

Solvolysis-Decomposition of 1-Adamantyl Chloroformate: Evidence for Ion Pair Return in 1-Adamantyl Chloride Solvolysis^{†,1,2}

Dennis N. Kevill,* Jin Burm Kyong,³ and Frederick L. Weigl

Department of Chemistry, Northern Illinois University, DeKalb, Illinois 60115

Received December 20, 1989

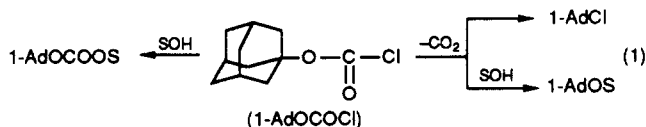
In hydroxylic solvents, 1-adamantyl chloroformate reacts with loss of carbon dioxide and formation of both solvolysis and decomposition products. The rates of both processes are appreciably sensitive to solvent ionizing power, with the solvolysis slightly more so. The influence of anionic additives is discussed. For mixtures of hydroxylic solvents, the selectivities for the formation of solvolysis products are very similar to those observed in conventional solvolyses of 1-adamantyl derivatives. It is suggested that 1-Ad⁺Cl⁻ ion pair intermediates are formed, and the observation of collapse requires that an identical collapse, corresponding to internal return, also occurs in 1-adamantyl chloride solvolysis. A comparison with solvolyses of other 1-AdOCOX compounds suggests that the initial ionization is not to 1-Ad⁺(OCOCl)⁻ and that the 1-Ad⁺Cl⁻ ion pair is formed either in a concerted process or via a very unstable (1-AdOCO)⁺Cl⁻ ion pair.

Introduction

A study of the decomposition of 1-adamantyl chloroformate to yield 1-adamantyl chloride in relatively inert solvents has been reported previously.⁴ Small amounts of accompanying solvolysis (<2% at 54 °C) were observed in benzene and nitrobenzene. Large rate variations correlated with Dimroth-Reichardt $E_T(30)$ values in a manner consistent with the originally proposed ionic process.⁵ In the relatively nucleophilic acetonitrile, the decomposition was accompanied by an appreciable amount (68% at 25 °C)⁵ of solvolysis to give the acetonitrilium chloride, which then slowly lost acetonitrile, affording an indirect route to the decomposition product. The *N*-(1-adamantyl)-acetonitrilium ion could be trapped by addition of water or azide ion to give 40–50% isolated yields of the acetamide or tetrazole, respectively.⁶

In hydroxylic solvents, chloroformates with a primary alkyl group usually solvolyze⁷ with attack at the carbonyl carbon. With a secondary alkyl group, the solvolyses have been found to be on the S_N1 – S_N2 borderline. Due to their instability,^{8,9} simple tertiary alkyl chloroformates have not been studied under solvolytic conditions. The bridgehead 1-adamantyl chloroformate is convenient to study because of both an increased stability¹⁰ and convenient solvolysis rates at around room temperature.

In the present study we report on the overall specific rates for solvolysis-decomposition in pure and mixed solvents, the dissected specific rates for solvolysis and decomposition, and the partitioning between the various possible solvolysis products (eq 1). The Grunwald-Win-



stein equation^{11,12} is applied to the specific rates. The partitioning within the solvolysis product is compared to behavior previously observed for the solvolyses of other adamantyl derivatives.

Results

Kinetics of Solvolysis-Decomposition. Specific rates were determined in methanol, ethanol, isopropyl alcohol, *tert*-butyl alcohol, 80% ethanol, and 90% dioxane at four to six temperatures in the 0–55 °C range. The specific rates of reaction were obtained using the observed infinity

titer for acid development, which, due to accompanying decomposition, was less than the value for the infinity titer calculated based upon complete solvolysis. The specific rates of solvolysis-decomposition and the percentages of reaction proceeding with solvolysis, from the ratio of the observed and calculated infinity titers, are reported in Table I. The activation parameters (at 25.0 °C) obtained from a treatment of this data in terms of the Eyring equation are reported in Table II. Specific rates of solvolysis-decomposition and percentages of reaction proceeding with solvolysis were measured at 25.0 °C for several aqueous methanol, aqueous ethanol, aqueous acetone, aqueous dioxane, and ethanol-2,2,2-trifluoroethanol (TFE) mixtures, and these values are also reported in Table I.

With the exception of runs in *tert*-butyl alcohol, constant integrated values for the first-order rate coefficient were obtained throughout each run. For reactions in *tert*-butyl alcohol, a stable infinity titer was not obtained, probably due to a slow removal of HCl by interaction with the reactive¹³ 1-adamantyl *tert*-butyl ether product. Runs in *tert*-butyl alcohol were analyzed in terms of a Guggenheim plot,¹⁴ omitting data obtained in the later stages of reaction. The specific rate of solvolysis-decomposition obtained could then be used to estimate the value that would have been obtained for the infinity titer in the absence of further reaction.

Product Studies by Acid Titration. For a range of aqueous acetone and aqueous dioxane concentrations of from 5 to 55% water content (volume/volume) and for a temperature range of 0–45 °C, the percentages of reaction with solvolysis were determined by a comparison of ob-

(1) For a preliminary communication of a portion of this work, see: Kevill, D. N.; Weigl, F. L. *Tetrahedron Lett.* 1971, 707.

(2) Presented at the 2nd European Symposium on Organic Reactivity, Padova, Italy, Aug 27–Sept 1, 1989, Abstract C6.

(3) On leave from Department of Chemistry, Hanyang University, Seoul 133, Korea.

(4) Kevill, D. N.; Weigl, F. L. *J. Am. Chem. Soc.* 1968, 90, 6416.

(5) Kevill, D. N.; Weigl, F. L. *J. Chem. Res. (S)* 1989, 318.

(6) Kevill, D. N.; Weigl, F. L. *J. Org. Chem.* 1970, 35, 2526.

(7) For a review, see: Kevill, D. N. In *The Chemistry of Acyl Halides*; Patai, S., Ed.; Interscience: New York, 1972; pp 410–415.

(8) Choppin, A. R.; Rodgers, J. W. *J. Am. Chem. Soc.* 1948, 70, 2967.

(9) Sakakibara, S.; Shin, M.; Fujino, M.; Shimonishi, Y.; Inoue, S.; Inukai, N. *Bull. Chem. Soc. Jpn.* 1965, 38, 1522.

(10) Haas, W. L.; Krumkalns, E. V.; Gerzon, K. *J. Am. Chem. Soc.* 1966, 88, 1988.

(11) Grunwald, E.; Winstein, S. *J. Am. Chem. Soc.* 1948, 70, 846.

(12) For a recent review, see: Bentley, T. W.; Llewellyn, G. *Adv. Phys. Org. Chem.*, in press.

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

(14) For a discussion of this method, see: Margerison, D. In *Comprehensive Chemical Kinetics*; Bamford, C. H., Tipper, C. F. H., Eds.; Elsevier: New York, 1969; Vol. 1, pp 388–390.

[†] Dedicated to Professor Paul v. R. Schleyer on the occasion of his 60th birthday.

Table I. Specific Rates of Solvolysis-Decomposition of 0.056 M 1-Adamantyl Chloroformate and Percentage of Reaction Proceeding with Solvolysis

| solvent ^a | T, °C | 10 ⁴ k, s ⁻¹ | % solv | Y ^a | |
|------------------------|------------------------|------------------------------------|-------------------|-------------------|--------------------|
| MeOH | 35.4 | 124 ± 3 | 75.5 | | |
| | 24.8 | 33.9 ± 0.5 | 74.6 ^b | -1.09 | |
| | 15.1 | 9.4 ± 0.1 | 73.3 | | |
| EtOH | 0.0 | 1.09 ± 0.02 | 70.8 | | |
| | 35.1 | 20.6 ± 0.5 | 64.5 | | |
| | 25.0 | 5.47 ± 0.05 ^c | 61.1 | -2.03 | |
| | 14.9 | 1.28 ± 0.03 | 58.0 | | |
| i-PrOH | 0.0 | 0.132 ± 0.001 | 57.4 | | |
| | 45.1 | 23.4 ± 0.5 | 58.6 | | |
| | 35.0 | 6.64 ± 0.06 | 52.0 | | |
| t-BuOH ^d | 25.0 | 1.71 ± 0.11 | 51.4 | -2.73 | |
| | 14.8 | 0.371 ± 0.006 | 49.5 | | |
| | 45.1 | 13.2 ± 0.7 | 31.7 ^e | | |
| | 35.1 | 3.87 ± 0.03 | 30.2 | | |
| 95% MeOH | 30.0 | 1.98 ± 0.06 | 29.1 | | |
| | 25.0 | 0.98 ± 0.01 | 27.5 | -3.26 | |
| | 25.0 | 72.5 ± 0.7 | 77.2 | -0.68 | |
| | 90% MeOH | 25.0 | 127 ± 5 | 80.0 | -0.30 |
| | 95% EtOH | 25.0 | 16.1 ± 0.1 | 62.2 | -1.29 |
| | 90% EtOH | 25.0 | 29.5 ± 0.8 | 67.1 | -0.75 |
| | 80% EtOH ^f | 30.0 | 232 ± 6 | 74 ^g | |
| | | 25.0 | 120 ± 3 | 69 ^g | 0.00 |
| | | 19.9 | 69.4 ± 2.0 | 65 ^g | |
| | | 15.0 | 35.1 ± 0.5 | 71 ^g | |
| 95% Me ₂ CO | 5.8 | 9.7 ± 0.3 | 68 ^g | | |
| | 0.0 | 3.55 ± 0.08 | 63 ^g | | |
| | 25.0 | 17.7 ± 0.2 | 68.1 | -2.76 | |
| | 90% Me ₂ CO | 25.0 | 41.8 ± 0.5 | 68.3 | -1.86 |
| | 85% Me ₂ CO | 25.0 | 82.7 ± 0.6 | 70.8 | -1.22 |
| | 80% Me ₂ CO | 25.0 | 146 ± 4 | 68.3 ^h | -0.67 |
| | 95% Dx ⁱ | 25.0 | 2.06 ± 0.01 | 49.5 | -2.94 ^j |
| | 90% Dx ⁱ | 55.0 | 153 ± 5 | 59.3 | |
| | | 50.0 | 102 ± 2 | 57.0 | |
| | | 35.1 | 24.6 ± 0.3 | 57.2 | |
| 85% Dx ⁱ | 25.0 | 8.5 ± 0.1 | 55.5 | -2.03 | |
| | 19.9 | 4.55 ± 0.03 | 53.9 | | |
| | 14.8 | 2.33 ± 0.05 | 55.3 | | |
| | 25.0 | 21.8 ± 0.3 | 63.1 | -1.38 | |
| | 80% Dx ⁱ | 25.0 | 48.7 ± 0.6 | 65.6 | -0.83 |
| 75% Dx ⁱ | 25.0 | 94.5 ± 1.7 | 70.2 | -0.38 | |
| 70% Dx ⁱ | 25.0 | 172 ± 9 | 70.8 | 0.01 | |
| 10T-90E ^k | 25.0 | 8.76 ± 0.14 | 59.5 | -1.77 | |
| 20T-80E | 25.0 | 20.7 ± 0.3 | 57.6 | -1.52 | |
| 30T-70E | 25.0 | 36.4 ± 0.9 | 61.6 | -1.22 | |
| 40T-60E | 25.0 | 69.4 ± 1.4 | 73.6 | -0.87 | |

^aFor mixed aqueous solvents, X % of organic solvent mixed with (100 - X) % of H₂O on volume-volume basis at 25.0 °C. Solvent ionizing power values from ref 18; some obtained by interpolation within the reported values. ^bA gravimetric analysis indicated 77.8% ionic chlorine and 20.4% covalent chlorine. ^cWith 0.0061 M 1-AdOCOCl, a value of 5.14 (±0.09) × 10⁻⁴ s⁻¹ was obtained. ^dStable infinity titer not obtained; *k* values and *V_∞* values in the absence of perturbation obtained by Guggenheim treatment. ^eAs an example of acid loss in this solvent, observed acid titer rose to 30.7% of theoretical (based on complete solvolysis) and then slowly declined. ^fSubstrate was dissolved in ethanol and the calculated volume of H₂O added (based on required composition at 25.0 °C and coefficients of expansion). ^gBecause of the way in which the mixed solvent was prepared (see footnote *f*), value is probably slightly low. ^hGLPC analysis of the products from 0.0068 M 1-AdOCOCl indicated 69.5% 1-AdOH and 30.5% 1-AdCl. ⁱ1,4-dioxane. ^jBy extrapolation of a plot of *Y* values for aqueous dioxane against those for corresponding aqueous acetone compositions. ^k2,2,2-Trifluoroethanol (T)-ethanol (E) mixtures (by volume).

served and calculated (for 100% solvolysis) infinity acid titers. To avoid nonhomogeneous reaction during the dissolving of the solid, a small amount of a concentrated solution of 1-adamantyl chloroformate in benzene was added to the appropriate mixed solvent. These results are reported in Table III.

Effect of Added Tetra-*n*-butylammonium Salts. The effects, at 25.0 °C in ethanol or methanol, of added

Table II. Enthalpies (Δ*H*[‡]) and Entropies (Δ*S*[‡]) of Activation for Solvolysis-Decomposition of 1-Adamantyl Chloroformate^a

| solvent | Δ <i>H</i> [‡] ₂₉₈ , kcal/mol | Δ <i>S</i> [‡] ₂₉₈ , eu |
|----------------------------|---|---|
| methanol | 21.82 ± 0.04 | +3.34 ± 0.14 |
| ethanol | 23.79 ± 0.12 | +6.34 ± 0.41 |
| 2-propanol | 24.42 ± 0.15 | +6.02 ± 0.55 |
| <i>tert</i> -butyl alcohol | 23.84 ± 0.40 | +3.08 ± 1.35 |
| 80% ethanol | 22.07 ± 0.26 | +6.72 ± 0.92 |
| 90% dioxane | 18.84 ± 0.30 | -9.37 ± 1.03 |

^aCalculated using the data of Table I; with associated standard errors.

tetra-*n*-butylammonium chloride, bromide, iodide, or perchlorate in concentrations of from 0.01 to 0.1 M upon both the specific rates and the percentages of reaction involving solvolysis (as determined from the magnitude of the infinity acid titers) are reported in Table IV. For addition of the iodide salt, a red color developed (presumably due to conversion of HI to I₂), and the observed acid titer passed through a maximum slightly lower than the value corresponding to the percentage of reaction with solvolysis. As with the reaction in *tert*-butyl alcohol, the reported specific rates of reaction, and the infinity titers used to calculate the percentage of reaction proceeding with solvolysis, were obtained by the Guggenheim procedure.¹⁴

Product Studies by GLPC. The products from the solvolysis-decomposition of 1-adamantyl chloroformate in aqueous ethanol (Table V), in ethanol containing bromide or chloride ion (Table VI), and in mixtures of TFE with water or ethanol (Table VII) have been determined by response-calibrated GLPC after reaction at 25.0 °C. Small percentages of 1-adamantanol found after solvolysis in TFE-ethanol mixtures probably result from reaction of the substrate with moisture during manipulation. In the calculation of solvent selectivity values (*S*) for aqueous-organic mixtures (eq 2), these percentages were first sub-

$$S = \frac{[\text{adamantanol}][\text{alcohol}]}{[\text{adamantyl alkyl ether}][\text{H}_2\text{O}]} \quad (2)$$

tracted from each of the determined percentages of 1-adamantanol before insertion into the equation.

For the reaction in TFE-ethanol mixtures the solvent selectivity value was calculated using eq 3.

$$S = \frac{[1\text{-AdOCH}_2\text{CF}_3][\text{EtOH}]}{[1\text{-AdOCH}_2\text{CH}_3][\text{TFE}]} \quad (3)$$

Small amounts of carbonate (<1% 1-adamantyl ethyl carbonate¹⁵) were found only for reaction in 100% ethanol. Other detected products all involved loss of carbon dioxide and either collapse to decomposition product or solvolysis to give alcohol or ether.

Effect upon the Ethanolysis of Added Sodium Ethoxide. A marked acceleration was observed upon addition of small (<0.01 M) concentrations of sodium ethoxide. The kinetics were followed in terms of second-order rate coefficients, first-order in both 1-adamantyl chloroformate and sodium ethoxide. Values at five temperatures and the activation parameters at 25.0 °C are reported in Table VIII.

Discussion

Extent of Fragmentation. The reactions under solvolytic conditions proceed almost exclusively with loss of

Table III. Percentage of Solvolysis Product^a in the Solvolysis-Decomposition of 0.0093 M 1-Adamantyl Chloroformate in Aqueous Acetone and Aqueous Dioxane at 0-45 °C

| % H ₂ O ^{b,c} | acetone-H ₂ O (°C) | | | dioxane-H ₂ O (°C) | | |
|-----------------------------------|-------------------------------|-------------------|------|-------------------------------|---------------------|----------|
| | 0.0 | 25.0 | 45.0 | 0.0 | 25.0 | 45.0 |
| 5 | 68.1 | 67.8 | 66.8 | <i>d</i> | 46.7 | 47.7 |
| 10 | | | | | 55.1 ^{d,f} | |
| 15 | 70.1 | 71.9 | 72.1 | 56.8 | 59.2 | 60.7 |
| 25 | 71.0 | 74.4 | 75.4 | 63.0 | 67.6 | 68.9 |
| 35 | 71.5 | 75.9 | 76.3 | 68.6 | 70.3 | 72.7 |
| 45 | 72.6 | 76.7 ^g | 78.2 | <i>h</i> | 74.3 | 77.7 |
| 55 | <i>h</i> | 80.3 | 81.9 | <i>h</i> | <i>h</i> | <i>h</i> |

^aFrom comparison of infinity acid titer with that predicted for 100% solvolysis. ^bWeight percentage of water in mixed solvent. ^cA 0.475 M solution in benzene (0.100 mL) added to 5.00 mL of mixed solvent. ^dSolvent freezes. ^eUsing 0.0932 M 1-AdOCOCl. ^fGravimetric analysis gave 56.2% ionic chlorine and 40.8% covalent chlorine. ^gValues of 76.3% with 0.75 M NaCl added and 75.3% with 0.75 M NaBr added. ^hPhase separation observed.

Table IV. Effect of Added Tetra-*n*-butylammonium Salts upon the Specific Rates of Reaction (*k*, s⁻¹)^a and Percentage of Reaction with Solvolysis for Reactions of 1-Adamantyl Chloroformate in Methanol and Ethanol at 25.0 °C

| | 0.0127 | 0.0253 | 0.0506 | 0.102 |
|---|--------|--------|-------------------|-------|
| (a) <i>n</i> -Bu ₄ NCl in MeOH | | | | |
| 10 ⁴ <i>k</i> (s ⁻¹) | 35.8 | 37.0 | 39.0 ^c | 40.0 |
| % solvolysis | 73.3 | 73.5 | 73.1 | 73.2 |
| (b) <i>n</i> -Bu ₄ NCl in EtOH | | | | |
| 10 ⁴ <i>k</i> (s ⁻¹) | 5.77 | 6.05 | 6.60 | 7.70 |
| % solvolysis | 61.1 | 63.2 | 61.7 | 61.5 |
| (c) <i>n</i> -Bu ₄ NBr in EtOH | | | | |
| 10 ⁴ <i>k</i> (s ⁻¹) | 6.05 | 6.18 | 6.78 | 7.75 |
| % solvolysis | 61.7 | 62.3 | 62.1 | 61.9 |
| (d) <i>n</i> -Bu ₄ NI in EtOH ^d | | | | |
| 10 ⁴ <i>k</i> (s ⁻¹) | 5.98 | 6.39 | 7.25 | 8.83 |
| % solvolysis | 62.6 | 62.1 | 62.2 | 62.1 |
| (e) <i>n</i> -Bu ₄ NClO ₄ in EtOH | | | | |
| 10 ⁴ <i>k</i> (s ⁻¹) | 5.95 | 6.44 | 7.25 | 8.76 |
| % solvolysis | 65.0 | 65.8 | 66.0 | 66.8 |

^aUnless otherwise indicated, standard deviations for specific rates are less than 1% of reported value. ^bFor values in absence of salt, see Table I. ^cStandard deviation of ±0.6. ^dAcid titers fall in the latter stages of reaction; a Guggenheim treatment was used to obtain *k* and *V*_∞. As an example, with 0.025 M salt, the acid titer passed through a maximum of 49% of the theoretical (based on 100% solvolysis) and a red color developed.

Table V. Percentages of Products in the Solvolysis of 0.0061 M 1-Adamantyl Chloroformate in Aqueous Ethanol at 25.0 °C

| solvent (% EtOH) ^{a,b} | 1-AdOEt (14.21) ^c | 1-AdCl (14.82) ^c | 1-AdOH (19.36) ^c | <i>S</i> ^{d,e} |
|------------------------------------|---------------------------------|--------------------------------|--------------------------------|-------------------------|
| 100 ^f | 55.7 | 40.9 | 2.7 ^g | |
| 95 | 44.6 | 40.0 | 15.4 | 1.66 (1.84) |
| 90 | 39.3 | 35.0 | 25.3 | 1.59 (1.72) |
| 80 | 30.1 | 32.6 | 37.3 | 1.41 (1.78) |
| 70 | 24.1 | 29.7 | 46.2 | 1.27 (1.40) |
| 60 | 19.9 | 26.7 | 53.3 | 1.17 (1.29) |
| 50 | 15.7 | 23.6 | 60.7 | 1.13 (1.27) |

^aOn volume-volume basis. ^bA pentane solution of 1-AdOCOCl (0.45 mL) added to 20.0 mL of ethanol or mixed solvent; essentially identical product ratios when 1 mL of stock solution in pentane (for ≥80% EtOH) or dioxane (for <80% EtOH) is added to 5 mL of the indicated solvent or when solid 1-AdOCOCl is added (100, 95, and 80% EtOH). ^cRetention time (min) under the GLPC conditions. ^dRatio of specific rates for the reaction of 1-adamantyl cation with water and ethanol, respectively (see eq 2). ^eValues in parentheses are with the larger amount of cosolvent (see footnote b). ^fAlso 0.67% 1-AdOCOEt. ^gThis value is deducted from the reported 1-AdOH percentages prior to calculation of *S* values.

carbon dioxide. Infrared spectra of the crude products from reaction in methanol and its three α -methylated derivatives showed no carbonyl absorption, and hence, at

Table VI. Effect of Added Halide Ion upon the Product Partitioning in the Reactions of 0.0081 M 1-Adamantyl Chloroformate in Ethanol at 25.0 °C^a

| [salt], M | % composition as a function of X in 1-AdX | | | | |
|-----------|---|-----------------------------------|------|-----|---------------------|
| | OEt | Cl | Br | OH | OCO ₂ Et |
| 0.0000 | 59.4 | 37.5 | | 2.1 | 1.00 |
| | | (a) <i>n</i> -Bu ₄ NBr | | | |
| 0.0101 | 60.6 | 36.3 | 0.35 | 1.9 | 0.86 |
| 0.0202 | 61.2 | 35.5 | 0.45 | 2.0 | 0.79 |
| 0.0403 | 63.2 | 33.4 | 0.62 | 2.0 | 0.75 |
| 0.0806 | 62.1 | 34.6 | 0.76 | 1.9 | 0.61 |
| | | (b) Et ₄ NCl | | | |
| 0.0800 | 61.3 | 36.0 | | 1.9 | 0.76 |

^aA 0.1-mL portion of 0.820 M 1-AdOCOCl solution in pentane added to 10 mL of ethanol containing the appropriate salt concentration.

Table VII. Percentages of Products in the Solvolysis of 0.0061 M 1-Adamantyl Chloroformate in Mixtures of 2,2,2-Trifluoroethanol (T) with Water (W) and Ethanol (E) at 25.0 °C

| solvent ^a (% v/v) | 1-AdOEt (14.21) ^b | 1-AdOTFE (14.46) ^b | 1-AdCl (14.82) ^b | 1-AdOH (19.36) ^b | <i>S</i> (TFE/ ROH) |
|---------------------------------|---------------------------------|----------------------------------|--------------------------------|--------------------------------|---------------------------|
| 100T | | 55.6 | 41.9 | 2.5 ^c | |
| 80T-20W ^d | | 30.9 | 24.7 | 44.4 | 1.03 |
| 90T-10E | 4.5 ^e | 53.0 ^e | 39.8 | 2.6 | |
| 70T-30E | 14.5 | 44.4 | 38.8 | 2.3 | 1.64 |
| 50T-50E | 27.0 | 31.9 | 39.0 | 2.1 | 1.46 |
| 40T-60E | 33.5 | 25.1 | 39.3 | 2.1 | 1.40 |
| 30T-70E | 36.4 | 16.2 | 44.7 | 2.6 | 1.29 |
| 20T-80E | 42.9 | 9.8 | 44.7 | 2.6 | 1.13 |
| 10T-90E | 48.4 ^e | 4.5 ^e | 44.5 | 2.6 | |
| 100E ^f | 55.7 | | 40.9 | 2.7 | |

^aA pentane solution of 1-AdOCOCl (0.1 mL) added to 5.0 mL of indicated solvent. ^bRetention time (min) under the GLPC conditions. ^cDeducted from percentage of 1-AdOH after reaction in 80T-20W before calculation of *S* value. ^dOn weight-weight basis. ^ePeaks with retention times of 14.21 min and 14.46 min not separated in the integration. The peak area of the minor component estimated from extrapolation of a plot of peak area against solvent composition and this value then subtracted from recorded combined peak area. ^fFrom Table V.

most, only traces of 1-adamantyl alkyl carbonate¹⁵ could have been formed. Control experiments showed that, under the (acidic) reaction conditions, the mixed carbonates remained unchanged over a period corresponding to 10 half-lives of the 1-adamantyl chloroformate reactions. More sensitive studies (GLPC) of the products from reaction in ethanol did show, either in the pure alcohol (Table V footnote f) or in the alcohol containing quaternary ammonium bromide or chloride (Table VI), small amounts of 1-adamantyl ethyl carbonate.

Table VIII. Second-Order Rate Coefficients for Reaction of 0.004 00 M 1-Adamantyl Chloroformate with Sodium Ethoxide in Ethanol at Various Temperatures^a

| T, °C | [NaOEt] | 10 ² k ₂ , M ⁻¹ s ⁻¹ |
|-------|----------|--|
| -10.0 | 0.005 97 | 7.63 ± 0.42 |
| 0.0 | 0.008 09 | 25.8 ± 1.8 |
| 0.0 | 0.006 07 | 23.7 ± 0.7 ^b |
| 0.0 | 0.003 98 | 19.8 ± 1.6 |
| 0.0 | 0.002 02 | 18.9 ± 0.6 |
| 6.0 | 0.005 97 | 39.3 ± 0.9 |
| 14.8 | 0.005 97 | 76.2 ± 2.7 |
| 25.0 | 0.005 97 | 174 ± 5 |

^aFor 0.005 97 M NaOEt, activation parameters, with standard errors, of $\Delta H^\ddagger_{298} = 13.11 \pm 0.48$ kcal/mol and $\Delta S^\ddagger_{298} = -13.5 \pm 1.6$ eu. ^bWith 0.006 M 1-AdOCOCl, a value of 23.2 ± 0.9 M⁻¹ s⁻¹ was obtained.

However, the 1-adamantyl ethyl carbonate was not observed after reaction in aqueous ethanol, even 5% of water was sufficient to lower its production to below the detection limit. This observation suggests that the competition is between a unimolecular solvolysis-decomposition (rate considerably increased by increase in solvent ionizing power) and bimolecular attack at the acyl carbon (rate of ethanolysis slightly reduced on addition of water), rather than a competition between decomposition and capture by ethanol for a preformed free or ion-paired carboxylium ion, (1-AdOCO)⁺. The observation (Table VIII) of a dominant second-order process, leading to the carbonate upon addition of small concentrations of the conjugate base, ethoxide ion, supports this interpretation.

Application of the Grunwald-Winstein Equation. The kinetic data of Table I have been analyzed in terms of the Grunwald-Winstein equation (4),¹¹ where for a given

$$\log k = mY + \log k_0 \quad (4)$$

substrate k and k_0 are the specific rates of solvolysis in a given solvent and in the standard solvent (80% ethanol) and m is the sensitivity of the specific rate of solvolysis to changes in solvent ionizing power Y . For the present system, a reasonable ionizing power scale to use would be that based on 1-adamantyl chloride solvolysis, Y_{Cl} .¹⁶ Unfortunately, the same factor that makes the solvolysis-decomposition reaction of 1-adamantyl chloroformate an excellent system to study, the very large difference in solvolytic reactivity between the substrate and the decomposition product (in contrast, for example, to 2-adamantyl azoxytosylate and 2-adamantyl tosylate¹⁷), leads to our studies being carried out in solvents where, due to extremely slow reaction of 1-adamantyl chloride, Y_{Cl} values are not available. We have accordingly used the original Y scale¹¹ based on *tert*-butyl chloride solvolysis.¹⁸

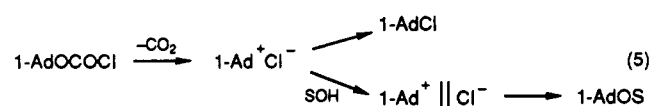
Three analyses have been carried out: in terms of the overall specific rates and those after partitioning into solvolysis and decomposition components; the latter two being obtained from the former by multiplying by the fractions of solvolysis and decomposition (Table I). The results are presented in Table IX. Using the data for all 23 solvents (Table IXA), the correlation coefficient was only a little over 0.9 and analysis showed, in each case, that the four points for aqueous acetone lay on a higher line of lower slope (Table IXB). The other 19 solvents give, in each analysis, good correlations with correlation coef-

Table IX. Calculated m Values for Reactions of 1-Adamantyl Chloroformate in Hydroxylic Solvents^a

| reaction | m | $\log k_0$ | r^b | n^c |
|--|---------------|--------------|--------|-------|
| (A) All Solvents | | | | |
| solvolysis | 0.620 ± 0.063 | -1.74 ± 0.27 | 0.907 | 23 |
| decomposition | 0.694 ± 0.072 | -1.84 ± 0.31 | 0.903 | 23 |
| decomposition | 0.520 ± 0.054 | -2.34 ± 0.23 | 0.904 | 23 |
| (B) Aqueous Acetone Mixtures | | | | |
| solvolysis | 0.440 ± 0.008 | -1.55 ± 0.01 | 0.9997 | 4 |
| decomposition | 0.443 ± 0.010 | -1.70 ± 0.02 | 0.9995 | 4 |
| decomposition | 0.432 ± 0.016 | -2.07 ± 0.02 | 0.9987 | 4 |
| (C) All Solvents except Aqueous Acetone Mixtures | | | | |
| solvolysis | 0.684 ± 0.031 | -1.76 ± 0.12 | 0.983 | 19 |
| decomposition | 0.773 ± 0.036 | -1.86 ± 0.15 | 0.982 | 19 |
| decomposition | 0.565 ± 0.030 | -2.37 ± 0.12 | 0.977 | 19 |

^a $\log k = mY + \log k_0$, where Y values are based on *tert*-butyl chloride solvolysis (ref 18). ^bCorrelation coefficient. ^cNumber of solvents.

ficients close to 0.98, with the m value for solvolysis about 0.12 higher than for decomposition, and with all three values appreciably below unity (Table IXC). The higher m values for solvolysis than for decomposition are consistent with the proposed¹ common formation of a 1-Ad⁺Cl⁻ ion pair (favored by high ionizing power), which then either collapses to decomposition product (disfavored by high ionizing power) or proceeds, via a solvent-separated ion pair (favored by high ionizing power), to solvolysis product (eq 5).



The higher than predicted rates and lower than predicted (based on the other solvents) value for m in the aqueous acetone solvents is not necessarily a consequence of fragmentation being a feature of the solvolysis-decomposition. Parallel behavior has been observed in some conventional solvolyses of adamantyl esters. For example, $\log(k/k_0)$ values (as defined in eq 4) for solvolysis in 95% acetone can cover a very wide range: -2.95 for 1-adamantyl tosylate,¹³ -2.18 for 2-adamantyl 2,2,2-trifluoroethanesulfonate,¹⁹ -2.11 for 2-adamantyl pentafluorobenzenesulfonate,²⁰ -1.15 (at 25 °C)²¹ or -0.79 (at -20 °C)²² for 2-adamantyl trifluoromethanesulfonate, and -0.23 for 2-adamantyl perchlorate.²³ The $\log(k/k_0)$ value of -0.83 for 1-adamantyl chloroformate solvolysis-decomposition is well within this range. In considering why $\log(k/k_0)$ values (Y values) are so variable in 95% aqueous acetone, it is noteworthy that the lower (more negative) values are observed when the leaving groups are reasonably nucleophilic and higher (less negative) values are observed when the very weakly nucleophilic trifluoromethanesulfonate and perchlorate are involved. Diminishing amounts of ion pair return in the 95% acetone could explain these trends. In the case of 1-adamantyl chloroformate, with a value for $\log(k/k_0)$ near the top of the range, extensive ion pair return to reactant could now be circumvented by fragmentation.

Possible Routes to 1-Ad⁺Cl⁻. While the m values observed are considerably less than unity, they are of

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

(17) Conner, J. K.; Maskill, H. *Bull. Chem. Soc. Fr.* **1988**, 342.

(18) The Y values are from: (a) Wells, P. R. *Chem. Rev.* **1963**, *63*, 171.

(b) Kaspi, J.; Rappoport, Z. *J. Am. Chem. Soc.* **1980**, *102*, 3829. (c) McManus, S. P.; Safavy, A. *J. Org. Chem.* **1986**, *51*, 3532. (d) Fainberg, A. H.; Winstein, S. *J. Am. Chem. Soc.* **1956**, *78*, 2770.

(19) Kevill, D. N.; Hawkinson, D. C. *J. Org. Chem.* **1989**, *54*, 154.

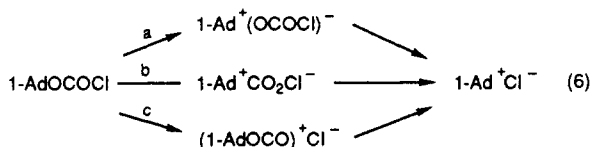
(20) Kevill, D. N.; Hawkinson, D. C. *J. Org. Chem.* **1988**, *53*, 3857.

(21) Bentley, T. W.; Roberts, K. *J. Org. Chem.* **1985**, *50*, 4821.

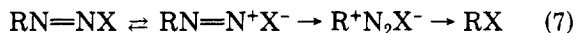
(22) Kevill, D. N.; Anderson, S. W. *J. Org. Chem.* **1985**, *50*, 3330.

(23) Kevill, D. N.; Bahari, M. S.; Anderson, S. W. *J. Am. Chem. Soc.* **1984**, *106*, 2895.

sufficient magnitude to strongly suggest ionic processes, both for solvolysis and for decomposition. Three basic pathways exist for the first step of eq 5, proceeding from 1-AdOCOCI to 1-Ad⁺Cl⁻; these pathways are presented in eq 6.



All three of the pathways of eq 6 can be given indirect support from comparison with related systems, and each requires serious consideration. Path a is, of course, the usual ionization step in substitution reactions of adamantyl derivatives, followed in this instance by loss of carbon dioxide from the unstable chloroformate anion. Path b involves a concerted fission of the 1-Ad-O and C-Cl bonds with CO₂ formation, it parallels the process proposed by Maskill for N₂O loss during reactions of 2-adamantyl and benzyl azoxyarenesulfonates.^{17,24} Path c proceeds via a carboxylium ion. Green and Hudson²⁵ proposed an intermediate carboxylium ion to explain differences between the relative rates of various cycloalkyl chloroformate solvolyses and the corresponding cycloalkyl halide or sulfonate solvolyses. Silver ion assisted reactions of chloroformate esters in the presence of weak nucleophiles have also been proposed to proceed via carboxylium ions.²⁶ A parallel pathway has been proposed²⁷ for decomposition of diazonium type compounds (eq 7).



Due to its close relationship to the pathway operating when esters solvolyze without fragmentation, path a is, at first sight, extremely attractive. We can attempt, by analogy with other solvolyses, to predict what the specific rate of ionization of 1-adamantyl chloroformate by this pathway might be and compare the prediction with our observed specific rates. In this regard, a very recently published²⁸ study of the solvolyses of 1-adamantyl trifluoroacetate in a variety of solvents is extremely valuable. The substrate is closely related structurally to 1-adamantyl chloroformate, with a trifluoromethyl group replacing the chlorine. In contrast to the solvolysis-decomposition of 1-adamantyl chloroformate, Bentley and Roberts found the solvolyses of the trifluoroacetate to be very slow. In 80% ethanol, an extrapolated (from higher temperatures) specific rate at 50 °C of $2.5 \times 10^{-7} \text{ s}^{-1}$ can be compared with an extrapolated specific rate (using the data at lower temperatures presented in Table I) for 1-adamantyl chloroformate of $2.5 \times 10^{-1} \text{ s}^{-1}$, a difference of 10^6 . The Charton σ_1 values²⁹ for Cl (0.47) and CF₃ (0.42) would suggest, for identical processes involving a remote substituent, only slightly higher rates for the chloroformate. For path a to operate, even if one assumes zero ion pair return for the chloroformate, almost a million contact ion pairs must return to the trifluoroacetate ester for every

one proceeding to product. While ion pair return in solvolyses of adamantyl derivatives is well established,^{1,17,30-32} ratios as enormous as 10^6 have not been suggested. Also arguing against path a is the observation³³ that 1-adamantyl fluoroformate, despite a σ_1 value for fluorine 0.05 units higher than for chlorine, solvolyzes much slower than 1-adamantyl chloroformate and predominantly by attack at acyl carbon.

Since path a is unlikely, the task of rationalizing why the observed m values are appreciably lower than the values of about unity usually observed for adamantyl ester solvolyses is removed. A lower value could presumably be a feature of concerted fragmentation or of carboxylium ion formation. The specific solvolysis rates of 1-adamantyl trifluoroacetate give a m value of only 0.68 when plotted against Y_{Cl} (based on 1-adamantyl chloride solvolysis);²⁸ however, the Y scale is in turn related to Y_{Cl} by $Y \approx 0.75 Y_{\text{Cl}}$ ^{12,16} and, therefore, the slope of a plot against Y values would be about 0.91, considerably higher than the values for 1-adamantyl chloroformate reactions.

Partitioning among the Products. The partitioning between solvolysis (with acid formation) and decomposition (without acid formation) has been studied for all solvents. For three mixtures of hydroxylic solvents, studies using GLPC allowed the partitioning of the solvolysis product into its two components.

Since the m value for solvolysis is larger than for decomposition (Table IX), there is a tendency for increased amounts of solvolysis as the solvent ionizing power is increased. For the 23 solvents studied, at 25.0 °C, the percentage of reaction with solvolysis varies from 29.1% in *tert*-butyl alcohol ($Y = -3.26$) to 80.0% in 90% methanol ($Y = -0.39$). For a given solvent, the amount of solvolysis rises slightly with temperature, consistent with the competition between separation of an ion pair and its (very low activation energy) collapse (Table I). The changes in the solvolysis-decomposition ratio (0.4 to 4.0) are, however, quite modest for a change in solvent ionizing power of about 3 units, consistent with the proposed very similar reaction pathways for solvolysis and decomposition and inconsistent with otherwise plausible alternatives, such as an ionic solvolysis accompanied by a four-centered transition state for decomposition. Paradisi and Bunnett³⁰ found similar behavior for the solvolysis of 2-adamantyl benzenesulfonate in three solvents; after ionization, the amount of internal return with ¹⁸O scrambling was found to vary only from 53 to 73%.

These observations provide a possible explanation as to why, even when ion pair return is expected, many scales of solvent ionizing power appear very similar for a majority of the solvents considered.^{16,19,20,34} This will be the case even if the extent of ion pair return varies appreciably with the leaving group provided that, as indicated in this study for 23 solvents and in the study of Paradisi and Bunnett for 3 solvents, for a given leaving group the collapse/solvolysis ratio is largely solvent independent. In so far as variation does occur, there is a general trend for a decrease in return relative to separation by solvent as solvent ionizing power increases, and the nature of the perturbation of the Y scale resulting from ion pair return will be a (usually small) expansion of the range of values covered by the scale relative to a scale based only on the relevant ionization process.

(24) (a) Maskill, H.; Jencks, W. P. *J. Am. Chem. Soc.* **1987**, *109*, 2062. (b) Maskill, H. 2nd European Symposium on Organic Reactivity, Padova, Italy, Aug 27-Sept 1, 1989, Abstract A19.

(25) Green, M.; Hudson, R. F. *J. Chem. Soc.* **1962**, 1076.

(26) For reviews, with leading references, see: (a) Reference 7, pp 427-433. (b) Beak, P. *Acc. Chem. Res.* **1976**, *9*, 230.

(27) White, E. H.; Aufdermarsh, C. A. *J. Am. Chem. Soc.* **1961**, *83*, (a) 1174, (b) 1179.

(28) Bentley, T. W.; Roberts, K. *J. Chem. Soc., Perkin Trans. 2* **1989**, 1055.

(29) Charton, M. *J. Org. Chem.* **1964**, *29*, 1222.

(30) Paradisi, C.; Bunnett, J. F. *J. Am. Chem. Soc.* **1985**, *107*, 8223.

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

(32) Maskill, H.; Thompson, J. T.; Wilson, A. A. *J. Chem. Soc., Perkin Trans. 2* **1984**, 1693.

(33) Kevill, D. N.; Kyong, J. B., unpublished results.

(34) Kevill, D. N.; Bahnke, R. W. *Tetrahedron* **1988**, *44*, 7541.

The solvolysis/decomposition ratio can be considered as a measure of the extent to which the 1-Ad⁺Cl⁻ ion pair proceeds to a solvent-separated ion pair and hence to solvolysis product as opposed to collapse to decomposition product. Since the ion pair is generated by fragmentation, the ions are initially almost certainly further separated than when directly generated from 1-AdCl and the fraction of reaction with collapse to covalent product must be regarded as a minimum value for the fraction of internal return during solvolysis of 1-adamantyl chloride.

Although the studies using GLPC analysis were done with a 10-fold reduction in the concentration of 1-adamantyl chloroformate, the values obtained for the partition between the sum of the solvolysis products and the decomposition product are in excellent agreement with those obtained by titration of developed acid. The nature of the subdivision of the solvolysis product has been studied for aqueous ethanol (Table V) and for mixtures of 2,2,2-trifluoroethanol (TFE) with water or ethanol (Table VII). In aqueous ethanol, the selectivity values for attack by water relative to ethanol (eq 2) exhibit the usual small preference shown by adamantyl derivatives for attack by the less nucleophilic water molecules,^{35,36} with values falling from 1.66 for 95% ethanol to 1.13 for 50% ethanol. These values are similar to those which have been observed in straight-forward solvolyses. Values have been reported,³⁶ in aqueous ethanol at 100 °C, of 2.10 for 1-adamantyl bromide, 2.13 for 1-adamantyl tosylate, and 1.73 for 1-adamantyl picrate. Other reported values include 1.94 for 1-adamantyl nitrate at 50 °C³⁷ and 1.26 for the 1-adamantyldimethylsulfonium ion at 70.6 °C.³⁸ Very similar values have been obtained for solvolyses of 2-adamantyl esters, including values at 25 °C of 1.52 for the trifluoromethanesulfonate²² and 1.75 for the perchlorate.²³ The values in the present study are a little lower than those usually obtained for 1-adamantyl halides or esters, and they are comparable to the value for the 1-adamantyldimethylsulfonium ion. The lower values may be a characteristic of the involvement of 1-AdX⁺ type species,³⁹ (1-AdOCO)⁺ in the present case, or they could result from the 1-Ad⁺Cl⁻ ion pair being more separated than when formed directly and, hence, a reduced preference for the smaller water relative to the larger ethanol.

In 80% TFE, at 25 °C, it is found that water and TFE are equally reactive ($S = 1.03$). This value is in remarkably good agreement with the value of 1.00 from 1-adamantyl bromide solvolysis at 35 °C⁴⁰ and in reasonable agreement with an earlier value^{18b} of 0.78. In TFE-ethanol mixtures, S values are obtained of 1.64 for 70% TFE-30% ethanol falling to 1.13 for 20% TFE-80% ethanol (S defined as in eq 3). The value of 1.64 is again in excellent agreement with the value, at 35 °C, of 1.63 for the 1-adamantyl bromide solvolysis in the same solvent composition,⁴⁰ and again rather higher than an earlier value^{18b} of 1.19. For 1-adamantyl bromide solvolysis, values have also been reported of 1.48 for solvolysis in 50% TFE-50% EtOH at 75 °C⁴¹ and of 1.66 for 80% TFE-20% EtOH and 1.34 for 40% TFE-60% EtOH at 25 °C.⁴² Values in the 50% TFE-50% EtOH solvent, at 25 °C, of very close to 1.7 have

been reported for three 1-adamantyl arenesulfonates.⁴¹ As with aqueous ethanol, the S values in TFE-EtOH mixtures are in excellent agreement with values obtained for conventional solvolyses of 1-adamantyl derivatives, giving strong support to the belief that the capture by solvent involves a 1-Ad⁺X⁻ ion pair, very similar in structure to those existing as intermediates in conventional solvolyses. Parallel results have been obtained in the solvolysis-decomposition of 2-adamantyl azoxytosylate, where the solvolysis products in aqueous ethanol and aqueous TFE are similar in relative amounts to those obtained from 2-adamantyl tosylate solvolysis.¹⁷

Temperature Effects. The positive entropy of activation for solvolysis-decomposition in 80% ethanol (Table II) is some 16–20 eu more positive than values reported for corresponding 1-adamantyl halide solvolyses.⁴³ In our preliminary communication,¹ it was suggested that this might result from the loss of CO₂ concurrent with, or subsequent to, the ionization process. However, a study of the conventional ethanolyses of several adamantyl arenesulfonates led to similar positive values, and the values could no longer be considered as a direct consequence of fragmentation.⁴⁴

Positive entropies of activation are also obtained in methanol, ethanol, 2-propanol, and *tert*-butyl alcohol. For 90% dioxane, however, a reduction in the activation energy is accompanied by a compensating reduction, to a negative value, in the entropy of activation. These trends are often a feature of the transfer of an ionization reaction from a protic to an aprotic (in this case largely aprotic) solvent, and it has been suggested that, at least in part, they are associated with an increase in ion pair return.⁴⁵ For 1-adamantyl chloroformate, this would have to be a true ion pair return to the chloroformate since, after fragmentation, combination of chloride ion and 1-adamantyl carbenium ion corresponds to reaction.

Effects of Added Salt. The effect of added quaternary ammonium salts has been considered both in terms of kinetics and product formation.

The effect of 0.01 to 0.1 M tetra-*n*-butylammonium salts upon the specific rate of acid production during solvolysis-decomposition at 25.0 °C showed for the chloride salt in methanol and the chloride, bromide, iodide, and perchlorate salts in ethanol modest rate increases, which were greater for the iodide and perchlorate salts (Table IV). These effects can be rationalized in terms of increases in solvent ionizing power upon addition of polar salts to relatively low ionizing power solvents. With regard to the percentage of reaction proceeding with solvolysis (Table IV), only very small changes (comparable with the probable experimental error) were observed. For the reactions in ethanol, these changes were, however, almost uniformly in the direction of increased solvolysis with added salt.

Added chloride ion slightly diverts the product away from 1-adamantyl chloride and toward the ethyl ether. This was confirmed (Table VI) by GLPC, using 0.08 M tetraethylammonium chloride. As with the influence on the kinetics, it appears that the important factor is the increase in solvent ionizing power, which favors solvolysis relative to decomposition (Table I).

A GLPC study in ethanol at 25.0 °C with 0.008 M 1-adamantyl chloroformate and an appreciable excess of tetra-*n*-butylammonium bromide (0.01–0.08 M) also

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

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

(37) Hawkinson, D. C. Ph.D. Dissertation, Northern Illinois University, August 1988.

(38) Kevill, D. N.; Anderson, S. W. *J. Am. Chem. Soc.* 1986, 108, 1579.

(39) McManus, S. P.; Crutcher, T.; Naumann, R. W.; Tate, K. L.; Zutaut, S. E.; Katritzky, A. R.; Kevill, D. N. *J. Org. Chem.* 1988, 53, 4401.

(40) Allard, B.; Casadevall, E. *Nouv. J. Chim.* 1985, 9, 725.

(41) Ando, T.; Tsukamoto, S. *Tetrahedron Lett.* 1977, 2775.

(42) McManus, S. P.; Zutaut, S. E. *Tetrahedron Lett.* 1984, 27, 2859.

(43) Schleyer, P. v. R.; Nicholas, R. D. *J. Am. Chem. Soc.* 1961, 83, 2700.

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

(45) Kevill, D. N.; Sutthoff, R. F. *J. Chem. Soc. B* 1969, 366.

showed only a small perturbation of the solvolysis–decomposition ratio, with a very small increase in the extent of solvolysis with increasing salt concentration (Table VI). Two important conclusions can be drawn because of the detailed nature of this GLPC study. First, the small percentage of 1-adamantyl ethyl carbonate falls slightly as the salt concentration is increased. This is consistent with the proposal that bimolecular attack by solvent at the acyl carbon is in competition with an ionic process, with the ionic process preferentially favored by increases in solvent ionizing power. Second, only a very small amount of 1-adamantyl bromide is observed in the products, reaching 0.8% for a 0.08 M salt concentration. For comparison, the reaction of this salt concentration in ethanol at 0 °C with the triethyloxonium ion leads to 97.1% ethyl bromide formation.⁴⁶ The very low percentage of 1-adamantyl bromide strongly indicates that the solvolysis–decomposition proceeds faster than halide ion exchange. In the presence of a 10-fold excess of the bromide salt, the exchange would be expected to move toward an equilibrium involving large amounts of 1-adamantyl bromoformate; if formed, this would result in the appearance of appreciable amounts of 1-adamantyl bromide after the subsequent solvolysis–decomposition reaction. Indeed, the small amount of 1-adamantyl bromide within the products could result from replacement of chloride by bromide at the 1-Ad⁺Cl⁻ stage. It is, however, more likely that it results primarily from a substitution reaction at the acyl carbon of the substrate. Indirect support for this view comes from the facile reaction of the more nucleophilic ethoxide ion to give the unreactive¹⁵ 1-adamantyl ethyl carbonate (Table VIII).

Summary and Conclusions. The reaction of 1-adamantyl chloroformate in hydroxylic solvents proceeds with both solvolysis and decomposition. In most solvents, all of the reaction is with loss of carbon dioxide, but in pure ethanol a trace of 1-adamantyl ethyl carbonate was observed; addition of very modest concentrations of ethoxide ion to the ethanol led to the carbonate becoming the dominant product. Additions of chloride, bromide, iodide, or perchlorate ion have little effect on either kinetics or product formation. Additions of bromide ion do lead to trace amounts of 1-adamantyl bromide, believed to be formed via 1-adamantyl bromoformate. The division among the solvolysis products for mixed hydroxylic solvents is virtually identical to that for conventional solvolysis of 1-adamantyl derivatives. The ratio of solvolysis to decomposition increases only modestly with solvent ionizing power; accordingly, the Grunwald–Winstein *m* value is only slightly greater for solvolysis than for decomposition.

Three routes to the 1-Ad⁺Cl⁻ intermediate require consideration: a concerted pathway to 1-Ad⁺·CO₂·Cl⁻ and ionization pathways to either 1-Ad⁺(OCOCi)⁻ or (1-AdOCOCi)⁺Cl⁻, followed by loss of CO₂. The pathway through 1-Ad⁺(OCOCi)⁻ is rendered unlikely by the observation that the solvolysis–decomposition proceeds several orders of magnitude faster than conventional solvolyses of 1-AdOCOX species, in instances where X has an inductive constant²⁹ similar to that of a chlorine atom.^{28,33} It is not possible at the present time to distinguish between the concerted pathway and that involving a carboxylium ion intermediate. If a carboxylium ion was to be involved it would, in pure alcohols, have to undergo fragmentation considerably faster than solvent capture (to give stable carbonates). We are presented with the common problem

of distinguishing between a concerted pathway and one involving a very reactive intermediate.⁴⁷

The observations are fully consistent with the formation of a 1-Ad⁺Cl⁻ ion pair, which either collapses or proceeds to solvolysis product via the solvent-separated ion pair. The study shows clearly that, despite arguments against ion pair return in solvolyses of adamantyl derivatives,^{48,49} 1-adamantyl chloride ion pairs do return to covalent substrate. Indeed, the percentage of decomposition in the present study must be regarded as a minimum value for this return, since the ion pairs formed after fragmentation are probably less tight than those formed by a simple ionization.

The rather low variation of the solvolysis–decomposition ratio with changes in solvent ionizing power may be a major clue as to why, despite extensive evidence for ion pair return,^{1,30–32,50} many *Y_x* scales have quite similar values for the majority of the usually included solvents. Widely varying extents of ion pair return, as the leaving group (X) is varied, will not affect the *Y* scale values if each of the 1-Ad⁺X⁻ intermediates shows little variation in its particular ratio of ion pair return relative to solvolysis as the solvent is varied.

Experimental Section

Materials. The purification of 2,2,2-trifluoroethanol was using a previously reported procedure.⁵¹ Other solvents were purified as previously described.¹³ Samples of 1-adamantyl chloroformate were prepared shortly before use by the procedure described earlier,⁴ except that, in some preparations, the phosgene was supplied as a solution in toluene rather than in benzene. The 1-adamantyl chloride (ROC/RIC) and 1-adamantyl bromide (Aldrich) were recrystallized from petroleum ether. Small quantities of 1-adamantyl ethyl carbonate,¹⁵ 1-adamantyl ethyl ether,¹³ and 1-adamantyl 2,2,2-trifluoroethyl ether,^{18b} required for calibrating the GLPC responses, were prepared as previously described. The tetra-*n*-butylammonium and tetraethylammonium salts (Eastman, K and K Labs, or G. F. Smith Chemical Co.) were recrystallized from acetone and dried overnight at low pressure.

Kinetic Procedures. Rates of solvolysis–decomposition in dry alcohols and several aqueous–organic mixtures (composition range limited by low solubility of substrate in more aqueous solvent mixtures) were studied in terms of acid production, using experimental infinity titers obtained after at least 10 half-lives. Typically, about 0.3 g of 1-adamantyl chloroformate was accurately weighed, and 25 mL of temperature equilibrated solvent was added to give a solution initially about 0.056 M in substrate. For runs in the presence of added tetra-*n*-butylammonium salts or sodium ethoxide, the required concentration of salt or alkoxide was already present in the solvent. After rapid shaking and temperature reequilibration, 2-mL portions were removed at suitable time intervals and quenched in 10 mL of neutral acetone containing resorcinol blue (Lacmoid) as indicator (maintained at acetone–solid CO₂ slush temperature). In the absence of sodium ethoxide, titration was against a standardized solution of triethylamine in toluene, chosen so as to avoid interference from unreacted chloroformate ester.⁵² In the presence of sodium ethoxide, ti-

(47) Jencks, W. P. *Acc. Chem. Res.* **1980**, *13*, 161.

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

(49) Raber, D. J.; Neal, W. C., Jr.; Dukes, M. D.; Harris, J. M.; Mount, D. L. *J. Am. Chem. Soc.* **1978**, *100*, 8137.

(50) (a) McManus, S. P.; Sedaghat-Herati, M. R.; Karaman, R. M.; Neamati-Mazraeh, N.; Cowell, S. M.; Harris, J. M. *J. Org. Chem.* **1989**, *54*, 1911. (b) In a paper published after the submission of this manuscript, substantial ¹⁸O scrambling was reported to accompany solvolysis of *cis*-3-(trimethylsilyl)cyclohexyl brosylate. Of especial interest is that similar ratios of return with scrambling relative to solvolysis are observed in 80% ethanol and 97% 2,2,2-trifluoroethanol, two solvents with very different nucleophilicities and ionizing powers: Shiner, V. J., Jr.; Ensigner, M. W.; Kriz, G. S.; Halley, K. A. *J. Org. Chem.* **1990**, *55*, 653.

(51) Rappoport, Z.; Kaspi, J. *J. Am. Chem. Soc.* **1974**, *96*, 4518.

(52) Brown, D. A.; Hudson, R. F. *J. Chem. Soc.* **1953**, 3352.

(46) Kevill, D. N.; Fujimoto, E. K. *J. Chem. Res. (S)* **1988**, 408.

tration was against a standardized solution of HCl in 99% aqueous ethanol.

For the relatively fast runs in 80% aqueous ethanol, slow dissolution of substrate was a problem and the procedure was modified. The substrate was dissolved in 20 mL of temperature equilibrated ethanol, 5 mL of temperature equilibrated distilled water was immediately added, and, after rapid shaking, the run started.

Determination of Infinity Acid Titrers. In addition to the infinity titers obtained directly from kinetic runs, others were determined by adding a small portion (usually 0.100 mL) of a freshly prepared stock solution of 1-adamantyl chloroformate in benzene to 5.00 mL of aqueous acetone or aqueous dioxane. For determinations in the presence of an added salt, the required concentration of salt was already present in the solvent. After 1 to 2 h, depending on the solvent composition, 10 mL of neutral acetone containing resorcinol blue (Lacmoid) indicator was added, and the acid developed was titrated against a standardized solution of sodium methoxide in methanol. In conjunction with the titer predicted for 100% solvolysis, the percentage of reaction involving solvolysis was calculated; averages of three experimental determinations for each mixed solvent are reported.

In a few instances the values obtained by acid titration for the partitioning between solvolysis and decomposition were checked by gravimetric analysis for free (solvolysis) and covalently bonded (decomposition) chloride. After at least 10 half-lives, the reactant solution was cooled to -15°C and the ionic chloride was precipitated by addition of an excess of aqueous silver nitrate. The silver chloride was collected on a tared glass crucible and 30 mL of concentrated H_2SO_4 (to create a good ionizing medium⁵³) was added to the filtrate. The additional silver chloride precipitated was collected on a second tared glass crucible. For example, from a reaction of 100% methanol at 24.8°C , a total silver chloride yield of 0.307 g was calculated, and the two weights observed were 0.239 and 0.063 g, respectively.

Infrared Spectrum of Crude Product Mixtures. For reaction at 25.0°C of 0.5 g of 1-adamantyl chloroformate in 5 mL of a pure alcohol, evolution of gas was immediately apparent. After

24 h (methanol, ethanol, *tert*-butyl alcohol) or 72 h (isopropyl alcohol), the solvent was removed by evaporation to leave a white residue. The infrared spectrum (hexane or KBr) showed no carbonyl absorption at $5.80\ \mu\text{m}$ and, with the exception of the product from reaction in *tert*-butyl alcohol, no hydroxyl absorption at $3.05\ \mu\text{m}$. From the reaction of *tert*-butyl alcohol, the spectrum of the product was consistent with a mixture of 1-adamantyl chloride and 1-adamantanol and, for the other three systems, it was consistent with a mixture of 1-adamantyl chloride with the appropriate 1-adamantyl alkyl ether.

Control Experiments in *tert*-Butyl Alcohol. A 0.0471 N solution of HCl in *tert*-butyl alcohol at 25.0°C gave an unchanged titer over at least 2 days when 1-mL aliquots were added to 10 mL of acetone prior to titration against a standardized solution of triethylamine in toluene. In contrast, when 0.052 M 1-adamantyl *tert*-butyl ether was also present in the solution, the acid titer fell in less than 16 h to a constant 52% of its value in the absence of ether. When aliquots containing the ether that had stood for in excess for 16 h were added to 50% aqueous ethanol and then allowed to stand for a further 10 h, the acid titer returned to its value in the absence of ether. Since 1-adamantyl chloride would solvolyze too slowly¹⁶ for complete acid regeneration under these conditions, it is believed that an acid-catalyzed cleavage of 1-adamantyl *tert*-butyl ether under the reaction conditions leads to 1-adamantanol and approximately equal amounts of *tert*-butyl chloride (incorporating HCl) and isobutylene.

Product Studies by GLPC. Solutions containing about 0.006 M 1-adamantyl chloroformate in ethanol, TFE, aqueous ethanol, aqueous TFE, or TFE-ethanol were allowed to react at 25.0°C for at least 10 half-lives. The products were directly analyzed by response-calibrated GLPC, as previously described.²³ Experiments were also carried out using 0.008 M substrate in ethanol in the presence of up to 0.08 M tetra-*n*-butylammonium bromide or tetraethylammonium chloride.

Acknowledgment. We wish to thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. J.B.K. thanks the Korea Science and Engineering Foundation for support during his participation in this project.

(53) Bentley, T. W.; Jurczyk, S.; Roberts, K.; Williams, D. J. *J. Chem. Soc., Perkin Trans. 2* 1987, 293.

Torsional Barriers in Quinolinone Hydroxylamine and Sulfenamide Derivatives

Morton Raban,* Van A. Martin,¹ and Leslie Craine¹

Department of Chemistry, Wayne State University, Detroit, Michigan 48202

Received January 24, 1989

The preparation of a 2-quinolinone hydroxylamine (*N*-(benzyloxy)-2(*1H*)-quinolinone) and sulfenamide derivatives of 2- and 4-quinolinone (*N*-[(2,4-dinitrophenyl)thio]-3-benzyl-4-methyl-2(*1H*)-quinolinone and *N*-[(2,4-dinitrophenyl)thio]-3-benzyl-2-methyl-4(*1H*)-quinolinone) are described. All three compounds exhibited chemical shift nonequivalence of diastereotopic benzyl methylene hydrogens, indicative of hindered rotation about the N-O or N-S bond which is slow on the NMR time scale. The torsional barriers were measured for the 2-quinolinone derivatives, while that for the 4-quinolinone sulfenamide was too large to be measured ($>22\ \text{kcal/mol}$), indicating that in this compound the N-S chiral axis is a stable stereogenic unit on the isolation time scale.

Introduction

Barriers to torsion about the N-X bonds (X = N, O, S) in hydrazines, hydroxylamines, and sulfenamides have been the subject of a large number of investigations and

have been reviewed a number of times.²⁻⁴ Such torsional barriers confer chirality on appropriately substituted systems, and as a result, they can be detected by using NMR spectroscopy at temperatures where torsion is slow

(1) Taken in part from the Ph.D. Dissertation of L.C. (Wayne St. University, 1986).

(2) Raban, M.; Kost, D. *Tetrahedron* 1984, 40, 3345.

(3) Riddell, F. G. *Tetrahedron* 1981, 37, 845.

(4) Oki, M. *Top. Stereochem.* 1983, 14, 83.