

# The Catalytic Effect of Silver Salts upon the Rate of Isomerization of Triphenylmethyl Isocyanide to Triphenylmethyl Cyanide in Acetonitrile

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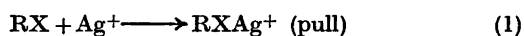
Triphenylmethyl isocyanide,  $\text{Ph}_3\text{CNC}$ , isomerizes very slowly in acetonitrile to triphenylmethyl cyanide,  $\text{Ph}_3\text{CCN}$ . The first order rate constant at  $35.0^\circ\text{C}$  is  $6.1 \times 10^{-7} \text{ s}^{-1}$ . The isomerization reaction is efficiently catalyzed by minute amounts of silver nitrate and silver perchlorate, the latter salt being the better catalyst.

The rate increase caused by the silver(I) catalysts is directly proportional to their concentrations. It is proposed that the rate determining step involves a cyclic intermediate involving the silver(I) ion.

Among the various methods for the preparation of alkyl isocyanides, the reaction between alkyl halides and silver cyanide<sup>1,2</sup> or onium dicyanoargentates<sup>3,4</sup> is well established. However, when using silver cyanide, the alkyl isocyanide formed is usually contaminated by the corresponding cyanide<sup>5</sup> which seriously limits the generality of this synthetic method. There are, however, no reports of such limitations when onium dicyanoargentates are used as reagents.

Organic reactions assisted by silver(I) ions are quite common and studies by Kornblum<sup>6-9</sup> and Kevill and Pocker<sup>10-12</sup> are repeatedly quoted. From kinetic studies on reactions of alkyl halides and silver nitrate the determined order in the alkyl halides is 1, while the order in the silver nitrate varies between 1.5 and 2.<sup>10-14</sup> These variations are explained by an electrophilic pull by the silver ion on the outgoing halide atom, eqn. 1, and a nucleophilic push by the nitrate ion on the central carbon atom, eqn. 2. The reaction order appears to be

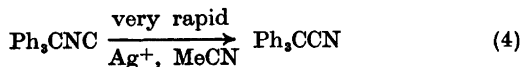
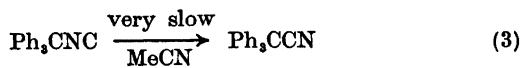
somewhat dependent upon the applied silver nitrate concentration.



The silver(I) ion, having its  $4d$  orbitals filled while the  $5s$  and  $5p$  orbitals are vacant, can readily be coordinated by electron-rich ligands and at the same time exert a stabilization due to back bonding from its  $d$ -orbitals to vacant or antibonding orbitals in the ligands. The silver(I) ion may even coordinate with strained  $\sigma$ -bonds in bicyclic ring systems exerting a catalytic effect upon the rearrangements of these systems as shown by Paquette.<sup>15</sup>

Recently Austad and Songstad<sup>16</sup> reported rates of isomerization of triphenylmethyl isocyanide to the corresponding cyanide in acetonitrile at various temperatures on samples of triphenylmethyl isocyanide synthesized from triphenylmethyl chloride and onium dicyanoargentates. However, we have been unable to reproduce their results from samples of triphenylmethyl isocyanide synthesized from *N*-triphenylmethyl formamide and 4-methylphenyl sulfonyl chloride,<sup>17</sup> a synthetic route which avoids the use of silver species.

Actually, we have found that triphenylmethyl isocyanide, synthesized by this method, is isomerizing extremely slowly in pure acetonitrile, eqn. 3, but that the isomerization is efficiently catalyzed by silver ions from added silver nitrate or silver perchlorate, eqn. 4.



In this work we have therefore performed a kinetic study on the effect of silver(I) ions upon the rate of isomerization to evaluate the mechanism of this reaction and to obtain further information on when silver species can be employed as reagents toward alkyl halides for the synthesis of alkyl isocyanides.

Silver nitrate and silver perchlorate are well suited as sources of the silver(I) ion in acetonitrile since the dissociation constants of these salts are  $9 \times 10^{-8}$  M and  $4.3 \times 10^{-4}$  M, respectively.<sup>10</sup> In the concentration range applied in the present study,  $< 1.5 \times 10^{-4}$  M, these salts can thus be considered fully dissociated. In acetonitrile the silver(I) ion is solvated by four acetonitrile molecules when the concentration is less than 0.5 M.<sup>18</sup> In this solvent the silver(I) ion should thus be formulated as  $[\text{Ag}(\text{MeCN})_4]^+$ .

## EXPERIMENTAL

**Solvents.** Acetonitrile, Baker Analyzed Reagent, was distilled from phosphorus pentoxide and finally from calcium hydride<sup>19</sup> and stored

on Linde 3 Å molecular sieves in a dry box under nitrogen. Cyclohexane and hexane were distilled from sodium. Formamide was distilled in vacuum prior to use.

**Materials.** Silver nitrate, Merck, *p.a.* grade, was dried at 120°C for 2 h. Anhydrous silver perchlorate, K & K Laboratories, was used without further purifications. *N*-Triphenylmethylformamide was prepared from triphenylmethyl chloride and formamide,<sup>20</sup> m.p. 203–204°C (MeCN). Triphenylmethyl isocyanide was prepared by two routes:

**Method A.** From *N*-triphenylmethylformamide and 4-methylphenylsulfonyl chloride in pyridine,<sup>17</sup> m.p. 132–133°C (hexane).

**Method B.** Purified triphenylmethyl chloride and tetramethylammonium dicyanoargentate yielded an impure product.<sup>19</sup> However, by addition of a trace amount of tetraphenylarsonium iodide to the reaction mixture immediately after the reaction was completed to complex catalytic amounts of silver species, the desired product was obtained, m.p. 131–132°C (hexane).

Tetramethylammonium dicyanoargentate was prepared from freshly prepared silver cyanide and dried tetramethylammonium chloride,<sup>3</sup> m.p. 194–195°C (MeCN). Tetraphenylarsonium iodide was prepared as reported by Songstad and co-workers.<sup>21</sup>

**Kinetic studies.** The rate studies were performed with a Unicam SP 200 Infrared Spectrophotometer by following the disappearance of the isocyanide peak at 2126  $\text{cm}^{-1}$  employing liquid IR cells with a cell length of 0.1 cm. The initial concentration of the substrate was  $2.0 \times 10^{-2}$  M in all runs. The logarithmic rate plots were linear throughout each run. When

*Table 1.* Rates of isomerization of triphenylmethyl isocyanide, RNC, to triphenylmethyl cyanide at 35°C at various concentrations of silver nitrate. The initial concentration of the isocyanide is  $2.0 \times 10^{-2}$  M.

$[\text{AgNO}_3] \times 10^6/\text{M}$	$k_{\text{obs}}/\text{s}^{-1}$	$k_1'K_A/\text{l s}^{-1} \text{mol}^{-1}$
0	$(6.1 \pm 0.4) \times 10^{-7}$	
1	$(3.2 \pm 0.2) \times 10^{-6}$	
2	$(8.8 \pm 0.4) \times 10^{-6}$	
5	$(7.2 \pm 0.4) \times 10^{-6}$	
10	$(2.3 \pm 0.1) \times 10^{-4}$	$31 \pm 3$
20	$(5.3 \pm 0.3) \times 10^{-4}$	
50	$(1.5 \pm 0.1) \times 10^{-3}$	
160	$(3.8 \pm 0.5) \times 10^{-3}$	
0 <sup>a</sup>	$(3.5 \pm 0.2) \times 10^{-4}$	
0 <sup>b</sup>	$(1.3 \pm 0.1) \times 10^{-6}$	
0 <sup>c</sup>	$3.34 \times 10^{-4}$	
$5.0 \times 10^{-5}$ Me <sub>4</sub> NAg(CN) <sub>2</sub>	$(1.7 \pm 0.1) \times 10^{-6}$	
$2.5 \times 10^{-5}$ M AgNO <sub>3</sub> + $2.3 \times 10^{-5}$ M Ph <sub>4</sub> AsCl	$(1.8 \pm 0.1) \times 10^{-4}$	

<sup>a</sup> With excess AgCN at 25°C. <sup>b</sup> Determined from triphenylmethyl isocyanide prepared by route B. <sup>c</sup> From Ref. 16 at 35°C.

Table 2. Rates of isomerization of triphenylmethyl isocyanide to triphenylmethyl cyanide at 35 °C at various concentrations of silver perchlorate. The initial concentration of the isocyanide is  $2.0 \times 10^{-3}$  M.

$[\text{AgClO}_4] \times 10^6/\text{M}$	$k_{\text{obs}}/\text{s}^{-1}$	$k_1/K_A/\text{s}^{-1} \text{ mol}^{-1}$
0	$(6.1 \pm 0.4) \times 10^{-7}$	
3	$(4.6 \pm 0.2) \times 10^{-6}$	
6	$(1.4 \pm 0.1) \times 10^{-4}$	
10	$(4.9 \pm 0.2) \times 10^{-4}$	$53 \pm 5$
20	$(9.1 \pm 0.4) \times 10^{-4}$	
40	$(1.9 \pm 0.1) \times 10^{-3}$	
60	$(2.5 \pm 0.5) \times 10^{-3}$	

the concentration of the added silver salts exceeded  $\sim 10^{-4}$  M the rates were too fast to be determined accurately by the technique employed.

## RESULTS AND DISCUSSION

The observed rates of isomerization at 35 °C in acetonitrile are listed in Tables 1 and 2. In pure acetonitrile, triphenylmethyl isocyanide, synthesized from *N*-triphenylmethylformamide and 4-methylphenyl sulfonyl chloride in pyridine, Method A, is isomerizing very slowly and with a first order rate constant of  $6.1 \times 10^{-7} \text{ s}^{-1}$ . The catalysis exerted by silver(I) ions is pronounced even for concentrations of silver salts of only  $1 \times 10^{-4}$  M, *i.e.*  $5 \times 10^{-3}$  % of the concentration of the organic substrate. At this concentration of the catalyst the rate of isomerization is five times as high as the uncatalyzed reaction (Tables 1 and 2).

In Fig. 1 the observed rate constants are plotted *versus* the concentration of added silver nitrate and silver perchlorate. For concentrations of the silver salts above  $\sim 3 \times 10^{-4}$  M, the observed rate constants are seen to be linearly related to the concentration of the silver salts fitting a rate equation  $k_{\text{obs}} = a + b[\text{AgX}]$ . The lack of linearity at very low concentrations of silver salt may be due to several factors. First of all, these low concentrations are considerably below the purification limit of the solvent. Furthermore, since the ratio between the concentration of the substrate and the silver catalyst in this non-linear region is more than  $7 \times 10^3$ , undetectable contaminations in the substrate may be the cause of the non-linearity observed. For concentrations of

silver salts above  $\sim 1 \times 10^{-4}$  M, the rates of isomerization were too rapid to be determined accurately by the technique employed. The possible deviation from linearity at high concentrations may thus be due to experimental error.

The results obtained in the present study suggest that the isomerization reaction studied takes place by an unassisted path, eqn. 3, with a first order rate constant  $k_1$ , along with an  $\text{S}_{\text{N}}1$   $\text{Ag}^+$  assisted step, eqns. 5 to 7.

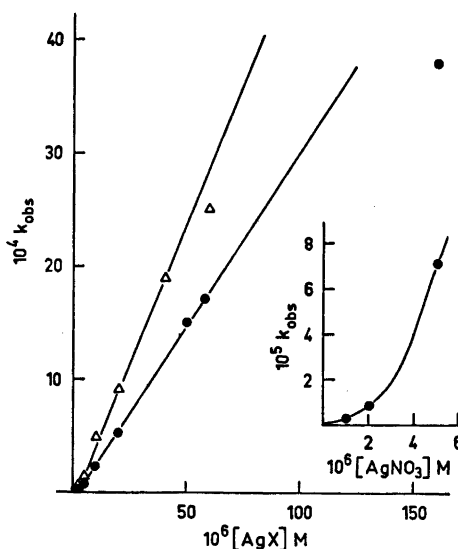
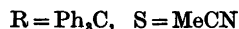
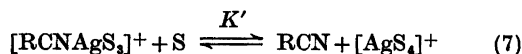
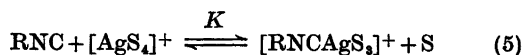


Fig. 1. The effect of added silver salts upon the observed rate constant,  $k_{\text{obs}}$ , for the isomerization of triphenylmethyl isocyanide to triphenylmethyl cyanide in acetonitrile at  $35.0 \pm 0.1$  °C. Filled circles, silver nitrate. Triangles, silver perchlorate.



The first step in the assisted reaction, eqn. 5, is supposed to be the displacement of a solvent molecule from the silver tetraacetonitrile ion followed by the intramolecular isomerization, eqn. 6. The final step in the sequence is the regeneration of the silver tetraacetonitrile ion together with the product, triphenylmethyl cyanide, eqn. 7. The latter step, being in principle an acid-base equilibrium, is set up very rapidly and is displaced completely to the right since triphenylmethyl cyanide is assumed to be a considerably weaker base toward the silver(I) ion than is the acetonitrile molecule.

Assuming the second step, eqn. 6, to be the rate determining one, the following rate equation is obtained:

$$k_{\text{obs}} = k_1 + k_1' \frac{K_a[\text{AgX}]}{1 + [\text{RNC}]} \quad (8)$$

where  $\text{X} = \text{ClO}_4^-, \text{NO}_3^-$  and  $K_a = K[\text{MeCN}]^{-1}$ . Eqn. 8 conforms with the linearity observed provided  $K_a[\text{RNC}] \ll 1$ , and we thus obtain:

$$k_{\text{obs}} = k_1 + k_1' K_a[\text{AgX}] \quad (9)$$

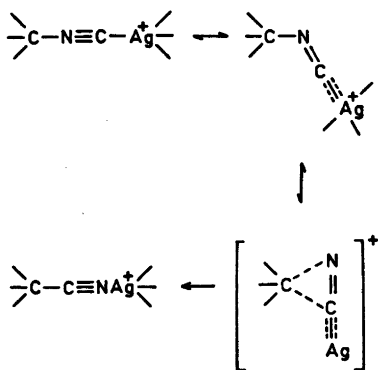
*Table 3.* The effect of water upon the rate of isomerization of triphenylmethyl isocyanide to triphenylmethyl cyanide at 35 °C in acetonitrile. The initial concentration of the isocyanide is  $2.0 \times 10^{-2}$  M.

$[\text{H}_2\text{O}] \times 10^2/\text{M}$	$k_{\text{obs}}/\text{s}^{-1}$
1.49	$(6.4 \pm 0.4) \times 10^{-7}$
14.9	$(8.3 \pm 0.5) \times 10^{-7}$
149	$(6.3 \pm 0.3) \times 10^{-7}$
820	$(6.9 \pm 0.4) \times 10^{-7}$
$5.8 \times 10^{-5}$ M $\text{H}_2\text{O}$ + $5.8 \times 10^{-5}$ M $\text{AgNO}_3$	$(1.7 \pm 0.2) \times 10^{-5}$

Addition of water along with silver nitrate causes the same catalytic effect as if the silver nitrate had been added alone, Table 3. The presence of water due to the hygroscopic nature of the solvent and silver perchlorate does not affect the rates. However, added tetraphenylarsonium chloride to a sample of the substrate and silver nitrate, (Table 1), shows a marked reduction of the expected rate acceleration due to the silver nitrate. This may be due to a complexing of the halide ion with the silver(I) ion forming traces of  $\text{AgCl}$  or preferably  $\text{AgCl}_2^-$ .<sup>22,23</sup> The rates reported by Austad and Songstad<sup>16</sup> for an uncatalyzed isomerization are too high compared to the results obtained in this paper. They also reported a rate depression by anions and assumed this to be caused by a salt effect due to the nucleophilic anions. In the light of the present work it now seem reasonable to assign these rate decelerations to a complexing of the added anions with impurities of silver(I) species in their employed triphenylmethyl isocyanide. From their reported rate constant,  $3.35 \times 10^{-4} \text{ s}^{-1}$ , and the results obtained in the present study one can estimate a concentration of approximately  $1.4 \times 10^{-5}$  M of active catalytic silver species in their applied reaction mixture, amounting to a contamination of 0.07 % (in mol) of the substrate. From Table 1 it can be seen that this contamination cannot be the pure tetramethylammonium dicyanoargentate alone since a concentration of  $5 \times 10^{-5}$  M of this salt only doubles the observed rate compared to the rate observed for the uncatalyzed isomerization.

Isocyanides are known to form stable complexes with the silver(I) ion although few of these complexes have been characterized.<sup>24-26</sup> However, the silver nitrate-triphenylmethyl isocyanide complex has been isolated in poor yield in acetonitrile at  $-20$  °C, while attempts to isolate the silver perchlorate complex have failed.<sup>27</sup> A preequilibrium step *via* the silver(I) isocyanide complex is therefore proposed.

In triphenylmethyl isocyanide the central carbon atom is surrounded by three phenyl groups. The silver(I) ion is attached to four acetonitrile solvent molecules<sup>18</sup> and for steric reasons the most possible attacking site is on the lone pair of the isocyanide carbon atom (Scheme 1).



Scheme 1.

In the complex formed a stabilization due to back donation from silver  $d^{10}$  orbitals to the antibonding orbitals of the isocyanide carbon atom is to be expected.<sup>28,29</sup> The negatively charged surroundings of the cyano groups in the solvent molecules will tend to increase this back donation due to their interactions with the electron rich  $d^{10}$  sphere of the silver(I) ion. It is assumed that this back donation will cause the isocyanide nitrogen atom to be  $sp^2$  hybridized and the C-NC bond angle approaches  $120^\circ$ , Scheme 1. Once formed, the isocyanide group in this complex will collapse to the product *via* an intermediate cyclic three center ion, with negligible separation of the alkyl and cyanide group in the transition state. This should be consistent with a synchronous mechanism as proposed by Casanova *et al.*<sup>28</sup> and calculated by Schaefer *et al.*<sup>30,31</sup> for similar uncatalyzed systems. Casanova and co-workers<sup>28</sup> found that *p*-substituted aryl isocyanides isomerize synchronously and unaffected by the substituents and for the isomerization of methyl isocyanide to methyl cyanide Schaefer and co-workers<sup>30,31</sup> calculated a transition state with a C-NC bond angle of  $106^\circ$ .

Yamada and co-workers<sup>32</sup> have shown that isocyanides may isomerize *via* a radical mechanism with racemization. A radical mechanism for the reaction studied is excluded as shown by Austad and Songstad.<sup>16</sup> Moreover, the enhanced rate reported when they added tetraphenylarsonium perchlorate or lithium perchlorate strongly supports a transition state with a charged alkyl carbon atom. The marked increase in the observed rates from silver

nitrate ( $k_1'K_A=31 \text{ l s}^{-1} \text{ mol}^{-1}$ ) to silver perchlorate ( $k_1'K_A=53 \text{ l s}^{-1} \text{ mol}^{-1}$ ) as catalyst supports a mechanistic route *via* a rate determining step with a positively charged intermediate as proposed. The perchlorate ion as a counter ion will be able to stabilize a positively charged transition state better than the nitrate ion. Songstad and Austad<sup>16</sup> could not isolate any triphenylmethyl azide when ionic azide was added to the reaction medium. Thus a long lived and stable carbenium ion can be excluded.<sup>33</sup>

The results reported in this paper suggest that the difficulties in preparing silver alkyl isocyanide complexes and in isolating alkyl isocyanides by applying silver compounds may be due to an isomerization of the isocyanide group which is catalyzed by the silver(I) ion. In other words, the initial product may be the desired complex or the alkyl isocyanide which then isomerizes to the corresponding cyanide in either case. One known exception to this is 4,4',4''-trinitrotriphenylmethyl isocyanide which can be obtained from the corresponding bromide and silver cyanide.<sup>3</sup> Furthermore, the reported stability of diphenylmethyl isocyanide and 4,4'-dimethyldiphenylmethyl isocyanide prepared *via* onium dicyanoargentates<sup>3</sup> suggests that the synthetic application of these silver salts is quite useful for alkyl substrates which do not readily ionize, or, when a silver complexing ion like ionic iodide is added to the reaction mixture.

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## REFERENCES

1. Gautier, A. *Ann. Chim. (Paris)* 7 (1869) 203, 215, 233.
2. Hartley, E. G. A. *J. Chem. Soc.* 109 (1916) 1296.
3. Engemyr, L. B., Martinsen, A. and Songstad, J. *Acta Chem. Scand.* 28 (1974) 255.
4. Songstad, J., Stangeland, L. J. and Austad, T. *Acta Chem. Scand.* 24 (1970) 355.
5. Guilmard, H. *Ann Chim. Phys.* 14 (1908) 311.
6. Kornblum, N., Fishbein, L. and Smiley, R. A. *J. Am. Chem. Soc.* 77 (1955) 6261.
7. Kornblum, N., Smiley, R. A., Blackwood, R. K. and Iffland, D. J. *J. Am. Chem. Soc.* 77 (1955) 6269.
8. Kornblum, N., Willard, J. J. and Hardies, D. E. *J. Am. Chem. Soc.* 88 (1966) 1704.

9. Kornblum, N. and Hardies, D. E. *J. Am. Chem. Soc.* 88 (1966) 1707.
10. Kevill, D. N. and Pocker, Y. *J. Am. Chem. Soc.* 87 (1965) 4760.
11. Kevill, D. N. and Pocker, Y. *J. Am. Chem. Soc.* 87 (1965) 4771.
12. Kevill, D. N. and Pocker, Y. *J. Am. Chem. Soc.* 87 (1965) 4778.
13. Hammond, G. S., Hawthorne, M. F., Waters, J. H. and Greybill, B. N. *J. Am. Chem. Soc.* 82 (1960) 704.
14. Kevill, D. N. and Held, L. *J. Org. Chem.* 38 (1973) 4445.
15. Paquette, L. A. *Acc. Chem. Res.* 4 (1971) 280.
16. Austad, T. and Songstad, J. *Acta Chem. Scand.* 26 (1972) 3141.
17. Alexandrou, N. E. *J. Org. Chem.* 30 (1965) 1335.
18. Balasubrahmanyam, K. and Janz, G. J. *J. Am. Chem. Soc.* 92 (1970) 4189.
19. Austad, T., Songstad, J. and Stangeland, L. J. *Acta Chem. Scand.* 25 (1971) 2327.
20. Brederbeck, H., Gompper, R. and Theilig, G. *Chem. Ber.* 87 (1954) 537.
21. Austad, T., Songstad, J. and Åse, K. *Acta Chem. Scand.* 25 (1971) 331.
22. Luehrs, D. C., Iwamoto, R. T. and Kleinberg, J. *Inorg. Chem.* 5 (1966) 201.
23. Alexander, R., Ko, E. C. F., Mac, Y. C. and Parker, A. J. *J. Am. Chem. Soc.* 89 (1967) 3703.
24. Klages, F. and Moenkmeier, K. *Chem. Ber.* 85 (1952) 109.
25. Cotton, F. A. and Zingales, F. *J. Am. Chem. Soc.* 83 (1961) 351.
26. Minghetti, G., Flavio, B. and Massobrio, M. *Inorg. Chem.* 14 (1975) 1974.
27. Martinsen, A. *To be published.*
28. Casanova, Jr., J., Werner, N. D. and Schuster, R. E. *J. Org. Chem.* 31 (1966) 3473.
29. Vogler, A. In Ugi, I., Ed., *Isonitrile Chemistry*, Academic, New York 1971, p. 217.
30. Liskow, D. H., Bender, C. F. and Schaefer, III, H. F. *J. Chem. Phys.* 57 (1972) 4509.
31. Liskow, D. H., Bender, C. F. and Schaefer, III, H. F. *J. Am. Chem. Soc.* 94 (1972) 5178.
32. Yamada, S., Takashima, K., Sato, T. and Terashima, S. *Chem. Commun.* (1969) 811.
33. Martinsen, A., Austad, T. and Songstad, J. *Acta Chem. Scand.* 29 (1975) 661.

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