cluding anomalous dispersion effects.[15] The value at the present time for the conventional R factor, $\Sigma||F_o| - |F_c||/\Sigma|F_o|$, is 0.063, and the error in an observation of unit weight, $[\Sigma w(|F_o| - |F_c|)^2/(NO - NV)]^{1/2}$, is 3.11. The only peculiarity in the location of any of the atoms in the cell concerns the water molecules of hydration which occur in a set of half-occupied eightfold general positions.

A view of the structure of the oxo-bridged dimer, $[(NH_3)_5Cr\text{-}O\text{-}Cr(NH_3)_5]^{4+}$, in the crystal is shown in Figure 1. Significant structural features of the complex are a linear (180°) Cr–O–Cr′ bond angle, an eclipsed configuration (required by symmetry) of the two pentaammine units, and a rather short Cr–O bond distance of 1.821 ± 0.003 Å. The Cr–Cr distance is 3.642 ± 0.001 Å. These features are entirely consistent with the weak paramagnetism of the complex,[11–13] which can imply either a strong antiferromagnetic superexchange coupling of the three unpaired electrons on each chromium ion center ($J/k > 200°$) or, alternatively, a pairing of chromium electrons through the formation of a system of π molecular orbitals involving the Cr dπ and bridging O pπ orbitals. In either description, the coupling is enhanced by the linear configuration of the three atoms. The Cr–N distances in the complex range from 2.098 to 2.136 Å (with esd's of ±0.010 Å) and do not reflect any significant trans influence from the implied strong Cr–O bridge bond. This seems surprising in view of the kinetic evidence,[6,16] which shows this complex to rapidly lose an ammonia ligand to form the basic erythro complex (see diagram above), thus suggesting strong activation of one of the ammine ligands.

In contrast to the oxo-bridged species, the binuclear acid rhodo, acid erythro, and basic erythro complexes, which presumably contain a bridging hydroxo ligand, exhibit electronic spectral and magnetic properties characteristic of weakly interacting mononuclear species.[10–14] We have examined crystallographically the acid rhodo salts $[(NH_3)_5Cr(OH)Cr(NH_3)_5]Cl_5 \cdot xH_2O$, where x = 1 or 3, and the acid erythro salts $[(NH_3)_5Cr(OH)Cr(NH_3)_4(H_2O)]X_5 \cdot H_2O$, where X = Cl or Br. Each of these has presented some insurmountable difficulty to a complete structural solution. To date the maximum information has been obtained from the acid erythro chloride salt which grows as large, red, twinned orthorhombic plates. The cell information and probable space group are a = 17.702 (9), b = 10.698 (7), c = 10.522 (7) Å, $D_2^5\text{-}C222_1$, $Z = 4$, D_m = 1.61, D_c = 1.630 g cm^{-3}. In the crystal the dimeric complex has a disordered orientation with respect to one of the twofold axes of the cell, and we have been unable to refine the structure below an R factor of 0.29. However, even at this stage two structural features are clear: (1) the $[(NH_3)_5Cr(OH)Cr(NH_3)_4(H_2O)]^{5+}$ cation has a bent Cr–O–Cr linkage with an exceptionally strained angle of 168 ± 5°; (2) the Cr–Cr distance of 3.91 ± 0.05 Å is significantly increased compared to that of the oxo-bridged dimer. In two recent structural determinations[17,18] of hydroxo-bridged tetranuclear chromium(III) complexes, the largest Cr–O–Cr bridge angle found was 133°; however, these were dihydroxo-bridged species. A more reasonable analog to the single-bridged dimer would probably be the μ-amido-bis(pentaamminecobalt(III)) ion which also has the rather strained bridge angle, Co–N–Co, of 153°.[19]

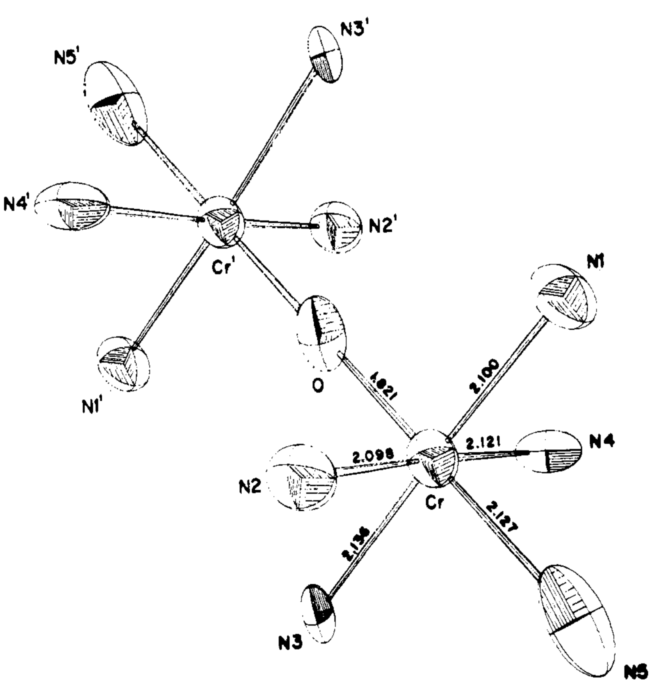

Figure 1. A view of the $[(NH_3)_5CrOCr(NH_3)_5]^{4+}$ cation. The atoms are represented by ellipsoids whose principal axes and sizes were derived from the final values of the anisotropic temperature parameters. Independent distances between bonded atoms are indicated in ångströms. Values for bond angles not shown are 180.0° for Cr-O-Cr′, 179.4° for O-Cr-N$_5$, and range from 90.8 to 92.6° for O-Cr-N$_{1-4}$. (Esd's of distances are ±0.010 Å, and for angles, ±0.4°, except for Cr-O-Cr′ which is symmetry determined.)

In order to strengthen these preliminary findings, we are presently examining other salts of these complexes in hopes of obtaining more suitable crystals.[20]

Acknowledgment. The partial support of this work by the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

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[15] Calculated and observed structure factors are deposited as Document No. NAPS-01345 with the ASIS National Auxilliary Publication Service, c/o CCM Information Corp., 909 3rd Ave., New York, N. Y. 10022. A copy may be secured by citing the document number and by remitting \$2.00 for microfiche and \$5.00 for photocopies.

[16] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, p 177.

[17] E. Bang, *Acta Chem. Scand.*, **22**, 2671 (1968).

[18] M. T. Flood, R. E. Marsh, and H. B. Gray, *J. Amer. Chem. Soc.*, **91**, 193 (1969).

[19] W. D. Schaeffer, A. W. Cordes, and R. E. Marsh, *Acta Crystallogr., Sect. B*, **24**, 283 (1968).

[20] NOTE ADDED IN PROOF. Since this paper was submitted, a report [A. Urushiyama, T. Nomura, and M. Nakahara, *Bull. Chem. Soc. Jap.*, **43**, 3971 (1970)] of a similar structural investigation of these complexes has appeared. The results of the above authors on the oxo-bridged, basic rhodo complex are in essential agreement with those we report here. In addition, however, they were able to refine the structure of a salt of the hydroxo-bridged, acid rhodo complex to a greater extent than we achieved on the acid erythro complex. They also find a bent Cr–O–Cr linkage and an increased Cr–Cr distance in the rhodo complex.

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Received November 7, 1970

Behavior of Bent Vinyl Cations Generated by Solvolysis of Cyclic Trifluoromethanesulfonates

Sir:

According to *ab initio* molecular orbital calculations, vinyl cations prefer a linear structure which can be

Table I.[a] Data for the Solvolysis of Cyclic Vinyl Triflates

Compd	Solvent	Temp, °C	k_1, sec^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
I	50% EtOH	176.45^b	$4.75 \pm 0.15 \times 10^{-5}$		
	60% EtOH	100.0^c	1.24×10^{-8}	33.0	−6.9
		151.0^b	$2.94 \pm 0.30 \times 10^{-6}$		
		176.45^b	$2.85 \pm 0.07 \times 10^{-5}$		
II	50% EtOH	100.0^c	5.47×10^{-7}	31.2	−4.1
		125.15^d	$8.16 \pm 0.16 \times 10^{-6}$		
	60% EtOH	100.0^c	2.15×10^{-7}	32.0	−3.8
		151.0^b	$4.10 \pm 0.15 \times 10^{-5}$		
		175.5^b	$3.88 \pm 0.14 \times 10^{-4}$		
III	50% EtOH	100.05^d	$5.61 \pm 0.31 \times 10^{-6}$	28.1	−7.7
		126.04^d	$6.10 \pm 0.12 \times 10^{-5}$		
	60% EtOH	100.0^c	2.81×10^{-6}	31.0	−1.3
		125.0^b	$4.13 \pm 0.17 \times 10^{-5}$		
		151.1^b	$4.86 \pm 0.19 \times 10^{-4}$		
	70% TFE	125.29^d	$7.47 \pm 0.06 \times 10^{-5}$		
	97% TFE	125.29^d	$1.12 \pm 0.09 \times 10^{-5}$		
IV	50% EtOH	75.55^d	$4.50 \pm 0.32 \times 10^{-6}$	26.9	−5.8
		100.0^d	$8.44 \pm 0.08 \times 10^{-5}$		
		125.44^d	$7.06 \pm 0.12 \times 10^{-4}$		
	60% EtOH	100.2^d	$3.73 \pm 0.25 \times 10^{-5}$	29.3	−0.8
		100.07^b	$3.48 \pm 0.17 \times 10^{-5}$		
		124.25^b	$4.08 \pm 0.23 \times 10^{-4}$		
	70% TFE	100.07^d	$1.18 \pm 0.01 \times 10^{-4}$	26.3	−6.5
		125.26^d	$1.20 \pm 0.01 \times 10^{-3}$		
	97% TFE	100.05^d	$3.89 \pm 0.04 \times 10^{-5}$	24.3	−14.1
		125.26^d	$3.36 \pm 0.04 \times 10^{-4}$		
V	50% EtOH	75.15^d	$3.43 \pm 0.19 \times 10^{-5}$	27.2	−1.2
		100.76^d	$5.44 \pm 0.12 \times 10^{-4}$		
VI	50% EtOH	100.07^d	$8.60 \pm 0.07 \times 10^{-5}$	25.9	−8.2
		125.40^d	$8.41 \pm 0.05 \times 10^{-4}$		
	60% EtOH	100.07^d	$3.39 \pm 0.07 \times 10^{-5}$	28.2	−4.0
		125.25^d	$4.01 \pm 0.02 \times 10^{-4}$		
	70% TFE	100.12^d	$1.31 \pm 0.02 \times 10^{-4}$		
	97% TFE	100.12^d	$4.06 \pm 0.07 \times 10^{-5}$		
VII	50% EtOH	75.20^{d,e}	$4.31 \pm 0.02 \times 10^{-5}$	26.3	−3.9
		99.82^{d,e}	$5.72 \pm 0.02 \times 10^{-4}$		
		100.45^d	$5.83 \pm 0.07 \times 10^{-4}$		
	60% EtOH	74.80^{d,e}	$1.66 \pm 0.01 \times 10^{-5}$	27.7	1.1
		99.84^d	$2.57 \pm 0.01 \times 10^{-4}$		
		100.10^b	$2.56 \pm 0.07 \times 10^{-4}$		
	70% TFE	75.2^{d,e}	$3.39 \pm 0.04 \times 10^{-5}$	27.0	−1.9
		100.65^{d,e}	$5.07 \pm 0.03 \times 10^{-4}$		
	97% TFE	75.27^{d,e}	$1.07 \pm 0.01 \times 10^{-5}$	23.2	−14.9
		99.80^{d,e}	$1.08 \pm 0.01 \times 10^{-4}$		
VIII	50% EtOH	49.4^{d,e}	$1.87 \pm 0.05 \times 10^{-5}$	26.7	2.4
		74.95^d	$4.32 \pm 0.06 \times 10^{-4}$		
		75.2^{d,e}	$4.81 \pm 0.05 \times 10^{-4}$		
		100.0^c	6.11×10^{-3}		
	60% EtOH	75.2^{d,e}	$2.18 \pm 0.04 \times 10^{-4}$	25.7	−1.7
		74.82^b	$2.24 \pm 0.12 \times 10^{-4}$		
		99.8^{d,e}	$2.67 \pm 0.06 \times 10^{-3}$		
		100.45^d	$2.86 \pm 0.02 \times 10^{-3}$		
	70% TFE	49.5^{de,}	$2.78 \pm 0.02 \times 10^{-5}$	25.7	0.1
		74.8^d	$5.36 \pm 0.01 \times 10^{-4}$		
		100.0^c	7.13×10^{-3}		
	97% TFE	75.25^{d,e}	$1.79 \pm 0.01 \times 10^{-4}$	24.3	−6.2
		99.95^d	$1.99 \pm 0.02 \times 10^{-3}$		

[a] All runs buffered in the ratio substance:2,6-lutidine = 1:3 unless otherwise indicated. [b] Determined by titration. [c] Calculated from data at other temperatures. In the case of II, the *mY* solvent relationship was also employed. [d] Determined by conductance. [e] Unbuffered.

considered to have an sp-hybridized carbon and a vacant p orbital.[1] Very little experimental evidence is available regarding the structure of vinyl cations.[2]

The stereochemistry of solvolysis of vinyl derivatives stabilized by attached aryl[2,3] or cyclopropane rings[4] indicates little or no stereoselectivity. This is consistent either with linear structures or, less likely, with bent cations which invert rapidly relative to solvent capture.

In cyclic systems, vinyl cations are rigidly held in bent geometries. If such bent structures are less favorable, then the rate of solvolysis of cycloalkenyl derivatives should be slower than that of similar acyclic

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(1) R. Sustmann, J. E. Williams, M. J. S. Dewar, L. C. Allen, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **91**, 5350 (1969), and references cited therein; W. A. Lathan, W. J. Hehre, and J. A. Pople, *ibid.*, **93**, 808 (1971).

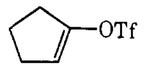
(2) For recent reviews see: M. Hanack, *Accounts Chem. Res.*, **3**, 209 (1970); H. G. Richey and J. M. Richey in "Carbonium Ions," Vol. II, G. A. Olah and P. v. R. Schleyer, Ed., Wiley, New York, N. Y., 1970, p 38; Z. Rappoport, T. Bässler, and M. Hanack, *J. Amer. Chem. Soc.*, **92**, 4985 (1970).

(3) Z. Rappoport and Y. Apeloig, *ibid.*, **91**, 6734 (1969); *cf.* G. F. P. Kernaghan and H. M. R. Hoffmann, *ibid.*, **92**, 6988 (1970).

(4) D. R. Kelsey and R. G. Bergman, *ibid.*, **92**, 228 (1970).

precursors. Peterson and Indelicato[5] attempted to study this problem by the examination of the behavior of cyclohexenyl arenesulfonates. In acidic solvents addition–elimination occurred[5a] while the prolonged action of 50% methanol at 130° failed to give reaction.[5b,c] In the aqueous alcohol solvent the solvolysis of acyclic arenesulfonates could be demonstrated. Nevertheless, it seems that bent vinyl cations might be capable of existence as indicated by the apparent ready formation of cyclic products *via* π-route closures of acetylene derivatives.[2,6]

The use of the highly reactive trifluoromethanesulfonate (triflate) leaving group[7] permits a detailed study of this probelm. Solvolysis data for eight cyclic triflates[8] are collected in Table I. Relative rates of solvolysis (k_{rel}) in 50% EtOH at 100° are: for *cis*-CH_3-$C{=}C(OTf)CH_3$, 1.0;[9] for VIII, 3.4; for VII, 3.2×10^{-1}; for II, 3.0×10^{-4}; for I, 1.1×10^{-5}. Relative rates (k_{rel}) of substituted compounds in 50% EtOH at 100° are: for II, 1.0; for III, 10; for IV, 160; for V, 920; for VI, 160.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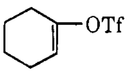
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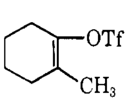
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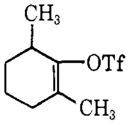
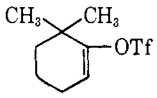

IV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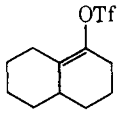
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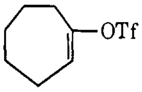
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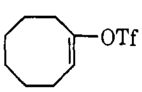
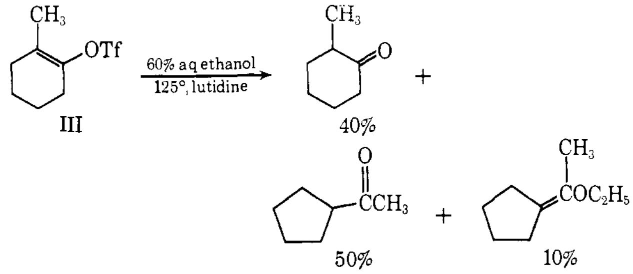
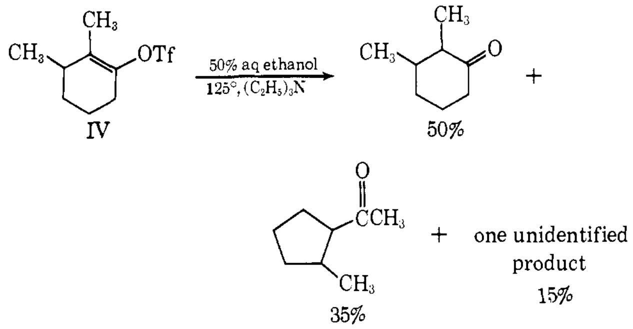

VIII

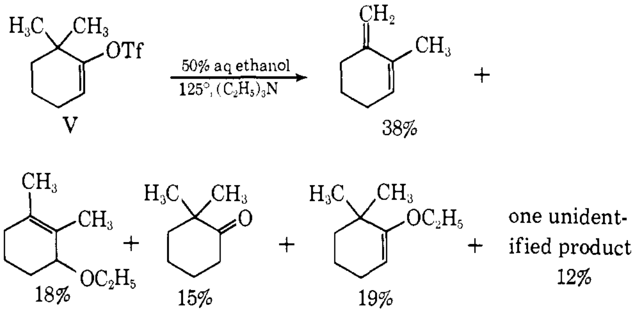
The solvolysis rates of the simple cycloalkenyl triflates fall off markedly as the ring size decreases: VIII > VII > II > I. This provides direct evidence for the instability of strongly bent vinyl cations. As the ring size decreases, the vinyl cations must be bent to an increasingly greater extent. A preferred linear structure for vinyl cations seems probable, but a slightly bent conformation cannot be excluded on the basis of our results.

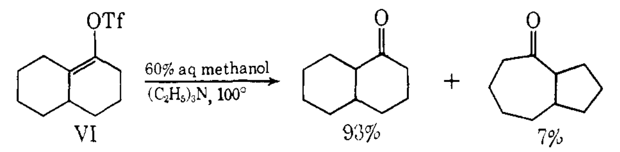
Solvolyses of the unsubstituted cyclic vinyl triflates at 100° in 50% aqueous ethanol (buffered with triethylamine) lead exclusively to the corresponding cycloalkanones. Treatment of 1-cyclohexenyl triflate with buffered CH_3COOD (4 weeks at 135°) gave a mixture consisting of cyclohexanone (85%) and 1-cyclohexenyl acetate (15%). Cyclohexanone was treated with CH_3-COOD under the same conditions. It was shown by mass spectral analysis that the amount of deuterium incorporation was the same in both samples of cyclohexanone. Therefore, it was concluded that little or none of the 1-cyclohexenyl triflate reacts *via* an addition–elimination mechanism, but rather by unimolecular ionization to form an intermediate vinyl cation.[2]

Vicinal alkyl substitution produces marked rate enhancements in the cyclohexenyl triflates III–VI. However, both rearranged and unrearranged products are found in each instance, as illustrated below.

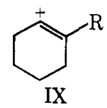




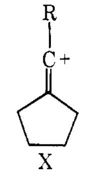




Ring-contracted products form only when the second vinyl carbon is substituted (III, IV, and VI), *e.g.*, by R = CH_3 in IX. When R = H in IX, rearrangement to X would yield a "primary" vinyl cation, a



IX



X

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[5] (a) P. E. Peterson and J. M. Indelicato, *J. Amer. Chem. Soc.*, **90**, 6515 (1968); (b) P. E. Peterson and J. M. Indelicato, *ibid.*, **91**, 6194 (1969).

(5c) NOTE ADDED IN PROOF. A similar lack of reactivity has been noted by C. A. Grob and H. R. Pfaendler, *Helv. Chim. Acta*, **53**, 2130 (1970), for a 2-bromo-1,3-cyclohexadiene, in contrast to acyclic bromodiene analogs.

[6] P. E. Peterson and R. J. Kamat, *ibid.*, **91**, 4521 (1969).

[7] R. L. Hansen, *J. Org. Chem.*, **30**, 4322 (1965); A. Streitwieser, Jr., C. L. Wilkins, and E. Kiehlmann, *J. Amer. Chem. Soc.*, **90**, 1598 (1968); T. M. Su, W. F. Sliwinski, and P. v. R. Schleyer, *ibid.*, **91**, 5386 (1969).

[8] For preparation details and physical constants see: T. E. Dueber, P. J. Stang, W. D. Pfeifer, R. H. Summerville, M. A. Imhoff, P. v. R. Schleyer, K. Hummel, S. Bocher, C. E. Harding, and M. Hanack, *Angew. Chem.*, **82**, 517 (1970).

[9] Calculated from unpublished data of P. J. Stang and R. H. Summerville; *cf. J. Amer. Chem. Soc.*, **91**, 4600 (1969); $k_1 = 1.83 \times 10^{-3}$ sec^{-1} at 100°.

highly unstable species. Quite analogous results have been obtained from π-route studies by Peterson and Kamat.[6] The only cyclized products from 6-heptyn-2-yl tosylate, a terminal acetylene, were six-membered rings. In contrast, solvolysis of 6-octyn-2-yl tosylate gave both five- and six-membered ring products in ratios rather similar to those found here from III, despite the different solvents which were employed in the two studies.

Despite the nonlinear nature of the vinyl cation in IX, these product results indicate that IX and X do not differ much in stability. This is to be expected, since methylenecyclopentane (a model for X) is nearly 5 kcal/mol (enthalpy) less stable due to ring strain than is 1-methylcyclohexene (a model for IX).[10] The $10^{-3.5}$ rate depression observed for II corresponds to an activation free-energy difference of 6 kcal/mol. Thus, ring strain and vinyl cation strain factors seem to balance in IX and X.

For this reason, it is difficult to attribute the tenfold rate enhancement of III over II to anchimeric assistance during rearrangement of IX to X. The rate enhancements in IV and V are an additional order of magnitude larger, but little rearranged product is found from VI. In short, rearrangements to more stable cations do not seem to provide driving force for the rate enhancements observed in Table III.

The situation is even more telling with V, which shows the largest rate enhancement, nearly 10^3 over II. Neither possible mode of ring contraction is observed; instead, the majority of products (but not all) form by methyl shift. Since the methyl groups cannot possibly be oriented at the backside of the departing triflate group, participation in this instance seems highly unlikely.

The rate enhancements observed for substituted compounds in 50% EtOH at 100° thus appear to be due to three possible causes: (1) formation of bridged ions more stable than their classical counterparts[6] (however, molecular orbital calculations do not support this possibility,[1] except, perhaps, for the smallest ring systems not considered in the present paper[11]). (2) inductive and hyperconjugative substituent effects of unusually large magnitude;[12] (3) relief of steric ground-state interactions between the substituents and the triflate leaving groups during solvolysis.[13] The detailed interpretation of the rate enhancements of substituted compounds, *e.g.*, III–VI, is under active investigation.

Acknowledgment. This work was supported at Princeton by grants from the National Science Foundation, the Petroleum Research Fund administered by the American Chemical Society (AI-07766), and Hoffmann-La Roche, Inc. At Tübingen the work was supported by Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. T. E. Dueber (University of Utah) provided us with samples of IV and VIII.

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[10] P. v. R. Schleyer, J. E. Williams, and K. R. Blanchard, *J. Amer. Chem. Soc.*, **92**, 2377 (1970).

[11] H. Fischer, K. Hummel, and M. Hanack, *Tetrahedron Lett.*, 2169 (1969); H. Fischer and H. Kollmar, *Theor. Chim. Acta*, **16**, 163 (1970).

[12] Compare the behavior of secondary alkyl tosylates in trifluoroacetic acid: P. E. Peterson, R. E. Kelly, Jr., R. Belloli, and K. A. Sipp, *J. Amer. Chem. Soc.*, **87**, 5169 (1965).

[13] The suggestion of a referee. Also see footnote 10a in J. L. Fry, J. M. Harris, R. C. Bingham, and P. v. R. Schleyer, *ibid.*, **92**, 2540 (1970), and footnote 20a in J. L. Fry, C. J. Lancelot, L. K. M. Lam, J. M. Harris, R. C. Bingham, D. J. Raber, R. E. Hall, and P. v. R. Schleyer, *ibid.*, **92**, 2538 (1970).

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Received October 12, 1970

Dispersion Force Contribution to Heats of Protonation[1,2]

Sir:

On comparing heats of protonation of homologous primary alcohols and amines referred to a gaseous reference state, we find a trend which is evidently due to a systematic contribution of dispersion or London forces.[3] Except for cases such as the ionization of neutral molecules to form large delocalized (polarizable) ions or transition states[4] in solution the effects of these forces are nearly equivalent in both the secondary and the initial states so that their presence is not normally brought to our attention.

Table I contains heats of solution of six primary alcohols and three primary amines in fluorosulfuric acid as well as $\Delta\bar{H}_s$ values for two of the amines in 96.5% H_2SO_4. Heats of transfer from the gas phase to high dilution in HSO_3F or H_2SO_4 (in which all the compounds are completely protonated[5]) are calculated by subtracting $\Delta\bar{H}_{vap}$ from $\Delta\bar{H}_s$ and are found in columns III and VIII. It is evident that the enthalpy of transfer of alcohols and amines from the gas state to solution in strong acid becomes more exothermic in direct proportion to the carbon number of the alkyl chain.

The stability of the protonated solutes in HSO_3F was shown in two ways. (a) Clean, easily interpreted nmr spectra were obtained at −60° for the alcohols. As previous workers have observed,[6] the protons on

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[3] These self-induced attractions result from the interaction of instantaneous dipoles produced by zero-point motions within molecules or parts of molecules. They occur between all types of matter, provided the distance separating the interacting pairs is large enough to make electron exchange negligible, and are sometimes the major contribution to van der Waals forces in liquids.

[4] E. Grunwald and E. Price, *J. Amer. Chem. Soc.*, **86**, 4517 (1964).

[5] E. M. Arnett, J. J. Burke, and R. P. Quirk, *ibid.*, **92**, 1260 (1970), estimate a value of −5.1 for the pK_{BH^+} of ethanol based on their enthalpimetric basicity scale. Since increasing the chain length has a negligible effect on the basicity of the aliphatic alcohols, HSO_3F, with an H_0 of −13.9, can be expected to protonate these alcohols completely.

[6] T. Birchall and R. J. Gillespie, *Can. J. Chem.*, **43**, 1045 (1965), record the nmr spectrum of EtOH in HSO_3F at 25, −82, and −95°. At 25° they note only CH_2 and CH_3 resonances, while at the lower temperatures a new peak appears at about −10 ppm from external TMS. They attribute this peak to the $-OH_2^+$ protons. Evidently at −60°, the temperature at which our spectra were recorded, exchange with the solvent is still too fast for the $-OH_2^+$ resonance to be observed. Alternatively, noting the temperature dependence of the $-OH_2^+$ peak observed by Birchall and Gillespie ($\Delta = -9.89$ ppm at −95°, −10.35 ppm at −82°), it is possible that at −60° the $-OH_2^+$ resonance is close enough to the solvent peak to be swamped by it.