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Heterogeneous Catalysis in Solution

Part 20.[1]—Catalysis by Silver Bromide and other Solids of the Solvolysis of t-Butyl Bromide in 80 vol% Ethanol + Water

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The S_N1 solvolysis of 2-bromo-2-methylpropane (t-butyl bromide) in 80 vol% (55.2 mol%) $EtOH + H_2O$ at 25 °C was found to be catalysed by silver and several insoluble silver and mercury salts but not by $BaSO_4$, SiO_2 or platinum. The relative catalytic effectiveness of these solids could be largely explained by Pearson's SHAB concept. The kinetics of the AgBr-catalysed process were studied in detail by a pH-stat technique. The results fitted a model in which t-BuBr molecules and product Br^- ions competitively adsorbed on the surface according to Langmuir isotherms. Calculations showed the surface reaction to be *ca.* 10^5 times faster than the homogeneous solvolysis and to possess a much lower activation energy. The heterogeneous reaction was found to be selective, forming no alkene product and a higher ratio t-BuOEt:t-BuOH than in the bulk solution. These findings have been discussed in terms of the structure of the interfacial region.

In this series we have been studying the heterogeneous catalysis of a wide range of solution reactions. For most such reactions the rate-determining step in the uncatalysed as well as in the catalysed process is a bimolecular one. The present paper is concerned with the heterogeneous catalysis of a reaction well known to be unimolecular in homogeneous solution, the solvolysis of a t-butyl halide.[2] It is generally accepted that the cleavage of carbon–halogen bonds is assisted homogeneously by ions such as Ag^+ and Hg^{2+} [2-5] and there have been reports of heterogeneous catalysis by AgBr[6] and of joint catalysis by Ag^+ ions and insoluble silver salts.[2, 3, 7] Systematic and kinetic work has been carried out for only one type of heterogeneously catalysed halide displacement[8] and none at all has previously appeared for S_N1 reactions.

We have studied the solvolysis of t-butyl bromide in the classical medium of 80 vol% $EtOH + H_2O$

$$(CH_3)_3CBr \xrightarrow{\text{r.d.s.}} (CH_3)_3C^+ + Br^- \xrightarrow{EtOH,H_2O}$$
$$\{(CH_3)_3COH, (CH_3)_3COC_2H_5, (CH_3)_2C{=}CH_2\} + H^+ + Br^-. \qquad (I)$$

The reaction was followed by monitoring the production of H^+ (glass electrode); to avoid inadvertent catalysis[9] we eschewed the use of metal electrodes and titration procedures leading to precipitate formation. Rates were obtained by a pH-stat method. With this technique the pH was maintained at its initial value by continuously and automatically titrating the acid formed in the solvolysis by a standard solution of alkali. Plots of volume of alkali required against time (t) were drawn on a chart recorder. These volumes could readily be converted to the concentration of H^+ that would have been formed in the solvolysis (x, in mol dm^{-3}).

RESULTS

HOMOGENEOUS EXPERIMENTS

All runs without added solid yielded good linear plots of $\ln(a-x)$ against t. The initial concentration a derived from the amount of t-BuBr used agreed within experimental error with that calculated from the total amount of NaOH required when the reaction proceeded to completion. Hastening the completion by adding a slight excess of silver nitrate gave similar values. The homogeneous rate constant k_1 was reproducible and agreed well with literature values.[10] Homogeneous runs were carried out regularly at 25 °C as a check on the system. Experiments at 4 temperatures between 15 and 25 °C yielded an activation energy of 97.3 ± 2.5 (1 s.d.) kJ mol^{-1} in reasonable agreement with the figure of 95.2 kJ mol^{-1} determined from Cooper and Hughes' data[11] within the same temperature limits.

EFFECTS OF ADDED SOLIDS

The effects on the solvolysis rate at 25 °C of a variety of added solids are summarised in table 1. All solids were present as well-stirred uniform suspensions. The pH values are those of the solvent with solid present before the addition of t-BuBr; the pH of the system was maintained at the stated value during each run. The sources and pretreatments of the solids are listed. Most of them were sieved and the fraction with particle size below 76 μm was generally used.

TABLE 1.—EFFECT OF VARIOUS SOLIDS (0.5 g) ON THE RATE OF SOLVOLYSIS OF t-BuBr (8.91×10^{-4} mol dm^{-3}) IN 80 vol% EtOH + H_2O (50 cm^3) AT 25.0 °C

solid	source and description	pH	effect on rate
$BaSO_4$	B.D.H. for X-ray examination, < 76 μm	8.1	no effect
Al_2O_3	Spence type H activated at 450 °C, 100–150 μm	9.3	slight catalysis
SiO_2	B.D.H. washed in $HClO_4$ to remove iron, < 76 μm	7.1	no signif. effect
C	H. and W. activated charcoal, < 250 μm	8.8	slight catalysis
C	Cabot Carbon Spheron 6[a]	5.9	slight inhibition
C	Akzo Chemie Ketjenblack E.C., < 250 μm[a]	8.6	slight inhibition
Pt	J.M.C. specpure sponge, < 710 μm	7.9	no effect
Ag	B.D.H. powder cleaned cathodically, < 76 μm	9.1	catalysis
AgBr	as batch 2, ref. (12)	6.4	catalysis
AgBr	as batch 0, ref. (12)	6.4	strong catalysis
AgI	B.D.H. treated as in ref. (8), < 76 μm	7.0	catalysis
Ag_2S	B.D.H., < 76 μm	6.1[b]	strong catalysis
Hg_2Br_2	B.D.H. < 76 μm	7.4	strong catalysis
HgS	B.D.H., half < 76 μm, half 76-152 μm	6.0	catalysis

[a] With 0.1 g of the powder. [b] The rate was too fast for the pH-stat to cope and the pH dropped to 3.8 during the reaction.

Inspection of table 1 shows that $BaSO_4$, SiO_2, carbon and platinum had little or no effect on the rate, Al_2O_3 and HgS produced a measurable rate increase while silver and the salts of silver and mercury(I) speeded up the reaction significantly. The best catalysts were AgBr, Ag_2S and Hg_2Br_2, each of which increased the rate more than tenfold. These differences in catalytic efficiency may be largely understood in the light of Pearson's principle of soft and hard acids and bases (SHAB).[13] We shall assume that on the polar inorganic solids employed, it is the bromide end of the t-BuBr molecule that is sitting on the surface. (Experimental evidence supporting this assumption is given below in the case of AgBr.) Bromide is a fairly soft base, so a surface with fairly soft acidic sites (Ag^+, Hg_2^{2+}) should adsorb the substrate better than a surface with hard acidic sites ($Ba^{2+}_?$ Al^{III}, Si^{IV}) or with acid sites that are too soft (Hg^{2+}). Silver metal may adsorb less well than silver salts because of a lower electrostatic interaction with the polar substrate molecule. The stronger the adsorption, the more the C—Br bond is weakened and the more its cleavage is facilitated: the greater, therefore, the catalysis. This simple model explains the general catalytic trends in table 1 fairly well and should prove helpful for predictive purposes. It should be added that fine distinctions cannot be drawn in table 1 because of lack of surface area information. The two experiments with AgBr show that different pretreatments produce different catalytic activities; freshly prepared precipitates would probably be several times more active still.[8, 14]

KINETIC EXPERIMENTS WITH SILVER BROMIDE CATALYST

A more detailed and quantitative study was undertaken with silver bromide, one of the best catalysts found. Material from two different sources was employed, B.D.H. and Johnson Matthey (Specpure); unless stated otherwise, the results refer to the latter material. Sets of kinetic experiments were carried out with different initial concentrations of t-BuBr (a) and both with and without the addition of different masses (m) of powdered silver bromide from the two sources. As fig. 1 illustrates, the solvolysis rate was faster the more AgBr was present.

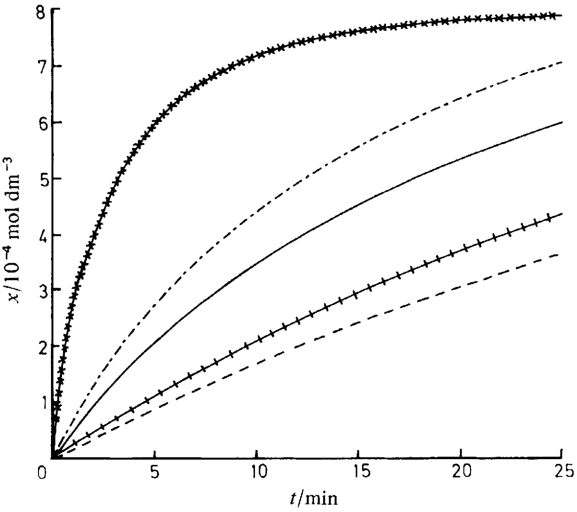
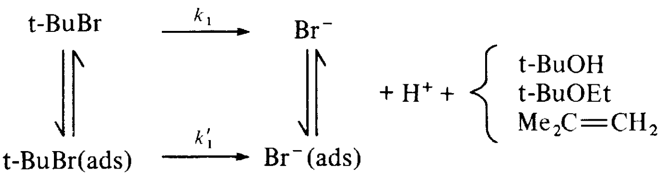


FIG. 1.—Kinetic plots of the solvolysis of 8.91×10^{-4} mol dm^{-3} t-BuBr in 80 vol % $EtOH + H_2O$ (50 cm^3) at 25 °C in the presence of: – – –, no added solid; ——, 0.5 g AgBr (J.M.); ++++, 0.5 g AgBr (J.M.) $+ 8.91 \times 10^{-4}$ mol dm^{-3} KBr; – - –, 1.0 g AgBr (J.M.); ×—×, 1.0 g AgBr (B.D.H.).

That the catalysis was heterogeneous was shown by runs carried out with samples of 80 vol% $EtOH + H_2O$ which had been previously stirred with AgBr powder (B.D.H. or J.M.) and the powder then filtered off. The solvolysis rate in these solvent samples was the same as the homogeneous rate in the case of J.M. AgBr. When B.D.H. AgBr had been used the rate was slightly faster, probably because a small amount of very finely divided powder had passed through the no. 3 sinter employed. Thus the first step in the catalysis must have involved adsorption of t-BuBr on the surface of AgBr powder. It seems likely on chemical grounds that the bromine ends of the molecules were sitting on Ag^+ ion sites. This was confirmed by competitive adsorption experiments. As fig. 1 shows, addition of KBr markedly reduced the catalytic effect of AgBr (though it did not affect the rate of the homogeneous solvolysis). Addition of KNO_3 produced a much smaller decrease in the catalysis and t-BuOH none at all. These results are easily explained if the Br and not the t-Bu end of t-BuBr is adsorbed on the AgBr surface so that t-BuBr molecules and Br^- ions compete for surface Ag^+ sites.

THEORETICAL TREATMENT OF DATA

The system under study may now be represented by the following scheme:



First-order C—Br bond cleavage can occur either homogeneously in solution (rate constant k_1) or on the catalyst surface (k_1'). In the latter case, adsorbed bromide ions remain behind while the liberated carbonium ions react further. Adsorption of H^+ (or OH^- or OEt^-) ions from the pH-statted solutions of pH 6-8 will be negligible. The back reactions of the homogeneous and heterogeneous processes need not be considered since the solvolysis goes to completion,[11] a point we confirmed both in the absence and presence of silver bromide. The above scheme then becomes a special case of the general theory of parallel first-order catalysed and uncatalysed reactions recently developed by one of us.[15] The basic differential rate equation for small extents of adsorption may be written

$$\mathrm{d}x/\mathrm{d}t = k_1(a-x)+(Am/V)k_1'\,c_{\mathrm{ads}} \qquad (1)$$

where A is the surface area of catalyst per unit mass, V the volume of solution and c_{ads} the surface concentration of substrate. Attempts to determine c_{ads} experimentally were unsuccessful because the amount of substrate adsorbed was too small. A theoretical relation is therefore required between c_{ads} and the bulk substrate concentration $c\,(=a-x)$ in order to integrate eqn (1). With the assumption that adsorption and desorption are fast processes we can regard the adsorbed t-BuBr and Br^- species as being in equilibrium with the corresponding species in the bulk solution. The surface concentrations can then be expressed by adsorption isotherms such as those of Henry, Langmuir or Freundlich. Feeding these in turn into eqn (1) gives differential equations which can be integrated.[15] The resulting equations will now be applied to the experimental data.

CATALYSIS WITH HENRY ADSORPTION

If t-BuBr and Br^- adsorb on the catalyst according to Henry's law, the integrated rate equation predicts[15] a straight-line relationship between $\ln(a-x)$ and t. For AgBr-catalysed runs, plots of $\ln(a-x)$ against t showed definite curvature. Henry-type adsorption is therefore not consistent with the observed kinetics.

CATALYSIS WITH FREUNDLICH ADSORPTION

If t-BuBr and Br$^-$ adsorb by independent Freundlich isotherms of the type

$$c_{\text{ads}} = gc^{\alpha} \quad (\alpha < 1) \tag{2}$$

then eqn (1) becomes

$$\mathrm{d}x/\mathrm{d}t = k_1(a-x)+k_1\phi(a-x)^{\alpha} \tag{3}$$

where $k_1\phi = Amgk_1'/V$ and g and α are Freundlich parameters. Graphical evaluation of the parameters α and ϕ cannot be achieved through the integrated form of eqn (3) because of its complex structure.[15] We therefore resorted to the differential equation itself which was treated as described in the Mathematical Appendix. This analysis of the data invariably produced values of α greater than unity. Since this is contrary to the requirement of Freundlich adsorption [eqn (2)], the latter cannot explain the experimental behaviour.

CATALYSIS WITH LANGMUIR ADSORPTION

If t-BuBr and Br$^-$ adsorb by Langmuir adsorption, they are likely to do so competitively on the same sites (Ag$^+$). Their monolayer coverage c_{mono} will then be the same but their adsorption coefficients σ and σ_{P} (P stands for product, Br$^-$) will differ. This converts eqn (1) into

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k_1(a-x)+\frac{Am}{V}\left\{\frac{\sigma c_{\text{mono}}k_1'(a-x)}{1+\sigma(a-x)+\sigma_{\text{P}}x}\right\}. \tag{4}$$

Analysis of the experimental data by this differential equation yielded approximate values of various parameters. For the final fitting, the integrated version of eqn (4) was tested against the recorded x against t plots. Details are given in the Appendix. Emphasis was placed on agreement over the early parts of all the curves up to times at which x had the same value (*ca.* 2.5×10^{-4} mol dm^{-3}). At constant x the concentration of adsorbed bromide ions ($c_{\text{P}_{\text{ads}}}$) will be similar in different runs since $\sigma_{\text{P}} > \sigma$. Bromide ions are less likely than t-BuBr molecules to follow simple Langmuir adsorption because of electrostatic Br$^-$–Br$^-$ repulsion on the surface, and so comparisons between runs are best made at the same low surface coverage of Br$^-$ ions. In this way values of $\sigma, \sigma_{\text{P}}$ and B [where $B \equiv Ak_1'\sigma c_{\text{mono}}/V(\sigma-\sigma_{\text{P}})$] were obtained which gave satisfactory agreement between the calculated and the experimental x against t curves over a 4-fold variation in both mass of catalyst (0.5-2 g) and initial t-BuBr concentration [$(4.5-18) \times 10^{-4}$ mol dm^{-3}]. Fig. 2 illustrates the fits obtained and shows, as expected, that deviations occur at high times when the degree of bromide coverage increases. The simple hypothesis of Langmuir adsorption is therefore consistent with the early stages of all the kinetic runs.

DISCUSSION

KINETIC PARAMETERS

The data for all the AgBr samples could be fitted with $\sigma = 400$ and $\sigma_{\text{P}} = 3800$ dm^3 mol^{-1}. It seems very reasonable that the adsorption coefficient of t-BuBr on AgBr should be less than that of Br$^-$. Molecules of t-BuBr must experience some steric hindrance in certain surface positions as well as much weaker electrostatic attraction to Ag$^+$ sites than Br$^-$ ions. The corresponding values of -10^7B (in mol dm^{-3} s^{-1} g^{-1}) were found to be 28 for the B.D.H. AgBr, 4.2_5 for the J.M. material and 25 for a later sample of J.M. AgBr used for the g.l.c. product analysis. Uncertainty limits for these parameters are hard to estimate since changes

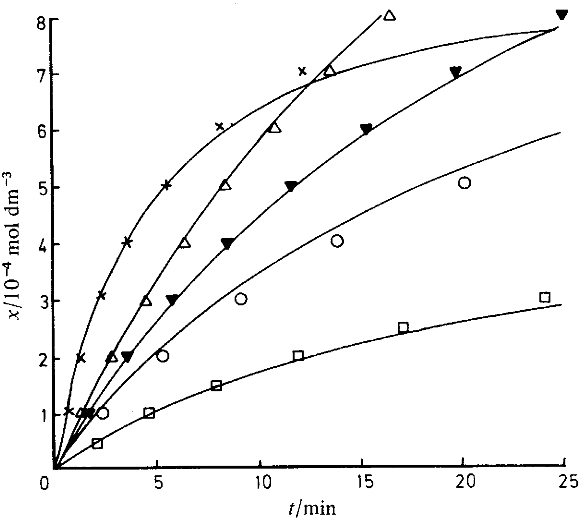


FIG. 2.—Agreement between experimental curves for runs with 0.5 g AgBr (J.M.) in 80 vol % EtOH+H_2O (50 cm^3) at 25 °C and the points calculated from eqn (A 4) using $\sigma = 400$ dm^3 mol^{-1}, $\sigma_P = 3800$ dm^3 mol^{-1}, $B = -4.2_5 \times 10^{-7}$ mol dm^{-3} s^{-1} g^{-1}: □, $a = 4.45 \times 10^{-4}$ mol dm^{-3}; ○, $a = 8.91 \times 10^{-4}$ mol dm^{-3}; ▼, $a = 13.36 \times 10^{-4}$ mol dm^{-3}; △, $a = 17.82 \times 10^{-4}$ mol dm^{-3}; ×, $a = 8.91 \times 10^{-4}$ mol dm^{-3} with 0.5 g AgBr (B.D.H.) using $B = -28 \times 10^{-7}$ mol dm^{-3} s^{-1} g^{-1}.

in B and in $(\sigma - \sigma_P)$ can to some extent balance each other to produce fits of similar goodness. It seems likely that the differences in the B values relate to differences in the specific surface areas (A) of the powders; their small magnitudes made it difficult to determine the areas experimentally. Taking A as 10^{-3} m^2 g^{-1} (see Experimental) and c_{mono} as 7×10^{-6} mol m^{-2} (equivalent to an area of 24 Å^2 per substrate molecule) leads to $k_1' \approx 10^2$ s^{-1}, a value over 10^5 times greater than the homogeneous rate constant k_1 (3.6×10^{-4} s^{-1}). Part of this increase may be attributed to the changed solvent composition at the AgBr surface. The standard Gibbs free energy of transfer for the reaction

$$\text{Ag}^+(\text{EtOH}) + \text{Br}^-(\text{EtOH}) \rightarrow \text{Ag}^+(\text{H}_2\text{O}) + \text{Br}^-(\text{H}_2\text{O}) \qquad \text{(II)}$$

is[16] -22 kJ mol^{-1} which suggests that the layer of solvent at the AgBr surface will be more aqueous than the bulk solvent. On the extreme view that the interfacial layer is pure water, the solvent effect would lead to a surface rate constant of[17] 0.76 s^{-1}. In reality the solvent at the interface will be partly alcoholic and the local solvent factor a smaller one. A large part of the heterogeneous catalysis of the solvolysis must therefore arise from the adsorption of t-BuBr molecules on the Ag$^+$ ion sites. These act as Lewis acids and cause inductive electron shifts in the adsorbed molecules which facilitate cleavage of the C—Br bonds.

Heterogeneous runs at 4 temperatures between 15 and 25 °C were similarly analysed on the crude assumption that σ and σ_P values change relatively little with temperature. The resulting B values, from data with both B.D.H. and J.M. AgBr, had an activation energy of 48 kJ mol^{-1}. The main temperature-dependent factor in B is the heterogeneous rate constant k_1'. Although its activation energy cannot be stated exactly as a result of these calculations it is clearly much lower than the activation energy for the homogeneous solvolysis.

PRODUCT ANALYSIS AND CATALYST SELECTIVITY

The homogeneous solvolysis of t-BuBr in 80 vol% (55.2 mol%) $EtOH+H_2O$ at 25 °C has been reported[18] as producing 12.6 mol% alkene. Our own bromine titrations and g.l.c. analyses led to 61 mol% t-BuOH, 28 mol% t-BuOEt and 11 mol% $Me_2C{:}CH_2$ for the homogeneous reaction. Thus the carbonium ion has preferentially reacted with water rather than ethanol molecules in forming the substitution products. This contrasts with the situation in highly aqueous alcoholic solutions where no 'solvent sorting' occurs.[19a]

In the presence of 1 g J.M. AgBr (new batch) in 50 cm³ solution the fully solvolysed mixture was found to contain 58 mol% t-BuOH, 40 mol% t-BuOEt and 2 mol% alkene. Some of these products resulted from the homogeneous solvolysis which always runs parallel with the heterogeneous reaction. The fraction f of solvolysis products formed by the homogeneous route is given by

$$f=\frac{1}{a}\int_0^\infty k_1(a-x)\,\mathrm{d}t \tag{5}$$

with x supplied by the integrated (Langmuir) rate equation, eqn (A 4). The mathematical basis of the calculation is derived in the Appendix. Application of the final eqn (A 8) and the appropriate σ, σ_P and B parameters shows that in the presence of 1 g AgBr some 20% of the solvolysis products were generated homogeneously. Thus the heterogeneous reaction by itself produced 57 mol% t-BuOH, 43 mol% t-BuOEt and no alkene at all. Other experiments with different masses of standard J.M. AgBr confirmed that the surface reaction formed no elimination products. Tests showed that the presence of silver bromide did not lead to hydration of the alkene. The AgBr catalyst thus acts selectively in this medium.

The literature contains some scattered evidence that corroborates these findings. Thus 5% alkene is formed[19b] when t-BuBr hydrolyses homogeneously in water at 25 °C, yet French *et al.*[20] detected no alkene at 30 °C and not more than 0.2% at 40 °C when the hydrolysis took place in the presence of excess silver hydroxide. No check was made to see if alkene disappeared by hydration in the presence of AgOH; the hydration reaction is, however, acid-catalysed. Buckson and Smith[21] found that the solvolysis of 2-chloro-2-phenylpropane in ethanol at 25 °C produced 11% 2-phenylpropene when excess 2,6-lutidine was present but only 2% alkene with excess silver nitrate. This effect was attributed[21] to anion involvement in a product-determining step. We think it likely that in the silver nitrate solution the concomitant formation of finely divided AgCl heterogeneously and selectively catalysed the solvolysis.

The selectivity of the heterogeneous reaction suggests that the intermediate carbonium ion reacts while still in the vicinity of the AgBr surface. The solvent in this region, as discussed above, is likely to contain less ethanol than the bulk mixture (55.2 mol% EtOH). Judging by the rather limited homogeneous studies available, this composition change would be expected to lead to a product mix containing less alkene[2, 19b] (as found) and less ether[2, 19a] (contrary to that found). One must therefore look more closely at the solvent structure in the interfacial region. It is known[22, 23] that at low ethanol contents profound structural changes occur in the solvent. The water structure is enhanced and this, together with its preferential adsorption on the polar surface, should make H_2O a less receptive acceptor for protons from the carbonium ions and lead to much decreased alkene formation. The interfacial alcohol, although present in smaller concentration than in the bulk, will be less hydrogen-bonded to other ethanol molecules and so may compete more effectively than the highly structured water for substitution into the Me_3C^+ ions. This could account for the increased ratio t-BuOEt: t-BuOH in the products of the heterogeneous reaction.

EXPERIMENTAL

MATERIALS

The A.R. ethanol (J. Burrough) was purified by reflux and distillation as described by Graham *et al.*;[24] very dry nitrogen, prepared by heating liquid nitrogen,[25] was bubbled through the alcohol throughout. The specific conductance of the centre cut product was 1.6×10^{-8} Ω^{-1} cm^{-1} and its density at 27 °C was 0.783 35 g cm^{-3} (interpolated I.C.T. value is 0.783 34). The water content of the distillate (*ca.* 0.1 wt%) was analysed by Karl Fischer titration using an electrometric end point.[26] This water was taken into account in preparing (by weight) a solvent mixture of such composition that it became 80.00 v/v% at 25 °C halfway through most runs. All water was doubly distilled. The 2-bromo-2-methylpropane (H. and W. or B.D.H., 25 cm^3) was shaken with well-dried (280 °C) A.R. Na_2CO_3 (2 g) and then distilled over fresh Na_2CO_3 in a 20 cm Vigreux column flushed with very dry nitrogen. The substrate was freshly distilled at least once a week and stored under nitrogen in 5 cm^3 vessels closed with Subaseal 25. The titrant was prepared from 0.5 mol dm^{-3} B.D.H. NaOH solution 'free from carbonate' by dilution under nitrogen. The exact concentration (*ca.* 0.2 mol dm^{-3}) was determined by potentiometric titration against dried A.R. potassium hydrogen phthalate. Silver bromide was finely ground in a mortar in the dark and sieved to obtain particles smaller than 76 μm. The solid was kept inside a black container and samples were weighed out in the dark.

KINETIC RUNS

The pH-stat measurements were carried out with a Radiometer TTT60 titrator, a REC61 Servograph with the REA160 Titrigraph module, a PHM62 pH meter and G202C glass and K401 saturated calomel electrodes. The pH was kept at the selected value during runs by delivering standardised NaOH solution *via* a Radiometer ABU12 autoburette fitted with a 0.25 cm^3 glass cylinder. The autoburette stopcock was regreased every few days with Radiometer grease or Apiezon N. The round-bottomed reaction vessel (*ca.* 70 cm^3) was made from a Quickfit FG35 flange joint. Its Vitrathene lid, held on with metal clips, contained four holes for the electrodes, the delivery tube for the titrant and addition of the substrate. The contents were stirred with a Rank immersible magnetic stirrer. The thermostat water was covered by a layer of polyolefin spheres and other precautions were taken to exclude light. The temperature could be controlled to ± 0.003 °C.

Before the runs the mixed solvent (50 cm^3) and the solid catalyst (if any) were thermostatted in the closed reaction vessel for 15 min. The pH of the contents was noted and the TTT60 titrator set to this value. The ABU12 tubing and capillary tip were filled with the NaOH titrant and the dried tip introduced into the solvent near the glass electrode. The t-BuBr was then injected below the surface with an S.G.E. 5 mm^3 syringe with no dead volume and the equipment set to pH-stat. The curve of alkali added against time was automatically recorded on the Servograph. The reproducibility of runs was satisfactory: values of x at 28 min showed a standard deviation of 1.8% for homogeneous runs and 3.2% for runs with 0.5 g J.M. AgBr. The rate was not affected by keeping the reaction mixture in a nitrogen atmosphere throughout. Deliberate exposure of the reaction mixture to light from a 60 W tungsten lamp decreased the catalytic effect of AgBr to half its usual value; care was always taken to carry out AgBr reactions in the dark and the powder retained its light yellow colour. The specific area of the AgBr was estimated to be of the order of 0.001 m^2 g^{-1} by thorough washing followed by e.m.f. measurement of the amount of bromide ion adsorbed on the powder from a number of very dilute (10^{-6} to 10^{-5} mol dm^{-3}) KBr solutions.

ANALYSIS OF PRODUCTS

The concentrations of alkene in equilibrium mixtures (50 cm^3) were of the order 10^{-5} to 10^{-4} mol dm^{-3}. Analyses were carried out by bromine titrations with dead-stop end-point.[26] 15 mV were applied cross the platinum-foil electrodes and the small currents were detected on a Telequipment double-beam cathode-ray oscilloscope connected across a 1000 Ω resistor in series with the cell. The bromine solution (*ca.* 1.6×10^{-3} mol dm^{-3}) was electrometrically standardised (*via* iodine) with A.R. sodium thiosulphate solution which had in turn been standardised against A.R. KIO_3. The method was checked with known amounts of 2-phenylpropene and solvent blanks allowed for. The presence of silver bromide did not affect the end-point nor did it remove any significant amount of alkene by hydration.

The three products of reaction (I) could be separated from each other and from the giant ethanol peak on a Pye Unicam 104 Chromatograph using a column filled with polyethylene glycol on Chromosorb P (Sil-O-Cel C22 firebrick) at 70 °C. The retention times of $Me_2C{:}CH_2$, t-BuOEt and t-BuOH were 0.8, 2.6 and 7.9 min, respectively, at a nitrogen flow rate of *ca.* 40 cm^3 min^{-1}. The percentages of t-BuOH and t-BuOEt in the product were derived from these g.l.c. results and the percentages of alkene from the more precise bromine titrations.

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APPENDIX

When the integrated rate equation is of complex form, it is easier in the first instance to compare the experimental data against the differential rate equation.[15] To evaluate dx/dt requires algebraic fitting. Pairs of x, t values were read off from the recorded graphs and were fitted to a polynomial:

$$x = a_0 + a_1 t + a_2 t^2 + \ldots + a_n t^n. \qquad \text{(A 1)}$$

The best coefficients were computed by a least-squares (matrix inversion) programme. Polynomials of degrees 3-7 all gave satisfactory fits of the points and the calculations were later standardised with 4th degree polynomials. Differentiation of eqn (A 1) was also carried out by computer, as was the calculation of the auxiliary function J defined by

$$J \equiv (dx/dt) - k_1(a-x). \qquad \text{(A 2)}$$

In the case of Freundlich adsorption, $J = k_1\phi(a-x)^\alpha$. A plot of $\ln J$ against $\ln(a-x)$ should then be a straight line of slope α. In fact such plots of AgBr-catalysed runs were linear at low times and curved at high times. The slopes of the linear portions invariably gave values of α greater than unity, contrary to the requirement of the Freundlich equation, eqn (2).

In the case of Langmuir adsorption, eqn (4) can be written

$$J = \frac{Bm(a-x)}{b-x} \qquad \text{(A 3)}$$

where $B \equiv Ak_1'\sigma c_{\text{mono}}/V(\sigma-\sigma_P)$, $b \equiv (1+\sigma a)/(\sigma-\sigma_P)$. Plots of $(a-x)/J$ against x should therefore be linear, with slopes of $-1/Bm$ and intercepts b/Bm. The experimental data gave plots that were straight lines or gentle curves at low times and became concave or convex at high times. Analysis of the low-time sections for runs with different masses of AgBr (m) and with different initial t-BuBr concentrations (a) then led to approximate values of σ, σ_P and B. The uncertainties produced by reading off the points, curve fitting and differentiating increased as the x against

t curves flattened out and were almost certainly responsible for the pronounced curving of the $(a-x)/J$ against x plots at large times. The values obtained, though approximate, were of reasonable magnitude and showed unambiguously that $\sigma < \sigma_P$.

More precise values of the Langmuir parameters were obtained by fitting the experimental x against t plots themselves with the integrated version[15] of eqn (4)

$$(1+\psi)\,k_1 t = \ln\left(\frac{a}{a-x}\right)+\psi\ln\left[\frac{b+\psi(b-a)}{b+\psi(b-a)-x}\right] \qquad \text{(A 4)}$$

where $\psi \equiv Bm/k_1(b-a)$. After approximate values of σ, σ_P and B obtained above had been fed into eqn (A 4) the value of each parameter was varied in turn to obtain better overall agreement with the experimental x against t curves. More weight was attached to fitting the early sections of these curves, for the reason explained in the text.

INTEGRATION OF EQN (5)

This is the basic equation for calculating the fraction of the reaction products formed by the homogeneous route. The required value of x as a function of time is given by the integrated rate equation for the overall reaction (homogeneous + heterogeneous). For the Langmuir model, eqn (A 4) becomes

$$y[y+\zeta(1+\psi)]^{\psi} = a[a+\zeta(1+\psi)]^{\psi}\exp[-(1+\psi)\,k_1 t] \qquad \text{(A 5)}$$

where $y \equiv a-x$ and $\zeta \equiv b-a$. Simplification is desirable to obtain a suitable x against t relationship. We note that for the system in question, $|y| < |\zeta(1+\psi)|$. Binomial expansion of the left-hand square bracket shows that for J.M. AgBr the term in y^2 is usually *ca.* 10% of the term in y in the most unfavourable case ($y = a$). We therefore neglect all terms in y^2 and above and, partly for reasons of symmetry, overcorrect for the error thus introduced by similarly expanding the right-hand side. This leads to

$$y+\frac{\psi y^2}{\zeta(1+\psi)} \approx \left[a+\frac{\psi a^2}{\zeta(1+\psi)}\right]\exp[-(1+\psi)k_1 t]. \qquad \text{(A 6)}$$

Writing $y' \equiv y/\zeta[1+\psi]$, $a' \equiv a/\zeta[1+\psi]$ and $A' \equiv 4\psi a'(1+\psi a')$ we obtain a quadratic in y' which can be solved and inserted into eqn (5) to give

$$f = \frac{k_1}{2\psi a'}\int_0^{\infty}(-1+\surd\{1+A'\exp[-(1+\psi)k_1 t]\})\,\mathrm{d}t. \qquad \text{(A 7)}$$

It may be noted that in the t-BuBr/AgBr system ζ, a' and A' are all negative because $\sigma < \sigma_P$ whereas ψ remains positive. To evaluate the above integral we require two further substitutions: $X \equiv \exp[-(1+\psi)k_1 t]$ and $P \equiv +\surd(1+A'X)$. This leads in a straightforward fashion to the final solution

$$f = -\frac{\zeta}{\psi a}\left\{[1-\surd(1+A')]+\ln\left(\frac{1+\surd(1+A')}{2}\right)\right\}. \qquad \text{(A 8)}$$

Although the binomial expansion and truncation of eqn (A 5) means that eqn (A 8) is not exact, the value of f will be correct within a few units percent. Eqn (A 8) also gives the correct answers in the extreme cases of $k_1 = 0$ ($f = 0$) and $k_1' = 0$ ($f = 1$).

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