Kinetics of Alkene Formation in the Homogeneous and in the Heterogeneously Catalysed Methanolyses of 2-Bromo-2-methylpropane (t-Butyl Bromide)

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The kinetics of the methanolysis of 2-bromo-2-methylpropane have been studied from 25 to 40 °C by a pH-stat method and the products analysed chromatographically. In dilute solutions both alkene and ether formation increased steadily with time but in concentrated solution the alkene concentration passed through a maximum. This allowed the rate constant of the acid-catalysed methanolysis of 2-methylprop-1-ene to be calculated. Addition of sodium methoxide to concentrated t-butyl bromide increased the alkene yield by *E*2 elimination. However, in the presence of silver bromide the percentage of alkene fell sharply while the rate of ether formation markedly increased. On the silver bromide surface the t-butyl bromide solvolysed *ca.* 10^5 times faster than in the bulk methanol solution.

THE solvolysis of a t-butyl halide in a pure alcohol normally yields a mixture of an ether and an alkene.[1] Thus Bu^tBr dissolved in dry ethanol was reported to produce 19.0 mol % $Me_2C{:}CH_2$ at 25 °C [2] and 27.9 mol % at 54.9 °C.[3] In methanol, by a short extrapolation to zero water content, the solvolysis of Bu^tCl was found [4] to form 18.3 mol % $Me_2C{:}CH_2$ at 24.8 °C and 19.7 mol % at 30 °C. It is therefore strange that Biordi and Moelwyn-Hughes [5] detected no alkene at all when 1 mol dm^{-3} Bu^tBr in dry methanol was allowed to react to completion at room temperature. We have now reinvestigated this reaction. The products were analysed chromatographically and the rate constants determined either this way or by pH-statting.[6,7] The effect of added AgBr was also studied since the strong heterogeneous catalysis by AgBr of the Bu^tBr solvolysis in 80% v/v $EtOH–H_2O$ was shown [6] to be a selective process which discriminates against alkene formation.

Concentrated Bu^tBr *Solutions.*—Several runs were carried out with Bu^tBr (1 mol dm^{-3}) in MeOH at 40 °C. One solution was initially neutral while NaOMe had been added to others to make them respectively 0.2 and 1 mol dm^{-3} in alkali. The reaction mixtures were chromatographically analysed every 15 min. Peak heights were found to be proportional to peak areas and concentrations were therefore calculated from the former. Plots of ln(Bu^tBr peak height) against time were initially linear and led to first-order rate constants k_1 of 2.3_3 ($\pm 0.1_5$) $\times$ 10^{-4} s^{-1} in satisfactory agreement with the values found in pH-stat runs with dilute solutions (see Table 1). The rate constant of the initially neutral run decreased with time because of the accumulation in solution of the common ion Br^-.

Peaks due to $Me_2C{:}CH_2$ appeared in every run, grew with time, and then declined. By extrapolating the ratios of the early composition peaks back to zero time, the mol fraction (α) of alkene product was found to be 0.11_3. A higher value of *ca.* 0.17 was determined from experiments with dilute solutions (see below) where volatility problems were less. In the 0.2 mol dm^{-3} NaOMe mixture $\alpha = 0.15_5$ and in the most concentrated solution (in which not all the added NaOMe had dissolved at the beginning) $\alpha = 0.30_5$. This rise in α represents a shift from *E*1 to *E*2 elimination [reaction (1)] with a rate constant of *ca.* 5×10^{-5} dm^3 mol^{-1} s^{-1} at 40 °C.

$$Me_3CBr + OMe^- \longrightarrow Me_2C{:}CH_2 + HOMe + Br^- \quad (1)$$

The analogous reaction between Me_3CBr and OEt^- in ethanol was discovered by Hughes, Ingold, and their co-workers [2,3] and Arrhenius interpolation of their data gives a rate constant of 2×10^{-4} dm^3 mol^{-1} s^{-1} for 40 °C.

The appearance of alkene and ether peaks showed that initially neutral Bu^tBr solvolyses in methanol in the usual manner, with parallel S_N1 and *E*1 pathways [reaction (2)]. For this solution at 40 °C the alkene peak reached a maximum height between 45 and 60 min and then decreased, falling to a quarter of its maximum value after 180 min. The decline is attributable to gradual solvolysis of the alkene [reaction (3)], catalysed by the H^+ ions that are progressively produced in reaction (2).

$$Me_3CBr \xrightarrow{MeOH} \{Me_3COMe,\ Me_2C{:}CH_2\} + H^+ + Br^- \quad (2)$$

$$Me_2C{:}CH_2 + MeOH \longrightarrow Me_3COMe \quad (3)$$

It is well known that acid catalyses alkene solvation and, in water, general acid catalysis and an $A–S_E2$ mechanism have been established.[8] Moreover, in the run with 0.2 mol dm^{-3} NaOMe where the generation of acid was delayed, the maximum appeared later. In the 1 mol dm^{-3} NaOMe solution a flat maximum was observed after 90 min, and this peak declined by only *ca.* 20% thereafter. That a maximum appeared at all under conditions where all the H^+ formed by the solvolysis would have been neutralised shows that some alkene was lost due to its volatility (b.p. −6.9 °C). A rise in alkene concentration followed by a fall was also recorded by Hughes and MacNulty [9] in their study of the solvolysis of initially neutral t-pentyl chloride in 80% aqueous ethanol at 50 °C, and they advanced a similar explanation for their finding.

The acid-catalysed removal of alkene during reaction (2) neatly accounts for the fact that Biordi and Moelwyn-Hughes[5] found no alkene at the end of their Bu^{t}Br methanolysis. The rate constant of the alkene solvation, k_{also}, can now be estimated from our results if it is assumed that reaction (3) is first order in [H$^+$]. At the maximum, equation (4) holds where a is the initial

$$\mathrm{d[alkene]}/\mathrm{d}t = \alpha k_1(a - x) - k_{\text{also}}x[\text{alkene}]_{\text{max.}} = 0 \quad (4)$$

concentration of Bu^{t}Br, x the concentration of H$^+$ and Br$^-$ formed by reaction (2), and t is the time. In the presence of b mol dm^{-3} NaOMe, the second term becomes $k_{\text{also}}(x - b)$ [alkene]$_{\text{max.}}$ Values of x and [alkene]$_{\text{max.}}$ were obtained from the peak heights at the times of the alkene maxima and, taking α as 0.17, the most likely k_{also} value was found to be 7×10^{-4} dm^3 mol^{-1} s^{-1}.

Chromatographic Experiments with Dilute Bu^{t}Br *Solutions.*—Runs with 8.91×10^{-4} mol dm^{-3} Bu^{t}Br in MeOH at 40 °C all exhibited progressively rising Bu^{t}OMe and $Me_2C{:}CH_2$ peaks throughout. The values of α were initially just below 0.17 and did not decline below 0.15 whatever the conditions: an initially neutral solution turned acid by reaction (2), a reaction mixture pH-statted to completion, or one to which 1×10^{-3} mol dm^{-3} NaOMe had been added. These facts are easily understood in the light of the rate constants calculated above. In the initially neutral solution the concentration of H$^+$ never exceeded 8.91×10^{-4} mol dm^{-3} and thus the rate of the acid-catalysed alkene methanolysis (3) was much too slow to reduce the alkene concentration significantly during the time of the Bu^{t}Br solvolysis run. This was even more true for the pH-statted solution. Similarly, the rate of alkene formation by reaction (1) was far too slow in the dilute NaOMe solution to have an effect on the concentration of alkene.

In the presence of AgBr (0.5 g) in the reaction mixture (50 cm^3) the overall solvolysis rate of Bu^{t}Br increased (see below) while α decreased to 0.06. A somewhat higher value, 0.08, was obtained when 1×10^{-3} mol dm^{-3} NaOMe had been added initially, presumably because OMe$^-$ ions were sitting on some of the Ag$^+$ sites on the surface. When the mass of AgBr (m) was increased to 1.0 g in a neutral solution, α fell to 0.04. Since the solvolysis of Bu^{t}Br always proceeded in part by the homogeneous route for which $\alpha = 0.17$, it can be calculated from the kinetic parameters derived below that α for the AgBr-catalysed solvolysis was only 0.02. We had previously found[6] α to be 0.00 for the AgBr-catalysed path of Bu^{t}Br solvolysis in 80% v/v EtOH–H$_2$O at 25 °C. In both solvents, therefore, the heterogeneous reaction on a AgBr surface discriminated against the formation of alkene. The explanation is that alcohol molecules which are 'datively' adsorbed on Ag$^+$ ion sites become less basic and thus poorer acceptors of protons from the carbonium ions produced nearby.

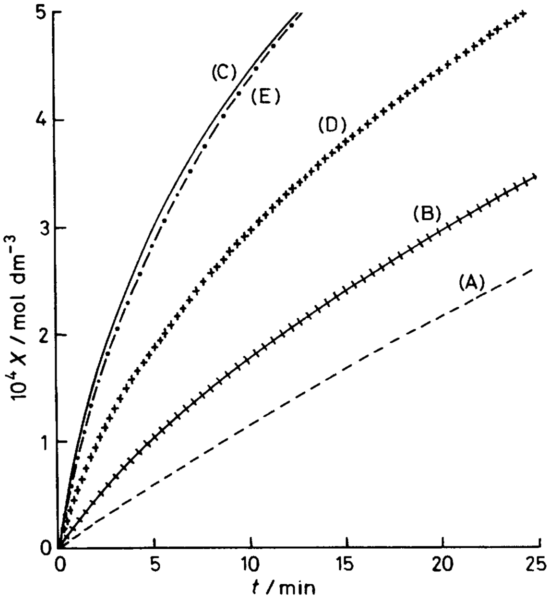
pH-Statting Experiments with Dilute Bu^{t}Br *Solutions.*—The rate of reaction (2) can be conveniently determined by continuous automatic titration of the H$^+$ ions formed with NaOMe solution. Details of the pH-stat technique have been given previously.[6,7] Straight-line plots of ln($a - x$) against t were obtained for all homogeneous runs and their slopes yielded the rate constants k_1. At a given temperature the k_1 values were reproducible, independent of the initial 'pH', independent of the initial Bu^{t}Br concentration a, and independent of whether the AnalaR methanol was used directly or four times distilled. The results are summarised in Table 1 and agree satisfactorily with literature values. The activation energy $E^‡$ derived from our data between 25 and 40 °C is 97.0 (±2.5) kJ mol^{-1} compared with 101 kJ mol^{-1} obtained from an Arrhenius plot of the literature data[5,10] between 14.9 and 50.0 °C.

TABLE 1

First-order rate constants for the methanolysis of Bu^{t}Br

	10^4k_1/s^{-1}	
T/°C	This work	Literature
25.0	0.362 ± 0.003	0.344,[10] 0.360 at 25.1 °C[5]
32.5	0.909 ± 0.009	
40.0	2.32 ± 0.06	2.46 at 39.93 °C[5]

The extent of catalysis by AgBr depended on the purity of the methanol used. The effect is clearly demonstrated in the Figure. The properties of the solvents involved are listed in Table 2, and it should be added that the water contents of the reaction mixtures after the runs were 0.02—0.03 wt % higher. It was at first thought that differences in water content were responsible for the spread of the rates: the more water was present, the more would be preferentially adsorbed on to the AgBr surface and the greater should be the



pH-stat plots of the solvolysis of 8.91×10^{-4} mol dm^{-3} Bu^{t}Br in different grades of methanol (50 cm^3) at 40 °C in the presence of 0.5 g AgBr: (A), homogeneous reaction (no AgBr present); (B), B.D.H. 'specially dried' methanol; (C), J. Burrough AnalaR methanol; (D), Burrough batch 2 methanol (4 times distilled); (E), Burrough batch 3 methanol (4 times distilled)

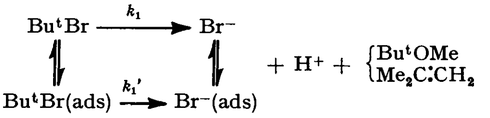
TABLE 2

Sources, purification methods, and properties of the various methanols used as solvent in the pH-stat experiments

Source	Treatment	' pH '	Water (wt %)	Conductivity (10^4 Ω^{-1} m^{-1})
B.D.H. ' specially dried '		9.25	0.02	13.9
B.D.H. ' water in methanol '		6.90	0.64	1.72
J. Burrough AnalaR		8.0	0.01—0.03	1.20
J. Burrough AnalaR batch 2	Distil over $Mg(OMe)_2$, redistil	8.82	0.008	
	Redistil over $Mg(OMe)_2$	9.97	0.004	
	Redistil	8.50	0.004	
J. Burrough AnalaR batch 3	Distil over $Mg(OMe)_2$	8.50		
	Redistil over $PhSO_3Na$	7.20	0.001	
	Redistil over $Mg(OMe)_2$ and Redistil over $PhSO_3Na$	7.0	0.004	0.44

heterogeneous catalysis.[6] However, a AgBr run with B.D.H. ' water in methanol ' containing 0.64 wt % water showed little increase in rate over runs with AnalaR methanol (0.01—0.03 wt % water). Moreover, additions of 0.10 cm^3 water to 50 cm^3 solutions made up with either B.D.H. ' specially dried ' or with Burrough quadruply distilled batch 2 methanol produced no significant changes in rate. It therefore seems more likely that the less active methanols were contaminated by impurities that poisoned the AgBr surface. The lowest catalytic rate was recorded with B.D.H. ' specially dried ' methanol with a very high conductivity corresponding to over 10^{-4} mol dm^{-3} electrolyte: if this solvent had been dried with, say, calcium chloride then the Cl^- ions so introduced would adsorb preferentially onto Ag^+ sites (*cf.* Table 3). The second lowest rate was found with Burrough batch 2 which may still have contained some Mg^{2+} and OMe^- ions—witness the relatively high pH. Redistillation over $PhSO_3Na$ in the batch 3 product appears to have removed these impurities. However, since this four-times distilled solvent led to almost the same rates as the AnalaR methanol itself, the latter was used directly for most of the later experiments.

The first step in the heterogeneous catalysis must involve adsorption of the substrate on the AgBr surface. On chemical grounds one would expect the bromide ends of the Bu^{t}Br molecules to adsorb on surface Ag^+ sites. If this is so, their adsorption and hence the catalysis should not be affected by adding another Bu^t compound like Bu^{t}OMe but should be significantly reduced in the presence of a competitive bromide adsorbate such as Br^-. The experiments listed in Table 3 show that this is exactly what happens. The catalysed solvolysis of Bu^{t}Br is therefore progressively inhibited by the Br^- ions produced by reaction (2). This is allowed for in the Scheme shown. The catalysis itself results from the formation at the surface of the adsorbed species $Me_3C \cdots Br \cdots Ag^+$ in which the C–Br bond is greatly weakened.



SCHEME

Catalytic runs were carried out with a range of Bu^{t}Br concentrations (a 4.45×10^{-4}—17.8×10^{-4} mol dm^{-3}) and masses of AgBr (m 0.25—2.00 g) in 50 cm^3 methanolic solution at 25 and at 40 °C. The reproducibility, as measured by the standard deviation of x values at 28 min, was 5%. The results were analysed by the theoretical Scheme based on parallel homogeneous (rate constant k_1) and heterogeneous (rate constant k_1') paths, with the surface concentrations of reactant Bu^{t}Br and product Br^- expressed in terms of various possible adsorption isotherms. Neither Henry nor Freundlich isotherms were consistent with the kinetic data and the results were therefore fitted to equation (5)

$$\frac{dx}{dt} = k_1(a - x) + \frac{mB(a - x)}{b - x} \qquad (5)$$

based on competitive Langmuir adsorption where $B = Ak_1'c_{mono}\sigma/V(\sigma - \sigma_p)$ and $b = (1 + \sigma a)/(\sigma - \sigma_p)$. Here A is the surface area per unit mass of catalyst (taken as [6] 10^{-3} m^2 g^{-1}), c_{mono} the monolayer coverage (assumed to be 7×10^{-6} mol m^{-2} at both temperatures), σ the adsorption coefficient of reactant and σ_p that of product (Br^-), and V the volume of the solution. However, even the Langmuir equation did not describe the total body of data in methanol as well as it had done in the 80% v/v EtOH–H_2O study.[6] For the methanolic solutions different values of the parameters were needed to fit the pH-stat curves under different conditions, as Table 4 shows.

TABLE 3

Effect of competitors on the solvolysis of Bu^{t}Br (4.45×10^{-5} mol) in J. Burrough AnalaR methanol (50 cm^3) in the presence of 0.5 g AgBr at 40 °C

' pH '	Additive	Amount added (10^{-5} mol)	Amount reacted at 28 min (10^{-5} mol)
	None (no AgBr present either)		1.44
8.08	None	—	3.46
7.82	Bu^{t}OMe	42.00	3.43
7.93	KNO_3	22.30	2.54
8.12	KBr	0.45	3.07
7.94	KBr	0.89	2.40
8.07	KBr	4.45	2.14
7.92	KBr	22.30	1.60

Two reasons can be put forward why equation (5) was less successful than before [6] at accounting for the kinetic curves. (1) The bulk and surface concentrations of substrate may not have been in equilibrium. Since

TABLE 4

Parameters required for best fits to equation (5) of the kinetic data of Bu^tBr methanolyses in the presence of AgBr

T/°C	Types of runs	σ/dm^3 mol^{-1}	σ_p/dm^3 mol^{-1}	-10^7B/mol dm^{-3} s^{-1} g^{-1}	k_1'/s^{-1}
25	Overall	700	22 000	1.4	30
25	Various *a* and low *m*	500	22 000	1.2_5	38
25	High *m*	400	22 000	1.6_5	64
40	Overall	1 600	10 000	9.0	34
40	Low *a* and low *m*	2 000	10 000	8.0	23
40	High *m*	1 800	10 000	10.0	33
40	High *a*	2 000	10 000	9.5	27

both σ and σ_p considerably exceed unity, the rate constants of desorption are much smaller than the rate constants of adsorption. There is already good evidence for the slow desorption of several substrates from the surfaces of carbons.[7,11] Although it is possible to go back to the original theory [12] and modify it accordingly, the mathematics becomes very cumbersome.[13] (2) Adsorbed Br^- ions will repel each other on the surface. This will be more important in pure methanol (with relative permittivity ε_r of 32.7 at 25 °C [14]) than in ethanol–water where the surface layer is predominantly water [6] (ε_r 78.3 at 25 °C). The electrostatic repulsion can be allowed for by incorporating a Boltzmann factor into the Langmuir equation but this leads to a transcendental equation in surface coverage which is difficult to manipulate.[13] Neither approach was therefore pursued further.

Let us consider the overall parameters in Table 4 as they stand. It is very reasonable that the adsorption coefficient of Br^- on AgBr is greater than that of Bu^tBr, as is the fact that σ_p decreases with increasing temperature. However, it is surprising that σ rises from 25 to 40 °C. It is possible, if not very likely, that at the higher temperature the methanol structure at the surface is more broken down and so makes Bu^tBr adsorption easier. The rate constant k_1' for the catalytic reaction at the AgBr surface is seen to be *ca.* 10^5 times greater than the methanolysis rate in the bulk solution, a result similar to that found for 80% v/v ethanol–water.[6] Moreover, the activation energy for the catalytic reaction is very small if not negative, as is the case with certain other heterogeneous reactions.[15] Finally, it must be pointed out that one cannot entirely rule out preferential adsorption of water as the reason both for the high surface rate and for the selective discrimination against alkene formation. Only 4×10^{-7} wt % water in the 50 cm^3 methanol solution would be enough to cover the whole of a 0.5 g AgBr sample of specific area 10^{-3} m^2 g^{-1} with a monolayer of water. None of the available methods of water purification (*cf.* Table 2) are capable of reducing the water content to such a low figure. On the other hand, small additions of water to the solvent did not affect the catalytic rate at all.

EXPERIMENTAL

Materials.—Bu^tBr was purified and stored as before.[6] Freshly distilled substrate was used for all runs. Silver bromide came from a 'new' batch of Johnson Matthey Specpure material. It was ground and sieved to <76 μm particle size in a darkroom, dried at 120 °C, and stored in a vacuum desiccator in the dark. Samples were weighed out in the dark and the pH-stat runs carried out with exclusion of light. Sodium methoxide (H and W Synchemica grade) was dried *in vacuo* for 1 h and dissolved in J. Burrough AnalaR methanol, presaturated with very dry nitrogen, in a nitrogen atmosphere. The solutions were standardised by potentiometric titration with AnalaR potassium hydrogen phthalate. The methanol solvents and the methods of their purification are listed in Table 2. Distillation over $Mg(OMe)_2$ was carried out by the Lund and Bjerrum procedure [16] and water contents determined by electrometric Karl Fischer titration.

Techniques.—The g.l.c. equipment was that used earlier. The retention times of the alkene, Bu^tOMe, Bu^tBr, and methanol were 0.8, 1.9, 3.8, and 10.0 min, respectively, at a nitrogen flow rate of 40 cm^3 min^{-1}.

The pH-stat equipment and reaction vessel were described previously.[6] In the main kinetic runs the reaction mixtures were titrated with a 0.02 mol dm^{-3} NaOMe solution in methanol in a 2.5 cm^3 autoburette. Although the Radiometer G202C glass electrode responded quickly in the methanolic solutions, its performance deteriorated after prolonged use in methanol (after *ca.* 1 week). A certain amount of water is necessary for proper functioning of a glass electrode,[17] and its pH response could be fully restored by soaking it in aqueous buffer of pH 4. It was then briefly soaked in methanol before transfer to the reaction vessel. The reference electrode was a Radiometer K401 aqueous saturated calomel electrode and pH value determined with this equipment are therefore designated 'pH'. The solvent junction potential does not of course affect the kinetic pH-stat curves.

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