Nemours Co. for providing us with a sample of the crown compound.
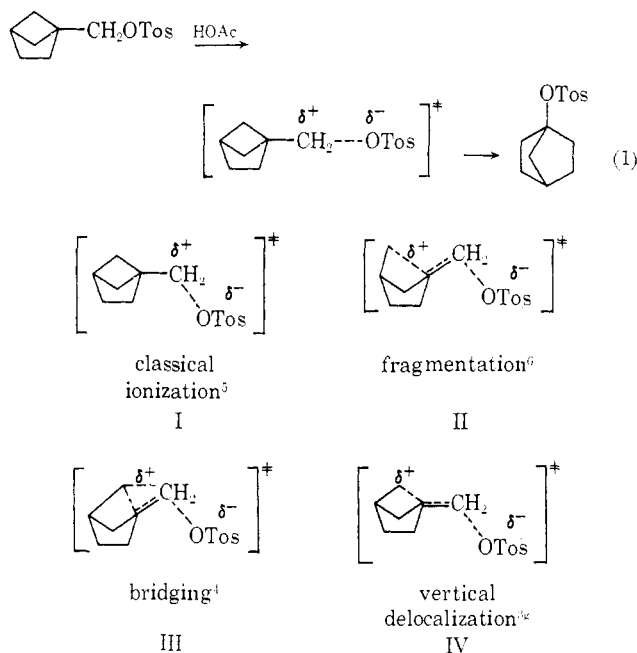
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Vertical Stabilization of Cations by Delocalization of Strained σ Bonds[1-3]

Sir:

We wish to report a successful demonstration that strained σ bonds can supply electrons by delocalization and that this delocalization is a "vertical"[3a,g] $\sigma-\pi$ conjugation in the systems studied.

Of the various concepts which might be applicable to the solvolysis of alkyl systems, as illustrated below for 1-[2.1.1]bicyclohexylmethyl tosylate (eq 1),

classical ionization[5]
I

fragmentation[6]
II

bridging[4]
III

vertical delocalization[3g]
IV

two kinds of differentiation are evident. First, I postulates no σ-bond delocalization and thus differs from II, III, and IV. Second, IV differs from II and III

because both II and III require nuclear movement in the strained system and can therefore be classified as "nonvertical stabilizations."[3a,g]

The recent development of quantitative correlations between solvolysis rates and ionization potentials[3g] makes possible both kinds of differentiations and allows us to decide which of the four concepts most accurately describes transition states for RCH_2X solvolyses. We here compare the relative rates of solvolysis of RCH_2X (*e.g.*, reaction 1) with the charge-transfer frequencies of the RC_6H_5–tetracyanoethylene (TCNE) complex (*e.g.*, reaction 2). In both cases some positive charge is created α to a strained bond. However, the process

TCNE   TCNE⁻
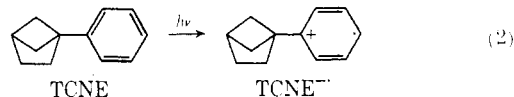
(eq 2) is vertical. If the classical mechanism (I) were applicable and the solvolysis (eq 1) were faster than solvolysis of neopentyl tosylate because of steric effects, then the charge-transfer frequency should increase with increasing strain in R of RC_6H_5 because the increasing s character in the R–C bond causes inductive electron withdrawal.[7,8] If mechanism IV were important then the frequency should decrease with increasing strain.[3g,9] However the contribution to rate acceleration from bond stretching (fragmentation) or bond making (bridging) would not be detected in the vertical process (eq 2). For this reason, a good correlation between reactions 1 and 2 is an implication[10a] that neither II nor III is very important in reaction 1.[10b]

We list the charge-transfer frequencies of a series of RC_6H_5 along with relative rates of solvolysis of RCH_2X in Table I and plot the data in Figure 1.

Considering that Figure 1 plots the solvolysis rates for alkyl derivatives (RCH_2X) against essentially the aromatic σ^+ substituent constants[3g] and that the relative rates span about 10^8, the correlation is remarkably good.[13] This correlation implies that acceleration of the reaction (eq 1) is primarily due to a vertical electronic effect involving $\sigma-\pi$ conjugation of one or more of the strained bonds. Strained or polarized[3] σ bonds

(1) Supported by the Air Force Office of Scientific Research, Grant No. AFOSR-69-1639. Some of the precursors used were synthesized for other purposes under Army Office of Ordnance Research, Durham, Grant No. DAHC-44-69-3-0060.

(2) Some of this work was presented at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, Abstract No. P 39.

(3) (a) The term "vertical stabilization" is defined as that stabilization which the group R supplies to a cation, $R-C^+R_2'$, or radical, $R\dot{C}R_2'$ (or the corresponding transition states), without any nuclear movement within the group R. This effect is discussed in more detail in ref 3g. Previous papers dealing with this subject are the following: (b) J. C. Ware and T. G. Traylor, *Tetrahedron Lett.*, 1295 (1965); (c) T. G. Traylor and J. C. Ware, *J. Amer. Chem. Soc.*, **89**, 2304 (1967); (d) T. T. Tidwell and T. G. Traylor, *ibid.*, **88**, 3442 (1966); (e) W. Hanstein and T. G. Traylor, *Tetrahedron Lett.*, 4451 (1967); (f) J. A. Mangravite and T. G. Traylor, *ibid.*, 4457 (1967); (g) W. Hanstein, H. J. Berwin, and T. G. Traylor, *J. Amer. Chem. Soc.*, **92**, 829 (1970).

(4) S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber, and J. Corse, *ibid.*, **74**, 1113 (1952). See footnote 19.

(5) (a) H. C. Brown, *Chem. Brit.*, **2**, 199 (1966); (b) H. C. Brown, *Chem. Soc., Spec. Publ.*, **16**, 140 (1962).

(6) C. A. Grob and F. Ostermayer, *Helv. Chim. Acta*, **45**, 1119 (1962).

(7) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965, p 48.

(8) R. A. Alden, J. Kraut, and T. G. Traylor, *J. Amer. Chem. Soc.*, **90**, 74 (1968).

(9) M. J. S. Dewar and S. D. Worley, *J. Chem. Phys.*, **50**, 654 (1969), observed that strained hydrocarbons have lower ionization potentials than their unstrained isomers and it follows that strained σ bonds are therefore more delocalizable than unstrained σ bonds.

(10) (a) But as a referee has pointed out, certainly not a proof, because our correlation could result from a proportionality between a nonvertical stabilization in solvolyses and a vertical charge-transfer stabilization. However the size of the vertical stabilization by strained bonds makes it quite clear that a large fraction of total acceleration in these solvolyses is available without nuclear movement. (b) This implication is made stronger if it is assumed that the cyclopropyl group provides vertical stabilization. References 11 and 12 summarize a plethora of evidence that this is probably true.

(11) (a) R. C. Hahn, T. F. Corbin, and H. Shechter, Abstracts, 139th National Meeting of the American Chemical Society, St. Louis, Mo., March 1961, p 35-O; (b) R. C. Hahn, T. F. Corbin, and H. Shechter, *J. Amer. Chem. Soc.*, **90**, 3404 (1968).

(12) E. Kosower, "An Introduction to Physical Organic Chemistry," Wiley, New York, N. Y., 1968, p 111.

(13) This correlation also suggests a simple means of predicting relative solvolysis rates. For instance, we believe that we can guess the rate of solvolysis of $RR'CHX$ fairly accurately from the color of the TCNE complex with $RR'C=C(CH_3)_2$. This prediction will, of course, fail where nonvertical acceleration is important. Notice the very large rate predicted for homocubylcarbinyl derivatives.

Table I. Charge-Transfer Frequencies for RC_6H_5 with Tetracyanoethylene $(TCNE)^{a,b}$ Compared with Relative Rates of Solvolysis of RCH_2X

	R^c	λ, nm	ν, cm$^{-1} \times 10^{-3}$	$k_{rel}{}^d$	log k_{rel}	$\sigma_R{}^+$
1	*tert*-Bu	438^e	22.8	1	0	~-0.3
2		450	22	8^g	0.9	~-0.4
3		465	21.5	190^h	2.28	-0.5
4		475	21	$5 \times 10^{4\ d}$	4.7	-0.54
5		485	20.6			-0.60
6		505	19.8	$1.1 \times 10^{7\ k}$	7.04	-0.69
7		510	19.6	$3 \times 10^{7\ l}$	7.48	-0.71
8		520	19.2			-0.75

^{a} Solvent CH_2Cl_2, room temperature. ^{b} The longer wavelength maxima are broad and overlap the second maxima. This makes the determination of λ_{max} rather inaccurate for shorter wavelengths (<450 nm) where the peaks do not separate. We will determine ionization potentials in other ways to determine these numbers more accurately. ^{c} Compounds were synthesized in several ways. Either the immediate precursor or the compound itself was identified with known structures. For example, phenylhomocubane was prepared from the perester of homocubanecarboxylic acid and benzene. All compounds have nmr and ir spectra consistent with assigned structures. ^{d} Most of the relative rate data shown here are from a tabulation of W. G. Dauben, J. L. Chitwood, and K. V. Scherer, Jr., *J. Amer. Chem. Soc.*, **90**, 1014 (1968). ^{e} Obtained by estimation from the band width and from a plot of charge-transfer maxima against ionization potentials. ^{f} Prepared from perester and benzene. ^{g} R. L. Bixler and C. Niemann, *J. Org. Chem.*, **23**, 742 (1958). ^{h} K. B. Wiberg and B. R. Lowry, *J. Amer. Chem. Soc.*, **85**, 3188 (1963). The phenyl derivative has a 5,5-dimethyl substitution. ^{i} See ref 3g. ^{j} Yu. S. Shabarov, T. P. Surikova, E. G. Treschova, and R. Ya. Levina, *Vestn. Mosk. Univ. Khim.*, **22** (2), 79 (1967); *Chem. Abstr.*, **68**, 21607 (1967). ^{k} P. von R. Schleyer and G. W. Van Dine, *J. Amer. Chem. Soc.*, **88**, 2321 (1966). ^{l} W. D. Closson and G. T. Kwiatkowski, *Tetrahedron*, **21**, 2779 (1965). ^{m} We are grateful to Dr. Alexander Sieber, who prepared homocubanecarboxylic acid for another project.

can therefore afford enormous stabilization of neighboring cations without any change in the structure of R to "relieve the strain."[14]

product (3)
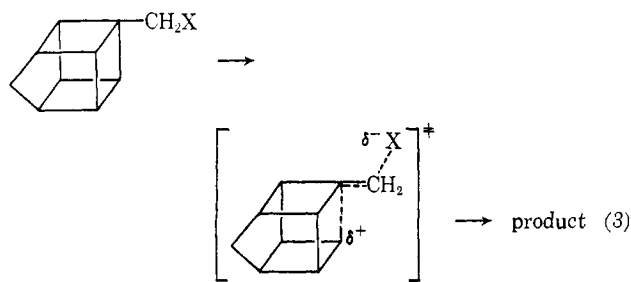
(14) Norbornyl groups were observed to accelerate electrophilic aromatic substitution by Tanida and Muneyuki[15] and by Jensen and Smart.[16] These rather small effects were attributed at least in part to delocalization. The present results confirm that the σ-bond participation[15] or hyperconjugation[16] discussed by these authors is a vertical stabilization similar to that of C–metal bonds.[3]

(15) H. Tanida and R. Muneyuki, *J. Amer. Chem. Soc.*, **87**, 4794 (1965).

(16) F. R. Jensen and B. F. Smart, *ibid.*, **91**, 5686 (1969).
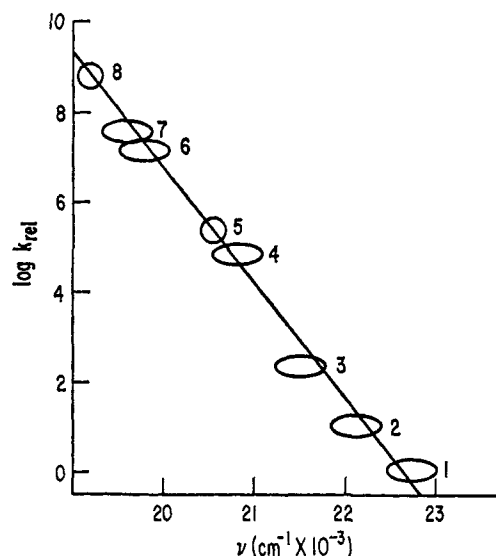
Figure 1. A plot of log relative solvolysis rates of RCH_2X against the longer wavelength charge-transfer frequencies of the complexes $RC_6H_5 \cdot$ tetracyanoethylene: ◯, experimental points; ◯, rates predicted from this plot.

A reinterpretation of many nonclassical accelerations as vertical[17] accelerations might also clarify many puzzling and apparently contradictory observations such as effects of substituents on norbornyl tosylate[18,19] or cyclopropylcarbinyl tosylate[20] solvolyses, the isotope effects *vs.* stereochemistry in neopentyl tosylate solvolyses,[21] etc. These will be discussed in a full report.

From these studies we draw two conclusions of significance to carbonium ion chemistry. (1) A carbonium ion generated α to a strained σ bond is delocalized (nonclassical) in proportion to the strain. There are no "classical"[5] carbonium ions having such strain. (2) The stabilization may be vertical or near-vertical and thus probes for migration to differentiate classical from nonclassical behavior may be inconclusive.

Although the primary tosylates discussed here appear to solvolyze with very nearly "vertical" acceleration,[11,12,25] *exo*-norbornyl tosylate seems to be accelerated at least in part by nonvertical stabiliza-

(17) Vertical, σ–π conjugation is, nevertheless, nonclassical. See ref 4.

(18) P. von R. Schleyer and D. C. Kleinfelter, Abstracts, 138th National Meeting of the American Chemical Society, New York, N. Y., Sept 1960, p 43P.

(19) J. W. Wilt and W. J. Wagner, *J. Amer. Chem. Soc.*, **90**, 6135 (1968).

(20) G. C. Robinson, *J. Org. Chem.*, **34**, 2517 (1969).

(21) In particular, the absence of CD_3 isotope effects[22,23] demands no migration whereas retention of configuration[24] seems to require bridging. But σ–π conjugation accommodates both of these observations.

(22) W. M. Schubert and P. H. LeFevre, *J. Amer. Chem. Soc.*, **91**, 7747 (1969).

(23) V. J. Shiner, Jr., R. D. Fisher, and W. Dowd, *ibid.*, **91**, 7748 (1969).

(24) (a) S. H. Liggero, R. Sustmann, and P. von R. Schleyer, *ibid.*, **91**, 4571 (1969); (b) J. E. Nordlander, S. P. Jindal, P. von R. Schleyer, R. C. Fort, Jr., J. J. Harper, and R. D. Nicholas, *ibid.*, **88**, 4475 (1966).

(25) S. Borčic, M. Nikoletic, and D. E. Sunko, *ibid.*, **84**, 1615 (1962). The inverse γ-isotope effect observed in cyclopropylcarbinyl tosylate solvolysis should be contrasted to the $(k_H/k_D)_\gamma = 1.10$ for *exo*-norbornyl tosylate solvolysis.[26,27] The latter result is difficult to explain in terms of vertical stabilization whereas no isotope effect or an inverse effect (inductive D effect) is consistent with vertical stabilization.

(26) B. L. Murr, A. Nickon, T. D. Swartz, and N. H. Werstiuk, *ibid.*, **89**, 1730 (1967).

(27) J. M. Jerkunica, S. Borčic, and D. E. Sunko, *ibid.*, **89**, 1732 (1967).

tion.[26,27] We hope to determine the extent of non-vertical acceleration in *exo*-norbornyl tosylate solvolysis by studying the ionization potentials of the appropriate structures.

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A Novel Vanadyl Pyrophosphate Trimer

Sir:

We wish to report the observation by esr spectroscopy and the preliminary characterization of a unique vanadium(IV) species: an anionic vanadyl pyrophosphate trimer.

The pH titration of a solution 0.02 M in $VO(ClO_4)_2$, 0.02 M in $Na_4P_2O_7$, 0.4 M in $NaClO_4$, and initially containing an excess of perchloric acid shows a sharp break at the point where all of the added acid has been titrated; see Figure 1. Thus, at the equivalence point,
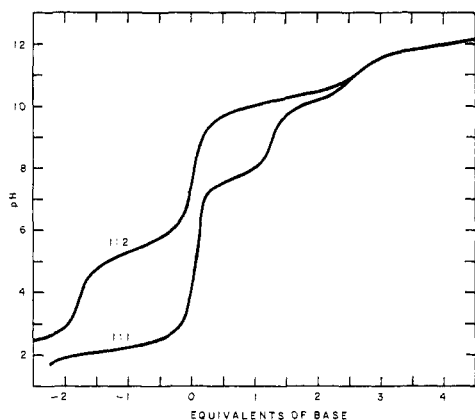

Figure 1. pH titration curve for the 1:1 and 1:2 VO^{2+}-$P_2O_7^{4-}$ solutions. Excess acid was added to the solutions to lower the initial pH to the desired value. The negative equivalents refer to the base needed to neutralize the excess acid added.

there are no protons remaining on pyrophosphate ions and all the pyrophosphates are bound in the complex. The esr spectrum at pH 1 shows the characteristic eight-line hyperfine spectrum due to interaction of the unpaired electron with the ^{51}V nucleus ($I = 7/2$), $a^V = 116$ G, $g = 1.965$, and is indistinguishable from that of the aquovanadyl ion. As base is added to the solution up to pH 2, the same eight-line spectrum persists. Above pH 2, the intensity of the original eight lines decreases and additional lines appear. To a first approximation, two new lines grow up between each pair of the original lines. At pH 5 the esr spectrum appears as in Figure 2. Twenty-two hyperfine lines are observed with intensity ratios very close to the expected ratios (1:3:6:10:15:21:28:36:42:46:48:48:46:42:...) for the interaction of an unpaired electron with three equivalent vanadium nuclei. The hyperfine splitting constant is 37 G, approximately one-third
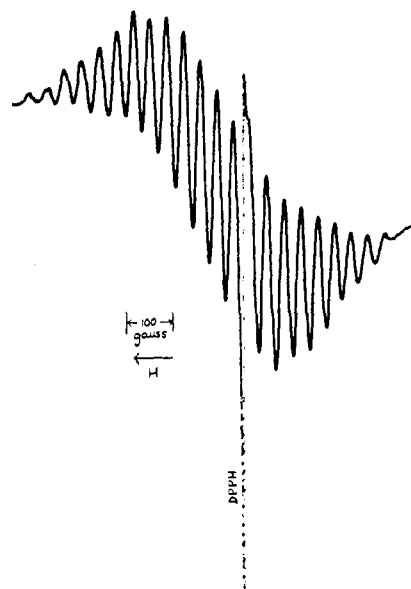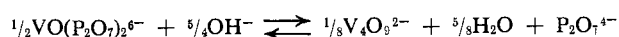

Figure 2. Esr spectra of $Na_6(VO)_3(P_2O_7)_3 \cdot 18H_2O$. The first derivative is plotted.

the usual splitting for monomeric vanadyl complexes; the g value is 1.964, very nearly the same as in the case of the aquo ion. As the titration is continued beyond pH 6, the 22-line spectrum decreases in intensity as a new eight-line spectrum grows up until, at pH 9, the trimer spectrum is gone and only a monomer spectrum is present with $a^V = 106$ G, $g = 1.965$. Addition of further base causes a decrease in the intensity of the esr spectrum, and at or above pH 11, no esr signal can be detected. The equilibria responsible for the buffer regions of pH 7–8 and pH 9.5–10.5 are, from the stoichiometry: (1) disproportionation of the vanadyl trimer to a monomeric vanadyl pyrophosphate (1:2) complex and an anionic vanadium(IV) species, perhaps $V_4O_9^{2-}$

$$1/3(VO)_3(P_2O_7)_3^{6-} + 5/4OH^- \rightleftarrows$$
$$1/2VO(P_2O_7)_2^{6-} + 1/8V_4O_9^{2-} + 5/8H_2O$$
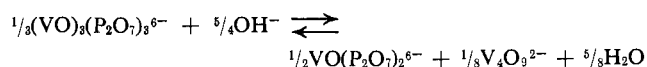
and (2) base hydrolysis of the 2:1 complex to give $V_4O_9^{2-}$

$$1/2VO(P_2O_7)_2^{6-} + 5/4OH^- \rightleftarrows 1/8V_4O_9^{2-} + 5/8H_2O + P_2O_7^{4-}$$

The above interpretation is supported by the results of a pH titration and esr spectra of a solution 0.02 M in $VO(ClO_4)_2$ and 0.04 M in $Na_4P_2O_7$. The titration curve is shown in Figure 1. From the esr spectra, we find that the dominant species at the first break in the titration curve (pH 3.8) is the trimer mentioned above. In the buffer region, pH 4.5–6.5, the trimer is in equilibrium with the high-pH monomer ($a^V = 108$ G) which is dominant at the second break (pH 8). Again, between pH 9.5 and 10.5, the esr spectrum decreases in intensity and is gone at pH 11. Further support is given by the appearance of the characteristic brownish-yellow color of $V_4O_9^{2-}$ in the 1:2 solutions above pH 10. The 1:1 solutions turned brown beginning around pH 7.5.

Addition of ethanol to a solution containing $VO(ClO_4)_2$ and $Na_4P_2O_7$ (1:1) at pH 6 causes precipitation of a greenish-gray solid which we believe to be $Na_6(VO)_3(P_2O_7)_3 \cdot 18H_2O$. *Anal.* Calcd. for $Na_6(VO)_3(P_2O_7)_3 \cdot 18H_2O$: V, 12.8; P, 15.7; Na, 11.7; H, 3.0.