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# THE MAGNITUDE OF DESTABILIZATION OF STABILIZED CATIONS BY CYANO AND TRIFLUOROMETHYL GROUPS

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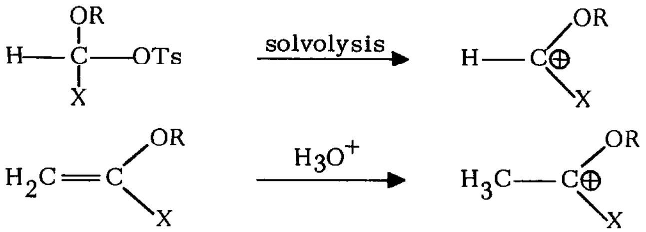
Summary: *Ab initio* calculations predict that cyano and trifluoromethyl groups both have large destabilizing effects on α-heteroatom stabilized cations, whereas CN is a much weaker destabilizer than $CF_3$ of less stabilized cations.

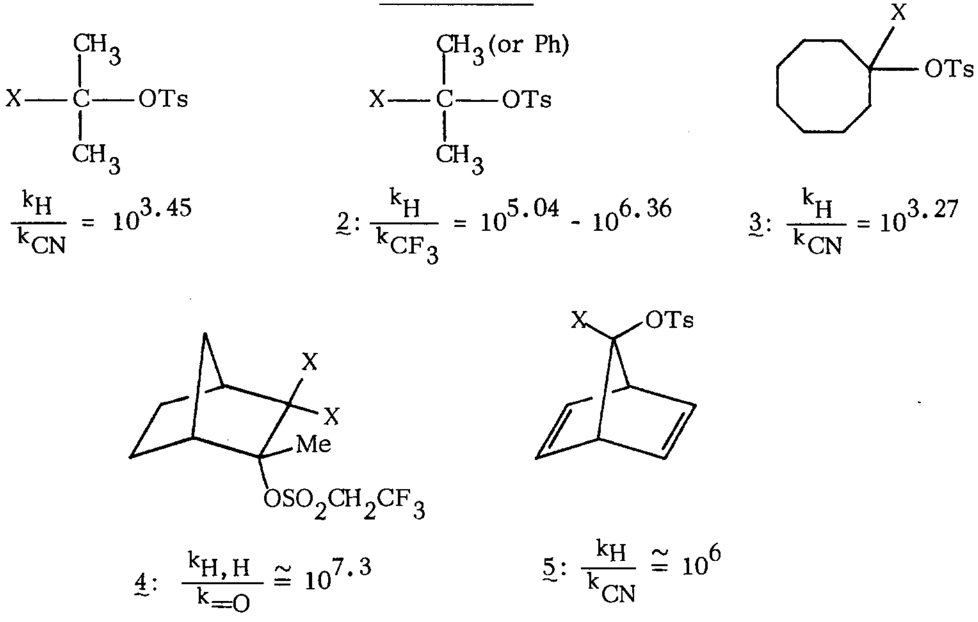
Electron-withdrawing groups traditionally have been considered as potent cation destabilizers, but recent experimental[1-6] and theoretical[7-10] studies indicate that certain electron-withdrawing groups may have a greatly attenuated destabilizing effect when directly attached to a highly electron-deficient cationic center. In conjunction with ongoing experimental studies of alkene hydrations and solvolyses involving substituents of this type,[11] we have carried out calculations on the influence of two electron-withdrawing groups, CN and $CF_3$, on the energy of the highly stabilized hydroxymethyl cation. These results provide predictions of CN and $CF_3$ rate effects for the following experimentally accessible systems, which are being studied in the Canadian laboratories.



X = H, CN, $CF_3$

Important experimental papers have recently appeared describing the effect of the electron-withdrawing $\alpha$-substituents, $CF_3$, CN, and RCO, on the stabilities of carbocations.[1-5] Scheme I summarizes the experimental data on the trifluoroethanolysis of various cyano compounds reported by Gassman and Talley,[1] the acetolysis of $\alpha$-keto-norbornyl derivatives reported by Creary,[2] and the solvolysis of trifluoromethyl derivatives described by Koshy and Tidwell,[3] and by Liu and Sheu.[4]

SCHEME I



1: $\frac{k_H}{k_{CN}} = 10^{3.45}$

2: $\frac{k_H}{k_{CF_3}} = 10^{5.04} - 10^{6.36}$

3: $\frac{k_H}{k_{CN}} = 10^{3.27}$

4: $\frac{k_{H,H}}{k_{=O}} \cong 10^{7.3}$

5: $\frac{k_H}{k_{CN}} \cong 10^{6}$

The smaller deceleration of solvolysis by cyano than by trifluoromethyl (cf. 1 and 2)[1,3] was taken as evidence that cyano is capable of $\pi$-donation which mitigates the strong $\sigma$ (inductive) electron-withdrawal by this substituent. That is, based on Taft polar substituent constants [$\sigma^*$ ($NCCH_2$) = 1.3; $\sigma^*$ ($CF_3CH_2$) = 0.92; $\sigma^*$ ($CH_3COCH_2$) = 0.00], cyano should be the most potent destabilizer of cations, in contrast to experimental results. The results of PRDDO calculations by Dixon, Charlier, and Gassman[7] and <u>ab initio</u> calculations by us support the anomalously low destabilization of cations by the cyano group.[9] For example, we have reported the 4-31G energies for the isodesmic reaction given below.[8]

$$\overset{\oplus}{C}H_3 + CH_3X \longrightarrow CH_4 + \overset{\oplus}{C}H_2X$$

| | |
|---|---|
| X = CN | +9.9 kcal/mol |
| CHO | +6.1 |
| $CF_3$ | +37.3 |

Thus, destabilization of the methyl cation by $CF_3$ is much larger than that by CHO and CN, which we interpreted to mean that CHO and CN could act as $\pi$ donors in cases of extreme electron demand.

On the other hand, the very large deceleration of the rate of solvolysis in case 5 by cyano[1] indicates that $\pi$-donation by cyano is small or nonexistent where the cation is highly stabilized. In order to probe this effect computationally for a highly stabilized cation, we have carried out calculations of substituent effects on highly stabilized hydroxymethyl cation.

$$\overset{\oplus}{C}H_2OH + HOCH_2X \longrightarrow HO\overset{\oplus}{C}HX + CH_3OH$$

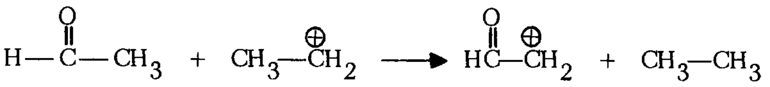
X = CN  +20.9 kcal/mole

$CF_3$  +35.6

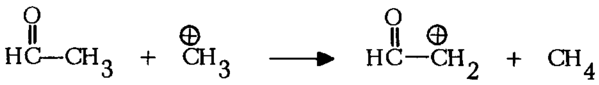
As before, full geometry optimizations were carried out at the STO-3G level, and single-point calculations were then performed using the 4-31G basis set.

On replacing a hydrogen in $^+CH_3$ by a strong donor, OH, the destabilizing effect of $CF_3$ is nearly equally large (37.3 kcal/mol for $^+CH_2CF_3$ vs. 35.6 kcal/mol for $HO\overset{+}{C}HCF_3$). However, the CN group becomes much more destabilizing for the stabilized cation: $HO\overset{+}{C}HCN$ is destabilized 11 kcal/mol more than $^+CH_2CN$ is destabilized by CN. Because the OH group is an excellent donor, the destabilization of $^+CHOHCN$ with respect to $^+CH_2CN$ may be taken as a lower bound to the $\pi$-donor stabilization (11 kcal/mol) by the CN afforded to the methyl cation. The large deceleration found in case 5 is an experimental example of the large destabilization of a stabilized cation by CN. $CF_3$ destabilizes an adjacent cation through inductive effects, and the deactivation of an adjacent cation is large and approximately constant, regardless of the nature of the other substituents attached to the cation.

Finally, we comment on the rate ratio for 4, which is the largest of those determined experimentally to date. The measured ratio is for replacement of $CH_2$ by C=O, which is modeled by reaction (1), whereas the other ratios listed earlier are for replacement of H by the substituent X, which for CHO is modeled by reaction (2). The 4-31G energies of



$$H-\overset{\overset{O}{\|}}{C}-CH_3 + CH_3-\overset{\oplus}{C}H_2 \longrightarrow H\overset{\overset{O}{\|}}{C}-\overset{\oplus}{C}H_2 + CH_3-CH_3 \qquad (1)$$



$$H\overset{\overset{O}{\|}}{C}-CH_3 + \overset{\oplus}{C}H_3 \longrightarrow H\overset{\overset{O}{\|}}{C}-\overset{\oplus}{C}H_2 + CH_4 \qquad (2)$$

these reactions are +37.0 and +6.1 kcal/mol, respectively.[12] Thus, these calculations indicate that replacement of H by CHO results in a much smaller destabilization than replacement of $CH_2$ by CO and suggest that CHO is comparable to CN (and different from

$CF_3$) in its ability to stabilize carbonium ions. This proposal can be subject to experimental tests, which will be awaited with interest.

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