Reactivity of Organic Molecules at Phase Boundaries

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1 Introduction

Interfaces are regions where two immiscible homogeneous phases come into contact. An organic molecule which is adsorbed from a bulk phase on to an interface often experiences a profound environmental change. For example, the dielectric constant and the concentration of reactants at an interface may differ substantially from those of the adjacent phases. Boundary state molecules would, therefore, be expected to exhibit interesting chemical properties, and the nature of these properties is the subject of this review.

Probably the outstanding boundary state property is molecular order. While the orientation of reactant species in solution is usually random, molecules at interfaces often have well-defined orientations. In certain cases, described later, the orientation of organic molecules at an interface can be measured and altered at will. The importance of the chemistry of 'arranged' molecules is seen, for example, in biological systems where the majority of reactions involve specific adsorption at surfaces of proteins, membranes, and cellular particles. Indeed, one may regard biochemistry as the organic chemistry of ordered molecules. Despite the relevance of interfacial organic chemistry to biochemistry (and to pharmacology, polymer chemistry, organic synthesis, *etc.*), there are few recent detailed investigations in the area. This is reflected in the fact that some of the most intriguing examples of boundary state reactions cited in this article are many years old.

One final point may be made by way of introduction. I have chosen to neglect theoretical considerations in favour of a more qualitative approach; perhaps the purpose of the present review is not so much to inform as to stimulate interest in a rather unique field of research.

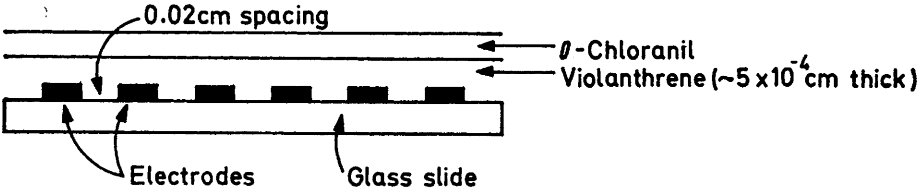
2 Solid Surfaces

Adsorption of light by a complex comprised of an electron donor D and an electron acceptor A gives rise to electron transfer, as in equation (1). Return to the ground state is rapid in homogeneous solutions. When the donor and

$$\mathrm{DA} \xrightarrow{h\nu} \mathrm{D}^{+}\,\mathrm{A}^{-} \qquad (1)$$

acceptor are solids in close contact with each other, the lifetime of the charge-transferred state is prolonged. An electron which moves across the interface can wander from one acceptor molecule to another; a 'hole' in the donor layer can similarly migrate among neighbouring molecules. The resulting separation of oxidized and reduced species enhances their lifetimes.

Kearns and Calvin[1] investigated the behaviour of solid donor–acceptor systems (see Figure). Violanthrene (a polynuclear aromatic hydrocarbon) was vacuum sublimed on to a glass slide plated with thin metal electrodes. A solution of a quinone, *o*-chloranil, was then sprayed on to the violanthrene surface. An e.s.r. signal and a new absorption band at 7200 Å were produced by the intimately-associated donor and acceptor compounds. Moreover, coating the violanthrene with the acceptor increased the dark current by almost 10^6. Illumination of the cell caused another current increase of about 10^5 which decayed exponentially with time when exposure to the light was terminated. These results may be rationalized in terms of an interfacial electron transfer. Once the positive and negative charges move several molecular diameters into their respective layers, they are relatively free to migrate and to carry a current. The photoconductivity is probably caused by mobile positive charges in the donor layer, because illumination of the donor surface generates larger photocurrents than acceptor-face illumination. Upon removal of the light, the electrons and holes drift back to the interface where the ground state is re-established. Not surprisingly, biological organelles involved in electron transport, such as chloroplasts, are characterized by highly-organized laminated structures.



Figure

If a multifunctional molecule positions itself at an interface so that one of the reactive groups is more exposed to an external reagent than the others, then a high degree of reaction selectivity is possible. One of the few examples of this type of selectivity was reported by Deno *et al.*[2] who studied the homogeneous and heterogeneous photochemical chlorinations of n-octanoic acid. Homogeneous chlorination in CCl_4 resulted in a mixture of monochlorinated isomers containing 17% 8-chloro-n-octanoic acid. When n-octanoic acid was first adsorbed on to alumina and then reacted heterogeneously with chlorine in CCl_4, the product mixture contained much more of the 8-isomer (33%). Apparently, the carboxy-groups of the n-octanoic acid adsorb on to the alumina surface such that the hydrocarbon tails are aligned more or less perpendicular to the surface. The methyl groups become the most accessible point of attack by the

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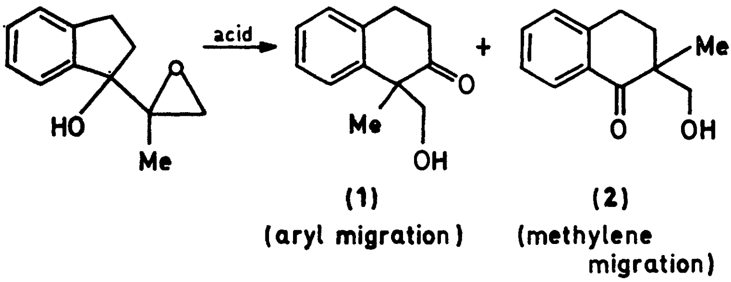
[1] D. R. Kearns and M. Calvin, *J. Amer. Chem. Soc.*, 1960, **83**, 2110.

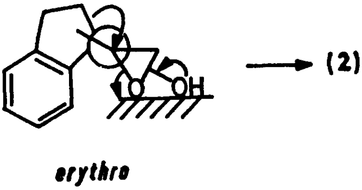
[2] N. C. Deno, R. Fishbein, and C. Pierson, *J. Amer. Chem. Soc.*, 1970, **92**, 1451.

chlorine free radical (particularly if the chains are tightly packed), and the amount of terminal chlorination increases substantially.

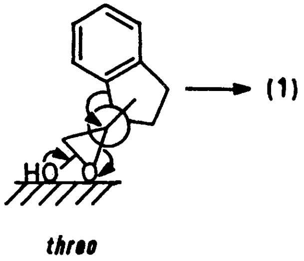
Cheer and Johnson[3] described another selective reaction carried out on an alumina surface [equation (2)]. Two products [(1) and (2)] are possible for this acid-catalysed rearrangement, depending upon whether the aryl or methylene group migrates. In a homogeneous reaction (boron trifluoride etherate in methylene chloride), *erythro*-epoxide gave (**1**) : (**2**) = 77 : 23 and *threo*-epoxide gave (**1**) : (**2**) = 90 : 10. The predominance of (**1**) in both cases was attributed to a greater migratory aptitude of the aryl group relative to that of the alkyl group. The heterogeneous rearrangement catalysed by alumina behaved quite differently: *erythro* led to >90% (**2**) and *threo* led to >90% (**1**). This remarkable stereoselectivity was explained by conformationally-immobile transition states in which both the epoxide and alcohol oxygen atoms of the substrate are fixed to the alumina surface [equations (3) and (4)].



(2)



(3)



(4)

Papain, a water-soluble proteolytic enzyme, was found by Katchalski and co-workers[4] to function heterogeneously when embedded in a collodion membrane.

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[3] C. J. Cheer and C. R. Johnson, *J. Amer. Chem. Soc.*, 1968, **90**, 178.

[4] R. Goldman, O. Kedem, I. H. Silman, S. R. Caplan, and E. Katchalski, *Biochemistry*, 1968, **7**, 486.

A 400 μm thick collodion film was immersed in an aqueous solution of papain and impregnated with enzyme. The membrane was then treated with a reagent which cross-linked the adsorbed enzyme molecules and prevented leaching from the membrane. (Cross-linking did not appear to affect enzymic activity.) A rate *vs.* pH profile for the 'enzyme-membrane', determined by adding membrane slices to solutions of benzoyl-L-arginine ethyl ester, showed a gradual rate increase from pH 6·0 to 9·6. On the other hand, native enzyme displayed a bell-shaped profile with a maximum rate of ester hydrolysis at pH 6·5—7·0.

The fact that the optimal pH of the embedded papain is not reached even at pH 9·6 suggests that the acidity within the membrane microenvironment is 2—4 pH units lower than the external pH. One reason for this difference may be that the local pH at the membrane is decreased by the protons generated from the enzyme-catalysed hydrolysis [equation (5)]. Another explanation for the distorted pH profile of the heterogeneous reaction is that a diminished enzymic activity, which normally results from an increase in pH above the pH maximum, is compensated by a subsequent increase in the steady-state concentration of the substrate within the membrane. The bell-shaped curve is thereby flattened.

$$RCO_2R \xrightarrow{\text{papain}} RCO_2^- + HOR + H^+ \qquad (5)$$

Interestingly, the enzyme-membrane hydrolyses gelatin much more extensively than does native enzyme. Perhaps the gelatin molecules adsorb on to the membrane surface, unfold, and expose a large number of peptide linkages to the hydrolytic action of the bound enzyme. Clearly, systems such as this are complex. Nevertheless, their study is necessary if we are ever to understand how enzymes function *in vivo* on the surfaces of membranes and subcellular particles.[5]

The investigation by Kornblum and Lurie[6] of the homogeneous and heterogeneous alkylations of phenol deserves mention since the results illustrate certain constraints imposed on a reaction proceeding on the surface of a crystal lattice. Homogeneous alkylation of sodium phenoxide by allyl bromide in ethylene glycol dimethyl ether (in which both reactants are soluble) gave 99% allyl phenyl ether [equation (6)]. Heterogeneous alkylation of sodium phenoxide (carried out by adding allyl bromide to a suspension of the phenoxide in ethyl ether) gave *o*-allylphenol as the major product [equation (7)]. There was also some ether formation in the latter reaction, but this was shown to arise from a competing homogeneous process. The difference in the reaction sites [equations (6) and (7)] is not a solvent effect, because homogeneous alkylation of *p*-t-octylphenoxide in diethyl ether yielded only ether product. Therefore, some feature of the surface reaction leads to a strong preference for attack at an *ortho* carbon of the benzene ring.

The absence of oxygen alkylation at the crystal surface [equation (8)] may have two causes. First, a halide ion departing into an aprotic solvent would be

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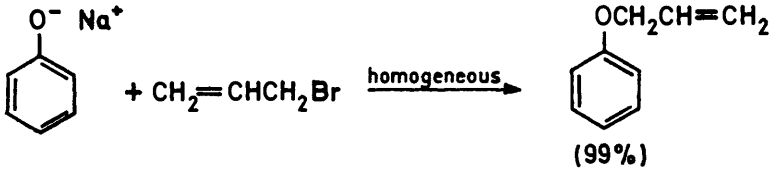
[5] For additional examples of matrix-bound enzymes, see K. Mosbach, *Acta Chem. Scand.*, 1970, **24**, 2084; K. Mosbach and B. Mattiasson, *ibid.*, 1970, **24**, 2093.

[6] N. Kornblum and A. P. Lurie, *J. Amer. Chem. Soc.*, 1959, **81**, 2705.



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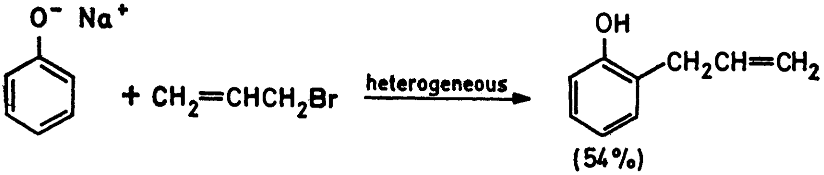
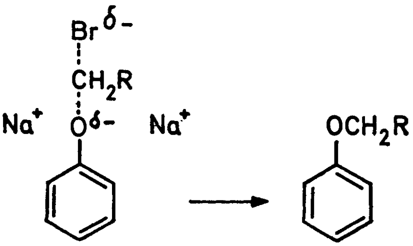


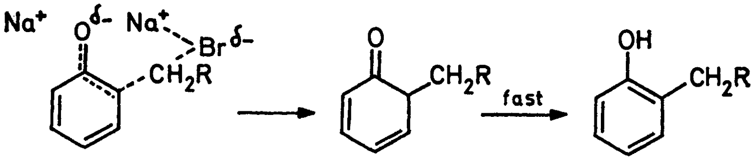
(7)

poorly solvated. Second, covalent bonding to the oxygen nucleophile would dissipate charge on the oxygen, thereby depriving the sodium ions in the proximity of the oxygen of one of their counterions. Since ion migration in a solid is less ready than in solution, the resulting coulombic repulsion between the sodium ions could not be easily relieved.



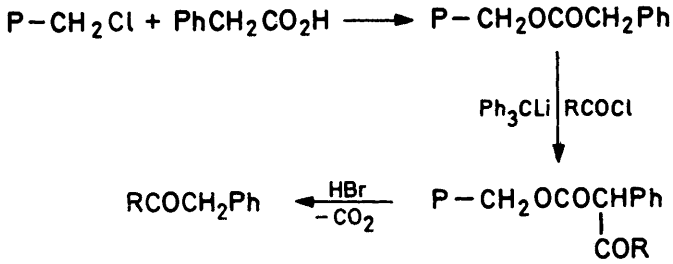
(8)

The above difficulties do not apply to carbon alkylation at the solid phenoxide surface [equation (9)]. The incipient bromide ion is stabilized by ion-pair formation with one of the sodium ions which presumably clusters about the oxygen anion. Since 'removal' of a sodium ion occurs concomitantly with loss of charge on the oxygen, there is little accumulation of unfavourable coulombic repulsion.



(9)

From a practical standpoint, a reaction at a solid surface may have an advantage over its homogeneous counterpart in the ease of product isolation. Thus, Leermakers and James[7] used small pieces of polyvinyl phenyl ketone as a sensitizer in the photolytic conversion of norbornadiene into quadricyclene. Removal of the sensitizer after the reaction was a simple matter. Another example is the Merrifield[8] solid-state synthesis of polypeptides. A polypeptide is constructed stepwise while the chain is attached to an insoluble resin. After each reaction, the system is freed of side products and excess reagents by thorough washing of the resin. Patchornik and Kraus[9] acylated phenylacetic acid by 'immobilizing' the acid on an insoluble polymeric carrier. Phenylacetic acid was treated with chloromethylated polystyrene [equation (10); P = polymer], and the resulting ester was acylated with an acid chloride and trityl-lithium. The derived polymer was isolated by filtration, washed, dried, and treated with HBr in trifluoroacetic acid to give the desired ketone. By immobilizing the ester on the polymer surface and by running the acylation heterogeneously, self condensation of the ester (an important side reaction in homogeneous acylations) was avoided.



$$\begin{tikzcd}
\mathrm{P{-}CH_2Cl + PhCH_2CO_2H} \arrow[r] & \mathrm{P{-}CH_2OCOCH_2Ph} \arrow[d, "\mathrm{RCOCl}", "\mathrm{Ph_3CLi}"'] \\
\mathrm{RCOCH_2Ph} & \mathrm{P{-}CH_2OCO\underset{\displaystyle COR}{\underset{|}{C}}HPh} \arrow[l, "\mathrm{HBr}", "-\mathrm{CO_2}"']
\end{tikzcd}$$

(10)

3 Films

Many water-insoluble organic substances having both hydrophilic and hydrophobic moieties can be readily spread on a water surface to form films one molecule thick. Valuable information concerning the reactivity of oriented molecules in such monomolecular films has been secured using an instrument known as a surface balance. The surface balance confines a film within a rectangular area bounded on two opposite sides by a movable barrier and by a float attached to a torsion wire arrangement. The surface pressure of the film, measured directly by means of the float system, may be increased by adjusting the movable barrier such that the area of the film is decreased. A decrease in area may have the effect of forcing molecules lying flat on the water surface into vertical posi-

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[7] P. A. Leermakers and F. C. James, *J. Org. Chem.*, 1967, **32**, 2898; see also G. R. De Mare, M. C. Fontaine, and P. Goldfinger, *ibid.*, 1968, **33**, 2528.

[8] S. Wang and R. B. Merrifield, *J. Amer. Chem. Soc.*, 1969, **91**, 6488.

[9] A. Patchornik and M. A. Kraus, *J. Amer. Chem. Soc.*, 1970, **92**, 7587.

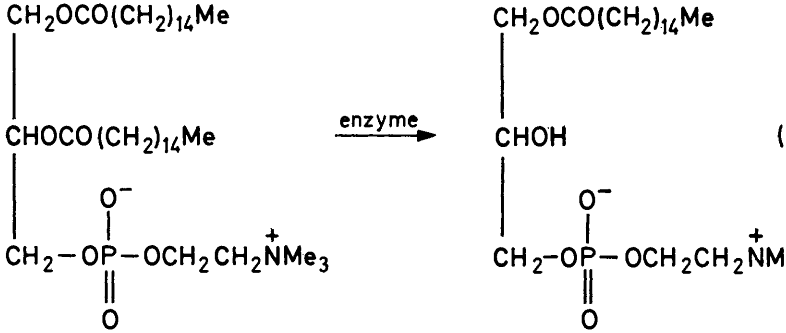
tions where they require less room. Therefore, the capability is available of manipulating the orientation of molecules and of determining their orientation by comparing the area per molecule in the film with the actual molecular area.

Over thirty years ago Mitchell[10] studied the light-induced hydrolysis of stearic anilide monolayers spread on 5N-HCl subphases [equation (11)]. He showed that the apparent quantum yield depended on the molecular area of the film.

$$PhNHCOC_{17}H_{35} \xrightarrow[H_3O^+]{h\nu} PhNH_2 + C_{17}H_{35}CO_2H \qquad (11)$$

When the film compression was increased, the area per molecule decreased, and the quantum efficiency increased up to a point where it levelled off. This behaviour was ascribed to a change in angle between the dipole axis of the stearic anilide chromophore and the direction of the incident light.

Shah and Schulman[11] injected cobra venom into the water phase beneath a dipalmitoyl lecithin film and measured the change in potential across the monolayer caused by an enzyme-catalysed ester hydrolysis [equation (12)]. The surface pressure remained nearly constant throughout the reaction, indicating that the hydrolysis products did not leave the monolayer. Although the reaction proceeded rapidly at applied surface pressures of 5—15 × 10^{-5} N cm^{-1}, there was virtually no ester hydrolysis at pressures greater than 20 × 10^{-5} N cm^{-1}. In other words, the reaction could be mechanically 'switched off'. Compression of the monolayer decreases the intermolecular spacing of the film and hence impedes the ability of the active site of the enzyme to penetrate the monolayer. This rationale is consistent with the finding that dioleoyl lecithin monolayers are subject to enzyme-catalysed hydrolysis even at pressures near 40 × 10^{-5} N cm^{-1}. The rigid olefinic linkages in the oleic acid side chains lead to a loosely-packed arrangement of molecules that is difficult to compress.



(12)

Marsden and Rideal[12] showed that the double bonds of unsaturated fatty

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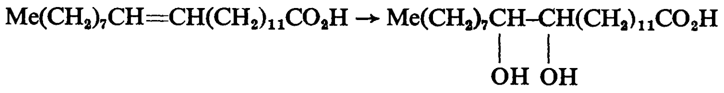
[10] J. S. Mitchell, *Proc. Roy. Soc.*, 1936, **A155**, 696.

[11] D. O. Shah and J. H. Schulman, *J. Colloid Interface Sci.*, 1967, **25**, 107.

[12] J. Marsden and E. K. Rideal, *J. Chem. Soc.*, 1938, 1163.

acid films are oxidized by aqueous subphases containing $KMnO_4$. The rate of oxidation of a monolayer of the *cis*-isomer of the fatty acid in equation (13) was found to decrease only 25% when the applied pressure was increased from 2 to 8×10^{-5} N cm^{-1}. An identical pressure increase on a monolayer of the corresponding *trans*-isomer led to 100-fold rate decrease. A reasonable explanation for this large difference follows. At low compressions, both the *cis*- and *trans*-compounds lie flat along the water surface where the double bonds, being in close proximity to the $KMnO_4$, are readily oxidized. When the *trans*-isomer is subjected to 8×10^{-5} N cm^{-1} pressure, the hydrocarbon chains are forced to stand vertically out of the water. Since most of the olefinic linkages are then no longer in contact with the aqueous $KMnO_4$, the reaction rate drops 100-fold. The *cis*-fatty acid resists a 90° change in orientation at 8×10^{-5} N cm^{-1} because the 'bent' chains fit less easily into a vertical array. Consequently, the pressure increase has only a small effect on the rate.



$$\mathrm{Me(CH_2)_7CH{=}CH(CH_2)_{11}CO_2H \rightarrow Me(CH_2)_7\underset{\displaystyle OH}{\underset{|}{CH}}{-}\underset{\displaystyle OH}{\underset{|}{CH}}(CH_2)_{11}CO_2H} \qquad (13)$$

The oxidation rate of double bonds in films of unsaturated steroids depends on the position of the double bond and on the stereochemistry of the steroid.[13] Unfortunately, very little is known about the regioselectivity and stereoselectivity of reactions of complex natural products at phase boundaries.

The photochemical decomposition of a monolayer of 4-hydroxystearic acid on 500 ml of 0·01-N H_2SO_4 is sensitized by trace quantities (3 μg) of nickel ion in the subphase.[14] Such an effect is reminiscent of the sensitivity of living systems to drugs and inhibitors. Langmuir and Schaefer[15] were able to detect the presence of 2×10^{-8}M aluminium ion in water by utilizing the efficient adsorption of cations by monomolecular films of fatty acids. Monolayers of stearic acid above metal solutions were crushed and skimmed off; the 'monoskims' were melted and their cooling observed under a polarizing microscope. Skims from monolayers lying upon 2×10^{-8}M aluminium ion gave distinctly-different crystal patterns from those lying upon pure water.

Davies[16] and Gaines[17] have cited further examples of monolayer reactions.

4 Liquid–Liquid Interfaces

The formation of nylon is one of the most vivid examples of an organic reaction which occurs rapidly at a liquid–liquid interface. When an aqueous solution of hexamethylenediamine is placed upon a solution of sebacoyl chloride in carbon tetrachloride, a milky film of polymer appears at the juncture of the two im-

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[13] J. F. Danielli and N. K. Adam, *Biochem. J.*, 1934, **28**, 1583.

[14] J. S. Mitchell, E. K. Rideal, and J. H. Schulman, *Nature*, 1937, **139**, 625.

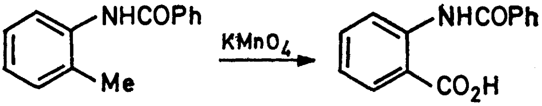
[15] I. Langmuir and V. J. Schaefer, *J. Amer. Chem. Soc.*, 1937, **59**, 2400.

[16] J. T. Davies, *Adv. Catalysis*, 1954, **6**, 1.

[17] G. L. Gaines, 'Insoluble Monolayers at Liquid-Gas Interfaces', Interscience, New York, 1966, chap. 7.

miscible liquids. A long thread of nylon may be slowly withdrawn from the film until one of the reagents is exhausted.

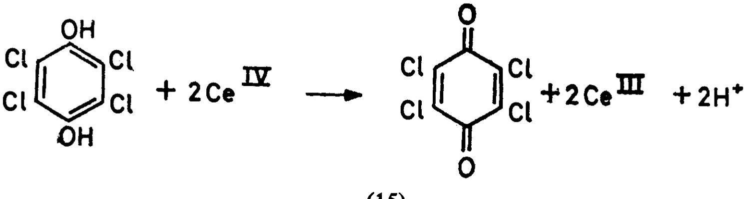
In 1928 Bell[18] published his work on the physical organic chemistry of reactions at liquid–liquid interfaces. Only a few papers on the subject have appeared since then. Bell treated benzoyl-*o*-toluidine in benzene with $KMnO_4$ in water to produce benzoylanthranilic acid [equation (14)]. The benzene and water solutions were allowed to remain in two layers, each of which was stirred separately.



(14)

Oxidation was assumed to take place exclusively at the horizontal boundary. The reaction rate was found to be independent of the stirring speed, first-order with respect to $KMnO_4$, and independent of the benzoyl-*o*-toluidine concentration above a certain level. There was also an amazing 13-fold rate increase with a 10 °C temperature rise. Bell concluded from these results that the interfacial reaction is caused by permanganate ions striking an adsorbed layer of benzoyl-*o*-toluidine. Highly-approximate calculations showed that at 25 °C only one in 10^7 of the permanganate ions reaching the interface manages to react successfully with a substrate molecule.

Mansoori and Madden[19] oxidized tetrachlorohydroquinone [equation (15)] by stirring solutions of the material (15—90 ml, 50% CCl_4–50% 2-octanone) with 1500 ml aqueous Ce^{IV}. The rate was zeroth-order with respect to Ce^{IV} but



(15)

directly proportional to the hydroquinone concentration in the organic phase. The reaction was believed to be homogeneous in nature (taking place either in an aqueous zone adjacent to the interface or throughout the aqueous phase). This requires that the tetrachlorohydroquinone molecules cross the interface prior to their oxidation. Since the reaction is zeroth-order in Ce^{IV}, the transfer of the substrate from the organic solvent into the water is probably rate-determining.

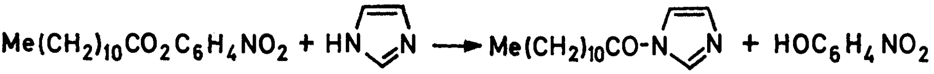
The mechanism of an imidazole-catalysed ester hydrolysis at a water–heptane

[18] R. P. Bell, *J. Phys. Chem.*, 1928, **32**, 882.

[19] G. A. Mansoori and A. J. Madden, *Amer. Inst. Chem. Engineers J.*, 1969, **15**, 245.

boundary was elucidated here at Emory.[20] Aqueous imidazole solutions were stirred rapidly under carefully-controlled conditions with heptane solutions of *p*-nitrophenyl laurate, and the rate of the resulting ester hydrolysis was determined as a function of the following reaction variables: stirring speed, concentration of reactants, temperature, viscosity of the hydrocarbon phase, volume of the heptane and water solutions, deuterium and salt content of the water, lauroylimidazole content of the heptane, presence of surfactant, and structure of the catalyst. Without going into details, the results of these experiments strongly support a true boundary reaction rather than a homogeneous process occurring in either the bulk water phase or the bulk heptane phase. The interfacial hydrolysis was found to be first-order in imidazole from 0·03 to 0·26M. A plot of the rate *vs.* concentration of ester in the heptane displayed a pronounced saturation effect above 3×10^{-3}M. There was no observable rate increase when the temperature was elevated from 15 to 30 °C. These results point to a diffusion-controlled process.

Remarkably small concentrations of laurate ion in the water phase (6×10^{-5}M) were found to impede significantly the interfacial ester hydrolysis. The surfactant adsorbs at the interface (according to a Freundlich isotherm) and inhibits the reaction by competing for adsorption sites and/or by perturbing the structure of the interfacial region. The laurate experiments were informative because they showed that the reaction between imidazole and ester at the interface involves nucleophilic attack [equation (16)] rather than general base catalysis. The latter mode of catalysis would produce laurate ion directly. Consequently, if general base catalysis were operative, a product inhibition should have been observed, and this was not the case. On the other hand, the interfacial hydrolysis catalysed by hydroxide ion did indeed exhibit product inhibition. One would expect this behaviour here because laurate ion is definitely a reaction product.



(16)

Synthetic organic chemists might be able to use reactions at liquid–liquid interfaces to good advantage, particularly with regard to controlling or altering stereochemistry. Some credence to this idea arises from preliminary experiments[21] on the oxidation of borneol and isoborneol to camphor [equation (17)]. Homogeneously, isoborneol is oxidized by aqueous chromic acid twice as fast as borneol.[22] In contrast, the two epimers are oxidized at virtually identical rates when the reactions are carried out heterogeneously (by stirring the alcohols in heptane with aqueous chromic acid). While no evidence exists which proves

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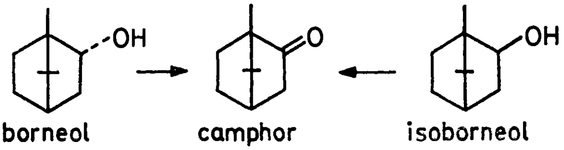
[20] F. M. Menger, *J. Amer. Chem. Soc.*, 1970, **92**, 5956.

[21] W. P. Bradley, unpublished results.

[22] H. Kwart and P. S. Francis, *J. Amer. Chem. Soc.*, 1959, **81**, 2116.

that these latter reactions are in fact completely interfacial, the fast borneol oxidation may result from a favourable adsorption of the borneol at the heptane–water boundary prior to formation and collapse of the chromate ester intermediate. This is reasonable because borneol has a less hindered alcohol group than isoborneol.



(17)

Starks[23] found that stirring octyl halides with aqueous solutions of inorganic anions did not lead to S_N2 substitution unless a quaternary salt was present in the organic phase. Thus, a mixture of 100 g 1-chloro-octane in 25 ml decane and 100 g NaCN in 25 ml water at 105 °C gave no 1-cyano-octane after 3 h. However, addition of 5 g hexadecyltributylphosphonium bromide resulted in a 95% yield of 1-cyano-octane after 1·8 h at 105 °C. The effect of the quaternary salt was termed 'phase-transfer catalysis' because cyanide ion must migrate from the aqueous phase into the organic phase and exchange with bromide ion before reaction with the alkyl halide. The cyanide–bromide exchange is reminiscent of an ion exchange resin. As cyanide is consumed in the organic phase, it is replenished by material in the aqueous cyanide pool. Although the substitution reaction is probably not interfacial, movement across the interface is an essential part of the mechanism. Starks also showed that quaternary salts which are soluble in non-polar solvents catalyse many other two-phase reactions involving anions such as the heterogeneous oxidation of olefins by aqueous permanganate and the reduction of ketones by aqueous sodium borohydride.

The concentration of reactants at a liquid–liquid interface may differ substantially from the concentration in the adjoining phases. An outstanding example was published by Fry and Reed[24] who electrochemically reduced 2,2-dichloronorborane [equation (18)] in DMF containing tetraethylammonium bromide. They obtained *endo*-norbornyl chloride (38%) and nortricyclene (62%) which were shown to arise from a common carbanion intermediate [equation (18)]. When one mole of water was added to the DMF, the ratio of products changed from 38 : 62 to 80 : 20. Addition of water, a proton donor, increased the relative amount of norbornyl chloride because proton capture by the carbanion competes more effectively with loss of chloride ion. In contrast to water, acetic acid and phenol hardly affected the ratio of 38:62. Furthermore, when both tetraethyl-ammonium bromide (0·1M) and phenol (1·0M) were present in the DMF, the *former* provided the protons required for norbornyl chloride formation

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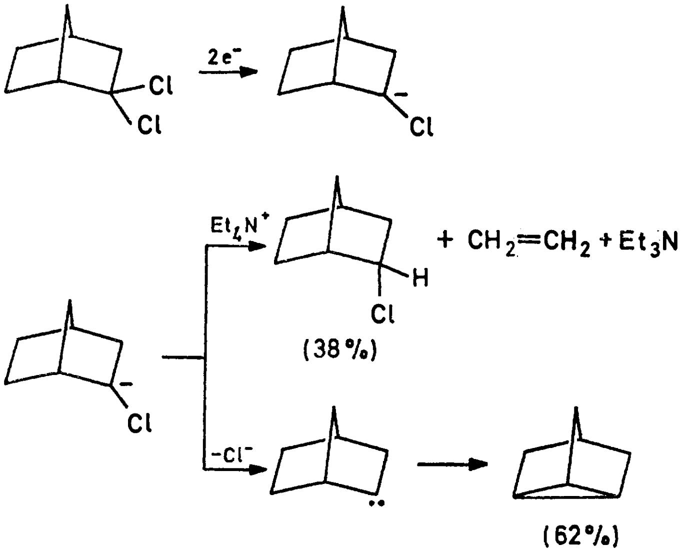
[23] C. M. Starks, *J. Amer. Chem. Soc.*, 1971, **93**, 195.

[24] A. J. Fry and R. G. Reed, *J. Amer. Chem. Soc.*, 1971, **93**, 553.

(as shown by ethylene production). Apparently, lack of adsorption of phenol at the mercury–DMF interface, where the carbanion forms and reacts, causes an enormous apparent reversal in acidity.



(18)

For reasons of brevity, the present review contains no discussion of emulsion polymerization and other applications of reactions of molecules at phase boundaries. This is unfortunate since the great practical importance of the subject should be emphasized. The world will be a better place when scientists—and nations—solve their respective boundary problems.