Nitrogen-bonded σ-Adducts from Amide Anions and 1,3,5-Trinitrobenzene. A ^{1}H Nuclear Magnetic Resonance Structural Study

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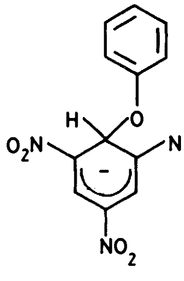
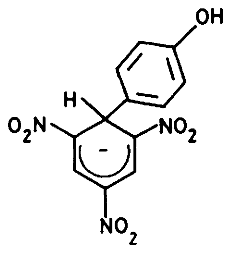
The reactions of several amide and imide anions with 1,3,5-trinitrobenzene (TNB) have been studied in acetonitrile and dimethyl sulphoxide. U.v.–visible and ^{1}H n.m.r. spectra have allowed complete characterization of the *N*-adducts but the formation of the isomeric *O*-adducts was not observed. Some *N*-adducts are found to exist as a mixture of *Z* and *E* isomers. In these instances the preferred isomer adopts the *E* configuration in which the bulky TNB substituent is *trans* to the carbonyl oxygen. Probable conformations around the $N–C_{sp^3}$ bond of the adducts are discussed in the light of the values of the $^3J_{HNCH}$ coupling constant. Most *N*-adducts have a thermodynamic stability which is of the same order as that of the TNB–methoxide adduct. This result as well as the failure to observe the *O*-adducts is shown to be consistent with literature data.

Among the various structure–reactivity relationships for σ-complex formation, one which has received considerable attention in the past few years is the generally observed kinetic preference for oxygen- or nitrogen-bonded and the thermodynamic preference for carbon-bonded adduct formation in the reactions of electron-deficient aromatic compounds with ambident bases.[1,2] The behaviour of phenoxide ions is typical of this trend.[1–5] These react with 1,3,5-trinitrobenzene (TNB) and related derivatives to give first an *O*-bonded adduct, *e.g.* (**1**), which subsequently rearranges to the much more stable *C*-bonded isomer (**2**). Similar observations have been made for indolide, pyrrolide, and imidazolide anions.[1,6–8] In these instances, an *N*-bonded adduct is initially formed, *e.g.* (**3**), but it is a *C*-adduct like (**4**) which is the final product of the reactions. The *C*-bonded rather than *N*-bonded adduct is also the thermodynamically favoured product in reactions of neutral bases like amidines or aromatic amines with some aromatic electrophiles.[9–12]

Another example of the thermodynamic preference for *C*-adduct formation is provided by the numerous studies devoted to the reactions of aromatic electrophiles with enolate anions of ketones, esters, and keto-esters.[1,2,13–17] Although these anions are potentially susceptible to react *via* their oxygen or carbon atom, the only adducts so far characterized are the *C*-adducts (**6**). No evidence for formation of the enolate *O*-adducts (**5**) could be found.[1,2,17]

In contrast with carbon *versus* nitrogen or oxygen base additions, nitrogen *versus* oxygen interactions have received no particular attention in the field of σ-complexes.[2,17] Thus, amide anions, which are strong bases susceptible to such competitive behaviour,[18–20] have been only occasionally studied.[2,17,21,22] We have therefore selected some structurally different amide and imide anions (**7**$^-$) and investigated their reactivity towards TNB by ^{1}H n.m.r. and u.v.–visible spectroscopy in dimethyl sulphoxide and acetonitrile. We report here our results which have led to complete characterization of the *N*-adducts (**9**) but did not allow the detection of the *O*-adducts (**8**), even to a small extent. The thermodynamic and kinetic implications of this observed selectivity with respect to the potential ambident reactivity of amide anions are discussed. The results obtained also provide interesting structural information on the *N*-adducts (**9**). In particular, the influence of the bulky anionic TNB substituent on the population of the *Z* and *E* configurations of the amide moieties is established.


(**1**)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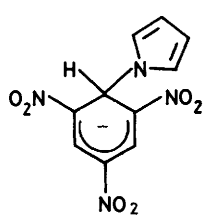
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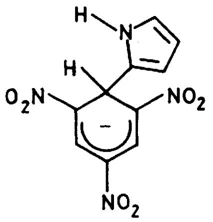
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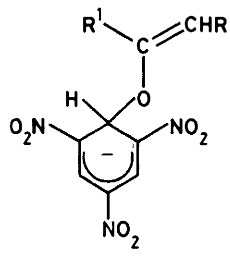
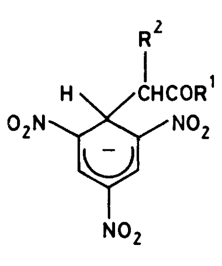
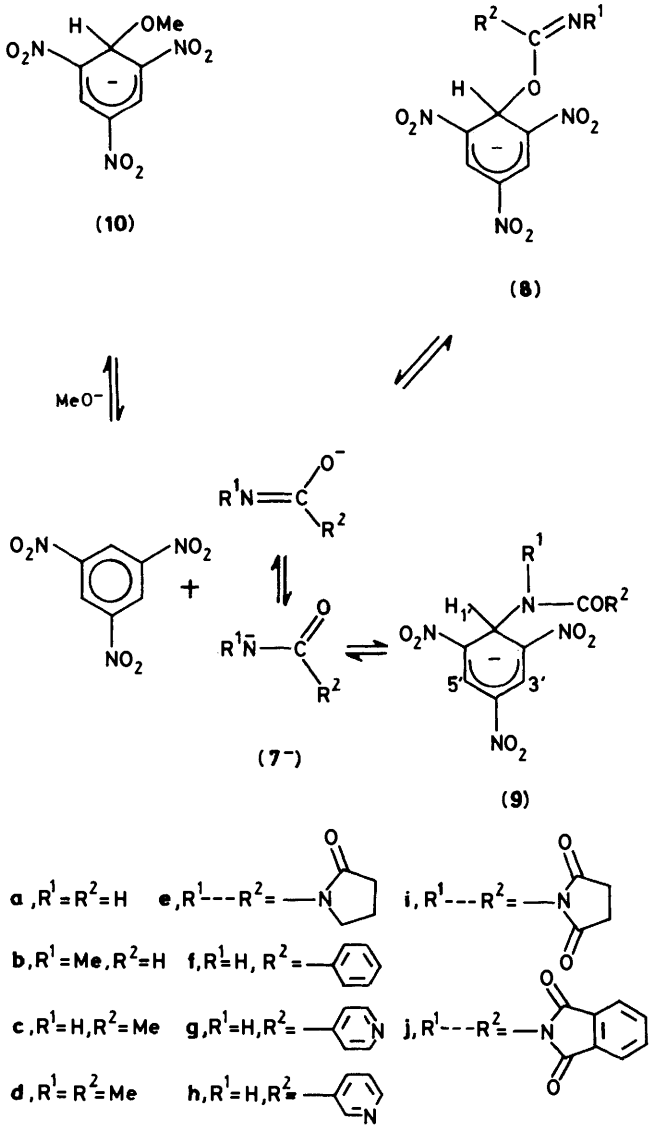

(**5**)


(**6**)

Results

Adduct Formation.—The reaction of TNB with the amide anions (**7**$^-$**a**—**h**) and imide anions (**7**$^-$**i**,**j**) listed in Scheme 1 was

$$\underset{(7)}{R^1NHCOR^2} + MeO^- \rightleftharpoons \underset{(7^-)}{R^1\overset{-}{N}COR^2} + MeOH \quad (1)$$

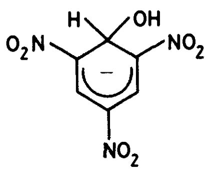


Scheme 1.

studied. Since the acidities of amides are known to be generally higher than those of alcohols,[23-25] amide anions (7^-**a**—**h**) were generated by adding an equimolar amount of concentrated methanolic potassium methoxide (5.5M) to a 0.4M solution of the parent amides in acetonitrile. Notwithstanding the fact that equilibrium (1) is only partially shifted towards the formation of (7^-**a**—**h**) in the case of the less acidic amides, this solution was added under stirring to a 0.4M solution of TNB in the solvent. In the case of the acidic imides (**7i**,**j**), acetonitrile solutions of the potassium salts were used directly. A strong orange-red colour typical of TNB σ-adducts[2] developed immediately in all cases. After some time, reddish to purple crystals deposited which were isolated (see Experimental section) and dissolved in $[^2H_6]Me_2SO$. Analysis of the n.m.r. and u.v.–visible spectra summarized in the Table shows that all the isolated adducts are the *N*-adducts of general structure (**9**).

These experiments provided a way to isolate the *N*-adducts (**9**) as pure crystalline potassium salts, but they did not allow us to assess whether the isomeric *O*-adducts (**8**) can form as transient species prior to (**9**). Since Me_2SO is a much better solvent of σ-adducts than acetonitrile,[2] *in situ* experiments were therefore carried out by adding an Me_2SO solution of TNB to an equimolecular amount of the amides (**7a**—**h**) and MeOK in $[^2H_6]Me_2SO$. N.m.r. spectra recorded rapidly after mixing showed the complete disappearance of the signal at δ 9.10 due to the TNB protons and the appearance of new peaks which indicated the concomitant formation of the *N*-adducts (**9**) and of the TNB–methoxide adduct (**10**). No signals ascribable to the isomeric *O*-bonded adducts (**8**) could be detected. A significant result, however, is the observation that the TNB–methoxide complex (**10**) was, in all cases, the major species initially present in solution. With time, partial conversion of (**10**) into (**9**) slowly occurred and the final equilibrium was reached after a few days when (**10**) and (**9**) coexisted in *ca.* 1 : 1 ratio in solution.

This result shows that the amide *N*-adducts (**9**) have a thermodynamic stability of the same order as that of the TNB–methoxide adduct (**10**). This conclusion was confirmed by the finding that the TNB–methoxide complex (**10**) forms partially at the expense of (**9**) when a small amount of methanol is added to Me_2SO solutions of the isolated *N*-adducts. This conversion is essentially complete in the case of the imide adducts (**9i** and **j**). Addition of water has a similar effect but affords the TNB–hydroxide adduct (**11**).



(**11**)

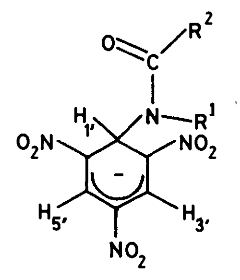
Discussion

Structure of the N-*Adducts.*—In every adduct, the protons of the cyclohexadienyl moiety give an A_2X system. While the chemical shifts observed for the 3′- and 5′-H lie in the narrow range commonly found for both *O*- and *N*-bonded TNB adducts, 1′-H resonates between δ 6.16 and 7.11, a range typical for *N*-adducts.[2,26] Furthermore, the $^4J_{1'\text{-}3',5'}$ coupling constants are 0.4—0.8 Hz, which agrees with *N*-adduct formation. For comparison, *O*-bonded adducts are associated with $^4J_{1'\text{-}3',5'}$ values of *ca.* 1.2—1.5 Hz.[2,26]

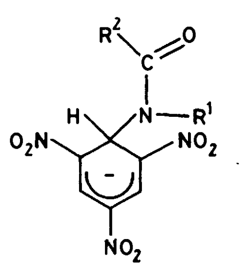
More compelling evidence that the adducts have structure (**9**) is obtained for systems involving acetamide (**7c**), benzamide (**7f**), isonicotinamide (**7g**), and nicotinamide (**7h**) as the parent amide (R^1 = H). In these cases, the resonance of the 1′-H is not a triplet but a doublet of triplets. Double resonance experiments show that the doublet splitting is due to a coupling of 1′-H with a broad NH doublet at low field. The magnitude of this coupling (7.5—8.4 Hz) agrees only with a vicinal coupling constant $^3J_{HNCH\text{-}1'}$, *i.e.* the negatively charged trinitrocyclohexadienylide moiety is necessarily bonded to the nitrogen atom, as in (**9**). A mixture of two adducts was formed in the reaction of TNB with formamide anion (7^-**a**); the 1′-H resonance of both AX_2 systems appears as a doublet of triplets, thus confirming that the two adducts have the same general structure (**9**) and are therefore the *Z* and *E* isomers of (**9a**).

In contrast with those of the aforementioned systems, the n.m.r. spectra relative to the *N*-adducts (**9b**, **d**, **e**, **i**, and **j**) involving *N*-methylformamide, *N*-methylacetamide, 2-pyrrolidone, succinimide, and phthalimide as the parent precursors ($R^1 \neq$ H) do not show a NH signal and therefore no splitting of the 1′-H triplet. Moreover, it should be noted that the spectra of the two imide adducts (**9i** and **j**) indicate that their structure is totally symmetrical, as is that of their parent imides, further confirming that we are dealing with *N*-adducts in all cases

N.m.r. data[a] of potassium salts of *N*-bonded σ-adducts formed from amide anions (7^-) with TNB in [$^2H_6$]Me$_2$SO



Z



E

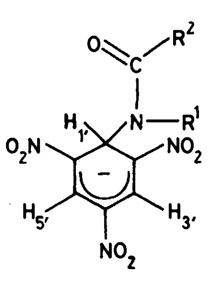
Compound	Configuration (%)	δ(3′,5′)	δ(1′)	δ(R¹)	δ(R²)	$^4J_{1'-3',5}$	$^3J_{\text{HNCH-1}'}$	^nJ(R¹–R²)		Visible maximum λ/nm (10^{-4} × ε)	
(9a)	(*Z*) (35)	8.39	6.50	8.38	7.79[b]	0.8	7.9	*n* 3	1.7	535	445
	(*E*) (65)	8.38	6.16	8.00	8.17[c]	0.7	8.4		11.1		
(9b)	(*Z*) (5)	8.52	6.78	2.66	7.83	0.7		*n* 4	0.3	535	435
	(*E*) (95)	8.54	6.44	2.32	8.24	0.7			0.5		
(9c)	(*Z*)	8.39	6.49	8.15	1.67	0.7	7.9			530 (1.76)	445 (2.8)
(9d)	(*Z*) (15)	8.50	6.83	2.74	1.83	0.5		*n* 5	N.o.	530	437
	(*E*) (85)	8.56	6.70	2.47	2.31	0.5			0.3		
(9e)		8.47	6.57	3.08	2.1[d]	0.7				530 (1.82)	443 (2.9)
(9f)	(*Z*)	8.49	6.81	8.77		0.7	7.7			535 (1.7)	447 (2.78)
(9g)	(*Z*)	8.48	6.81	9.03	*e*	0.7	7.6			535 (1.617)	445 (2.585)
(9h)	(*Z*)	8.49	6.81	8.96	*f*	0.7	7.5			535 (1.58)	445 (2.55)
(9i)		8.45	6.87		2.53	0.5				530 (0.815)	440 (1.28)
(9j)		8.58	7.11		*g*	0.4				540 (0.93)	438.5 (2.45)

[a] Chemical shifts in p.p.m. relative to Me$_4$Si as internal standard, *J* in Hz, N.o.: not observed. [b] ^4J(H-1′–CHO) 0.5. [c] ^4J(H-1′–CHO) 1.2. [d] Centre of the multiplet (second-order spectrum); C–CH$_2$–C δ *ca.* 1.8. [e] δ_2 8.68, δ_3 7.71, $|J_{23} + J_{23'}|$ *ca.* 6.0. [f] δ_2 8.95, δ_4 8.16, δ_5 7.45, δ_6 8.68; J_{24} 2.2, J_{25} 0.9, J_{45} 8.0, J_{46} 1.6, J_{56} 4.6. [g] Aromatic protons: singlet at δ 7.85.

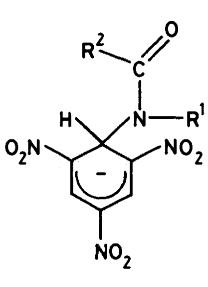
studied. The data for the succinimide adduct (**9i**) are in agreement with previous reports.[2,17,21,22]

Complementary evidence for the formation of *N*-adducts (**9**) is provided by the visible spectra which all exhibit absorption maxima at *ca.* 430 and 530 nm (Table), in agreement with values found for previously reported *N*-adducts.[2]

Configuration of the N-*Adducts.*—It is well known that amides can adopt *Z* and/or *E* configurations due to the partial double-bond character of nitrogen–carbonyl bond.[27,28] This isomerism is also effective in the TNB–amide adducts as shown by the formation of two *N*-bonded isomers in the formamide, *N*-methylformamide, and *N*-methylacetamide systems (**9a**, **b**, and **d**).



Z



E

The stereochemical dependence of the $^3J_{\text{HN-CHO}}$ coupling constant has been previously studied for formamide.[29] This coupling was found to be much greater in the *E* (13.5 Hz) than in the *Z* configuration (1.7 Hz). A similar pattern is observed when the $^3J_{\text{HN-CHO}}$ values found for the two isomeric *N*-adducts of formamide (**9a**) are compared. On this basis, the *E* configuration can be assigned to the most abundant isomer ($^3J_{\text{HN-CHO}}$ 11.1 Hz) and the *Z* configuration to the minor one ($^3J_{\text{HN-CHO}}$ 1.7 Hz). Similarly, the four-bond coupling, $^4J_{\text{MeN-CHO}}$, which is known to be greater when the formyl and *N*-methyl protons are *trans*,[30] indicates that the major isomer of the TNB–*N*-methylformamide adduct (**9b**) has *E* configuration. The observation of a weak $^5J_{\text{MeN-COMe}}$ coupling[30–32] in the major isomer of the TNB–*N*-methylacetamide adduct (**9d**) and the lack of a similar coupling in the minor one suggests an *E* configuration for the most populated isomer. The populations of the observed *Z* and *E* isomers are given in the Table.

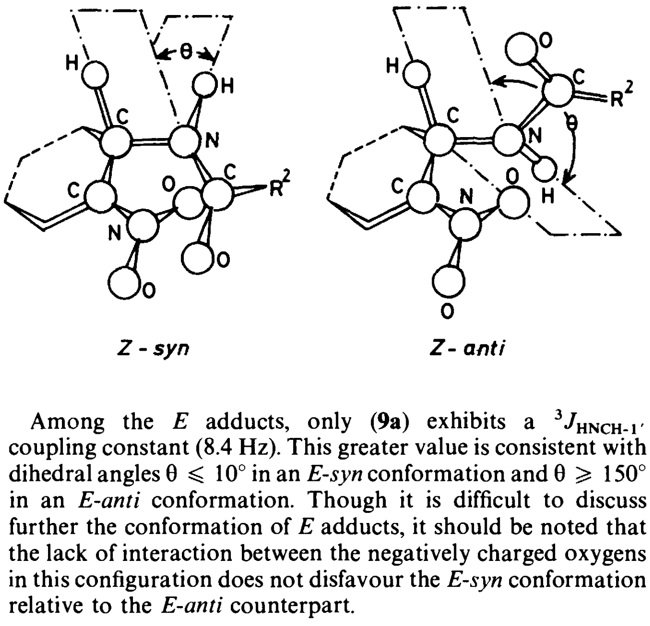
The above conclusions are confirmed by the chemical shifts of the various protons observed in the three couples of adducts (**9a**, **b**, and **d**). The R^2 protons (R^2 = H, Me) are deshielded in the *E* isomer relative to the *Z*, while a reverse sequence is observed for 1′-H). The R^1 protons (R^1 = H, Me) are shielded in the *E* isomer where they are *cis* to the carbonyl oxygen, as observed in the parent amides.[27,28] This is in agreement with the anisotropic effect of the amide group.[33]

A single isomer is observed for the four adducts (**9c**, **f**, **g**, and **h**). Since it is known that mono-*N*-arylated acetamides and benzamides exist exclusively in the *Z* form[34] (within the limits of n.m.r. detection), it was to be expected that the corresponding adducts, where the nitrogen is bonded to a TNB moiety instead of an aryl group, also adopt a *Z* configuration. This conclusion is supported by the chemical shift of 1′-H; on the one hand, identical figures (δ 6.81) are observed for the three *C*-arylated adducts (**9f**, **g**, and **h**); on the other hand, the 1′-H shift observed in the adduct (**9c**) is similar to that observed in the *Z* isomer of (**9a**).

Conformation of the N-*Adducts with* R^1 = H.—A $^3J_{\text{HNCH-1}'}$ coupling constant is observed in the adducts in which R^1 = H. On experimental and theoretical grounds, this coupling constant has been shown to exhibit a Karplus-like dependence,[35–41] so that values for the dihedral angle θ between the H(1′)–C(1′)–N and C(1′)–N–H planes can be evaluated from the $^3J_{HNCH\text{-}1'}$ value. We have applied this treatment to our systems, but due to the low precision of the reported relationships and known disparities between experimental and theoretical results, only minimum and maximum θ values will be considered.

For the five *Z* adducts (**9a**, **c**, and **f**—**h**), this coupling lies between 7.5 and 7.9 Hz, suggesting similar conformations around the N–C(1′) bond. This coupling is consistent with θ values $\leqslant 20°$ or $\geqslant 140°$. Examination of Dreiding molecular models indicates that when $|\theta|$ is *ca.* 20°, *i.e.* when NH and CH(1′) are synperiplanar (conformation *Z-syn*), the carbonyl oxygen lies in the vicinity of a nitro oxygen. Such an interaction between two negatively charged oxygens disfavours this *Z-syn* conformation. This type of interaction does not exist when $|\theta|$ is *ca.* 140°, *i.e.* when NH and CH(1′) are antiperiplanar (conformation *Z-anti*). Hence the conformation *Z-anti* is probably preferred, but the equivalence of the cyclohexadienyl 3′- and 5′-H implies a rotation around the N–C(1′) bond, so that the two symmetrical positions θ *ca.* ±140° are equally populated.

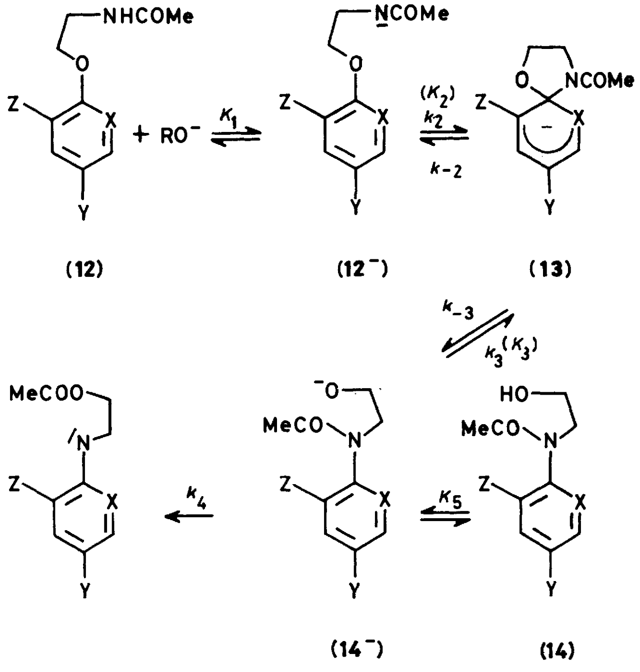
It should be noted that the R^2 substituent, which lies away from the cyclohexadienyl moiety in the *Z* configuration, does not affect the conformation. This explains the narrow range of $^3J_{HNCH\text{-}1'}$ observed in these five *Z* adducts.



Z - syn *Z - anti*

Among the *E* adducts, only (**9a**) exhibits a $^3J_{HNCH\text{-}1'}$ coupling constant (8.4 Hz). This greater value is consistent with dihedral angles $\theta \leqslant 10°$ in an *E-syn* conformation and $\theta \geqslant 150°$ in an *E-anti* conformation. Though it is difficult to discuss further the conformation of *E* adducts, it should be noted that the lack of interaction between the negatively charged oxygens in this configuration does not disfavour the *E-syn* conformation relative to the *E-anti* counterpart.

N-*Adduct versus* O-*Adduct Formation*.—Efforts to obtain some reliable kinetic data on the reactions of TNB with amide anions (7^-**a**—**h**) have been unsuccessful because of the competitive formation of the TNB–hydroxide or TNB–methoxide adducts in H_2O–Me_2SO or MeOH–Me_2SO mixtures. That this competition occurs and that the thermodynamic stability of the *N*-adducts (**9a**—**h**) is finally of the same order of magnitude as that of (**10**) and (**11**) constitute, however, interesting features which are consistent with results recently reported by Sekiguchi in studies of the Smiles rearrangement of Scheme 2.[25,42–44] First, Sekiguchi found that the equilibrium constant K_1 for deprotonation of the *N*-substituted acetamide moieties of the two ethers (**12a** and **b**) by OH^- is 131 and 93, respectively in 96% Me_2SO–4% H_2O.[42,43] Such K_1 values imply that the ionization of the NH group of (**12a** and **b**) according to the equilibrium $R^1CONHR^2 + OH^- \rightleftharpoons R^1CO\bar{N}R^2 + H_2O$ cannot be completely achieved in the solvent mixture and therefore that appreciable amounts of both R^1–$CO\bar{N}R^2$ and OH^- anions are available for a competitive attack on an electrophilic substrate. While such competition does not occur in Sekuguchi's system because spirocomplex formation is much favoured, it is actually observed in the TNB–amide systems studied in this work. The results obtained in MeOH–Me_2SO mixtures are explicable along similar lines.



a, X = C—Br, Y = NO_2, Z = H

b, X = N, Y = NO_2, Z = H

c, X = C—NO_2, Y = H, Z = NO_2

Scheme 2.

Another interesting report is that the equilibrium constants for formation of the spiro adduct (**13c**) *via* cyclization of the ether (**12c**) (K_1K_2) or the aniline (**14c**) (K_3K_5) are similar in 60% Me_2SO–40% MeOH (K_1K_2 232 at 25 °C; K_3K_5 221 l mol^{-1} at 20 °C) and 20% Me_2SO–80% Pr^iOH (K_1K_2 6 400 at 25 °C; K_3K_5 2 800 l mol^{-1} at 20 °C).[25,44] In these cases, kinetic analysis has shown that the rates of formation of (**13c**) are consistent with the basicity order, being somewhat greater *via* the alkoxide than *via* the amide pathway: K_1k_2 26.6; K_5k_3 1 480 l mol^{-1} s^{-1} at 30 °C in 60% Me_2SO–40% MeOH; K_1k_2 774; K_5k_3 7.1 × 10^4 l mol^{-1} s^{-1} in 20% Me_2SO–80% Pr^iOH. In contrast, the decomposition of (**13c**) occurs more rapidly *via* C–O than *via* C–N bond breaking, indicating that the amide anion has a lower leaving group ability than the more basic RO^- ion: k_{-2} 0.118; k_{-3} 7.45 s^{-1} at 30 °C in 60% Me_2SO–40% MeOH; k_{-2} 0.12; k_{-3} 25.8 at 20 °C in 20% Me_2SO–80% Pr^iOH.[25,44] Although it is relatively unexpected, this difference in the k_{-2} and k_{-3} values compensates for that in the rates of formation, accounting for the observed similarity of the equilibrium constants K_1K_2 and K_3K_5. Significantly this result compares well with our observation that the *N*-adducts (**9**) and the TNB–methoxide adduct (**10**) have close thermodynamic stabilities in MeOH–Me_2SO mixtures.

In general, the thermodynamic stability of a σ-adduct decreases with decreasing basicity of the potential leaving group.[1,2] It is thus to be expected that the stability of the *N*-adducts would decrease on going from amides like formamide, acetamide, or *N*-methylacetamide to imides like succinimide or phthalimide. On this basis, the complete decomposition of the adducts (**9i** and **j**) on water or methanol addition is readily understood.

Considering the potential ambident reactivity of amide anions, the failure to observe the *O*-adducts (**8**) indicates that there is a large thermodynamic preference for the formation of the *N*-isomers (**9**), and therefore greater thermodynamic affinity of the electrophilic TNB molecule for the nitrogen than for the oxygen atom of the amide anions. This result compares well with the estimate that the thermodynamic affinity of common amide anions for the proton is 10^8 times greater at the nitrogen than at the oxygen centre.[4,5] Furthermore, the possibility that amide anions attack first *via* their oxygen atom but that the resulting *O*-adducts (**8**) are undetectable because they isomerize too fast into the *N*-adducts (**9**) is unlikely. The reason is that the rate and equilibrium parameters found for formation of *N*-amide and alkoxide adducts are finally not very different despite the greater basicity of the oxygen atom of the RO^- than of the nitrogen atom of the $R^1CO\bar{N}R^2$ [*e.g.* see (**13**)]. This implies that attack *via* a process involving a much less basic oxygen nucleophile than RO^-, *i.e.* the amide anion, is probably neither kinetically nor thermodynamically favoured.

Although primary and secondary carboxamide anions normally react at their nitrogen atom in alkylation reactions, alkylation at the oxygen atom has been observed in some specific instances,[18–20] notably in reactions involving bulky alkylating reagents.[20] In this respect, our results also show that steric factors are not significant in determining the preferred thermodynamic site of the electrophilic addition of the TNB to the amide anions studied.

Experimental

Preparation of σ-Adducts.—Amide anions were generated by adding an equimolar amount of methanolic potassium methoxide (*ca.* 5.5M) to a solution of the parent amide (*ca.* 0.4M) in $[^2H_6]Me_2SO$. The resulting solution was added to a $[^2H_6]Me_2SO$ solution of TNB (*ca.* 0.4M) and the strong colours typical of TNB σ-adducts developed immediately.

Owing to their low solubility in acetonitrile, the same σ-adducts could be isolated by using this solvent instead of Me_2SO. After evaporation of the solvent *in vacuo*, the crystals were washed with copious amounts of ether and dried *in vacuo*. The ^1H n.m.r. spectra of these potassium salts dissolved in $[^2H_6]Me_2SO$ were similar to those observed in the *in situ* generation of these adducts.

It should be noted that some of these adducts are relatively explosive so that preparation was carried out only on a small scale (<0.5 g TNB). This also prevented a reliable determination of the m.p.s.

^1H *N.m.r. and U.v.-Visible Spectra.*—^1H N.m.r. spectra were recorded at 100 MHz (Varian XL-100, continuous wave mode, probe temperature 31 °C) and/or 60 MHz (Varian A60, probe temperature 37 °C), using tetramethylsilane as an internal standard. Double resonance experiments were performed using the gyrocode XL decoupler.

U.v.-visible spectra were recorded on a Beckman Acta III spectrometer (3×10^{-5}M; solvent Me_2SO).

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