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# A Kinetic Study of the Formation and Dissociation of the Meisenheimer Complex Formed between 1,3,5-Trinitrobenzene and the Hydroxide Ion in Micellar Dodecyltrimethylammonium Bromide Solution

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The rates of formation and dissociation of the thermoaddition complex of 1,3,5-trinitrobenzene with $OH^-$ has been investigated in micellar solutions of dodecyltrimethylammonium bromide (DTABr) using a stopped-flow spectrometer. We have observed and measured three processes which proceed under different conditions of acidity: (*a*) formation of the $\sigma$ complex, (*b*) spontaneous (equilibrium) dissociation in less basic solutions and (*c*) dissociation *via* proton attack in acid solutions. These processes are influenced by the background KBr electrolyte. The interphase potential $\Delta\phi = \phi_m - \phi_w$, depicted in the pseudophase model, allows us to explain the variations of the rate constants.

The catalytic effect of cationic detergents, for example dodecyltrimethylammonium bromide solutions with water (DTABr), on nucleophilic aromatic substitution reactions has been studied by several workers.[1–13] 1-Halogeno-2,4-dinitrobenzene compounds have often been used and reacted with the hydroxide ion, $OH^-$, to form the corresponding phenate; the catalytic effect on such reactions is significant. In contrast, few investigations[14–16] have been made on aromatic substitutions in which $\sigma$ addition complexes (or Meisenheimer complexes) are formed, *e.g.* when the aromatic substrate is a trinitrosubstituted benzene compound. The aim of this work is to investigate whether a cationic detergent (DTABr) has an active effect on the rate of formation of such complexes between 1,3,5-trinitrobenzene (TNB) and the $OH^-$ ion.

This aromatic substrate shows simple behaviour in sodium hydroxide solutions because there is no substitutable group (or leaving group) and the reaction is limited to

$$\mathrm{TNB}+\mathrm{OH}^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{TNBOH}^- \tag{1}$$

in which the $\sigma$ addition complex ($TNBOH^-$) is stable in micellar solutions. We have already studied these reactions for several mixtures of water and methanol[17] and, depending upon the conditions of acidity used, we were able to describe several reaction processes. When the medium is strongly basic, the principal reaction is to give the $\sigma$ complex $TNBOH^-$ and only the rate constant $k_1$ may be determined experimentally. For a less basic range, the rate constant $k_{-1}$ is also accessible and corresponds to dissociation of the Meisenheimer complex, caused by thermal motion of solvent molecules. For strongly acid mixtures, dissociation occurs by direct attack and the reaction scheme is written as

$$\mathrm{TNBOH}^- \xrightarrow{k_2[\mathrm{H}^+]} \mathrm{TNB}+\mathrm{H_2O}. \tag{2}$$

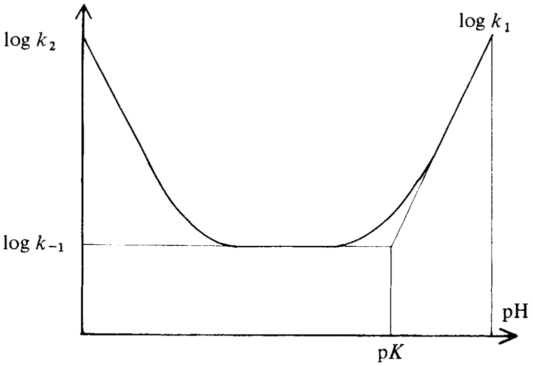

**Fig. 1.** Theoretical diagram showing the logarithm of the apparent constant $\lambda$ for the processes of ionization of TNB [reaction (1)] and dissociation of the TNBOH⁻ complex [reaction (2)]. $\lambda = k_1[\mathrm{OH^-}]+k_{-1}+k_2[\mathrm{H^+}]$.

The overall behaviour is summarized diagrammatically in fig. 1. The effects of DTABr upon these three processes have now been investigated and this paper reports our results.

## EXPERIMENTAL

DTABr detergent was used at a concentration of $2 \times 10^{-2}$ mol dm$^{-3}$, higher than the critical micellar concentration (c.m.c. = $1.56 \times 10^{-2}$ mol dm$^{-3}$), and normally in the presence of an excess of background electrolyte in order to mask the secondary effects of the various buffer salts in solution, even though the background electrolyte is expected to affect the rates of reaction[10-18].

The rates of reaction were always high and a stopped-flow Durrum Gibson spectrometer was used with the measurement cells thermostatted at $20 \pm 0.1$ °C, as were the two syringes for injection of reagents. The experimental kinetics curves were displayed on the screen of a Tektronix oscilloscope connected directly to the stopped syringe. However, the use of such a method with micellar solutions is difficult and tedious because many microbubbles are formed in the mixing jet during the injections of reagents. Thus, the different solutions had to be injected three or four times for each measurement in order to obtain reproducible results.

## RESULTS

When TNB in micellar DTABr solutions is reacted with a range of concentrations of micellar sodium hydroxide solutions, we can calculate the rate constants $k_1$ and $k_{-1}$, see fig. 2 and 3. On the other hand, the determination of the rate constant $k_2$ is experimentally more difficult. The reagents are mixed quickly in the mixing jet of the stopped-flow spectrometer, one being the preformed TNBOH⁻ complex with an excess of OH⁻ ions and the other being a weak acid solution chosen to obtain the desired final pH value. The two solutions of reagents were made up in such a way that, in every one, there were the same concentrations of surfactant ($2 \times 10^{-2}$ mol dm$^{-3}$) and background electrolyte ($4 \times 10^{-2}$, $8 \times 10^{-2}$, $2 \times 10^{-1}$ or $4 \times 10^{-1}$ mol dm$^{-3}$ KBr). Such reagent conditions were necessary in order to ensure that there were no problems caused by viscosity differences in the mixing jet. The excess of salt enables not only the interphase potential but also the ionic surroundings of the micellar structure to be obtained. The preformed TNBOH⁻ complex with an excess of OH⁻ is stable in solutions of DTABr and KBr and the reaction observed after mixing with weak acid solutions corresponds to reaction (2). Indeed, in the measurement

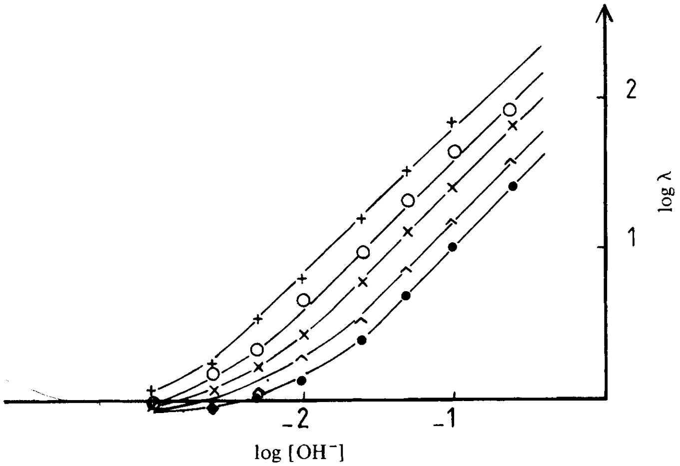

**Fig. 2.** Plot of the pseudo-first-order rate constant $\lambda$ against log[OH⁻]. [DTABr] = $2 \times 10^{-2}$ mol dm$^{-3}$ and $T = 20$ °C. +, Without background electrolyte; ○, $4 \times 10^{-2}$; ×, $8 \times 10^{-2}$; △, $2 \times 10^{-1}$ and ●, $4 \times 10^{-1}$ mol dm$^{-3}$ KBr.

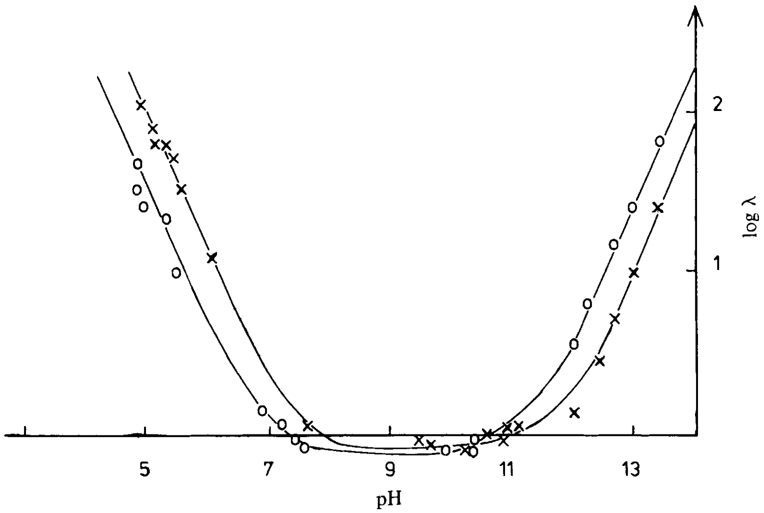

**Fig. 3.** Plot of the pseudo-first-order rate constant $\lambda$ defined by $k_{app} = \lambda[OH^-]$ against pH. Circles and crosses refer to KBr concentrations of $8 \times 10^{-2}$ and $4 \times 10^{-1}$ mol dm$^{-3}$, respectively. [DTABr] = $2 \times 10^{-2}$ mol dm$^{-3}$ and $T = 20$ °C.

cell there occurs fast neutralization of the weak acid by the excess of OH⁻ and formation of the buffer solution *in situ*, which sets the final pH value. Acetic acid and butylammonium, dibutylammonium or pyridinium salts were used in various proportions for obtaining the correct pH value over a range of *ca.* 6 pH units.

The kinetic curves were recorded on the screen of the oscilloscope at a wavelength $\lambda = 460$ nm, corresponding to the maximum absorbance of the $\sigma$ complex. For reaction (2) we followed the decreasing absorbance at the same wavelength. In all experiments the concentration of TNB was very low ($10^{-4}$–$10^{-5}$ mol dm$^{-3}$) and under

**Table 1.** Variation of $\log {}^{m}\lambda$ (pseudo-first-order rate constant in $s^{-1}$) with $\log[OH^-]$ for different concentrations of KBr. $C_{DTABr} = 2 \times 10^{-2}$ mol $dm^{-3}$, $T = 20$ °C; $\log \lambda = \log(k_{-1} + k_1[OH^-])$

| $\log[OH^-]$ | $C_{KBr}$/mol $dm^{-3}$ | | | | |
|---|---|---|---|---|---|
| | 0 | $4 \times 10^{-2}$ | $8 \times 10^{-2}$ | $2 \times 10^{-1}$ | $4 \times 10^{-1}$ |
| −0.7 | — | 1.94 | 1.83 | 1.60 | 1.40 |
| −1.0 | 1.85 | 1.65 | 1.40 | 1.20 | 1.00 |
| −1.3 | 1.52 | 1.34 | 1.12 | 0.88 | 0.70 |
| −1.6 | 1.20 | 0.98 | 0.78 | 0.54 | 0.40 |
| −2.0 | 0.80 | 0.66 | 0.43 | 0.29 | 0.13 |
| −2.3 | 0.53 | 0.33 | 0.21 | 0.07 | 0.01 |
| −2.6 | 0.23 | 0.17 | 0.06 | −0.02 | −0.08 |
| −3.0 | 0.05 | −0.02 | −0.03 | −0.10 | −0.10 |

such conditions the concentrations of $OH^-$ may be considered to be constant. Fig. 2 shows the variation of the pseudo-first-order rate constant, $\lambda$, with $\log[OH^-]$ ($k = \lambda/[OH^-]$; *cf.* caption to table 1) for solutions with and without KBr electrolyte (KBr $= 4 \times 10^{-2}, 8 \times 10^{-2}, 2 \times 10^{-1}$ and $4 \times 10^{-1}$ mol $dm^{-3}$). All the data are summarized in table 1, and fig. 2 leads to several conclusions. When the reaction occurs in the absence of electrolyte, the plot of $\log \lambda$ against $\log[OH^-]$ function is represented by a straight line whose slope is unity. The micellar catalysis is at a maximum compared with the results in the presence of KBr. On the other hand, when the reaction occurs in the presence of electrolyte, the rate constant is decreased in proportion to the increasing concentrations of KBr. For $\log[OH^-] > -2$, the plots of $\log \lambda$ against $\log[OH^-]$ are represented by straight lines whose slopes are unity and for $\log[OH^-] < -2$ these they tend towards a constant value corresponding to $k_{-1}$.

The variations of the pseudo-first-order rate constants $\lambda$ with pH are illustrated (fig. 3) for solutions with two KBr concentrations, $8 \times 10^{-2}$ and $4 \times 10^{-2}$ mol $dm^{-3}$. The form of the curves leads to several conclusions depending on the pH range. When pH > 11, the plot of $\log \lambda$ against pH is represented by a straight line whose slope is unity. The reaction is thus second order as expected. When $8 < \text{pH} < 11$, $\log \lambda$ is independent of pH. When $5 < \text{pH} < 8$, as is seen in the third part of the kinetic diagram, the plot of $\log \lambda$ against pH is a line whose slope is $-1$, corresponding to the $\sigma$ complex dissociation reaction with the protons present in solution. In this case, we note that the proton reacts with the $TNBOH^-$ complex despite the repulsion of the positive micellar charges. Such a result has not previously been observed with cationic micelles, but the corresponding reaction with anionic surfactants (symmetrical trend) has been described for micellar dodecylsulphate in alkaline media.[13]

When the concentration of the KBr electrolyte is increased, the rate constant $k_1$ invariably decreases. However, the $k_{-1}$ rate constant is modified very little by added salt. Finally, the dissociation rate, following reaction (2), is increased by adding KBr and we notice a comparable translation for the two lines of slope 1 and $-1$ in the presence of salt. Thus the rate constants $k_1$ and $k_2$ are changed by almost the same absolute value. We were careful to check that this was not due to pH variation in the micellar solution.

## DISCUSSION

Two theories are able to show the logical development of the effects of ionic surroundings on micellar catalysis, one being based on the interphase potential of the two phases $\Delta\phi = \phi_M - \phi_W$ ($\phi_M$ and $\phi_W$ are the potential of the micellar and bulk phases, respectively) and the other on ionic exchange on the micellar surface. These two models have been applied by different workers and from time to time they have been considered as mutually exclusive. However, we believe that they are compatible but that the interphase potential model is able to explain our experiments more simply.

In this paper we have chosen to show the influence of the addition of a salt on the micellar catalysis of a model reaction [reactions (1) and (2)]. The presence of the salt enable us to set the interphase potential and for that reason we used different concentrations in order to experiment with several values of $\Delta\phi$. It is known that the presence of salt generally involves a decrease in the rate of the reaction: either by competition between two anions ($Br^-$, the common anion of the surfactant and the background electrolyte, and the $OH^-$ anion) or by decreasing the interphase potential and correspondingly the rate constant.

The three processes of the reaction are influenced differently by increasing concentration of electrolyte: (*a*) a decrease of the rate constant $k_1$, as has been described by several authors, (*b*) an unmodified value of the rate constant $k_{-1}$ and (*c*) an increase of the rate constant $k_2$.

A qualitative interpretation becomes obvious if we use the interphase potential expression. We have already developed[23, 24] an expression for the interphase potential using the pseudophase model:

$$\Delta\phi = \Delta\phi_i^\circ + \frac{2.3\boldsymbol{RT}}{\boldsymbol{F}} \log \Sigma s_i [a_i]^{b_i} \tag{i}$$

where $s_i$ and $b_i$ are the parameters of each species of ion which are determined experimentally for kinetic results, $[a_i]$ is the ionic concentration in the bulk phase and $\Delta\phi_i^\circ$ is a constant depending on amphiphiles, counter ion, solvent and temperature. Using eqn (i) we are able to foresee the effect of a variation of electrolyte concentration and we believe, in accord with other workers,[25, 26] that an excess of salt will give rise to an interphase potential difference.

If we develop eqn (i), taking account of the anions present in solution, we use a cationic amphiphile ($DTA^+$, $Br^-$), a reactive anion $OH^-$ and a fixed excess of background electrolyte ($K^+$, $Br^-$), whose anion is common with the counter ion of the surfactant. Consequently eqn (i) may be written as

$$\Delta\phi = \Delta\phi_i^\circ + \frac{2.3\boldsymbol{RT}}{\boldsymbol{F}} \log (s_{OH^-}[OH^-]^{b_{OH^-}} + s_{Br^-}[Br^-]^{b_{Br^-}}). \tag{ii}$$

Eqn (ii) explains the variation of $\Delta\phi$ with varying concentration of background electrolyte. We do not need the values of $s_i$ and $b_i$ for explaining qualitatively our kinetic results, nevertheless we have determined[23, 24, 27] these coefficients using other kinetic results and also for shifts of the deprotonation equilibria. Thus, choosing the $OH^-$ ion as a reference $s_{OH^-} = 1$, we have obtained $s_{Br^-} = 25$. Consequently the micellar structure has a selectivity which is 25 times larger for $Br^-$ than the $OH^-$. We are in agreement with the selectivity magnitude for these ions found by Bunton *et al.*[10, 21] The contribution of the $[OH^-]$ term in eqn (ii) is thus very small in comparison with that for the $Br^-$ ion and eqn (ii) may therefore be simplified to

$$\Delta\phi \approx \Delta\phi_i^\circ + \frac{2.3\boldsymbol{RT}}{\boldsymbol{F}} b_{Br^-} \log s_{Br^-}[Br^-]. \tag{iii}$$

The charge transfer between two phases involves the development of the transfer rate concurrently with $\Delta\phi$:

$$\log {}^{\mathrm{m}}k = \text{constant} - \frac{\boldsymbol{F}}{2.3\boldsymbol{RT}}\Delta\phi \qquad \text{(iv)}$$

where ${}^{\mathrm{m}}k$ is the kinetic micellar rate constant (second order) and the constant is the sum of several constants: one being the value of the kinetic rate constant in water and the other the ratio of transfer activity coefficients of several species in solution.

We mentioned previously that we have determined experimentally the pseudo-first-order rate constant ${}^{\mathrm{m}}\lambda$, which can be reproduced by taking account of the expressions for $\log {}^{\mathrm{m}}k$ and $\Delta\phi$:

$$\log {}^{\mathrm{m}}\lambda = C + \log[\mathrm{OH}^-] - b_{\mathrm{Br}^-} \log s_{\mathrm{Br}^-}[\mathrm{Br}^-]. \qquad \text{(v)}$$

When the salt concentration increases, the interphase potential decreases and consequently the rate of the TNB ionization reaction decreases (slope $+1$ in fig. 2 and 3). The thermal dissociation process (rate constant $k_{-1}$) cannot be modified by a $\Delta\phi$ potential variation, as is observed. On the contrary, for the dissociation of the complex caused by proton attack (slope $-1$ in fig. 3), we obtain an inversion of reactivity, the rate constant $k_2$ increasing with the increasing electrolyte concentration. Again, a decrease in $\Delta\phi$ causes a reduction in ionic repulsion between the proton and the micelles and reaction is promoted. This is a very interesting experimental example of an increase of rate constant obtained by increasing the electrolyte concentration, the opposite effect having always been described for cationic amphiphiles previously.

The kinetic interpretations based on the ion-exchange model of the micellar surface[22] are not able to explain such results without recourse to other assumptions such as the introduction of a local pH at the micellar surface;[13] on the other hand our approach gives a plausible and direct interpretation. If the kinetic variations are due only to the variation in interphase potential that is determined by the change of electrolyte concentration in the bulk, then the acceleration of proton attack has to correspond exactly to the decrease of the TNB reaction with OH⁻ ions, as observed.

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