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COMPLEX FORMATION BETWEEN 1,3,5-TRINITROBENZENE AND 1,8-DIAZABICYCLO-[5,4,0]-UNDEC-7-ENE

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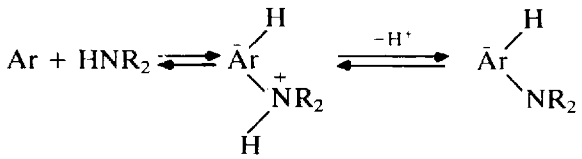
ABSTRACT

The title reaction is an instance of a simple nucleophilic attack of neutral nitrogen on aromatic sp^2 carbon. The kinetic data (obtained in dimethyl sulphoxide) are compared to the results reported by the literature for the same reaction of aliphatic amines. Some possible interactions (substrate/nucleophile, substrate/salt) preceding the attack of the nucleophile are discussed.

The formation of σ complexes between nitro-aromatic compounds and primary or secondary amines was extensively investigated.[1] The formation of zwitterionic complexes may be complicated by the deprotonation of the positive nitrogen by an equilibrium affording σ anionic complexes,[2] according to Scheme 1.

Scheme 1



Generally, tertiary amines show[3] weak interactions with very activated nitroaromatic compounds (such as 1,3,5-trinitrobenzene, TNB) and few examples of formation of zwitterionic complexes are reported[4] in the literature. Tertiary amines are interesting nucleophiles to investigate the simple attack on sp^2 electron deficient carbon atom, without the following equilibria of proton abstraction.

In principle, cyclic imines or imidines are better nucleophiles[5,6] than tertiary amines which are sterically hindered nucleophiles.

To learn more about the attack of the nucleophile in S_NAr reactions, we present some quantitative results on σ complex formation between TNB and 1,8-diazabicyclo-[5,4,0]-undec-7-ene (DBU) in dimethylsulphoxide (DMSO).

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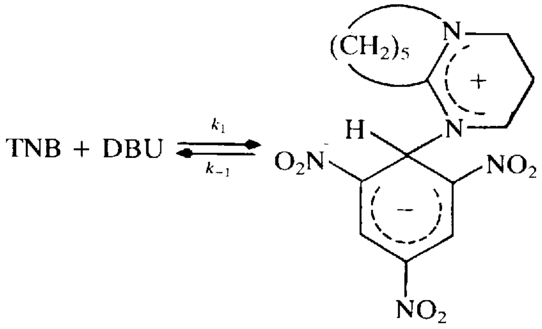
RESULTS

When appropriate solutions (in DMSO) of TNB and DBU are mixed, a red colour rapidly develops and the visible spectrum shows two new absorbance maxima (at λ 517 and 438 nm) which were ascribed by us[7] to the presence of the σ complex **1**

Scheme 2



1

Addition of H^+ (H_2SO_4, HCl) to the reaction mixtures gave a fading of colour.

The absorbance values recorded at infinite reaction time (A_∞) were satisfactorily stable. Feeble variations (less than 5%) were observed after a time longer (2–3 times) than that used to obtain infinite absorbance values.

K value (for the equilibrium of Scheme 2) calculated by the Benesi–Hildebrand plot (see 'Experimental') from the A_∞ values ($K = 2{\cdot}5 \times 10^4$ mol^{-1} l $\varepsilon = 1{\cdot}97 \times 10^4$ at $\lambda = 517$ nm) under the experimental conditions $[DBU]_0 > [TNB]_0$, agrees (within the experimental errors) with the K value ($= 1{\cdot}9 \times 10^4$ mol^{-1} l; $\varepsilon = 1{\cdot}92 \times 10^4$; at $\lambda = 517$ nm) calculated from the A_∞ values obtained under the experimental conditions $[TNB]_0 > [DBU]_0$. $[\,]_0$ indicates the initial concentration values.

Finding close K and ε values under both experimental conditions, indicates (in most of the range of concentrations used here) that the red colour development may be related to the simple formation of a complex according to the stoichiometry (1:1) required by the equilibrium of Scheme 2 and it is unlikely to be related to the presence of some impurities of DBU.[8]

In principle it is possible to assume that the red colour development arises from the presence of OH^-, arising from the equilibrium between DBU and traces of water:[8] $DBU + H_2O \rightleftarrows DBUH^+ + OH^-$.

In addition to the previously reported indications,[7] we emphasize that the observed absorbance values at infinite time of reaction (A_∞) under the experimental conditions $[TNB]_0 > [DBU]_0$ agrees well with the A_∞ values obtained when DBU is used in excess. Consequently, the presence of a σ complex involving water or a hydroxyl ion may be ruled out. In any case, we carried out some runs in the presence of water. The water influence on the A_∞ values, under both experimental conditions, ($[DBU]_0 > [TNB]_0$ and $[TNB]_0 > [DBU]_0$) is very feeble. A_∞ value is 10% higher than A_∞ value obtained in the absence of added water, for the run with the highest water concentration ($5{\cdot}5 \times 10^{-2}$ mol l^{-1}).

A_∞ enhancement is also observed for the runs carried out in the presence of tetraalkylammonium halides. In this case A_∞ value is 5–8% lower than the value calculated by

Table 1. Reactions between TNB and DBU in DMSO at 25 °C

$[\mathrm{TNB}]_0 = 7{\cdot}8 \times 10^{-5}$ (mol l^{-1})										
$10^4 \times [\mathrm{DBU}]_0$ (mol l^{-1})	2·55	2·81	3·06	3·83	4·04	5·11	5·91	7·66	8·90	10·2
$10^4 \times k_{\mathrm{obs}}$ (s^{-1})	2·12	2·25	2·46	3·20	3·26	4·15	4·50	6·00	6·50	7·50
$[\mathrm{DBU}]_0 = 6{\cdot}4 \times 10^{-5}$ (mol l^{-1})										
$10^4 \times [\mathrm{TNB}]_0$ (mol l^{-1})	2·60	3·47	4·96	6·61	8·02					
$10^4 \times k_{\mathrm{obs}}$ (s^{-1})	1·26	1·62	2·20	2·87	3·37					
$10^4 \times [\mathrm{TNB}]_0$ (mol l^{-1})	2·46	2·46	2·46	2·46	0·794	0·794	0·794			
$10^4 \times [\mathrm{DBU}]_0$ (mol l^{-1})	0·695	0·695	0·695	0·695	3·90	3·83	4·76			
$10^3 \times [\mathrm{H_2O}]_0$ (mol l^{-1})	—	0·0736	0·147	55	—	0·175	0·175			
$10^4 \times k_{\mathrm{obs}}$(s^{-1})	1·24	1·33	1·32	1·40	3·25	4·00	4·50			

the Benesi–Hildebrand plot and the measurements are unreliable for evaluating K value, because the equilibrium of Scheme 2 is too strongly shifted to the right.

Kinetic results (k_{obs} in s^{-1}) are collected in Table 1. In the same table the results obtained in the presence of water are also reported. The reaction rate is hardly affected by the presence of the water.

In the range of concentrations here used, the plot of k_{obs} values (calculated by the initial rate method) against $[\mathrm{DBU}]_0$ values is linear. Also under the conditions $[\mathrm{TNB}]_0 > [\mathrm{DBU}]_0$ at constant initial concentration value of DBU, the plot of k_{obs} values against $[\mathrm{TNB}]_0$ values is linear.

Table 2 collects some kinetic results obtained in the presence of tetra-n.butylammonium bromide (TBAB) or chloride (TBAC) and of tetraethylammonium chloride (TEAC).

Table 2. Reactions between TNB and DBU in DMSO at 25 °C in the presence of ammonium salts. $[\mathrm{TNB}]_0 = 8{\cdot}22 \times 10^{-5}$ (mol l^{-1})

$[\mathrm{DBU}]_0 = 5{\cdot}91 \times 10^{-4}$ (mol l^{-1})					
$10^3 \times [\mathrm{TBAB}]^a$ (mol l^{-1})	—	0·603	0·905	1·51	2·11
$10^3 \times k_{\mathrm{obs}}$(s^{-1})	0·450	0·724	0·775	1·04	1·29
$[\mathrm{TBAB}]^a = 1{\cdot}18 \times 10^{-3}$ (mol l^{-1})					
$10^4 \times [\mathrm{DBU}]_0$ (mol l^{-1})	2·78	3·06	4·59	5·91	
$10^4 \times k_{\mathrm{obs}}$ (s^{-1})	4·28	4·50	6·97	8·70	
$[\mathrm{TBAC}]^b = 1{\cdot}12 \times 10^{-3}$ (mol l^{-1})					
$10^4 \times [\mathrm{DBU}]_0$ (mol l^{-1})	3·06	4·59	5·63	6·12	
$10^4 \times k_{\mathrm{obs}}$ (s^{-1})	6·15	9·72	11·2	12·3	
$[\mathrm{DBU}]_0 = 5{\cdot}91 \times 10^{-4}$ (mol l^{-1})					
$10^3 \times [\mathrm{TBAC}]^b$ (mol l^{-1})	0·578	1·16	1·44	1·73	
$10^3 \times k_{\mathrm{obs}}$ (s^{-1})	1·07	1·27	1·34	1·36	
$(\mathrm{BDU}]_0 = 5{\cdot}91 \times 10^{-4}$ (mol l^{-1})					
$10^3 \times [\mathrm{TEAC}]^c$ (mol l^{-1})	0·914	1·22	1·52		
$10^3 \times k_{\mathrm{obs}}$ (s^{-1})	1·24	1·32	1·34		

[a] TBAB = tetra-n.butylammonium bromide.
[b] TBAC = tetra-n.butylammonium chloride.
[c] TEAC = tetraethylammonium chloride.

DISCUSSION

The reactions between TNB and amidines are reported by the literature to afford zwitterionic carbon-bonded complexes or *meta*-bridged complexes, via undetected nitrogen bond complexes.[6,9] The different products obtained depend on the structure of the starting amidine, of the nitro derivative and of the solvent. Preliminary investigation in weakly polar solvents (tetrahydrofuran, toluene) shows that some reactions different from that reported here (between TNB and DBU) take place. Under our experimental conditions, the step of formation of the zwitterionic complex **1** appears to be well separated from other possible processes. The present system is an example of zwitterionic complex formation without following equilibrium of proton abstraction.

From the data in Table 1, k_1 (in s^{-1} mol l^{-1}) and k_{-1} (in s^{-1}) values are calculated by using equation 1

$$k_{obs} = k_{-1} + k_1[R]_0 \qquad (1)$$

where $[R]_0$ means the initial concentration values of the reagent used in excess. k_1 and k_{-1} values (together with some significative parameters) are collected in Table 3.

k_1 value, calculated from the data of the runs carried out by using an excess of TNB, is lower than the k_1 value calculated from runs with an excess of DBU. This difference is not very large, but is significant and it requires some comments. In the literature, the experimental conditions $[\text{nucleophile}]_0 < [\text{substrate}]_0$ are unusual. In our previous investigations,[10] we proposed that the first interaction between substrate and nucleophile, in scarcely polar solvents, is a rapidly established equilibrium yielding a molecular complex. Present experimental conditions do not allow investigations (at higher concentration of reagents) into molecular complex presence. The molecular complex mechanism is a difficult question[11] in aromatic substitution reactions. Many established examples of molecular complex intervention in electrophilic substitution reactions, leading to complications in kinetics, are reported.[12] Some nucleophilic aromatic substitution reactions (showing anomalous kinetic features) are also reported to occur[10,13,14] via molecular complexes.

Owing to the simplicity of the present system, the interactions substrate/nucleophile, may be considered responsible for the observed difference in k_1 values. In fact, it is reasonable to assume that in a polar solvent,[15] (under the experimental conditions $[\text{substrate}]_0 > [\text{nucleophile}]_0$) the possible presence of a molecular complex depresses the reactivity of the system by depressing the concentration of the nucleophile, and thus the reactivity of the complexed substrate is lower than that of the free substrate. On the other hand, in a solvent of low polarity the substrate reactivity is enhanced by the presence of substances of high polarity (such as the same nucleophile, or the so-called catalyst: α-pyridone, tertiary amines) which assist the attack of the nucleophile by a molecular complex formation.[13] In this way the lower k_1 obtained from runs with a low concentration nucleophile is a logical consequence of the depression of the nucleophile concentration and of the lower reactivity of the complexed substrate in comparison to the reactivity of the 'free' substrate.

k_1 values here reported are lower than k_1 values reported by the literature (in DMSO) with primary and secondary amines.

For n-butylamine, benzylamine, i-propylamine, piperidine, pyrrolydine, k_1 values are (in s^{-1} $mol^{-1}l$) $4{\cdot}5 \times 10^4$, $1{\cdot}3 \times 10^4$, 8×10^3, $> 6 \times 10^4$ and 9×10^3 respectively.[1] The nucleophilic power of the amidine used here is lower than that of the aliphatic amines.

k_{-1} value for DBU is lower than the values reported for the above-mentioned amines. For instance,[16] $k_{-1(\text{piperidine})}/k_{-1(\text{DBU})} > 2 \times 10^8$. Since k_{-1} refers to the back reaction from the

Table 3. Kinetic and equilibrium constants for the reaction between TNB and DBU, in DMSO at 25 °C

$10^5 \times [TNB]_0$ (mol l^{-1})	$10^4 \times [DBU]_0$ (mol l^{-1})	$10^3 \times$ [salt] (mol l^{-1})	k_1[a] (s^{-1} mol l^{-1})	$10^5 \times k^a_{-1}$) (s^{-1})	$10^4 \times K_c$[b] (mol^{-1} l)	n[c]	r[d]
7·8	from 2·55 to 10·2	—	0·70 ± 0·1	3·9 ± 0·1	1·8 (2·2)	10	0·9978
from 26·0 to 80·2	0·64	—	0·39 ± 0·02	2·6 ± 0·02	1·5 (1·6)	5	0·9997
8·2	from 2·78 to 5·91	TBAB 1·18	1·45 ± 0·1	1·8 ± 2·3	8·0	4	0·9986
8·2	from 3·06 to 6·12	TBAC 1·12	2·01 ± 0·3	1·7 ± 6	12	4	0·9962

[a] Errors are standard deviations.
[b] $K_c = k_1/k_{-1}$; in brackets the values obtained from Benesi–Hildebrand plot, by using the 'infinite' absorbance values.
[c] Number of points.
[d] Correlation coefficient.

zwitterionic complex, the comparison between k_{-1} values of DBU and k_{-1} values of the aliphatic amines is a clear indication of the stabilisation of the adduct (**1**) of Scheme 2 by delocalization of the positive charge on the nucleophile moiety.[17] Thermodynamic stability (K_c values, see Table 3) of the complex between TNB and DBU is higher than the values of the stability constant of the TNB/aliphatic amines complexes, reported in the literature.[1]

The data from the reactions carried out at constant concentration values of NBAB and NBAC, and at increasing initial concentration values of DBU (see Table 2) allow us to calculate the related k_1 and k_{-1} values (see Table 3). The presence of 1×10^{-3} mol l^{-1} of NBAB enhances the k_1 value twofold. A similar amount of NBAC enhances k_1 value by 2·8 times. k_{-1} value (although the statistical errors are very large, as expected when the intercept of the plot of equation 1 is very near to zero value) is slightly reduced by the salts presence; this effect may be related to a simple salt effect.[18]

Interesting details are from reactions carried out at constant initial concentration values of TNB and DBU and at variable [salt] values. The salt presence in the reaction mixture, in every case, enhances the k_{obs} value, as expected when the reaction starts from neutral reagents to yield a transition state with strong charge separation.[18] This effect is moderate, as expected by considering the high polarity of the solvent (DMSO) here used. The k_{obs} values (reported in Table 2) are linearly increased by increasing the salt concentration only in the case of the ammonium bromide. Both the chlorides used give plots of k_{obs} values against [salt] values with a downward curvature. The levelling off in k_{obs} values by increasing the salt concentration is known[19] to arise at a higher salt concentration value than that here used, and the 'saturation' evidence is easily explained by the ion pairs presence. Under our experimental conditions, the structure of the counter ions and the range of concentration of the salts are arguments against this interpretation. Some effecs of the addition of salts to the reactions between nitro-activated substrates and primary or secondary amines are reported in the literature. The main efforts to explain the results, conceive the influence of salts on steps following the attack of the nucleophile. The assistance of salts to the leaving group departure[20] or to the proton abstraction[21] from the zwitterionic intermediates (see Scheme 1) is claimed to be operative in generating some particular kinetic behaviour.

Salt effects similar to the salt effects reported by the literature are observed in the present system which does not show further steps after the attack of the nucleophile.

A reasonable explanation of our data is the presence of a specific interaction between the substrate and the chloride ion. Recently the reactions between TNB and the hydroxide ion show evidences of the presence of π complex and of a charge-transfer complex on the reaction pathway affording a Meisenheimer complex.[22]

A similar interaction (by a rapidly established equilibrium preceding the attack of the nucleophile) may be assumed in the case of the chloride ion and the shapes of the curves of plots of k_{obs} against [salt] are probably from overimposition of the complexation effect and the usual salt effect.

EXPERIMENTAL

Materials

TNB and DBU were commercial samples (Carlo Erba RPE) purified by previously described procedures.[7] DMSO was purified by the usual procedure.[23] TBAB, TBAC and TEAC were commercial specimens recrystallized from anydrous tetrahydrofuran, and dried by warming in vacuum for 5 hs.

Kinetics

Kinetic runs were performed by the usual method following the appearance of the reaction product (with a Perkin Elmer spectrophotometer model Lambda 5) at $\lambda = 517$ nm. All the runs followed first-order kinetics. The reproducibility of k_{obs} values, calculated by the initial rate method, was ± 3%.

Determination of σ complex formation constant

The u.v./vis. spectrophotometric method was used.[10,24] K and ε values (see text) for the zwitterionic complex (**1**) formation are calculated from the plots of $[\text{TNB}]_0[\text{DBU}]_0/A_\infty$ values vs. $[\text{DBU}]_0$ or $[\text{TNB}]_0$ values. The linear relationship can be expressed algebraically by the following equations (calculated by least squares method)
$[\text{TNB}]_0[\text{DBU}]_0/A_\infty = (5{\cdot}08 \times 10^{-5} \pm 5 \times 10^{-10}) \times [\text{DBU}]_0 + (2{\cdot}04 \pm 0{\cdot}3) \times 10^{-9}$; ($n^0$ of points = 9, $r = 0{\cdot}9979$).
$[\text{TNB}]_0[\text{DBU}]_0/A_\infty = (5{\cdot}2 \pm 0{\cdot}6) \times 10^{-5} \times [\text{TNB}]_0 + (2{\cdot}78 \pm 0{\cdot}7) \times 10^{-9}$; ($n^0$ of points = 5, $r = 0{\cdot}9985$), under the experimental conditions $[\text{TNB}]_0 < [\text{DBU}]_0$ and $[\text{TNB}]_0 > [\text{DBU}]_0$ respectively (see Table 1). Errors are standard deviations.

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