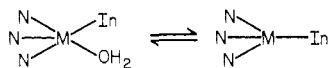data points out that the hydroxo species is the active one. Inhibitors of the enzyme that act as coordination ligands give rise to the general equilibrium



The importance of five-coordination is reflected on the catalytic pathway: indeed, five-coordinate intermediate species with bicarbonate bound, which have been detected, allow the detachment of bicarbonate through an equilibrium of the type of that shown above. Finally, the rapid OH⁻ exchange is accounted for by assuming the existence of an intermediate of the type
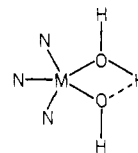
# Electron-Deficient Carbocations

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To refer to a carbocation as "electron deficient" may appear superfluous. Carbocations did not even gain respectability as organic intermediates until 1932,[1] and it was only with the advent of the direct observation of carbocations, particularly by the use of NMR in the early 1960's,[2] that these species became commonly studied as discrete entities in solution. However, they are now quite routinely examined and it is appropriate to consider gradations of stability.

What we consider as electron-deficient carbocations are those species, **1**, in which the substituent R is less



**1**

electron donating than hydrogen. The classification of substituents as to their electron-donating ability relative to hydrogen is well-known to organic chemists from their influence on electrophilic aromatic substitution. These are categorized in a qualitative fashion in all introductory textbooks in organic chemistry; most usually as ortho,para directing and activating (e.g., alkyl,

NR₂, OH, OR, O₂CR); ortho,para directing and deactivating (F, Cl, Br, I); and meta directing and deactivating (NO₂, NR₃⁺, SO₃H, CO₂R, COR, CF₃, and CN).[3]

The class of deactivators, but ortho,para directors, clearly reflects the operation of two effects, namely, inductive electron withdrawal and resonance electron donation. In fact, for fluorine, even though the inductive electron withdrawal due to electronegativity ought to be the greatest of any element, the compensating resonance donation (eq 1) is so strong that this
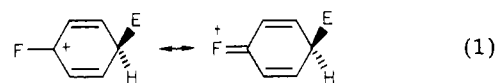
  (1)

group is frequently a net activator. Thus, the partial rate factors for electrophilic aromatic substitution in fluorobenzene range from 0.68 to 2.98,[4a] and the $\sigma_p^+$ constant for fluorine derived from cumyl chloride solvolysis is $-0.07$.[4b] The activating effect of fluorine is also manifested in aliphatic reactivity; for example, the rate ratio $k(\text{2-fluoropropene})/k(\text{propene})$ toward addition of trifluoroacetic acid via an intermediate carbocation is 71 (eq 2).[5]

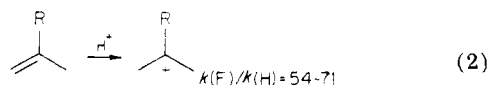(1) Whitmore, F. C. *J. Am. Chem. Soc.* **1932,** *54,* 3274–3283.
(2) (a) Olah, G. A.; Tolgyesi, W. S.; Kuhn, S. J.; Moffatt, M. E.; Bastier, I. J.; Baker, E. B. *J. Am. Chem. Soc.* **1963,** *85,* 1329–1334. (b) Deno, N. C.; Richey, H. G., Jr.; Hodge, J. D.; Wisotsky, M. J. *Ibid.* **1962,** *84,* 1498–1499.
(3) (a) Streitwieser, A., Jr.; Heathcock, C. H. "Introduction to Organic Chemistry", 2nd ed.; Macmillan: New York, 1981. (b) Pine, S. H.; Hendrickson, J. B.; Cram, D. J.; Hammond, G. S. "Organic Chemistry", 4th ed.; McGraw-Hill: New York, 1980. (c) Roberts, J. D.; Caserio, M. C. "Basic Principles of Organic Chemistry", 2nd ed.; W. A. Benjamin, Menlo Park, CA: 1977.
(4) (a) Stock, L. M.; Brown, H. C. *Adv. Phys. Org. Chem.* **1963,** *1,* 35–154. (b) Brown, H. C.; Okamoto, Y. *J. Am. Chem. Soc.* **1958,** *80,* 4979–4987.

$$(2)$$

The Brown–Hammett $\sigma^+$ parameters provide a useful quantitative measure of the electron-donating abilities of groups (eq 3) as conveniently derived from solvolysis

$$\log k = -4.54\sigma^+ - 3.91 \qquad (3)$$

rates of cumyl chlorides in 90% acetone at 25 °C (eq 4).



$$(4)$$
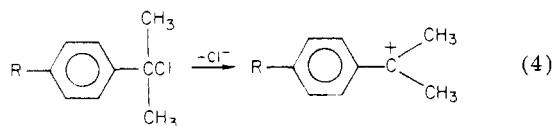
Efforts have been made to decrease the electron-donating ability of the aryl group in such reactions by placing one or more electron-withdrawing groups (R) on the ring. The most deactivated aryl groups that have been studied are the 3,5-bis(trifluromethyl)phenyl($\sigma^+$ = 1.04) and the 3,5-dichloro-4-cyanophenyl ($\sigma^+$ = 1.22);[6a] however, in relationships such as those of eq 5, derivatives substituted with these groups are still vastly more reactive than the corresponding hydrogen-substituted compounds.[6b–e]



$$(5)$$

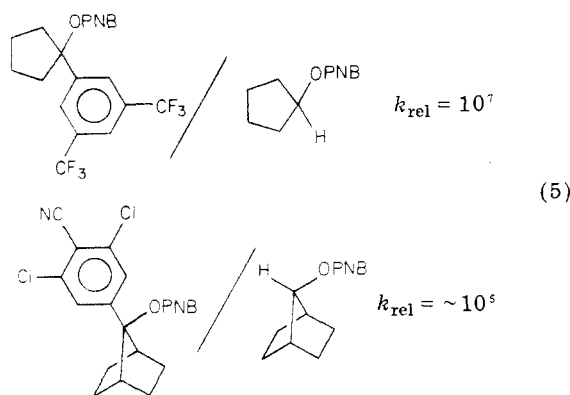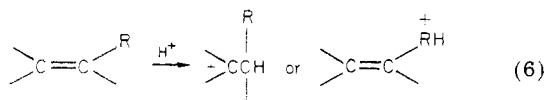Much more drastic effects should be observable if the phenyl group is excised and the substituent is attached directly to the center where the positive charge is generated. Previous studies along this line have included several 1,2-disubstituted alkenes bearing electron-withdrawing groups such as cyano or carbonyl.[7] However, in all these cases the compounds appeared to react with protonation either on the substituent or on the carbon bearing the substituent so that the positive charge in the intermediate was not generated $\alpha$ to the original substituent (eq 6). Thus, the substituents were



$$(6)$$

exercising a powerful directing effect, but their influence on the rate of generation of adjacent positive charge could not be evaluated.

Similarly, studies of electrophilic additions to alkenes substituted with a variety of electron-withdrawing groups (particularly halogens) with reagents such as halogens, sulfenyl halides, and others have been reported.[8] However, these reactions largely involve cycloadditions and other non-carbocation processes and do not allow quantitative measurements of the substituent effects on carbocation formation.

Better quantitative measurements of the effect of destabilizing groups on carbocation generation were found in studies of solvolysis of allylic systems. Thus, Poulter et al.[9] reported a high $CH_3/CF_3$ rate ratio in 2, and Harrington[10] found large $H/CF_3$ ratios in 3 and 4.
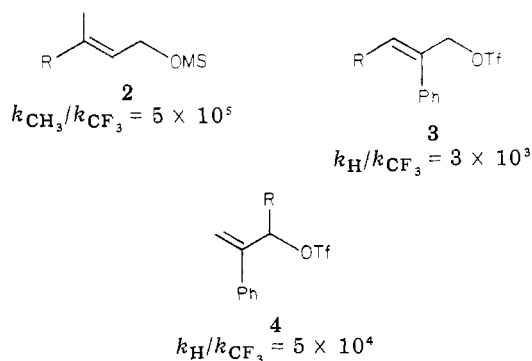


Evidently all of these systems reacted with formation of allylic cations that were strongly destabilized by the $CF_3$ group. An earlier[10b] study had revealed $CF_3CH$-(OBs)CH=CH$_2$ to be unreactive in 70% acetone at 50 °C.

In the norbornyl systems shown (eq 7[11] and 8[12]), large



$$k_{rel} = 4.0 \times 10^6 \qquad (7)$$



$$k_{rel} = 2.0 \times 10^7 \qquad (8)$$
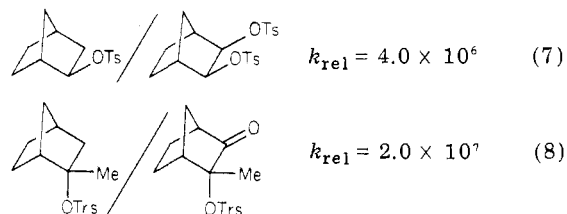
rate retardations due to $\alpha$-CHROTs and $\alpha$-RC=O groups were observed. In these systems, the reference substituent to which the electron-withdrawing group is being compared is $CH_2$, and because of the bicyclic nature of the substrates, comparison of these electron-withdrawing groups to hydrogen is not simple. There have also been many studies of the effect of electron-withdrawing substituents in other positions of the norbornyl ring system (eq 9).[13] These may be com-

(5) (a) Peterson, P. E.; Bopp, R. J. J. Am. Chem. Soc. 1967, 89, 1283–1284. (b) Allen, A. D.; Tidwell, T. T. Ibid. 1982, 104, 3145–3149.

(6) (a) Gassman, P. G.; Fentiman, A. F., Jr. Tetrahedron Lett. 1970, 1021–1024. (b) Peters, E. N.; Ravindranathan, M.; Brown, H. C. Aspects Mech. Organomet. Chem., Proc. Symp. 1978, 1–40. (c) Brown, H. C.; Ravindranathan, M.; Peters, E. N.; Gundu Rao, C.; Rho, M. M. J. Am. Chem. Soc. 1977, 99, 5373–5378. (d) Peters, E. N. Ibid. 1976, 98, 5627–5632. (e) Gassman, P. G.; Fentiman, A. F., Jr. Ibid. 1970, 92, 2549–2551.

(7) (a) Brynes, S. D.; Fedor, L. R. J. Org. Chem. 1979, 44, 1928–1931. (b) Jensen, J. L.; Carré, D. J. Ibid. 1974, 39, 2103–2107. (c) Noyce, D. S.; Jorgenson, M. J. Ibid. 1963, 28, 3208–3209. (d) Noyce, D. S.; Reed, W. L. J. Am. Chem. Soc. 1958, 80, 5539–5542. (e) Chiang, Y.; Kresge, A. J.; Young, C. I. Can. J. Chem. 1978, 56, 461–464.

(8) (a) Schmid, G. H.; Garratt, D. G. In "Chemistry of the Alkenes", Zabicky, J., Ed.; Wiley-Interscience: New York, 1977; Vol. 2, Suppl. A. (b) Bolton, R. In "Comprehensive Chemical Kinetics"; Banford, C. H., Tipper, C. F. H., Ed.; Elsevier: New York, 1973; Vol. 9.

(9) Poulter, C. D.; Rilling, H. C. Acc. Chem. Res. 1978, 11, 307–313. Poulter, C. D.; Satterwhite, D. M.; Rilling, H. C. J. Am. Chem. Soc. 1976, 98, 3376–3377.

(10) (a) Gassman, P. G.; Harrington, C. K., unpublished results. Harrington, C. K., Ph.D. Thesis, The Ohio State University, Columbus, OH, 1976; Diss. Abstr. 1976, 37, 2248B. (b) Pegalotti, J. A.; Young, W. G. J. Am. Chem. Soc. 1961, 83, 3251–3258.

(11) Lambert, J. B.; Mark, H. W.; Holcomb, A. G.; Magyar, E. S. Acc. Chem. Res. 1979, 12, 317–324.

(12) Creary, X. J. Org. Chem. 1979, 44, 3938–3945. For synthetic applications of $\alpha$-acylcarbocations, see Bégué, J.-P.; Charpentier-Morize, M. Acc. Chem. Res. 1980, 13, 207–212.

$$\text{(9)}$$



$$2 \times 10^3 \qquad \text{(10)}$$
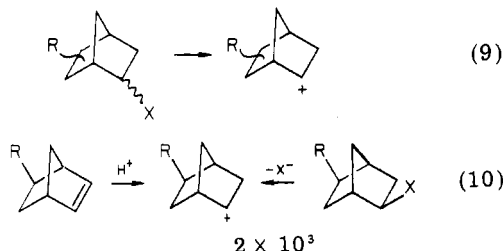
pared with the effect of electron-withdrawing substituents in the hydration of 5-substituted norbornenes,[14] as illustrated for the cyano group (eq 10).

Recently, we and others have been studying various manifestations of the effect of trifluoromethyl, cyano, carbonyl, and other groups on reactivity in alkene protonations and solvolysis by both experimental and theoretical means. Different aspects of this work are considered separately below.

Protonation of alkenes has been systematically elucidated,[15] and the reactivity of alkenes in acid-catalyzed hydration according to eq 11 has been correlated by eq



$$\text{(11)}$$

12 in which the $\sigma_p^+$ constants of the substituents were

$$\log k_{H^+} = -10.5 \textstyle\sum \sigma_p^+ - 8.92 \qquad \text{(12)}$$

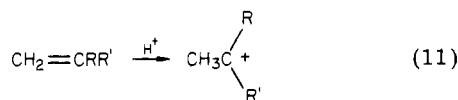used directly. This equation gives a reasonable account of the rates of all of the more than 110 known hydrations proceeding by eq 11. The least reactive alkene observed in this reaction was ethylene itself, and the question arose if an alkene even less reactive could be found. To answer this question, $\alpha$-(trifluoromethyl)-styrenes were studied,[16] and in reaction 13, rate ratios



$$\text{(13)}$$
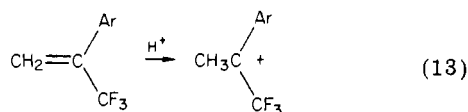
for Ar = *p*-Anis, *p*-Tol, Ph, *p*-ClC$_6$H$_4$, and *m*-ClC$_6$H$_4$ of approximately 10, 1, 0.1, 0.01, and 0.001 relative to ethylene were observed. Furthermore, the rates of these derivatives fit on an extension of the same correlation line of eq 12 that had already been published.[15] Thus, the reactivity of alkenes deactivated relative to ethylene could not only be studied but the entire family of all of the alkenes appeared to follow the same pattern of behavior.

Another aspect of the protonation described in eq 13 was the $\rho^+$ value of $-4.0$ for the rate dependence of this reaction on aryl substituents.[16] On the one hand this value is the most negative observed for a large family of protonations of styrenes (ArCR=CH$_2$) with different R groups. This is exactly the behavior predicted by the "reactivity–selectivity" principle, which requires greater

aryl substituent stabilization in a system of high electron demand, as illustrated by the observed rate ratio of $k[\text{PhCH}{=}\text{CH}_2]/k[\text{PhC(CF}_3){=}\text{CH}_2]$ of $10^7$. However, the value of $\rho^+$ of $-4.0$ is not of extraordinarily large magnitude for a carbocation reaction, and an even greater value might have been expected.

In a related recent study,[17] reduction of trifluoromethyl aryl ketones by NaBH$_4$ according to eq 14 was



$$\text{(14)}$$
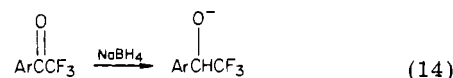
compared to the reduction of the corresponding acetophenones (ArCOCH$_3$). Such reductions have been taken to be inversely related to carbocation formation in solvolysis, in that the relatively positive sp$^2$ carbon in the ketone is converted to an sp$^3$ structure. Surprisingly, the data led to the conclusion[17] that "in the case of hydride addition, replacing the hydrogen atoms of the methyl group with fluorine atoms causes virtually no change in the transmission of ring effects to the reaction site". There was some scatter in the data in both systems, but it is clear that there is no notable operation of the reactivity–selectivity principle in this example, even though the trifluoromethyl ketones react faster than their methyl analogues by $10^5$.

Another method used[18] for the study of electrophilic substituent effects is a linear correlation between $\sigma^+$ for groups R and the carbonyl stretching frequencies of aryl ketones (RC$_6$H$_4$COCH$_3$), from which data[18] we calculate a slope of 11.7 (correlation coefficient 0.986). Stretching frequencies of 17 ketones (ArCOCF$_3$) were also reported,[17] and while the measurements were not made in a way to test for a linear correlation (some were measured as films, some in solution), nevertheless, a correlation is observed (slope = 24.2, $r = 0.93$). It is striking that the magnitude of this slope is double that of nonfluorinated acetophenones, indicating a strong effect of electron demand on the sensitivity of the carbonyl stretching frequency to substituent effects.

A test of eq 12 in a purely aliphatic system has now been made.[19] The alkene, 5, was found to undergo hydrolysis to acetic acid in 8–10 M H$_2$SO$_4$. The kinetic behavior was consistent with rate-limiting hydration on carbon as shown in eq 15, and the $k_{H^+}$ value is 1.13 $\times$



$$\text{(15)}$$

5
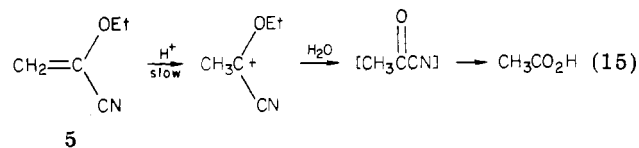
$10^{-7}$ M$^{-1}$ s$^{-1}$ at 25 °C, in remarkable agreement with the value of $0.73 \times 10^{-7}$ M$^{-1}$ s$^{-1}$ predicted from eq 12, using the $\sigma_p^+$ values of $-0.83$ for EtO[15] and 0.66 for CN.[4b] This result is considerably better than could be reasonably expected because of the various extrapolations involved in these comparisons but provides powerful confirmation of the utility of this approach.

## Solvolytic Studies

**The Trifluoromethyl Substituent.** Solvolytic studies of CF$_3$-substituted derivatives have been con-

(13) For leading references, see (a) Fischer, W.; Grob, C. A.; von Sprecher, G.; Waldner, A. *Helv. Chim. Acta* **1980**, *63*, 928–937. (b) Grob, C. A.; et al. *Tetrahedron Lett.* **1981**, *22*, 835–838, 1211–1214, 3231–3234. (c) Apeloig, Y.; Arad, D.; Lenoir, D.; Schleyer, P. v. R. *Ibid.* 879–882. (d) Gassman, P. G.; Marshall, J. L.; Macmillan, J. G.; Hornback, J. M. *J. Am. Chem. Soc.* **1969**, *91*, 4282–4284. (e) Grob, C. A. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 87–96. (f) Wilcox, C. F., Jr.; Tuszynski, W. J. *Tetrahedron Lett.* **1982**, *23*, 3119–3122.

(14) Lajunen, M.; Wiksten, P. *Finn. Chem. Lett.* **1980**, 17–20.

(15) Nowlan, V. J.; Tidwell, T. T. *Acc. Chem. Res.* **1977**, *10*, 252–258.

(16) Koshy, K. M.; Roy, D.; Tidwell, T. T. *J. Am. Chem. Soc.* **1979**, *101*, 357–363.

(17) Stewart, R.; Teo, K. C. *Can. J. Chem.* **1980**, *58*, 2491–2496.

(18) Traylor, T. G.; Ware, J. C. *J. Am. Chem. Soc.* **1967**, *89*, 2304–2316.

(19) Allen, A. D.; Shahidi, F.; Tidwell, T. T. *J. Am. Chem. Soc.* **1982**, *104*, 2516–2518. For a theoretical discussion of this hydration, see Paddon-Row, M. N.; Houk, K. N.; Tidwell, T. T. *Tetrahedron Lett.* **1982**, *23*, 383–386.
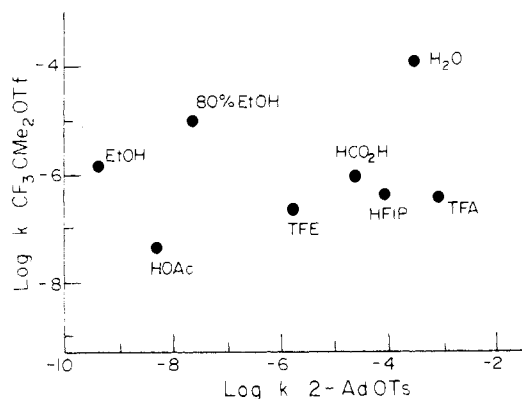
**Figure 1.** Effect of solvent on the reactivity of CF₃CMe₂OTF (6).



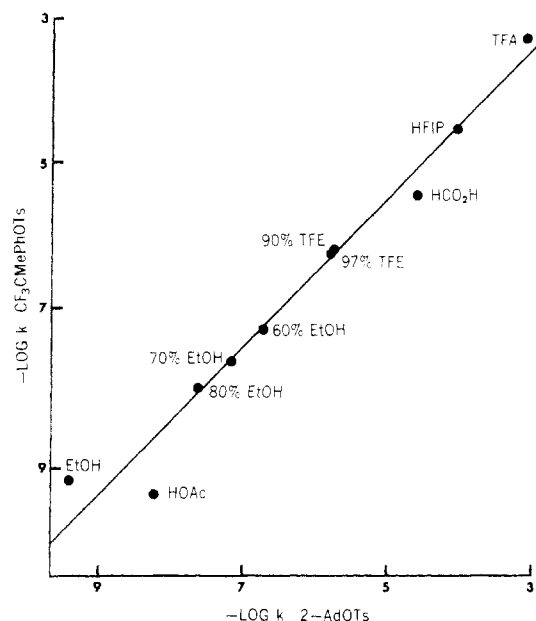**Figure 2.** Effect of solvent on the reactivity of CF₃CMeArOTs (7).

centrated on the substrates $CF_3CMe_2OTf$ (**6**)[20a,b] and $CF_3CMeArOTs$ (**7**).[20a,c,21] These systems show very high $H/CF_3$ rate ratios that vary between $10^5$ and $10^7$ depending on the solvent, but, interestingly, they react by quite different mechanisms. The most striking evidence for this is the dependence of the rates on solvent: with **6** there was no correlation of the rates with those of 2-adamantyl tosylate (2-AdOTs)(Figure 1), whereas with **7** (Ar = Ph) a good correlation was observed (Figure 2). 2-Adamantyl tosylate is the prototype of a system reacting by rate-limiting ionization to form a carbocation (eq 16),[22] and so the interpretation of these

$$\text{2-AdOTs} \xrightarrow[\text{slow}]{k_c} \text{2-Ad}^+ \text{ OTs}^- \xrightarrow{\text{fast}} \text{products} \quad (16)$$
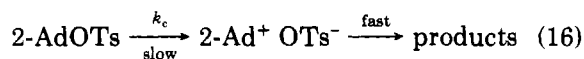
data is that **6** does not react by a route analogous to eq 16 but that **7** (Ar = Ph) does (eq 17). The available evidence indicates that **6** reacts by initial ionization to

(20) (a) Koshy, K. M.; Tidwell, T. T. *J. Am. Chem. Soc.* **1980**, *102*, 1216–1218. (b) Jansen, M. P.; Koshy, K. M.; Mangru, N. N.; Tidwell, T. T. *Ibid.* **1981**, *103*, 3863–3867. (c) Allen, A. D.; Jansen, M. P.; Koshy, K. M.; Mangru, N. N.; Tidwell, T. T. *Ibid.* **1982**, *104*, 207–211.

(21) (a) Liu, K.-T.; Sheu, C.-F. *Tetrahedron Lett.* **1980**, *21*, 4091–4094. (b) Liu, K.-T.; Kuo, M.-Y.; Sheu, C.-F. *J. Am. Chem. Soc.* **1982**, *104*, 211–215.

(22) Bentley, T. W.; Schleyer, P. v. R. *Adv. Phys. Org. Chem.* **1977**, *14*, 1–67.

(17)
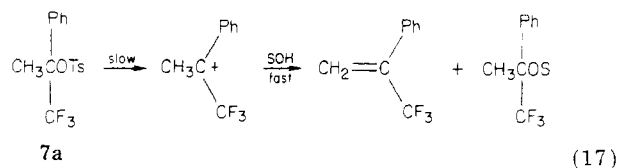
form an ion pair, and this undergoes rate-limiting elimination to give alkene as the only observed product (eq 18). Cation formation prior to, or during, the



(18)
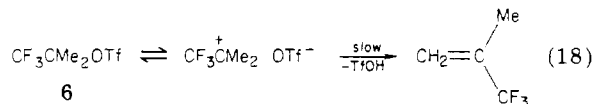
rate-limiting step for both **6** and **7a** is indicated by the $k(H)/k(CF_3)$ ratio of $10^5$–$10^7$. Confirmatory evidence for the mechanisms of eq 17 and 18 comes from the effects of salts: for **7a**, $NaClO_4$, NaCl, NaOAc, and $NaN_3$ all cause modest increases in rate (10–30% for 0.06 M salt), which are independent of the nature of the salt. This behavior parallels that of 2-AdOTs[23] and is expected for a $k_c$ process. On the other hand NaOAc and $NaN_3$ have much larger effects on the reactivity of **6** (a rate increase by a factor of 2.9 for 0.06 M salt) that parallel the acceleration induced for *i*-PrOTs.[23] Interestingly, this latter substrate is a model for processes involving nucleophilic participation by salt or solvent, whereas for **6** only alkene is formed, thus indicating a close parallel of the kinetic effects of salts acting as bases or as nucleophiles.

Structural isotope effects, $k(CH_3)/k(CD_3)$, are also consistent with paths 17 and 18. Thus, for **7a**, values around 1.3 were found in the more ionizing solvents, whereas values near 1.6 were found in the less ionizing solvents. The larger effects in the latter cases are as expected in a situation with less stabilization of the developing positive charge by solvent, resulting in a greater demand for hyperconjugative stabilization by the methyl group and, hence, a larger isotope effect.

For **6**, the isotope effect $k(CH_3)/k(CD_3)$ for deuteration of one of the methyl groups gave values of about 1.8 independent of the solvent; however, the effect for deuteration of both methyl groups was 3.8, showing that the isotope effect exceeded that for a cumulative effect $(1.8^2 = 3.2)$ and suggesting a primary isotope effect was significant. A rate/product correlation based on the extent of deuterium elimination in the alkene from 6-$d_3$ was consistent with this conclusion. A possible alternative explanation for the reaction of **6** is a direct elimination to give products without the intervention of an ionic intermediate. The large rate retardation by the $CF_3$ and the large secondary isotope effect both indicate that the transition state in such a process must have a large degree of positive charge development; thus, mechanism 18 appears to be a more direct interpretation of the data.

A detailed study of the solvolysis of a series of derivatives of $CF_3CMeArOTs$ (**7**) has also been reported by Liu and co-workers.[21] Although their initial report[21a] indicated that a mechanistic change may have occurred as a function of the aryl substituent, their latter studies[21b] failed to support this contention. For the system indicated, these workers observed a $mY_{OTs}$ plot with $m$ = 1.09 for the parent system.[22,24] This indicated a

(23) Raber, D. J.; Harris, J. M.; Hall, R. E.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1971**, *93*, 4821–4828.

### Table I
#### Comparative $\sigma_p^+$ and $\gamma^+$ Values

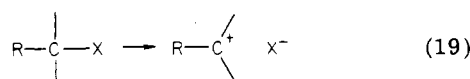| substit | $CF_3$ | H | Ph | Me | c-Pr | ferrocenyl | MeO |
|---|---|---|---|---|---|---|---|
| $\sigma_p^+$ | 0.61 | 0.0 | −0.18 | −0.31 | −0.47 | −0.7 | −0.78 |
| $\gamma^+$ | 3.7 | 2.56 | 0.0 | 0.63 | −0.68 | −1.4 | −1.4 |

rate-limiting ionization process (without solvent participation). A Hammett-Brown $\rho\sigma^+$ plot of the solvolytic data from the 1-aryl-1-(trifluoromethyl)ethyl tosylates in 80% ethanol (25 °C) gave a $\rho$ of −7.46. Omission of the p-methoxy derivative, which was extrapolated from the corresponding bromide, gave a $\rho$ of −6.85.

Secondary systems $ArCH(OTs)CF_3$ and $ArCH(OTf)_3$ have now been studied in a variety of solvents with different aryl substituents.[25a] For the tosylates, correlations with $\sigma^+$ values gave $\rho$ values of −6.7 to −12, depending upon the solvent, although only a limited number of substituents have been examined to date. Optically active $PhCH(OTf)CH_3$ reacted with racemization in highly ionizing trifluoroacetic acid in hexafluoropropan-2-ol, but with significant inversion in the strongly nucleophilic solvents ethanol and acetic acid. These results indicate rate-limiting cation formation in the less nucleophilic solvents, whereas in more nucleophilic but less ionizing solvents there is probably formation of an ion pair that undergoes substantial substitution by solvent with inversion of configuration.

Systems such as $Ar_2C(OTs)CF_3$ have been examined by Sneen and co-workers, who have obtained results comparable to some of those discussed above.[25b]
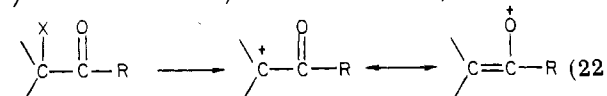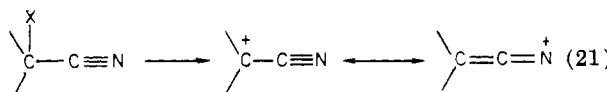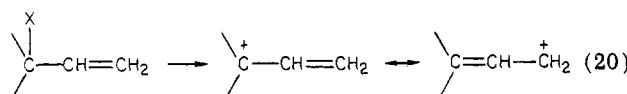
In an extension of these studies to even more destabilizing conditions, the substrate $PhC(CF_3)_2OTf$ was demonstrated to solvolyze in methanol at 60 °C via a carbocation bearing two electron-withdrawing trifluoromethyl groups.[25c] One of us (T.T.T.) is involved in a systematic study of these interesting systems.

**The Cyano Substituent.** While systems of the type shown in eq 19 are clearly dependent primarily on the

$$R\!-\!\overset{|}{\underset{|}{C}}\!-\!X \;\longrightarrow\; R\!-\!\overset{+}{C}\diagdown \quad X^- \tag{19}$$

inductive nature of R when R is $CF_3$, the situation is much more complex when R has either nonbonding or $\pi$-type electrons available for conjugative stabilization.

The series represented by eq 20–22 represent some

$$\overset{X}{\underset{\diagup}{\diagdown}}\overset{|}{C}\!-\!CH\!=\!CH_2 \;\longrightarrow\; \overset{+}{\underset{\diagup}{\diagdown}}C\!-\!CH\!=\!CH_2 \;\longleftrightarrow\; \overset{\diagdown}{\underset{\diagup}{\phantom{.}}}C\!=\!CH\!-\!\overset{+}{C}H_2 \tag{20}$$

$$\overset{X}{\underset{\diagup}{\diagdown}}\overset{|}{C}\!-\!C\!\equiv\!N \;\longrightarrow\; \overset{+}{\underset{\diagup}{\diagdown}}C\!-\!C\!\equiv\!N \;\longleftrightarrow\; \overset{\diagdown}{\underset{\diagup}{\phantom{.}}}C\!=\!C\!=\!\overset{+}{N} \tag{21}$$

$$\overset{X}{\underset{\diagup}{\diagdown}}\overset{|}{C}\!-\!\overset{O}{\overset{\|}{C}}\!-\!R \;\longrightarrow\; \overset{+}{\underset{\diagup}{\diagdown}}C\!-\!\overset{O}{\overset{\|}{C}}\!-\!R \;\longleftrightarrow\; \overset{\diagdown}{\underset{\diagup}{\phantom{.}}}C\!=\!C\!-\!R \tag{22}$$

of the possibilities that exist. It is well recognized that the vinyl group is extremely carbocation stabilizing even

though it is slightly electron-withdrawing relative to an alkyl group. What has only been recognized recently is that the cyano and carbonyl groups, while strongly electron withdrawing, are capable of considerable resonance stablization. In eq 20–22, the resonance structure on the right would be a carbocation, nitrenium ion,[26] and oxenium ion, respectively. Since the stability of these species should decrease in the order given, the balance between inductive destabilization and conjugative stabilization should differ for each of the systems.

The first of the strong electron-withdrawing groups, which also possessed conjugative possibilities, to be investigated in detail was the cyano group.[27] On the basis of the relatively large rate retardation observed for carbocation generation in the presence of a β-CN moiety,[27d,28] it had been generally assumed that extreme difficulty would be encountered in the generation of a carbocation with a directly attached cyano group. In addition, on the basis of the Taft polar substituent constants $[(\sigma^*_{N\equiv CCH_2} = 1.30)$, $(\sigma^*_{CF_3CH_2} = 0.92)$, and $(\sigma^*_{CH_3COCH_2} = 0.60)]$,[29] it might have been predicted that an α-cyano group would have a greater rate-retarding effect than either the α-trifluoromethyl or α-keto groups. For four different sets of H/β-CN rate ratios, the values were found to be $10^4$–$10^7$. When observations of H/α-CN rate ratios were compared for six different systems,[27a,c,d] the ratios were found to vary from 1.30 × $10^3$ to 5.15 × $10^3$.[30] Thus, it is evident that a β-cyano group is more rate retarding than an α-cyano group. This is clearly demonstrated by the relative rates of 8, 9, and 10.[27c]



|  | **8** | **9** | **10** |
|---|---|---|---|
| $k_{rel}$ | 1 | $10^{-3}$ | $10^{-5}$ |
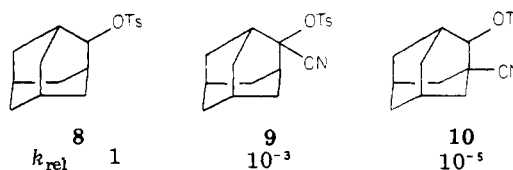
Since the α-cyano group is less rate retarding than would be expected on the basis of a purely inductive effect, a conjugative effect must be involved as indicated by eq 21. In systems where the charge is localized on a single carbon, extensive electron demand is placed on an α-cyano moiety and a considerable amount of charge delocalization to nitrogen occurs. For systems in which the other groups attached to the carbocation are unable to provide resonance stabilization, H/α-CN rate ratios

(24) Bentley, T. W.; Bowen, C. T.; Morten, D. H.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 5466–5475.

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(27) (a) Gassman, P. G.; Talley, J. J. *J. Am. Chem. Soc.* **1980**, *102*, 1214–1216. (b) *Ibid.* **1980**, *102*, 4138–4143. (c) Gassman, P. G.; Saito, K.; Talley, J. J. *Ibid.* **1980**, *102*, 7613–7615. (d) Gassman, P. G.; Saito, K. *Tetrahedron Lett.* **1981**, *22*, 1311–1314. (e) Gassman, P. G.; Talley, J. J. *Ibid.* **1981**, *22*, 5253–5256.

(28) (a) Muneyuki, R.; Yano, T. *J. Am. Chem. Soc.* **1970**, *92*, 746–748. Lenoir, D. *Tetrahedron Lett.* **1974**, 1563–1566. (b) Farcasiu, D. *J. Am. Chem. Soc.* **1976**, *98*, 5301–5305. (c) Farcasiu, D. *J. Org. Chem.* **1978**, *43*, 3878–3882.

(29) Taft, R. W. In "Steric Effects in Organic Chemistry"; Newman, M. S., Ed.; Wiley: New York, 1956; Chapter 13.

(30) Prof. P. Schleyer has recently informed us of an unpublished result for the solvolysis of acetone cyanohydrin tosylate that agrees quite well with our published rate data on this substrate.[27a] E. A. Hyson and P. Schleyer, unpublished results, 1971.

are approximately $10^3$. However, for systems in which the charge on the carbocation can be delocalized by neighboring group participation or by conjugation, the H/$\alpha$-CN rate ratios are much larger.[27b,e] *This demonstrates that the balance between inductive destabilization and conjugative stabilization by the cyano group is a function of the stability of the incipient carbocation.* For example, the H/$\alpha$-CN rate ratio for 11 is $10^6$.[27b]
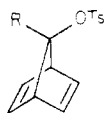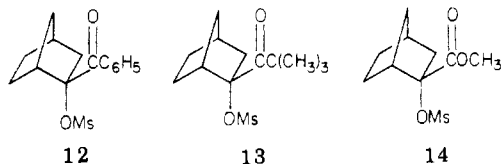


11

A Hammett–Brown $\rho\sigma^+$ study has been carried out for the $\alpha$-hydroxy-$\alpha$-methylbenzeneacetonitrile mesylates. A $\rho$ of $-6.70$ was obtained.[31] Both solvent capture and the formation of $\alpha$-cyanostyrenes were observed upon product analysis. The absence of a concerted elimination process was established through the observation of $k_{CH_3}/k_{CD_3} = 1.56$.[31] These results (eq 23)
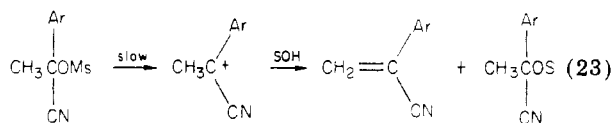


imply that there is only limited charge delocalization onto nitrogen when the charge on the carbocation can be delocalized into an aromatic ring. The linearity of the $\sigma\rho^+$ plot requires that the charge delocalization to the nitrogen of the cyano group involve a linear balance between inductive destabilization and conjugative stabilization *in this system.* Recent studies by Olah of substituted benzophenone cyanohydrins in superacid solutions at $-78\ ^\circ$C support the existence of such a linear balance.[32] However, it is difficult to ascertain the exact extent to which $^{15}$N NMR shifts are a measure of the amount of positive charge on nitrogen.

**The Carbonyl Substituent.** Detailed studies that permit a comparison of H/$\alpha$-carbonyl rate ratios have been reported only recently.[33] Results from the laboratory of Creary have provided unequivocal evidence for stabilization of the type shown in eq 22. Examination of systems 12–14 showed that, in comparison to



12    13    14

bicyclo[2.2.1]hept-*endo*-2-yl methanesulfonate, H/$\alpha$-carbonyl rate ratios were 8, 0.3, and 76, respectively. In each case extensive rearrangement of the bicyclic skeleton was observed. In spite of the extensive formation of rearrangement products, 12 and 13 exhibited

$mY_{OT_8}$ values of 0.77 and 0.69. These transition states clearly have considerable cationic character. It would appear that the $mY_{OT_8}$ values may be sensitive to other factors in the ionization of 12 and 13.

More definitive evidence was provided[33] by examples 15–18, where the H/$\alpha$-carbonyl rate ratios were 21, 13,



15    16

17    18

200, and 1.5, respectively.[34] A study of optically active 17 showed that the rate of racemization exceeded the rate of solvolysis in trifluoroacetic acid by a factor of 8.2. The use of trifluoroacetic acid-*O-d* gave no deuterium incorporation. Thus, no enolization was involved in the racemization step and ion-pair formation is indicated. Further support for the ion-pair concept was provided by an $mY_{OT_8}$ of 1.0. The $mY_{OT_8}$ for loss of methanesulfonate anion from 17 was 0.87. The various factors discussed above provide convincing evidence for the existence and relative ease of generation of $\alpha$-carbonyl-substituted carbocations.

**Theoretical Studies**

Considerable theoretical interest has been expressed in carbocations bearing $\alpha$-keto and $\alpha$-cyano groups.[19,35] In general, calculations resulting from a variety of different theoretical approaches are in reasonable agreement with each other, and, more importantly, with the experimental results. For instance, in the case of $\alpha$-cyano carbocations, the carbon–nitrogen bond distance is found to lengthen as the stability of the attached carbocation is decreased. At the same time, the C–C bond length of the carbocation–cyano bond is found to shorten. Analogous results are found for $\alpha$-carbonyl-substituted carbocations.

**Further Discussion**

The success of the correlation of protonation reactivities of alkenes by eq 12[15] leads to an interest in whether solvolytic reactivities as in eq 19 are also amenable to such a treatment. This approach was suggested some time ago by Traylor and Ware[18] and has been developed more recently by Peters[6c,36] and by Harris and McManus.[37] The term $\gamma^+$ has been adopted for the substituent parameter of the group R in eq 19, where $\gamma^+$ for phenyl is defined as 0.0 so that the $\gamma^+$ values of substituted aryl groups are the same as the $\sigma^+$ parameters of the substituents themselves. It has been found that there is a significant variation in the
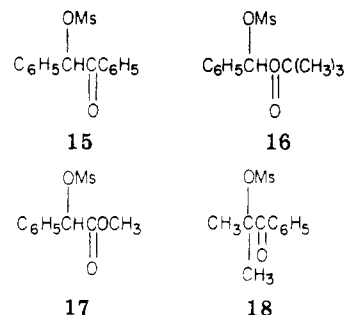
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(34) The relative rates for 15–17 were compared to that of the hydrogen analogue in hexafluoroisopropyl alcohol. Extrapolations from acetic acid were involved in the case of 16.

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(37) McManus, S. P.; Harris, J. M. *J. Org. Chem.* 1977, 42, 1422–1427.

values of $\gamma^+$ for particular substituents according to the substrate used in eq 19, but, nevertheless, it appears that these parameters will be quite useful in the interpretation of reaction mechanisms. Only a small portion of the development work needed to establish the limits of this correlation has been done, but some of the comparative data available at this early stage are listed in Table I.

When a similar calculation of $\gamma^+$ for the cyano moiety ($\sigma_p^+ = 0.66$) was carried out for five different systems, values of 2.77, 3.14, 3.26, 3.49, and 4.00 were obtained.[19] The most likely explanation of this relatively large variation in $\gamma^+$ is that the balance that exists between inductive destabilization and mesomeric stabilization for the cyano group is a function of the stability of the incipient carbocation. As a result, there is no single value for $\gamma^+$ that would fit all situations. A similar circumstance should exist for the $\alpha$-carbonyl group.

The results discussed above are relevant to several important recent studies of solvolysis theory. Bentley et al. have carefully examined the rate dependence on solvent of many solvolytic reactions and have concluded that relatively few (but including 2-AdOTs and **7a**) react by $k_c$ routes.[24] Other systems such as cyclooctyl and *endo*-norbornyl tosylates that have been claimed to react by $k_c$ processes are proposed by the authors to react with solvent participation.[24] The value of ^{18}O-labeling studies has been demonstrated again by Paradisi and Bunnett,[38] who have shown that, even in 2-adamantyl benzenesulfonate solvolysis, scrambling of the [18]O label occurs during solvolysis (eq 24). One

$$2\text{-AdOSC}_6\text{H}_5 \rightleftharpoons 2\text{-Ad}^{18}\text{OSC}_6\text{H}_5 \qquad (24)$$
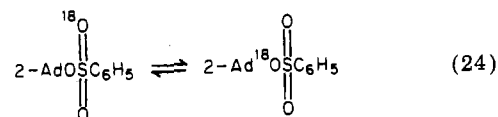
interpretation of this result is that reversible formation of an ion pair occurs before the rate-limiting step in this solvolysis. Finally, there is the conclusion of Knier and Jencks[39] that even typical secondary cations are not sufficiently stable in the presence of "reasonably good nucleophiles" to form intimate ion pairs but must react through one-step processes. It appears certain that further study of destabilized carbocations will be a powerful tool for the clarification of these new theories of carbocation behavior.

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# Catalysis of Photochemical Reactions

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"The process resembles the creation of a work of art, which is firmly guided by the final whole even though the whole can be definitely conceived only in terms of its yet undiscovered particulars".[1]

There is no reason why a reaction originating in an excited state cannot be catalyzed. Catalysis of ground-state reactions, both homogeneous and heterogeneous, is of course a well-developed concept; it enables us to explain many natural phenomena[2] and has fostered chemical changes of commercial value.[3] Perhaps owing to the lack of a clear definition, catalysis of excited-state reactions has not emerged as an identifiable field of study, despite significant activity in this and related areas and conspicuous progress in understanding of photochemical reaction mechanisms.[4] In this Account we propose a definition of a catalyst of a photochemical reaction and examine and classify according to the definition a variety of reported acceleratory phenomena for photochemical reactions.

Chemists have applied a bewildering assortment of terms to reactions exhibiting enhanced quantum yields, examples of which include catalyzed, sensitized, promoted, accelerated, enhanced, stimulated, protonated, induced, and assisted. These words are often joined to the words light or photo or to a word designating a substance. The manifest lack of clear terminology in this area indicates that the chemistry being reported has outstripped the conceptual basis for describing it and that some new attention to definitions is needed. This Account is prompted by that recognition and by the conviction that a new phenomenon clearly recognizable as homogeneous catalysis in photochemistry is

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