Evidence against Appreciable Internal Ion Pair Return in the Solvolyses of Tertiary Aliphatic Halides. Measurement of α-Methyl/Hydrogen Rate Ratios in Hexafluoropropan-2-ol–Water

By **T. William Bentley** * and **Christine T. Bowen**, Department of Chemistry, University College of Swansea, Singleton Park, Swansea SA2 8PP
(the late) **William Parker**, Department of Chemistry, University of Stirling, Stirling FK9 4LA
C. Ian F. Watt,* Department of Chemistry, University of Manchester, Manchester M13 9PL

A good linear correlation between the logarithms of rate constants for solvolyses of 1-adamantyl (I) and 2-methyl-2-adamantyl (III) chlorides is interpreted as evidence that these solvolyses proceed by the same mechanism, rate-determining formation of contact ion pairs. This interpretation conflicts with two previous interpretations based on β-deuterium kinetic isotope effects for solvolyses of tertiary substrates, (i) suggesting the occurrence of rate-determining elimination from contact ion pairs; (ii) claiming a linear correlation between log (CH_3/H) and log (CH_3/CD_3) rate ratios, where log (CH_3/H) is the logarithm of rate ratios for solvolyses of tertiary substrates ($R^1R^2CH_3CX$) and the corresponding secondary substrate (R^1R^2HCX). Kinetic techniques for relatively fast solvolyses are used to study reactions in 97% w/w hexafluoropropan-2-ol–water, where nucleophilic solvent assistance is small, and so carbocation stabilities can be evaluated kinetically. Reaction of 2-chloro-2-methyladamantane is $10^{7.4}$ times more rapid than that of 2-chloroadamantane, in agreement with studies using more nucleophilic solvents. The corresponding rate ratio for 2-bromo-2-methylpropane and 2-bromopropane is only $10^{6.2}$, a higher ratio than is obtained in more nucleophilic solvents. It is proposed that nucleophilic solvent assistance is significant even for solvolysis of propan-2-yl† substrates in hexafluoropropan-2-ol. Kinetic data measured directly at 25° for 2-*exo*- and 2-*endo*-norbornyl methanesulphonates give an *exo/endo* rate ratio of 1.59×10^3, in agreement with results obtained by temperature extrapolations. Some of the factors influencing (or helping to prevent) internal ion pair return are discussed.

One of the most intriguing problems in solution kinetics is assessing the extent to which a short-lived pair of ions in a solvent cage can return to starting material rather than proceed to product, *i.e.* k_{-1} compared with k_2 in equation (1). Such competing processes complicate

$$\text{Y–Z} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (\text{Y}^+\text{Z}^-)_{\text{solvated}} \xrightarrow{k_2} \text{product} \qquad (1)$$

studies both of reaction mechanisms and interpretation of structure–reactivity relationships. For aliphatic nucleophilic substitutions during which a 1,2-shift occurs to a more stable carbocation, it has been assumed that ion-pair return cannot occur, *e.g.* solvolyses of neophyl (2,2-dimethyl-2-phenylethyl) [1,2] and pinacolyl (3,3-dimethyl-2-butyl) [3] substrates. Unfortunately use of these substrates as reference compounds is complicated by two factors, (i) the 1,2-shift may be concerted with ionization or may occur after formation of the first ion pair; [3,4,5,6a] (ii) there may be competing nucleophilic solvent-assisted ionization.[7,8] Clearer evidence for ion pair return can be obtained when an optically active substrate racemizes more rapidly than it solvolyses; the extent of internal ion pair return can be estimated by comparing the rate constant determined polarimetrically with that determined titrimetrically.[9a] Similar conclusions can be drawn from ^{18}O-scrambling experiments in sulphonates [9b] or carboxylates,[9c] but in nearly all cases the rate effects are quite small.[6b] Unfortunately, it has not been demonstrated that the same ion pair is common to solvolysis and racemization (or scrambling) pathways.[10]

It has also been proposed that configurationally stable ion pairs undergo internal ion pair return, *i.e.* without racemization or ^{18}O-scrambling.[3] This proposal is intuitively reasonable, particularly when a nucleophilic leaving group (*e.g.* Cl^-) is displaced by a less nucleophilic species such as a protic solvent,‡ but is difficult to substantiate experimentally because only relatively indirect evidence is available (*e.g.* kinetic isotope effects [3,11,12]). There have been extensive criticisms of the evidence for appreciable internal ion pair return during solvolyses of secondary aliphatic substrates.[6a,8,13,14] We now present experimental results which lead us to doubt the existence of appreciable internal ion pair return even during solvolyses of tertiary aliphatic systems. Our research in this general area [15] has required kinetic studies of relatively fast solvolytic reactions, and we include in this paper detailed discussion of our experimental techniques. We also summarize our experience with hexafluoropropan-2-ol as a solvolysis medium.

RESULTS

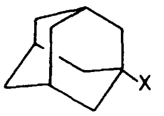
Included in this paper are rate constants for solvolyses of 1-adamantyl (I), 2-adamantyl (II), 2-methyl-2-adamantyl (III), 2-*exo*-norbornyl (IV), 2-*endo*-norbornyl (V), 1-propan-2-yl, and t-butyl substrates. Kinetic data for 2-chloro-2-methyl-2-adamantane (III; X = Cl) in various solvents are given in Table 1. Kinetic data for 97% w/w hexafluoropropan-2-ol–water are summarized in Table 2. Batches of solvent were checked by determining rate constants for solvolysis of t-butyl chloride. Our values for many independent measurements are slightly lower than

---

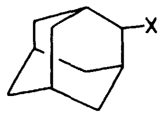
† Although application of the IUPAC rules leads to the numbering of the radical position in an alkyl radical as 1, for reasons of clarity this rule has not been strictly followed.

‡ For a reactivity–selectivity argument in favour of internal return, see D. N. Kevill and G. M. L. Lin, *J. Amer. Chem. Soc.*, 1979, **101**, 3916 (footnote 38).

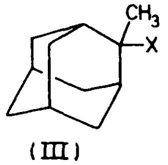
the published value, determined by continuous potentiometric titration;[16] it may be that the latter determination includes small rate increases due to salt effects, and that there are slight differences between the solvent compositions. The effect of added water is significant, *e.g.* in 90% hexafluoropropan-2-ol–water t-butyl chloride solvolyses three times less rapidly than in 97%.[16] For solvolyses of sulphonates but not for halides, agreement between observed and calculated conductance readings for >99% reaction was not always satisfactory. There appears to be an upward drift in conductance readings, possibly due to oxidation or to acid catalysed decomposition of the solvent. As a routine precaution to try to minimize such side reaction(s), oxygen was excluded from the solvent. Additional kinetic data relevant to the discussion of our results are given in Table 3.



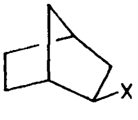
(I)



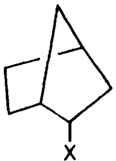
(II)



(III)



(IV)



(V)

TABLE 1

Solvolytic rate constants (k) for 2-chloro-2-methyl-2-adamantane (III; X = Cl) [a]

Solvent	T/°C	k/s^{-1}
97% Hexafluoropropan-2-ol [b]	-17.5 [d,e]	$(5.70 \pm 0.06) \times 10^{-2}$
	-14.3 [d,e]	$(7.57 \pm 0.22) \times 10^{-2}$
	-10.6 [d–f]	$(1.05 \pm 0.05) \times 10^{-1}$
	-8.8 [d–f]	$(1.26 \pm 0.06) \times 10^{-1}$
	25.0 [c,g,h]	1.72 ± 0.07
97% Trifluoroethanol [b]	25.2 [e]	$(2.31 \pm 0.01) \times 10^{-2}$
40% v/v Ethanol–water	25.0 [e,f,i]	$(1.18 \pm 0.08) \times 10^{-2}$
50% v/v Ethanol–water	25.0 [j]	3.398×10^{-3}
70% v/v Ethanol–water	25.0 [j]	2.451×10^{-4}
80% v/v Ethanol–water	25.0 [j]	6.430×10^{-5}

[a] Determined conductometrically in duplicate except where otherwise noted; errors shown are average deviations. [b] % w/w with water as co-solvent. [c] Calculated from data at other temperatures. [d] Method A, see experimental section. [e] Error limit is standard error of triplicate runs. [f] The relatively high error limits are probably due, at least in part, to difficulties caused by the low solubility of the substrate. [g] Error limit is estimate of error in k combined with extrapolation error. [h] $\Delta H^{\ddagger}$ 11.6 ± 0.3 kcal mol^{-1}, $\Delta S^{\ddagger}$ -18.7 ± 0.9 cal mol^{-1} K^{-1}. [i] To increase the rate of dissolution, a solution of the chloride in tetrahydrofuran (2 μl) was injected into the solvent (10 ml). [j] Ref. 12.

DISCUSSION

For solvolyses of t-butyl halides in 97% w/w trifluoroethanol–water and 2-methyl-2-adamantyl halides (III) in 80% v/v ethanol–water, it has been reported that the yield of alkene products and the β-deuterium kinetic isotope effects are higher than for comparable solvolyses (Table 4). This could imply that the rate-determining and product-determining steps are the same and, after arguing against an $E2$ mechanism, it was proposed that these solvolyses proceeded by rate-determining elimination from contact ion pairs.[11,12] This proposal implies that there is appreciable internal ion pair return, and suggests that solvolyses of t-butyl halides in trifluoroethanol should be slower than would be predicted on the basis of rate-determining formation of contact ion pairs. A linear free energy relationship (l.f.e.r.) between logar-

TABLE 2

Solvolytic rate constants (k) for solvolyses in 97% hexafluoropropan-2-ol [a,b]

Substrate	T/°C	k/s^{-1}
$(CH_3)_3CCl$	25.0 [g]	$(2.45 \pm 0.03) \times 10^{-3}$
	25.0 [h]	$(2.60 \pm 0.07) \times 10^{-3}$
	25.0 [i]	$(2.69 \pm 0.05) \times 10^{-3}$
$(CH_3)_3CBr$	16.7 [e]	$(9.66 \pm 0.08) \times 10^{-3}$
	25.0 [e,j]	$(2.20 \pm 0.03) \times 10^{-2}$
	31.4 [e]	$(3.95 \pm 0.05) \times 10^{-2}$
$(CH_3)_2CHBr$	25.0 [c,k]	$(1.4 \pm 0.5) \times 10^{-8}$
(I; X = Cl)	25.0	$(9.7 \pm 0.5) \times 10^{-4}$
(I; X = Br)	25.0	$(9.1 \pm 0.2) \times 10^{-3}$
(II; X = Cl)	25.0 [c,l]	$6.9\ (4.8 < k < 10) \times 10^{-8}$
(II; X = Br)	84.5	$(1.61 \pm 0.03) \times 10^{-4}$
	69.5	$(4.94 \pm 0.13) \times 10^{-5}$
	25.0 [c,m]	$3.7\ (2.3 < k < 5.9) \times 10^{-7}$
(II; X = OSO_2CH_3)	25.0	$(1.13 \pm 0.03) \times 10^{-4}$
(II; X = OTs)	25.0	$(8.84 \pm 0.10) \times 10^{-5}$
	25.0 [n]	9.75×10^{-5}
(IV; X = OSO_2CH_3)	25.0	$(1.37 \pm 0.03) \times 10^{-1}$
(V; X = OSO_2CH_3)	25.0	$(8.59 \pm 0.08) \times 10^{-5}$

[a–f] As Table 1. [g] Average of five independent solvent preparations; solvent distilled from calcium hydride. [h] Average of four independent solvent preparations; solvent distilled from 3A molecular sieves. [i] Ref. 16. [j] $\Delta H^{\ddagger}$ 16.2 ± 0·1 kcal mol^{-1}, $\Delta S^{\ddagger}$ -11.7 ± 0.4 cal mol^{-1} K^{-1}. [k] 10^6k (T): 44.9 (100.5°); 6.95 (80.5°); 0.57 (55.6°); $\Delta H^{\ddagger}$ 23.1 ± 0.3 kcal mol^{-1}, $\Delta S^{\ddagger}$ -17.0 ± 0.7 cal mol^{-1} K^{-1}. [l] 10^6k (T): 14.2 (71.5°); 6.41 (63.2°); 2.42 (54.7°); 0.696 (43.4°); $\Delta H^{\ddagger}$ 22.8 ± 0.3 kcal mol^{-1}, $\Delta S^{\ddagger}$ -14.7 ± 0.9 cal mol^{-1} K^{-1}. [m] Additional data 10^6k (T): 5.90 (49.5°); 3.66 (44.6°); 2.03 (39.6°); $\Delta H^{\ddagger}$ 21.3 ± 0.4 kcal mol^{-1}, $\Delta S^{\ddagger}$ -16.6 ± 1.1 cal mol^{-1} K^{-1}. [n] Ref. 13*b*.

TABLE 3

Solvolytic rate constants (k) for solvolyses of 1-adamantyl halides (I) [a]

Substrate	Solvent [b]	T/°C	k/s^{-1}
(I; X = Br)	90%E	25.0 [c,d]	$(4.7 \pm 1.1) \times 10^{-8}$
	90%E	25.0 [c,e]	2.47×10^{-8}
(I; X = Cl)	40%E	25.0 [c,f]	4.7×10^{-6}
	50%E	25.0 [c,g]	1.0×10^{-6}
	70%E	25.0 [h]	4.28×10^{-8}
	80%E	25.0 [h]	1.32×10^{-8}
	80%E	25.0 [i]	7.59×10^{-9}
	97%T	25.0 [f]	5.4×10^{-6}

[a] As Table 1. [b] %E = % v/v ethanol–water; %T = % w/w trifluoroethanol–water. [c] Calculated from data at other temperatures. [d] Solvent batch 1, using titration with 0.01M-NaOH and phenolphthalein as indicator, $10^{-6}k$ (T): 22.6 (72.25°); 1.26 (49.67°); solvent batch 2, 10^6k (T): 23.6 (75.17), determined conductometrically; 1.28 (49.9), determined titrimetrically: $\Delta H^{\ddagger}$ 24.9 ± 0.2 kcal mol^{-1}, $\Delta S^{\ddagger}$ -8.5 ± 0.6 cal mol^{-1} K^{-1}. [e] Data from ref. 17 cited in ref. 18. [f] T. W. Bentley and P. v. R. Schleyer, unpublished result. [g] Ref. 19. [h] Estimated from published rate data for 1-adamantyl bromide[18] and the Br/Cl rate ratios obtained from t-butyl substrates in the appropriate solvent.[20] This method of estimation can be checked for 1-adamantyl chloride in 40 and 50%E, and it appears to be accurate to within *ca.* 10%. Br/Cl rate ratios appear to be slightly lower for 1-adamantyl than for t-butyl. [i] Ref. 21, based on an extrapolation from 75° and considered to be less reliable than the estimate based on Br/Cl ratios (footnote *h*\).

ithms of solvolytic rate constants for t-butyl and 1-adamantyl halides (a bridgehead system from which rate-determining elimination cannot occur because elimination is prohibitively energetic) in a wide range of solvents appeared to substantiate this mechanism because the rate constant for 97% trifluoroethanol did not fit the correlation.[18] We have recently suggested as an alternative explanation of this l.f.e.r. that the rates of solvolyses of t-butyl halides are influenced by effects of solvent nucleophilicity.[22]

TABLE 4

Evidence for rate-determining elimination

Substrate		β-Deuterium effect	Mole fraction alkene
$(CH_3)_3CCl$	97% w/w $CF_3CH_2OH-H_2O$	1.378 [a]	0.30
	cf. 70% w/w $CF_3CH_2OH-H_2O$	1.356 [a]	0.17
(III; X = Cl)	80% v/v $EtOH-H_2O$	1.68 [b]	0.33
	cf. 50% v/v $EtOH-H_2O$	1.48 [b]	0.07

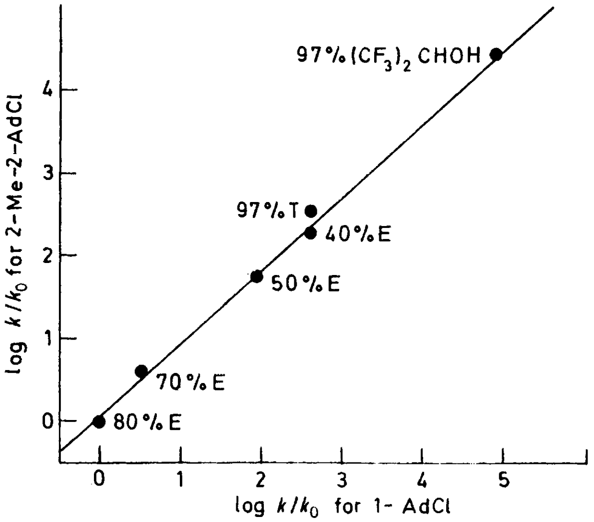
[a] $(k_H/k_{D9})^{⅓}$.[11] [b] k_H/k_{D3}.[12]

The 2-methyl-2-adamantyl system (III) should be even less susceptible to nucleophilic attack at the α-carbon atom than the secondary 2-adamantyl system, which for steric reasons shows negligible susceptibility to nucleophilic attack.[15b,23] Consequently if solvent nucleophilicity effects on carbon are influencing the l.f.e.r. between t-butyl and 1-adamantyl halides, these should be absent in solvolyses of (III) and a linear correlation should be expected between solvolytic rate constants for (III) and (I). This reasoning is complicated by the possibility of nucleophilic attack on β-hydrogen (*i.e.* *E*2 like reaction), which we also regard as nucleophilic solvent assistance.[7] If however rate-determining elimination is significant for solvolyses of t-butyl halides in weakly nucleophilic media, it is expected to occur to a greater extent in (III), because the cation from (III) is expected to be more stable than the t-butyl cation, and should be more effective in preferentially selecting the leaving group and collapsing to covalent starting material rather than solvolysing.* It has been proposed that (III; X = Cl) undergoes rate-determining elimination even in 80% ethanol–water [12] (see also Table 4), and this effect should be more marked in weakly nucleophilic media (*e.g.* trifluoroethanol and hexafluoropropan-2-ol),[8] but the kinetic isotope data are not yet available.

The experimental results (Figure) show a good l.f.e.r. including trifluoroethanol, hexafluoropropan-2-ol, and 80% ethanol–water in marked contrast to our expectations based on the mechanism involving rate-determining elimination. The results suggest that there is no change in the rate-determining step and can be explained if *formation* of the contact ion pair is rate determining for solvolyses of (I; X = Cl) and (III; X = Cl) as well as t-butyl halides.[7,22]

The solvent dependence of β-deuterium kinetic isotope effects (k.i.e.) may not be directly related to the formation of alkene, but they could be indirectly related. Solvolyses of t-butyl halides in the less nucleophilic solvent (more trifluoroethanol) has a higher β-deuterium k.i.e. (Table 4), suggesting that the ion pair intermediate has a higher carbocation character; such an intermediate may be more prone to elimination than to substitution. From these correlations we cannot rule out small amounts of internal return and rate-determining elimination [$k_2 \sim k_{-1}$ in equation (1)], but most of the experimental data can be explained by rate-determining formation of contact ion pairs. Neither mechanism provides a complete explanation why solvolysis of (III; X = Cl) has a higher β-deuterium k.i.e. in 80% ethanol–water than in 50% ethanol–water and/or why the former gives more alkene (*e.g.* why rate-determining elimination should be more important in 80% than in 50% ethanol–water).

Other factors influencing the effect of solvent on kinetic isotope effects can be considered, based on our proposals that both (III) and t-butyl substrates react by rate-determining formation of contact ion pairs and that t-butyl substrates are susceptible to effects of solvent nucleophilicity. In the case of (III; X = Cl), where solvent nucleophilicity is not important, changes in solvent ionizing power should move the transition state along the co-ordinate for ionization, and the observed decrease of k.i.e. with increasing ionizing power is in accord with the Bell–Evans–Polanyi principle.[25] For t-butyl substrates the transition state will vary with both ionizing power and nucleophilicity of solvent.[22] From



Rates of solvolysis of 2-chloro-2-methyladamantane (III; X = Cl) *versus* 1-adamantyl chloride (I; X = Cl). Solvent code: %E, % v/v ethanol/water; %T, % w/w trifluoroethanol–water; k_0 refers to 80% E. Slope 0.90 ± 0.02, correlation coefficient 0.998

---

* *E.g.* (III; X = Cl) solvolyses more rapidly than t-butyl chloride and carbocation stabilities do parallel solvolytic reactivities.[24] Alternatively this argument may be presented as a strictly limited application of reactivity–selectivity concepts. Several reactivity–selectivity correlations have been observed based on solvolytic rate constants and nucleophilic attack by ethanol and water or by azide ion and water. Studies of common rate depressions are also relevant as the reactivity–stability factors influencing such external ion pair return would be expected to parallel those influencing internal ion pair return (see A. Pross, *Adv. Phys. Org. Chem.*, 1977, **14**, 96).

the low kinetic isotope effects observed in solvolyses of ethyl and propan-2-yl halides and arenesulphonates,[11,26] increased nucleophilic assistance is expected to reduce the observed k.i.e. The total change in k.i.e. for a solvent change from weakly nucleophilic and strongly ionizing to more nucleophilic and less strongly ionizing should be a balance of two opposing trends, resulting in much smaller changes than in (III; X = Cl), with the direction of change depending on the balance between the effects (see Table VI of ref. 11). These arguments suggest that the equilibrium CH_3/CD_3 isotope effects for ionization (irrespective of their origin [27]) should be larger than the value of 1.45 previously suggested on the basis of a relationship between CH_3/H effects and CH_3/CD_3 isotope effects.[12,28] (We show later that this relationship has a tenuous basis in experiment.) The above interpretation could be expressed as More O'Ferrall–Jencks diagrams,[29] but we will defer more detailed discussion until additional experimental data have been obtained.

The slope of the correlation (Figure) is less than unity, suggesting that there is greater charge dispersion in the transition state from solvolyses of (III; X = Cl) than of (I; X = Cl), and this may be due to electron release from the methyl group in (III). A similar correlation for (III; X = Cl) and t-butyl chloride in ethanol–water mixtures has a slope of 1.03.

Two general points can be made about correlations such as that in the Figure. First, we suggest that it is important to compare solvolyses having the same leaving group, so that solvation effects of the leaving group do not interfere with mechanistic interpretations, *e.g.* a comparison of 1-adamantyl bromide with t-butyl chloride (*i.e. Y* values) was altered significantly when t-butyl bromide was used instead of the chloride (compare Figure 1 of ref. 18 with Figure 1 of ref. 22). Secondly, it is important to minimize errors due to extrapolations of rate constants from one temperature to another. Small experimental errors in rate constants determined at one temperature can be greatly increased by extrapolation to different temperatures. Two examples are given in Table 3. We redetermined rate constants for solvolysis of 1-adamantyl bromide (I; X = Br) in 90% ethanol–water at 75°, and then studied the reaction at *ca.* 50°. Extrapolation of the previously published data over 55° (from 80 to 25°), which the original authors [17] did not attempt, gave a rate constant almost double that based on our extrapolation over 25°; both sets of results agreed satisfactorily at 75°. A similar error appears to be present in the rate constant for solvolysis of 1-adamantyl chloride in 80% ethanol–water at 25° (see Table 3).

We can also compare the results obtained in 97% hexafluoropropan-2-ol (Table 2) with other solvolyses, with gas-phase data, and with data obtained in strongly acidic media. Recently it has been shown that the differences in energies between secondary and tertiary carbocations in the gas phase are very similar to the differences measured in strongly acidic media, *e.g.* for propan-2-yl and t-butyl cations differences of 1.4 ± 0.5 * and 14—16 kcal mol^{-1} have been obtained for SbF_5–SO_2ClF solution [31] and for the gas-phase,[32] respectively. If the transition states for solvolyses of secondary and the corresponding tertiary substrate reflected all this energy difference, it would be expected that the tertiary substrate would react *ca.* 10^{10} times faster than the secondary substrate. A similar rate enhancing effect of substitution of an α-hydrogen for an α-methyl group is referred to as an α-methyl/hydrogen rate ratio (*i.e.* comparisons are made between substrates having different numbers of carbon atoms). *In principle* this mechanistic criterion could provide information about the mechanistic aspects and solvation effects in the more nucleophilic media used for solvolytic reactions. Large α-methyl/hydrogen rate ratios (*ca.* 10^8) have been observed for 7-norbornyl toluene-*p*-sulphonate (tosylate),[33] and for 2-adamantyl bromide (II; X = Br) [34] and 2-adamantyl nitrophenyl ethers.[5] To obtain an estimate of this large rate change at one temperature (25°) required extrapolations of rate constants obtained for the less reactive substrate at much higher temperatures (100—150°). More accurate estimates could be obtained titrimetrically by studying the less reactive substrate at lower temperatures, but half-lives of reaction would then be of the order of weeks. Alternative approaches use different leaving groups [5] or fast reaction techniques to extend the experimentally accessible range. To reduce the possibility that the secondary bromide reacted by nucleophilically solvent assisted process, we studied solvolyses in 97% w/w hexafluoropropan-2-ol–water.[13b] Preliminary studies showed that the tertiary bromide (III; X = Br) was too reactive to study accurately and so we compared the corresponding chlorides (II; X = Cl) and (III; X = Cl). To obtain comparisons of rate constants at one temperature (25°) required temperature extrapolations for both compounds but each was over a range of $<35°$. The resulting α-methyl/hydrogen rate ratio ($k_{\text{III}}/k_{\text{II}}$) of $10^{7.4}$ is in satisfactory agreement with values of $10^{8.1}$ for acetolysis (from 125° extrapolation) and of $10^{7.5}$ for 80% ethanolysis (from 75° extrapolation) of the corresponding bromides.[34] The similarity of these values supports our proposal that these solvolyses all proceed by the same rate-determining step, *formation* of the contact ion pair.

A consistent pattern of reactivity has emerged from these and earlier studies. We have previously argued that solvolyses of 2-adamantyl tosylate (II; X = OTs) does not involve appreciable internal return, and that correlations such as that in the Figure are capable of detecting internal return (ref. 7, particularly, the Appendix). We have also correlated solvolyses of 2-adamantyl tosylate and the bridgehead bicyclo[2.2.2]-octyl tosylate (see Figure 15 of ref. 15*b*), which suggests that solvolyses of this bridgehead substrate do not involve appreciable internal return. Consequently, these solvolyses probably involve rate determining

---

* This value is higher than previously reported values of *ca.* 9 kcal mol^{-1}.[30]

formation of contact ion pair. Our proposal that solvolyses of t-butyl chloride and of (I; X = Cl), (II; X = Cl), and (III; X = Cl) all occur by rate-determining formation of contact ion pair is consistent with this earlier work and with the trends expected from studies of carbocations in the gas phase.[22] It should be realised that the arguments for appreciable internal ion pair return are not well based on experimental evidence. Furthermore, if internal ion pair return were appreciable correlations such as that in the Figure would be expected to be non-linear because $k_2/(k_{-1} + k_2)$ in equation (1) would be expected to be dependent on both solvent and substrate. Whilst small amounts [*e.g.* $k_2/k_{-1} + k_2)$ *ca.* 0.5 in equation (1)] of internal ion pair return cannot be ruled out, it appears that the wide range of solvolytic reactivity of tertiary aliphatic substrates is determined exclusively or almost exclusively by k_1, the rate of formation of contact ion pair.

There has been some discussion of the possibility that the methyl/hydrogen rate ratio for 2-adamantyl systems is affected by steric factors,[5,34b] and so we have attempted to obtain an α-methyl/hydrogen rate ratio for simple aliphatic systems, *e.g.* 2-substituted propanes ($\mathrm{Pr^iX}$) and 2-methyl-2-substituted propanes ($\mathrm{Bu^tX}$). This presents various difficulties, *e.g.* for tosylates (OTs) the secondary substrate ($\mathrm{Pr^iOTs}$) has been examined in detail,[7,35,36] but the tertiary tosylate ($\mathrm{Bu^tOTs}$) would be too reactive;[37] bromides can be studied directly but there are uncertainties in the interpretation of the results (see below). The ratio of rates for $\mathrm{Bu^tBr}$ and $\mathrm{Pr^iBr}$ is $10^{6.2}$, significantly lower than for adamantyl systems but higher than any other published values for this ratio; *e.g.* for bromides acetolysis at 100° gives $10^{4.2}$ and formolysis at 25° gives *ca.* $10^{5.3}$;[36a] hydrolysis of chlorides at 25° gives a ratio of $10^{5.15}$.[38,*] These results suggest that more nucleophilic solvents or solvents of lower ionizing power lead to lower α-methyl/hydrogen rate ratios. As a partial check whether reaction of $\mathrm{Pr^iBr}$ in $97\%(CF_3)_2CHOH/H_2O$ is nucleophilically assisted by solvent, we applied equation (2), which is analogous to the equation used to calculate k_s/k_c ratios for tosylates in various solvents,[13b,35] and leads to a k_s/k_c value of only 2.1 for solvolysis of $\mathrm{Pr^iBr}$

$$\text{nucleophilic solvent assistance} = k_s/k_c = [k_{\mathrm{Pr^iBr}}/k_{\mathrm{2\text{-}AdBr}}]/[k_{\mathrm{Pr^iOTs}}/k_{\mathrm{2\text{-}AdOTs}}] \quad 97\%(CF_3)_2CHOH\text{–}H_2O \qquad (2)$$

in $97\%(CF_3)_2CHOH\text{–}H_2O$. If taken literally this would increase the calculated α-methyl/hydrogen rate ratio to $10^{6.5}$ but, as the value of 2.1 is probably within combined experimental and theoretical uncertainties, it will be ignored until further experimental checks can be performed, *e.g.* it is necessary to re-examine the provisional assumption that solvolyses of all secondary sulphonates in trifluoroacetic acid or hexafluoropropan-2-ol are free from nucleophilic solvent assistance.[22] Our results do not provide definitive evidence on whether α-methyl/hydrogen rate ratios of 10^8 in 2-adamantyl systems are partially steric in origin, and our lower values for $\mathrm{Bu^tX/Pr^iX}$ ratios suggest a need to investigate rates of solvolytic reactions in even less nucleophilic media [one possibility is $(CF_3)_3COH$]. Not surprisingly our results imply less development of charge in solvolytic transition states than in stable cations.[24,40]

The above discussion indicates several possible limitations of α-methyl/hydrogen rate ratios as a mechanistic criterion; the tertiary and secondary substrates may not solvolyse by the same mechanism—the tertiary substrate *could* (in principle) react by rate-limiting attack on contact ion pairs, the secondary and tertiary substrates could react by nucleophilically solvent assisted processes, and steric effects could be significant[5] (*e.g.* in 2-norbornyl systems, α-methyl/hydrogen rate ratios are 10^5).[41] Also in the above discussion we have called into question the current interpretation of β-deuterium kinetic isotope effects. These results have led us to examine critically a proposal that there is a linear relationship between α-methyl/hydrogen rate ratios (CH_3/H) and corresponding CH_3/CD_3 ratios.[42] This relationship has been used as a basis for further quantitative work,[12,28] but as discussed below it appears to have a rather tenuous basis in experiment.

In the original ' correlation ' seven experimental results [for chlorides: cyclopropylmethyl, *exo*-2-norbornyl (IV), cyclohexyl and cyclopentyl, cyclobutyl, α-phenylethyl, and α-*p*-methoxyphenylethyl] were included with an estimated α-CH_3/H rate ratio of 10^6 for 2-chloropropane.[42] This estimate of 10^6 has now been closely approximated experimentally (Table 2), but the published ' correlation '[42] includes data for the secondary substrates in solvents likely to provide nucleophilic solvent assistance. The ' correlation ' would be affected very adversely if a consistent set of kinetic data were used for the secondary halides, *e.g.* if 2-chloropropane in 80% ethanol–water were plotted, a much lower α-CH_3/H rate ratio (*ca.* 10^4) would be expected. Then four of the eight substrates would show a ' correlation ' having a variety of CH_3/CD_3 rate ratios and approximately constant α-CH_3/H rate ratio of 10^4. Conversely, if the secondary and tertiary halides were examined in hexafluoropropanol, mechanistic complications from the effects of solvent nucleophilicity would be reduced but the ' correlation ' would be based on at least four substrates having approximately constant α-CH_3/H rate ratios of 10^6. As the CH_3/CD_3 rate ratios are also somewhat dependent on solvent and 7-norbornyl[12,28] and other substrates[43] are known to deviate substantially from the ' correlation ' it does not appear to be sound to use this ' correlation ' as the basis for further quantitative work.

exo/endo-2-*Norbornyl Rate Ratios*.—The *exo-endo* rate ratio ($k_{\mathrm{IV}}/k_{\mathrm{V}}$) has been studied in various solvents to evaluate the degree of nucleophilic solvent assistance.[44,45] For this purpose solvolyses in weakly nucleophilic media are of particular interest. For tosylates in trifluoroacetic acid an *exo-endo* rate ratio of 1.12×10^3 has been reported,[46,47] and for *p*-bromobenzenesulphonates in 97%

---

[*] Similarity between nucleophilic solvent assistance in formolysis and hydrolysis has been noted recently.[39]

$(CF_3)_2CHOH-H_2O$ a ratio of 1.75×10^3 has been found;[48] the latter result included extrapolations from lower temperatures but we expected that methanesulphonates (ROMs) could be studied directly at 25° because they dissolve rapidly even in water.[39] Our *exo-endo* rate ratio from Table 2 is 1.59×10^3 and using the OTs/OMs rate ratio of 0.78 from 2-adamantyl sulphonates we obtain a rate constant for *exo*-2-norbornyl tosylate $(1.37 \times 10^{-1}) \times 0.78 = 1.07 \times 10^{-1}$ s^{-1} in good agreement with the rate constant of 1.10×10^{-1} s^{-1} obtained independently by extrapolation from lower temperatures.[49] It now appears that our previously reported *exo-endo* rate ratio of 2.55×10^3 in water is the highest reliable value obtained for 25°.[39] The lower ratios in less nucleophilic solvents may be due to small amounts of internal ion pair return.

In *exo*-norbornyl systems (IV) it is known that racemization of sulphonates may occur up to five times faster than solvolysis.[50] As discussed above, internal return is expected to be greater in weakly nucleophilic media; polarimetric data for solvolyses of *exo*-norbornyl sulphonates in trifluoroacetic acid or hexafluoropropan-2-ol are required. These would be difficult to obtain but methanesulphonates should dissolve sufficiently rapidly. Despite that lack of direct experimental data one can infer from the reduction in *exo-endo* rate ratio (k_{IV}/k_V) from 2.55×10^3 in water to 1.59×10^3 in $97\%(CF_3)_2$-$CHOH-H_2O$ to 1.12×10^3 in CF_3CO_2H that internal ion pair return in the *exo*-isomer is becoming more significant. Increased nucleophilicity of the leaving group appears to favour internal return because racemization of bromides occurs 24 times faster than acetolysis.[51]

It should be emphasised that effects of internal ion pair return are atypically large for *exo*-norbornyl systems, compared with other secondary aliphatic systems. This system does provide possible insights into the factors influencing internal ion pair return. Thus, as might be expected, the extent of internal ion pair return appears to depend on the environment of the contact ion pair [equation (1)]; more nucleophilic leaving groups and/or less nucleophilic solvents appear to favour k_{-1} over k_2, which could be explained readily if k_2 involved nucleophilic attack on the contact ion pair. For other mechanisms in which k_2 represented further dissociation to a solvent-separated ion pair, more complex dependence on various solvent parameters would be expected. This evidence indirectly supports the intuitive argument discussed above that substantial internal ion pair return ' ought to be ' present in many other solvolyses, but experimental evidence suggests that return is not extensive. It is important to reconcile these two lines of experimental evidence. We have previously suggested that nucleophilic solvation of ion pair intermediates may help to prevent internal ion pair return.[7] In systems where this rearside nucleophilic solvation cannot occur, *e.g.* 1-adamantyl (I), it may be that the nucleophilicity of the leaving group is greatly reduced by electrophilic solvation.[52] Differences in behaviour between ion pairs from solvolysis and ion pairs from additions to double bonds [13,53] may also be due, at least in part, to different solvation of the anions.

Leaving Group Effects.—There is now considerable evidence that leaving group effects in solvolytic reactions are not very sensitive to mechanistic changes.[54] The marked increase in tosylate/bromide rate ratios in solvolyses of tertiary compared with secondary systems appears to reflect steric effects,[55] as does the low tosylate/bromide rate ratios in solvolyses of certain vinyl substrates.[56] For 2-adamantyl substrates (I) the tosylate/bromide rate ratios of 240 for $97\%(CF_3)_2CHOH-H_2O$ is similar to the published value [23] of 231 for 80% ethanol–water. For t-butyl bromides and chlorides ratios (k_{Br}/k_{Cl}) at 25° vary from *ca.* 50 in pure ethanol to 30 in 50% ethanol–water.[20] Smaller ratios are observed for 97% CF_3CH_2OH (22),[11,57] for acetic acid (14),[20] and for formic acid (9.1).[20] Our bromide/chloride rate ratios in 97% $(CF_3)_2CHOH-H_2O$ are *ca.* 9 for both t-butyl and 1-adamantyl halides (I) and slightly lower (*ca.* 5.4) for 2-adamantyl halides (II). The latter value is probably the least reliable but overall these ratios show the self-consistency of our results, and their compatibility with earlier studies.

Kinetic Methods.—Relatively fast solvolytic reactions have been studied by u.v. spectroscopy,[46] and faster reactions in aqueous acetone mixtures have been examined in flow systems,[58] but the technique requires complex apparatus and is only applicable to solvolyses in which the substrate can be dissolved in a relatively inert co-solvent prior to mixing. We used a fast response conductivity amplifier connected to a suitable recording system to measure the change in conductance of the solution against time. The conductivity amplifier, designed at Stirling in 1973 for stopped-flow kinetic measurements,[59] was also used to study the high reactivity of 1-chlorobicyclo[3.3.3]undecane.[60] Additional amplifiers have now been in operation in Manchester and Swansea for several years.

The fastest reaction we have studied to date is the solvolysis of 2-chloro-2-methyladamantane (II; X =Cl). In a preliminary series of kinetic runs the following rate constants were observed: $k/s^{-1}(T/°C)$: 2.77×10^{-1} (−4.4°), 3.33×10^{-1} (−2.0°), 4.39×10^{-1} (0.5°), 6.14×10^{-1} (3.4°). Extrapolation to 25° gave a value of *ca.* 4.8 s^{-1} in fair agreement within combined experimental errors with the more reliable value of 1.7 s^{-1} obtained from more detailed results (Table 1). The compound does not dissolve rapidly enough to permit faster reactions to be examined with satisfactory accuracy, and the temperature extrapolation is probably a major source of error. However, these results suggest that, if solubility permits, rate constants for reactions with half-lives <1 s can be obtained with surprisingly good precision. The less reactive *endo*-isomer (V) was studied under the same conditions, showing that the conductivity amplifiers are also suitable for following slow reactions.

Various recording systems were tried, *e.g.* Servoscribe 1s, Honeywell 194, Tekman *X/t* recorders, and Tektronix 5103N storage oscilloscope. The screen of the latter was found to be rather too small to obtain accurate values of *k*. For $t_{\frac{1}{2}}$ *ca.* 5 s the fastest chart speed of the Servoscribe (1 cm s^{-1}) produced a sufficiently accurate time base and for the faster reactions a faster chart speed (*e.g.* Honeywell; 2 cm s^{-1}) was found to be better. Although we have not yet tried them ourselves we note that data systems capable of displaying the results on a television screen are available at prices competitive with chart recorders.[61] Alternatively, digital voltmeters with data storage might be used; we connected a digital voltmeter to the conductivity amplifier and found that the precision of the results was markedly better than that obtained with the chart recorder.

Conclusions.—These results illustrate the utility of the adamantyl framework (I)—(III) as a model system with which to compare other compounds. Our results in 97% hexafluoropropan-2-ol confirm the α-methyl/hydrogen rate ratio for 2-adamantyl of *ca.* 10^8 and the lower rate ratio for t-butyl/propan-2-yl of $10^{6.2}$ may be due to nucleophilic solvent assistance accelerating the propan-2-yl substrate. The linear correlation (Figure) suggests that both 1-adamantyl (I) and 2-methyl-2-adamantyl (III) systems solvolyse by the same mechanism, presumably rate-determining formation of contact ion pair. Further work is needed on solvolyses in even less nucleophilic media than hexafluoropropan-2-ol and on the interpretation of β-deuterium kinetic isotope effects.

Considering the difficulties on the interpretation of both α- and β-deuterium kinetic isotope effects and also the complex variation in products from solvolytic reactions, it appears that all these reflect subtle changes in the potential energy surfaces, which are difficult to fit into a consistent pattern. In contrast the solvent effects considered in our research[15b] reflect larger energy changes and do appear to fit into a consistent pattern, if effects of solvent nucleophilicity and leaving group are allowed for.

EXPERIMENTAL

Apparatus.—The conductivity amplifiers were built as described earlier;[59] the connection to the conductivity cell was made using shielded wire and the apparatus was adequately earthed. Various recording systems were tried (see Discussion section) but most of the data were obtained using Tekman *X*/*t* and Servoscribe 1s recorders.

Kinetic Techniques.—In addition to standard conductometric techniques described previously,[7] two additional methods (A and B) were developed for rapid solvolyses.

Method A. Solvolyses of solids were carried out in a stirred conductivity cell comprising a 12 mm i.d. Pyrex tube fitted with platinum electrodes (0.002 in foil) and two B10/14 Quickfit joints. The connections to the electrodes were arranged so that the cell could be suspended in a constant temperature bath of the appropriate temperature. A standard Quickfit MU 0/8 air driven stirrer was fitted through the top joint (white spot nitrogen was used to drive the stirrer), and an extended stopper with a flattened end through the side arm. For a typical run, solvent (7 ml) was placed in the cell, and the cell and stirrer were placed in the constant temperature bath to equilibrate, and the side-arm was fitted with a standard stopper. Using a 25 μl syringe, between 5 and 10 μl of standard solution (0.2 g ml^{-1}) of 2-chloro-2-methyladamantane (III; X = Cl) in light petroleum was spread over the flattened end of the extended stopper. The petroleum was evaporated in a stream of nitrogen to leave a fine powdery coating of the halide on the stopper. The stopper was then equilibrated to temperature in a test tube suspended in the constant temperature bath for 10 min. The stirrer motor was then started. (Some small fluctuations in conductivity occurred when the stirrer was started, but the blank runs showed that, after this initial variation, the base line was constant to within 1% over the reaction time.) The extended stopper carrying the substrate was then fitted in the side-arm and the reaction monitored in the usual way. Good first-order fits were obtained with readings taken from 3 s after the start [corresponding to 30% reaction of (III; X = Cl) at −8.8°]. The rate constants did not depend on stirring rate, provided that the stirrer speed was over *ca.* 150 r.p.m.

Method B. Solvolyses of readily soluble liquids were studied by rapidly injecting 1—2 μl of the liquid into the conductivity cell containing pre-equilibrated solvent (7 cm^3) using a 10 μl syringe having a long (25 cm) needle. The cell may be shaken manually very briefly (<1 s) but satisfactory results can be obtained by quickly 'pumping' the syringe a few times before withdrawing the needle.

The less reactive compounds provided some difficulties in experimental procedure. For reactions of the bromides $(CH_3)_2CHBr$ and (II; X = Br) over 70° a light yellow solution developed in the cell as the reaction proceeded, but this did not appear to affect the kinetic results. For (II; X = Cl) at 85° one of our cells 'blew up' and the solvent boiled in another.

Raw kinetic data were fitted to the first-order rate equation using a version of LSKIN least square computer program.[62]

Preparation of Solvents.—*CAUTION:* Hexafluoropropan-2-ol has a high vapour pressure and an unpleasant odour; manipulations were carried out in a fume cupboard and/or using syringes.

Method A. Hexafluoropropan-2-ol (B.D.H.; 50 ml) and calcium hydride (2 g) was stirred under nitrogen, and the mixture heated under reflux for 30 min. The condenser was then exchanged for a 36 cm Vigreaux column and distillation head, and the mixture distilled under nitrogen. The pot temperature was not allowed to rise above 80°.* The fraction boiling between 58.5 and 59.5° was collected in a weighed flask. To this fraction (77.958 2 g) was added distilled and deionized water (2.411 08 g) to make the mixture 97 : 3 w/w $(CF_3)_2CHOH-H_2O$.

Method B. Hexafluoropropan-2-ol (Eastman) was distilled under nitrogen from 3A molecular sieves,[63] through a triple pass Widmer column (effective column length 100 cm). The fraction boiling between 58 and 59° was collected in a flask which was later fitted with a tap adaptor and serum cap. The water content of the solvent was <0.06 wt % (Karl Fischer determination). The 97% wt % solution was prepared ignoring the water content in the purified solvent; because 0.06% water was regarded as an upper limit the solution was between 96.94 and 97.00 wt %.

Preparation of Substrates.—The following substrates are available commercially: $(CH_3)_3CCl$, $(CH_3)_3CBr$, $(CH_3)_2CHBr$, (I; X = Br) (II; X = Br) (Aldrich), but all adam-

---

* The sodium salt of $(CF_3)_2CHOH$ decomposes explosively at 140°, see H. J. Koetzsch, *Chem. Ber.*, 1966, **99**, 1143.

antyl compounds were prepared by standard methods and had m.p.s in agreement with literature values: (I; X = Cl[21,64] or Br[18]); (II; X = Cl;[64] Br,[65] OMs,[39] or OTs[7]); (III; X = Cl[66] or Br[67]). Methanesulphonates (IV; X = OMs) and (V; X = OMs) were prepared as described previously.[39]

We thank Miss D. Stief for technical assistance, Mr. D. S. Jones for constructing the Swansea amplifiers, and Dr. J. S. Littler and Professor P. v. R. Schleyer for helpful discussions. This research was financially supported by an S.R.C. research studentship to C. T. B., and by the University of Manchester.

[9/1638 *Received, 16th October*, 1979]

REFERENCES

[1] A. H. Fainberg and S. Winstein, *J. Amer. Chem. Soc.*, 1957, **79**, 1608; S. G. Smith, A. H. Fainberg, and S. Winstein, *ibid.*, 1961, **83**, 618.

[2] H. Yamataka, S.-G. Kim, T. Ando, and Y. Yukawa, *Tetrahedron Letters*, 1973, 4767; V. J. Shiner, jun., and R. C. Seib, *J. Amer. Chem. Soc.*, 1976, **98**, 862.

[3] V. J. Shiner, jun., R. D. Fisher, and W. Dowd, *J. Amer. Chem. Soc.*, 1969, **91**, 7748.

[4] T. Ando and H. Morisaki, *Tetrahedron Letters*, 1979, 121.

[5] J. R. Pritt and M. C. Whiting, *J.C.S. Perkin II*, 1975, 1458.

[6] D. J. Raber, J. M. Harris, and P. v. R. Schleyer, in 'Ion and Ion Pairs in Organic Reactions,' ed. M. Szwarc, Wiley, New York, 1974, vol. 2, (*a*) p. 302; (*b*) pp. 279—297.

[7] T. W. Bentley and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, 1976, **98**, 7658.

[8] J. M. Harris, D. L. Mount, M. R. Smith, W. C. Neal, jun., M. D. Dukes, and D. J. Raber, *J. Amer. Chem. Soc.*, 1978, **100**, 8147.

[9] (*a*) S. Winstein, B. Appel, and A. Diaz, Chem. Soc. Publ. No. 19, 1965, pp. 109—130; (*b*) A. F. Diaz, I. Lazdins, and S. Winstein, *J. Amer. Chem. Soc.*, 1968, **90**, 1904; (*c*) H. L. Goering and H. Hopf, *J. Amer. Chem. Soc.*, 1971, **93**, 1224; H. L. Goering and R. P. Anderson, *ibid.*, 1978, **100**, 6469.

[10] D. J. McLennan, *Accounts Chem. Research*, 1976, **9**, 281 (footnote 74); D. J. Raber and J. M. Harris, *J. Chem. Educ.*, 1972, **49**, 60. See also L. P. Hammett, 'Physical Organic Chemistry,' McGraw-Hill, New York, 1970, 2nd edn., pp. 165—167.

[11] V. J. Shiner, jun., W. Dowd, R. D. Fisher, S. R. Hartshorn, M. A. Kessick, L. Milakofsky, and M. W. Rapp, *J. Amer. Chem. Soc.*, 1969, **91**, 4838.

[12] R. D. Fisher, R. C. Seib, V. J. Shiner, jun., I. Szele, M. Tomić, and D. E. Sunko, *J. Amer. Chem. Soc.*, 1975, **97**, 2408.

[13] (*a*) T. W. Bentley, S. H. Liggero, M. A. Imhoff, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, 1974, **96**, 1970; (*b*) F. L. Schadt, T. W. Bentley, and P. v. R. Schleyer, *ibid.*, 1976, **98**, 7667.

[14] For a reply see V. J. Shiner, jun., D. A. Nollen, and K. Humski, *J. Org. Chem.*, 1979, **44**, 2108.

[15] For reviews of the background to this work see (*a*) J. M. Harris, *Progr. Phys. Org. Chem.*, 1974, **11**, 89; (*b*) T. W. Bentley and P. v. R. Schleyer, *Adv. Phys. Org. Chem.*, 1977, **14**, 1.

[16] D. E. Sunko and I. Szele, *Tetrahedron Letters*, 1972, 3617.

[17] J. Delhoste, G. Lamaty, and P. Pajanacci, *Compt. rend.*, 1968, **266**, 1508.

[18] D. J. Raber, R. C. Bingham, J. M. Harris, J. L. Fry, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, 1970, **92**, 5977.

[19] P. v. R. Schleyer and V. Buss, *J. Amer. Chem. Soc.*, 1970, **92**, 1660.

[20] A. H. Fainberg and S. Winstein, *J. Amer. Chem. Soc.* (*a*) 1956, **78**, 2770; (*b*) 1957, **79**, 1602.

[21] P. v. R. Schleyer and R. D. Nicholas, *J. Amer. Chem. Soc.*, 1961, **83**, 2700.

[22] T. W. Bentley, C. T. Bowen, W. Parker, and C. I. F. Watt, *J. Amer. Chem. Soc.*, 1979, **101**, 2486.

[23] J. L. Fry, C. J. Lancelot, L. K. M. Lam, J. M. Harris, R. C. Bingham, D. J. Raber, R. E. Hall, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, 1970, **92**, 2538.

[24] E. M. Arnett, C. Petro, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, 1979, **101**, 522.

[25] M. J. S. Dewar and R. C. Dougherty, 'The PMO Theory of Organic Chemistry,' Plenum Press, New York, 1975, pp. 212—220.

[26] K. T. Leffek, J. A. Llewellyn, and R. E. Robertson, *Canad. J. Chem.*, 1960, **38**, 1505, 2171.

[27] Believed to be hyperconjugative, 'Isotope Effects in Chemical Reactions,' eds. C. J. Collins and N. S. Bowman, A.C.S. Monograph 167, Van Nostrand–Reinhold, New York, 1970, pp. 140—145 and 168—171; see also D. J. DeFrees, M. Taagepera, B. A. Levi, S. K. Pollack, K. D. Summerhays, R. W. Taft, M. Wolfsberg, and W. J. Hehre, *J. Amer. Chem. Soc.*, 1979, **101**, 5532.

[28] (*a*) D. E. Sunko, I. Szele, and W. J. Hehre, *J. Amer. Chem. Soc.*, 1977, **99**, 5000; (*b*) D. E. Sunko, S. Hiršl-Starčević, S. K. Pollack, and W. J. Hehre, *ibid.*, 1979, **101**, 6163.

[29] R. A. More O'Ferrall, *J. Chem. Soc.* (*B*), 1970, 274; W. P. Jencks, *Chem. Rev.*, 1972, **72**, 705.

[30] H. Hogeveen, *Adv. Phys. Org. Chem.*, 1973, **10**, 29.

[31] E. M. Arnett and C. Petro, *J. Amer. Chem. Soc.*, 1978, **100**, 2563; E. W. Bittner, E. M. Arnett, and M. Saunders, *ibid.*, 1976, **98**, 3734.

[32] T. W. Bentley in 'Mass Spectrometry,' Specialist Periodical Reports, The Chemical Society, London, vol. 4, p. 55; vol. 5, p. 72.

[33] H. Tanida, Y. Hata, S. Ikegami, and H. Ishitobi, *J. Amer. Chem. Soc.*, 1967, **89**, 2928.

[34] J. L. Fry, J. M. Harris, R. C. Bingham, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, 1970, **92**, 2540; J. L. Fry, E. M. Engler, and P. v. R. Schleyer, *ibid.*, 1972, **94**, 4628.

[35] P. v. R. Schleyer, J. L. Fry, L. K. M. Lam, and C. J. Lancelot, *J. Amer. Chem. Soc.*, 1970, **92**, 2542.

[36] D. J. Raber, W. C. Neal, jun., M. D. Dukes, J. M. Harris, and D. L. Mount, *J. Amer. Chem. Soc.*, 1978, **100**, 8137.

[37] H. M. R. Hoffmann, *J. Chem. Soc.*, 1965, 6748.

[38] R. E. Robertson, *Progr. Phys. Org. Chem.*, 1967, **4**, 233.

[39] T. W. Bentley and C. T. Bowen, *J.C.S. Perkin II*, 1978, 557.

[40] M. H. Abraham and G. F. Johnston, *J. Chem. Soc.* (*A*), 1971, 1610.

[41] H. C. Brown, M. Ravindranathan, C. G. Rao, F. J. Chloupek, and M.-H. Rei, *J. Org. Chem.*, 1978, **43**, 3667; J. M. Harris and S. P. McManus, *J. Amer. Chem. Soc.*, 1974, **96**, 4693.

[42] K. L. Servis, S. Borčić, and D. E. Sunko, *Tetrahedron*, 1968, **24**, 1247.

[43] X. Creary, M. Keller, and J. P. Dinnocenzo, *J. Org. Chem.*, 1978, **43**, 3874.

[44] J. M. Harris, D. L. Mount, and D. J. Raber, *J. Amer. Chem. Soc.*, 1978, **100**, 3139.

[45] H. C. Brown, M. Ravindranathan, F. J. Chloupek, and I. Rothberg, *J. Amer. Chem. Soc.*, 1978, **100**, 3143.

[46] J. E. Nordlander, R. R. Gruetzmacher, and J. E. Stuehr, *Rev. Sci. Instruments*, 1972, **43**, 1835.

[47] J. E. Nordlander, R. R. Gruetzmacher, W. J. Kelly, and S. P. Jindal, *J. Amer. Chem. Soc.*, 1974, **96**, 181.

[48] D. Lenoir, W. Röll, E. Weiss, and G. Wenke, *Tetrahedron Letters*, 1976, 1991.

[49] D. Lenoir and R. Frank, unpublished result cited in ref. 45.

[50] Data summarised in Table IV of reference 7.

[51] S. Winstein, J. S. Gall, M. Hojo, and S. Smith, *J. Amer. Chem. Soc.*, 1960, **82**, 1010.

[52] For a theoretical study of protonated alkyl chlorides see W. L. Jorgensen, *J. Amer. Chem. Soc.*, 1978, **100**, 1049.

[53] P. v. R. Schleyer in 'The Non-classical Ion Problem,' Plenum, New York, 1977, p. 233.

[54] J. M. Harris, S. G. Shafer, J. R. Moffatt, and A. R. Becker, *J. Amer. Chem. Soc.*, 1979, **101**, 3295.

[55] R. C. Bingham and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, 1971, **93**, 3189; J. Slutsky, R. C. Bingham, P. v. R. Schleyer, W. C. Dickeson, and H. C. Brown, *ibid.*, 1974, **96**, 1969.

[56] Z. Rappoport, J. Kaspi, and Y. Apeloig, *J. Amer. Chem. Soc.*, 1974, **96**, 2612.

[57] F. L. Scott, *Chem. and Ind.*, 1959, 224.

[58] C. G. Swain and A. Maclachlan, *J. Amer. Chem. Soc.*, 1960, **82**, 6095.

[59] A. C. Knipe, D. McLean, and R. L. Tranter, *J. Phys. E: Scientific Instruments*, 1974, **4**, 586.

[60] W. Parker, R. L. Tranter, C. I. F. Watt, L. W. K. Chang, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, 1974, **96**, 7121.

[61] J. S. Littler and R. M. Reeves, *Chem. Brit.*, 1978, **14**, 118.

[62] D. F. Detar in 'Computer Programs for Chemistry,' ed. D. F. Detar, Benjamin, New York, 1968, vol. 1, pp. 126—173; W. F. Sliwinski, Ph.D. Thesis, Princeton University.

[63] M. A. Matesich, J. Knoefel, H. Feldman, and D. F. Evans, *J. Phys. Chem.*, 1973, **77**, 366.

[64] P. Kovacic and J.-H. Chen Chang, *J. Org. Chem.*, 1971, **36**, 3138.

[65] W. Hoek, J. Strating, and H. Wynberg, *Rec. Trav. chim.*, 1966, **85**, 1045.

[66] D. Kovačević, Z. Majerski, S. Borčić, and D. E. Sunko, *Tetrahedron*, 1972, **28**, 2469.

[67] B. D. Cuddy, D. Grant, A. Karim, M. A. McKervey, and E. J. F. Rea, *J.C.S. Perkin I*, 1972, 2701.