The Mechanism of Alkylation Reactions. Part 2.[1] The Effect of Pressure and Substituents on the Reaction of Phenacyl Bromide with Pyridine in Methanol

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Rate constants have been determined for the reaction of *p*-bromophenacyl bromide with pyridine and three substituted pyridines in methanol at 313.2 K. The reaction of phenacyl bromide in methanol at 313.2 K was investigated for pressures up to 100 MPa and the effect of substituents on the volume of activation, ΔV^*, determined. From the partial molar volumes of reactants and products, the values of ΔV^* were interpreted in terms of the intrinsic volume of the transition state, solvent electrostriction in the transition state and differences in hydrogen bonding between the initial and the transition state. The results support a transition state in which (*a*) bond forming leads over bond breaking and (*b*) considerable charge dispersal occurs. *A priori* calculations of ΔV and ΔV^* are compared with experimental values and their utility discussed.

In Part 1,[1] a mechanism was proposed to account for both the high reactivity of phenacyl halides in general and the Hammett ρ values for substituents in phenacyl bromide and in pyridine, $+0.28$ and -1.87, respectively, for their reaction in methanol at 313.2 K. As the selectivity of the nucleophile was found to be insensitive to change in temperature[1] and Arnett and Reich have recently found[2] the selectivity of the same nucleophile to be independent of the reactivity of the alkylating agent, both the selectivity of the more reactive *p*-bromophenacyl bromide and substituent effects on ΔV^* for the reaction were investigated. In response to the suggestion of the referees, we have determined the reaction volumes, ΔV, and hence determined the contributions of electrostriction and of changes in hydrogen-bonding to the volumes of the initial, final and transition states. By application of Drude–Nernst theory we have calculated the electrostriction of the reaction products and found excellent agreement between the calculated values and values of ΔV obtained by experiment. We have calculated the volumes of activation, ΔV^*, for several reactions calculating the electrostrictive component, $\Delta_2 V^*$, in the same way and obtain good agreement with experimental values. Applying this theory to our experimental results, we discuss the extent of bond-formation and bond-breaking, charge dispersal and solvent interactions in the transition state.

Experimental

Materials.—Materials were purified as before.[1]

Products.—Phenacylpyridinium halides were synthesised by mixing methanolic solutions of the appropriate phenacyl halide and pyridine under a nitrogen atmosphere for three weeks. For the less reactive *m*-acetylpyridine and *o*-picoline after nine months, unreacted phenacyl halide remained. In all cases a large excess of the pyridine was used. The reaction mixtures were diluted with water and extracted with ether to remove the pyridine, excess phenacyl halide and any traces of phenacyl methyl ether, and then dried using cyclohexane by the method of Dean and Stark. The dry residues, where possible, were recrystallised from dry methanol.

The pyridinium and both *p*-picolinium salts gave colourless or fawn needles. The *o*-picolinium salt gave dark green transparent needles and the *meta*-acetyl compound gave a pale amber glass.

Table 1 IR frequencies/cm^{-1} of carbonyl groups for X-phenacyl-Y-pyridinium bromides in Nujol

	Y			
X	H	*p*-CH$_3$	*o*-CH$_3$	*m*-COCH$_3$
H	1708[a]	1710	—	—
p-Br	1705	1711, 1704[b]	1712	1712, 1700[c]

[a] Also the chloride. [b] In MeOH. [c] *meta*-Acetyl CO *ν* value.

Characterisation of the Products.—Using polarography, the rate of loss of the reduction steps characteristic of the phenacyl halides were identical with the appearance of a new step corresponding to the isolated products. For the phenacylpyridinium halides in aqueous solution, the $E_{\frac{1}{2}}$ value agreed[3] with that given by Zuman and Horàk.[4] For the reactions of the less reactive *m*-acetylpyridine and *o*-picoline, unreacted phenacyl halide was present but no phenacyl ether (from solvolysis) was detected[5] for either base. The rate constants obtained for the decomposition of the salts in water by hydroxide ions at 298 K were in excellent agreement with those reported by Pearson and Dillon[6] using a different technique. No decomposition was observed in methanol in the presence of pyridine and with high activation energies reported[7] for the reaction of quaternary ammonium ions, with the extremely small concentration of methoxide ions present, the reaction products are stable under reaction conditions.

We conclude that although the *meta*-acetyl salts were obtained as glasses and could not be crystallised after treatment with charcoal and other adsorbants, they were the sole product of these reactions.

Kinetic Measurements.—Anticipating a possible solvolysis correction, all reactions were conducted with the same molarity of solvent, since pyridine solutions were shown to be devoid of any excess volume of mixing, Table 8. Solvents 10^{-3} mol dm^{-3} in phenacyl halide and typically 0.1240, 0.1014, 0.1508, 0.1027 and 0.1365 mol dm^{-3} in pyridine and its *ortho*-, *meta*- and *para*-methyl and *meta*-acetyl derivatives, respectively, were all

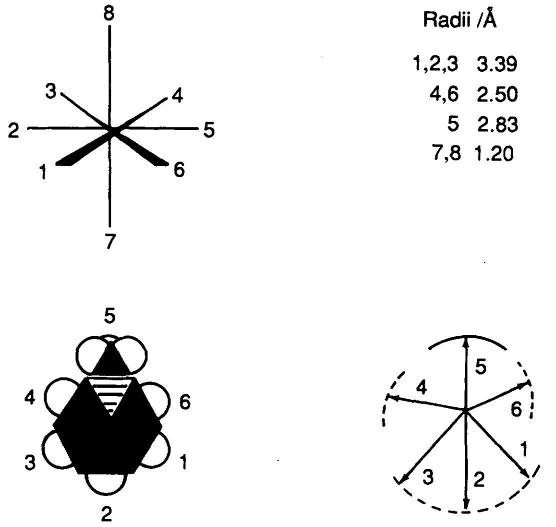

Fig. 1 The dimensions of the *N*-methylpyridinium ion used in the calculation of electrostriction

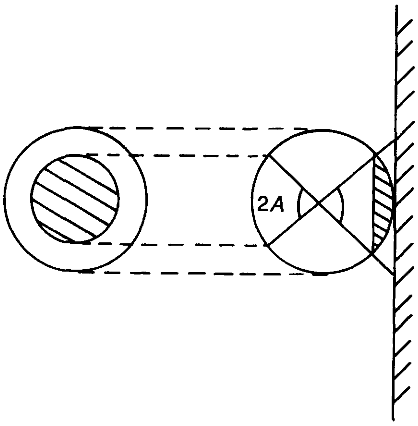

Fig. 2 The loss of electrostricted solvent on contact ion-pair formation. The planar surface is either the pyridine ring or the plane containing the spectator groups in the transition state. The area of the zone, expressed as a fraction of a spherical anion, is (1 − cos*A*)/2. For *A* = 45°, the fraction is 0.1464.

24.3063 mol dm^{-3} in methanol and gave apparent first-order kinetics which were followed conductimetrically using a Wayne–Kerr B641 autobalance bridge. High-pressure measurements were conducted using the conductance cell and equipment previously described[8] and were taken when thermal equilibrium was established after 30 min.

Reactions were followed for at least three half-lives with the exception of the slow reactions of phenacyl bromide with *o*-picoline and of phenacyl chloride with pyridine, for which only the initial 20% of the reaction was followed. The first-order rate constants, *k*, were determined from the relation, $\ln(C_\infty - C_t) = \ln C_\infty - kt$, where C_∞ and C_t are, respectively, the final conductance and the conductance at time *t* and had standard deviations < 1% and corresponding errors of estimate 0.005 or less. Duplicate runs agreed to within 1%.

Density Measurements.—Solutions were assayed in a pycnometer of the type described by Robertson[9] and weighed using a Precisa 80A electronic precision balance and a standard technique.[10]

Conductance Measurements.—Λ_0 values for the reaction products were obtained in the normal way[11a] by dilutions of millimolar solutions. For the phenacylpyridinium chloride in methanol and the phenacyl-*p*-toluidinium bromide in water, the extended Debye–Hückel expression[12] given below, holds at all concentrations up to saturation where $A = 1.8953$ (0.5115),

$$-\log f_\pm = AI^{\frac{1}{2}}/(1 + BaI^{\frac{1}{2}}) + bI$$

$B = 0.5093$ (0.2300), $a = 8.55$ (3.57) and $b = 0.38$ (0.1) in methanol (or water). For the bromides in methanol deviations from ideal behaviour were treated using Fuoss' theory of ionic association.[11b]

Calculations of Electrostriction.—Because experimental values for partial molar volumes and other properties of *N*-alkylpyridinium salts have been determined in a variety of solvents, we calculate the electrostriction for the *N*-methyl cation to illustrate the method. Considering the solvent around the charged nitrogen atom, access is through the pyridine ring in positions 1, 2 and 3 of Fig. 1, obliquely through an *ortho*-hydrogen in positions 4 and 6, through the methyl group in position 5 and in direct contact in positions 7 and 8 perpendicular to the plane of the ring. Each position has been given an eighth of the total solid angle and an appropriate radius. Thus for position 5, the radius of the tetramethylammonium ion was used[13] (Fig. 1) and the contribution to electrostriction calculated from the Drude–Nernst equation.[14] This is repeated for each position and a value of 26.5 cm^3 mol^{-1} is found for the electrostriction in methanol at 298.2 K. Thus, since the electrostriction of the iodide ion in the same solvent is 26.5 cm^3 mol^{-1}, the predicted electrostriction on the formation of *N*-methylpyridinium iodide is 26.5 + 26.5 = 53.0 cm^3 mol^{-1}.

With *N*-ethylpyridinium an acceptable model for the *gauche* conformer of the phenacylpyridinium ions, the elimination of solvent from the 7-position (Fig. 1) by the adjacent carbonyl group in the *cis*-conformer and finally the elimination of solvent from the 8-position in contact ion-pairs give electrostrictions of 26.1, 20.1 and 12.1 cm^3 mol^{-1}, respectively.

For the anions the area of a spherical zone traced out by rotation of a sector with angle, *A*, expressed as a fraction of the total area of the spherical ion, is given by 0.5 (1 − cos*A*), Fig. 2. For a 45° angle this fraction is 0.1464, and represents the fractional loss of anionic electrostriction on ion-pair formation. Summing both contributions the increase in volume from ion-pairing can be calculated for any solvent. Thus the increase in molar volume accompanying ion-pair formation for *N*-methylpyridinium iodide in methanol at 298.2 K is $6.0 + 0.1426 \times 26.5 = 9.9$ cm^3 mol^{-1}.

Calculations of Partial Molar Volumes Taking Account of Ion-pairing.—Since in all cases the reaction products were completely ionised at the concentrations used for the kinetic studies, the partial molar volumes have been corrected for the amount of association in Table 2.

Knowing K_{ass}, α and f may be calculated iteratively for any concentration, *c*, from the expression[11b] $\alpha = [-1 + (1 + 4f^2cK)^{0.5}]/2f^2cK$. In principle the equation $\varphi v = \varphi v_0(\text{ions}) + \varphi v(\text{ion pair})$, where $\varphi v(\text{ions}) = \varphi v_0 + 15.77\,(\alpha c)^{0.5} + bc$ and $\varphi v(\text{ion pair}) = V'_0 + b'c$ can be solved for the four unknowns, V_0, V'_0, b and b'. Unfortunately, because values of φv are only obtained over a reasonable concentration range when K and α are small, the solutions of the four simultaneous equations are ill-conditioned.

Using our calculated value of 10.2 cm^3 mol^{-1} for the loss of electrostriction on ion-pair formation, the partial molar volumes for the reaction products were redetermined from plots of $\varphi v - 15.77(\alpha C)^{0.5} - 10.2\,(1 - \alpha)$ *vs.* both αC and C. These plots are equivalent to assuming b' to be zero and b, respectively. It will be seen from the results in Table 2 that the value of b' has little effect on the calculated limiting partial molar volumes.

Table 2 Partial molar volumes of X-phenacyl-Y-pyridinium bromides in methanol at 298.2 K corrected for ion-pairing

		$b' = 0$				$b' = b$			
X	Y	V^0	$-m$[a]	$-R$[b]	s[c]	V^0	$-m$[a]	$-R$[b]	s[c]
H	H	166.9	16	0.67	0.61	166.8	13.7	0.65	0.62
p-Br	H	180.96	3	0.59	0.14	180.93	2.2	0.57	0.14
p-Br	*p*-CH_3	192.8	19	0.17	1.5	192.8	15	0.17	1.5
p-Br	*o*-CH_3	193.5	15	0.17	2.2	193.3	10	0.12	2.2

[a] Coefficient of regression of $\varphi_v - 15.77(\alpha C)^{0.5} - 10.2(1 - \alpha)$ on αC or C, respectively. [b] Correlation coefficient. [c] Standard error of estimate.

Table 3 Electrostriction of ions in methanol at 298.2 K

Ion	Electrostriction/ $cm^3\ mol^{-1}$
Chloride	31.6 (27.0)[a]
Bromide	29.4 (25.1)[a]
Iodide	26.5 (22.6)[a]
N-CH_3-pyr	29.1
N-RCH_2-pyr	28.6
N-RCH_2-pic	27.8
O-RCH_2-metox	33.9
N-RCH_2-anil	25.9
N-RCH_2,*N*,*N*-Dimethyl-anil	15.7
N,*N*,*N*-Trimethyl-anil	18.9

[a] Corrected for steric hindrance in a transition state or a contact ion pair; pyr = pyridinium, pic = *o*-picolinium, metox = methylhydroxonium, R = aryl or phenacyl (*gauche*-conformer) and anil = anilinium ion.

Table 4 Volume contractions, $\Delta V/cm^3\ mol^{-1}$, on bond formation

Bond	ΔV	Bond	ΔV
C–N	8.09	C–B′	3.82
C–O	2.47	C–I	5.10
C–Cl	3.72	π[a]	3.26

[a] Shrinkage of a carbon atom on re-hybridisation from sp^3 to sp^2.

Table 5 Rate constants at 313.2 K for the reactions of *p*-bromophenacyl bromide with substituted pyridines in methanol

Substituent	$k/10^{-4}\ dm^{-3}\ mol^{-1}\ s^{-1}$	Substituent	$k/10^{-4}\ dm^{-3}\ mol^{-1}\ s^{-1}$
p-CH_3	31.4	*m*-$COCH_3$	2.35
m-CH_3	13.9	*o*-CH_3	0.48[a]
H	9.63	H[b]	1.15[a]

[a] Interpolated from the first-order values in Table 6. [b] Phenacyl chloride.

The values are marginally better for the first case, $b' = 0$, and those values of V are collected in the second column of Table 10.

Calculation of ΔV* *Values From Theory*.—We illustrate the method for the reaction[15] of benzyl bromide with pyridine in nitrobenzene at 303.2 K. As before, the electrostriction of the *N*-alkylpyridinium ion is calculated using the appropriate value of $d\varepsilon^{-1}/dP$, 0.575 $cm^2\ N^{-1}$, and found to be 18.1 $cm^3\ mol^{-1}$. ρ for the substituent effect in pyridine[16] is -2.94 at 313.2 K and hence the fractional charge q_+ is 0.495 and the fractional electrostriction, v_+ is $(0.495)^2 = 0.245$. The electrostriction due to the developing charge on the nitrogen, V^+, is therefore $0.245 \times 18.1 = 4.4\ cm^3\ mol^{-1}$. The ρ value[16] for the substituent effect on the benzyl bromide, -0.82, gives the fractional charge at the reacting carbon atom, 0.286, which taken with the fractional charge on the nitrogen atom gives the fractional charge at the leaving bromide group, q_+ as 0.781. With the electrostriction of the bromide ion, 18.6 $cm^3\ mol^{-1}$ less the small 15% steric correction, 15.9 $cm^3\ mol^{-1}$, V_- is $(0.781)^2 \times 15.9 = 9.7\ cm^3\ mol^{-1}$ and hence $(V_+ + V_-)$, the electrostrictive component of $\Delta_2 V^*$, is 14.1 $cm^3\ mol^{-1}$. $\Delta_1 V^*$ includes shrinkage at the reacting carbon of 3.26 $cm^3\ mol^{-1}$ due to the change in bonding, an increase due to bond-breaking of $0.786 \times 3.82\ cm^3\ mol^{-1}$ and a decrease due to the bond-formation with the bulky pyridine of $0.495 \times 8.09\ cm^3\ mol^{-1}$ to give a net shrinkage of 4.26 $cm^3\ mol^{-1}$. This is converted to a molar volume giving $\Delta_1 V^*$ as $-7.7\ cm^3\ mol^{-1}$. Assuming $\Delta_2 V^*$ is wholly due to electrostriction gives a value for $-\Delta V^*$ of 21.8 $cm^3\ mol^{-1}$ in agreement with the observed value,[15] 23.7 $cm^3\ mol^{-1}$. For the corresponding reaction in methanol, allowance has to be made for the loss of hydrogen bonding to the nucleophile on entering the transition state using the value obtained from partial molar volumes discussed above.

Except where stated otherwise, substituent effects were either obtained at, or interpolated from, a ρ *vs.* T^{-1} plot to the temperature at which the ΔV^* measurements were made. As tabulated values of the Drude–Nernst factor[17,18] are available, we give some calculated ionic electrostrictions for methanol at 298.2 K for which the factor is 0.92 $cm^2\ N^{-1}$, Table 3. Volume changes for bond-formation (or breaking) used in the calculation of $\Delta_1 V^*$ values are collected in Table 4.

The technique requires accurate ρ values for the calculation of ΔV^*. Thus for the calculation for phenacyl chloride in Table 15, changing q_+ from 0.550 to 0.555 gives a similar change in q_-, 0.1 to $\Delta_1 V^*$ but 1.3 $cm^3\ mol^{-1}$ to $\Delta_2 V^*$.

Results

Rate constants for the reaction of *p*-bromophenacyl bromide with substituted pyridines are collected in Table 5. The measured first-order rate constants for reactions under pressure are collected in Table 6 and the derived volumes of activation are in Table 7. No significant change in $d\ln k/dP$ was observed[19] in the range 0.1–100 MPa. Variations in pyridine concentration gave first-order rate constants which both confirmed the derived second-order constants in Table 5 and indicated no requirement for any corrections for the slow solvolysis reaction.[1] Partial molar volumes for the reactants were obtained from plots of apparent partial molar volume *vs.* concentration.[20] The apparent partial molar volumes for the ionic products were initially plotted using the Redlich and Rosen equation,[20] which incorporates an ionic strength correction, but the results indicate ion-pair formation. Partial molar volumes and information on the plots are given in Table 8, which includes apparent values for the pyridinium bromides.

Λ_0 Values for the reaction products were obtained in the normal way[11a] by dilutions of millimolar solutions, since at these concentrations, corresponding to those at the end of the kinetic measurements, there is no ionic association. For the bromides in methanol deviations from ideal behaviour at the higher concentrations required for density measurements were treated using Fuoss' theory of ionic association.[11b] The results are collected in Table 9.

Since in all cases the reaction products were completely

Table 6 Rate constants, $k/10^{-4}\ s^{-1}$, at 313.2 K for the reactions of X-substituted phenacyl halides with Y-substituted pyridines in methanol at different pressures

Substituents		Pressure/MPa							
X	Y	0.10	10	20	30	40	50	60	100
H	H	0.980	1.06	1.15	1.12	1.36	1.46	1.54	2.10
p-Br	H	1.20		1.37		1.64		1.87	2.55
p-Br	*p*-CH_3	3.22		3.66		4.18		4.83	6.13
p-Br	*m*-$COCH_3$	0.320		0.371		0.454		0.518	0.746
p-Br	*o*-CH_3					0.099		0.143	0.404
H[a]	H					0.22		0.29	0.448

[a] Phenacyl chloride.

Table 7 Volumes of activation for the reactions of X-substituted phenacyl bromides with Y-substituted pyridines at 313.2 K in methanol

Substituents		
X	Y	$-\Delta V^*/cm^3\ mol^{-1}$
H	H	19.9 ± 0.2
p-Br	H	19.8 ± 0.4
p-Br	*p*-CH_3	16.9 ± 0.2
p-Br	*m*-$COCH_3$	22.1 ± 0.6
p-Br	*o*-CH_3	48
H[a]	H	30

[a] Phenacyl chloride.

ionised at the concentrations used for the kinetic studies, the partial molar volumes have been corrected for the amount of association. The corrected and uncorrected values are compared with values calculated using partial molar increments and Drude–Nernst theory in Table 10.

The values are marginally better for the first limiting case, $b' = 0$ and those values of V are collected in column two of Table 10 alongside the uncorrected values from Table 8. In this table the partial molar volumes of the phenacyl pyridinium ions are compared with calculated values for the *cis*-conformer.

Discussion

For the reaction of *p*-bromophenacyl bromide with *meta*- and *para*-substituted pyridines, Table 5, a Hammett ρ value[21] of -1.94 ± 0.25 was obtained. This value is similar to the value of -1.82 ± 0.17 obtained previously[1] for the phenacyl bromide reaction. In fact for the *para*-bromo compound a better correlation is obtained using Hammett σ^+ values,[22] $\rho^+ = -1.66 \pm 0.06$, which indicates a greater charge on nitrogen, possibly the result of more bond forming in the transition state for this compound. We merely note that different blends of σ values have been used to describe the ionisation of pyridines in different media[23,24] and that Fischer, Galloway and Vaughan have discussed the anomalous behaviour of *para*-alkylpyridines.[23] What is significant is the near absence of change in selectivity. Our Brønsted-type plot[25] in which the nucleophile replaces the catalyst, gives a gradient of 0.326 ± 0.02 close to the value of 0.30 obtained[2] by Arnett and Reich for the alkylation of pyridines by a wide spread of reagents.

In general the values of ΔV^* for the reactions of the phenacyl bromides, Table 7, are less negative than for the corresponding reactions of pyridine with methyl iodide[26] and benzyl bromide[15] in the same solvent, $\Delta V^* = -46.1$ and $-27.2\ cm^3\ mol^{-1}$, respectively. Apparently as bond making becomes more important, the resultant contraction in the transition state is offset by a reduction in solvent electrostriction. This could be due either to charge dispersal or to the effect of bringing the developing charges closer as noted for ion-pairs and zwitterions.[27]

The insignificant change in ΔV^* on introducing the *para*-bromo group into the phenacyl bromide is not unexpected when the magnitude of the ρ value, 0.28, is considered. The observed change in ΔV^* with change in pyridine substituent is $-9.5\ cm^3\ mol^{-1}\ unit^{-1}$, where one unit corresponds to a tenfold change in rate constant. Clearly the less important bond forming, the further bond breaking has to progress with greater charge development on the leaving group. A combination of a looser transition state and the decreasing importance of the dispersed charge on the pyridine leads to a net increase in electrostriction of the solvent when electron-withdrawing substituents are introduced into the nucleophile.

Taking the observed Hammett ρ values for substituents in the phenacyl group and in pyridine as measures of their effect in altering the balance of bond-forming relative to bond-breaking, a change in ΔV^* with change of phenacyl substituent of $1.4\ cm^3\ mol^{-1}\ unit^{-1}$ is calculated. This is smaller than the $-4.9\ cm^3\ mol^{-1}\ unit^{-1}$ observed[28] for the hydrolysis of benzyl chlorides in 14% aqueous acetone and also in the opposite direction; the expected behaviour of a reaction with $\rho = -2.26$ in which bond-breaking is dominant. The predicted positive shift of $0.3\ cm^3\ mol^{-1}$ in ΔV^* for the introduction of the *para*-bromo group is within experimental error.

Changing the leaving group from bromine to chlorine gives a reduction in ΔV^* of a further $10\ cm^3\ mol^{-1}$, as observed for the methanolysis of ethyl halides.[29a] This additional volume reduction is in accord with a poorer leaving group, for which bond breaking has to proceed further in the transition state unless more bond making occurs, since the combined effect of greater charge development in the transition state and the smaller ionic radius of the leaving-group[27,28] give a more negative ΔV^*.

Whereas the reaction of phenacyl bromide in nitrobenzene with pyridine is reduced tenfold on the introduction of an *ortho*-methyl group in the nucleophile,[30,31] a twenty-fold reduction is indicated for the reaction in methanol, Table 5. A very negative ΔV^* value is characteristic of steric hindrance in the transition state.[27c,29c,32] Steric interactions in the transition state between the spectator groups and the *ortho*-group on the nucleophile hinder bond-forming and result in bond breaking having to proceed further with consequent additional charge development in the leaving group. This looser transition state allows more solvent electrostriction around the developing charges.

Since other workers have suggested[27b,32–34] that further information can be obtained by comparisons between the volumes of activation and the corresponding reaction volumes, volumes of reaction, ΔV, were calculated from the partial molar volumes of the reactants and products for each reaction.

The partial molar volume for *o*-picoline in methanol, Table 8, is close to the value of 93.93 obtained in water,[35] but differs from the value of 99.8 obtained in nitrobenzene,[31] an aprotic solvent

Table 8 Partial molar volumes of compounds and related parameters

		V_0/cm^3 mol^{-1}	m[a]	n[b]	R[c]	s[d]	C_{max}[e]/mol dm^{-3}
X-Phenacyl-Y-pyridinium bromides							
X	Y						
H	H[f]	160.9 ± 0.1	8.0 ± 0.9	6	0.82	0.27	0.254
H	H	165.9 ± 0.15	0.2 ± 0.4	9	0.15	0.32	0.240
4-CH_3	H	190.2 ± 0.9	−70 ± 11	8	0.94	0.86	0.140[g]
H	4-Br	181.52 ± 0.07	2.58 ± 0.72	6	0.53	0.15	0.170[g]
4-CH_3	4-Br	210.8 ± 3.3	−179 ± 56	9	0.82	2.5	0.084[g]
2-CH_3	4-Br	212.7					0.132
3-$COCH_3$	4-Br	220					0.06[g]
4-CH_3	H	193.5[h]	54.4 ± 0.4	4	0.80	1.9	0.1974[g]
Pyridine		78.25[i]					
2-Methylpyridine		95.15 ± 0.18	0.25 ± 0.42	6	0.22	0.20	0.634
4-Methylpyridine		95.38 ± 0.08	−0.09 ± 0.20	7	0.12	0.15	0.630
3-Acetylpyridine		104.91 ± 0.07	−0.52 ± 0.20	6	0.49	0.13	0.546
Phenacyl chloride		120.68 ± 0.15	3.77 ± 0.81	4	0.81	0.16	0.254[g]
Phenacyl bromide		120.5 ± 0.7	28 ± 9	4	0.91	0.51	0.181[j]
4-Bromophenacyl bromide		128.7					0.080[g]
Chloride ion		11.3[k]					
Bromide ion		18.6[k]					

[a] Coefficient of regression of $\varphi_v - 15.77C^{\frac{1}{2}}$ or φ_v on C. [b] Number of readings. [c] Correlation coefficient. [d] Standard error of estimate. [e] Highest concentration. [f] Chloride. [g] Saturated solution. [h] In water. [i] Ref. 34. [j] Supersaturated solution. [k] F. J. Millero, *J. Phys. Chem.*, 1969, **73**, 2417.

Table 9 Λ_0 and association constants, K, for X-phenacyl-Y-pyridinium bromides in methanol at 298.16 K

X	Y	Λ_0/S cm^2 mol^{-1}	K/dm^3 mol^{-1}	a/Å
p-Br	m-$COCH_3$	118.5	5	7.34
p-Br	o-CH_3	117.0	12	5.77
p-Br	p-CH_3	112.0	17	4.84
p-Br	H	102.0	8	6.65
H	H	105.1	4.5	7.34
H	H[a]	88.5[b]	0.0	—

[a] Chloride. [b] 293.2 K.

Table 10 Partial molar volumes of X-phenacyl-Y-pyridinium bromides in methanol at 298.2 K, a comparison between observed and calculated values for the cations and the errors resulting from neglect of ionic association

		Phenacyl Pyridinium Bromides		Phenacyl Pyridinium Ions		
X	Y	V[a]	V[b]	V[b]	V[c]	V[b] − V[c]
H	H[d]	160.9 ±0.1	—	149.6[a]	147.8	1.8
H	H	167.1 ±0.2	166.9 ±0.2	148.3	147.8	0.5
p-Br	H	181.52 ±0.07	180.96 ±0.05	162.3	158.8	3.5
p-Br	p-CH_3	188.2 ±1.2	192.8 ±0.6	174.2	173.3	0.9
p-Br	o-CH_3	191.7 ±0.8	192 ±1	175	176.1	−1
p-Br	m-$COCH_3$	220 ±20	202 ±10	183	184	—

[a] No association correction. [b] Corrected for association. [c] Calculated using Drude–Nernst electrostriction. [d] Chloride.

Table 11 Partial molar volumes and conformers of phenacyl halides in different states

Halide	Solid	Solution	Methanol	*gauche* (%)
Chloride	116.8[a]	122.3[b]	120.7	50[c]
Bromide	120.9[a]	128.3[b]	120.5	70[c]

[a] Molar volume (*cis*-conformer); ref. 38. [b] Calculated from molar increments. [c] Ref. 39.

with a relative permittivity similar to that of methanol. This observed constriction appears to be associated with nitrogen hydrogen bonding in the hydroxylic solvent.[34,36] Our values for the picolines together with literature values[34] for pyridine and lutidines in methanol, give a similar pattern to the very accurate values obtained[35] for these compounds in water.

Similarly, the observed partial molar volumes in methanol for all three phenacyl halides are less than the values calculated from molar increments,[37] whereas the value of 127.6 obtained for phenacyl bromide in propionitrile,[31] is close to the expected value. For the two parent phenacyl halides in the solid state, both in the *cis*-conformation and having similar unit cells,[38] molar volumes differ in the expected way, see Table 11.

The observation of nearly identical partial molar volumes in methanol is the expected result of the greater proportion of the *cis*-isomer in the phenacyl chloride solution, with a consequent decrease in solvent striction due to hydrogen bonding with the keto-group.[39] Since both the conformer ratio[39] and the partial molar volumes[31] in different aprotic and non-ketonic solvents are related to the solvent parameter,[40] E_T, it may be deduced that the intrinsic molar volumes of the *cis*-conformers are less than the corresponding *gauche*-conformers. In hydroxylic solvents the volume changes associated with hydrogen bonding predominate. Allowing for the proportions of each conformer in solution in dichloromethane,[39] the observed partial molar volume[31] may be divided up as 128.3 and 131.3 cm^3 mol^{-1} for the *cis*- and *gauche*-isomers respectively. The volume associated with the conformational change is close to that reported for the conformers of chloroacetone in carbon disulphide.[41] Using these values, the conformer ratio[39] and the observed partial molar volume in Table 8, the striction due to changes on hydrogen bonding and the net shrinkage associated with the *cis*

Table 12 Λ_0 values for *N*-pyridinium and related cations in hydroxylic solvents at 298.2 K, values in parentheses obtained by Walden's rule[a]

Cation	Solvent Water	 Methanol	 Ethanol
Octadecyl, trimethylammonium	19.9[b]	35.1,[c] (32.5)	
Octadecylpyridinium	20.0[b]	(32.7)	
Decylpyridinium	29.5[b]	(48.2)	
Methylpyridinium	(33.3)	(52.9)	26.7[d]
2-Bromopropylpyridinium	(53)	(85)	43[e]
3-Bromopropylpyridinium	(61)	(97)	49[e]
Phenacylpyridinium	(29.8)	48.7[f]	

[a] Ref. 13, p. 638. [b] *CRC Handbook of Chemistry*, 67th edn., ed. R. C. Weast, CRC Press, Boca Raton, 1987, p. D168. [c] *Handbook of Electrochemical Constants*, ed. R. Parsons, Butterworths, London, 1959, p. 86. [d] Ref. 46. [e] Ref. 42. [f] This work.

to *gauche* conformational change in methanol are 13.9 and 10.9 cm^3 mol^{-1}, respectively.

Discussion of the partial molar volumes of the products requires a consideration of ionic association before any discussion of conformations.

Conductimetric studies indicated, Table 9, that although phenacylpyridinium chloride is dissociated throughout the concentration range used for the partial molar volume estimations, all the pyridinium bromides were to some extent associated as ion pairs. The Λ_0 values agree with observed or calculated values for pyridinium salts in methanol, collected in Table 12.

The values of mean ion-pair distance, Table 9, are less than the distance which would allow solvent-separated ion-pairs. Ionic association is greatest for compounds with an electron-withdrawing substituent for which little dispersal of the charge on the quaternary nitrogen occurs. There is little steric hindrance to ion pairing for the *o*-picolinium bromide with the *ortho*-methyl group in the plane of the pyridine ring, Fig. 2, although this has been reported for groups projecting out of this plane.[42]

We have calculated the electrostriction for all product conformations and because experimental values for partial molar volumes and other properties of *N*-methylpyridinium salts have been determined in a variety of solvents, we illustrate the method for the *N*-methylpyridinium ion and for an ion pair in the experimental section. With *N*-ethylpyridinium an acceptable model for the *gauche* conformer of the phenacylpyridinium ions, the elimination of solvent from the 7-position (Fig. 1) by the adjacent carbonyl group in the *cis*-conformer and finally the elimination of solvent from the 8-position in contact ion-pairs give electrostrictions of 26.1, 20.1 and 12.1 cm^3 mol^{-1}, respectively.

If as has been suggested,[17] ΔV for the alkylation is almost wholely due to electrostriction of the product, then the observed value[34] of -46.1 cm^3 mol^{-1} for the reaction of pyridine with methyl iodide in methanol should be close to the electrostriction, -53.0 cm^3 mol^{-1}. That the values differ is due to two factors, the loss of hydrogen bonding to the reactant pyridine and the ion-pairing of the product.

Using 70.4 cm^3 mol^{-1} as the partial molar volume for the *N*-methylpyridinium ion,[34,43] the electrostriction at 298 K in methanol can be obtained as 25.0 and 29.4 cm^3 mol^{-1}, relative to *p*-picoline in methanol and *o*-picoline in nitrobenzene,[31] respectively, as uncharged model compounds for the comparison method[33,44,45] and may be compared with our calculated value, 26.5 cm^3 mol^{-1}. As nitrobenzene and methanol have similar relative permittivities we believe the difference in partial molar volumes for *o*-picoline in these solvents, 4.7 cm^3 mol^{-1}, to represent in part a contraction due to hydrogen bonding of the picoline with the alcohol.[34,36]

In a medium of similar relative permittivity, 80% ethanol, Hemmes, Constanzo and Jordan[46] found *N*-methylpyridinium iodide to have an association constant of 271 mol^{-1} and this is higher than that for any of our products (Table 9). There seems no doubt that ion-pairing is important, and that our treatment is generally applicable.

For the same reaction in acetone, a solvent precluding hydrogen bonding, the predicted electrostriction for *N*-methylpyridinium iodide, 108 cm^3 mol^{-1}, is greater than the observed reaction volume,[47] 95 ± 3 cm^3 mol^{-1}, by an amount less than either the observed[48] or the calculated volume changes on ion-pair formation, 16 and 20.2 cm^3 mol^{-1}, respectively. K_{ass} is 5501 mol^{-1} for this salt[49] and for the mean concentration employed for the partial molar volume determination, 0.1 mol dm^{-3}, the degree of dissociation, α, is 0.38 and the activity coefficient for the dissociated salt, f, is 0.273, corresponding to an apparent partial molar volume of 95.6 cm^3 mol^{-1}.

Since in all cases the reaction products were completely ionised at the concentrations used for the kinetic studies, the partial molar volumes have been corrected for the amount of association in Table 2. Finally, the corrected and uncorrected values are compared with values calculated using partial molar increments and Drude–Nernst theory in Table 10.

The Conformation of the Reaction Products.—The IR solution spectra in Table 1 give single carbonyl peaks compatible with (*a*) an inductive frequency increase relative to acetophenones due to the attached positively-charged nitrogen atom and (*b*) a frequency lowering due to the carbonyl group either hydrogen bonding with solvent in the *gauche*-conformation or undergoing a through-space polarisation with the adjacent quaternary nitrogen in the *cis*-conformation. Since both IR and NMR spectra lead to the same interpretation[1] of through-bond inductive polarisation of σ and π bonds in opposite directions by a neighbouring group and the pyridine-ring substituent effects observed by Harsch, Johnson and Boykin[50] for the methylene and carbonyl carbon atoms of phenacyl pyridinium ions in aqueous solution are contrary to this interpretation, then the ions must be in the *cis*-conformation with a direct through-space interaction between the carbonyl oxygen atom and the quaternary nitrogen atom. X-Ray diffraction studies[51] have shown that the related 9-phenacyl-3-phenylbenzimidazo[2,1-*b*]thiazole bromides exists in the *cis*-conformation in the solid state.

Corrected and uncorrected partial molar volumes for the reaction products are compared with values calculated using partial molar increments and Drude–Nernst theory in Table 10. It will be seen from the last three columns of Table 10 that the partial molar volumes calculated for the *cis*-conformer, 6.0 cm^3 mol^{-1} greater than the corresponding *gauche*-conformer, are close to the observed values. We conclude that the reaction product exists both in water and in methanol as the *cis*-conformer.

In Table 13 are collected the activation volumes, the reaction volumes and for comparison apparent reaction volumes when ion-pairing is neglected. It is immediately apparent that neglect of ionic association would lead to the false conclusion that electrostriction in the transition state could exceed that in the final state.

We have adopted the suggestion of Evans and Polyani,[52] accepted by most workers,[27c,34,53,54a] that ΔV^* may be divided into a part due to the change in intrinsic molar volume on the formation of the transition state, $\Delta_1 V^*$, and a part due to changes in the solvent, $\Delta_2 V^*$. $\Delta_1 V^*$ can be calculated from the difference between the molar volumes of the reactants and the estimated volume of the transition state.

Table 13 Collected values of ΔV^*, ΔV corrected and uncorrected for ion-pairing for the reactions of X-phenacyl bromides with Y-pyridines in methanol at 313.2 K

X	Y	$-\Delta V^*$	$-\Delta V^a$	$-\Delta V^b$
H	H	19.9	31.7	31.9
p-Br	H	19.8	25.5	26.0
p-Br	*p*-CH_3	16.9	35.9	31.3
p-Br	*m*-$COCH_3$	22.1	14	32
p-Br	*o*-CH_3	48	7.3	32
H	H[c]	30	38.1	—

[a] No association corrections. [b] Corrected for ion-pairing. [c] Phenacyl chloride.

Table 14 Charge distributions in the transition state and volumes of activation for reactions of benzyl bromide with pyridine at 302.2 K

Solvent	Methanol[a]		Nitro-benzene[b]	Acetone[c]
q_+	0.45	0.46[d,e]	0.495	0.43
q_c	0.381	0.19	0.286	0.09
q_-	−0.831	−0.65	−0.781	−0.52
$-\Delta_1 V^{*d}$	6.7	4.1	7.7	8.7
$-\Delta_2 V^{*d}$	24.9	18.1	14.1	26.1
$-\Delta V^{*f}$	26.9[g]	22.2	21.8	34.8
$-\Delta V^{*h}$	27.2	22.8	23.7	34.9

[a] Sources used for substituent effects: ref. 82; H. B. Song and I. Lee, *J. Korean Chem. Soc.*, 1988, **32**, 416; F. Quemeneur and B. Bariou, *J. Chem. Res. (M)*, 1979, 2344. Value interpolated from a reactivity–selectivity plot: ref. 76; R. F. Hudson and G. Klopman, *Helv. Chim. Acta*, 1961, **44**, 1914; S. C. J. Olivier and A. P. Weber, *Recl. Trav. Chim. Pays-Bas*, 1934, **53**, 869; from ref. 21(*b*). [b] Refs. 16 and 77. [c] Ref. 76. [d] Calculated for an S_N2 reaction with a protonated benzyl alcohol as the initial reaction product. The calculation for an S_N1 reaction gave $q_\pm$ as 0.88 and as bond breaking has made much less progress in the transition state for the bimolecular displacement, we conclude that the mechanism is S_N2. No allowance was made in the S_N1 calculation for any loss of electrostriction due to the shorter distance between the developing charges, which could possibly lead to an underestimate of $q_\pm$. [e] Methanolysis of the bromide. [f] Calculated value. [g] 4.7 cm^3 mol^{-1} added for loss of hydrogen bonding. [h] Ref. 15.

Table 15 Charge distributions in the transition state and volumes of activation for the reaction of phenacyl bromide with pyridine at 313.2 K

Solvent	Methanol[a]		Nitro-benzene[b]	Acetone[c]
q_+	0.315	0.55[d]	0.692	0.45
q_c	−0.196	−0.416	−0.307	−0.39
q_-	−0.119	−0.134	−0.385	−0.06
$-\Delta_1 V^*$	9.6	13.0	13.1	12.0
$-\Delta_2 V^*$	4.0	10.4	12.6	3.4
$-\Delta V^{*e}$	8.9[f]	18.7[f]	25.9	15.4
$-\Delta V^*$	19.9[g]	30[g]	—	15.4[h]

Sources for substituent effects: [a] this paper and ref. 87; [b] ref. 30; [c] ref. 72. [d] Phenacyl chloride. [e] Calculated value. [f] 4.7 cm^3 mol^{-1} added for loss of initial-state hydrogen bonding. [g] This work. [h] J. V. Hwang, J. J. Chung, S. D. Yoh and J. G. Jee, *Bull. Korean Chem. Soc.*, 1983, **4**, 237.

As estimates of $\Delta_1 V^*$ for S_N2 reactions vary from 0 to −16 cm^3 mol^{-1}, we have used the usual cylindrical space-filling model[27a,53,54a] and inserted the extent of bond making and bond forming to calculate the intrinsic change in molecular volume in the formation of the transition state. To allow for the changes in void volume, this value is multiplied by the factor of 1.8, suggested by Kondo, Shinzawa and Tokura,[45] to give the intrinsic change in molar volume, $\Delta_1 V^*$. This factor is higher than that found for water,[55] but is in accord with recent theoretical calculations of void volumes for non-aqueous less-structured solvents.[56] Since in the final state ΔV is found to approximate to the electrostriction of the ionic product, Brower suggested[33] the use of $\Delta_2 V^*/\Delta V$ as an indicator of the extent of reaction in the transition state. This was based on the then best empirical model for the electrostriction of electrolytes which has now been superceded.[20b] Because of this and the difficulties in determining $\Delta_2 V^*$ when the Drude–Nernst relation is applied,[54b] this suggestion has received little support.[15,34]

Provided electrostriction is the only factor, then for exchange reactions only, the square-root of this ratio indicates[14] the fractional charges developed in the transition state. For reactions for which the leaving and entering groups differ an estimate of at least one partial charge as determined by Hammett values is necessary. For both cases small allowances for steric hindrance of solvation in the transition state are required.

Encouraged by the results of our *a priori* calculations of partial molar volumes and reaction volumes, we have calculated fractional volume changes due to electrostriction in the transition state as $(\Delta V^* - \Delta_1 V^* \pm V^*h)/\Delta V$, where V^*h represents any change due to a change in hydrogen bonding. Because the electrostricted solvent is closer to either of the developing charges on the pyridine nitrogen or the departing halogen than the distance between the partial charges, the electrostriction must be treated as that at two separate poles rather than at a dipole. The electrostriction in the transition state is now the sum of two volumes, v_+ and v_-, representing the electrostriction at each pole. For convenience in calculation, we define fractional electrostrictions, V_+ and V_-, as the electrostrictions expressed as a fraction of those in the product allowing for the additional steric exclusions of solvent in the transition state. Dropping the suffixes for each pole and applying the Drude–Nernst relation, $v = q^2$ where q is the partial charge. Values of q are determined from the appropriate Hammett ρ value relative to that of a suitable standard equilibrium reaction in the usual way.[1] Finally, we assume the steric inhibition to solvation in the transition state to be that at the product cation for the nitrogen atom and for the leaving groups at the product anion in a contact ion-pair, Fig. 2.

We illustrate the method for the reaction[15] of benzyl bromide with pyridine in nitrobenzene at 303.2 K giving a specimen calculation in the experimental section above.

Where less information is available, as long as the partial charge at one pole is known, then the remaining ΔV^* can be distributed by iterative calculation between $\Delta_1 V^*$ and the electrostriction at the other pole. This gives a unique result whose validity is dependent on electrostriction being the sole contribution to ΔV^*.

These results are included in Table 14, along with calculations for related reactions. Calculations for the reactions of phenacyl halides with pyridine and with *o*-picoline are collected in Tables 15 and 16, respectively. For comparison, Table 17 contains information for the reaction of methyl iodide with pyridine in the two aprotic solvents.

Comparing the results in Tables 14 and 15, the effect of either different solvents or of different leaving-group affects the charges at carbon, nitrogen and departing halogen atoms at first glance in an apparently random manner. However, when bond-forming leads over bond-breaking for the reactions of the phenacyl halides, tighter transition states are found. That the phenacyl chloride reaction with a poorer leaving group has a tighter transition state than that for the reaction of the more reactive phenacyl bromide is confirmed.

Comparing the results in Tables 14, 15 and 17, it is clear that in acetone, conjugation by both phenyl and benzoyl groups allows more bond formation than for methyl iodide in their

Table 16 Transition-state charge distributions in the reaction of phenacyl bromide with *o*-picoline at 303.2 K

Solvents	Methanol		Nitro-benzene	Acetone
q_+	0.315	0.60	0.50	0.48
q_c	−0.196	0.35	0.231	−0.173
q_-	−0.119	−0.95	−0.731	−0.307
$-\Delta_1 V^*$	9.7	8.1	8.1	10.8
$-\Delta_2 V^*$	4.0	40.9	13.0	19.2
$-\Delta V^{*a}$	9.0[b]	45.3[b]	21.0	29.5
$-\Delta V^*$	48.0[c]	48.0[c]	21.2[d]	30.2[d]

[a] Calculated value. [b] 4.7 cm^3 mol^{-1} added for loss of initial-state hydrogen bonding. [c] This work. [d] Ref. 31.

Table 17 Transition state charges and volumes of activation for the reactions of methyl iodide with pyridines at 323.2 K[a]

Solvent	Nitrobenzene	Acetone
q_+	0.50	0.36
q_c	0.19	0.11
q_-	−0.69	−0.47
$-\Delta_1 V^*$	6.6	6.7
$-\Delta_2 V^*$	14.7	26.5
$-\Delta V^*$	21.3	33.2

[a] The volumes of activation are taken from ref. 26 and the q_+ values taken from U. Berg, R. Gallo, G. Klatte and J. Metzger, *J. Chem. Soc., Perkin Trans. 2*, 1980, 1350.

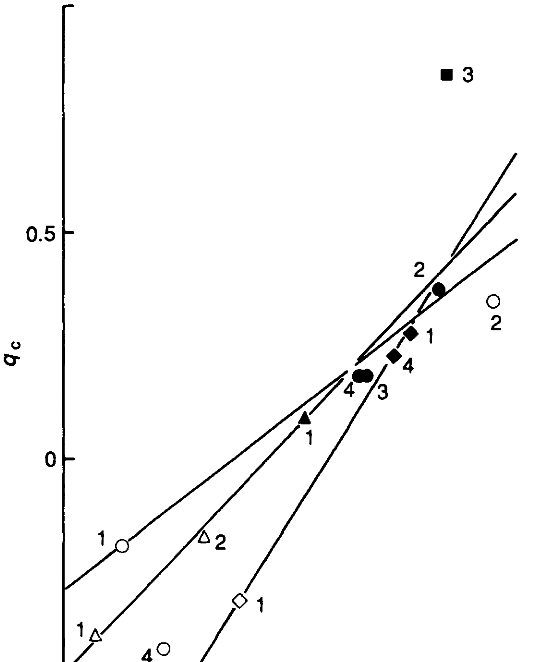

Fig. 3 The relationship between q_c and q_-. Reactions of phenacyl bromide (open symbols) and benzyl bromide (filled symbols) in methanol (○, ●), acetone (△, ▲) and nitrobenzene (◇, ◆) with: 1, pyridine; 2, *o*-picoline; 3, methanol and 4, aniline. The S_N1 methanolysis of *tert*-butyl chloride is indicated by ■.

respective transition states. In nitrobenzene this only happens with the benzoyl group. This occurs by either reducing the partial positive charge on carbon in the case of the benzyl halide, or by stabilising the partial negative charge in the case of the phenacyl halides.

As the electron density on the reacting carbon atom is increased, so the ease of bond breaking should increase. Thus, comparing the reactions of phenacyl halides with the corresponding benzyl halide reaction, Tables 14 and 15, for all four sets bond breaking is facilitated and has made less progress in the transition state for the more reactive phenacyl compounds.

In fact we have some evidence, Fig. 3, that for a given solvent and a given leaving-group, there is a linear relationship between q_c and q_-, *i.e.* the amount of bond-breaking in a transition state is directly proportional to the formal charge at the reacting carbon atom. Furthermore, provided there is no mechanistic change, the relationship is independent of the nucleophile. Thus, for the reactions of benzyl bromide in methanol with aniline[57] and with the solvent, Table 14, the relation holds, Fig. 3.

This implies that bond breaking in the transition state is dependent solely on the charge on the reacting carbon and on the interaction between the incipient ion and the solvent. For bond forming in methanol, a solvent that promotes bond breaking, less bond forming is required for the phenacyl bromide transition state relative to the benzyl bromide, but for the aprotic solvents, the reverse holds.

For the reaction of phenacyl halides in methanol, in addition to the loss of hydrogen bonding with pyridine in the initial state,[34,35] consideration has to be given to changes in hydrogen bonding associated with conformational changes in the phenacyl halides, any tightening of the hydrogen bonds between the keto-oxygen of the phenacyl group and the solvent and, finally, any changes in electrostriction due to charge dispersal on to the substituents.

Evidence for charge dispersal in pyridines has been given by Arnett and Chawla who identified changes in the enthalpy of solution in water with the ability of the substituent to facilitate hydrogen bonding at the nitrogen atom.[36b] Similarly, we have related both solubility and the stability constants for contact ion-pair formation with the inability of electron-withdrawing substituents to disperse the charge on the pyridinium nitrogen atom in the products.

As pyridine substituents affect the amount of hydrogen bonding in water and methanol as measured by the enthalpies of solution,[36] the 4.7 cm^3 mol^{-1} loss of striction for pyridine itself will also change with substituent. It is clear that the observed change in ΔV^* with change in Hammett σ value, −9.5 cm^3 mol^{-1} unit^{-1}, could in part arise from large losses of striction from the breaking of strong hydrogen bonds to pyridines with electron-releasing substituents (and smaller losses for the weaker bases) on entering the transition state. Moreover, since for hydrogen bonding ΔH is directly proportional to the IR frequency shift,[58,59] an estimate of the substituent effect on the magnitude of the strictional changes due to loss of hydrogen bonds may be made. This is −0.6 cm^3 mol^{-1} unit^{-1} and obviously cannot account for all of the observed substituent effect. It follows that changes in bond-forming and bond-breaking must contribute most to the substituent effect. The weaker the pyridine, the more bond making and breaking will occur, probably accompanied by a decrease in the partial negative charge at the reaction centre. This behaviour is in accord with the conclusions of Songstad and his co-workers[60] and recent theories[61,62] that the more polarisable the nucleophile with the ability to donate charge to the transition state, the faster the reaction.

In methanol the *gauche*-conformer of phenacyl bromide is favoured relative to the *cis*-conformer due to hydrogen bonding with the solvent.[39] Irrespective of the route postulated,[63a] the *gauche*-conformer should undergo further striction as the hydrogen bonds to the ketone oxygen strengthen in the transition state. The *cis*-conformer must in addition form new hydrogen bonds. The substituent effect on the conformer ratio is small[64] and may be neglected.

Earlier we estimated the net change of volume on going from the *cis*- to the *gauche*-conformer to be $-10.9\ \text{cm}^3\ \text{mol}^{-1}$. Taking the *gauche*-conformer as a model for the transition state, since both have solvent molecules hydrogen bonded to the ketone group, and knowing the equilibrium concentration of the *cis*-conformer,[39] a net striction of $4.0\ \text{cm}^3\ \text{mol}^{-1}$ is obtained for additional hydrogen-bond formation. Using the relationship between ΔH and ν for hydrogen bonding between phenol and acetophenones,[65] we estimate $-\Delta H$ for *p*-acetylphenoxide to be $21.8 \pm 0.8\ \text{kJ mol}^{-1}$. Using the decrease in ΔH on changing the donor from phenol to an alcohol,[66,67] $-\Delta H$ for acetophenone and *p*-acetylphenoxide hydrogen bonding to an alcohol are, respectively, 10.5 and $17.2\ \text{kJ mol}^{-1}$. Since the unit charge in the phenoxide ion is attenuated by the benzene ring to a third of unit charge,[21b] then this compound is a good model for the solvent methanol hydrogen bonding to the phenacyl keto-group in the transition state with $q_c = -0.3$, and acetophenone is a model for the *gauche*-conformer in the initial state. Because these values lie in the quadratic region[68] of the hydrogen bond length relation,[67] the hydrogen bonds will shorten by at least 0.2 Å on entering the transition state. With two bonds being formed,[69] this corresponds to a striction of $3.3\ \text{cm}^3\ \text{mol}^{-1}$.

Although the *gauche* conformers of phenacyl halides offer the least steric hindrance to attack at the reacting carbon, as discussed previously, most authors[1] assume preferential attack on the *cis*-comformer. In the solid state this conformer is slightly skew with the plane containing the haloacetyl group at a small angle to that of the benzene ring.[38,70] This in solution would reduce steric hindrance between the nucleophile and the *ortho*-hydrogen of the benzene ring reported for the reactions of groups held rigidly in the plane of the ring.[71] In methanol, with ΔH 30 kJ mol^{-1} for the *gauche–cis* conversion, a similar favourable contribution occurs as the ketone of the *cis*-conformer hydrogen bonds to the solvent on entering the transition state.

We note that for benzyl bromide reactions E_a in methanol is 21 kJ mol^{-1} greater than for the reactions in nitrobenzene, acetone and acetonitrile,[15] presumably due to the loss of initial hydrogen bonding to the pyridine. For phenacyl bromide reactions in methanol and acetone[72] the difference is only 13 kJ mol^{-1}, indicating that the interaction between the transition-state complex and methanol is exothermic relative to that for benzyl bromide. This may be interpreted as stabilisation of the partial charge on the ketone group through solvent hydrogen bonding accompanied by the expected decrease in entropy.

Within the uncertainties in predicting molar volumes,[20b,55,56,73] all the additional striction found in the phenacyl transition state in methanol is accounted for by structural changes involving hydrogen bonding with the solvent.

In Part 1,[1] it was noted that an isoenthalpic relation could not be ruled out for the substituent effect in the pyridine ring. We can say definitely that for this reaction in methanol[1] and in acetone[72] and for the related reaction of pyridines with phenacyl *p*-toluenesulphonate in acetonitrile[74] there is some compensating effect leading to no significant change in selectivity with temperature as measured by either Hammett ρ values or Brønsted-type coefficients. This is in marked contrast to the corresponding reactions of benzyl bromides, which show substantial changes in ρ with temperature.[75,76] Possibly, knowing the low thermal stability of hydrogen bonds, the compensation lies in a crude balance of hydrogen-bond making and breaking on entering the transition state for the reaction of pyridine with phenacyl bromide, Fig. 4.

ortho-*Effect*.—Although no ΔV^* measurements have been reported for the reaction of *o*-picoline with benzyl bromides in acetone, Baker and Nathan[76] found <1% change in the substituent effect over a 20 K temperature range. Relative to the pyridine reaction there are 61% and 91% increases in ρ at 293.2 and 313.2 K, respectively, corresponding to a more positive value for q_c. Panigahi and Sinha[77] obtained a 50% greater effect for the reaction of benzyl chlorides in nitrobenzene at 353.2 K and for the weaker base, quinoline, the substituent effect was double that for the reaction with pyridine. Thus, either bond breaking has increased, bond forming decreased or a combination of both occurs: the expected result for steric hindrance. With bond breaking for the reaction of pyridine with benzyl bromide greater in nitrobenzene than in acetone, it seems reasonable to assume more bond breaking for the reaction with benzyl chloride in nitrobenzene. At a common temperature, it is clear that steric hindrance is less for the chlorides because bond breaking has already made more progress for the reaction of the parent pyridine in nitrobenzene than for the reaction of pyridine with benzyl bromide in acetone. For the reactions of phenacyl bromide in acetone and nitrobenzene, assuming that the $\Delta_2 V^*$ values are solely due to electrostriction, the unique solutions in Table 16 are obtained. In the transition states for these reactions, bond forming is almost unchanged in acetone and in nitrobenzene is appreciably reduced. For both solvents bond breaking has to proceed further, for nitrobenzene[30] to such an extent that the enhanced reactivity due to the phenacyl group is lost and the transition state resembles closely that for the reaction of benzyl bromide in the same solvent,[16,77] Table 14. For both reactions the relation between q_c and q_- holds, Fig. 3.

Because of the uncertainty in hydrogen bonding, no unique solution is possible for the reaction in methanol. The transition state could lie between two extremes, from a charge distribution, (*a*) which resembles that for the reaction with pyridine to one, (*b*), in which bond breaking is dominant without any conjugation with the phenacyl keto-group and striction due to hydrogen bonding much reduced with the keto-group next to a positive charge, Table 16. Calculated ΔV^* values favour a transition state close to the latter limit, Fig. 3.

Although Asano and LeNoble found two *ortho*-methyl groups to have a modest effect on either ΔG or ΔV for the alkylation of pyridines with methyl iodide in acetone,[34] we, in agreement with Heydtman and his co-workers,[31] found a very large steric factor when the alkylating group was phenacyl. This presumably is a result of steric hindrance between the *ortho*-methyl group on the nucleophile and the benzoyl spectator group, which is apparent using space-filling molecular models and is not present in the methylation. Under these conditions with a greater proportion of sp^3 hybridisation,[78] conjugation with the phenacyl group is lost but front strain[79] is reduced as the spectator groups bend back out of the plane normal to the π-bond at the reaction centre as the Walden inversion proceeds.

In Part 1,[1] the higher reactivity of aniline with regard to its pK_b in its reaction with phenacyl bromide and the lower *m* value for the solvolysis of phenacyl bromide than that for the reaction with pyridine were explained by transition states in which hydrogen bond formation between the phenacyl keto-group and an amino-hydrogen from the nucleophile occurred with substantial charge dispersal. Such charge dispersion, because of the dependence of electrostriction on the square of the charge, would reduce electrostriction and in Fig. 3, the points for this reaction, unlike the corresponding benzyl bromide reactions, lie off the line in the sense of more bond breaking than would be expected for the formal charge, q_c, as predicted. For the reactions in methanol and nitrobenzene, these dispersed partial charges are 0.22 and 0.20, respectively. Such an effect has been observed for the alkylation of *o*-(hydroxymethyl)benzylamine by an epoxide[80] and Parker and Rockett[81] have explained similarities in the behaviour of the two alkylating agents in hydroxylic solvents as the result of both reactions being subject

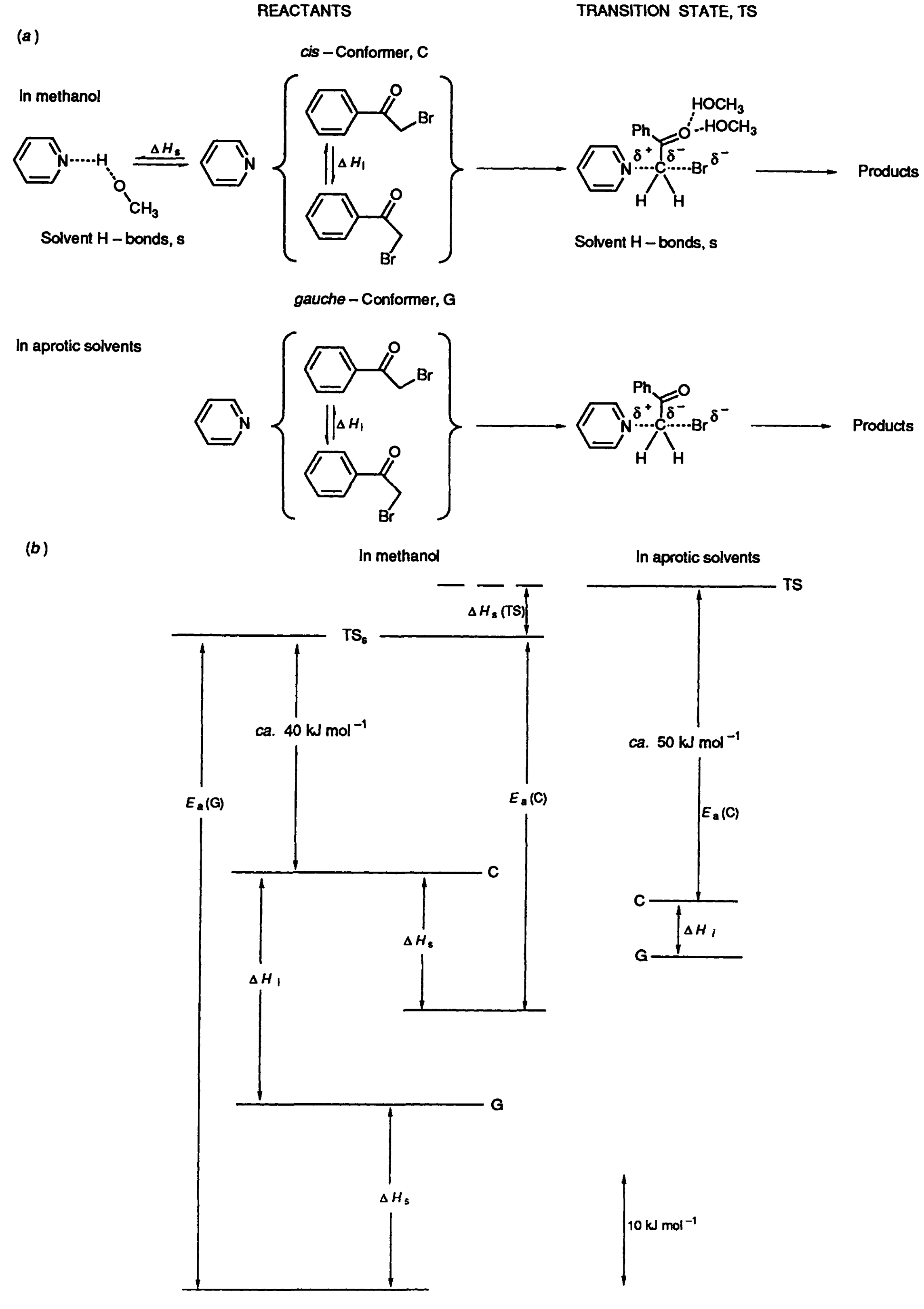

Fig. 4 The factors contributing to the observed E_a values for the reaction of phenacyl bromide with pyridine. (*a*) '*cis*-' and '*gauche*-' precede conformer. The Gibbs' free energy changes for the conformational change are not available. However, assuming the conformers have similar extinction coefficients for the bands used to obtain the ΔH values, gives a value of 3 kJ mol^{-1} and consideration of leaving groups, 2 kJ mol^{-1} for $\delta\Delta G^*$. These smaller values correspond to only a two- to three-fold advantage for the *cis*-conformer. The 65-fold reduction in reactivity on changing from *p*- to *o*-picoline, $\delta\Delta G^* = 10.9$ kJ mol^{-1}, is only in part due to loss of conjugation between the phenacyl keto-group and the reaction centre.

to general acid catalysis at a developing negative charge and to general base catalysis when a primary or secondary amine is the nucleophile.

Cram stressed[82] the importance of σ^R rather than σ for the ability of groups to stabilise carbanions which like radical anions[5,83] and the transition state for phenacyl reactions with good nucleophiles,[1,60] carry an excess negative charge. There is a perfect rank correlation between the ability of groups to facilitate the reactions of methyl halides[84] and to stabilise carbanions.[82] Two theoretical valence bond[61] and molecular orbital[62] calculations have emphasised the similarity with carbanions and have confirmed the transition state proposed in Part 1.[1] Because of cross-conjugation at the phenacyl keto-group,[85] as a more electron rich π-bond appears in the transition state, so conjugation is switched preferentially from the substituted benzene ring to the new π-system and stabilises the excess charge in the transition state. Moreover, since less conjugation takes place in the initial state with electron-withdrawing substituents, we concluded that these substituents promoted the reaction by allowing the greatest potential change in polarisation of the keto-group in the transition state. We further concluded that the σ-values in the ground state might well be replaced by σ^1 or σ^0 values in the transition state. This appears to be confirmed by the inversion of the normal σ sequence for *meta*- and *para*-nitro found by Baker for the reaction of phenacyl bromides with either pyridine or aniline.[71,86]

Previously we also concluded[1] that low steric requirements were a requisite for substantial bond forming in the transition state. From Sisti and Memeger[87] and our results, E_a and log A for the reaction of phenacyl chloride with pyridine in methanol may be obtained as 104 kJ mol^{-1} and 14.3, respectively. As bond breaking becomes more important in the chloride relative to the bromide in the transition state, then log A increases as Ingold's 'basket'[88] widens, but corresponding to the work of bond-stretching, E_a increases

Berg and his co-workers[89] found that the selectivity of *ortho*-substituted pyridines towards methylating agents decreased the better the leaving group. This is the expected result when bond breaking requires little assistance with consequently less bond forming in the transition state.

In this paper evidence that the better the leaving group the less bond forming is required for a given nucleophile in a given solvent implies that for poorer activating groups insufficient bond making is possible before steric hindrance is encountered in the transition state. A number of recent studies confirm the earlier conclusion[1] that activating groups bulkier than a ketone require a polarisable nucleophile,[90] a good leaving group[90] or an ionising solvent.[91]

Summarising our results in Fig. 4, a favourable combination of low steric hindrance, the ability to stabilise a partial negative charge in the transition state, and conformational isomerism all contribute to the enhanced reactivity of phenacyl halides. Without a suitable solvent and a sufficiently polarisable nucleophile, no advantage is obtained for reactions in which bond breaking leads over bond forming.

In conclusion, it is possible to calculate ΔV^* values from two values provided there are no other structural changes such as hydrogen bonding in alcohols. We believe that the calculated electrostrictions are most useful and in certain cases more informative than values of ΔV alone. Where the reaction product is sparingly soluble, calculated values of electrostriction are possible.

We believe we may have shed some light on what Arnett and Reich termed[2] 'a complex interplay of poorly understood influences' by the use of a variety of well-established methods seldom used in conjunction.

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