STUDY OF REACTIONS IN TWO-PHASE SYSTEMS HYDROLYSIS OF TRIPHENYLMETHYL CHLORIDE IN WATER-ORGANIC SOLVENT SYSTEMS

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The rate of hydrolysis was studied for triphenylmethyl chloride in water-organic solvent systems with an unstirred interface of a known area. The hydrolytic reaction was found to take place at the interface only. The temperature dependence of the reaction rate indicates that at lower temperatures (up to 60°C) the rate-determining step is the chemical reaction, whereas at higher temperatures a deviation from the Arrhenius type dependence is observed, which along with the low activation energy value points to the diffusion as the governing phenomenon. The effect of salts added to the aqueous phase is consistent with the expected behaviour for the S_N1 mechanism, but surprising is the inhibiting effect of some quaternary ammonium salts. In the study of the effect of the organic solvent, the reaction rate was found to correlate satisfactorily with the solubility of the organic solvent in water, but no correlation was established with the solubility of water in the solvent. From the results obtained it can be inferred that the reaction site is the laminary layer adjacent to the interface from the aqueous phase side.

A number of organic reactions are accomplished in systems of two immiscible liquids that are stirred together vigorously; this approach has found application particularly since the successful introduction of phase transfer catalysts. Still, only few works have been aimed at gaining detailed information concerning the reactions taking place in this arrangement[1-3]. The main problem of such a study lies in the fact that the true interface area, which is a crucial parameter of the treatment, is difficult to determine and reproduce experimentally. The simplest way of circumventing this difficulty consists in performing the reaction without mutually stirring the two liquid phases; the phases are allowed to form two separate layers that are stirred gently so as to avoid disturbances of the interface. In such an arrangement the interface area in the macroscopic sense is determined readily and accurately, and moreover, it remains constant during the process. The reason why this simple approach has been so far employed only rarely is to be sought in the fact that most organic reactions suitable for an aqueous-organic two-phase system are too slow if the phases are not mixed intimately, so that the kinetic parameters are difficult to determine.

In the present work, use has been made of aqueous hydrolysis of triphenylmethyl chloride as a model reaction which proceeds with a measurable rate even if the two phases rest in a simple contact, yet is amenable to measurement without special provisions also if the system is stirred vigorously. Furthermore, the reaction mechanism is known in principle beyond doubts[4,5], and this knowledge can be utilized when interpreting the interface phenomena.

EXPERIMENTAL

Triphenylmethyl chloride was prepared by the Friedel–Crafts reaction of benzene with tetrachloromethane catalyzed by aluminium chloride[6], and purified by crystallization from a benzene–light petroleum mixture. The melting point of the product used for the kinetic measurements was 111–112°C, its purity was checked by IR spectroscopy and elemental analysis. The organic solvents were redistilled prior to use.

Apparatus. The hydrolytic reactions were carried out in cylindrical vessels of diameters 45 to 80 mm with sealed-on jackets for thermostating (Fig. 1). The bottom of the vessels was provided with a sealed-in salt bridge with a glass filter for a calomel electrode and an opening for introducing an ion-selective electrode. The two electrodes used were CRYTUR, RCE 101 (calomel) and 17-17 (chloride) electrodes manufactured by Monokrystaly, Turnov. In the case of organic solvents heavier than water there were no openings in the bottom, the electrodes being introduced into the upper aqueous layer from above. The two phases — water or an aqueous solution of a salt and the solution of triphenylmethyl chloride in the solvent chosen — were placed in the reactor with care so as to prevent any appreciable mixing at the interface. The separate, very cautious stirring of the phases was accomplished either with a combination of a magnetic stirrer from below and a propeller stirrer from above (Fig. 1), or with a precisely adjustable vibrating stirrer after Hančil, Rod and Řeháková[7]. As long as the stirring intensity is held at a level low enough to prevent the interface from disturbances, there is no substantial difference between the two ways of stirring.

The kinetic measurements were performed using triphenylmethyl chloride in the solvent of choice, solution concentrations 0·025—0·250 mol l^{-1}. The course of the reaction was monitored by measuring the potential changes of the chloride electrode on an OP-205 precision

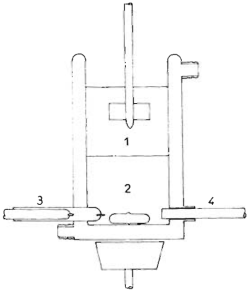


FIG. 1

Layout of the reaction vessel. **1** Organic phase, **2** aqueous phase, **3** calomel electrode, **4** ion- selective electrode

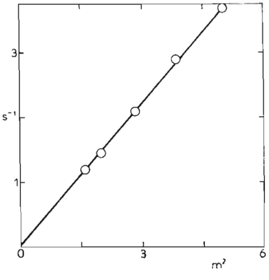


FIG. 2

Dependence of the experimental rate constant k_{exp} on the interface area A in the toluene–water system at 50°C pH-meter (Radelkis, Budapest), the increment of the chloride concentration was determined by using a calibration plot. The results were evaluated by applying the rate equation

$$r_A = k_A c_{org} , \qquad (1)$$

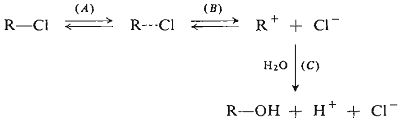
in which r_A is the rate per unit area (mol s^{-1} m^{-2}) and k_A is the rate constant normalized with respect to the organic phase volume and the interface area,

$$k_A = k_{exp} V_{org}/A , \qquad (2)$$

where k_{exp} is the 1st order rate constant determined from the time dependence of the degree of conversion of the reactant, V_{org} is the volume of the organic phase, and A is the macroscopic interface area.

RESULTS AND DISCUSSION

The mechanism of the model reaction under study can be, with a high reliability, thought of as consisting of a typical sequence of steps of a monomolecular nucleophilic substitution, referred to as the S_N1 mechanism. This mechanism can be formulated as a gradual lengthening of the C—Cl bond (step (*A*)), a monomolecular dissociation of the bond as the rate-determining step (step (*B*)), and finally a rapid attack of the nucleophilic agent (water) on the carbonium ion formed (step (*C*)) (refs[4,5]):



($R = (C_6H_5)_3C$).

In the two-phase system, the conditions for the reaction will change dramatically on the transition from the inert solvent to the aqueous phase. Owing to the rapid increase in the polarity of medium, the reaction should be so substantially accelerated in a close vicinity to or directly at the interface that it should take place just here and only to a low extent in the bulk of one or the other phase. From a mechanistic model it also follows that the reaction should obey the 1st order kinetics, and as the products are efficiently separated from the unreacted substrate, the typical side effects of S_1N reactions, such as the reversibility effect, should be suppressed.

The hydrolysis experiments carried out applying different substrate concentrations in the organic phase and using vessels of different diameters gave evidence that these assumptions are essentially satisfied. The time dependences of the chloride ion concentration in the aqueous phase obeyed the 1st order kinetics, and the experiment performed in vessels of different diameters demonstrated a linear dependence of the rate on the interface area (Fig. 2). These facts are documented by Table I, in which the k_A constant is seen to be independent of the substrate concentration in the organic phase over a fairly wide concentration region.

The question as to whether the determining phenomenon is the chemical reaction at the interface or the substrate diffusion towards the reaction site could be settled based on the temperature dependence of the hydrolytic reaction. Over the temperature

TABLE I

Dependence of the rate constant k_A on the concentration of triphenylmethyl chloride in the organic phase; solvent: toluene, $t = 50°C$

Concentration in the organic phase mol l^{-1}	$k_A \cdot 10^6 \pm s_X$[a] m s^{-1}
0·025	1·19 ± 0·02
0·050	1·27 ± 0·08
0·100	1·23 ± 0·11
0·200	1·26 ± 0·05
0·250	1·31 ± 0·05

[a] Standard deviation of the average from five experiments.

TABLE II

Activation energy of hydrolysis of triphenylmethyl chloride

System	Activation energy kJ mol^{-1}	Reference
Toluene–water[a]	46·8 (45—60°C)	this work
	6·9 (>65°C)	this work
Ethanol–water[b]	52·3	8
Acetone–water[b]	61·8	9
Acetone–water[b] (7—1%)	52·7—62·8	10

[a] Two-phase system; [b] homogeneous system.

region 45 – 70°C two types of temperature dependences were found: at lower temperatures, approximately 45 – 60°C, the reaction rate obeys well the Arrhenius equation, whereas at higher temperatures the rate increment diminishes markedly (Fig. 3).

TABLE III

Effect of salts added to the aqueous phase on the rate of hydrolysis of triphenylmethyl chloride in the toluene–water system at 50°C

Salt	Salt concentration mol l^{-1}	$k_A \cdot 10^6 \pm s_x^a$ m s^{-1}
—	—	1·33 ± 0·04
NaCl	0·1	1·07 ± 0·03
NaCl	1·0	0·86 ± 0·06
KBr	0·1	2·04 ± 0·05
$(C_4H_9)_4NCl$	0·1	0·58 ± 0·06
$(C_4H_9)_4NBr$	0·1	0·66 ± 0·04
Sodium lauryl sulphate	0·1	1·35 ± 0·07

[a] Standard deviation of average from five experiments.

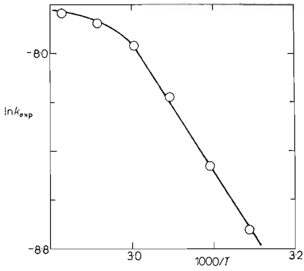


FIG. 3

Dependence of the rate constant in the toluene–water system on temperature

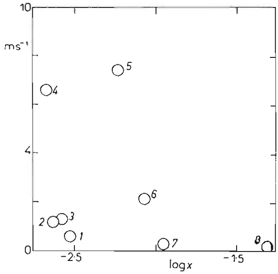


FIG. 4

Dependence of the rate constant at 50°C on the solubility of water in the organic solvent (x). *1* Benzene, *2* toluene, *3* ethylbenzene, *5* chloroform, *6* 1,1,2,2-tetrachloroethane, *7* dibutyl ether, *8* dibutyl phthalate

This can be interpreted in a straightforward way, namely so that at lower temperatures the overall rate is determined by the kinetics of the chemical reaction itself, but at higher temperatures this process is accelerated to such an extent that it becomes commensurable with the rate of the diffusion, which then – at temperatures above 65°C – becomes the rate-determining step.

The activation energy calculated from the linear part of the temperature dependence and that estimated from the dependence for higher temperatures are 47·8 and 6·9 kJ . . mol^{-1}, respectively. The latter is consistent with the low temperature coefficient values commonly encountered in transport phenomena, the former agrees with the values obtained by various authors for the hydrolysis of triphenylmethyl chloride in homogeneous alcohol–water or acetone–water systems (Table II). Of the values published, of great interest are those reported by Golomb[8], who investigated the activation energy also in dependence on the content of water in acetone (over the range of 1–7% vol.) and found a marked decreasing trend of the activation energy values with increasing water content. From the fact that the activation energy obtained by us is still lower we can thus deduce that the concentration of water in the transition state of the rate-determining step is even higher and hence, the reaction site is more likely than not on the aqueous side of the interface rather than on the organic phase side.

The same conclusion could be drawn from the study of the so-called salt effects. Sodium chloride – a salt with a common ion – added to the aqueous phase depresses the hydrolysis rate, whereas potassium bromide – a salt with no common ion – enhances it. By their extent these effects are comparable to those encountered in homogeneous systems. These results are perfectly consistent with the theory of effects of salts with various anions on the rate of monomolecular substitutions proceeding *via* the S_N1 mechanism. In view of the fact that the solubility of salts such as NaCl or KBr in toluene is virtually zero, the hydrolytic reaction obviously takes place in a medium whose aqueous nature si pronounced enough for the specific effects of the dissolved salts to be able to appear. In other words, the hydrolytic reaction can only occur after the passage across the interface – though in its close vicinity, still on the aqueous side.

If, however, a common or a foreign ion is applied in the form of a quaternary ammonium salt, a marked inhibition of the hydrolytic reaction is observed (Table III). The inhibiting effect is obviously associated with the amphipatic nature of the bulky quaternary cations, which to a higher extent occupy the interface, interfering thus with the reaction. This interference is, obivously, of a specific nature, as the analogous anion-active tenside, sodium lauryl sulphate, which also concentrates at the interface, does not affect the hydrolytic reaction. These results are in contrast to the theory of action of quaternary ammonium salts as phase transfer catalysts. This is probably due to the fact that for an efficient catalytic function of quaternary salts, the reaction must take place more or less in the organic phase bulk, to which the salts are transported by the appropriate agents. Unless the reaction proceeds, even in part, within the organic phase, there is no reason for catalysis by the reagent transport across the interface. From this viewpoint the results obtained bear out our conclusion that the hydrolytic reaction only occurs at the interface, on its aqueous side. On the other hand, however, the marked inhibition observed is a new and unexpected effect.

If the hydrolytic reaction really takes place only after the passage across the interface, the nature of the organic solvent should not essentially have a bearing on the reaction rate. This assumption has not been confirmed: even in our static system, where all the hardly examinable effects associated with the dispersibility of water and the organic solvent are eliminated, great differences were found in the rate of hydrolysis of triphenylmethyl chloride in systems with different solvents. We attempted to correlate the values with the mutual solubilities of water and the organic solvents; the results are presented in Figs 4 and 5. While there is evidently no relation between the rate constant values and the solubility of water in the organic solvent (Fig. 4), an indication is observed of a correlation with the solubility of the organic solvents in water ($r^2 = 0{\cdot}73$) (Fig. 5). This different correlatability again is in accordance with the above conclusion that it is in the laminary layer adjacent to the interface from the aqueous side that the reaction occurs. The extent to which the organic solvent dissolves in this layer agrees qualitatively with the extent to which the reaction is affected by it.

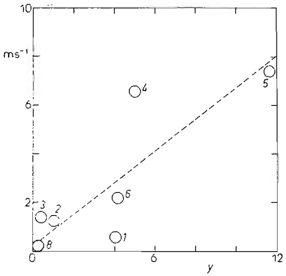


FIG. 5

Dependence of the rate constant at 50°C on the solubility of the organic solvent in water (y). Solvent numbering as in Fig. 4

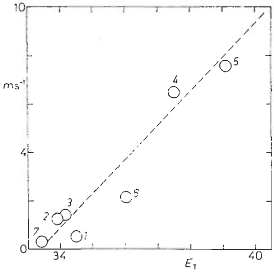


FIG. 6

Dependence of the rate constant at 50°C on the E_T parameter. Solvent numbering as in Fig. 4

So far it is difficult to decide whether the polarity of the solvent plays a dominant part or whether the effect involved is a mere increase in the solubility and, consequntly, in the concentration at the reaction site. Of the various ways of monitoring the effect of the solvent polarity on the reaction rate, the most convenient Y parameter method, derived based on a reaction of the same mechanism as the studied one[11], S_1N, is unfortunately inapplicable to our case as the parameters are only available for more or less aqueous systems such as ethanol–water, acetone–water, dioxane, dioxane–water, *etc*., hence for solvents miscible with water. Of the other parameters available, the most suitable is the ample set of the E_T parameter data[12,13] based on spectroscopic measurements; these values were found to correlate very well with the rate constants measured $(r^2 = 0{\cdot}94)$ (Fig. 6).

We can conclude that aqueous hydrolysis of triphenylmethyl chloride represents a suitable model reaction for a two-phase liquid system. By combining some kinetic and mechanistic concepts we were able to give evidence that the reaction takes place directly at the interface or in its close vicinity, and so its rate is a function of the interface area. This conclusion was further refined so – speaking in terms of the simple film theory – that the reaction site is the laminary layer adjacent to the interface from the aqueous phase side. The approach used also indicates the potentialities of a study of a static reaction system with unstirred interface in conjunction with the exploitation of the available data of the analogous homogeneous systems.

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