J. Am. Chem. Soc. **1984**, *106*, 2895–2901 2895

One reaction gave 60.0/40.0 for PrOz-d_0–/PrOz-d_1 by NMR and 60.4/39.6 from microwave (MW) transitions. The second reaction gave 46.3/53.7 by NMR and 46.2/53.8 by MW. Five MW transitions[2c] were used; the precision of the MW and NMR ratios were similar.

MW spectroscopy was employed to determine the relative amounts of EtOz-d_0, -d_2, and -d_4. The intensities of five microwave transitions ($10_{6,4} \rightarrow 10_{7,3}$ and $13_{11,3} \rightarrow 13_{12,2}$ for EtOz-d_0; $13_{9,4} \rightarrow 13_{10,3}$ and $14_{10,4} \rightarrow 14_{11,3}$ for EtOz-d_2; $13_{8,5} \rightarrow 13_{9,4}$ for EtOz-d_4) were used following procedures previously worked out.[7a] Because of the spectral complexity and the slow decomposition of EtOz in the MW cell, the uncertainties cannot be further reduced without considerable effort.

Overall yields were determined by manometric methods. In order to remove most of the acetaldehyde from the ozonides, the mixture was distilled from a −78 °C trap for ~1 h. The NMR indicated that the acetaldehyde was reduced to about 5% or less. Some ozonide may also have been lost during the long distillation, but their overall yields still ranged from 70% to 85%. No systematic differences were evident between runs at low and high acetaldehyde concentrations.

One of the parameters difficult to evaluate precisely is the actual acetaldehyde concentration during the ozonolysis. The initial amount added to the reaction was determined by a pressure measurement assuming only the monomer in the gas phase.[25] However, trimer formation is favored at the reaction temperature if the data for liquid CH_3CHO can be extrapolated to these conditions.[25] Nevertheless, it appears that the rate of trimer formation may be slow since the acetaldehyde exhibits monomer behavior under reaction conditions and incorporates extensively into the ozonide. Until this ambiguity can be better resolved, the reported acetaldehyde concentrations are considered upper limits and ignore any trimerization. In terms of the kinetic analysis, this implies that the dipolarophilicity of the CH_3CHO may be underestimated.

Computer Analysis. The algorithm for Scheme II used Euler's[26] method to approximate the solutions to the differential equations. It was written in Fortran-77 for a PDP-11/23 system. A calculation of yields for a single set of assumptions typically took 2 min. Some iterations, such as testing various combinations of KSIEs, consisted of several hundred calculations. A flow diagram and listing of the program as well as some additional calculations and examples of rate constants are available as supplementary material.

Acknowledgment. This work was supported by Grants CHE-8005471 and CHE-8303615 from the National Science Foundation. We are grateful to Dr. Kurt Hillig for help on ozonolysis and computer techniques.

Supplementary Material Available: Nine examples of rate constant assumptions (Table 1S) and calculated yields (Table 2S) and flow diagram and listing for the Fortran program, called KINET, predicting the product yields (15 pages). Ordering information is given on any current masthead page.

---

(25) Busfield, W. K.; Lee, R. M.; Merigold, D. *J. Chem. Soc., Faraday Trans. 1* **1973**, *69*, 936.

(26) Johnson, K. J. "Numerical Methods in Chemistry"; Marcel Dekker: New York, 1980; Chapter 7.

Perchlorate Esters. 7.[1] Solvolysis of 2-Adamantyl Perchlorate: Rate and Product Studies

Dennis N. Kevill,* Mohd. S. Bahari, and Steven W. Anderson

Contribution from the Department of Chemistry, Northern Illinois University, DeKalb, Illinois 60115. *Received July 25, 1983. Revised Manuscript Received January 10, 1984*

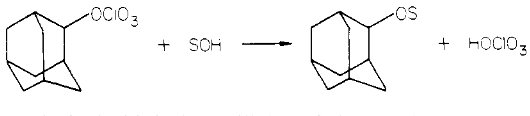
Abstract: The solvolysis of 2-adamantyl perchlorate proceeds at a convenient rate at temperatures close to ambient in a wide variety of pure and aqueous organic solvents. The nucleofugality of the perchlorate ion in S_N1 reactions is shown to be several orders of magnitude higher than for more conventional leaving groups, such as *p*-toluenesulfonate or bromide. Entropies of activation in pure organic solvents and in 80% ethanol are unusually high. Grunwald–Winstein plots are markedly curved, with deviations being especially marked for aqueous-acetone and aqueous-2,2,2-trifluoroethanol mixtures. A scale of Y_{OClO_3} values is developed and compared with scales for a variety of other leaving groups. In aqueous ethanol there is a preference for product formation by interaction with water molecules by a factor of ca. 1.7, essentially independent of solvent composition (96–50% ethanol) and temperature.

It has recently been reported that both methyl perchlorate[2] and 2-adamantyl perchlorate[3] can exhibit maxima in Grunwald–Winstein plots (eq 1) of log k against Y. In eq 1, k and k_0

$$\log (k/k_0) = mY \qquad (1)$$

represent the specific rates of solvolysis in the solvent under consideration and in the standard solvent (80% ethanol), Y represents the solvent ionizing power of the solvent under consideration, and m represents the sensitivity of the substrate to changes in solvent ionizing power.

The observation of a shallow maximum and an almost constant specific rate of solvolysis over the full range of composition of methanol–acetone mixtures for 2-adamantyl perchlorate[3] parallels the results of Luton and Whiting[4] for the solvolysis of 1-adamantyl picrate in methanol-tetramethylene sulfone mixtures. The perchlorate ion has a lipophilicity lower than picrate ion but higher than more familiar nucleofuges, such as *p*-toluenesulfonate (tosylate), bromide, and chloride ions, and one aim of the present investigation is to see, for several organic and aqueous organic systems, to what extent S_N1 solvolysis of perchlorate esters, such as 2-adamantyl (eq 2), shows unusual effects which can be related to the relatively high lipophilicity of the perchlorate ion. Such effects could be reflected in Y values required for a perchlorate



(2)

---

(1) Part 6: Kevill, D. N.; Posselt, H. S. *J. Chem. Res. Synop.* **1983**, 264.

(2) Kevill, D. N.; Wang, A. *J. Chem. Soc., Chem. Commun.* **1981**, 83.

(3) Kevill, D. N.; Bahari, M. S. *J. Chem. Soc., Chem. Commun.* **1982**, 572.

(4) Luton, P. R.; Whiting, M. C. *J. Chem. Soc., Perkin Trans. 2* **1979**, 1507.

(5) Dehmlov, E. V.; Dehmlov, S. S. "Phase Transfer Catalysis"; Verlag Chemie: Weinheim, 1980; pp 13, 14.

0002-7863/84/1506-2895$01.50/0

Table I. First-Order Rate Coefficients for the Solvolysis of 2-Adamantyl Perchlorate[a,b] and Comparison of Y_{OClO_3} with Other Solvent Ionizing Power Scales

	$10^6 k$(s^{-1})					
temp, °C	80% EtOH	MeOH	EtOH	*i*-PrOH	*t*-BuOH	CH_3COOH
0.0	33.9[c]	4.77[c]	0.451[c]	0.123	(0.071)[d]	(1.48)[d]
12.7	250	41.9	4.81	1.12		
17.3						17.6
25.0	1490	227	30.5	6.83	(3.47)[d]	47.9
26.7					4.45	
32.2		929	86.3	23.5	8.53	125
41.2						378
49.7					85.0	
Y_{OClO_3}[e]	0.000	−0.852	−1.876	−2.440	−2.68	−1.36
Y[f]	0.000	−1.090	−2.033	−2.73	−3.26	−1.675
Y_{OTs}[g]	0.000	−0.924	−1.962	−2.829	−3.736	−0.896
Y_{Cl}[h]	0.000	−1.2	−2.5			−1.6
Y_{Br}[h]	0.000	−1.12	−2.4			−2.1
Y_{Pic}[i]	0.000	−0.87	−1.12			−1.01

[a] Solvolysis of ~0.004 *M* 2-AdOClO_3 in a solvent consisting of 98% of indicated composition plus 2% pentane; all runs performed in duplicate. [b] Standard deviations for k_1 were within 3% of the reported values. [c] For value with 2% dioxane substituted for 2% pentane, see Table III. [d] Calculated using the Arrhenius equation. [e] Log $(k/k_0)_{2\text{AdOClO}_3}$ at 0.0 °C, where k_0 refers to the specific rate in 80% ethanol. [f] Traditional Grunwald–Winstein *Y* values (ref 28). [g] Log $(k/k_0)_{1\text{-AdOTs}}$ at 25.0 °C (ref 27). [h] From ref 31. [i] Log $(k/k_0)_{1\text{-AdPic}}$ at 49.1 °C. Value for k_0 (407×10^{-5} s^{-1}) obtained by interpolation within data of ref 30; specific rates for methanolysis (ref 4 and 30) and acetolysis (ref 26) calculated, using Arrhenius equation, from data at neighboring temperatures.

ion leaving group (Y_{OClO_3}) being quite different from the classical *Y* values and from the *Y* values based on 2-adamantyl tosylate (Y_{OTs}) or 1-adamantyl halide (Y_{Cl} and Y_{Br}) solvolyses.

During the acetolysis of 2-adamantyl tosylate, less than 0.3% 1→2 or 4→2 hydride shifts was observed,[6] and the product was almost entirely 2-adamantyl acetate (formed with a preference for retained configuration[7]), with only a 0.4–0.5% contribution from the much less stable *exo*-4-protoadamantyl acetate, formed by a 1→2 skeletal rearrangement.[8] Since side products are formed only in very small amounts,[6,8] it has been possible to consider product formation from the solvolyses of 2-adamantyl arenesulfonates and bromide in aqueous ethanol in terms of only 2-adamantanol and 2-adamantyl ethyl ether formation.[9-11]

While it has been suggested that 2-adamantyl derivatives solvolyze with a rate-determining step involving a simple ionization,[12-15] it has also been proposed both that weak σ-bond participation occurs[7,8] and that the rate-determining step involves conversion of the first formed intimate ion pair to the solvent-separated ion pair.[9,16] The observation of O^{18} scrambling in unreacted substrate during the solvolysis of 2-adamantyl benzenesulfonate[17] has not been universally accepted as strong evidence for internal ion-pair return because the O^{18} scrambling could be occurring by an independent concerted process.[15]

A concerted process could also superficially explain the observation of 1-adamantyl chloride formation, concurrent with 1-adamantanol and/or 1-adamantyl alkyl ether formation, during solvolyses of 1-adamantyl chloroformate.[18] However, the observation of very similar Grunwald–Winstein *m* values for both decomposition and solvolysis strongly suggests that both processes involve an initial ionization with internal return of chloride, after loss of carbon dioxide from the chloroformate anion, competing with solvolysis. A parallel observation has been made of 2-adamantyl tosylate formation competitive with the solvolysis of 2-adamantyl azoxytosylate.[19]

Table II. Enthalpies ($\Delta H^{\ddagger}$) and Entropies ($\Delta S^{\ddagger}$) of Activation for Solvolysis of 2-Adamantyl Perchlorate[a]

solvent	$\Delta H^{\ddagger}{}_{298}$°, kcal/mol	$\Delta S^{\ddagger}{}_{298}$°, eu
80% ethanol[b]	24.0 ± 0.1	+9.0 ± 0.3
methanol	26.3 ± 0.3	+13.2 ± 1.1
ethanol	26.4 ± 0.4	+9.4 ± 1.6
2-propanol	26.2 ± 0.4	+5.6 ± 1.4
tert-butyl alcohol	24.2 ± 0.5	−2.2 ± 1.8
acetic acid	22.8 ± 0.2	−1.9 ± 0.6

[a] Calculated using the data of Table I, with associated standard errors. [b] On a volume–volume basis at 25.0 °C.

The lack of reaction of 2-adamantyl perchlorate with *N,N*-dimethylaniline in benzene,[20] conditions under which isopropyl perchlorate reacts readily to give a quaternary ammonium salt, and the high temperatures (>110 °C) needed for reaction of 2-adamantyl tosylate with azide ion in toluene[21] confirm the resistance of 2-adamantyl derivatives toward bimolecular nucleophilic attack.[12] It is of interest to determine just how much more nucleofugic[22] the perchlorate ion is in S_N1 reactions of 2-adamantyl derivatives than previously studied tosylate,[23,24] bromide,[25] and picrate[26] ions.

Results

Solvolyses in Dry Alcohols, Acetic Acid, and 80% Ethanol. Rates of solvolysis were determined at three or four temperatures in the

---

(6) Sinnott, M. L.; Whiting, M. C. *J. Chem. Soc., Perkin Trans. 2* **1975**, 1446.

(7) Bone, J. A.; Pritt, J. R.; Whiting, M. C. *J. Chem. Soc., Perkin Trans. 2* **1975**, 1447.

(8) Storesund, H. J.; Whiting, M. C. *J. Chem. Soc., Perkin Trans. 2* **1975**, 1452.

(9) Harris, J. M.; Becker, A.; Fagan, J. F.; Walden, F. A. *J. Am. Chem. Soc.* **1974**, *96*, 4484.

(10) Karton, Y.; Pross, A. *J. Chem. Soc., Perkin Trans. 2* **1978**, 595.

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

(12) Fry, J. L.; Lancelot, C. J.; Lam, L. K. M.; Harris, J. M.; Bingham, R. C.; Raber, D. J.; Hall, R. E.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1970**, *92*, 2538.

(13) Bentley, T. W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1976**, *98*, 7658.

(14) Bentley, T. W.; Bowen, C. T.; Parker, W.; Watt, C. I. F. *J. Chem. Soc., Perkin Trans. 2* **1980**, 1244.

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

(16) Shiner, V. J., Jr.; Fisher, R. D. *J. Am. Chem. Soc.* **1971**, *93*, 2553.

(17) Paradisi, C.; Bunnett, J. F. *J. Am. Chem. Soc.* **1981**, *103*, 946.

(18) Kevill, D. N.; Weitl, F. L. *Tetrahedron Lett.* **1971**, *707*.

(19) Maskill, H.; Thompson, J. T.; Wilson, A. A. *J. Chem. Soc., Chem. Commun.* **1981**, *1239*.

(20) Kevill, D. N.; Shen, B. W. *J. Am. Chem. Soc.* **1981**, *103*, 4515.

(21) Banert, K.; Kirmse, W. *J. Am. Chem. Soc.* **1982**, *104*, 3766.

(22) Kevill, D. N.; Lin, G. M. L. *Tetrahedron Lett.* **1978**, 949.

(23) Schleyer, P. v. R.; Fry, J. L.; Lam, L. K. M.; Lancelot, C. J. *J. Am. Chem. Soc.* **1970**, *92*, 2542.

(24) Kevill, D. N.; Kolwyck, K. C.; Shold, D. M.; Kim, C.-B. *J. Am. Chem. Soc.* **1973**, *95*, 6022.

(25) Fry, J. L.; Harris, J. M.; Bingham, R. C.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1970**, *92*, 2540.

(26) Sinnott, M. L.; Whiting, M. C. *J. Chem. Soc. B* **1971**, 965.

Table III. First-Order Rate Coefficients for the Solvolysis of 2-Adamantyl Perchlorate[a] in Aqueous-Organic Solvents, at 0.0 °C, and Comparison of Y_{OClO_3} with Other Solvent Ionizing Power Scales

solvent[b,c]	10^6k, s^{-1} [d]	Y_{OClO_3}[e]	Y[e,f]	Y_{OTs}[e]	Y_{Pic}[e,g]
100% EtOH	0.545	−1.835	−2.033	−1.962	−1.12
90% EtOH	7.43	−0.701	−0.747	−0.768	−0.43
80% EtOH	37.3	0.000	0.000	0.000	0.000
70% EtOH	125	0.525	0.595		0.33
60% EtOH	622	1.222	1.124		0.64
50% EtOH	3392	1.959	1.655		0.94
100% MeOH	5.41	−0.839	−1.090	−0.924	−0.87
90% MeOH	32.2	−0.064	−0.301	−0.048	
80% MeOH	204	0.738	0.381		
70% MeOH	741	1.298	0.961		
60% MeOH	4454	2.077	1.492		
100% TFE[h]	610	1.214	1.045		
97% TFE	735	1.295	1.148		
90% TFE	1647	1.645	1.245		
80% TFE	3085	1.918	1.461		
70% TFE	4378	2.070	1.659		
60% TFE	4977	2.125	1.894		
50% TFE[i]	7146	2.282	2.229		
95% acetone	22.0	−0.229	−2.76	−2.954	
90% acetone	54.1	0.161	−1.856	−1.986	−0.65[j]
80% acetone	236	0.801	−0.673	−0.942	
70% acetone	764	1.311	0.130		0.13[j]
60% acetone	2160	1.763	0.796		
50% acetone[i]	5550	2.173	1.398		
90% dioxane	29.5[k]	(−0.970)[l]	−2.030	−2.409	
80% dioxane	232[k]	(−0.074)[l]	−0.833	−1.302	
70% dioxane	1063[k]	(0.587)[l]	0.013		
70% dioxane	196	0.721	0.013		
60% dioxane	807	1.335	0.715		
50% dioxane[i]	3940	2.024	1.361		

[a] Concentration 0.004–0.005 M, unless otherwise stated. [b] On a volume–volume basis (at 25.0 °C) and with water as the other component, except for TFE–H_2O mixtures which are on a weight percentage basis. [c] Actual solvent composition is 98% of the composition indicated plus 2% dioxane (volume–volume); all runs performed, at least, in duplicate. [d] Standard deviations for k_1 within 3% of reported value. [e] For definitions, see footnotes *e–g* and *i* of Table I. [f] For several Y_{Cl} and Y_{Br} values (based on 1-adamantyl halides), see Table IV of ref 31. [g] Specific rates in aqueous ethanol obtained by interpolation within the data of ref 30; essentially identical values obtained by multiplying Y values by 0.564 (the reported m value). [h] 2,2,2-Trifluoroethanol. [i] $[2\mathrm{AdOClO}_3] \sim 0.002$ M. [j] Specific rates at 50 °C (ref 30) were adjusted to 49.1 °C by multiplying by 0.914 (ratio of specific rates of methanolysis at these temperatures). The acetone–water compositions of ref 30 are *by volume* (Whiting, M. C. personal communication). [k] At 12.7 °C. [l] Using values at 12.7 °C; k_0 value from Table I corrected by factor of 1.10 (ratio of specific rates at 0 °C with 2% dioxane and 2% pentane as cosolvent).

Table IV. Percentage of Product Present[a] as 2-Adamantanol after the Solvolysis of 2-Adamantyl Perchlorate[b] in Aqueous Ethanol and Selectivity Values (S)[c]

	0.1 °C		24.7 °C	
% EtOH[d]	AdOH	S	AdOH	S
100	3.1[e]		3.8[e]	
96			21.3	1.65
90	42.4[f]	1.91	38.4[f]	1.57
85	51.8[f]	1.76	50.5	1.67
80	60.7[f]	1.83	61.9	1.91
70[g]	70.3[f]	1.65	73.5	1.91
65	74.0[f]	1.57	77.5[f]	1.89
60	77.7[f]	1.56	80.2	1.81
50	85.3	1.75	84.3[f]	1.61

[a] Only 2-adamantanol and 2-adamantyl ethyl ether detected as products. [b] Concentration within range of 10^{-2} to 10^{-3} M. [c] Ratio of specific rate constants for reaction of intermediate ionic species with water and ethanol, respectively (see text). [d] On volume–volume basis and actual composition is 91% of the solvent of indicated composition plus 9% dioxane. [e] Corresponds to percentage of 2-adamantanol impurity in the 2-adamantyl perchlorate stock solution. [f] A 5% excess of pyridine was present. [g] Using a stock solution of 2-adamantyl perchlorate in pentane rather than in dioxane, values obtained for % AdOH and S were 69.8 and 1.58 and 72.2 and 1.78 at 0.1 and 24.7 °C, respectively; reaction was in presence of 5% excess pyridine, and 2-adamantanol present after solvolysis in 100% EtOH was, at each temperature, 3.8%.

0–50° range. Constant integrated values for the first-order rate coefficient were obtained throughout each run, including runs in *tert*-butyl alcohol (where autocatalysis was observed in a study of the solvolysis of 1-adamantyl tosylate[27]). All of the values for duplicate runs were averaged and these averages are reported in Table I, together with three values for temperatures below the freezing points of the solvents, calculated using the appropriate Arrhenius parameters of Table II. Solvent ionizing power values (Y_{OClO_3}) based on 2-adamantyl perchlorate as the standard substrate are also presented in Table I, where they are compared with the traditional Y values based on *tert*-butyl chloride solvolysis[28] and with related scales based upon the solvolysis of 1-adamantyl tosylate[27,29] (Y_{OTs}), 1-adamantyl picrate[4,26,30] (Y_{Pic}), 1-adamantyl chloride[31] (Y_{Cl}), and 1-adamantyl bromide[31] (Y_{Br}).

Solvolysis in Solvents of Varying Ionizing Power. A study has been made at 0.0 °C in the following aqueous-organic mixtures: 100–50% ethanol (six compositions), 100–60% methanol (five compositions), 100–50% 2,2,2-trifluoroethanol (TFE) (seven compositions), 95–50% acetone (six compositions), and 70–50% dioxane (three compositions). Attempts to extend to solvents of higher water content were thwarted by a combination of low solubility and high reaction rate. A study was also made, at 12.7 °C, of a 90–70% dioxane range (three compositions). The averages of all of the values for the integrated first-order rate coefficients of duplicate runs are reported within Table III; also, this table contains the Y_{OClO_3} values calculated from the data and, for comparison, other Y values which are either directly available or can be calculated or estimated from previously reported rate coefficients.

Product Studies. The products from the reactions in aqueous-ethanol mixtures were studied at 0.1 and 24.7 °C for the same solvent composition range as the kinetic studies. In some of the runs, a 5% excess of pyridine was added with the intention of protecting against the acid-catalyzed equilibration of the alcohol and ethyl ether products that had been observed for the solvolyses in aqueous ethanol of other adamantyl derivatives.[10,32] However, the milder conditions and shorter reaction times made possible by the much better leaving group rendered such precautions superfluous, and identical results were obtained with or without addition of pyridine. Essentially identical product partitioning was also found when a stock solution of 2-adamantyl perchlorate in pentane, rather than in dioxane, was employed. The results from the product study are summarized in Table IV.

The approximately 3.5% of 2-adamantanol found after solvolysis in 100% ethanol is ascribed as being due to contamination of the 2-adamantyl perchlorate within its stock solution. Since an identical value was obtained with use of a solution in either dioxane or pentane, it appears that the alcohol is formed competitive with the perchlorate ester during the heterogeneous reaction of silver perchlorate with 2-adamantyl bromide and not during transfer from pentane to dioxane. Although the hygroscopic silver perchlorate was dried before use, a little moisture is probably adsorbed on the surface, where the substitution reaction takes place, during the preparation of the reaction mixture.

---

(27) Kevill, D. N.; Kolwyck, K. C., Weitl, F. L. *J. Am. Chem. Soc.* **1970**, *92*, 7300.

(28) Wells, P. R. *Chem. Rev.* **1963**, *63*, 171.

(29) These Y values are also presented in: Bentley, T. W.; Carter, G. E. *J. Org. Chem.* **1983**, *48*, 579. We wish to thank Dr. Bentley for providing us with a copy of this manuscript prior to publication.

(30) Luton, P. R.; Whiting, M. C. *J. Chem. Soc., Perkin Trans. 2*, **1979**, 507.

(31) Bentley, T. W.; Carter, G. E. *J. Am. Chem. Soc.* **1982**, *104*, 5741.

(32) Luton, P. R.; Whiting, M. C. *J. Chem. Soc., Perkin Trans. 2* **1979**, 646.

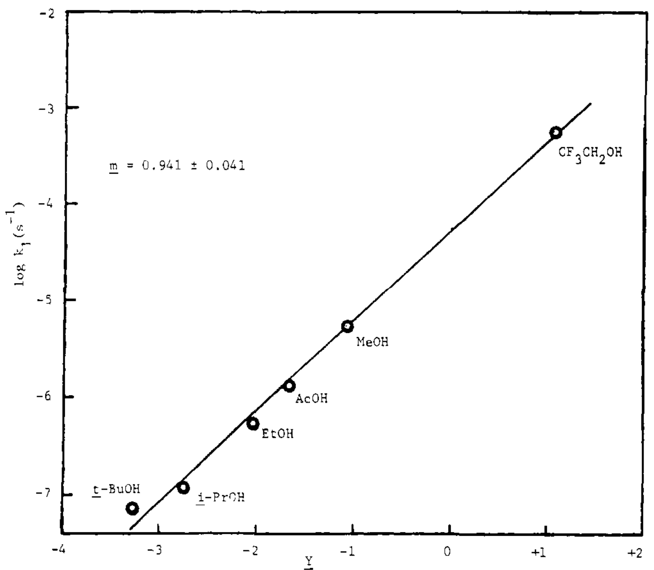


Figure 1. Grunwald–Winstein plot for solvolysis of 2-adamantyl perchlorate in organic solvents at 0.0 °C.

In the calculation of the selectivity values (S) reported in Table IV (eq 3), the percentage of 2-adamantanol found after solvolysis

$$S = \frac{[\text{adamantanol}][\text{ethanol}]}{[\text{adamantyl ethyl ether}][\text{water}]} \quad (3)$$

in 100% ethanol was subtracted from each of the values reported for the solvolysis in aqueous ethanol before insertion into eq 3.

Discussion

In considering the variation in the first-order rate coefficient for the solvolysis of 2-adamantyl perchlorate as a function of solvent ionizing power, the question arises as to which scale of solvent ionizing power is best employed.

The original *tert*-butyl chloride Y scale has been shown[31,33] to include a small nucleophilic solvation component over and above any nucleophilic component which might be present in the solvolyses of adamantyl derivatives. The Y_{OTs} scale based on 2-adamantyl tosylate solvolysis[29,34,35] might appear, at first sight, to be more suitable, but tosylate esters have been found[27] to be subject to a marked specific electrophilic catalysis, not present to any appreciable degree with other studied nucleofuges, and, further, the rather sluggish solvolyses have led to directly determined values only for solvents of reasonably high ionizing power. The sluggish solvolyses of 1-adamantyl halides have limited also the range of values available for Y_{Cl} and Y_{Br} scales.[31] In particular, the adamantane-based scales do not include values for the aqueous-acetone and aqueous-dioxane mixtures rich in the organic component, where effects due to the relatively high lipophilicity of the perchlorate ion should be maximized.

However, where values are available, they do not vary very much from scale to scale except for the less nucleophilic media, such as carboxylic acids and fluorinated alcohols.[31] In aqueous ethanol, it had been estimated[33] that an adjustment of only 10% is required when the nucleophilic component is factored out from the traditional Y values. Also, it has been shown that the rates of solvolysis of tosylate esters can be very well correlated in terms of the extended (four-parameter) Grunwald–Winstein equation using the traditional Y values rather than Y_{OTs} values.[36] Accordingly, we have used the traditional Y values for the correlation of our data, knowing that (with the possible exception of the aqueous-2,2,2-trifluoroethanol system[31]) only very minor changes would result from the use of Y_{OTs},[29,34,35] Y_{Cl},[31] or Y_{Br}[31] scales.

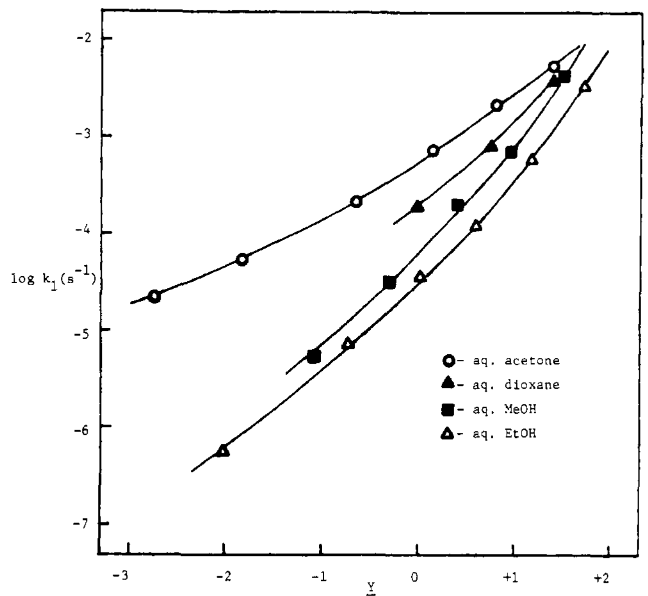


Figure 2. Grunwald–Winstein plot for the solvolysis of 2-adamantyl perchlorate in aqueous-organic solvents at 0.0 °C.

Table V. Calculated m Values for Solvolysis of 2-Adamantyl Perchlorate at 0.0 °C

solvents	no. of points	$m^{a,b}$	log k_0 ^{a,b}
100–70% ethanol	4	0.900 ± 0.008	−4.440 ± 0.009
100–60% ethanol	5	0.949 ± 0.038	−4.385 ± 0.042
100–50% ethanol	6	1.008 ± 0.051	−4.333 ± 0.062
70–50% ethanol	3	1.354 ± 0.011	−4.716 ± 0.007
100–70% methanol	4	1.055 ± 0.028	−4.132 ± 0.021
100–60% methanol	5	1.115 ± 0.043	−4.108 ± 0.041
95–70% acetone	4	0.533 ± 0.028	−3.229 ± 0.047
95–60% acetone	5	0.561 ± 0.026	−3.177 ± 0.040
95–50% acetone	6	0.582 ± 0.023	−3.144 ± 0.035
70–50% acetone	3	0.679 ± 0.002	−3.206 ± 0.002
70–50% dioxane	3	0.965 ± 0.054	−3.741 ± 0.048
90–70% dioxane[c]	3	0.761 ± 0.010	−2.990 ± 0.012
100–70% TFE	5	1.469 ± 0.209	−4.727 ± 0.228
100–60% TFE	6	1.139 ± 0.197	−4.322 ± 0.283
100–50% TFE	7	0.908 ± 0.157	−4.021 ± 0.247
80–50% TFE	4	0.449 ± 0.058	−3.143 ± 0.107

[a] Using the data of Table III; plots are curved (Figures 2 and 3) but values are calculated according to log $k = mY +$ log k_0.
[b] With associated standard errors. [c] At 12.7 °C.

When the specific rates at 0 °C for the pure organic solvents from Table I and the value for solvolysis in 2,2,2,-trifluoroethanol from Table III are used to construct a linear free energy relationship (LFER) plot against Y values[28,37] (Grunwald–Winstein plot), a good linear relationship (Figure 1) is obtained with a slope of 0.941 ± 0.041, consistent with the generally accepted[38] S_N1 mechanism for the solvolyses of 2-adamantyl derivatives. The linearity of the plot is in contrast to that for the solvolysis of 1-adamantyl tosylate,[27] where marked curvature was observed and where the acetolysis proceeded about five times faster than would be predicted based upon the other solvents. The specific electrophilic assistance proposed[27] to operate in the acetolysis of *p*-toluenesulfonate esters is, apparently, much weaker for perchlorate esters (and, also, for picrate esters[4]). For perchlorate esters any specific assistance must be comparable to that for the standard substrate, *tert*-butyl chloride.

---

(33) Kevill, D. N.; Kamil, W. A.; Anderson, S. W. *Tetrahedron Lett.* **1982**, *23*, 4635.

(34) Bentley, T. W.; Bowen, C. T.; Brown, H. C.; Chloupek, F. J. *J. Org. Chem.* **1981**, *46*, 38.

(35) Schadt, F. L.; Bentley, T. W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1976**, *98*, 7667.

(36) Kevill, D. N.; Lin, G. M. L. *J. Am. Chem. Soc.* **1979**, *101*, 3916.

(37) The Y values for TFE–H_2O systems are from: Shiner, V. J., Jr.; Dowd, W.; Fisher, R. D.; Hartshorn, S. R.; Kessick, M. A.; Milakofsky, L.; Rapp, M. W. *J. Am. Chem. Soc.* **1969**, *91*, 4838.

(38) See, for example, Harris, J. M. *Prog. Phys. Org. Chem.* **1974**, *11*, 89. Bentley, T. W.; Schleyer, P. v. R. *Adv. Phys. Org. Chem.* **1977**, *14*, 1.

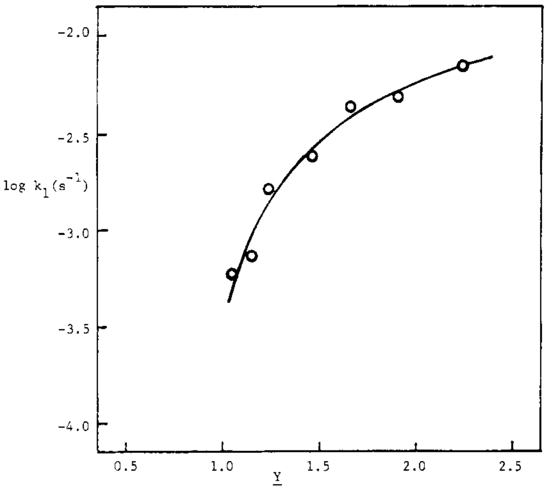


Figure 3. Grunwald–Winstein plot for the solvolysis of 2-adamantyl perchlorate in 2,2,2-trifluoroethanol–water mixtures at 0.0 °C.

The dispersion of the Grunwald–Winstein plot into a separate branch for each aqueous-organic solvent system, previously observed with 1-adamantyl tosylate,[27] is also observed with 2-adamantyl perchlorate. The dispersion in the 1-adamantyl tosylate study was essentially lateral in nature, and each mixed-solvent system, studied only in the highly organic region, had a slope (*m* value) of close to unity. In the order of decreasing rates at any given *Y* value, the plots lay with aqueous methanol > aqueous ethanol > aqueous acetone > aqueous dioxane. The corresponding plots for 2-adamantyl perchlorate are shown in Figure 2 and the calculated *m* values for varying ranges of composition are given in Table V. The plots all curve upward, with behavior similar to that observed for 2-adamantyl *p*-toluenesulfonate in the more aqueous regions of aqueous ethanol and aqueous acetone.[34] Further, the ordering of the plots is such that, relative to 1-adamantyl tosylate, the rates in water–aprotic solvent mixtures have been lifted above the rates in the aqueous-alcohol mixtures; i.e., aqueous acetone > aqueous dioxane > aqueous methanol > aqueous ethanol. For the more limited data available for 1-adamantyl picrate,[30] the ordering is aqueous acetone > aqueous ethanol > methanol.

For 2-adamantyl perchlorate solvolysis, it can be seen qualitatively from Figure 2 and quantitatively from Table V that the *m* values vary appreciably, from 0.53 in 95–70% acetone to 1.06 in 100–70% methanol, or, if one wishes to compare two regions with approximately the same range of *Y* values, from 0.53 in 95–70% acetone to 0.90 in 100–70% ethanol. While the *m* values in the aqueous alcohols remain close to or above unity throughout the range studied, rising to as much as 1.35 in the 70–50% ethanol range, the values in aqueous acetone are consistently lower, rising only to 0.68 in the 70–50% acetone range. Dioxane–water mixtures lead to intermediate values for *m* of 0.76 in the 90–70% dioxane range (at 12.7 °C), rising to 0.96 for the 70–50% dioxane range. The previous study[30] of 1-adamantyl picrate led to consistently low values for *m*, not only in 90–70% acetone (0.39) but also in 100–44% ethanol (0.56).

The Grunwald–Winstein plot for the study in TFE–water mixtures is given in Figure 3 and the analysis of the data in Table V. Unlike the other plots, the plot curves markedly *downward*, with a *m* value of 1.47 for 100–70% TFE, decreasing to 0.45 for 80–50% TFE. Since all of the plots for aqueous-organic mixtures must eventually converge upon the (unknown) log *k* value for pure water, either the TFE–H_2O plot must turn upward or the other plots must turn downward (with the possibility, of course, of a compromise) in the highly aqueous region. Depending upon the probe employed, quite different scales of solvent ionizing power for TFE–H_2O mixtures have been obtained.[39] Recently, three Y_{Cl} values have been reported[31] for TFE–H_2O mixtures. These are based on 1-adamantyl chloride solvolysis, and they minimize contributions from nucleophilic solvation of the developing cation.[31,33] However, use of these values leads to an even more markedly downward-curving plot.

The present study shows very clearly that for a given substrate, especially when of a type not previously studied, considerable care must be exercised in quoting values for the *m* parameter. For example, the comparison of a *m* value for 2-adamantyl trifluoromethanesulfonate measured in acetone-rich acetone–water mixtures with values for other 2-adamantyl derivatives measured in aqueous ethanol in terms of the relative stabilities of the incipient anions[40] is clearly a dangerous procedure. Indeed, for 2-adamantyl perchlorate, one cannot quote a value for *m* independent of the identity of the mixed solvent and the range of composition studied. A brief study in a limited range of one of the mixed solvent systems could have resulted in any value for *m* between 0.4 and 1.5.

In addition to 1-adamantyl picrate solvolysis[30] and some of the presently reported solvolyses, at least one other solvolysis believed to be S_N1 in character has exhibited low *m* values. Solvolysis of 1-adamantyl chloroformate[18] exhibited *m* values of 0.68 in aqueous-ethanol mixtures and 0.44 in aqueous-acetone mixtures. For solvents where temperature variation of rate has also been studied, solvolyses of the adamantyl derivatives exhibiting the unusually low *m* values normally exhibit entropies of activation which are considerably more positive than for solvolyses in which the leaving group is one which leads to *m* values closer to unity. For example, in methanol, the $\Delta S^{\ddagger}$ values (eu) are −4.2 for 1-adamantyl tosylate,[27] −1.5 for 1-adamantyl methanesulfonate,[29] +7.0 for 1-adamantyl picrate,[4] +3.8 for 1-adamantyl chloroformate,[18] and +13.2 for 2-adamantyl perchlorate (Table II). While it can be dangerous to base mechanistic conclusions only on entropy of activation values, we agree with Luton and Whiting[4] that the observation of relatively positive $\Delta S^{\ddagger}$ values coupled with low *m* values is very reasonably explained in terms of reduced solvation, which in turn leads to less loss of freedom of solvent molecules. Consistent with this explanation is the observation that the entropies of activation for the ethanolyses of both 1-adamantyl and 2-adamantyl arenesulfonates rise in value with the Hammett σ value of the substituent;[24] as the leaving group becomes better able to internally disperse the developing negative charge, there is less need for dispersal through solvation and less loss of freedom of solvent molecules.

The very different kinetic responses to variation in solvent composition exhibited by perchlorate, arenesulfonate, and picrate esters strongly support the viewpoint that each leaving group requires separate consideration.[31,34,35] It was emphasized several years ago,[41] from a study involving a large number of anions, that each anion responds differently to transfer from a protic to a dipolar aprotic solvent, and, as a general guide, small anions which are strong hydrogen bond acceptors are much more solvated by protic than by dipolar aprotic solvents, whereas large polarizable anions (such as perchlorate), which do not have strong hydrogen-bonding interactions with protic solvents, show the reverse behavior. These solvation considerations will be an important factor in determining the detailed nature of the solvation of incipient anions in mixed solvents. A scale of *P* values was developed;[41] these measure the ease of transfer of an anion, relative to thiocyanate, from water to a new solvent. For tranfer to *N*,*N*-dimethylformamide, the values obtained included 5.1 for chloride, 0.4 for tosylate (positive values imply a relative loss of solvation and vice versa), −3.2 for picrate, and −3.4 for perchlorate. The higher lipophilicities of perchlorate and picrate are confirmed by consideration of the extraction constants for tetra-*n*-butylammonium salts from water to chloroform; values of 0.78 for chloride, 214 for tosylate, 3020 for perchlorate, and 8.1 × 10^5 for picrate have been assembled.[5]

Luton and Whiting[4] suggested that chlorides respond kinetically to variations in the composition of an aqueous-organic system more

---

[39] Rappoport, Z.; Kaspi, J. *J. Am. Chem. Soc.* **1974**, *96*, 4518.

[40] Creary, X. *J. Am. Chem. Soc.* **1976**, *98*, 6608.

[41] Alexander, R.; Ko, E. C. F.; Mac, Y. C.; Parker, A. J. *J. Am. Chem. Soc.* **1967**, *89*, 3703.

markedly than picrates because solvation of the halide ion by water is the largest energy term involved in going from the reactant to the transition state. This view has been supported by the demonstration for several pure solvents that solvation of the developing chloride ion in the solvolysis of *tert*-butyl chloride is indeed the major factor controlling variation of rate with solvent composition.[42] Presumably, with the more lipophilic leaving groups, solvation by the organic component can become competitive with solvation by water, leading to a reduced falloff in rate as the proportion of the organic component is increased. In extreme cases, where the bulk dielectric constant varies only modestly, as in methanol–tetramethylene sulfone[4] or methanol–acetone[3] compositions, solvolyses of adamantyl derivatives with lipophilic leaving groups can proceed at a rate almost independent of the proportions of the two components.

However, the rationalization of the solvolysis of 1-adamantyl picrate in "pure" tetramethylene sulfone in terms of a small water content (ca. 0.01 M) forming water-separated ion pairs competitive with internal return[4] should probably be modified to allow for an initial separation by the sulfone molecules in a process eventually leading to 1-adamantanol. Similarly, it has been shown that 1-adamantyl arenesulfonates solvolyze quite readily in acetonitrile to give (even in the presence of azide ion) the 1-adamantylacetonitrilium ion, presumably via an actonitrile-separated ion pair.[43]

The differing kinetic responses to solvent variation are, in turn, reflected in the scales of Y values presented in Tables I and II and, for several of the solvents of Table II, also in Table IV of a report by Bentley and Carter.[31] In addition to the first values for a perchlorate leaving group ($Y_{\mathrm{OClO_3}}$), additional values are also reported for a tosylate leaving group, based upon a previously reported[27] study of 1-adamantyl tosylate; since it has been shown[29] that a good LFER exists between the specific rates of solvolysis of 1-adamantyl and 2-adamantyl tosylates, with a slope of close to unity, values from either scale can be used interchangeably. Since 1-adamantyl and 2-adamantyl derivatives differ in solvolysis rates[24,44] by a factor of about 10^5, use in tandem allow Y_{OTs} values to be determined over a wide range of solvent composition without the need for temperature or solvent composition extrapolations. The Y_{OTs} values in 95–80% acetone are especially valuable in that they extend the 60–0% acetone range of Y_{OTs} values previously reported.[29,34]

For some leaving groups, large variations in Y values from the traditional Y values occur for aqueous acetone compositions that are rich in acetone. In 95% acetone, reflecting both dispersion and curvature (Figure 2), the $Y_{\mathrm{OClO_3}}$ value of -0.23 is some 2.5 units higher than either the Y or Y_{OTs} values. In 90% acetone, the Y and Y_{OTs} values are similar, the Y_{Pic} value is about 1.25 units higher, and the $Y_{\mathrm{OClO_3}}$ value about 2.1 units higher. The $Y_{\mathrm{OClO_3}}$ values also differ appreciably from Y values for aqueous-dioxane compositions, but they are similar to Y values for aqueous-ethanol (unlike Y_{Pic} values), aqueous-methanol, and aqueous-TFE systems.

For some solvents, the specific rate of solvolysis can be combined with values obtained by extrapolation of data at higher temperatures for other 2-adamantyl derivatives, to give a measure of the relative nucleofugality of the perchlorate ion in S_N1 reactions. Since these extrapolations must span a fairly large temperature gap, the error in the extrapolated value can be as large as 30%. However, since several orders of magnitude of nucleofugality are involved, such errors would not seriously distort the comparisons. In 80% ethanol, using literature values for the solvolyses of 2-adamantyl tosylate[23] and 2-adamantyl bromide[25] and the value for 2-adamantyl perchlorate solvolysis from Table I, a $\mathrm{OClO_3}$:OTs:Br ratio of specific solvolysis rates at 25 °C of $1{:}1.6 \times 10^{-5}{:}7.0 \times 10^{-8}$ is obtained. In ethanol[24] at 25.0 °C, the $\mathrm{OClO_3}$:OTs ratio is essentially identical, $1{:}1.4 \times 10^{-5}$. From data reported[45] for 97% TFE, an extrapolated specific rate of solvolysis of 2-adamantyl tosylate at 0 °C of $2.58 \times 10^{-8}\ \mathrm{s^{-1}}$ can be calculated; together with the value for this solvent from Table III, this leads to a $\mathrm{OClO_3}$:OTs ratio of $1{:}3.5 \times 10^{-5}$. For acetolysis at 25.0 °C, using literature values for 2-adamantyl tosylate[23] and 2-adamantyl bromide,[25] an extrapolated value of $1.94 \times 10^{-10}\ \mathrm{s^{-1}}$ for 2-adamantyl picrate,[26] and the value for 2-adamantyl perchlorate from Table I, a $\mathrm{OClO_3}$:OTs:Pic:Br ratio of specific solvolysis rates of $1{:}1.2 \times 10^{-4}{:}\ 4.1 \times 10^{-6}{:}0.9 \times 10^{-8}$ is obtained.

Averaging the S values within Table IV for the relative sensitivities toward attack by water and ethanol molecules, values (with standard deviations) of 1.72 ± 0.13 at 0.1 °C and of 1.75 ± 0.14 at 24.7 °C are obtained. Other studies of 1- and 2-adamantyl derivatives in aqueous ethanol[10,32] have also shown a perference for reaction with water by a factor of about 2. The previously observed insensitivities of the S values to solvent composition ratio,[10,32] temperature,[10,32] and large changes in lipophilicity of the leaving group[32] are confirmed in the present study, and, in addition, it is shown that even an extremely large variation in leaving group ability (ca. 10^8 between bromide and perchlorate) does not significantly change the S values observed.

The observation that the S values with either 9% dioxane or 9% pentane present are essentially identical suggests that no significant perturbation results from an initial nucleophilic intervention by dioxane.[46]

Karton and Pross[10] did bring about a change in the S values by addition of large quantities of acetone (≥20%) to solvolyses of adamantyl derivatives in 60% ethanol. They interpreted this observation in terms of an enhancement of water nucleophilicity relative to ethanol nucleophilicity. However, it is probable that the dominant factor controlling the formation of products is the ability of the solvent components to participate in the formation of the solvent-separated ion pair,[9] with nucleophilicity considerations being only a secondary factor. Futher, acetone has been shown to be an effective nucleophile, capable, for example, of competition with methanol.[46] If an acetone molecule was to insert itself to give a solvent-separated ion pair involving a dipolar aprotic solvent molecule,[43] collapse to an acetoxonium ion would frequently follow. While in other systems[46] the presence[10] of lutidine has negated the subsequent alcohol formation resulting from an acid-catalyzed decomposition of a mixed ketal of acetone, one must also consider the probability that, as the acetone content is increased, an increasing proportion of products will result from further reaction of an intermediate acetoxonium ion and not directly from the ionization of the initial substrate.

Experimental Section

Materials. The purifications of acetone, *tert*-butyl alcohol, dioxane, ethanol, methanol, and 2-propanol were as previously described.[27] The purifications of acetic acid,[47] formic acid,[48] and 2,2,2-trifluoroethanol[39] were also performed using previously reported procedures. The 2-adamantyl bromide (Aldrich) was recrystallized from methanol and dried under vacuum. Silver perchlorate (Alfa) was dried at 120 °C for 24 h and allowed to cool over P_2O_5 in a desiccator.

2-Adamantyl Perchlorate. A modification of a method previously used to prepare *n*-alkyl perchlorates[49] was employed. A 0.860-g portion of 2-adamantyl bromide was dissolved in 20 mL of pentane, and a tenfold excess (8.33 g) of silver perchlorate was added. After 2 days, the 2-adamantyl perchlorate solution was decanted from precipitated silver bromide and excess silver perchlorate. For transfer to dioxane, 10 mL of the pentane solution was treated with 14 mL of dioxane and the mixture evaporated to 10 mL using a vacuum desiccator. A control experiment showed that such an evaporation produced a solvent with less than 7% residual pentane.

Kinetic Procedures. To 49 mL of the solvent under investigation was added 1 mL of the stock solution of 2-adamantyl perchlorate in pentane

---

[42] Abraham, M. H.; Taft, R. W.; Kamlet, M. J. *J. Org. Chem.* **1981**, *46*, 3053.

[43] Kevill, D. N.; Kim, C.-B. *J. Org. Chem.* **1974**, *39*, 3085.

[44] Fort, R. C., Jr.; Schleyer, P. v. R. *Chem. Rev.* **1964**, *64*, 277.

[45] Allard, B.; Casadevall, A.; Casadevall, E.; Largeau, C. *Nouv. J. Chim.* **1979**, *3*, 335.

[46] Weiner, H.; Sneen, R. A. *J. Am. Chem. Soc.* **1965**, *87*, 287. Hammett, L. P. "Physical Organic Chemistry", 2nd ed.; McGraw-Hill: New York, 1970; pp 160–161.

[47] Swain, C. G.; Kaiser, L. E.; Knee, T. E. C. *J. Am. Chem. Soc.* **1958**, *80*, 4092.

[48] Winstein, S.; Marshall, H. *J. Am. Chem. Soc.* **1956**, *74*, 1126.

[49] Radell, J.; Connolly, J. W.; Raymond, A. J. *J. Am. Chem. Soc.* **1961**, *83*, 3958.

or dioxane. For runs in water, alcohols, and aqueous-organic mixtures, 5-mL portions were removed at suitable time intervals into 25 mL of acetone, containing Lacmoid (resorcinol blue) indicator, and cooled in a solid CO_2–acetone slush bath. The acid produced was titrated against a standardized solution of sodium methoxide in methanol. The procedure for runs in acetic acid and the calculation of first-order solvolytic rate coefficients were as previously described.[36] All runs were performed, at least, in duplicate.

Product Studies. A stock solution of 2-adamantyl perchlorate in dioxane was used to prepare reaction mixtures in 100–50% ethanol (by volume). These reaction mixtures were allowed to stand at the appropriate temperature for in excess of 10 half-lives. The products were directly analyzed by response-calibrated GLC using a Packard instrument (Model GC-430) with flame ionization detector and microprocessor integrator. The stationary phase consisted of 15% Carbowax-20M on Chromosorb WNAW, within a 6 ft × 1/4 in. column. All determinations were made at least in duplicate and an error of ±5% is estimated for the product ratio.

Acknowledgments. This research was supported, in part, by the award of a Doctoral Research Fellowship to S.W.A. by the NIU Graduate School. One of us (D.N.K.) wishes to thank Professor M. Hanack, Lehrstuhl Für Organische Chemie 2, Universität Tübingen, for hospitality during the time that this manuscript was prepared.

Registry No. 2-Adamantyl perchlorate, 83187-55-7; 2-adamantyl bromide, 7314-85-4; silver perchlorate, 7783-93-9.

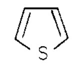
Reactions of the π-Thiophene Ligand in (η-C_4H_4S)$Mn(CO)_3^+$. Mechanistic Possibilities for Catalytic Hydrodesulfurization

David A. Lesch, James W. Richardson, Jr., Robert A. Jacobson, and Robert J. Angelici*

Contribution from the Department of Chemistry and Ames Laboratory,[1] Iowa State University, Ames, Iowa 50011. *Received September 26, 1983*

Abstract: Reaction of $Mn(CO)_5OSO_2CF_3$ with refluxing thiophene gives a high yield of $[Mn(CO)_3(\text{thiophene})]SO_3CF_3$ (**1**). This complex reacts with CN^- to give $Mn(CO)_3(\text{thiophene}\cdot CN)$ (**2a**) and with BH_4^-, $HFe(CO)_4^-$, and $HW(CO)_5^-$ to give $Mn(CO)_3(\text{thiophene}\cdot H)$ (**2c**). A single-crystal X-ray diffraction study of **2a** shows that it crystallizes in the monoclinic cell $P2_1/c$ with $a = 12.008$ (2) Å, $b = 6.6935$ (8) Å, $c = 12.172$ (2) Å, $\beta = 95.63$ (2)°, and four molecules per unit cell. The structure demonstrates that cyanide addition occurs at a carbon atom adjacent to sulfur causing this now-saturated carbon to be 0.59 Å out of the plane of the thiophene ring. Compound **1** reversibly adds $P(n\text{-}Bu)_3$ to form $Mn(CO)_3(\text{thiophene}\cdot PBu_3)^+$. Protonation of **2c** by HCl, HSO_3CF_3, HI, and CF_3CO_2H yields an unstable complex of 2,3-dihydrothiophene. The dihydrothiophene is readily displaced by MeCN or CO. Hydride addition to the π-bonded thiophene in **2c**, followed by protonation, is suggested as a possible model for the first steps in hydrodesulfurization of thiophene.

The mechanism of catalytic hydrodesulfurization (HDS) of thiophene has been the subject of numerous investigations.[2] In general, these studies have involved commercial Co–Mo/Al_2O_3 catalysts. Two key features of the mechanism which are not well



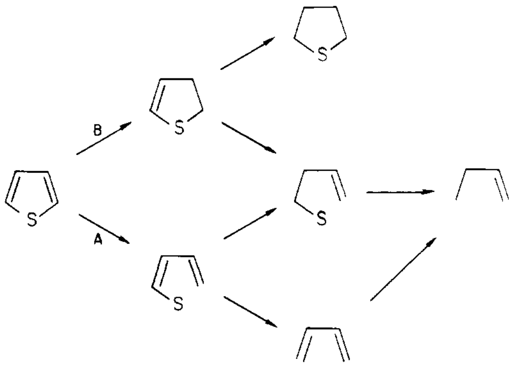
$+ 3H_2 \longrightarrow$ 1- and 2-butenes $+ H_2S$ (1)

defined are (1) the initial mode of bonding of thiophene to the catalyst surface and (2) the nature of the first step in the HDS process; does it involve C–S bond cleavage or hydrogenation of an unsaturated carbon–carbon bond?

The most commonly invoked mode of thiophene adsorption is via the sulfur lone-electron pair to a metal cation. Kwart and co-workers recently reviewed this "one point" model and also discussed its shortcomings.[3a] Kwart proposed instead a model whereby thiophene adsorbed by coordination through a C=C double bond. Earlier Cowley[3b] and Zdrazil[3c] suggested that the entire aromatic π system of thiophene is coordinated to metal sites on the surface.

The detection of small amounts of butadiene among the HDS products has been the basis for suggesting that C–S bond cleavage occurs prior to carbon–carbon bond hydrogenation (path A).[4] The presence of tetrahydrothiophene, on the other hand, suggests a mechanism involving initial hydrogenation of unsaturated carbon–carbon bonds (path B).[5,6]

Scheme I. Possible Pathways for Thiophene HDS



arrows indicate H_2 addition

As is true in all catalytic systems, determining the nature of shortlived intermediates is very difficult. The use of discrete metal complexes has proven useful in modeling types of substrate reactivity which might occur on heterogeneous catalysts.[7] A number

---

[1] Ames Laboratory is operated for the U. S. Department of Energy by Iowa State University under Contract No. W-7405-Eng-82. This research was supported by the office of Basic Energy Sciences, Chemical Sciences Division.

[2] Mitchell, P. C. H. In "Catalysis"; Kemball, C., Ed.; The Chemical Society: London, 1977; Vol. 1, p 223; Vol. 4, p 203 ("Special Periodical Report").

[3] (a) Kwart, H.; Schuit, G. C. A.; Gates, B. C. *J. Catal.* **1980**, *61*, 128. (b) Cowley, S. W., Pd.D. Thesis, Southern Illinois University, 1975. (c) Zdrazil, M. *Collect. Czech. Chem. Commun.* **1977**, *42*, 1484.

[4] Desikan, P.; Amberg, C. H. *Can. J. Chem.* **1964**, *42*, 843.

[5] Zdrazil, M. *Collect. Czech. Chem. Commun.* **1975**, *40*, 3491.

[6] Devanneaux, J.; Maurin, J. *J. Catal.* **1981**, *69*, 202.

[7] Muetterties, E. L.; Stein, J. *Chem. Rev.* **1979**, *79*, 479 and references therein.

0002-7863/84/1506-2901$01.50/0