 1–13 the solutions were made up to constant ionic strength 1.0M with sodium perchlorate. ^b Calculated with values of K_1 4 000 l mol⁻¹, K_2 50 l mol⁻¹, ϵ (2; R = Et) 1.36×10^4 , ϵ (4; R = Et) 2.72×10^4 l mol⁻¹ cm⁻¹.

of 1 : 1 stoichiometry.⁶ This strongly suggests that in the more concentrated base solutions a di-adduct is formed by ethoxide attack on each of the aromatic rings and, in view of the n.m.r. evidence the most likely structure is (4; R = Et). We analysed the results according to equations (4) and (5), assuming the



extinction coefficient of (2; R = Et) at 480 nm to be one-half the value of (4; R = Et). Results at low base concentrations, items 1–4 in Table 2, where little 1 : 2 adduct will be present allowed an approximate value to be obtained for K_1 . Similarly the results at high base concentrations, items 10–15, where little free HNS will remain gave an approximate value for K_2 . Iteration gave values for K_1 4 000 l mol⁻¹ and K_2 50 l mol⁻¹ which gave a good fit of calculated and observed optical densities. The considerably lower value for K_2 shows that even through the 2,4,6-trinitrobenzene rings are separated by two carbon atoms attack of alkoxide on one ring inhibits attack on the second ring. We limited kinetic studies to very low base concentrations ($[\text{NaOEt}] < 0.005\text{M}$) where 1 : 1 interactions will be dominant. In these solutions two rapid colour-forming reactions were observed which we attribute to formation of the 3-ethoxy-adduct (1; R = Et) and the 1-ethoxy-adduct (2; R = Et). Rate expressions exactly analogous to equation (1) and (2) will apply to these processes. A linear plot of k_{fast} versus base concentration gave values for k_3 1.2×10^4 l mol⁻¹ s⁻¹, and k_{-3} 25 s⁻¹ leading to K_3 ($= k_3/k_{-3}$) 480 l mol⁻¹. The values of k_{med} are accommodated by equation (2) with k_1 300 l mol⁻¹ s⁻¹ and k_{-1} 0.075 s⁻¹.

Comparison with Related Compounds.—In Table 4, kinetic and equilibrium data relating to alkoxide additions to ring positions of HNS are compared with similar data for 2,2',-4,4',6,6'-hexanitrobenzyl (HNBB), 2,4,6-trinitrobenzyl chloride (TNBCl), 2,4,6-trinitrobenzene (TNT), and 1,3,5-trinitrobenzene (TNB). The values for HNS and HNBB, where two equivalent aromatic rings are available for alkoxide attack, have not been statistically corrected. The results are in

Table 3. Kinetic results for formation of 1 : 1 adducts from HNS (1×10^{-5} M) and sodium ethoxide in ethanol at 25°

[NaOEt]/M	$k_{\text{fast}}/\text{s}^{-1}$	$k_{\text{med}}/\text{s}^{-1}$	k_{med} (calc.) ^a
0.0006	30 ± 3	0.210 ± 0.02	0.21
0.0008	32	0.245	0.24
0.0010	37	0.28	0.28
0.0015	48	0.34	0.33
0.0020	51	0.40	0.38
0.0030	62	0.43	0.43
0.0040	72	0.45	0.47

^a Calculated from equation (2) with k_1 300 l mol⁻¹ s⁻¹, k_{-1} 0.075 s⁻¹, and K_3 480 l mol⁻¹.

accord with the generally higher basicity of ethoxide solutions compared to methoxide solutions. The values of the equilibrium constants for reaction of HNS fall between those for the analogous reactions for HNBB and TNBCl, and are in accord with the increased electron-withdrawing ability¹⁴ of the unsaturated side-chain CH=CHPic compared with its saturated analogue CH₂CH₂Pic.

As with HNBB and TNBCl alkoxide attack at the unsubstituted 3-position of HNS is a faster process than at the 1-position but leads to a thermodynamically less stable product. This contrasts with the behaviour of TNT where attack has been observed only at the 3-position.¹⁵ The difference may be due to the electron-withdrawing ability of the 1-substituents in HNS, HNBB, and TNBCl which will encourage addition at the 1-position and also to the greater steric bulk of the 1-substituents. Thus greater steric relief may be obtained on rotating these substituents from the ring-plane on formation of the 1-alkoxy-adducts than for TNT.

A third reversible 1 : 1 interaction of HNS with alkoxide ions has been observed giving rise to species with high thermodynamic stability. E.s.r. measurements* of HNS in the presence of alkoxide ions indicate that very small quantities of radicals are produced accounting for <0.1% of the substrate so that the species is unlikely to be a radical. A likely possibility involves attack of alkoxide at the olefinic part of the molecule to give (3). This species is formed most readily in methanolic methoxide solutions. In more basic media such as ethoxide in ethanol or methoxide in methanol–DMSO its production is slow and is in competition with irreversible decomposition of the substrate. This observation can be rationalised in terms of equation (3) which indicates that the rate of its production will decrease as the stability of ring adducts increases.

Experimental

Reaction of TNT with sodium hypochlorite³ gave the *trans*-isomer of HNS as pale yellow crystals, m.p. 316° (lit.,³ 316°). Recrystallisation from nitric acid gave a second crystalline modification HNS(II) with m.p. 324° . The two forms gave identical ¹H n.m.r. spectra when dissolved in DMSO. Kinetic measurements were made by using HNS(II). Stock solutions of substrate were prepared in DMSO so that reaction mixtures in alcohol solvents contain 1% v/v DMSO. Solutions of sodium alkoxides were prepared by solution of clean pieces of sodium in AnalaR alcohol and were titrated against standard acid.

¹H N.m.r. measurements were made with either a Varian EM 360L instrument or with a Bruker HX 90E instrument

* We thank Dr. B. C. Gilbert, University of York, for these measurements.

Table 4. Comparison of kinetic and equilibrium data for HNS with those for related compounds

	$k_3/l \text{ mol}^{-1} \text{ s}^{-1}$	k_{-3}/s^{-1}	$K_3/l \text{ mol}^{-1}$	$k_1/l \text{ mol}^{-1} \text{ s}^{-1}$	k_{-1}/s^{-1}	$K_1/l \text{ mol}^{-1}$
HNS-methoxide			10	145	0.75	200
HNBB-methoxide ^a				23	1.15	20
TNBCl-methoxide ^b			<20	770	2.2	350
TNT-methoxide ^c	280	3 000	0.07			
TNB-methoxide	7 300	300	20			
HNS-ethoxide	12 000	25	480	300	0.075	4 000
HNBB-ethoxide ^a	4 000	32	125	84	0.07	1 200
TNBCl-ethoxide ^b	10 000	14	700	7 000	<1	>10 000
TNB-ethoxide ^d	40 000	20	2 000			

^a Ref. 5. ^b Ref. 4. ^c Ref. 15. ^d Ref. 16 (refers to addition at unsubstituted position).

modified for Fourier transform operation and using a deuterium lock. Chemical shifts were measured relative to internal tetramethylsilane. Visible spectral measurements were made with Unicam SP 500, Beckman 25, or Hi-Tech SF-3C stopped-flow spectrophotometers by using freshly prepared solutions of reagents. All rate measurements were made at 25° under first-order conditions. Rate coefficients are in most cases the mean of five separate determinations and are precise to $\pm 5\%$.

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