the calculations for temperature rise. Corrections were made graphically for heat leak where appropriate; since the heat leak for the calorimeter was about 5×10^{-5} s^{-1} (half-time for cooling of about 200 min) reactions with half-lives of as much as 20 min could conveniently be followed. Since the response lag of all the various components of the calorimeter was only a few seconds, rates could be measured for reactions with half-lives of only a fraction of a minute.

Acknowledgment. This research was supported by the National Science Foundation and by the Cope Award of the American Chemical Society. We thank Professor J. P. Guthrie for helpful criticisms.

Registry No. Trimethyl phosphate, 512-56-1; trimethyl phosphite, 121-45-9; triethyl phosphate, 78-40-0; triethyl phosphite, 122-52-1; dimethyl methylphosphonate, 756-79-6; dimethyl hydrogenphosphonate, 868-85-9; diethyl methylphosphonate, 683-08-9; diethyl hydrogenphosphonate, 762-04-9.

Thin-Layer Phase-Transfer Catalysis in the Reaction of Alkyl Chlorides and Solid Formate Salt

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Contribution from the Casali Institute of Applied Chemistry, The Hebrew University of Jerusalem, 91904 Jerusalem, Israel. Received June 2, 1987

Abstract: A systematic study of the quaternary ammonium catalyzed solid–liquid esterification of alkyl chlorides by alkali formate has been undertaken. The maximum conversion and the kinetics of the reaction were found to be strongly dependent on the type of formate salt used. The reaction rate was highest when a definite amount of water was added. The optimal water content varied strongly when the inorganic cation, the reaction temperature, or the catalyst concentration was changed. When the amount of water was limited, most of it was found surprisingly in the organic phase as water of hydration of the quaternary ammonium ion pair, reducing the rate of the homogeneous reaction step. At very low water concentrations the overall rate was limited by slow mass transfer, which could be enhanced by application of ultrasound.

The coextraction of water in liquid–liquid phase-transfer catalysis (PTC) has a negative influence on certain types of reactions.[1-3] Two methods have been suggested to solve this problem. One of them, the application of highly concentrated aqueous solutions of KOH and NaOH,[4,5] suffers from catalyst decomposition when onium salts are used as catalysts. Therefore the second, the use of solid–liquid systems, is widely employed.[1,6-8] It is quite surprising that only very little effort has been made to evaluate the influence of various parameters on this type of reaction. It has been found by different workers that the reaction velocity in various systems is a function of the amount of water employed and that an optimum amount of water results in the fastest rates.[8-12] Since the influence of various reaction parameters on this optimum amount has not been tested, the conclusions drawn were quite limited. Furthermore, the amount of water present is generally represented as a fraction of the solid phase,[8-11] thereby suggesting that this is its actual location in the system, although this has never been examined.

Table I. Solubility Ratio and Formation of Decyl Formate with Different Formate Salts[a]

type of cation[b]	solubility ratio[c]	max conversion (%) after 48 h	rate constant (min^{-1}) × 10^3
Ca^{2+}	0.1	0%	
Li^+	0.4	11%	0.1[d]
Na^+	4	98%	2.0[e]
K^+	12	100%	11.4[e]

[a] Reaction conditions: chlorodecane, 18 mmol; Aliquat, 1.05 mmol, made up to 12.0 mL with *o*-dichlorobenzene; inorganic formate (36 mmol)–1% (w/w) H_2O; mechanical agitation at 800 rpm; 100 °C. [b] The data obtained with ammonium formate are irrelevant due to (a) sublimation of the solid out of reach of the organic phase and (b) formation of formic acid by hydrolysis of the salt, which causes depression of the substitution reaction.[17] [c] Ratio of solubilities of formate and chloride salts, at 100 °C.[16] [d] Approximate pseudo-first-order rate constant. [e] Pseudo-first-order rate constant.

It has been proposed that in the presence of a slight amount of water, dissolution of the inorganic salt in the aqueous film precedes the ion exchange with the catalyst salt.[9,13] If this is true, then the kinetics of the overall reaction should be strongly dependent on the relative solubilities of the attacking (Y^-) and the displaced (X^-) ions in this film, as can be seen from eq 1 and 2,[14] where Q represents the quaternary onium cation.

$$-d[RX]/dt = k_2[RX][QY] \qquad (1)$$

$$[QY] = [QX]_{org} K^{sel}_{Y/X} \frac{[Y^-]_{aq}}{[X^-]_{aq}} \qquad (2)$$

This correlation between solubility and reaction rate has been confirmed experimentally.[15]

Recently, it has been shown that the maximum conversion obtainable in different solid–liquid exchange reactions varies with the amount of water present in the system.[9,11,13] In the case of bromide/chloride exchange the results could be correlated to the

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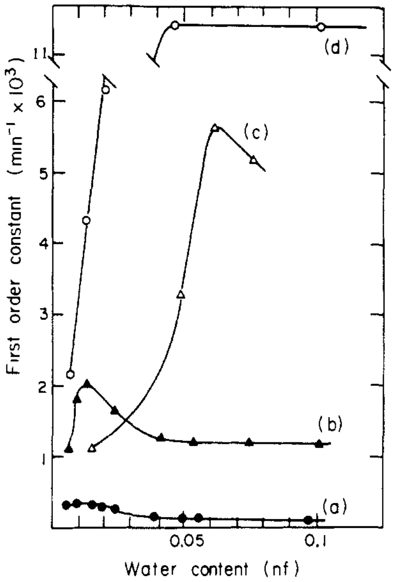

Figure 1. First-order rate constants as a function of the water content (n_f; total mol of H_2O per mol of formate). Reaction conditions: chlorodecane, 18 mmol; formate, 27 mmol; Aliquat 336, made up to 12 mL with *o*-dichlorobenzene; agitation, 800 rpm. Cation, temperature, and catalyst quantity (mmol) as follows: (a) Na^+, 75 °C, 1.05; (b) K^+, 75 °C, 1.05; (c) K^+, 75 °C, 3.5; (d) K^+, 100 °C, 1.05.

relative solubilities of different inorganic halides in water.[13]

This paper reports a study of the various factors affecting the onium salt catalyzed formate–chloride exchange in a solid–liquid system.

Results and Discussion

Reactions with Different Formate Salts. The reaction of 1-chlorodecane with solid formate salts containing 1% (w/w) water was studied at 100 °C using *o*-dichlorobenzene as solvent and trioctylmethylammonium chloride (Aliquat 336) as catalyst (eq 3). The maximum conversion (48 h) and the reaction kinetics

$$C_{10}H_{21}Cl + MO_2CH \xrightarrow{QCl} C_{10}H_{21}O_2CH + MCl \quad (3)$$

were compared to the solubility ratio of the respective formate and chloride salts. As data on this three-component system (1% H_2O!) are not available, we had to correlate our results to the solubilities of the pure salts (in water, 100 °C) as published in the literature.[16]

With sodium formate and potassium formate pseudo-first-order kinetics according to eq 4 was observed up to at least 70% conversion.

$$d[RO_2CH]/dt = k_1[RCl] \quad (4)$$

When eq 4 and 1 are compared, it is evident that the concentration of QO_2CH in the organic phase must be constant throughout this range and that the first-order rate constant is the product of this concentration and the second-order rate constant.

The results are summarized in Table I. The significant correlation between the solubility ratio of the salts and their performance in the overall displacement reaction is evident.

In the following experiments our interest was focused on the well-performing sodium and potassium formates.

Influence of Various Parameters on the Reaction Kinetics. We studied the effect of the water on the reaction (eq 3, with sodium and potassium formates) as a function of temperature (75 and 100 °C) and the catalyst amount (1.05 and 3.50 mmol). The results were analyzed according to the water content measured at the end of each run. (At 100 °C small water losses occurred during the reaction.)

All reactions obeyed pseudo-first-order kinetics in the range studied. In Figure 1 the first-order rate constants are plotted versus the water content of the systems (n_f = total moles of water per mole of formate salt). The curves obtained are rather puzzling:

(1) At n_f = 0.01 the reaction with potassium formate is hardly accelerated by an increase in the temperature. This indicates a mass transfer controlled process, although curve b (75 °C) has its maximum at this water content.

(2) At the same water content the reaction rate is *reduced* by the addition of catalyst (compare curves b and c).

(3) Potassium formate and sodium formate (curves a and b) behave similarly up to n_f = 0.06. Above this water content the rate with potassium formate is constant, whereas the rate with sodium formate continues to decrease. (This is more easily observed when the curves are drawn to a larger scale.)

(4) Curve d, obtained for reactions with potassium formate at 100 °C, has no definite optimum. Instead the rate constant increases with water content, until a certain plateau is reached.

These facts will be investigated and discussed in the following sections.

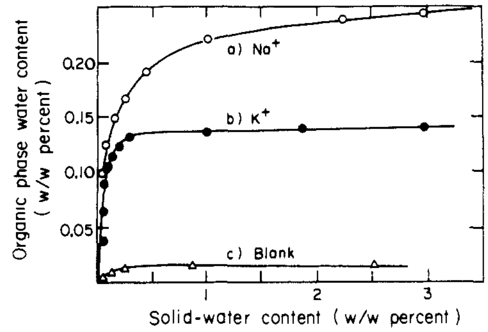

Figure 2. Water distribution between the solid and the liquid phases. Reaction conditions for curves a and b as in Figure 1. Reaction conditions for curve c are the same as for curve b but *without* Aliquat 336.

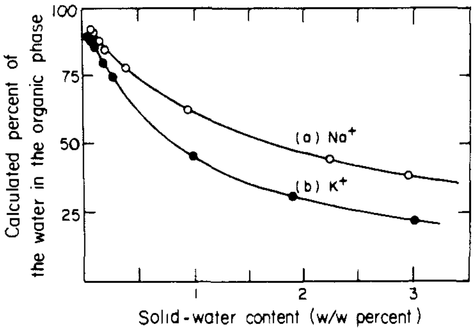

Figure 3. Fraction of water found in the organic phase. Calculated from curves a and b in Figure 2.

Distribution of Water between the Organic and the Solid Phases. When the water content of the different phases in the kinetic experiments of the former sections was measured, we found that the water distribution between the two phases reached equilibrium after approximately 10–20 min and that most of the water had drifted from the inorganic solid phase to the organic phase. We investigated the distribution for different initial amounts of water at 75 °C, after 100 min of mechanical agitation. Mass balance showed that at this temperature the water loss or gain was less than 15%, throughout *all* the water concentration range.

The higher the catalyst concentration in the organic phase (up to 0.3 M), the more water it extracted. In the absence of any PTC (control), the organic phase remained relatively dry. The results obtained with 1.05 mmol of catalyst[18] and without catalyst

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(18) Whereas the water concentration of the organic phase can be measured directly, the water content in the solid must be calculated from the measurable water concentration of a solid–liquid mixture (60–80% solid), which is obtained after the solid is allowed to settle. When the water *concentration* in the organic phase exceeded the water concentration in the solid by far, this determination was very inexact. Any attempt to separate the mixture prior to the water determination resulted in a great increase in the water content of the solid during handling. Therefore the distribution of water between a catalyst-rich organic phase (0.3 M) and the solid could not be determined quantitatively.

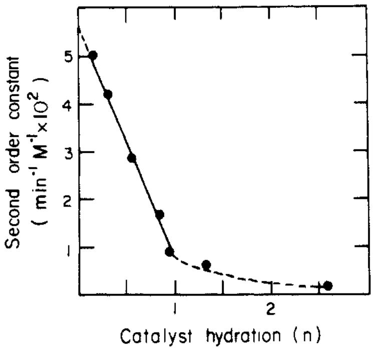

Figure 4. Effect of the catalyst hydration (mol of H_2O per mol of catalyst) on the homogeneous reaction rate. Reaction conditions: chlorodecane, 10 mmol; trioctylmethylammonium formate, 3.2 mmol, made up to 10 mL with *o*-dichlorobenzene; 75 °C.

are presented in Figures 2 and 3. The catalyst ion pair (1.05 mmol corresponds to only 4 mol % of the formate salt present) evidently competes well, even with a very hygroscopic salt such as potassium formate, for the water available, especially when the reaction system is extremely short of water. At higher water concentrations, the water content in the organic phase rises only with the less hygroscopic sodium formate.

The degree of catalyst hydration can be calculated by deducing the control value from the total water content of the organic phase.

Effect of Catalyst Hydration on the Reaction Rate. When trioctylmethylammonium formate was prepared by the method of Bar et al.[19] and the homogeneous step of the reaction (eq 5)

$$C_{10}H_{21}Cl + (C_8H_{17})_3CH_3N^+{}^-OOCH \rightarrow C_{10}H_{21}COOCH + (C_8H_{17})_3CH_3N^+Cl^- \quad (5)$$

was performed separately, irreversible second-order kinetics was observed, up to at least 70% conversion. Afterward the reaction rate deviated downward, in the reactions where the average catalyst hydration (n) was less than 0.4. The final conversion was 100%. The second-order rate constant decreased linearly by 85%, when n increased from 0.1 to 1 mol of water per mol of catalyst (Figure 4). This linear behavior together with the low rate observed at $n = 1$ might suggest that the *nonhydrated* quaternary ammonium formate (quat formate) is a much more efficient nucleophile in this reaction than its monohydrated form. Its concentration increases linearly with the water content decrease of the organic phase. The ratio of the rate constants at $n = 0$ (extrapolated value) and $n = 1$ is approximately 7.

Considering the strong influence of the catalyst hydration on the reaction rate, the observation of second-order kinetics throughout 70% of the reaction requires a constant ratio of monohydrated to nonhydrated quat formate molecules in that time. The slowdown of the reaction toward its end could then be explained by a slow increase of this ratio. In other words, the quat chloride formed during the reaction must have a similar but somewhat lower affinity for water than its formate counterpart. For chloroform solutions this has been shown by Bar et al.[20]

Solid–Liquid Mass Transfer. There has been some disagreement concerning the question of whether solid–liquid mass transfer *can* occur by direct attack of the quat molecule on the ions bound in a crystal; if mass transfer cannot occur, prior dissolution of the salt in an aqueous film is required. The curves shown in Figure 1 already suggested that in the absence of water, mass transfer is at least extremely slow.

We studied the buildup of quat formate when a solution of quat chloride in *o*-dichlorobenzene is mixed with solid sodium formate and potassium formate (Figure 5) containing different amounts of water. The following results were obtained:

(1) The equilibrium concentration of quat formate is by far higher with potassium than with sodium formate (greater than 80% compared to 17%).

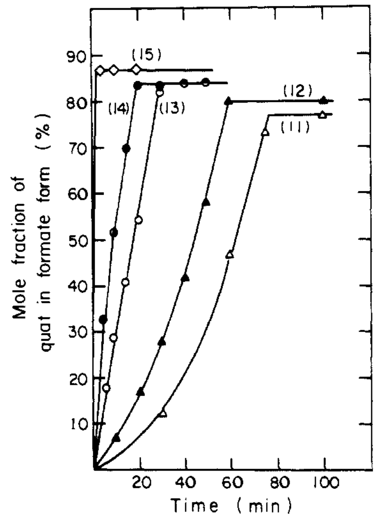

Figure 5. Solid–liquid mass transfer with potassium formate. Reaction conditions: formate, 27 mmol; Aliquat 336, made up to 12 mL with *o*-dichlorobenzene: agitation, 800 rpm. Temperature, catalyst amount, and water content in the solid (approximately[18]) and liquid phases as follows: (11) 25 °C, 3.5 mmol, 0.03%, 0.081%; (12) 75 °C, 3.5 mmol, 0.03%, 0.080%; (13) 75 °C, 3.5 mmol, 0.05%, 0.098%; (14) 75 °C, 1.75 mmol, 0.05%, 0.054%; (15) 75 °C, 3.5 mmol, 0.3%, 0.305%.

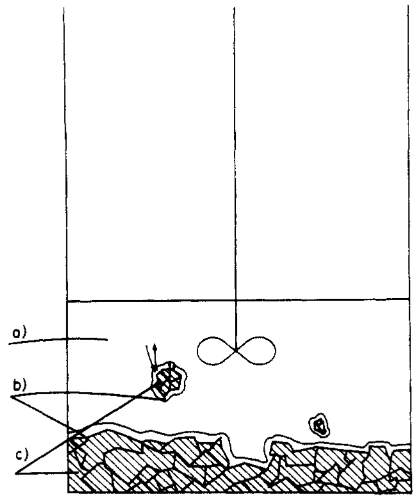

Figure 6. Mass transfer in thin-layer phase-transfer catalysis: (a) organic phase; (b) aqueous film; (c) solid.

(2) Whereas the equilibrium composition is only slightly dependent on the water content (87% (curve 11) compared to 80% (curve 12)), the rate of the exchange process is strongly enhanced by the addition of water.

(3) As expected, the activation energy of the mass transfer process is low.

(4) The curves obtained at low water content (curves 11–14) clearly show that the rate of mass transfer is not dependent on the concentration of quat chloride. Therefore quat chloride is not participating in the rate-determining step of the process.

In order to account for these facts, we propose the following mechanism for mass transfer (Figure 6):

$$MOOCH_{crystal} \rightarrow MOOCH_{aq\ film} \qquad \text{rate determining}$$

$$MOOCH_{aq\ film} + QCl_{org} \rightleftharpoons QOOCH_{org} + MCl_{aq\ film} \qquad \text{fast}$$

$$KCl_{aq\ film} \rightarrow KCl_{crystal}$$

Since the catalyst takes part only in the second step in this mechanism, we have termed the overall process "thin-layer phase-transfer catalysis".

Comparison of the Heterogeneous and the Homogeneous Reactions. In Figure 7 the heterogeneous first-order constants (Figure 1) obtained with potassium formate are shown as a

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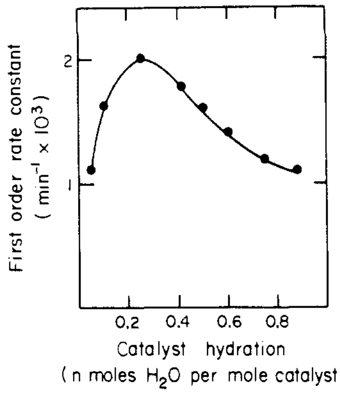

Figure 7. First-order rate constant as a function of the catalyst's hydration in heterogeneous reactions with potassium formate. Reaction conditions, as in Figure 1b; 75 °C.

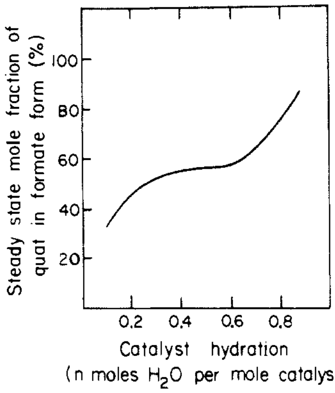

Figure 8. Calculated steady-state concentration of quat formate as a function of catalyst hydration in heterogeneous reactions with potassium formate.

function of the catalyst hydration. The rate constant is greatest at $n = 0.2$ (mol of water per mol of catalyst). We calculated the steady-state concentration of quat formate (ssc) in the heterogeneous reaction (Figure 8) from the measured rate constants of the homogeneous and the heterogeneous reactions (compare eq 1 and 4). Experimental determination of the ssc confirmed these calculated results approximately.[21] The curve in Figure 8 has a rather puzzling form, but if the ssc is plotted against the corresponding water content of the solid (Figure 9), it becomes clear that the rise in the ssc between $n = 0.7$ and $n = 0.88$ (Figure 8) is caused by the simultaneous great increase in the water content of the solid. Efficient mass transfer is therefore (as expected) a function of the water content of the solid, and not dependent on the total water content of the system.

Thus, when the overall heterogeneous reaction rate is plotted as a function of the total water content, four regions are observed (three of which are shown in Figure 1b). Initially the addition of water increases the rate (until a maximum is reached) due to improved mass transfer. Further addition of water causes reduction of the rate, since the rate-limiting homogeneous reaction step is slowed down by the higher catalyst hydration. With even more water the rate becomes insensitive to changes in the water content, since (although the organic phase is still far from saturation) most of the added water is held as an aqueous film on the solid, where it has no influence on the homogeneous step. (A rise in the water content of the solid phase from 0.35 to 1.75% (w/w) results in an increase in the catalyst hydration from $n = 0.88$ to $n = 0.9$ only; compare to Figure 2.) Finally, with enough water (more than 10% (w/w)) to allow for competitive dissolution of

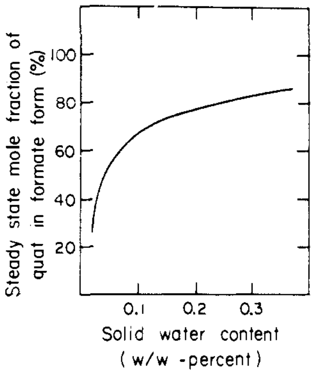

Figure 9. Calculated steady-state concentration of quat formate as a function of the water content of the solid.

the displaced salt (alkali chloride in this study) the rate reduces according to eq 2.[15] To conclude, in relatively dry systems, addition of catalyst reduces the aqueous film on the solid (by competing for the available water), and therefore the overall reaction rate decreases (Figure 1c). At 100 °C, the mass transfer keeps up with the homogeneous reaction rate only when the water content of the solid is above the limit where the catalyst hydration remains approximately constant and the reaction rate is hardly affected by the addition of more water (Figure 1d).

Mechanical Agitation and Ultrasonic Mixing in Mass Transfer Controlled Reactions. At 100 °C the heterogeneous reaction of 1-chlorodecane and potassium formate has a maximum rate constant $k = 11.4 \times 10^{-3}$ min^{-1} (Table I, Figure 1). As we have shown before, reduction in the amount of water causes the reaction rate to decrease, due to hindered mass transfer. We found that this reduction cannot be avoided by increasing the agitation speed. The reaction rate increased with the agitation speed only up to 600 rpm. At higher speeds (up to 1100 rpm) the rate constant was unaffected ($k = 6.2 \times 10^{-3}$ min^{-1}). Thus, a reaction rate that is not increased by improved agitation might still be controlled by slow mass transfer.

When ultrasonic mixing was used instead of mechanical agitation, mass transfer could be improved.[22] Thus at $T < 75$ °C (see Experimental Section) the rate constant obtained with potassium formate was $k = 2.9 \times 10^{-3}$ min^{-1} (compared to 2×10^{-3} min^{-1} with mechanical agitation at $T = 75$ °C; see Figure 7). We could demonstrate that this rate increase is caused by improved mass transfer. Under ultrasonic irradiation the solid–liquid mass transfer (which is hardly affected by any temperature increase) was about twice as fast compared to the mass transfer observed with mechanical agitation (Figure 5).

Summary. In this paper we have demonstrated the multiple role of water in the heterogeneous reaction of chlorodecane and solid formate salts. Although some of the effects observed might be specific to the reactions studied, some general conclusions can be drawn:

(1) Solid–liquid PTC reactions do not guarantee anhydrous conditions in the organic phase.

(2) It seems that the dissolution of the salt in an aqueous film is a necessary step of the reaction mechanism. Therefore the process should be termed "thin-layer phase-transfer catalysis".

(3) The solubility ratio (see Table I) can be of help for choosing the appropriate salt for any nucleophilic substitution.

(4) Quaternary ammonium salts and inorganic salts compete for the water available in the system.

(5) When the reaction medium is short of water, the reaction may be controlled by mass transfer. This does not mean that the reaction rate can be improved by better agitation.

(6) The optimum amount of water for any reaction may be strongly varied with such parameters as reaction temperature,

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[21] Due to the low molar ratio of catalyst to both substrate and formate, exact ssc measurement would require extremely fast separation of the liquid and the solid phases (to prevent any further mass transfer), as well as quick cooling (to prevent any further reaction with the substrate), after sampling. This was achieved only partly, and the results showed relatively great fluctuation.

[22] The ultrasonic source used required the use of an open reaction system. Thus water losses occurred. Within minutes the water content was reduced to a certain value, which was independent of the initial water content. At 65 °C (bath temperature), this value corresponds approximately to the optimum found for the reaction with potassium formate at 75 °C (Figure 7).

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mixing speed, catalyst amount, or the cation used (for nucleophilic substitution). An investigation on the effect of the water content in any reaction should account for these variables at least.

Experimental Section

Materials. *n*-Chlorodecane, Aliquat 336, *o*-dichlorobenzene (anhydrous), and sodium and potassium formates were purchased from Aldrich and were used without further purification. The molar concentration of the onium salt was determined by titration.

Trioctylmethylammonium formate was prepared from Aliquat 336 by ion exchange as described by Bar et al.[19] Complete substitution of the chloride was checked by titration.

Calcium formate and lithium formate were prepared by titration of the corresponding hydroxides with analytical grade formic acid (Merck).

Hydranal reagents and solvent for Karl Fischer titration were purchased from Riedel de Haen.

All reagents were dried under reduced pressure (0.5 mbar): the onium salts (to 0.15% (w/w) water) and the ammonium formate (to 1%) in a rotavapor at 80 °C and the other formates (to 0.02%) in a vacuum oven at 140 °C.

Analysis. The conversion of chlorodecane to decyl formate was determined by gas chromatographic analysis.

A solution of trioctylmethylammonium chloride in *o*-dichlorobenzene can be titrated argentometrically (0.02 N $AgNO_3$) when a mixture of acetone, ethanol, and water (equal weights of each) containing sodium bicarbonate (10 mM) and potassium chromate (indicator, 2 mM) is used as the medium. The trioctylmethylammonium formate concentration is obtained by subtracting the titrated value from the initial quat concentration.

The water determination by Karl Fischer titration was precise to 30 ppm. All reagents were titrated prior to the experiments. At the end of each experiment, after the solids had settled, the water content of the liquid phase and of the solid–liquid mixture was determined. Afterward the solid fraction of the mixture was measured (60–80%), and the water content of the solid was calculated.[18]

Water Addition. In all the heterogeneous reactions water was added to the solid by means of a 10-μL syringe. The mixture was allowed to equilibrate overnight in a closed vial. With potassium formate the equilibration time was shortened, by allowing the hygroscopic solid to absorb the required amount of water (indicated by the gain in the weight (analytical balance)) from the air.

In the homogeneous reaction water was added to the solution of the onium salt in *o*-dichlorobenzene, and the mixture was stirred for 30 min.

Reactions. The reactions were carried out in a closed system, consisting of a round-bottom flash (20 mL) equipped with a stoppered side arm and a small condenser through which a mechanical glass stirrer was introduced (Teflon seal).

Heterogeneous Reactions. The dried Aliquat had a gelatinous constitution. Thus, in order to ensure identical initial composition of the organic phase, large batches of solvent, catalyst, and substrate were prepared in advance. This mixture (12 mL) and the contents of one vial of formate salt (27 mmol) were poured into the reaction flask, which was immediately closed. The system was placed in a thermostated bath (±0.5 °C) and stirred at 800 rpm. Samples were withdrawn at fixed time intervals and the liquid phase composition was determined by GC. In order to exclude initial irregularities, the kinetic behavior was investigated only above 5% conversion.

Ion Exchange of Quat Chloride and Solid Formates. The formates were premixed with water as before and added to the solution (12 mL) of trioctylmethylammonium chloride (3.5 mmol) in *o*-dichlorobenzene. The system was held at constant temperature and stirred at 800 rpm. Samples of the liquid phase alone were withdrawn, immediately filtered (GF/A paper, Whatman), and analyzed by argentometric titration. At the end of each run the water content was determined.

Ultrasonic Mixing. An ultrasonic generator (W-375, Heat Systems-Ultrasonics Inc.) with a flat tip was used at an output level of 50 W. The experimental procedure was identical with the mechanically agitated heterogeneous reactions, except for two things:

(1) Since the ultrasonic head had to be immersed in the reaction medium, the reaction had to be performed in an open system. (It is strictly forbidden to introduce the tip through any kind of seal.) Therefore an open vial was used as the reaction vessel.

(2) In order to account for the heat released by the ultrasonic source, the thermostated bath was held at 65 °C. The reaction temperature, which was measured inside the vessel with a thermocouple, varied between 72 and 74 °C but 75 °C was never reached.

Regioselective Trans–Cis Photoisomerization of *m*-Styrylstilbenes

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Abstract: Trans–cis photoisomerizations of *m*-styrylstilbenes, i.e., 2,4,6-triisopropyl-3′-styrylstilbene (TISS), 2,4,6-trimethyl-3′-styrylstilbene (TMSS), and 3-styrylstilbene (SS), and of stilbenes, i.e., 2,4,6-triisopropylstilbene (TIS), 2,4,6-trimethylstilbene (TMS), and stilbene (S), are studied under direct or benzophenone-sensitized irradiation in hexane. Measurements of quantum yields for isomerization have revealed that although the styrylstilbene molecule bears two styryl groups, the reaction is highly regioselective, depending upon the excitation conditions and reactant structures. For example, isomerizations of *trans,trans*-TISS and *trans,cis*-TISS occurred either at the 2,4,6-trisubstituted styryl side upon direct excitation or at the unsubstituted styryl side upon sensitized excitation. When the starting material carries an unsubstituted *cis*-styryl group, the major isomerization always occurred at this moiety by either direct or sensitized excitation, e.g., *cis,trans*-TISS → *trans,trans*-TISS, *cis,cis*-TISS → *trans,cis*-TISS, and *cis,trans*-SS → *trans,trans*-SS. Furthermore, the photoisomerization of *cis,cis*-SS was found to be one-way. These results are interpreted in terms of the usual "energy sink" concept: the excited-state energies (E_S and E_T) of the stilbene chromophores depend on molecular distortion in a subtle manner. It seems that an extremely rapid cis → trans isomerization rate of the unsubstituted *cis*-styryl group is also responsible for the observed preferential photoisomerization of this group. Finally, the cis,cis isomers of TISS, TMSS, and SS underwent upon sensitized excitation minor but substantial one-photon two-double-bond isomerization (cis,cis → trans,trans) in addition to major one-double-bond isomerization. This reaction is not common, since the two isomerizing double bonds are cross-conjugated.

Energy-transfer processes in molecular assemblies such as solids, membranes, and polymers, where electronic interactions between chromophores are frequently strong, can be very rapid (even $>10^{12}$ s^{-1}).[1] As a result, photochemical reactions in these organized

0002-7863/88/1510-0189$01.50/0