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Modification of the Order of Reaction and Reaction Rate of Nucleophilic Aromatic Substitution in Micellar Solutions

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The rate of formation of 2,4,6-trinitrodiphenylamine following the attack of aniline on 1-methoxy-2,4,6-trinitrobenzene has been studied in micellar media. The partial order with reference to the nucleophilic reagent (aniline) is unity in solutions of cationic detergents (positive micelles) and 3/2 in water or solutions of anionic detergents. For such reactions there are two main steps in the reaction scheme: first, the formation of an adduct between reagents, favoured by the effect of local higher concentration in the two kinds of micellar solutions and secondly, ejection of a proton from the adduct formed. The latter reaction is catalysed largely by positive micelles and in this case the kinetics are not limited by the deprotonation step. On the other hand, negative micelles inhibit the ejection of a proton and this opposes, in part, the effect of higher local concentrations.

Aqueous solutions of surfactants often form micelles and the kinetics of numerous chemical reactions have been shown to be modified in the presence of these micelles. The catalytic properties of such solutions have recently been the subject of many publications and several workers have shown the complex nature of such phenomena.[1–24] We propose to recall briefly the main proposals made to explain the observed features micellar catalysis.

Fundamental Elements of Micellar Catalysis

When a chemical reaction is set up in the presence of micelles, the reagents can remain in the aqueous phase or may be extracted partly or wholly into the core of the micelles and they can be adsorbed into the polar sheath. Many different situations have been described, according to the nature of the reagents and substrates. For organic substrates, extraction into the micellar bulk is favoured and the catalysis usually results from a local higher concentration in this phase.[25–30]

This description is applied generally to neutral solutes and non-ionic micelles and in this case the rate equation of micellar catalysis is calculated on the enzymatic model.[30–33] However, if we use ionic micelles, the aqueous and micellar phases both contain an excess charge and there is an interphase potential $\Delta\phi$ between the two phases.

When one of the reagents is an ion whose charge is opposite to the micellar charge and the other is a neutral species dissolved in the organic phase, we can expect a catalytic effect that can be explained in two complementary ways: (i) a local higher concentration of reagents occurs and therefore there is an increase of probability of reaction; or (ii) the reaction implies a charge transfer of the ionic reagent from the aqueous phase to the core of the micelle through the potential difference $\Delta\phi$.

Very often these two explanations are proposed separately or have been proposed to be opposed,[8] whereas they are completely complementary.[34–36] The first explanation is attractive because it uses the same terminology and the same formulation used in the case of neutral systems.

In order to include in the theory the decrease in the rate of reaction observed on the addition of background electrolyte *in situ*, we have to introduce competition between the several ions having opposite charge to the micelles for the occupation of the superficial sites. If we consider two ions (i) and (j) having the same charge z [$z(\text{i}) = z(\text{j})$], we can write an exchange equilibrium:

$$\text{i}^{(\text{mic})} + \text{j}^{(\text{aq})} \rightleftharpoons \text{i}^{(\text{aq})} + \text{j}^{(\text{mic})}$$

with a constant $K([\text{i}]/[\text{j}])$. If ion j is the reagent, it is obvious that the introduction of an ion i will decrease more or less strongly [according to the value of K] the number of j ions bound to the micelles and consequently will decrease the potential reactivity. This explanation has been used in many papers[8–19, 37–39] and proves generally to be very satisfactory. However, difficulties appear in some systems[20–23, 40] and when the ionic reagent has the same sign of charge as the micelle.

The interphase potential appears in the second explanation and it was used in the earliest papers.[41–44] We have already shown that it was not incompatible with the above interpretation and that these two explanations are complementary in a simple model,[34–36, 45–47] which leads to the same formulation in every case, independent of whether the reagents are molecules or ions.

The previous theories can be applied directly for systems in which the reaction scheme has only one determinant process. The aim of this work is to investigate whether the previous methods can be applied to examples of reactions involving several processes. We have chosen nucleophilic aromatic substitution in which the kinetics may or may not be controlled by the pH, according to whether the step involving ejection of a proton from the intermediate complex is the predominate one or not.

Mechanism of the Reaction

The whole mechanism of the reaction of nucleophilic substitution of aniline (AnH_2) on 1-methoxy-2,4,6-trinitrobenzene (TNA) has been described in previous papers[48, 49] and it follows the general mechanism established by Bunnett *et al.* and in ref. (51). The reaction scheme is explained in detail in fig. 1. A zwitterionic intermediate complex (HI) is formed by attack of aniline on TNA according to equilibrium (1) of the reaction scheme. This complex can rapidly eject a proton to form an anion I^- that decomposes to 2,4,6-trinitrodiphenylamine (TNDPA) and CH_3O^-. The two intermediate complexes HI and I^- never accumulate in the system (stationary state) and the general equation established from the reaction scheme is written:

$$\frac{\mathrm{d}x}{(a-x)(b-x)} = \frac{KK'k_1k_2}{[(\text{H}^+)+K][k_{-1}(\text{H}^+)+K'k_2]}\,\mathrm{d}t = k\,\mathrm{d}t \tag{1}$$

where a and b are the initial concentrations of TNA and AnH_2, respectively, and x is the concentration of the final product TNDPA.

Generally we used very low concentrations of TNA in comparison with other reagents because the TNDPA formed is a dye that allows us to study the kinetics spectrometrically. Consequently, the kinetic curves always degenerated to first order and the equation of rate is written:

$$v = \mathrm{d}x/\mathrm{d}t = kb(a-x) = k_{\text{app}}[\text{TNA}] \tag{2}$$

where k_{app} is the apparent rate constant. We have already studied this reaction in non-micellar solutions and the results show that this system can be interpreted in accordance with two kinetic laws. (i) When the medium is basic, ($K \gg [\text{H}^+] \ll K'k_2/k_{-1}$) the zwitterionic complex HI ejects the proton completely and instantaneously. Then the reaction (1) (fig. 1) is the determinant step because k_2 (loss of the leaving group) is very high. k_{app} is dependent only on the concentration of aniline:

$$k_{\text{app}} = k_1[\text{AnH}_2]. \tag{3}$$

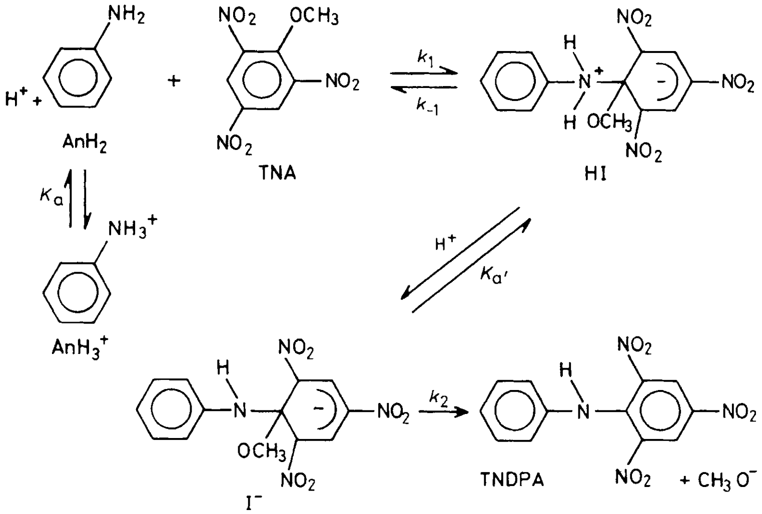

Fig. 1. Reaction scheme of nucleophilic substitution of aniline (AnH_2) on 1-methoxy-2,4,6-trinitrobenzene (TNA). The complexes HI and I^- are not accumulated during the reaction and 2,4,6-trinitrodiphenylamine (TNDPA) formation is followed by means of a spectrophotometer.

(ii) On the contrary, for a less basic range ($K \gg [H^+] \gg K'k_2/k_{-1}$) the intermediate complex exists mainly in the HI form and dissociates principally to give the initial reagents because it is very unstable [process (−1)]. The rate of formation of TNDPA is thus determined by means of the ratio of the rates corresponding to the two processes of dissociation of the intermediate complex HI, and this ratio is controlled by the pH:

$$k_{app} = \frac{k_1 k_2}{k_{-1}} \frac{K'}{[H^+]} [AnH_2]. \tag{4}$$

If we use only TNA and AnH_2 as reagents, the pH value of the solution is fixed by the aniline concentration and $[H^+]$ is calculated as:

$$[H^+] = (K^w K_a/c)^{1/2} \quad [pH = 0.5(pK^w + pK_a + \log c)]$$

and eqn (4) becomes:

$$k_{app} = \frac{k_1 k_2}{k_{-1}} \frac{K'}{(K^w K_a)^{1/2}} [AnH_2]^{3/2}. \tag{5}$$

The partial order of the reaction according to aniline is 1 for case (i) and 3/2 for case (ii).

Using different systems (see below) we can obtain one or other type of behaviour. Nevertheless the experimental range in which this occurs is restricted by parasitic reactions. (i) When the medium is acid, the aniline is more or less in the form of the anilinium cation AnH_3^+ which is unreactive. The best range for study is where pH values are higher than the pK value of the couple AnH_3^+/AnH_2 in the micellar solution. (ii) When the medium is basic, two other reactions can occur: (*a*) the product formed (TNDPA) is a weak acid and is thus able to ionize in solution, but this ionization has no effect on the kinetics of the reaction. (*b*) The nucleophilic attack of aniline [process (1), fig. 1] can be in competition with reaction with OH^- ions, which indeed predominates when the pH value is high enough. The product of this reaction is not TNDPA (the molecule or the corresponding ion) but the picrate anion formed from 2,4,6-trinitrophenol (picric acid). (iii) If we use buffer solutions for controlling the pH value, the basic species in the buffer can compete with the aniline.

Table 1. C.m.c. values for surfactants, concentrations of stock solutions and minimum concentrations for plateau rate

surfactant	c.m.c. /mol dm^{-3}	concentration of stock solution /mol dm^{-3}	plateau-rate concentration /mol dm^{-3}
HDTABr	9.2×10^{-4}	5×10^{-2}	10^{-2}
TDTABr	3.5×10^{-3}	5×10^{-2}	2×10^{-2}
DDTABr	1.5×10^{-2}	2×10^{-2}	2.5×10^{-2}
DTABr	6.5×10^{-2}	2.5×10^{-1}	10^{-1}
NaDDS	8.1×10^{-3}	2×10^{-1}	1.5×10^{-2}
NaDS	3.3×10^{-2}	2×10^{-1}	5×10^{-2}
NaOS	1.4×10^{-1}	2.5×10^{-1}	

Experimental

1-Methoxy-2,4,6-trinitrobenzene (TNA) was prepared in our laboratory from picryl chloride and sodium hydroxide in methanol solution. This aromatic substrate is not very soluble in water and it was used in the form of stock micellar solutions. The concentration of TNA was in the range $(4-5) \times 10^{-5}$ mol dm^{-3}. The aniline was a commercial reagent, purified by distillation and the stock aqueous solutions ([aniline] = 0.2 mol dm^{-3}) were stored at low temperature.

We have already studied the reaction in water and several H_2O–CH_3OH mixtures[48, 49] and shown that a plot of $\log k_{\text{app}} = f(\text{pH})$ was principally composed of two linear parts with slopes 1 and 0, corresponding to the limiting laws (4) and (5). The system discussed here has been investigated in aqueous solutions of several surfactants. The kinetics were carried out in a micellar solution of TNA and an aqueous solution of aniline without any other compound. In those solutions the pH value is determined by the concentration of aniline and though the medium is basic, the pH is not high enough and there is no other nucleophilic reagent to be in competition with AnH_2.

We used (Sigma Chemical Co.) for hexadecyl-, tetradecyl- and dodecyl-trimethylammonium bromide (HDTABr, TDTABr and DDTABr, respectively) and decyltrimethylammonium bromide and sodium dodecyl-, decyl- and octyl-sulphate (DTABr, NaDDS, NaDS, NaOS, respectively, from Eastman Kodak). Table 1 shows the values of critical micelle concentrations (c.m.c.) and the concentrations of stock solutions used.

An Acta III Beckman spectrophotometer was used with the measurement cells thermostatted at 25 ± 0.1 °C. The maximum of absorption of TNDPA is at $\lambda = 400$ nm and all the kinetic data have been carried out at this wavelength and were extracted using an Apple IIe microcomputer and a program written in our laboratory. We checked, in every case, that the kinetic development was always pseudo-first-order in terms of aniline.

Results

By using several surfactants with different aliphatic chainlengths we were able to study a variety of solutions with different c.m.c. Below the c.m.c. the kinetics of reaction were modified little by surfactants. For concentrations higher than the c.m.c., the rate increased in every case and we found a flat maximum of micellar catalysis.

The increase in rate of reaction is illustrated in fig. 2 for a fixed concentration of aniline. The micellar catalysis occurs, in every case, for a concentration close to the value of the c.m.c. of every detergent; we could not illustrate the catalytic effect for NaOS in this figure because this effect is observed for a very high concentration (*ca.* 0.2 mol dm^{-3}).

The progressive increase in the number of micelles allows an increased extraction of

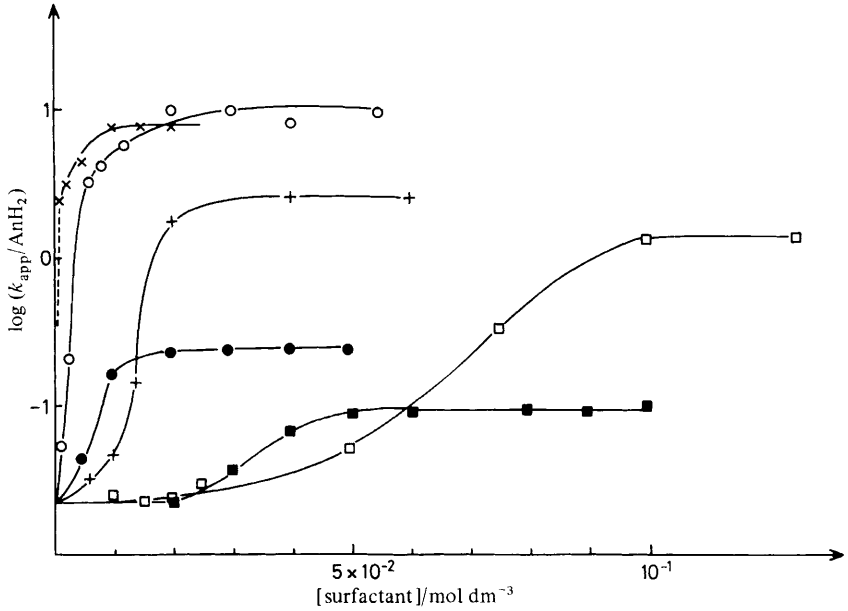

Fig. 2. Plot of the pseudo-first-order rate constant k_{app} over concentration of aniline *vs.* concentration of several detergents. The concentration of aniline is fixed (4×10^{-3} mol dm^{-3}) and $T = 25$ °C. ×, HDTABr; ○, TDTABr; +, DDTABr; □, DTABr; ●, NaDDS; ■, NaDS.

the two reagents (AnH_2 and TNA) from the aqueous phase and the rate of reaction reaches a maximum value when extraction is practically complete. For higher concentration of surfactants, the observed rate (for fixed concentration of AnH_2) remains constant and it is depicted in fig. 2 by a plateau. The increased rate of reaction obtained for the conditions of maximum extraction (when the concentration of aniline is 4×10^{-3} mol dm^{-3}) is greater than in water by a factor of: 4 for NaDS solutions, 10 for NaDDS solutions, 60 for DTABr solutions, 100 for DDTABr solutions and 400 for TDTABr solutions and HDTABr solutions.

This increase is obviously the result of a local higher concentration of reagents in the micelles. But, in fact, it is difficult to interpret these values in terms of actual concentrations for several reasons: (i) the volume of the micellar phase is not properly defined because the boundary of the reaction between the aqueous phase and the micelle is not clearly specified. (ii) The increase of rate is the result not only of the change of concentration but also the modification of free enthalpy of each reagent by transfer from the water phase to the organic phase. We would be able to take into account the change of medium only if we knew the free enthalpies of extraction of the two reagents (deduced from the partition constants) and this information is not available.† (iii) Finally, the main reason why the rate ratios are not significant in an absolute way is because their value is dependent upon the concentration of aniline: any other value of [AnH_2] would give similar behaviour, but other numerical values (see below).

The results obtained show that the rate of reaction depends on the pH according to the kind of surfactants used. As the pH is determined by the concentration of aniline in our experimental conditions, this concentration modifies the overall rate in a different

† A binding constant $K = 14$ has been proposed by Bunton *et al.*[50] for AnH_2 with NaDDS, but we have no corresponding value for TNA.

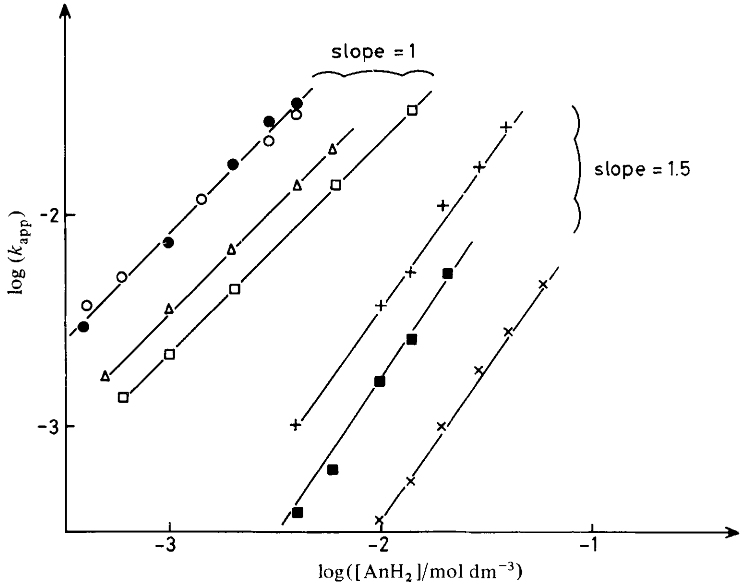

Fig. 3. Plot of the pseudo-first-order rate constant k_{app} in several solutions of detergents: ●, HDTABr (0.015 mol dm^{-3}); ○, TDTABr (3×10^{-2} mol dm^{-3}); △, DDTABr (4×10^{-2} mol dm^{-3}); □, DTABr (0.15 mol dm^{-3}); +, NaDDS (4×10^{-2} mol dm^{-3}); ■, NaDS (8×10^{-2} mol dm^{-3}); ×, water. For cationic detergents the plots are represented by straight lines whose slopes are unity and thus k_{app} is given by eqn (3); for anionic detergents and aqueous solutions plots are represented by straight lines whose slopes are 1.5. For these experimental cases, k_{app} is given by eqn (5).

way in every situation. For a constant concentration of AnH$_2$, a comparison between the different kinds of surfactants by use of fig. 2 is inevitably not significant.

For comparing the catalytic efficiencies of every surfactant we have proceeded as follows: we have chosen to use for every surfactant a concentration such that the rate of the reaction had attained its maximum constant value. Under these conditions the effect of concentration of amphiphile is eliminated and the influence of variations of the concentration of nucleophilic reagent AnH$_2$ can be investigated without interference from this effect (fig. 3). Then we notice that we find again a first-order kinetic law in terms of aniline when salts of alkyltrimethylammonium are used and formed positive micelles. In contrast, when the reaction is carried out in aqueous media (or in H_2O–CH_3OH) or using negative micelles formed by alkylsulphate ions, the kinetic law has experimentally an order of 3/2 in terms of aniline. The previous experiments in water–methanol mixtures have proved the validity of the reaction scheme. Consequently, these two different orders are explained by the two kinetic equations (3) and (5).

The last result is significant because it is a demonstration that micelles are able to modify not only the rate of the process but also the kinetic laws; that is to say the intervention of several processes contributing to the total rate. We have shown in the previous paragraph that the reaction is controlled by process (1), fig. 1, if the intermediate species HI ejects a proton rapidly and totally while this control is modulated by the ratio of rates of dissociation of the intermediate complex HI into I$^-$ and H$^+$, or alternatively TNA and AnH$_2$ if the ejection of proton occurs with more difficulty. Consequently, the plateau shown in fig. 2 does not have the same meaning for the two cases: in the presence of cationic detergents the plateau value is equal to log(k_1) and the micelles greatly increase the first kinetic step. On the contrary, for an aqueous solution or anionic detergent solutions, the plateau value depends on the concentration of aniline and increases with this concentration: the k_1 value cannot be obtained straightforwardly from the graph and the influence of anionic and cationic detergents upon the first step cannot be compared directly from this figure.

These findings are confirmed in another way. It is well known that an addition of background electrolyte is almost ineffective on the rate of reaction between two neutral species enclosed in the micellar core but, in comparison, such an addition can be very effective on the reaction rate if there is charge transfer between the micelle and the bulk. In our case, if we add background electrolyte to our solutions (TNA–AnH_2), two experimental trends are observed. When the micellar system in use gives an order of 1 in terms of aniline there is no modification of the reaction rate, but when the order is 3/2 there is a decrease of the reaction rate. These effects are in good agreement with the proposed mechanism.

Finally, the part played by each type of surfactant is very clear: when the micelles are positive, the charge of the medium thermodynamically favours the ejection of H^+ from HI and this process is easier than in aqueous solution; the rate of reaction is controlled simply by the process of formation of the HI complex with a rate constant k_1. On the contrary, in water the ejection of H^+ is more difficult and the order in terms of aniline is 3/2, which is a demonstration of the influence of pH. When we use anionic micelles this effect is reinforced, the charge of the micelle is opposed to the ejection of a proton from HI and this process becomes even more difficult (the pK of the intermediate complex is lowered by cationic micelles and enhanced by anionic ones). Thus, in the case of anionic micelles, the influence of surfactant is felt in two opposing ways: the extraction of reagents into the micelles creates an increased probability of encounter between reagents, but the complex appears in a region of negative potential that is opposed to the reaction path which leads to the usual final product. However, the first effect is the dominating one and the reaction is faster than in water (10 times higher for NaDDS solutions) but slower than in cationic surfactants. For positive micelles the alkyl chain length seems to influence the degree of extraction and the rates are 5 times less for C_{12} chains than for C_{14} and C_{16} chains and 10 times less for C_{10} chains.

The results carried out in the presence of the same detergents, but for concentrations where the reaction has not reached its maximum value are not reported here. In this case, the concentration of the detergent cannot be eliminated and the values of the slopes of the experimental lines giving the apparent order of the reaction in terms of aniline are not necessarily in the range 1–1.5, owing to the progressive incorporation of AnH_2 into the micelles.

Conclusion

Investigation of the reaction between aniline and 1-methoxy-2,4,6-trinitrobenzene shows a more complex influence of a micellar system than in ordinary cases. For such a system, with several determining steps, the kinetic study in micellar solutions can be used to confirm the reaction scheme. In the present case, for the first process of the kinetic scheme where two molecules are reacting (TNA + AnH_2), the micellar catalysis is only the effect of a higher concentration in the micelles and consequently a larger probability for the reaction. The adduct formed during this first process is able to react later according to two different ways, either splitting up into two molecules (return to the initial components) or losing a proton. The charge of the micellar system has a large influence upon this last process and the cationic detergents are good catalysts of this transformation because they favour the ejection of the proton. On the contrary, this ejection is largely inhibited by the use of anionic detergents: the effect of a higher concentration in the micelles is partially compensated and the concentration of the nucleophilic reagent becomes essential (order 3/2) because the ejection of the proton is favoured by the increase of this concentration.

These conclusions are confirmed by experiments carried out in other conditions (additions of background electrolytes and buffer solutions). These experiments imply the intervention of other parameters and of some parasitic reactions; they will be described in a later paper. However, it is interesting to report now that the whole set of experimental data can be interpreted using the theoretical model which has been recalled in the first paragraph.

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