Autocatalytic alkaline hydrolysis of tri-*n*-butyl phosphate

David J. Burgess and Geoffrey Stedman *

Chemistry Department, University of Wales Swansea, Singleton Park, Swansea, UK SA2 8PP

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Although the alkaline hydrolysis of tri-*n*-butyl phosphate, TBP, in homogeneous aqueous solution shows normal second order kinetics, the hydrolysis of a solution with a hydrocarbon diluent by concentrated sodium hydroxide at 388 K shows an induction period followed by an autocatalytic reaction. The reaction starts with two liquid phases, and ends with three, the third phase consisting mainly of sodium di-*n*-butyl phosphate, NaDBP, together with hydrocarbon, TBP, Bu^{n}OH, H_2O and NaOH. The autocatalysis arises from the fact that the third phase dissolves appreciable concentrations of both TBP and NaOH, and serves to bring the reactants together, although the second order rate constant for reaction in the third phase is not much greater than it is in water. As hydrolysis proceeds the volume of the third phase increases while the other phases shrink, thus increasing the rate and resulting in autocatalysis.

The alkaline hydrolysis of the triesters of *ortho*-phosphoric acid, $(RO)_3PO$, has been intensively studied,[1] and the kinetics and mechanism are well understood. In homogeneous aqueous or aqueous–organic solution, the kinetics are simple second order, first order in [ester] and in [OH^-], and phosphorus–oxygen bond cleavage[2] occurs yielding the sodium salt of the diester $Na[P(O)_2(OR)_2]$. Further hydrolysis to the monoester is very much slower[3] so that it does not significantly overlap the first stage. TBP is of technological importance in nuclear fuel reprocessing[4] where it acts as a ligand/solvent extraction agent in the Purex Process, usually in the form of a 30% v/v solution with odourless kerosene, OK, as a diluent. It has very low solubility in water,[5] 1.59×10^{-3} mol dm^{-3} at 25 °C, but alkaline hydrolysis converts it to water soluble NaDBP + Bu^{n}OH. This hydrolysis is part of current reprocessing chemistry[6] in the disposal of waste TBP. The present paper describes a study of the alkaline hydrolysis of the TBP–hydrocarbon diluent solution, where the behaviour is much more complex than it is in homogeneous aqueous solution. Work on pilot-plant scale showed[6] that the reaction had a variable induction period, followed by an autocatalytic reaction, and that although reaction started with two liquid phases it finished with three. This third phase had a density intermediate between the 'light' TBP–OK and the 'heavy' aqueous sodium hydroxide phase. Practical considerations in the industrial situation make it desirable to have a system that reacts to completion in less than two hours, and this imposes constraints on temperature, [NaOH] and the mole ratio NaOH : TBP. The present work was designed to provide an understanding of these unusual phenomena which, in addition to their practical importance, have an intrinsic interest.

Experimental

Materials

TBP and OK were supplied by BNFL, Sellafield. AnalaR NaOH was a Fisons product while *n*-dodecane and the other hydrocarbons used were supplied by Aldrich. All were used without further purification. Samples of solid NaDBP were obtained by separating off some of the third phase from an infinity solution and allowing it to evaporate to dryness. The waxy product contained traces of NaOH.

Analytical methods

Analysis for TBP was carried out by gas chromatography (FID detectors) using added tridecane or nonadecane as internal standards. Calibration solutions were made up by weight. The instruments used were a Pye Unicam GC104 and a Pye Unicam GCD attached to a Hewlett Packard A integrator. A third GC used was a Phillips PU 4400 attached to a Phillips S computer with a data acquisition package. The columns used were a 7 ft (3 mm internal diameter) glass column packed with 10% OV-17 on Chromosorb W (80–100 mesh) from Jones Chromatography and a 10 ft (3 mm internal diameter) glass column packed with 5% OV-17, supplied by a colleague, Dr J. A. Ballantine. Injection volumes were typically 1 µl.

Analysis for NaDBP was carried out by FTIR[7] at 1036 cm^{-1}. TBP absorbs close to this frequency, and had to be first removed by extraction with *n*-dodecane. The aqueous solution of NaDBP was then acidified to produce HDBP which can be extracted into a range of organic solvents for FTIR analysis. Another procedure was to remove TBP by solvent extraction, hydrolyse the NaDBP in concentrated hydrochloric acid at 115 °C for 4 h and then determine H_3PO_4 colorimetrically as vanadomolybdo-phosphoric acid. Analysis by NMR was carried out on a Bruker AC 400 instrument for proton measurements. Some spectra were run on a Bruker WM 250 instrument.

Kinetic methods

Two essential requirements for the kinetic method were that the solution should be very vigorously stirred in order to ensure that equilibrium was maintained between the phases and that it should run at 388 K. Reactions were carried out in a 700 cm^3 thick walled cylindrical vessel with a separate lid fitted with ground glass flange joints. To prevent the lid sealing to the vessel under the influence of splashed droplets of hot, concentrated NaOH solution, a thin Gorex gasket was fitted between the upper and lower flanges, and the lid was held tightly in place by metal clamps. The lid had four apertures to take the stirrer shaft, a condenser, a thermometer pocket and a sampling port. The reaction vessel was immersed up to the lower flange in a constant temperature silicone oil bath. The reaction mixture was stirred by a four-blade stainless steel stirrer. The very vigorous stirring necessarily splashed hot liquid onto the lid, causing heat losses. These were minimised by insulating the lid but inevitably there was some heat loss and it was necessary to keep a regular check on the temperature of the reaction mixture which was controlled to ±1 °C. Because of the catalytic effect of

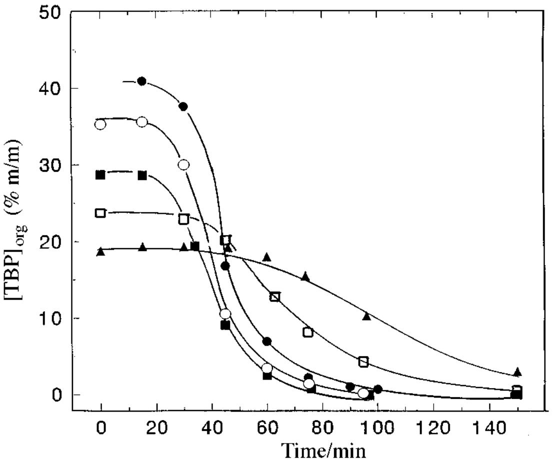

Fig. 1 Variation of $[TBP]_{org}$ with time for hydrolysis with 8.5 mol dm^{-3} NaOH at 388 K. $[TBP]_{org}$ (% m/m): ●, 41.2; ○, 35.7; ■, 30.2; □, 24.5; ▲, 18.7.

traces of NaDBP very thorough cleaning of the reaction vessel was essential at the end of each run. The kinetics were followed by removing samples at known times with a pipette and allowing the layers to separate out while the sample was in a narrow tube. Samples of the top layer (TBP–hydrocarbon) were removed for GC analysis.

Solubility and partition measurements

Partition experiments involving the third phase were carried out by taking an infinity three phase system and carefully separating a samples of the third phase. This was then equilibrated with TBP–*n*-dodecane to measure partition of TBP between the organic and the third phase. To measure the distribution of NaOH between the aqueous and the third phases a portion of the third phase was equilibrated with 8.5 mol dm^{-3} NaOH and TBP–*n*-dodecane at various temperatures. The equilibrated third phase was separated off and the NaOH concentration determined by pH titration.

Results

The standard reaction mixture was 250 cm^3 of 30% v/v TBP–*n*-dodecane (35.7% m/m, 1.096 mol dm^{-3}) and 100 cm^3 of 8.5 mol dm^{-3} NaOH at 388 K. Because the analysis was carried out by GC it was much easier to use *n*-dodecane as the hydrocarbon than OK which has an average composition close to that of a C_{12} paraffin but which contains a large number of components with a wide range of GC retention times. A limited number of experiments using TBP–OK showed no significant differences from TBP–*n*-dodecane. Under these conditions the induction period lasted 10–20 min, and was followed by the onset of autocatalysis. Typical traces are shown in Fig. 1 for a range of TBP concentrations. As there is more than one way of defining the term 'induction period', we specify that in this paper we mean the time over which there was no detectable change in the TBP concentration in the organic layer at the start of reaction. At about the end of the induction period, there was the first appearance of the third liquid phase. It was not practicable to detect this by visual observation of the stirred reaction mixture, and the statement is based upon observations, after settling, of samples taken early in the run for a large number of experiments.

Autocatalysis implies one of the products is acting catalytically, presumably either Bu^{n}OH or NaDBP. Checks with added Bu^{n}OH confirmed, as expected, that it was not the autocatalyst; reactions in which samples of NaDBP were added to the initial reaction mixture showed no induction period, but the immediate onset of autocatalysis. This was observed both for the addition of dried samples of NaDBP, and also for the addition of a liquid sample of the third phase taken from an infinity sample of a reaction mixture. It was found that scrupulous attention to cleaning out the reaction vessel between runs was essential, as even small traces of NaDBP markedly reduced the length of the induction period. During the course of a run the concentration of TBP in the organic phase decreases from the initial value to zero, so a group of runs was carried out in which $[TBP]_{org}$ was varied from 35 to 15% v/v (Fig. 1). All showed an induction period followed by autocatalysis, but as the initial value of $[TBP]_{org}$ decreased the length of the induction period increased, and below 25% v/v the maximum rate of the autocatalytic stage decreased also. Reaction with pure TBP also showed autocatalytic behaviour, but in this case there was no sign of a third phase.

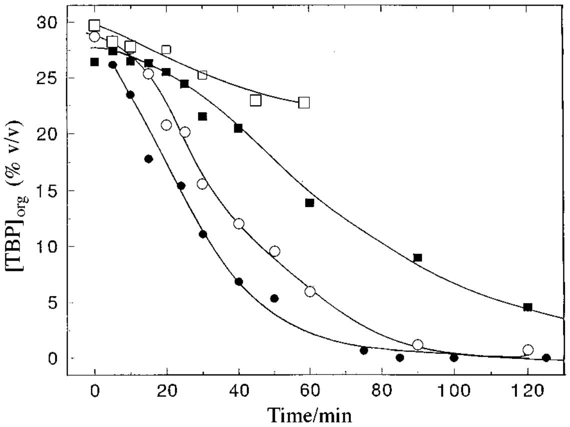

Fig. 2 Experimental data on the effect of $[NaOH]_{aq}$ on the hydrolysis of TBP in the presence of added infinity third phase to eliminate the induction period. $[NaOH]_{aq}$/mol dm^{-3}: ●, 8.5; ○, 7.0; ■, 6.0; □, 4.5.

A few experiments were carried out using lower initial concentrations of NaOH, but with the addition of an aliquot of an infinity third phase to eliminate the induction period. The results, shown in Fig. 2, show that as [NaOH] decreases so does the rate of reaction, and that in the most dilute alkali, 4.5 mol cm^{-3} NaOH, there was no autocatalysis. Experiments in which a larger volume of 4.25 mol dm^{-3} NaOH was used again showed no sign of autocatalysis. In order to obtain a more quantitative understanding of the system our kinetic measurements were extended to homogeneous, single liquid phase systems, and we also examined the partition equilibria between the phases.

Kinetics in aqueous solution

The solubility of TBP in relatively dilute sodium hydroxide at 298 K (<1 mol dm^{-3}) was sufficient for us to study the kinetics of the homogeneous reaction. Individual runs give good first order plots of ln $[TBP]_{aq}$ *versus* time and k_1 was proportional to $[OH^-]$. Measurements from 298–344 K gave an Arrhenius plot for $k_2 = k_1/[OH^-]$ with $E_a = 62.1 \pm 0.6$ kJ mol^{-1} and $10^{-5} A = 2.46 \pm 0.50$ mol^{-1} dm^3 s^{-1}. At 300 K the value of $k_2 = 3.8 \times 10^{-6}$ mol^{-1} dm^3 s^{-1}. Kennedy and Grimley[8] studied the hydrolysis of pure TBP, and also of 20% TBP–OK shaken in contact with 1.02 mol dm^{-3} aqueous NaOH from 303–373 K, following the growth of NaDBP in the aqueous layer. The TBP was labelled with ^{32}P, and the kinetics followed by radioactive counting. From this data for the 100% TBP organic phase k_2 at 300 K is calculated to be 1.6×10^{-6} mol^{-1} dm^3 s^{-1}. The fact that this is somewhat lower than our value may be due to the fact that they washed their aqueous samples with CCl_4 to remove unreacted TBP prior to determining $[NaDBP]_{aq}$. We have found that NaDBP has some solubility in *n*-dodecane, and also in $CHCl_3$, so the possibility of some losses of NaDBP in the CCl_4 wash must exist. An independent estimate of the order of

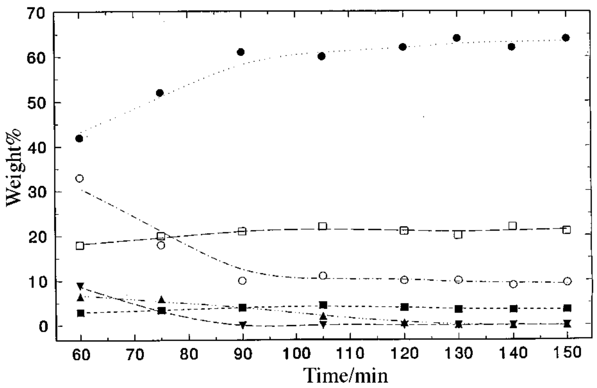

Fig. 3 Variation of composition of third phase with time for hydrolysis of 250 dm^3 of 20% v/v TBP–OK with 7.5 mol dm^{-3} NaOH. ●, NaDBP; ○, OK; ■, NaOH; □, H_2O; ▲, Bu^nOH; ▼, TBP.

magnitude of k_2 can be obtained from the work[5] of Higgins *et al.* They state that for a solution of ^{32}P labelled TBP in 1 mol dm^{-3} NaOH at 25 °C that 'had stood overnight' 18% of the radioactivity was non-extractable into CCl_4. If one regards 'overnight' as being *ca.* 16 h (5 pm to 9 am) then this corresponds to k_2 of 3.4×10^{-6} mol^{-1} dm^3 s^{-1}. Clearly this can be only a rough figure, but it is in the same region as the two other values.

Kinetics in the third phase

The fact that both TBP and NaOH are appreciably soluble in the third phase made it possible to study the hydrolysis reaction under homogeneous conditions in this medium. A sample of the third phase was carefully separated from an infinity reaction mixture. Titration showed it contained 0.82 mol dm^{-3} of NaOH. A fresh aliquot of TBP was then added to a sample of the third phase so that $[NaOH]_0 \gg [TBP]_0$, and reaction was followed by removing 1 cm^3 portions at known times and quenching in 20 cm^3 of water. The NaDBP went into aqueous solution and the mixture was extracted with $CHCl_3$ so that the dodecane and unreacted TBP went into the organic layer (together with a small amount of NaDBP). The TBP concentration was then determined by GC analysis. Individual runs gave good first order kinetic plots (k_1/s^{-1}). It was assumed by analogy with reaction in aqueous media that k_1 was proportional to [NaOH] and a second order rate constant k_2 was calculated. Measurements made over the range 36–65.1 °C gave Arrhenius parameters $E_a = 79.4 \pm 3.2$ kJ mol^{-1} and 10^{-8} $A = 2.7 \pm 1.1$ mol^{-1} dm^3 s^{-1}. This corresponds to a value of k_2 of 4.0×10^{-6} mol^{-1} dm^3 s^{-1} at 300 K, very close to the value observed for the aqueous phase.

Composition of the third phase

This was established in the original pilot plant work to consist of TBP, NaDBP, OK, H_2O, NaOH and a trace of Bu^nOH. The low concentration of the alcohol was because the experiments were run with most of the butanol being distilled off during the course of reaction. Fig. 3 shows the composition of the middle phase during reaction and it can be seen that the TBP concentration falls as it is destroyed by hydrolysis while the concentration of NaDBP rises. We have confirmed the behaviour in our TBP–*n*-dodecane system done under total reflux by ^1H NMR analysis of samples of the third phase. It was easy to resolve and integrate the peak areas for the $-OCH_2$ protons of TBP, NaDBP and Bu^nOH. Use of ^{31}P NMR also yielded analyses for TBP and NaDBP. The original pilot plant work showed the shrinkage of the organic and aqueous phases as the volume of the third phase grew, and the present work has confirmed this result. The ^{31}P NMR results showed that with more concentrated NaOH, up to 11 mol dm^{-3}, significant hydrolysis to the monoester Na_2MBP occurred.

Table 1 Partition and solubility data

Partition data for TBP at 296 K						
$[TBP]_{org}$ (% m/m)	33.9	20.4	15.8	10.5	5.3	
K_1	1.01	1.10	1.11	1.00	1.04	
Solubility data for NaDBP at 296 K						
$[NaOH]_{aq}/mol\ dm^{-3}$	8.5	7.2	6.0	5.1	4.3	3.0
$10^4[NaDBP]_{aq}/mol\ dm^{-3}$	9	14	42	81	154	336

Partition and solubility measurements

The interpretation of the kinetic data requires additional physical data. The solubility of TBP in aqueous NaOH presents some difficulty because of its low value. Measurements at 295 K for [NaOH] = 0, 0.05 and 1.0 mol dm^{-3} gave $10^4[TBP] = 15.7$, 7.44 and 4.06 mol dm^{-3}. This corresponds to a Setschenow coefficient k_s ($\log f = k_sC_s$) of 0.59 mol^{-1} dm^3 in reasonable agreement with a very careful study[5] by Higgins, Baldwin and Soldano using ^{32}P labelled TBP which yielded $k_s = 0.65$ at 25 °C. These workers found no variation in k_s for measurements at 278, 286 and 298 K. In terms of absolute solubilities, Higgins *et al.* found $10^4[TBP] = 15.8$ mol dm^{-3} at 298 K, very close to our value at 295 K.

The partition of TBP between the organic phase and the third phase was examined at 296 K and values of $K_1 = [TBP]_{org}/[TBP]_{thd}$ (concentration units in mol dm^{-3}) are shown in Table 1. There is no significant variation of K_1 with $[TBP]_{org}$. The measurements were extended to cover a range of temperatures from 298–337 K yielding the equation $\ln K_1 = 3.955 - 1225/T$. Solubility data for NaDBP in aqueous NaOH are also in Table 1. The partition of the other reactant, NaOH, between 8.5 mol dm^{-3} aqueous sodium hydroxide and the third phase was also examined as a function of temperature, and values of $K_2 = [NaOH]_{thd}/[NaOH]_{aq}$ fitted the equation $\ln K_2 = -5.25 + 862/T$. From this equation the concentration of NaOH in the middle phase at 388 K is calculated as 0.4/mol dm^{-3}.

Solubility and kinetic measurements on trimethyl phosphate

The low solubility of TBP in aqueous NaOH limited measurements to concentrations up to $[OH^-] = 1$ mol dm^{-3}. In order to get some feel for the likely magnitude of the salt effects of more concentrated alkali we have examined a more tractable triester, trimethyl phosphate, $(MeO)_3PO$, TMP, which has a much greater solubility in aqueous media and a higher reactivity towards OH^-. Solubility plots of $\ln [TMP]_{aq}$ *vs.* [NaOH] over the range 3.49–5.95 mol dm^{-3} sodium hydroxide at 295 K were linear with a slope of -0.39 mol^{-1} dm^3, corresponding to a *decrease* in solubility of a factor of 1.48 per mol dm^{-3} increase in [NaOH]. Kinetic measurement made at 298 K over the range 2–5 mol dm^{-3} [NaOH] yielded a linear plot of $\ln k_1$ *vs.* [NaOH] with a slope of 0.61 mol^{-1} dm^3, an increase in k_1 by a factor of 1.84 per mol dm^{-3} of sodium hydroxide. Thus the net increase in $k_1[TMP]_{aq}$ is 1.84/1.48 = 1.25 per mol dm^{-3} of NaOH. If the plots were linear over the whole range 1 to 8.5 mol dm^{-3}, a bold assumption, the increase in rate for TMP would only be a factor of 5.3. Obviously, this approach can only give a very rough idea of the effect expected for TBP where salting out is likely to be much greater but the figures suggest that the increase in rate of hydrolysis from 1 to 8.5 mol dm^3 NaOH may only be around an order of magnitude because of opposing effects on solubility and nucleophilic reactivity.

Discussion

We begin by considering briefly the rate data for reaction in homogeneous aqueous solution. From the literature it is known[1] that at 308 K values of k_2/mol^{-1} dm^3 s^{-1} for $(MeO)_3PO$

and $(EtO)_3PO$ are 3.35×10^{-4} and 3.56×10^{-5} respectively, which compare with 7.3×10^{-6} for $(Bu^nO)_3PO$. This trend could be due to steric effects and/or leaving group effects. A similar trend but on a smaller scale can be seen for a series of triesters with a common leaving group, the *p*-nitrophenate ion, $(RO)_2(p\text{-}NO_2C_6H_4O)PO$ where $10^2k_2 = 8.8$, 2.67 and 1.8 mol^{-1} dm^3 s^{-1} for R = Me, Et and Bu^n respectively at 310 K. The smaller spread in k_2 values is probably due to the much greater reactivity arising from the excellence of the *p*-nitrophenate anion as a leaving group, but even so it appears that steric effects due to the increased size of the *n*-butyl group are modest. This is confirmed by the observation that differences between the normal, iso and secondary butyl esters $(RO)_2(p\text{-}NO_2C_6H_4O)PO$ are small. We conclude that the low reactivity of $(Bu^nO)_3PO$ is largely due to poor leaving group character, probably poor solvation of the incipient Bu^nO^- ion associated with the hydrocarbon chain.

A more important observation is the similar k_2 value for hydrolysis in the third phase, and in aqueous solution. The much larger solubility of TBP in the middle phase compared to the aqueous phase results in a much greater rate of hydrolysis in the former case. Using the known partition coefficient K_1 the concentration of TBP for the third phase in contact with 30% v/v TBP–*n*-dodecane would be *ca.* 1 mol dm^{-3}. Thus the value of k_2 [TBP][OH$^-$] is 3.3×10^{-6} mol dm^{-3} s^{-1} for the third phase compared with 1.5×10^{-9} mol dm^{-3} s^{-1} for 1 mol dm^{-3} NaOH at 300 K. However, the actual reaction system uses 8.5 mol dm^{-3} NaOH at 388 K. If we use the rate data for TMP to estimate the increase in nucleophilic reactivity from 1 to 8.5 mol dm^{-3} NaOH one should get an increase in rate of a factor of 97, and if we use the Setschenow coefficient of TBP we estimate a decrease in $[TBP]_{aq}$ by a factor of 1.1×10^{-5}. If we used the solubility data for TMP the estimated decrease in solubility would be a factor of 1.2×10^{-3}. Either way, the effect of the decrease in solubility of TBP far outweighs the effect of increased nucleophilic reactivity of the concentrated NaOH. The change in temperature from 300 to 388 K will again favour reaction in the third phase; the activation energies are 79.4 compared to 61.2 kJ mol^{-1} corresponding to an increase of a factor of 5 for k_2 (third phase)/k_2 (aq. phase). One factor that has a slight influence in the opposite sense is that $[OH^-]_{thd}$ decreases by a factor of 2, but this is trivial compared with the other effects. As already mentioned, Higgins[5] found no effect of temperature on the Setschenow coefficient for TBP in aqueous NaOH.

The conclusion seems indisputable that the rate of hydrolysis of TBP in the third phase is orders of magnitude greater than it is in 8.5 mol dm^{-3} aqueous sodium hydroxide, and that this is mainly due to the much greater solubility of TBP in the former phase. It seems clear that the autocatalysis is due to the fact that the third phase, of which the main component is NaDBP, is able to act as an efficient solvent to both TBP and NaOH. The solubility of NaOH is probably enhanced by the significant amount of water in the third phase.

The one stage where the rate of reaction in the aqueous phase is important is in determining the length of the induction period. This is presumably the length of time needed for sufficient TBP to be hydrolysed to saturate both aqueous and organic phases with NaDBP at 388 K. We have measured the solubility of NaDBP in aqueous sodium hydroxide at 296 K and find the data fits the expression ln $[NaDBP]_{aq} = 1.286 - 0.69[NaOH]$ where all concentrations are in mol dm^{-3}. This corresponds to [NaDBP] = 9×10^{-4} mol dm^{-3} in 8.5 mol dm^{-3} sodium hydroxide. However, we do not have data that can be extrapolated to 388 K and in any case we also need data on the solubility in the organic phase at the same temperature. Thus we cannot use our data to make any *prediction* of the length of the induction period at 388 K.

We did carry out a single experiment under standard conditions at 298 K, which was, of course, a very slow reaction. This single experiment yielded an induction period of *ca.* 8×10^5 s. From our solubility of [NaDBP] in the aqueous phase, and assuming a constant rate of hydrolysis of TBP until the end of the induction period one may calculate that $k_2[TBP]_{aq} > 10^{-10}$ s^{-1} in 8.5 mol dm^{-3} NaOH at 298 K.

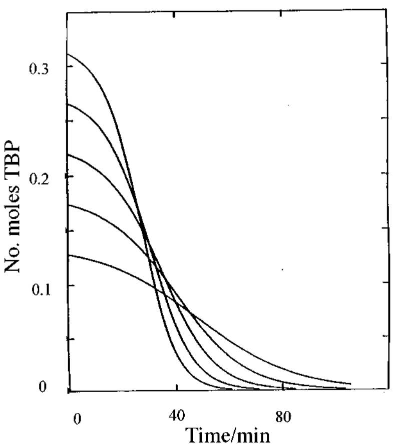

Fig. 4 Curves of number of moles TBP *versus* time computed for various initial amounts of TBP reacting with 8.5 mol dm^{-3} NaOH at 388 K. Calculations for 250 cm^3 organic phase containing 35, 30, 25, 20 and 15% v/v TBP.

As a check on whether our mechanism gave a reasonable account of reaction during the important autocatalytic stage, we have compared the maximum rate of consumption of TBP (at the point of inflexion) with the rate predicted by our other measurements. For reaction under standard conditions at 388 K we measured a maximum rate of 7.6×10^{-5} mol TBP s^{-1} is hydrolysed. To predict the expected rate, it was necessary to extrapolate values of k_2 (third phase), K_1 and K_2 to 388 K and estimate the volume of the third phase (*ca.* 63 cm^3). On the assumption that every reaction in the third phase leads to hydrolysis we predict a rate of *ca.* 3.6×10^{-5} mol TBP s^{-1}. In view of the assumptions made and the inevitable extrapolation of data, we consider the difference of a factor of 2 to be acceptable.

Our mechanism accounts qualitatively for the effect of varying $[TBP]_{org}$ and $[NaOH]_{aq}$. A decrease in the initial value of $[TBP]_{org}$ will necessarily reduce $[TBP]_{aq}$, slow the rate of hydrolysis at the start and hence increase the induction period. Again the rate of the autocatalytic stage is determined by what happens in the third phase, and the volume of the third phase will be related to the amount of hydrolysis that has occurred. Clearly, if we compare rates at a given volume of the third phase, then as the initial value of $[TBP]_{org}$ decreases, the rate of the autocatalytic stage must decrease. The effect of changes in $[NaOH]_{aq}$ can be explained similarly. A reduction in [NaOH] greatly increased the solubility of NaDBP in the aqueous phase, and thus much more hydrolysis (taking a longer time) is required to saturate the aqueous phase. A decrease in $[NaOH]_{aq}$ will also reduce the sodium hydroxide concentration in the third phase and hence slow down the rate of the autocatalytic stage.

We have attempted to develop a computer model for the autocatalytic stage of the system, assuming that all the hydrolysis occurs in the third phase, that the volume of the third phase is proportional to the amount of TBP hydrolysed and that equilibrium is maintained between the phases. To avoid the problem of the induction period all calculations were started with an amount of third phase equivalent to the hydrolysis of 0.01 mol TBP for our standard mixture of 250 cm^3 30% TBP–*n*-dodecane and 100 cm^3 8.5 mol dm^{-3} NaOH at 388 K. Rate constants and partition coefficients were values obtained in the present work, extrapolated to 388 K. Fig. 4 shows the effect of varying the number of moles of TBP initially present and shows how as $[TBP]_{org}$ decreases the rate of the autocatalytic reaction decreases. Fig. 5 shows the effect of decreasing [Na-

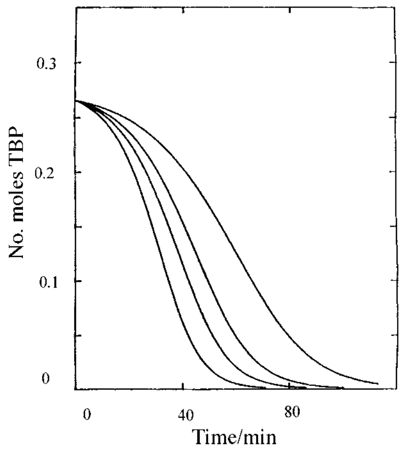

Fig. 5 Curves showing the computed effect of varying $[NaOH]_{aq}$ for reaction with TBP at 388 K. Calculations for 250 cm^3 organic phase containing 30% v/v TBP.

$OH]_{aq}$. These calculations serve to show that our model describes the broad features of this complicated system. We have not made any attempt to optimise the calculation by varying the numerical values for the parameters as the model is clearly a very simplified one. Thus the composition of the third phase must vary during the course of reaction as the composition of the organic phase varies, and this in turn must lead to changes in k_2, K_1 and K_2. For the higher values of $[TBP]_{org}$ there is probably some NaDBP dissolved in the organic phase. Indeed for the hydrolysis of pure TBP with 8.5 mol dm^{-3} NaOH autocatalysis is observed, but there is no detectable third phase. We suggest that NaDBP dissolves in TBP, possibly to form inverse micelles, and thereby solubilises H_2O and NaOH into the organic phase, thus increasing the rate of reaction. The work of McKay *et al.*[9] shows that the increase in solubility of TBP in water from 30% v/v to 100% is not very large, so it seems certain that the increase in rate is due to solubilisation of NaOH into TBP. This suggests that one effect of the hydrocarbon diluent is to make the organic phase much less polar, reducing the solubility of NaDBP and leading to the formation of the NaDBP rich third phase. It is clear also that the effect of using concentrated NaOH also drives the system to form the third phase reducing the solubility of NaDBP in the aqueous phase. The third phase, which can dissolve both TBP and NaOH, serves to bring the reactants together. The physical chemistry of this complex six component solvent is an unexplored area.

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