Heterogeneous Catalysis in Solution. Part 21.[1] The Effect of Various Carbons on the Solvolysis of 2-Chloro-2-methyl-1-phenylpropane in 50% v/v Ethanol–Water

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The first-order solvolysis of $PhCH_2CMe_2Cl$ in 50% v/v $EtOH–H_2O$ at 40 °C was found to be inhibited by two types of carbon, Hopkin and Williams activated charcoal and Akzo Ketjenblack E.C. Competitive adsorption experiments indicated that the substrate was adsorbed at its phenyl end. The surface solvolysis was found by a combination of kinetic and adsorption measurements to have a rate constant 1/4 as large as the homogeneous solvolysis and a greater activation energy. The main reason for the slower solvolysis of the adsorbed molecules was preferential adsorption of ethanol on the carbon surface. The adsorption isotherm on charcoal of $PhCH_2CMe_2Cl$ in 50% v/v $EtOH–H_2O$ was also derived from the experimental data.

BARBOSA *et al.*[1] have studied the heterogeneous catalysis of the S_N1 solvolysis of t-butyl bromide in 80% v/v $EtOH–H_2O$ by silver bromide and other solids. Various forms of carbon were found to have only a slight effect on the rate. Since carbons often possess large surface areas and are known to catalyse many other types of reaction (substitutions,[2] additions,[3] racemisations,[4-6] and redox processes [7]), this result suggests that Bu^tBr molecules were not sufficiently strongly adsorbed on the carbon surfaces. These surfaces are at least partly graphitic and adsorption should therefore be much stronger for a substrate containing a phenyl group.[4,5,8] Framework models of appropriate tertiary halides showed that in molecules of type $PhCMe_2X$ the methyl groups were likely to hinder adsorption: a more promising substance was $PhCH_2CMe_2X$. Here planar adsorption of the phenyl group would leave the rest of the molecule exposed and the halide end free to leave. We therefore chose 2-chloro-2-methyl-1-phenylpropane for a detailed kinetic study of the effect of carbons on an S_N1 reaction.

The homogeneous solvolysis rate of $PhCH_2CMe_2Cl$ has been measured by two different groups [9-11] in 80% v/v $EtOH–H_2O$ at several temperatures. These data showed that a rate convenient for our purposes would only be attained above 60 °C where volatility problems could arise. We therefore selected instead a medium of 50% v/v $EtOH–H_2O$ in which the homogeneous reaction proceeded at a suitable speed at 40 °C. Since each molecule that solvolyses causes one H^+ ion to be formed, the rate could be followed by means of a pH-stat. Keeping the pH constant is a considerable advantage in work with carbon surfaces because any attached quinonoid, phenolic, and carboxylic groups [12-14] are then ionised to the same extent throughout. Furthermore, if the pH stays at a fairly neutral value, one avoids appreciable H^+ adsorption on the carbons; it is known [15] (and we have confirmed) that such adsorption does occur from acid solutions. Each kinetic run thus produced a recorded plot, against time (t), of the volume of NaOH solution [V_t(NaOH)] that had been automatically added to the reaction mixture (of volume V) to maintain a constant pH. Clearly equation (1) applies where xV equals the moles of H^+ (and of Cl^-, and of the organic products [9,10]) formed by the solvolysis at time t. Thus

$$c(\mathrm{NaOH})V_t(\mathrm{NaOH}) = xV \qquad (1)$$

x represents the concentration of product if it were all present in the bulk solution. In the case of H^+ the product is actually removed by titration and, as described below, some of the organic products are adsorbed on the carbons.

Homogeneous Experiments.—The initial concentration of substrate (a) was normally derived from the syringe volume. It could be checked by determining how much titrant NaOH was required after the reaction had reached completion. In practice the mixture was then pH-statted for 70 min, removed from the reaction vessel, refluxed for *ca.* 15 min to complete the reaction, replaced, re-equilibrated thermally, and titrated with alkali to the initial pH. Good straight lines were always obtained on plotting $\ln(a—x)$ against t.

The first-order rate constant k_1 at 40.00 °C was 2.21 ($\pm$0.03) $\times 10^{-4}$ s^{-1}, and the activation energy over the range 35—50 °C was 94.0 kJ mol^{-1}. That k_1 is greater in 50% than in 80% $EtOH–H_2O$ (where $k_1 = 1.3 \times 10^{-5}$ s^{-1} at 40 °C [9,10]) is typical of S_N1 solvolyses in mixed solvents.[16] The homogeneous solvolysis in 50% $EtOH–H_2O$ produced 36 mole % alkene of which just over half (19%) was $PhCH{:}CMe_2$.

The Effect of Added Solids.—To test for heterogeneous effects, various powdered solids (mass m) were added to the stirred 50% v/v $EtOH–H_2O$ solvent (50 cm^3) at 40 °C. When after a time t(stab) the pH had stabilised, the pH-stat was switched on to maintain the pH at this value and $PhCH_2CMe_2Cl$ (5 µl) was injected to start the solvolysis. The reaction was usually followed for 70 min. The results are summarised in Table 1. The only marked catalysis was shown by silver powder. The emphasis in the present study was on the addition of carbons most of which, somewhat surprisingly, did not alter the solvolysis rate. However, Hopkin and Williams' activated charcoal and Akzo Chemie's Ketjenblack E.C. significantly inhibited the reaction. A quantitative study of this effect was then undertaken, principally with the activated charcoal. Experiments were carried out with a range of initial substrate concentrations ($a = 2.9$—11.6×10^{-4} mol dm^{-3}) and with different masses of carbon (m 0.05—0.30 g). Figure 1 shows clearly that inhibition of the solvolysis was greater the more carbon was present.

Adsorption Measurements on Carbons.—Since many carbons possess large surface areas they can adsorb appreciable quantities of substrate. Quantitative adsorption experiments were therefore possible and were used to supplement the information derived from kinetic runs. To measure how much $PhCH_2CMe_2Cl$ was adsorbed, the solvolysing reaction mixtures were pH-statted as usual but, at a given time t, were filtered to remove the carbon. The filtrate was then refluxed to solvolyse the remaining substrate completely and the extra H^+ ions thus formed were titrated to the initial pH. Further details are given in the Experimental section. Of the initial aV moles of substrate, xV moles will have solvolysed at time t and a further Amc_{ads} moles will have been adsorbed on the carbon [where V is the volume of solution, A the area per unit mass of the carbon, Am the area of the carbon employed, and c_{ads} the surface concentration (in mol m^{-2}) of the substrate]. The concentration c of substrate remaining in solution at time t is therefore given by equation (2). Now a is known, x has been determined by the amount of NaOH added up to time t [*cf.* equation (1)] and c by the

$$c = a - x - Amc_{\text{ads}}/V \qquad (2)$$

further amount of NaOH needed to titrate the completely solvolysed filtrate. We can thus calculate the number of moles of $PhCH_2CMe_2Cl$, Amc_{ads}, adsorbed from the reaction mixture.

TABLE 1

Effect of various solids on the rate of solvolysis of $PhCH_2CMe_2Cl$ (5.80×10^{-4} mol dm^{-3}) in 50% v/v EtOH–H_2O (50 cm^3) at 40.0 °C

Solid	Source and description	m/g	t(stab)/min	pH	Effect on rate
Al_2O_3	Spence type H	0.5	8	8.7	Very slight catalysis
Ag	JMC powder EC, <76 μm	0.1	2	6.7	Catalysis
AgCl	JMC specpure, <100 μm or <250 μm	0.5	2	6.5	No effect
AgCl	Freshly precipitated, dried, ground, <100 μm	0.5	2	6.3	Slight catalysis
SiC	Carborundum Ltd.	0.5		6.9	No effect
C	B.D.H. synthetic graphite powder	0.5	35	6.0	No effect
C	Thos. Hill-Jones 01/S synthetic graphite, <53 μm	0.5	50	7.3	No effect
C	Union Carbide Grafoil, cut to 5 mm × 5 mm pieces	0.5	30	4.9	No effect
				7.0 [a]	No effect
C	Cabot Carbon Spheron 6	0.5	60	4.7	No effect
			180	7.3 [b]	No effect
C	Cabot Carbon Black Pearls 2	0.5	80	3.6	No effect
C	Cabot Carbon Vulcan 9X87, graphitised	0.1	5	6.7	No effect
C	H and W decolourising charcoal	0.5	5	6.3 [b]	Slight inhibition
C	H and W activated charcoal for gas adsorption, <250 μm	0.1	30	8.9	Inhibition
C	Akzo Chemie Ketjenblack E.C., <250 μm	0.1	17	8.1	Inhibition

[a] Addition of Grafoil to the solvent gave pH 4.9. When the Grafoil was separated off and added to a fresh solvent mixture, the pH remained at 7.0. Runs were done in both cases. [b] With alkali added to raise the pH.

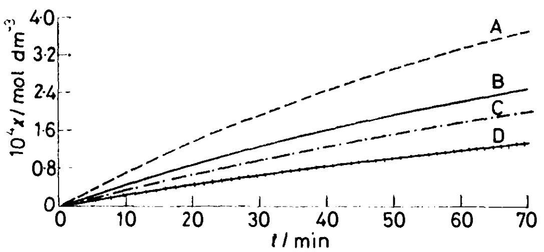

FIGURE 1 Kinetic plots of the solvolysis of 5.80×10^{-4} mol dm^{-3} $PhCH_2CMe_2Cl$ in 50% v/v EtOH–H_2O (50 cm^3) at 40 °C in the presence of: A, no added solid; B, activated charcoal (0.05 g); C, activated charcoal (0.1 g); D, activated charcoal (0.3 g)

Table 2 summarises the results obtained with solutions containing $PhCH_2CMe_2Cl$ (2.90×10^{-5} mol). The extent of substrate adsorption on various carbons can be seen to correlate well with their effects on the solvolysis rate (Table 1). The two carbons that adsorbed appreciable amounts of reactant also inhibited the solvolysis reaction while those carbons that adsorbed little did not influence the rate significantly. This lack of effect can in some cases be attributed to a relatively low surface area. Grafoil is a good example since even the low area obtained by nitrogen adsorption would be only partly accessible to the large substrate molecules.

TABLE 2

Moles of $PhCH_2CMe_2Cl$ adsorbed on to carbons (0.1 g) from a 5.8×10^{-4} mol dm^{-3} solution in 50% v/v EtOH–H_2O at 40 °C after 70 min solvolysis

Carbon	A [a]/ m^2 g^{-1}	10^4x/ mol dm^{-3}	10^4c/ mol dm^{-3}	10^5Amc_{ads}/ mol
B.D.H. graphite [b]		2.50	3.20	0.05
Grafoil	20 [17]	3.84	1.96	0.00
Spheron 6	90	3.84	1.70	0.13
Decolourising charcoal	2 400	3.44	1.88	0.24
Activated charcoal	1 046 [c]	1.90	0.67	1.62
Ketjenblack E.C.	929	2.13	1.14	1.27

[a] By B.E.T. (N_2) determination. Suppliers' data except where noted. [b] Using graphite (0.5 g) and filtering after 40 min. [c] Present work.

Adsorption of the substrate on activated charcoal was also measured under other conditions, and these results are discussed in the Analysis section (*cf.* Table 4). Measurements in the presence of other adsorbates are treated in the section following.

Competitive Adsorption Experiments with Charcoal.—Pincock and his co-workers [4,5] obtained useful insight into the heterogeneous process by competitive adsorption experiments. We therefore tried the effect of adding various kinetically inert substances to a 'standard' charcoal run of activated charcoal (0.1 g) and $PhCH_2CMe_2Cl$ (2.90×10^{-5} mol) in 50% v/v $EtOH-H_2O$ (50 cm^3) at 40 °C. Most of the additives were present in 10-fold excess over the reactant. The results are listed in Table 3. That the additives do adsorb competitively was directly tested in certain cases by measuring the amount of substrate adsorbed after 70 min solvolysis: the values of Amc_{ads} in column 3 are seen always to be less in the presence of an additive. Closer examination of the adsorption figures reveals that benzene hardly impedes adsorption of the substrate whereas $PhCH_2CMe_2OH$ and naphthalene both compete strongly for adsorption sites.

TABLE 3

Effect of the presence of various soluble additives on a 'standard' charcoal run after 70 min

Additive	Moles additive present	10^5 moles reactant adsorbed at 70 min	10^5 moles product formed at 70 min	Comments
None (no carbon present either)			1.80	Homogeneous run
None		1.62	1.00	'Standard' run
NaCl	3.0×10^{-4}		1.00	No effect
$PhCH_2CMe_2OH$	5.8×10^{-5}	1.24	1.19	Less inhibition
	2.9×10^{-4}		1.42	Much less inhibition
CH_3CMe_2OH	2.9×10^{-4}		1.00	No effect
Benzene	2.9×10^{-4}	1.51	0.94	No significant effect
Toluene	3.0×10^{-4}		1.23	Less inhibition
Naphthalene	3.0×10^{-5}		1.12	Less inhibition
	2.9×10^{-4}	0.37	1.42	Much less inhibition

A measure of the effect of the additives on the solvolysis rate is given, in column 4, by the moles of product formed after 70 min. Qualitatively, the more a given additive adsorbs competitively with the reacting substrate, the less will be the inhibition produced by the charcoal and the nearer will the rate be to that in homogeneous solution. Let us now consider each additive in turn, beginning with two products of the solvolysis itself, Cl^- and $PhCH_2CMe_2OH$. Chloride ions did not affect the inhibition by charcoal which suggests that the reactant $PhCH_2CMe_2Cl$ was not adsorbed by its chloride end. The product alcohol $PhCH_2CMe_2OH$ did adsorb competitively with the reactant although CH_3CMe_2OH appeared not to: adsorption of the reactant is therefore likely to involve the phenyl group. The experiments with hydrocarbon additives now show that a phenyl group by itself is insufficient. Thus benzene played no significant competitive role on the surface, nor did it do so in Pincock's experiments.[4,5] This small molecule can probably penetrate inside the charcoal structure: the suppliers state that the activated charcoal can absorb 35% benzene. Bigger aromatic molecules should be largely restricted to surface positions. It is therefore not surprising that toluene definitely reduced the extent of charcoal inhibition and that naphthalene showed a more pronounced effect still. Naphthalene and $PhCH_2CMe_2OH$ in fact exhibit very similar competitive abilities. The low solubilities of anthracene and of cumene ($PhCHMe_2$) in 50% $EtOH-H_2O$ prevented tests with these materials. The experiments thus indicate that a phenyl group with an attached side chain is required for good adsorption on this charcoal surface, and that it is the phenyl and not the chloride end of the substrate molecule that sits on surface sites.

Analysis of Kinetic and Adsorption Experiments.—It has been shown above that the substrate $PhCH_2CMe_2Cl$ solvolyses by a first-order process in the bulk ethanol–water medium, that both the substrate and the product alcohol are adsorbed competitively on activated charcoal, that the other organic products should be likewise adsorbed, and that the overall solvolysis rate is less in the presence of this charcoal. These facts can be conveniently accommodated by Spiro's Scheme [18] of parallel first-order homogeneous and heterogeneous processes. Alkene forms as well and also adsorbs on the carbon. Only the two forward rate constants are shown in the Scheme since the reaction was found to go to completion. A kinetic analysis of the Scheme then leads [18] to the basic rate equation (3). It should be noted that the derivation of this equation required no assumptions about the rates of adsorption on, or desorption from, the surface, nor about the adsorption isotherms for either reactant or products.

$$\begin{tikzcd} \mathrm{PhCH_2CMe_2Cl} \arrow[r, "k_1"] \arrow[d, shift left] & \mathrm{PhCH_2CMe_2OR} \arrow[d, shift left] & + \mathrm{H^+} + \mathrm{Cl^-} \\ \mathrm{PhCH_2CMe_2Cl(ads)} \arrow[u, shift left] \arrow[r, "k_1'"] & \mathrm{PhCH_2CMe_2OR(ads)} \arrow[u, shift left] & \end{tikzcd}$$

R = H or Et

SCHEME

$$dx/dt = k_1(a - x) + Am(k_1' - k_1)c_{ads}/V \quad (3)$$

One of our major objectives was the determination of k_1', the first-order heterogeneous rate constant. This was achieved by the following steps. (i) The kinetic runs had yielded recorded plots against time of V_t(NaOH) and thus, by equation (1), of x. Values of x were read off and fitted to a polynomial of the type (4). The best coefficients were evaluated by computer using a least squares (matrix inversion) program. Three types of fitting were tried: a third-degree polynomial, a sixth-degree polynomial, and three third-degree polynomials covering short overlapping sections of the plot. All

$$x = a_0 + a_1t + a_2t^2 + \ldots + a_nt^n \quad (4)$$

gave very good fits of the experimental data, and the overall third degree polynomial was finally adopted.

(ii) The derivative dx/dt was computed from the polynomial (4) at various points, and so was the useful auxiliary function J defined by equation (5).

$$J \equiv (dx/dt) - k_1(a - x) = (Amc_{\text{ads}}/V)(k_1' - k_1) \quad (5)$$

(iii) Measurements of the adsorption of $PhCH_2CMe_2Cl$ had been carried out at various times during 'standard' charcoal runs. These yielded values of Amc_{ads}. Combination with J values for the same times then enabled us to evaluate k_1'.

Some details of these calculations are given in Table 4. It should be borne in mind that J depends upon a differential as well as upon a difference between two functions, and that Amc_{ads}/V is derived from differences between experimental quantities. Both J and Amc_{ads}/V values are therefore subject to appreciable uncertainty and their quotients $(k_1' - k_1)$ even more so. The evaluation of k_1' from these quotients involves another calculation in which k_1' is the small difference between two large quantities. When due allowance is made for these possible sources of error in k_1' we must conclude that the k_1' values in the last column of Table 4 are really remarkably constant. This result confirms that the surface reaction is a first-order process. The mean value of $10^5\ k_1'/s^{-1}$ is changed from 5.86 to 5.96 if three overlapping third-degree polynomials are used to fit the $x - t$ data instead of one overall third-degree polynomial, and the mean is altered to 6.02 if we choose $k_1 = 2.15 \times 10^{-4}\ s^{-1}$ and to 5.71 on choosing $k_1 = 2.25 \times 10^{-4}\ s^{-1}$. Data from another run, and three other determinations under different conditions, led to similar but somewhat lower values for k_1'. Taking all the data together we can say that k_1' for this system is constant and equal to $5.6 \times 10^{-5}\ s^{-1}$, with an uncertainty of *ca.* ±10%. This value is approximately one-quarter of the homogeneous rate constant k_1 so that the solvolysis proceeds four times faster in the bulk medium than it does on the surface of the activated charcoal. However, the solvolysis rate of the adsorbed substrate is certainly not zero as might naively have been thought from the fact that the carbon inhibits the solvolysis.

TABLE 4

Evaluation of the first-order heterogeneous rate constant k_1' for a 'standard' charcoal run, using $k_1 = 2.20 \times 10^{-4}\ s^{-1}$

t/min	10^4x/ mol dm^{-3}	10^8J/ mol dm^{-3} s^{-1}	10^4Amc_{ads} V^{-1}/ mol dm^{-3}	$10^5k_1'$/ s^{-1}
4	0.114	−6.47	4.00	5.80
14	0.486	−6.18	3.70	5.30
35	1.094	−5.66	3.42	5.44
70	1.900	−4.96	3.23	6.64
140	3.116	−3.62	2.28	6.13
				Mean
				5.86

A kinetic and an adsorption experiment carried out at 50 °C led to $k_1' = 2.8 \times 10^{-4}$ (±20%) s^{-1} and hence to an activation energy for the surface reaction of 135 ± 20 kJ mol^{-1}. This is much greater than the activation energy of 94 kJ mol^{-1} found for the faster homogeneous reaction.

Like the activated charcoal, Ketjenblack E.C. inhibits the solvolysis (Table 1). A kinetic run was carried out at 40 °C with this carbon (0.1 g) and the amount of substrate adsorbed on it was measured at 70 min. Application of the normal computer analysis and equation (5) gave $k_1' = 6.1 \times 10^{-5}\ s^{-1}$. This result is surprisingly similar to that obtained for the activated charcoal.

Adsorption Isotherm of the Substrate.—Values of Amc_{ads}/V have been measured experimentally under certain conditions (*cf.* Tables 2—4). We can now calculate values of Amc_{ads}/V for any other points of the various kinetic x–t curves by evaluating the J function at these points and dividing by $(k_1' - k_1)$. From the known area per unit mass of the charcoal [$A = 1\,046\ m^2\ g^{-1}$ by the B.E.T. (N_2) method] we obtain directly the adsorbed concentrations of $PhCH_2CMe_2Cl$, c_{ads}. The corresponding bulk concentrations c are calculable by equation (2). Graphs can then be drawn of c_{ads} against c. For all initial reactant concentrations and for the various masses of charcoal employed, these plots show c_{ads} rising in a monotone fashion with increasing c although the shapes of the curves differ. These curves are adsorption isotherms of $PhCH_2CMe_2Cl$ in mixed solutions of reactant and products, and are therefore not easy to interpret theoretically. However, one point in each curve, that corresponding to $x = 0$, refers to the adsorption of reactants from 50% EtOH–H_2O containing reactant only. This point was obtained for each of the curves by replotting them as c_{ads} against x and extrapolating to $x = 0$. The resulting adsorption isotherm for $PhCH_2CMe_2Cl$ in the absence of other solutes is depicted in Figure 2.

The six charcoal points in Figure 2 were derived by extrapolation of data from six different kinetic runs, and it is reassuring to see that they all fit fairly well on a single smooth curve. Somewhat unexpectedly, the point for adsorption on Ketjenblack lies on the same curve. The fact that the isotherm for charcoal is not a straight line rules out Henry's law adsorption. Within the extrapolation uncertainties of the charcoal points they are reasonably consistent both with Freundlich adsorption (with an exponent of 0.57) and with Langmuir adsorption. The latter interpretation will be adopted as it provides greater physical insight. In equation form, this is (6) where σ is the adsorption coefficient of $PhCH_2CMe_2Cl$ and c_{mono} the monolayer coverage. From the intercept and slope of a plot of $1/c_{\text{ads}}$ against $1/c$ we can derive $\sigma = 3\,400\ dm^3\ mol^{-1}$ and $c_{\text{mono}} = 5.3 \times 10^{-7}\ mol\ m^{-2}$. The last figure is equivalent to an area of 300 Å^2 per molecule at monolayer coverage compared with an area of *ca.* 45 Å^2 estimated from the molecular model of $PhCH_2CMe_2Cl$. This indicates that not as many sites on the surface are accessible to substrate

$$c_{\text{ads}} = \sigma c c_{\text{mono}}/(1 + \sigma c) \quad (6)$$

molecules as to the much smaller N_2 molecules, a not unreasonable result. When surface areas of carbons are estimated by adsorption of large organic molecules, it is quite common to obtain areas smaller by factors of 2—3 than those determined by the B.E.T. method.

A curious result emerges when the isotherm for pure $PhCH_2CMe_2Cl$ is compared with the isotherms derived for mixed solutions of reactant and products. In almost all cases more $PhCH_2CMe_2Cl$ appears to be adsorbed in the mixed solutions than in the pure substrate ones (for given bulk concentrations of substrate). A likely explanation is that desorption from the surface of either the slowly formed $PhCH_2CMe_2^+$ ion or of $PhCH_2CMe_2Cl$ molecules, or of both, is a relatively slow process. The concentration on the surface then decreases more slowly than that in the bulk medium where the substrate solvolyses relatively quickly. The adsorbed substrate concentration is therefore greater than would be expected from *equilibrium* considerations throughout a kinetic run, except near the very beginning and at completion. This conclusion does not contradict that drawn from Table 3 where less substrate was found to be adsorbed when product alcohol was initially added to the solution, for here such a large excess of product was added that competitive adsorption became the dominant factor. It should be emphasized that the derivation and use of equation (3) in no way assumed c_{ads} to be the equilibrium concentration of adsorbed substrate.

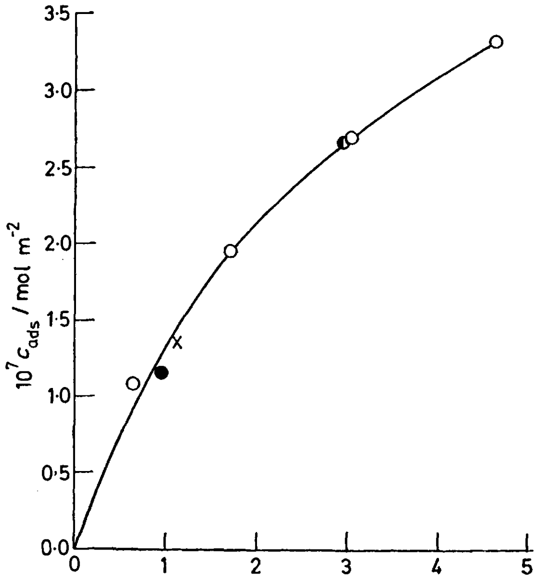

FIGURE 2 Adsorption isotherm of $PhCH_2CMe_2Cl$ in 50% v/v EtOH–H_2O (50 cm^3) at 40 °C on activated charcoal and on Ketjenblack: ◐, charcoal (0.05 g); ●, charcoal (0.2 g); ○, charcoal (0.1 g) with various initial substrate concentrations; ×, Ketjenblack (0.1 g)

DISCUSSION

The reasons for the low rate of solvolysis on both carbons must lie in the environment of adsorbed $PhCH_2CMe_2Cl$ molecules. Probably the most important factor is the change in solvent composition around the surface. Adsorption experiments carried out with the charcoal suspended in 50% v/v EtOH–H_2O, and described in the Experimental section, showed that the surface preferentially adsorbed ethanol from the bulk solvent. Similar findings have been reported for three other carbons.[20] By equation (7) [19] we can then estimate the difference between the mole fraction of ethanol on the surface (x^s_{EtOH}) and that in the bulk (x_{EtOH}). In equation (7)

$$x^s_{EtOH} - x_{EtOH} = \frac{w_0 \Delta c}{m n^s}\left(\frac{x_{EtOH}}{M_{HOH}} + \frac{x_{HOH}}{M_{EtOH}}\right) \quad (7)$$

Δc is the decrease in weight fraction of EtOH brought about by equilibrating w_0 gram of solvent with m gram of charcoal, M is the molecular weight of the subscripted component, and n^s the total number of moles in the adsorbed layer per unit mass of solid. It we assume that this layer is one molecule thick, and that molecules of dinitrogen, ethanol, and water occupy areas of comparable size, we obtain from the B.E.T. experiment $n_s = 0.010\,9$ mol g^{-1}. Insertion of the other experimental results into (7) then gives $x^s_{EtOH} =$ *ca.* 0.64 compared with $x_{EtOH} = 0.23$. Although the surface composition should not be regarded as more than semi-quantitative, there is little doubt that the surface layer is much richer in ethanol than is the bulk solvent. Even with the Cl atom of the $PhCH_2CMe_2Cl$ molecule raised somewhat above the surface, as the molecular model suggests, the average ethanol content of the solvent surrounding the C–Cl bond will be significantly greater than 50% v/v. The adsorbed molecule therefore solvolyses more slowly than its counterpart in the bulk medium. The change in solvent composition by itself should not cause a major increase in the activation energy $E^‡$: for the homogeneous solvolyses in 50% and in 80% v/v EtOH–H_2O the $E^‡$ values are 94.0 and 95.8 kJ mol^{-1},[10] respectively. However, the higher the temperature the greater will be the thermal motion and hence the more similar will be the surface and bulk solvent compositions. The surface reaction at 50 °C will therefore take place in less ethanolic surroundings than the surface reaction at 40 °C, and the activation energy calculated from the experimental rates must reflect this change in medium. To take an exaggerated example: $E^‡$ calculated from the homogeneous rate in 50% v/v EtOH at 50 °C and from that in 80% v/v EtOH at 40.5 °C [10] is 343 kJ mol^{-1}. It follows that even a small shift in surface solvent composition with temperature can produce a large apparent activation energy, as was found in the present research.

Three other environmental factors will also play a role. First, the adsorbed solvent molecules will have lost some of their degrees of freedom. Second, for steric reasons the transition state on the surface is less likely than the transition state in the bulk to assume a cyclic phenonium form. Finally, the presence of the carbon surface itself must be considered. The phenyl end of a substrate molecule probably adsorbs parallel to the basal plane of the carbon. The electron density in this plane is usually less than in the edge region since the exchange current densities of several electrode reactions (hydrogen evolution,[21-23] oxygen reduction,[24] chlorine evolution,[25] the Fe^{3+}–Fe^{2+} couple [26]) are greater on the edge than on the face of graphite electrodes. The resulting inductive electron shift would affect the rate of cleavage of the C–Cl bond. These factors will be the predominant ones for solvolysis in pure ethanol or pure water. However, in the 50% v/v EtOH–H_2O solvent employed here the major influence on k_1' is likely to have been the changed solvent composition at the carbon surface.

EXPERIMENTAL

Materials.—2-Hydroxy-2-methyl-1-phenylpropane was synthesised by a Grignard reaction followed by hydrolysis as described in the literature,[9] b.p. 74—75 °C at 4 mmHg. Hydrochlorination yielded the 2-chloro-compound, b.p. 58 °C at 2.5—3 mmHg, 67—69 °C at 5.5 mmHg, *d* 0.981 g cm^{-3} at 22 °C. The structure was checked by n.m.r.

Hopkin and Williams granular activated charcoal for gas adsorption 2 996 was ground in a mortar and sieved to give particles <250 μm. The Akzo Chemie Ketjenblack E.C. was treated similarly. Ethanol was purified as described previously [1] and analysed for water by Karl Fischer titration. The solvent was prepared by weight so as to give a 50% v/v mixture at 40 °C, and was stored under nitrogen. Sodium hydroxide solution was made up and analysed as before.[1]

Kinetic Experiments.—The Radiometer pH-stat apparatus and the reaction vessel have been described in the preceding paper.[1] The procedure, too, was similar except that the solvent + carbon had to be thermostatted for 30 min before the pH became constant. The reactant was less soluble and took up to 2 min to dissolve completely: the *x–t* plots therefore exhibited a short horizontal section during the first minute. The standard deviation of the *x* value at 70 min of the standard charcoal run was 5%. Homogeneous runs were carried out regularly as a check on the experimental procedure.

Adsorption Measurements.—To determine the amount of adsorbed substrate, the whole of the stirred reaction mixture with suspended carbon powder was removed with an insulated pipette that had been kept at 40 °C. The mixture was filtered through a no. 3 sinter funnel that was largely submerged in the 40 °C thermostat bath. This filtration took 3—4 min. Certain carbons could not be removed in this way, and instead the mixture was separated with filter paper. This operation was quicker (*ca.* 1 min) and could be carried out at room temperature without markedly lowering the temperature of the solution. Neither the sinter nor the filter paper adsorbed a significant amount of substrate. The filtrate was refluxed for 10—15 min to solvolyse the remaining substrate. The solution was then cooled, returned to the reaction vessel at 40 °C, and titrated with alkali to the initial pH. The NaOH required for this corresponds to the amount of substrate in the filtrate. The total amount of substrate in the system before filtration is known from the initial concentration and the titre required up to filtration; the amount adsorbed is given by the difference in equation (2).

The extent of preferential adsorption of ethanol from 50% v/v (44.1 wt%) EtOH–H_2O (10 cm^3) on to charcoal (1—2 g) was determined at room temperature by stirring the suspension for 30 min, filtering, and measuring the refractive index of the filtrate. Blank experiments were done without suspended charcoal. According to the results, 1 g charcoal decreased the bulk ethanol concentration from 44.1 to 41.6 wt%. The real decrease was in fact closer to 1.6_5 wt%, from 43.2 to 41.6%, because some water had been introduced with the charcoal powder itself. The amount involved was estimated by further adsorption and blank experiments with charcoal suspended in pure ethanol.

The area of the charcoal was determined by the B.E.T. method using nitrogen. The charcoal had first been outgassed *in vacuo* at 300 °C for >48 h.

Alkene Analysis.—The concentration of alkene was determined by bromine titration using the dead-stop end-point procedure.[1] A homogeneous solvolysis mixture left at 40 °C until completion gave 36% alkene. Bromine titrations of mixtures containing charcoal were unsuccessful, the currents rising and then falling with time. The bromine appeared to react more slowly with adsorbed alkene and bromine was also adsorbed onto and/or reacted with the charcoal surface. Similar effects have been observed by other workers.[19] The concentration of PhCH:CMe$_2$ was determined from the absorbance at 244 nm.[27]

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