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# SILVER-ION ASSISTED REACTIONS OF 1-ADAMANTYL HALIDES IN ETHANOL[1]

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For several years, the relative reactivities of bridgehead halides have been correlated by a semi-quantitative evaluation of the rates of reaction with silver nitrate in ethanol or aqueous ethanol[3]. Prior to the present investigation of silver-ion assisted reactions of 1-adamantyl halides in ethanol, there does not appear to have been a detailed study of any one of these reactions.

1-Adamantyl halides react with silver nitrate in ethanol to give a mixture of 1-ethoxyadamantane, corresponding to solvolysis, and 1-adamantyl nitrate, corresponding to anion exchange. The overall reaction can be monitored by potentiometric titration of aliquots against potassium chloride and the extent of acid formation (corresponding to solvolysis) can be monitored by titration of aliquots against sodium methoxide. 1-Adamantyl nitrate was synthesized by the heterogeneous reaction of 1-adamantyl bromide with powdered silver nitrate in hexane [mp 103-103.5°; ir (KBr) includes 6.28, 7.89, 9.08, 9.63, 11.56 (broad), 14.26μ; pmr ($CCl_4$) τ 7.73 (s,3), 7.85 (s with fine structure, 6), 8.28 (s with fine structure, 6); satisfactory analyses for C, H, and N] and it was shown to be essentially unreactive to ethanol at 25.0; after two weeks a 0.04M solution had developed only 0.8% acid.

A study of the partitioning between the two products for the chloride, bromide, and iodide showed that, at 25.0° and over a wide range of silver nitrate concentration, the ratio of ether to nitrate ester does not vary by a large amount. Even for silver nitrate concentrations of below 0.01M, the nitrate ester was the dominant product (Table I). Addition of nitrate ions as tetraethylammonium nitrate also had only a minor influence on the product ratio.

The small variation in the product ratio with nitrate ion concentration suggests that only a minor contribution to the overall reaction scheme involves a competition for initially formed free 1-adamantyl carbonium ions between solvent molecules and nitrate ions and most acts of substitution involve along the reaction path the elements of an ion-pair (perhaps associated also with other entities) containing a 1-adamantyl carbonium and a nitrate ion[4,5]. Within this ion-pair there is either collapse to 1-adamantyl nitrate or separation, which is mainly followed by solvolysis.

TABLE I

Percentage of Solvolysis (Acid Development) after Completion of the Reaction of Silver Nitrate with Excess (0.144M) 1-Adamantyl Halides in Ethanol at 25.0°.

| | | | % Solvolysis | | |
|---|---|---|---|---|---|
| $[AgNO_3]$ | $[NEt_4NO_3]$ | X = | Cl | Br | I |
| 0.0050 | | | 20.7 | 25.7 | 43.1 |
| 0.0100 | | | 19.8 | 21.4 | 39.5 |
| 0.0200 | | | 20.3 | 20.6 | 36.0 |
| 0.0200 | 0.0200 | | 15.8 | 17.4 | 31.5 |
| 0.0200 | 0.0400 | | 14.0 | 16.0 | 30.4 |
| 0.0200 | 0.0800 | | 11.9 | 15.0 | 28.6 |
| 0.0400 | | | 19.6 | 18.1 | 35.7 |
| 0.0800 | | | 17.7[a] | 16.6[a] | 35.4[a] |

[a] Confirmed in semi-quantitative manner by use of 0.072M 1-adamantyl halide and analysis of the pmr spectrum ($CCl_4$) of the product.

Kinetic studies on the system of 1-adamantyl chloride and ethanolic silver nitrate were carried out at 25.0° (Table II). Keeping the concentration of 1-adamantyl chloride constant (0.144M) and varying the initial silver nitrate concentration (0.0025-0.08M), an analysis of the variation in initial velocity with concentration indicated an order in silver nitrate of 1.57. A similar study (Table II) for silver perchlorate indicated an order of higher than unity and increasing with concentration. Within the concentration range studied, silver nitrate gave a faster reaction than silver perchlorate but indications were that at higher concentrations (not attainable due to limited solubility of silver nitrate) this situation would have been reversed. Addition of tetraethylammonium nitrate showed that the faster reaction of silver nitrate was unlikely to be due to nucleophilic assistance from the nitrate ion. The addition had little effect upon the rate and actually caused a slight retardation. During seven days, a solution 0.144M in 1-adamantyl chloride and 0.070M in tetraethylammonium nitrate did not develop any free chloride ion.

The next two series of runs involved a constant (0.02M) concentration of silver nitrate or silver perchlorate and varying initial concentrations of 1-adamantyl chloride (Table III). The kinetic order in 1-adamantyl chloride was not unity, as we had expected, but about 1.7 for reaction with silver nitrate and about 1.5 for reaction with silver perchlorate.

TABLE II

Initial First-order Rate Coefficients with Respect to 0.144<u>M</u> 1-Adamantyl Chloride for Reaction with Silver Nitrate or Silver Perchlorate in Ethanol at 25.0.

| $10^2$[AgNO$_3$] | 0.250 | 0.500 | 1.00 | 2.00 | 4.00 | 8.00 |
|---|---|---|---|---|---|---|
| $10^7 k_1(\mathrm{sec}^{-1})$ | 0.52 | 1.6 | 5.6 | 14[a] | 53. | 160. |

| $10^2$[AgClO$_4$] | 0.508 | 1.01 | 2.03 | 4.18 | 7.97 | 12.0 | 15.0 |
|---|---|---|---|---|---|---|---|
| $10^7 k_1(\mathrm{sec}^{-1})$ | 0.17 | 0.76 | 3.2 | 13.4 | 79. | 246. | 515. |

[a] For additions of NEt$_4$NO$_3$ of 0.02, 0.04, and 0.08<u>M</u>, value is reduced to 12 x $10^{-7}$, 12 x $10^{-7}$, and 11 x $10^{-7}$ sec$^{-1}$ respectively.

TABLE III

Initial First-order Rate Coefficients with Respect to 0.0200 <u>M</u> Silver Nitrate or Silver Perchlorate for Reaction with 1-Adamantyl Chloride in Ethanol at 25.0°.

| [C$_{10}$H$_{15}$Cl] | 0.0359 | 0.072 | 0.144 | 0.288 | 0.576 |
|---|---|---|---|---|---|
| $10^5 k_1^{\mathrm{AgNO_3}}(\mathrm{sec}^{-1})$ | 0.12 | 0.40 | 1.04 | 3.6 | 13.3 |
| $10^5 k_1^{\mathrm{AgClO_4}}(\mathrm{sec}^{-1})$ | 0.028 | 0.066 | 0.227 | 0.66 | 1.82 |

Due to the complex kinetic patterns, valid determinations of the influence upon the reaction rate of varying the identity of the halide leaving group required comparisons under identical conditions and the large rate differences found to be involved made this difficult. Results for the compromise concentrations selected are shown in Table IV.

TABLE IV

Leaving Group Effects upon the Specific Rates of Reaction of Silver Nitrate or Silver Perchlorate with 0.0072<u>M</u> 1-Adamantyl Bromide or 1-Adamantyl Chloride in Ethanol at 25.0°.

| | $10^8 k_1(\mathrm{sec}^{-1})$ | | |
|---|---|---|---|
| [AgNO$_3$] | <u>X</u> = Cl | <u>X</u> = Br | Ratio |
| 0.0020 | 5.2 | 90,000 | 1.7 X $10^4$ |
| 0.0040 | 6.6 | 129,000 | 2.0 X $10^4$ |
| [AgClO$_4$] | | | |
| 0.0020 | 2.9 | 34,000 | 1.2 X $10^4$ |
| 0.0040 | 3.7 | 43,000 | 1.2 X $10^4$ |
| 0.0160 | 6.7 | 101,000 | 1.5 X $10^4$ |

The 1-adamantyl chloride was reacting slower and the 1-adamantyl bromide was reacting faster than for an ideal investigation. Also, autocatalysis, which was not very marked at the higher concentrations, became appreciable at these lower concentrations and accurate assessment of initial rates was more difficult. The data do not have the accuracy of those obtained at higher concentrations and the ratios may be in error as much as 25%. There can be no doubt, however, but that the rate ratios are fantastically higher than the ratios of 30-100 usually obtained for alkyl bromide/alkyl chloride comparisons in hydroxylic solvents[6] and, also, much higher than the value of 450, at 45°, for the reactions of 2-octyl halides with silver nitrate in acetonitrile[5], an aprotic solvent in which leaving-group effects are magnified over those in hydroxylic solvents[7].

The mechanisms for these silver-ion assisted reactions are clearly complex and they possibly take place largely through clusters containing silver ions, counterions, 1-adamantyl carbonium ions, and halide ions. Although a detailed mechanism cannot be presented at the present time, it is clear that these reactions, commonly used to establish relative reactivities of bridgehead halides, cannot be considered as classical $S_N1Ag^+$ solvolyses. In particular, any reasonable mechanism would have to account for the extremely large rate differences between reaction of the bromide and the chloride and for the formation of 1-adamantyl nitrate as the dominant product. In contrast, 1-adamantyl p-toluenesulfonate solvolyzes in 0.15 M ethanolic tetraethylammonium chloride without concurrent formation of 1-adamantyl chloride[8].

## REFERENCES

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(2) National Science Foundation High School Teacher Research Participant.

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