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SOLVOLYSIS OF ARYL TRIFLUOROMETHANESULFONATES.

Andrew Streitwieser, Jr.* and Alan Dafforn[1]
Department of Chemistry, University of California
Berkeley, Calif. 94720

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We wish to report some observations demonstrating the high stability of aryl trifluoromethanesulfonates (ArOTf) under solvolytic conditions and thus the extreme instability of aryl cations. This instability may be easily seen in the gas phase by considering a typical reaction leading to cations, $RCl \rightarrow R^+ + Cl^-$. The heat of reaction $\Delta H_r°$ for several such reactions has been calculated and is given in Table I. Formation of $C_6H_5^+$ in the gas phase is seen to be almost as difficult as formation of CH_3^+ and significantly more difficult than formation of such cations as vinyl and ethyl. The only well-documented route to aryl cations in solution is solvolysis of arenediazonium ions,[2] but this reaction is of limited use in determining the relative stabilities of aryl cations because of ground-state resonance effects. Solvolysis of aryl trifluoromethanesulfonates (triflates) might be expected to be a good alternate source of unstable aryl cations, since triflate is an excellent leaving group (10^4 -10^5 better than tosylate)[3,4,5] and has proven quite useful for studying species such as vinyl cations.[6] Such a reaction would be particularly useful for mechanistic studies of aryl cations because little resonance interaction would be expected between the CF_3SO_3-group and an aromatic ring. It might also have synthetic utility for replacement of a phenolic hydroxyl group by a nucleophile.

Hansen has shown that phenyl triflate is inert to 80% aqueous CF_3SO_3H for 18 hours at 150° and that several aryl triflates are unreactive in methanol at 95° for 18-24 hours.[7] While this study was underway, Schleyer and co-workers reported that phenyl and p-methoxyphenyl triflates are stable in acetic acid for one week at 200° and in CF_3COOH for 4 days at 125°, but decompose to unknow products after more than one week at 125° in CF_3COOH.[5]

Phenyl triflate and 2-n-propylphenyl triflate were prepared by reaction of the potassium salt of the phenol with CF_3SO_2Cl in pyridine at room temperature, aqueous work-up, and distillation. Solvolysis reactions were carried out in sealed, thick-walled glass tubes. Solutions were de-gassed or sealed under nitrogen. Approximate temperatures were maintained with an oil bath or a heated autoclave. Some reactions were monitored directly by comparing the uv spectrum of starting and product solution. Others were monitored by aqueous work-up of product followed by glpc. Appropriate control solutions were worked up in the same manner to assure that no products were lost.

Table I

Heats of Reaction for Cation Formation

Reaction	$\Delta H_r°$ (kcal/mole)
$CH_3Cl \longrightarrow CH_3^+ + Cl^-$	+ 226
$C_6H_5Cl \longrightarrow C_6H_5^+ + Cl^-$	+ 222
$C_2H_3Cl \longrightarrow C_2H_3+ + Cl^-$	+ 206
$CH_3CH_2Cl \longrightarrow CH_3CH_2^+ + Cl^-$	+ 191
$(CH_3)_2CHCl \longrightarrow (CH_3)_2CH^+ + Cl^-$	+ 169

$\Delta H_r°$ in the gas phase at 298° was calculated from $\Delta H_f°$.

$\Delta H_f°$ for neutral molecules were taken from J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds," Academic Press., Inc., London, 1970.

$\Delta H_f°$ for Cl^- was taken as -54.4 kcal/mole, calculated using $\Delta H_f°$ = 29.94 kcal/mole for Cl· from D. R. Stull and G. C. Sinke, "Thermodynamic Properties of the Elements," American Chemical Society, Washington, D. C., 1956 and an electron affinity of 3.613 ev for Cl· from R. S. Berry and C. W. Reimann, *J. Chem. Phys.*, *38*, 1540 (1963).

$\Delta H_f°$ for cations except $C_6H_5^+$ were taken from J. L. Franklin, J. G. Dillard, and F. H. Field, "Ionization Potentials, Appearance Potentials, and Heats of Formation of Gaseous Positive Ions," Nat. Stand. Ref. Data Ser., Nat. Bur. Stand. (U.S.) 26, 1969.

$\Delta H_f°$ for $C_6H_5^+$ was taken as +289. A value of 292 was calculated using an ionization potential of 9.20 ev for $C_6H_5\cdot$ from Franklin (*ibid*) and $\Delta H_f°$ = +80 for $C_6H_5\cdot$ from A. S. Rodgers, D. M. Golden, and S. W. Benson, *J. Amer. Chem. Soc.*, *89*, 4578 (1967). This value was averaged with a value of +286 from photoionization of benzene, also quoted by Franklin et al.

Results are summarized in Table II. The most striking feature of these results is the very low reactivity of the triflates. Reactions were observed only after prolonged heating at temperatures well above 200° or in strong base. Given the high reactivity of alkyl triflates, this is convincing evidence of the instability of aryl cations. The only identifiable reaction product ever observed was phenol, the product expected from nucleophilic attack at sulfur. Although no independent controls were run, it is unlikely that phenyl trifluoroethyl ether would decompose to phenol in acidic trifluoroethanol, especially in view of the low reactivity of even trifluoroethyl tosylate.[9] When substantial reaction occurred, reaction mixtures were carefully examined for products resulting from aryl cations or nucleophilic attack at carbon; no such products were found.

A few of these reactions deserve further comment. Solvolysis in trifluoroethanol at >240° is of interest because the reaction may have occurred

Table II

Solvolyses of Aryl Triflates

Triflate	Solvent	Time	Temp.	% Triflate Recovered	Products	Products <u>not</u> Present
Phenyl	Ethanol	69 hr	161°	100%[a]	---	---
Phenyl	Ethylene Glycol	20 hr	220-240°	85-95%[a,b]	5% Phenol[a]	---
Phenyl	CF_3COOH	53 hr	160°	0%[a]	unknown	---
Phenyl	CF_3CH_2OH	157 hr	150°	100%[c]	---	---
Phenyl	CF_3CH_2OH	27 hr	176°	100%[c]	---	---
Phenyl	CF_3CH_2OH	196 hr	189°	100%[c]	---	---
Phenyl	CF_3CH_2OH	217 hr	240-250°[d]	36%[c]	~75% Phenol[a]	$PhOCH_2CF_3$[c]
Phenyl	3M $NaOCH_3$ in CH_3OH	$t_{1/2}$~15 min[e]	~35°	0%	Phenol[a]	$PhOCH_3$[a]
Phenyl	0.17M LiBr in 95% EtOH	30 hr	Reflux	100%[a]	---	Phenol,[a] C_6H_5Br[a]
2-n-Propyl-Phenyl	Sulfolane	78 hr	250°	92%[c]	unknown	Indan,[c] 2-n-Propylphenol[c]
"	Sulfolane	179 hr	276°	32%[c]	tar	"

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a. Determined by uv absorption.
b. In a second experiment under similar conditions, a 2.5% yield of phenol was obtained, but no remaining starting material was apparent in the uv spectrum.
c. Determined by glpc or extraction and glpc.
d. Due to equipment malfunction, temperature rose to 278° at one point, and may have remained there *for as long as 20 hr.*
e. Observed directly in cuvette.

above the critical temperature. Using a group equivalent treatment,[10] we estimate the critical temperature of trifluoroethanol as 174°. 2-n-propylphenyl triflate was decomposed in Sulfolane in an attempt to trap an aryl cation in an essentially non-nucleophilic system. In the 2-n-propylphenyl cation, intramolecular hydride abstraction and cyclization might be expected to yield indan, since diazotization of *o*-neopentylaniline yields 2,2-dimethylindan.[11] No indan or other hydrocarbons extractable into hexane were observed.

The general conclusion from this and earlier work is that simple aryl triflates are not useful compounds for generating aryl cations. Under extreme solvolytic conditions or in strong base, the only observable reaction is nucleophilic attack at sulfur.

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References and Notes

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