The Stabilities of Meisenheimer Complexes. Part IV.[1] Methoxide Adducts from 1-X-3,5-Dinitrobenzenes

By **Michael R. Crampton** * and **Hassan A. Khan**, Chemistry Department, The University, Durham

The σ complexes from 1-X-3,5-dinitrobenzenes and methoxide ions have been examined by ^{1}H n.m.r. and visible spectroscopy. Initial addition of base occurs at C-4 but rearrangement occurs with time so that at equilibrium mainly the C-2 adducts are present. However the free-energy difference between the isomeric adducts is usually small. The measurement of indicator ratios in methanol–dimethyl sulphoxide mixtures containing 0·098M-sodium methoxide allowed the simultaneous determination of the J_M acidity function for these media, which is compared with other J_M functions, and the thermodynamic equilibrium constants K for complex formation. Values of K are X = CN, K = 1·0 l mol^{-1}; SO_2Me, 0·50; CF_3, 1·2 × 10^{-2}; CO_2Me, 8·5 × 10^{-3}; I, 8·9 × 10^{-4}; $CONEt_2$, 1·1 × 10^{-4}; SMe, 3·9 × 10^{-5}; H, 1 × 10^{-6}; SO_3^-, *ca.* 10^{-4}—10^{-5}. The stabilities of these adducts are compared with those from similarly activated anisoles.

METHOXIDE addition to substituted anisoles has been the subject of many investigations.[2-5] In general addition at an unsubstituted ring position to give a 1,3-complex (I) is kinetically favoured but rearrangement occurs to give the thermodynamically more stable 1,1-complex (II).

---

[1] Part III, M. R. Crampton and H. A. Khan, *J.C.S. Perkin II*, 1972, **2286**.

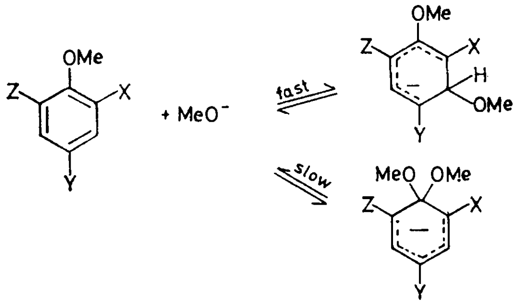
[2] For recent reviews on Meisenheimer complexes see M. R. Crampton, *Adv. Phys. Org. Chem.*, 1969, 211; M. J. Strauss, *Chem. Rev.*, 1970, 667.

[3] M. R. Crampton and H. A. Khan, *J.C.S. Perkin II*, 1972, 1173.

[4] M. R. Crampton, M. A. El Ghariani, and H. A. Khan, *J.C.S. Perkin II*, 1972, 1178.

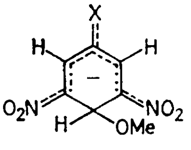
[5] F. Terrier, F. Millot, and R. Schaal, *J.C.S. Perkin II*, 1972, 1192 and references therein; C. F. Bernasconi, *J. Amer. Chem. Soc.*, 1971, **93**, 6975; E. J. Fendler, E. Ernsberger, and J. H. Fendler, *J. Org. Chem.*, 1971, **36**, 2333.

In this paper we are concerned with methoxide addition to 1-X-3,5-dinitrobenzenes, where again isomeric addition is possible. In the cases of 1-methoxycarbonyl-3,5-dinitrobenzene[6] or 1-cyano-3,5-dinitrobenzene[7] previous results indicate that in dimethyl sulphoxide addition occurs first at C-4 to give (III). Rearrangement occurs with time so that at equilibrium a mixture of the adducts (III) and (IV) is present. When X = CO_2Me the ratio (III) : (IV) is 3 : 7 while when X = CN the ratio is 1 : 19. Fendler *et al.*[8] have shown in the case of the cyano-compound that initial complex formation is followed by decomposition resulting in nucleophilic substitution of a nitro-group by methoxide. In the present investigation points of particular interest are the effects of different substituents X on (i) the position of initial base addition, (ii) the equilibrium ratio of isomers, and (iii) the overall equilibrium constant for adduct formation. In the course of determining these equilibrium constants we have measured the J_M acidity function[9] relating to methoxide addition to these compounds in methanol–dimethyl sulphoxide mixtures containing either 0·098M-sodium methoxide or 0·080M-tetra-n-butylammonium methoxide.

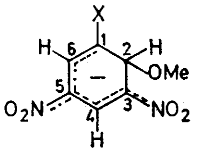


(I)

(II)



(III)



(IV)

EXPERIMENTAL

Parent compounds containing the following substituents were purified commercial specimens; X = H, I, CN, and NO_2. 3,5-Dinitrobenzotrifluoride, m.p. 50 °C (lit.,[10] 50 °C) was prepared in good yield by nitration of 3-nitrobenzotrifluoride and was recrystallised from methanol. *NN*-Diethyl-3,5-dinitrobenzamide, m.p. 92 °C (lit.,[11] 91 °C), was prepared by reaction of 3,5-dinitrobenzoyl chloride with diethylamine in benzene. Diazotisation of 3,5-dinitroaniline followed by reaction with KSCN–CuSCN yielded 3,5-dinitro-1-thiocyanatobenzene. Reaction of this product with trimethyl phosphite gave 3,5-dinitrothioanisole, m.p. 121 °C (lit.,[12] 121 °C). Oxidation of the thioanisole with peracetic acid gave the methylsulphonyl derivative, m.p. 238 °C (lit.,[12] 240 °C). 3,5-Dinitrobenzenesulphonic acid was prepared[13] by direct sulphonation of 1,3-dinitrobenzene and was crystallised as the potassium or barium salt. Other nitro-compounds, solvents, and base solutions were prepared as before.[1,3,6]

^1H N.m.r. measurements were made on 0·2M solutions with a Varian A56/60 instrument, using tetramethylsilane as internal reference. Visible spectral measurements were made with Unicam SP 800 and SP 500 instruments with substrate concentrations of *ca.* 4×10^{-5}M. The former recording instrument was used for the determination of spectral shapes while the latter instrument was used for the accurate determination of optical densities.

RESULTS

N.m.r. studies.—Spectra of the parent molecules were recorded in dimethyl sulphoxide. Spectral analysis was carried out using standard methods.[14] The ring protons gave in each case an AB_2 spectrum with J_{AB} *ca.* 2 Hz. Chemical shifts are in Table 1.

TABLE 1

Chemical shifts [δ (p.p.m.) downfield from internal tetramethylsilane] for 1-X-3,5-dinitrobenzenes in dimethyl sulphoxide

	Ring protons		
X	2-H and 6-H	4-H	Methyl protons
NO_2 [a]	9·21	9·21	
CN [b]	9·16	9·08	
SO_2Me	9·07	9·14	3·52
CF_3	8·98	9·14	
CO_2Me [c]	8·95	9·08	4·05
I	8·96	8·87	
$CONEt_2$	8·62	8·90	
SMe	8·43	8·58	
SO_3^-	8·70	8·85	

[a] M. R. Crampton and V. Gold, *J. Chem. Soc.* (*B*), 1966, 893. [b] Ref. 8. [c] Ref. 6.

The addition of 1 equiv. of concentrated sodium methoxide solution in methanol to solutions of the parent compounds in dimethyl sulphoxide produced intensely coloured solutions. Spectra were recorded *ca.* 1 min after mixing of the solutions and showed bands characteristic of the methoxide adducts (IV). Data for these compounds and some data from the literature are collected in Table 2. For the parent compounds with X = CO_2Me or CN n.m.r. bands have been observed[6,7] due to the isomeric adducts with structure (III). No such bands were observed in the present study for the other compounds used. We estimate that our measurements are sufficiently sensitive to detect 10% of these species thus setting an upper limit on their equilibrium concentrations.

Visible Spectra.—Evidence for the initial addition of methoxide at C-4 to give adducts of structure (III) comes

---

[6] M. R. Crampton and H. A. Khan, *J.C.S. Perkin II*, 1971, 733.

[7] F. Terrier, F. Millot, and M. P. Simmonin, *Tetrahedron Letters*, 1971, 2933.

[8] E. J. Fendler, J. H. Fendler, N. L. Arthur, and C. E. Griffin, *J. Org. Chem.*, 1972, **37**, 812.

[9] C. H. Rochester, 'Acidity Functions,' Academic Press, New York, 1970.

[10] G. C. Finger and F. H. Reed, *J. Amer. Chem. Soc.*, 1944, **66**, 1972.

[11] B. Voláková, *Coll. Czech. Chem. Comm.*, 1961, **26**, 1332.

[12] K. Pilgram and F. Korte, *Tetrahedron*, 1964, **20**, 177.

[13] R. H. Griffith, *J. Chem. Soc.*, 1924, 1401.

[14] J. A. Pople, W. G. Schneider, and H. J. Bernstein, 'High Resolution N.M.R. Spectroscopy,' McGraw-Hill, New York, 1959.

from visible spectroscopy. For example with the trifluoromethyl substituted compound the addition of sodium methoxide (10^{-3}M) to a solution in dimethyl sulphoxide gave a red colour which changed to orange. The colour change was moderately fast ($t_{\frac{1}{2}}$ *ca.* 1 min) and in order to obtain the visible spectrum of the initially produced red species results were extrapolated back to zero time. Spectra are shown in the Figure. The n.m.r. results show that the C-2 adduct (IV) is favoured at equilibrium, so that the initial visible spectrum corresponds to the adduct of structure (III). It seems likely that at least some of this adduct (III) will be present at equilibrium, and if we assume that the absorption beyond 550 nm in the final spectrum results from this isomer we obtain the ratio (III) : (IV) = 7 : 93. In media containing more methanol the rate of the isomerisation of (III) to (IV) increased although the spectral shapes indicated that the ratio of isomers present at equilibrium was unchanged.

TABLE 2

Chemical shifts [δ (p.p.m.)] and coupling constants for methoxide adducts (IV) of 1-X-3,5-dinitrobenzenes in dimethyl sulphoxide

	Ring protons						
X	2-H	4-H	6-H	OMe	$J_{2,4}$/Hz	$J_{4,6}$/Hz	$J_{2,6}$/Hz
NO_2 [a]	6·14	8·42	8·42	3·10	1·5		1·5
CN [b]	5·60	8·48	7·77	3·08	1·2	2·2	0·3
SO_2Me [c]	6·13	8·62	8·05	3·08	1·2	2	<0·5
CF_3	5·83	8·60	7·70				
CO_2Me [d]	5·83	8·51	8·09	3·06	1·4	2	0·5
I	5·65	8·52	7·67	3·05	1	2	<0·5
$CONEt_2$	5·92	8·50	7·15	3·08	1·2	2	0·3
SMe	5·50	8·45	6·90	3·00	1	2	<0·5
H [e]	5·35	8·36	6·96				

[a] M. R. Crampton and V. Gold, *J. Chem. Soc.* (*B*), 1966, 893. [b] Ref. 8. [c] SO_2Me protons absorb at δ 3·37 in the complex. [d] Ref. 6. [e] C. A. Fyfe, 'The Chemistry of the Hydroxyl Group,' ed. S. Patai, Interscience, New York, 1971, p. 51.

TABLE 3

Visible spectra of methoxide adducts of 1-X-3,5-dinitrobenzenes in dimethyl sulphoxide

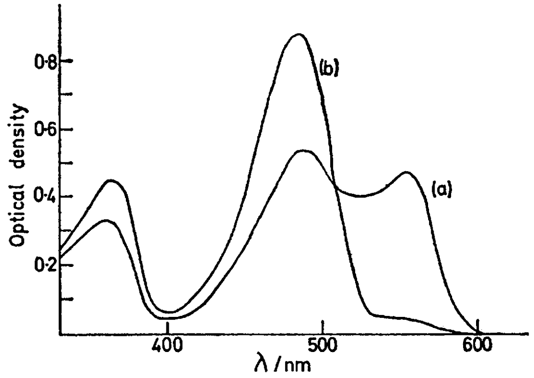
	C-2 Adduct (IV)			C-4 Adduct (III)		% of (III) present at equilibrium
X	$\lambda_{max.}$/nm [a]	$\lambda_{max.}$/nm [a]	$\lambda_{max.}$/nm [a]	$\lambda_{max.}$/nm [a]	$\lambda_{max.}$/nm [a]	
NO_2	431 (2·8)	505 (1·95)		431 (2·8)	505 (1·95)	
CN	390 (2·1)	490 (2·2)	380	490	550	5 [b]
SO_2Me	376 (1·7)	481 (2·3)	372 (1·3)	485 (2·2)	540 (0·8)	10
CF_3	362 (1·35)	490 (2·6)	360 (1·0)	488 (1·6)	555 (1·5)	7
CO_2Me	392 (1·85)	496 (2·2)	378 (1·8)	514 (1·75)	550 (1·75)	30
I	363 (1·6)	513 (2·5)		Not observed		<5
$CONEt_2$	370 (1·6)	510 (2·7)	370 (1·5)	520 (1·8)	580 (1·6)	<5
SMe	366 (1·4)	534 (1·9)		Not observed		<5
SO_3^-	360 (1·4)	520 (2·2)	360	530	600	5
H		520 (2·7)		Not observed		

[a] Values of $10^{-4}\varepsilon$ (mol^{-1} l cm^{-1}) accurate to ±10% are given in parentheses. [b] Ref. 7.

Similar general behaviour was observed with compounds containing the substituents X = SO_2Me, $CONEt_2$, or SO_3^-. With the iodo-substituted compound a colour change from purple to red could be observed by eye but the change was too fast for the initial spectrum to be obtained. With X = H or SMe no changes in spectral shapes were observed on our time scale (measurements were begun after 15 s). This does not necessarily mean that adducts of structure (III) are not formed with these latter compounds. It may be that the rate of isomerisation is very fast.

Visible spectral data for these adducts together with estimates of the proportions present at equilibrium are collected in Table 3.

Measurement of Indicator Ratios.—In order to determine the thermodynamic equilibrium constants for methoxide addition measurements were made in methanol–dimethyl sulphoxide mixtures containing 0·098M-sodium methoxide. The resulting data enabled the equilibrium constants to be determined and the J_M acidity function for these media to be evaluated. The experimental determination of the indicator ratios ($\log_{10}$ [complex]/[parent]) required the knowledge of the extinction coefficients of the coloured adducts. By increasing the proportion of dimethyl sulphoxide in the solvent it was possible for each indicator to obtain virtually complete conversion into complex and hence obtain a value for the extinction coefficient in that medium. However previously we have shown[4] that the spectra of similar complexes are affected by the change in solvent from methanol to dimethyl sulphoxide and undergo a bathochromic shift and increase in extinction coefficient. The present results show a similar effect for 1,3,5-trinitrobenzene (Table 4). Thus the absorption maximum shifts from 425 to 431 nm on going from pure methanol to 70% (v/v) dimethyl sulphoxide. In addition in media where conversion to complex is virtually complete (30—70% dimethyl sulphoxide) there is an increase in extinction coefficient as the proportion of dimethyl sulphoxide is increased. Due account of these changes of extinction coefficient with solvent composition was taken in the deter-



Visible spectra of 3,5-dinitro-1-trifluoromethylbenzene (3·3 × 10^{-5}M) in dimethyl sulphoxide containing sodium methoxide: (a), initially after mixing corresponding to adduct of structure (III); (b), time-stable spectrum mination of the indicator ratios for this and the other compounds studied. As before[4] a linear correlation between wavelength of maximum absorption and extinction coefficient was found.

For 1,3,5-trinitrobenzene, spectra measured in media containing >70% dimethyl sulphoxide indicated some formation of 1 : 2 adducts (two methoxide ions per molecule of parent). However no evidence for the formation of 1 : 2 adducts was found for the other, less reactive, parent molecules studied.

TABLE 4

Indicator ratios at 25 °C with 0·098M-sodium methoxide for 3 × 10^{-5}M-parent

% Dimethyl sulphoxide (v/v)	$\lambda_{max.}$/nm	Optical density	$\log_{10}$ (Indicator ratio)
1,3,5-Trinitrobenzene			
0	425	0·512	0·27
5	425	0·641	0·61
10	426	0·700	0·86
15	426	0·759	
20	427	0·775	
30	428	0·815	
40	428	0·825	
50	429	0·825	
60	430	0·835	
70	431	0·840	
3,5-Dinitrobenzonitrile			
0	484	0·063	−0·94
5	484	0·110	−0·66
10	484	0·172	−0·41
15	484	0·270	−0·11
20	484	0·400	+0·26
25	484	0·485	+0·55
30	485	0·585	
35	486	0·595	
40	487	0·616	
50	488	0·637	
60	489	0·642	
70	490	0·652	
80	490	0·655	
Methyl 3,5-dinitrophenyl sulphone			
5	473	0·061	−0·96
10	473	0·112	−0·65
15	474	0·185	−0·35
20	474	0·289	−0·06
25	475	0·393	+0·23
30	475	0·494	0·58
35	476	0·558	0·89
40	477	0·604	(1·22)
50	478	0·651	
60	479	0·665	
70	480	0·679	
80	481	0·680	
1,3-Dinitro-5-trifluoromethylbenzene			
25	484	0·028	(−1·41)
30	485	0·063	−1·04
35	485	0·127	−0·70
40	486	0·252	−0·31
45	486	0·439	+0·12
50	487	0·605	+0·54
55	488	0·708	(+0·96)
60	488	0·767	
70	489	0·792	
80	489	0·795	
Methyl 3,5-dinitrobenzoate			
30	493	0·036	(−1·17)
35	494	0·074	−0·83
40	494	0·150	−0·45
45	495	0·270	−0·06
50	495	0·402	+0·35
55	496	0·518	+0·85
60	497	0·570	
70	498	0·597	
80	499	0·603	
1-Iodo-3,5-dinitrobenzene			
45	510	0·064	−1·02
50	510	0·146	−0·61
55	511	0·302	−0·17
60	511	0·494	+0·29
65	512	0·653	+0·80
70	512	0·716	
80	513	0·757	
85	513	0·761	
NN-Diethyl-3,5-dinitrobenzamide			
55	507	0·064	−1·04
60	507	0·158	−0·59
65	508	0·331	−0·13
70	508	0·550	+0·37
75	509	0·700	+0·89
80	509	0·752	
86	510	0·790	
91	510	0·806	
3,5-Dinitrothioanisole			
60	532	0·043	−1·07
65	532	0·113	−0·59
70	533	0·251	−0·09
75	533	0·411	+0·43
80	534	0·534	
85	534	0·567	
90	534	0·570	
95	534	0·571	
1,3-Dinitrobenzene			
70	519	0·015	(−1·72)
75	519	0·051	−1·17
80	520	0·172	−0·57
85	520	0·569	+0·36
90	520	0·750	(+1·06)
95	520	0·815	
3,5-Dinitrobenzenesulphonate			
60	519	0·022	(−1·45)
65	519	0·054	−1·04
70	520	0·130	−0·61
75	520	0·267	−0·17
80	520	0·495	+0·48
85	520	0·614	
90	520	0·655	
95	520	0·665	

Similar sets of measurements were made for solutions containing 0·080M-tetra-n-butylammonium methoxide instead of sodium methoxide.

For all compounds studied the formation of coloured adducts was fast and in these media, containing appreciable proportions of methanol, resulted in the immediate production of the equilibrium ratio of isomers (III) and (IV). In some cases, notably for the cyano[8] and trifluoromethyl substituted compounds, this initial fast complex formation was followed by slower irreversible substitution reactions. In order to determine the initial optical densities corresponding to adduct formation measurements were made at 15 s intervals and extrapolated to zero time.

DISCUSSION

The ^{1}H n.m.r. spectra (Table 2) produced on the addition of concentrated sodium methoxide in methanol to solutions of the parent 1-X-3,5-dinitrobenzenes in dimethyl sulphoxide give clear evidence of the formation of adducts of structure (IV). The spectra show three spin-coupled bands of equal intensity due to ring protons in the adducts. The resonances of the protons at C-2 absorb at δ 5·3—6·2 and are shifted considerably to high field from the positions for the parent molecules. This is consistent with the change in hybridisation from sp^2 to sp^3 on base addition. The hydrogen at C-4 between the nitro-groups is relatively insensitive to the nature of the substituent and absorbs at δ 8·4—8·6, while the ring-proton at C-6 is more dependent on the nature of the substituent, X. The added methoxy-group gives a resonance in the range δ 3·00—3·10. Only in the cases of the methoxycarbonyl[6] or cyano[7]-substituents have the distinctive n.m.r. bands due to the isomeric adducts (III) been observed. We estimate that our measurements would be sufficiently sensitive to detect a proportion of $>10\%$ of these isomers.

The visible spectra, in agreement with the n.m.r. results, indicate that for most substituents X adducts of structure (IV) are thermodynamically favoured. However measurements with low base concentrations in dimethyl sulphoxide show that initially base addition occurs at C-4 to give the adducts (III). Rearrangement occurs with time. It was possible to estimate from the visible spectra the proportions of isomers present at equilibrium (Table 3). Except for the methoxycarbonyl substituent the percentage of (III) is in the range 0—10. We note however that there is a statistical factor of 2 favouring the adducts of structure (IV) and the free energy differences between the isomers may be quite small. For example with the trifluoromethyl compound the ratio 93 : 7 favouring the C-2 adduct corresponds to an energy difference between the isomers of only 1 kcal mol^{-1}.

The importance of a strongly electron-withdrawing group *para* to the position of addition has frequently been raised in discussion of the stabilities of Meisenheimer complexes. In the present case there appears to be some tendency for the proportion of C-4 adduct present at equilibrium to increase with the electron-withdrawing ability of X (Hammett σ^- values decrease in the order $NO_2 > CN,SO_2Me > CO_2Me,CF_3 > I,\ SO_3^- > SMe > H$).[15,16] However the correlation is not very good as indicated by the fact that the greatest proportion of (III) occurs with the CO_2Me substituent.

In order to determine the equilibrium constants K for methoxide addition indicator ratios were measured in methanol–dimethyl sulphoxide mixtures containing base.

$$\text{Parent} + \text{MeO}^- \xrightleftharpoons{K} \text{Complex} \qquad (1)$$

The results allowed the simultaneous determination of the thermodynamic values of the equilibrium constants, referred to pure methanol as solvent, and the J_M acidity function for these media.[9]

$$J_M = pK_{MeOH} + \log_{10}\,[\text{complex}]/[\text{parent}] \qquad (2)$$

where K_{MeOH} is the auto-protolysis constant of methanol ($pK_{MeOH} = 16{\cdot}92$). The starting point of the scale is 0·098M-sodium methoxide in methanol and the J_M value (15·96) for this solution is obtained from measurements with 1,3,5-trinitrobenzene. Values for K for this compound have been reported as 15·4 l mol^{-1} at zero base concentration[17] of 23 l mol^{-1} at ionic strength 0·2M.[18] Our measurements[19] give a value of 17 l mol^{-1} at zero ionic strength which increases only slightly with increasing sodium methoxide concentration. The construction of the J_M scale was then carried out using the usual stepwise technique.[6,9] The agreement amongst individual indicators was excellent except for the SO_3^- substituted compound which is of a different charge type to the other indicators, the complex being a dianion.

In view of the specific effects of cations[1] sometimes found in similar systems measurements were also made with 0·08M-tetra-n-butylammonium methoxide in place of sodium methoxide. The higher starting value of the scale ($J_M = 16{\cdot}21$) derives from the non-ideal behaviour of the 1,3,5-trinitrobenzene–tetrabutylammonium methoxide system in methanol.* However, the two J_M scales are strictly parallel throughout the entire solvent composition range (Table 5). The present J_M scale, involving methoxide addition at an aromatic carbon atom carrying hydrogen, increases somewhat more rapidly with dimethyl sulphoxide content than that previously determined[4] for methoxide addition to substituted anisoles [giving structure (II)]. However it parallels exactly the acidity scale derived from the

TABLE 5

J_M values (25 °C) for base addition to 1-X-3,5-dinitrobenzenes

% Dimethyl sulphoxide (v/v)	J_M (0·098M-NaOMe)	J_M (0·080M-Bu_4NOMe)
0	15·96	16·21
5	16·27	16·50
10	16·54	16·70
15	16·84	17·01
20	17·17	17·30
25	17·46	17·61
30	17·82	17·95
35	18·15	18·29
40	18·53	18·69
45	18·94	19·11
50	19·35	19·55
55	19·80	20·00
60	20·26	20·47
65	20·74	20·92
70	21·24	21·42
75	21·76	21·90
80	22·36	22·58
85	23·29	23·47

---

* Results indicate that the stoicheiometric equilibrium constant K_e increases from 17 l mol^{-1} at zero base concentration to 34 l mol^{-1} at 0·08M-base.

[15] H. van Bekkum, P. E. Verkade, and B. M. Wepster, *Rec. Trav. chim.*, 1959, 815.

[16] G. B. Barlin and D. D. Perrin, *Quart. Rev.*, 1966, **20**, 75.

[17] V. Gold and C. H. Rochester, *J. Chem. Soc.*, 1964, 1692.

[18] C. F. Bernasconi, *J. Amer. Chem. Soc.*, 1970, **92**, 4682.

[19] M. R. Crampton and H. A. Khan, unpublished observations.

ionisation of α-cyanostilbenes[20] where methoxide addition occurs at a carbon atom carrying hydrogen in a conjugated system. Calorimetric studies[21] have shown that the increase in the basicity of the medium with dimethyl sulphoxide concentration results partly from the destabilisation of the methoxide ions and partly from stabilisation of the adducts formed. The present results indicate that the adducts (IV) produced from 1-X-3,5-dinitrobenzenes are slightly better solvated by dimethyl sulphoxide relative to methanol than are the adducts (II) produced from substituted anisoles.

The values for the thermodynamic equilibrium constants for methoxide addition to the 1-X-3,5-dinitrobenzenes are in Table 6, where comparison is made with some previously determined values. The measured values will be the sum of those for the formation of structures (III) and (IV). However since, with one exception, the former adducts are present only in low concentration at equilibrium, they will be close to the values for formation of adducts of structure (IV). The exception occurs with the methoxycarbonyl substituent where we calculate values of 6×10^{-3} l mol^{-1} for the formation of (IV).

TABLE 6

Thermodynamic equilibrium constants for methoxide addition to 1-X-3,5-dinitrobenzenes in methanol at 25 °C

X	K/l mol^{-1} M^{-1}	K/l mol^{-1} (literature)
NO_2	17	15·4,[a] 23[b]
CN	1·0	1·3, 1·9[c]
SO_2Me	0·50	
CF_3	$1{\cdot}2 \times 10^{-2}$	
CO_2Me	$8{\cdot}5 \times 10^{-3}$	$2{\cdot}9 \times 10^{-3}$[d]
I	$8{\cdot}9 \times 10^{-4}$	
$CONEt_2$	$1{\cdot}1 \times 10^{-4}$	
SMe	$3{\cdot}9 \times 10^{-5}$	
H	1×10^{-6}	5×10^{-7}[e]
SO_3^-	$(10^{-4}$—$10^{-5})$	

$K = 2{\cdot}5 \times 10^{-3}$ l mol^{-1} for formation of (III).

Ref. 17. [b] Ref. 18. [c] Ref. 8. [d] Ref. 6. [e] Ref. 2.

It is of interest to compare these equilibrium constants with those for Meisenheimer complex formation from similarly activated anisoles. Such data are collected in Table 7. The considerably greater stabilities of the adducts from the anisoles probably results largely from the relief of steric strain on their formation. The methoxy-group in the parent anisoles will be sterically compressed by the presence of *ortho*-substituents but such strain will be largely removed in the adducts where the two methoxy-groups lie out of the plane of the aromatic ring. There will be no similar relief of steric strain resulting from adduct formation with 1-X-3,5-dinitrobenzenes. The smaller difference in stabilities between the adducts from 2,4-dinitroanisole and 1,3-dinitrobenzene reflects the smaller relief of steric strain on adduct formation from 2,4-dinitroanisole than from the 2,4,6-trisubstituted anisoles. In addition Bernasconi[18] has argued that multiple alkoxy-substitution will have a large stabilising effect on an sp^3 hybridised carbon atom relative to a non-substituted sp^3 carbon. This factor may also account for the enhanced stabilities of the dimethoxy-adducts.

TABLE 7

Comparison of equilibrium constants for methoxide addition to 1-X-3,5-dinitrobenzenes and 2-X-4,6-dinitro-anisoles

X	Adduct (IV) from 1-X-3,5-$(NO_2)_2$-C_6H_3 K/l mol^{-1}	Adduct (II) from 2-X-4,6-$(NO_2)_2$-C_6H_2OMe K/l mol^{-1} [a]	Ratio[b]
NO_2	17	17,000	3000
CN	1	2600	5200
CF_3	$1{\cdot}2 \times 10^{-2}$	14	2300
CO_2Me	6×10^{-3}	10	3300
H	1×10^{-6}	$4{\cdot}6 \times 10^{-5}$	92

[a] Data from ref. 3. [b] In working out these ratios account has been taken of the statistical factor favouring adduct formation from 1-X-3,5-dinitrobenzenes. In general there are two equivalent ring positions leading to the formation of (IV) although with 1,3,5-trinitrobenzene the factor is three.

[2/2597 *Received, 16th November, 1972*]

---

[20] D. J. Kroeger and R. Stewart, *Canad. J. Chem.*, 1967, **45**, 2163.

[21] J. W. Larsen, K. Amin, and J. H. Fendler, *J. Amer. Chem. Soc.*, 1971, **93**, 2910.