### Experimental Section

**Materials.**—Palladium acetate was purchased by Engelhard Industries. Absence of nitrate ions in the compound was confirmed by ir. Reagent grade chemicals were used without further purification.

**Rate Studies.**—The rate of naphthalene consumption and product formation was followed by vpc. A Hewlett-Packard Model 5750 research chromatograph, equipped with a flame ionization detector and a 6-ft column of 10% Apiezon L on Chromosorb W maintained at 220°, was employed. Products were identified by vpc retention time and ir comparison with authentic samples.

**Acetoxylation of Naphthalene.**—$Pd(OOCCH_3)_2$ [1.485 g (6.6 mmol)], $C_{10}H_8$ [1.024 g (8.0 mmol)], and $CH_3COONa$ [0.584 g (7.1 mmol)] were dissolved in 10 ml of 99% glacial acetic acid and allowed to react at the reflux temperature of the solvent. The mixture assumed a dark color after 10 min and the reaction continued for 4 hr.

The Pd black isolated (0.725 g) indicated quantitative conversion. The acetic acid filtrate was suspended in ether–aqueous $NaHCO_3$, and the ether extract was evaporated to obtain the products. Vpc analysis of the solid products indicated the following compounds to be present (yields): α-naphthylacetate (25%), β-naphthylacetate (25%), α-naphthol (6%), β-naphthol (6%), and binaphthyls (2%).

**A Typical Catalytic Reaction.**—$C_{10}H_8$ [2.096 g (16.4 mmol)], $Pd(CH_3COO)_2$ [0.498 g (2.2 mmol)], $Cu(CH_3COO)_2 \cdot H_2O$ [0.890 g (4.5 mmol)], $LiOOCCH_3 \cdot 2H_2O$ [1.356 g (13.3 mmol)], and LiCl [0.291 g (6.9 mmol)] were suspended in 15 ml of $CH_3COOH$ in a 100-ml, three-neck flask. The mixture was heated at the reflux temperature for 12 hr while oxygen was sparged through the solution. The yield (based on $Pd^{2+}$) of isolable[5] monomeric products was highest in about 4 hr after the start of the experiment: α-naphthylacetate (39%) and α-chloronaphthalene (11%).

**Control Run.**—The above reaction was repeated without $Pd(CH_3COO)_2$. Only traces of monosubstituted products could be detected *via* vpc.

**Registry No.**—$Pd(OOCCH_3)_2$, 3375-31-3; naphthalene, 91-20-3.

**Supplementary Material Available.**—A table containing 14 oxidative reactions of naphthalene in the presence of $Pd(OOCCH_3)_2$ with various redox systems and three kinetic figures depicting two of the runs will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JOC-73-4443.

---

## Kinetics and Mechanism of the Reactions of Allyl Halides with Silver Nitrate in Acetonitrile

DENNIS N. KEVILL* AND LUCETTE HELD

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

*Received June 28, 1973*

Kinetic studies of the reactions of methyl, primary, and secondary alkyl halides with acetonitrile solutions of silver nitrate have indicated a mechanism in which electrophilic assistance by the silver ion is accompanied, in the rate-determining step, by nucleophilic attack by nitrate ion.[1,2] Alkyl halides found to exhibit these characteristics include methyl,[1] ethyl,[1,3] neopentyl,[1] and isopropyl[1] iodides, 1-octyl and 2-octyl bromides,[2] and 2-octyl chloride.[2] For concentrations of silver salt within the range 0.002–0.2 *M* the overall kinetic order approximates 2.5, first order in alkyl halide, first order in silver ion, and one-half order in nitrate ion.[2]

If the reasonably nucleophilic nitrate ion is replaced by the weakly nucleophilic perchlorate ion, the rate of precipitation of silver halide is considerably reduced; for example, with 0.03 *M* silver salt at 44.6°, silver nitrate reacts with 2-octyl bromide 80 times faster than silver perchlorate.[4] Additional evidence for SN2 character in the rate-determining step comes from a considerably slower reaction for the appreciably sterically hindered neopentyl iodide than for the considerably less hindered, but also primary, ethyl iodide.[1]

A reconsideration[1,2] of product data obtained for reactions of silver nitrate with ethyl iodide in ethanol[5,6] suggested that an ion pair containing the carbonium ion and the nitrate ion is formed, which then either collapses to product or undergoes solvolysis. A recent study of the reactions of 1-adamantyl halides with silver nitrate in ethanol[7] also implicated such an ion pair. The complex kinetics and the variation observed for the product partitioning between solvolysis and anion exchange with changing identity of the halogen suggested that, in the product-determining step, the halide ion is still in the vicinity of the carbonium ion. They may well be contained within an ion quadruplet or an even more complex aggregate.[7]

While it is reasonable to suppose that the scheme postulated for reactions in ethanol[1,2,7] can also be extended to reactions in other solvents, it should be emphasized that there is no *direct* evidence for formation of ion pairs between a carbonium ion and the anion of the silver salt during reactions in acetonitrile. An argument developed earlier[1] in favor of such an ion pair within reactions of alkyl iodides with silver perchlorate was based on the assumption that covalent alkyl perchlorates would not be solvolyzed by acetonitrile. It has, however, been shown that 2-octyl perchlorate has, in acetonitrile at 25.0°, a half-life of less than 1 min.[8] Nucleophilic attack within the rate-determining step and intermediate ion-pair formation has also been suggested for the reaction in acetonitrile between *tert*-butyl bromide and silver *p*-toluenesulfonate.[9]

A study of the reactions of the tertiary α-halogenated ketone, α-bromo-*p*-phenylisobutyrophenone, with silver salts in acetonitrile[10] also suggested nucleophilic participation by nitrate ion within the rate-determining step of the reaction with silver nitrate.

Previous studies of silver ion assisted reactions of allylic halides have usually been interpreted (in the Hughes–Ingold terminology[11]) as SN1 $Ag^+$ reactions, involving in the rate-determining step an electrophili-

---

[1] G. S. Hammond, M. F. Hawthorne, J. H. Waters, and B. M. Graybill, *J. Amer. Chem. Soc.*, **82**, 704 (1960).

[2] Y. Pocker and D. N. Kevill, *J. Amer. Chem. Soc.*, **87**, 4760 (1965).

[3] F. G. Donnan and H. E. Potts, *J. Chem. Soc.*, **97**, 882 (1910); for a reassessment of these data see ref 2.

[4] Y. Pocker and D. N. Kevill, *J. Amer. Chem. Soc.*, **87**, 4771 (1965).

[5] A. K. Burke and F. G. Donnan, *J. Chem. Soc.*, **85**, 555 (1904).

[6] F. G. Donnan and A. K. Burke, *Z. Phys. Chem.* (*Leipzig*), **69**, 148 (1909).

[7] D. N. Kevill and V. M. Horvath, *Tetrahedron Lett.*, 711 (1971).

[8] Y. Pocker and D. N. Kevill, *J. Amer. Chem. Soc.*, **87**, 5060 (1965).

[9] H. M. R. Hoffmann, *J. Chem. Soc.*, 6748 (1965).

[10] D. N. Kevill and N. H. Cromwell, *J. Org. Chem.*, **29**, 499 (1964).

[11] See, for example, C. K. Ingold, "Structure and Mechanism in Organic Chemistry," 2nd ed, Cornell University Press, Ithaca, N. Y., 1969, pp 479–483.

TABLE I

AVERAGE VALUES FOR THE INTEGRATED 2.5-ORDER RATE COEFFICIENTS,[a] $k_{2.5}$ ($M^{-1.5}$ sec$^{-1}$), FOR REACTION OF ALLYL BROMIDE WITH SILVER NITRATE OR SILVER PERCHLORATE IN ACETONITRILE AT VARIOUS TEMPERATURES

| [$C_3H_5Br$] | [$AgNO_3$] | [$AgClO_4$] | Temp, °C | $10^3 k_{2.5}$ |
|---|---|---|---|---|
| 0.0400 | 0.00500 | | 45.0 | 29.9 ± 1.1 |
| 0.0400 | 0.0100 | | 45.0 | 26.1 ± 0.8 |
| 0.0400 | 0.0200 | | 45.0 | 30.0 ± 2.0 |
| 0.0400 | 0.0400 | | 45.0 | 28.4 ± 0.7[b] |
| 0.0800 | 0.0400 | | 45.0 | 26.7 ± 1.1 |
| 0.160 | 0.0400 | | 45.0 | 25.1 ± 2.1 |
| 0.0400 | 0.0800 | | 45.0 | 23.0 ± 1.5 |
| 0.0800 | 0.160 | | 45.0 | 22.1 ± 0.6 |
| 0.0800 | 0.0400 | | 25.0 | 5.3 ± 0.2 |
| 0.0812 | 0.0406 | | 35.0 | 9.5 ± 0.5 |
| 0.0766 | 0.0383 | | 55.0 | 65.7 ± 2.5 |
| 0.0400 | | 0.0435 | 45.0 | 0.0159 ± 0.0010 |
| 0.200 | | 0.0435 | 45.0 | 0.0171 ± 0.0009 |
| 0.200 | | 0.0870 | 45.0 | 0.0164 ± 0.0005 |

[a] Calculated from appropriate integrated form of $-d[Ag^+]/dt = k_{2.5}[C_3H_5Br][AgX]^{1.5}$, where X = $NO_3$ or $ClO_4$. [b] A solution initially 0.0800 $M$ in both reactants and allowed to react to 50%, with precipitation of silver bromide, before start of run (35 min) gave an essentially identical value of 0.0268 ± 0.0021 $M^{-1.5}$ sec$^{-1}$.

cally assisted ionization. Systems which have been interpreted in this way include reactions with silver acetate in acetic acid,[12] silver oxide suspended in water,[13] and silver nitrate in water[14] or ethanol.[15] The present investigation was undertaken to determine whether reactions of allyl halides with silver nitrate in acetonitrile follow the S<sub>N</sub>1 Ag+ type mechanism previously postulated for silver ion assisted reactions of allylic halides or the alternate type of mechanism with concurrent nucleophilic assistance, previously postulated for reactions of acetonitrile solutions of silver nitrate with a variety of organic halides.

It is known that acetonitrile solutions of silver nitrate react with the analogous 2-methallyl chloride to give the replacement product, 2-methallyl nitrate.[16] Silver ion assisted solvolytic reaction (Ritter reaction[17]) could to some extent compete with collapse to nitrate ester. Such reaction would produce an imidoyl nitrate which on addition to moist acetone would be rapidly hydrolyzed to *N*-allylacetamide plus an equivalent amount of nitric acid. Any elimination reaction to give allene would also produce an equivalent amount of nitric acid. An acetonitrile solution, 0.08 $M$ in allyl bromide and 0.16 $M$ in silver nitrate, was allowed to react to completion and acid–base titration after addition to moist acetone indicated less than 0.2% acid development; presumably, allyl nitrate is formed in better than 99.8% yield based on allyl bromide consumed.

The kinetics of the reaction of allyl bromide with silver salts in acetonitrile was analyzed in terms of integrated 2.5-order rate coefficients. The reactions of alkyl bromides with silver perchlorate in acetonitrile have been shown to exhibit complex and variable kinetic orders[4] but at the concentrations of silver perchlorate employed (0.04–0.08 $M$) the kinetic order closely approximates 1.5 in silver salt and unity in alkyl or allyl bromide. The averages of the integrated rate coefficients (with standard deviations) are shown in Table I. Corresponding rate coefficients for reaction of allyl chloride with silver nitrate in acetonitrile at 45.0°, together with the ratio of the rate coefficients for allyl bromide (from Table I) relative to those for allyl chloride at each silver nitrate concentration, are shown in Table II.

TABLE II

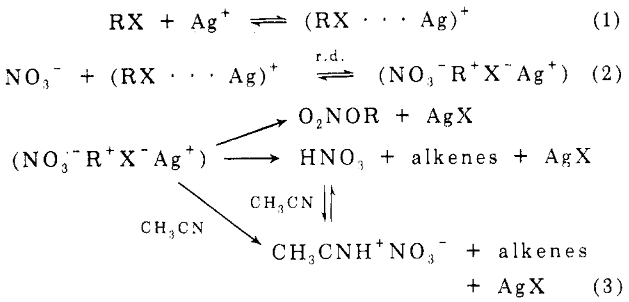
AVERAGE VALUES FOR THE INTEGRATED 2.5-ORDER RATE COEFFICIENTS,[a] $k_{2.5}$ ($M^{-1.5}$ sec$^{-1}$), FOR REACTION OF ALLYL CHLORIDE WITH SILVER NITRATE IN ACETONITRILE AT 45.0° AND COMPARISON OF THESE COEFFICIENTS WITH THOSE FOR REACTION OF IDENTICAL CONCENTRATIONS OF SILVER NITRATE WITH ALLYL BROMIDE

| [$C_3H_5Cl$] | [$AgNO_3$] | $10^5 k_{2.5}$ | $k_{2.5}^{Br}/k_{2.5}^{Cl}$ |
|---|---|---|---|
| 0.0800 | 0.0100 | 10.8 ± 0.5 | 242 |
| 0.0800 | 0.0200 | 8.7 ± 0.8 | 345 |
| 0.0800 | 0.0400 | 10.3 ± 0.4 | 259 |
| 0.0800 | 0.0800 | 9.1 ± 0.6 | 253 |
| 0.0800 | 0.160 | 6.8 ± 0.7 | 324 |

[a] Calculated from appropriate integrated form of $-d[Ag^+]/dt = k_{2.5}[C_3H_5Cl][AgNO_3]^{1.5}$.

Reaction of both allyl chloride and allyl bromide with 0.005–0.16 $M$ silver nitrate in acetonitrile shows essentially the same overall 2.5-order kinetics as previously observed[2] for identical reaction of 1-octyl and 2-octyl halides and, presumably, a mechanism is operating which is closely related to that which was previously proposed (Scheme I).[2]

SCHEME I



There does appear to be, in the present investigation, a tendency for the 2.5-order rate coefficients to fall off slightly in value at the higher silver nitrate concentrations.

From Table I, it can be seen that, for reaction at 45.0° with approximately 0.04 $M$ silver salt, allyl bromide reacts with silver nitrate some 1600 times faster than with silver perchlorate. This can be compared with data available for 2-octyl bromide where, at 44.6°, reaction with silver nitrate is governed[2] by a 2.5-order rate coefficient of $3.27 \times 10^{-3}$ $M^{-1.5}$ sec$^{-1}$ and reactions with silver perchlorate[4] have initial second-order rate coefficients of $0.578 \times 10^{-5}$ $M^{-1}$ sec$^{-1}$ at 0.0155 $M$ salt and $0.715 \times 10^{-5}$ $M^{-1}$ sec$^{-1}$ at 0.0310 $M$ salt. These second-order rate coefficients correspond to 2.5-order rate coefficients of $4.65 \times 10^{-5}$ $M^{-1.5}$ sec$^{-1}$ and $4.06 \times 10^{-5}$ $M^{-1.5}$ sec$^{-1}$, respectively. For 0.03 $M$ silver salt at 44.6°, silver nitrate reacts with 2-octyl

---

[12] J. D. Roberts, W. G. Young, and S. Winstein, *J. Amer. Chem. Soc.*, **64**, 2157 (1942).

[13] W. G. Young and L. J. Andrews, *J. Amer. Chem. Soc.*, **66**, 421 (1944).

[14] W. G. Young, S. H. Sharman, and S. Winstein, *J. Amer. Chem. Soc.*, **82**, 1376 (1960).

[15] S. Oae and C. A. Vanderwerf, *J. Amer. Chem. Soc.*, **75**, 2724 (1953).

[16] A. F. Ferris, K. W. McLean, I. G. Marks, and W. D. Emmons, *J. Amer. Chem. Soc.*, **75**, 4078 (1953).

[17] J. J. Ritter and P. Minieir, *J. Amer. Chem. Soc.*, **70**, 4045 (1948).

TABLE III

A. Temp, 45.0°; 5-ml aliquots; [$C_3H_5Br$], 0.0400 *M*; [$AgNO_3$], 0.0100 *M*; Titers, ml of 0.00625 *M* KCl

| | | | | | |
|---|---|---|---|---|---|
| Time, min | 0 | 10.15 | 15.20 | 20.34 | 24.95 |
| Titer | 7.88 | 7.40 | 7.19 | 7.02 | 6.85 |
| $10^2$ $k_{2.5}$, $M^{-1.5}$ sec$^{-1}$ | | 2.64 | 2.60 | 2.47 | 2.53 |
| Time, min | 30.51 | 40.02 | 49.90 | | |
| Titer | 6.57 | 6.22 | 5.92 | | |
| $10^2$ $k_{2.5}$, $M^{-1.5}$ sec$^{-1}$ | 2.67 | 2.69 | 2.66 | | |

B. Temp, 45.0°; 5-ml aliquots; [$C_3H_5Br$], 0.0800 *M*; [$AgNO_3$], 0.160 *M*; Titers, ml of 0.100 *M* KCl

| | | | | | |
|---|---|---|---|---|---|
| Time, min | 0 | 1.30 | 2.03 | 2.66 | 3.28 |
| Titer | 7.70 | 7.30 | 7.12 | 7.00 | 6.83 |
| $10^2$ $k_{2.5}$, $M^{-1.5}$ sec$^{-1}$ | | 2.29 | 2.22 | 2.11 | 2.23 |
| Time, min | 3.96 | 4.54 | 5.18 | | |
| Titer | 6.71 | 6.57 | 6.50 | | |
| $10^2$ $k_{2.5}$, $M^{-1.5}$ sec$^{-1}$ | 2.18 | 2.26 | 2.15 | | |

C. Temp, 45.0°; 5-ml aliquots; [$C_3H_5Br$], 0.200 *M*; [$AgClO_4$], 0.087 *M*; Titers, ml of 0.0500 *M* KCl

| | | | | | |
|---|---|---|---|---|---|
| Time, min | 0 | 1343 | 2835 | 4215 | 5630 |
| Titer | 8.70 | 8.05 | 7.48 | 7.04 | 6.58 |
| $10^5$ $k_{2.5}$, $M^{-1.5}$ sec$^{-1}$ | | 1.70 | 1.62 | 1.57 | 1.60 |
| Time, min | 9970 | 11458 | 12903 | 14393 | |
| Titer | 5.38 | 5.17 | 4.84 | 4.60 | |
| $10^5$ $k_{2.5}$, $M^{-1.5}$ sec$^{-1}$ | 1.63 | 1.64 | 1.69 | 1.69 | |

D. Temp, 45.0°; 5-ml aliquots; [$C_3H_5Cl$], 0.0800 *M*; [$AgNO_3$], 0.0400 *M*; Titers, ml of 0.0250 *M* KCl

| | | | | | |
|---|---|---|---|---|---|
| Time, min | 0 | 1452 | 2897 | 4282 | 8649 |
| Titer | 8.04 | 7.00 | 6.23 | 5.50 | 4.32 |
| $10^4$ $k_{2.5}$, $M^{-1.5}$ sec$^{-1}$ | | 0.97 | 1.03 | 1.12 | 1.02 |
| Time, min | 10077 | 11511 | 12953 | 14363 | |
| Titer | 3.98 | 3.70 | 3.48 | 3.28 | |
| $10^4$ $k_{2.5}$, $M^{-1.5}$ sec$^{-1}$ | 1.03 | 1.03 | 1.02 | 1.01 | |

bromide 80 times faster than silver perchlorate. The corresponding ratio of 1600 for allyl bromide is some 20 times larger and this suggests that in reaction with silver nitrate nucleophilic assistance is more pronounced for allyl bromide than for the secondary 2-octyl bromide or the tertiary *α*-brominated ketone, *α*-bromo-*p*-phenylisobutyrophenone, where, at 74.0° and for reaction with 0.16 *M* salt, a ratio of 130 was observed.[10]

The leaving-group effect (Table II) has an average value of 285, which can be compared to a corresponding bromide/chloride ratio of 467 for reaction of 2-octyl halides.[2] While the difference between these ratios is quite small, its direction is consistent with the proposal of more pronounced nucleophilic assistance (less S$_N$1 character) for reaction of the allyl bromide.

At 45°, silver nitrate reacts with allyl bromide about eight times faster than with 2-octyl bromide. Streitwieser[18] reports that, on the average, allyl derivatives react under S$_N$2 conditions some 1600 times faster than isopropyl derivatives; the rates of isopropyl derivatives can be considered to represent an upper limit for the possible S$_N$2 rates of 2-octyl derivatives. In the presence of accompanying electrophilic assistance, the spread between the rates of nucleophilic attack upon allyl bromide and secondary bromides is considerably reduced.

### Experimental Section

**Materials.**—Allyl chloride and allyl bromide were purified by fractional distillation. Silver nitrate was used as received. Acetonitrile and silver perchlorate were purified as described previously.[2]

**Kinetic Procedures.**—Potentiometric titration to determine the concentration of silver ion remaining in solution and titration of developed acid, in the presence of silver ion, were carried out as described previously.[2] Reaction solutions were prepared by appropriate dilution of concentrated stock solutions within 50-ml volumetric flasks and, after shaking and temperature equilibration, 5-ml aliquots of solution were removed at appropriate time intervals. Heterogeneous catalysis by precipitated silver bromide was shown to be unimportant by allowing a solution initially 0.08 *M* in both allyl bromide and silver nitrate to react to 50% completion and then showing the subsequent kinetics to be identical with those of a solution initially 0.04 *M* in each reactant. Integrated 2.5-order rate coefficients were calculated using the appropriate form for the integrated rate equation.[2,19] Four illustrative runs are reported in Table III.

**Registry No.**—Allyl bromide, 106-95-6; allyl chloride, 107-05-1; silver nitrate, 7761-88-8; silver perchlorate, 7783-93-9; acetonitrile, 75-05-8.

---

[18] A. Streitwieser, Jr., *Chem. Rev.*, **56**, 571 (1956).

[19] We wish to thank Mr. K. C. Kolwyck for writing a computer program for this operation and Mr. A. Wang for applying the program to the experimental results.

---

## Onium Ions. VIII.[1] Selenonium and Telluronium Ions and Their Comparison with Oxonium and Sulfonium Ions

GEORGE A. OLAH,* JAMES J. SVOBODA, AND ALICE T. KU

*Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106*

*Received August 7, 1973*

A series of trialkyl(aryl)selenonium and telluronium ions are known.[2] However, neither were acidic selenonium (telluronium) ions previously obtained, nor

---

[1] Part VII: G. A. Olah, J. R. DeMember, Y. K. Mo, J. J. Svoboda, P. Schilling, and J. A. Olah, *J. Amer. Chem. Soc.*, in press.

[2] For a summary and references see H. Reinboldt in "Houben-Weyl Methoden der Organischen Chemie," Vol. 9, Georg Thieme Verlag, Stuttgart, 1955, pp 1034, 1975.