Solvolysis of 1-Aryl-2,2,2-trihalogenoethyl Toluene-*p*-sulphonates. Generation of Carbocations Destabilized by Trichloro- or Tribromo-methyl Groups

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The kinetics of solvolysis of the title compounds, leading to the formation of carbocations destabilized by a CCl_3 or a CBr_3 group, have been studied in various solvents. Destabilization by the CX_3 group increases with the electronegativity of the halogen X. Plots of log *k* *vs.* Y_{OTs} for the 1-(*p*-methoxyphenyl)-2,2,2-trihalogenoethyl *p*-toluenesulphonates yield m_{OTs} values which are indicative of some deviation from a pure k_c process, probably due to anchimeric assistance by the halogen substituents.

Considerable effort has been devoted in the past decade to the study of destabilized carbocations of general structure $R^1R^2ZC^+$, where Z is an electron-withdrawing group. Substituents Z include CN,[1] COR,[2] PS(OEt)$_2$,[3] PO(OEt)$_2$,[4] SOR,[5] SO_2R [5] and CF_3 [6–8] groups.

The destabilizing effect of the trifluoromethyl group has been particularly well investigated. Kinetic studies have revealed intriguing behaviour even by these species. For the solvolysis of *p*-XArCHRY, substitution of α-CF_3 for α-Me causes a large decrease in the rate constant, pointing to a large destabilizing effect of the α-CF_3 group upon the incipient adjacent positive charge.[6e] On the other hand, measured rate constants for the capture of these intermediates by the solvent or acetate anion suggest little or no change in the carbocation reactivity when α-Me is substituted by an α-CF_3 group.[7] In addition to this unexpected kinetic stability, a further unusual behaviour of these species as regards certain nucleophiles was also observed.[8] In the presence of amines, nucleophilic addition to the C-4 ring position of *p*-MeOArCH$(CF_3)^+$ was detected, an observation which reinforced a previous report of nucleophilic aromatic substitution in the ethanolysis of *p*-MeOArCH(CF_3)OTs.[6g]

By comparison with the amount of work devoted to carbocations destabilized by the CF_3 group, it is surprising that this interest has not yet been extended to other analogous trihalogenomethyl species. In fact, the formation of the aryltrichloromethyl carbocations ArCH$(CCl_3)^+$ as intermediates in such a classical reaction as the preparation of DDT and its analogues from arenes and chloral was postulated nearly fifteen years ago.[9] Nevertheless, in spite of their suggested intermediacy in such long established processes, these species have not yet been investigated in detail and no attempt has been made to compare the destabilizing effects of the CCl_3 and CBr_3 groups with that of the well studied trifluoromethyl group.

We have been interested for some time in the influence of a trihalogenomethyl group upon the reactivity of a neighbouring electrophilic centre.[10–12] As a natural extension of this work, we decided to study the solvolysis of 1-aryl-2,2,2-trihalogenoethyl *p*-toluenesulphonates.

The results presented in this paper, besides providing kinetic evidence for the formation of carbocations destabilized by an adjacent trichloro-or tribromomethyl group, allow the direct comparison of these groups with the CF_3 substituent in these intermediates.

Experimental

M.p.s were obtained with a Kofler hot-stage apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 781 model. NMR spectra were taken with a Bruker AC-80 instrument, using tetramethylsilane as internal standard. All coupling constant values (*J*) are given in Hz. Light petroleum refers to the fraction boiling point 30–60 °C.

Materials.—2,2,2-Trifluoroethanol (TFE) and 1,1,1,3,3,3-hexafluoropropan-2-ol (HFP) were purchased from Aldrich. Absolute ethanol and methanol were dried following standard procedures.[13] Aqueous binary mixtures were prepared with twice-distilled water.

1-(p-*Methoxyphenyl*)-2,2,2-*trichloroethyl* p-*Toluenesulphonate* **1a**.—To a cooled (0–5 °C) solution of 1-(*p*-methoxyphenyl)-2,2,2-trichloroethanol[14] (3.7 g, 14.5 mmol) in chloroform (50 cm^3) were added, with stirring, a 70% suspension in oil of sodium hydride (1.1 g, 32 mmol) and then, in portions, *p*-toluenesulphonyl chloride (1.9 g, 10 mmol). The resulting cooled suspension was stirred for 2 h, until almost all of the sulphonyl chloride had been consumed, as shown by TLC (silica gel HF_{254}, $CHCl_3$ eluant) of the mixture. The precipitated sodium chloride was filtered off and the filtrate was washed with 10% aqueous HCl, then water and dried (anhydrous $MgSO_4$). The chloroform solution was evaporated under reduced pressure to yield an oily residue, which solidified to a white powder after being triturated with light petroleum. The p-*toluenesulphonate* after being filtered, was washed with light-petroleum, dried, weighed (2.3 g, 56%) and recrystallized from diethyl ether, m.p. 89–91 °C (Found: C, 46.6; H, 3.7. $C_{16}H_{15}Cl_3O_4S$ requires C, 46.9; H, 3.7%); ν_{max}(KBr)/cm^{-1} 1600, 1375, 1250, 1190, 1170, 970, 860 and 800; δ($CDCl_3$) 2.3 (3 H, s, ArMe), 3.8 (3 H, s, ArOMe), 5.8 [1 H, s, CH(CCl_3)OTs], 6.95 (2 H, d, J_{AB} 7), 7.15 (2 H, d, J_{AB} 8), 7.4 (2 H, d, J_{AB} 7) and 7.6 (2 H, d, J_{AB} 8).

1-(p-*Methylphenyl*)-2,2,2-*trichloroethyl* p-*Toluenesulphonate* **1b**.—This was prepared as described above for compound **1a** (52%), m.p. 133–135 °C (from $CHCl_3$–light petroleum) (Found: C, 48.5; H, 3.9. $C_{16}H_{15}Cl_3O_3S$ requires C, 49.8; H, 3.8%); ν_{max}(KBr)/cm^{-1} 1600, 1370, 1180, 980, 860, 810 and 760.

1-(p-*Methoxyphenyl*)-2,2,2-*tribromoethyl* p-*Toluenesulphonate* **2a**.—To a cooled (0 °C), stirred suspension of sodium hydride (0.5 g of a 70% suspension in oil, 14.5 mmol) in dry THF (10 cm^3) was added dropwise a solution of 1-(*p*-methoxyphenyl)-2,2,2-tribromoethanol[14] (2.7 g, 7 mmol) in dry tetrahydrofuran (THF) (20 cm^3). The resulting mixture was stirred at 0 °C for a further 15 min. A solution of *p*-toluenesulphonyl chloride (1.9 g, 10 mmol) in THF (10 cm^3) was then added and the reaction was allowed to proceed for 4 h at 0 °C. The suspension was then filtered, the filtrate was evaporated under reduced pressure and the residue extracted with chloroform (50 cm^3). The chloroform extract was washed with 10% aqueous HCl, then water and was finally dried (anhydrous $MgSO_4$). Evaporation of solvent left the crude product, which was recrystallized from hexane–chloroform to give 0.76 g (20%) of the p-*toluenesulphonate* **2a** m.p. 99–100 °C (Found: C, 35.25; H, 2.8. $C_{16}H_{15}Br_3O_4S$ requires C, 35.35; H, 2.8%); ν_{max}(KBr)/cm^{-1} 1610, 1510, 1370, 1250, 1170, 960 and 850; $\delta(CDCl_3)$ 2.3 (3 H, s, ArMe), 3.8 (3 H, s, ArOMe), 5.9 [1 H, s, $CH(CBr_3)OTs$], 6.8 (2 H, d, J_{AB} 7), 7.2 (2 H, d, J_{AB} 8), 7.5 (2 H, d, J_{AB} 7) and 7.7 (2 H, d, J_{AB} 8).

1-(p-*Methylphenyl*)-2,2,2-*tribromoethyl* p-*Toluenesulphonate* **2b**.This was prepared as described above for compound **2a**, yield 25%, m.p. 171–173 °C ($CHCl_3$–light petroleum) (Found: C, 36.7; H, 2.8. $C_{16}H_{15}Br_3O_3S$ requires C, 35.1; H, 2.85%); ν_{max}/cm^{-1} 1370, 1170, 960, 850 and 800; $\delta[(CD_3)_2CO]$ 2.2 (3 H, s, ArMe), 2.3 (3 H, s, ArMe), 5.9 [1 H, s, $CH(CBr_3)OTs$] and 6.9–7.5 (8 H, m, ArH).

1-*Phenyl*-2,2,2-*tribromoethyl* p-*Toluenesulphonate* **2c**.—This was prepared as described above for compound **2a**, yield 75%, m.p. 134–136 °C ($CHCl_3$–light petroleum) (Found: C, 34.7; H, 2.5. $C_{15}H_{13}Br_3O_3S$ requires C, 35.1; H, 2.5%); ν_{max}(KBr)/cm^{-1}: 1370, 1170, 960 and 850; $\delta_H[(CD_3)_2CO]$ 2.3 (3 H, s, ArMe), 6.0 [1 H, s, $CH(CBr_3)OTs$], 7.0–7.3 (5 H, m, ArH) and 7.4–7.7 (4 H, m, ArH).

Product Characterization.—The characterization of the solvolysis products was carried out for the acetolysis of 1-(*p*-methoxyphenyl)-2,2,2-tribromo- and 1-(*p*-methoxyphenyl)-2,2,2-trichloroethyl *p*-toluenesulphonates. In both cases, refluxing each of these tosylates (*ca.* 0.1 g) in acetic acid (5 cm^3) until completion of the acetolysis (as shown by TLC) yielded the corresponding 1-(*p*-methylphenyl)-2,2,2-tribromo-and 1-(*p*-methoxyphenyl)-2,2,2-trichloro-ethyl acetates, respectively, as sole products of solvolysis. The identity of these products was established by spectral comparison of the isolated acetates with authentic samples prepared by the action of acetic anhydride on the corresponding trihalogenoethanol.[15]

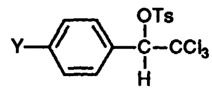
Kinetic Measurements.—Kinetic runs were followed spectroscopically with a Shimadzu 210-A UV-vis. spectrophotometer.

In a typical run, *ca.* 10 mm^3 of a freshly prepared ethanolic solution (*ca.* 10^{-2} mol dm^{-3}) of the *p*-toluenesulphonate was added to a thermostatted (±0.1 °C) water-jacketed cell containing the solvent. After thermal equilibrium was attained, the absorbance variations were recorded at 235 nm for compounds **1** and **2** in ethanol, methanol, TFE, HFP or in aqueous solutions of these alcohols, and at 275 nm for *p*-toluenesulphonate **1a** in acetic acid. A total of 250 absorbance readings, spanning over at least three half-lives, were automatically acquired and processed by means of an iterative kinetic data program (Microquímica) which yielded rate constants with errors $< 1\%$.

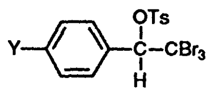
Alternatively, for slower reactions, the rate constants were obtained by applying the Guggenheim method[16] to the absorbance readings of 3 cm^3 aliquots of the substrate in the appropriate solvent, sealed in ampoules and withdrawn periodically from a constant temperature bath. Every ampoule withdrawn was immediately frozen and stored until at least twenty absorbance readings had been made over a period of 3–4 half-lives.

Results and Discussion

The solvolysis of the 1-aryl-2,2,2-trihalogenoethyl *p*-toluenesulphonates **1** and **2** was studied at different temperatures in various solvents.



1a Y = OMe
1b Y = Me



2a Y = OMe
2b Y = Me
2c Y = H

In all cases the reactions yielded the corresponding substitution products. Thus, from the acetolysis of **1a** and **2a** in refluxing acetic acid, the corresponding acetates were isolated as sole reaction products.

The solvolytic rate constants are given in Table 1. Estimated rate constants at 25 °C were obtained by extrapolation from the Arrhenius plots of the rate constants at higher temperatures, whenever the reactions were too slow to be followed directly at that standard temperature.

Comparison of the rate constants obtained for the solvolyses of compounds **1a** and **2a** with those reported by Tidwell and co-workers[6e] for the fluorinated analogue suggests a similar behaviour for these substrates. As expected, the tribromoethyl *p*-toluenesulphonate **2a** solvolyses more readily than the trifluoro- and trichloro- analogues. As an example, the solvolytic rate constant at 25 °C in 80% ethanol reported for the 1-(*p*-methoxyphenyl)-2,2,2-trifluoroethyl *p*-toluenesulphonate[6e] was 1.19×10^{-3} s^{-1}, similar to the value estimated by us for compound **1a** under the same conditions (7.82×10^{-4} s^{-1}), and *ca.* three times smaller than the rate constant obtained for the tribromo analogue **2a** in the same solvent.

Plots of log *k vs.* Y_{OTs} values[17] for substrates **1a** and **2a** yield straight lines with good correlation coefficients (Fig. 1). The slopes of these lines yield m_{OTs} values of 0.69 ($r = 0.994$) and 0.70 ($r = 0.990$) for compounds **1a** and **2a**, respectively. As for its fluorinated analogue,[6e] the point corresponding to the rate constant for acetolysis of the trichloroethyl *p*-toluenesulphonate **1a** was omitted from the correlation, because of the negative

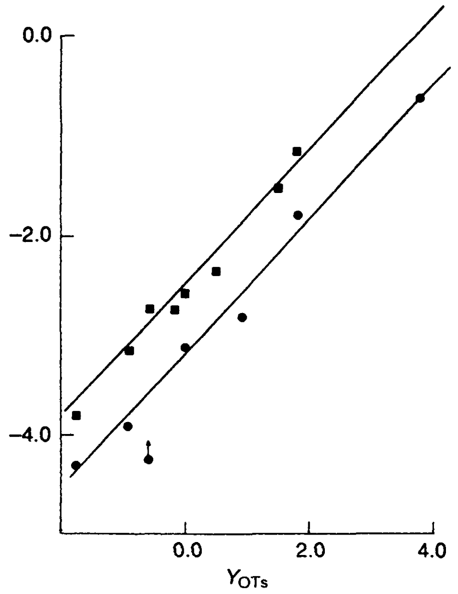


Fig. 1 Plots of log *k vs.* Y_{OTs} for the solvolysis of compounds **1** (●) and **2** (■) in various solvents at 25 °C

deviation of this point from the line, arising from protonation of the *p*-OMe substituent in this acidic solvent.

The m_{OTs} value reported for the solvolysis of the 1-(*p*-methoxyphenyl)-2,2,2-trifluoroethyl *p*-toluenesulphonate was 0.76,[6e] somewhat larger than our values. This would imply that the solvolysis of the fluorinated compound is closer to a pure k_c process than the solvolysis of its chlorinated or brominated analogues. Tidwell and co-workers have indeed contended that, in spite of the rather low value of 0.76, theirs was in fact a pure k_c process.[6e] In our case, deviation from a pure k_c solvolysis may arise from either solvent participation or anchimeric assistance in the rate-determining carbocation formation. It is difficult to see why backside attack from the solvent would be required in the solvolysis of *p*-toluenesulphonates **1a** and **2a** and not in the formation of the more electron-demanding, less sterically hindered trifluoromethyl carbocation. Anchimeric assistance by the more polarizable Cl and Br atoms seems to be a better rationalization of the smaller m_{OTs} values. The fact that no rearranged products were detected in the acetolysis of substrates **1a** and **2a** does not preclude the neighbouring participation of Cl and Br in the formation of the intermediate carbocations. An actual 1,2-halogen shift would mean rearrangement of a destabilized secondary benzyl carbocation $ArCH(CX_3)^+$ to an even less stable primary species $ArCHX{-}CX_2^+$. The absence of rearranged products arising from such an unfavoured process should not be a surprise.

Hammett plots of log *k vs.* σ^+ for substrates **1** and **2** in various solvents (graphs not shown) yield large negative ρ^+ values. Thus, for the trichloroethyl *p*-toluenesulphonates, ρ^+ values in EtOH, 80% and TFE were -9.2 and -8.5, respectively. For the solvolysis of the tribromoethyl *p*-toluenesulphonates **2** in TFE and HFP these values were -7.5 and -6.6, respectively. These figures should be treated with some caution, because of the scarcity of the available points. In fact, these are estimated ρ^+ values, being obtained from only two points each, very much like those reported for the solvolysis of the 1-aryl-2,2,2-trifluoroethyl *p*-toluenesulphonates.[6e] Nevertheless, two trends emerge from the comparison of our estimated ρ^+ values with those reported under similar conditions by Tidwell and co-workers.[6e]

Table 1. Solvolytic rate constants for *p*-toluenesulphonates **1** and **2** at different temperatures and in various solvents

Compound	Solvent	T/°C	k[a]/s^{-1}
1a	EtOH, 100%	59.0	1.47×10^{-3}
		52.0	7.95×10^{-4}
		42.5	3.10×10^{-4}
		25.0[b]	4.94×10^{-5}
	EtOH, 80%	61.0	2.43×10^{-2}
		52.0	1.07×10^{-2}
		42.0	4.39×10^{-3}
		25.0[b]	7.82×10^{-4}
	EtOH, 60%	58.0	2.26×10^{-2}
		52.0	1.62×10^{-2}
		43.0	7.13×10^{-3}
		25.0[b]	1.54×10^{-3}
	MeOH, 100%	59.0	4.37×10^{-3}
		48.0	1.48×10^{-3}
		41.5	0.76×10^{-3}
		25.0[b]	1.21×10^{-4}
	TFE	25.0	1.64×10^{-2}
	HFP	25.0	2.53×10^{-1}
	HOAc	62.0	2.59×10^{-3}
		52.0	9.60×10^{-4}
		44.0	4.49×10^{-4}
		25.0[b]	5.51×10^{-5}
1b	EtOH, 80%	113.5[c]	6.62×10^{-4}
		95.5[c]	8.83×10^{-5}
		83.5[c]	4.42×10^{-5}
		25.0[b]	3.52×10^{-8}
	EtOH, 60%	95.5[c]	5.58×10^{-4}
		85.4[c]	1.98×10^{-4}
		75.5[c]	7.80×10^{-5}
		25.0[b]	1.64×10^{-7}
	TFE	78.0	6.54×10^{-4}
		70.0	2.64×10^{-4}
		62.0	1.35×10^{-4}
		25.0[b]	1.77×10^{-6}
	HFP	59.0	1.82×10^{-3}
		50.0	1.32×10^{-3}
		40.7	8.85×10^{-4}
		25.0[b]	4.48×10^{-4}
2a	EtOH, 100%	49.5	2.22×10^{-3}
		39.5	7.93×10^{-4}
		30.5	3.01×10^{-4}
		25.0[b]	1.61×10^{-4}
	EtOH, 90%	49.7	1.62×10^{-2}
		39.7	6.95×10^{-3}
		30.0	3.17×10^{-3}
		25.0[b]	2.00×10^{-3}
2a	EtOH, 80%	40.0	1.05×10^{-2}
		29.7	4.17×10^{-3}
		25.0[b]	2.81×10^{-3}
		22.0	2.17×10^{-3}
	MeOH, 100%	47.5	6.85×10^{-3}
		39.5	3.22×10^{-3}
		30.5	1.31×10^{-3}
		25.0[b]	7.37×10^{-4}
	MeOH, 90%	38.5	7.68×10^{-3}
		31.5	3.88×10^{-3}
		25.0[b]	1.87×10^{-3}
		21.5	1.26×10^{-3}
	MeOH, 80%	40.5	1.86×10^{-2}
		32.0	8.26×10^{-3}
		25.0[b]	4.55×10^{-3}
		21.3	3.26×10^{-3}
	MeOH, 60%	25.0	3.15×10^{-2}
	TFE	25.0	7.00×10^{-2}
2b	TFE	59.5	8.93×10^{-4}
		49.0	3.16×10^{-4}
		40.3	1.23×10^{-4}
		25.0[b]	2.12×10^{-5}
	HFP	25.0	2.55×10^{-3}
2c	HFP[d]	60.0	7.78×10^{-5}
		50.0	4.39×10^{-5}
		40.0	2.33×10^{-5}
		25.0[b]	8.53×10^{-6}

[a] Rate constants obtained from duplicate runs, unless noted. [b] Values obtained by extrapolation or interpolation from Arrhenius plots of rate constants at other temperatures. The probable uncertainty in the extrapolated values of $\log k_{25}$ from these plots does not exceed 6% in most cases. This result is compatible with the average uncertainty calculated from data reported for analogous studies.[6e] [c] Rate constants obtained from absorbance readings of sealed aliquots immersed in a constant temperature bath. [d] Rate constants from single runs.

For the three series of trihalogeno derivatives, the magnitude of the ρ^+ values decreases with the solvent ionizing power. This is what one would expect from the application of the Hammond postulate to the carbocation formation. In a poorly ionizing solvent like ethanol, this step should be more endergonic than in a powerfully dissociating medium such as HFP. The transition state in the first solvent should therefore occur later, with greater charge development than in HFP.

A second trend emerges from the comparison of the ρ^+ values for the solvolysis of the three trihalogeno derivatives in TFE. The absolute values of ρ^+ decrease from the fluorinated analogue (-9.8)[6e] to the trichloro- (-8.5) and tribromo-derivative (-7.5), showing that, in this family of carbocations, the destabilizing effect of the CX_3 group upon the neighbouring positive charge increases with the electronegativity of the halogen X.

In conclusion, our results show that the solvolysis of the trihalogeno *p*-toluenesulphonates **1** and **2** takes place *via* formation of highly electron-demanding carbocations, a process which is very similar to that described for the solvolysis of their trifluoro analogues.[6e]

Solvolytic rate constants for compounds **1** are close to the values reported for the related fluorinated compounds. The tribromo *p*-toluenesulphonates **2** solvolyse faster. This probably reflects the decreased destabilizing effect of the CBr_3 group upon the adjacent positive charge of the carbocationic intermediate, as compared to the CCl_3 and CF_3 groups. *p*-Toluenesulphonates **1** and **2** are also more prone to anchimeric assistance in the formation of their corresponding carbocations. This conclusion is based upon the m_{OTs} values obtained for these substrates, which are smaller than that reported for the fluorinated analogue. Anchimeric assistance, rather than nucelophilic solvent participation, seems to be responsible for the deviations, implied by these smaller m_{OTs} values, from a pure k_c dissociation process.

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