

Francesco P. Ballistreri and Gaetano A. Tomaselli*

Istituto Dipartimentale di Chimica e Chimica Industriale, Università di Catania, Viale A. Doria 6
95125 Catania, Italy
Received February 20, 1981

Hydrolysis reactions of substituted thiophene-2-sulphonyl chlorides (5-methyl, 5-H, 5-chloro, 5-nitro) catalysed by silver nitrate and silver nitrite salts have been studied in water at 25°. Salt effects by potassium nitrate, sodium perchlorate and mercuric bromide have also been investigated. For the catalysis effected with silver nitrate, the pseudo-first order rate constants depend on the first power of silver ion concentration, while nitrate anion is not involved in the transition state. The corresponding curved Hammett plot suggests a transition state with a partially developed sulphonylium character. With silver nitrite, the rate dependence on both silver and nitrite ion concentrations would indicate that silver is involved in the transition state as well as nitrite. Also, in this case the curved Hammett plot obtained suggests a partial positive charge on the sulphur atom in the transition state. A comparison with uncatalysed hydrolysis reactions would support a previous interpretation that thiophene-2-sulphonyl chlorides hydrolyze by an S_N2 type mechanism which can shift toward an S_N1 or an $S_A N$ process depending on the ring substituent.

J. Heterocyclic Chem., **18**, 1229 (1981).

Introduction.

Hydrolysis of substituted thiophene-2-sulphonyl halides has been interpreted in terms of an S_N2 type mechanism which can shift toward an S_N1 or an S_N2 process depending on the ring substituent and on the leaving group mobility (1-2).

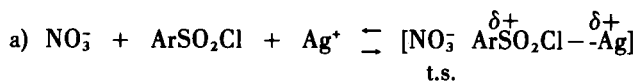
To test the above interpretation further we studied the hydrolysis of substituted thiophene-2-sulphonyl chlorides in the presence of silver salts in water. It is known that nucleophilic substitution reactions of alkyl halides are catalysed by electrophilic metal ions such as silver ion and that the transition states, involved in such reactions, have both S_N1 and S_N2 character (3-4).

The use of silver salts in the system studied by us would allow a reaction model which implies a transition state with a developed sulphonylium character (S_N1 -like). In such a case, a comparison with the uncatalysed hydrolysis reactions would be meaningful.

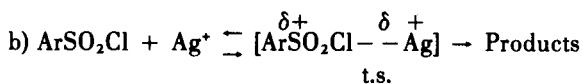
Results and Discussion.

i) Catalysis by Silver Nitrate.

The hydrolysis of thiophene-2-sulphonyl chlorides catalysed by silver nitrate might occur as follows (5).



→ Products



We neglect the possibility that the undissociated nitrate might be involved during the catalysis process, since its degree of dissociation α ranges from 1 to 0.95 for the concentrations used in our experiments (6). Furthermore, hydrolysis of thiophene-2-sulphonyl chloride in the presence of mercuric bromide (8) (molar ratio with respect to substrate 1:1 and 10:1, $k_{obs} = 0.000483$ and 0.000466 s^{-1} , respectively) has the same rate as the solvolysis made without mercuric bromide ($k_{obs} = 0.000478$) (1). Since mercuric bromide is dissociated very little, this indicates that the catalysis by undissociated salt does not occur. Likewise, catalysis by undissociated silver nitrate or by the silver chloride (9) produced during the reaction is unimportant.

Reaction a) involves the participation of nitrate ion in the transition state. It can be ruled out on the basis that observed rate constants k_{obs} , reported in Table 1 (experiments 1-11), appear to be affected by the silver ion concentration only.

The process b) can be described by the following rate law:

$$v = k_c[\text{ArSO}_2\text{Cl}][\text{Ag}^+] = k_c[\text{ArSO}_2\text{Cl}][\text{AgNO}_3] \quad (1)$$

assuming the degree of dissociation of silver nitrate α and the activity coefficient are close to unity and incorporating $[\text{H}_2\text{O}]$ in k_c . In addition, if we consider the uncatalysed hydrolysis route, equation 1 becomes:

$$v = k_{unc}[\text{ArSO}_2\text{Cl}] + k_c[\text{ArSO}_2\text{Cl}][\text{AgNO}_3], \text{ or} \\ k_{obs} = k_{unc} + k_c[\text{AgNO}_3] \quad (2)$$

Table 1

Solvolysis Rate Constants k_{obs} of Substituted Thiophene-2-sulphonyl Chlorides (a) in Water at 25° in the Presence of Silver Nitrate, Potassium Nitrate and Sodium Perchlorate, respectively

Experiment No.	Substituent	$10^4[\text{AgNO}_3]$, M	$10^4[\text{KNO}_3]$, M	$10^4[\text{NaClO}_4 \cdot \text{H}_2\text{O}]$, M	$10^4 k_{obs}$, s^{-1} (e)
-	5-CH ₃	-	-	-	1.27 (b)
1	5-CH ₃	0.0309	30.4 (c)	-	0.500
2	5-CH ₃	3.68	26.8 (c)	-	1.63
3	5-CH ₃	6.49	24.0 (c)	-	2.25
4	5-CH ₃	9.04	21.4 (c)	-	2.89
5	5-CH ₃	0.0309	-	30.4 (c)	0.454
6	5-CH ₃	3.68	-	26.8 (c)	1.24
7	5-CH ₃	6.49	-	24.0 (c)	1.92
8	5-CH ₃	9.04	-	21.4 (c)	2.82
9	5-CH ₃	6.49	1.63	-	2.24
10	5-CH ₃	6.49	3.26	-	2.12
11	5-CH ₃	6.49	0.326	-	2.18
12	5-CH ₃	0.0309 (d)	-	-	0.621
13	5-CH ₃	0.310 (d)	-	-	0.764
14	5-CH ₃	1.52 (d)	-	-	1.34
15	5-CH ₃	3.68 (d)	-	-	2.16
16	5-CH ₃	6.49 (d)	-	-	3.14
17	5-CH ₃	-	0.317	-	0.719
18	5-CH ₃	-	1.61	-	0.680
19	5-CH ₃	-	3.69	-	0.691
20	5-CH ₃	-	7.44	-	0.691
-	H	-	-	-	0.478 (b)
21	H	0.310 (d)	-	-	0.461
22	H	1.52 (d)	-	-	0.594
23	H	6.49 (d)	-	-	1.47
24	H	-	0.317	-	0.384
25	H	-	3.69	-	0.385
26	H	-	6.49	-	0.401
-	5-Cl	-	-	-	0.164 (b)
27	5-Cl	0.310 (d)	-	-	0.0979
28	5-Cl	1.52 (d)	-	-	0.130
29	5-Cl	3.68 (d)	-	-	0.179
30	5-Cl	-	1.49	-	0.0956
31	5-Cl	-	3.67	-	0.0942
32	5-Cl	-	8.06	-	0.0926
-	5-NO ₂	-	-	-	0.301 (b)
33	5-NO ₂	0.310 (d)	-	-	0.234
34	5-NO ₂	1.52 (d)	-	-	0.226
35	5-NO ₂	3.70 (d)	-	-	0.251
36	5-NO ₂	5.94 (d)	-	-	0.272
37	5-NO ₂	-	0.394	-	0.287
38	5-NO ₂	-	1.49	-	0.283
39	5-NO ₂	-	4.11	-	0.283
40	5-NO ₂	-	8.16	-	0.280
41	5-NO ₂	-	-	7.55	0.320
42	5-NO ₂	-	-	22.8	0.247
43	5-NO ₂	-	-	35.8	0.263

(a) 0.00326M in all cases. (b) Reference 1. (c) $[\text{AgNO}_3] + [\text{KNO}_3] = [\text{AgNO}_3] + [\text{NaClO}_4 \cdot \text{H}_2\text{O}] = 0.3044M$. (d) The values of catalytic rate constants are (number of the experiment, catalytic rate constant k_c $l\ m^{-1}\ s^{-1}$, correlation coefficient): 12-16, 0.0388, 0.998; 21-23, 0.0167, 0.998; 27-29, 0.00239, 0.999; 34-36, 0.00104, 0.998 for 5-CH₃, H, 5-Cl and 5-NO₂, respectively. (e) Values of k_{obs} are accurate to $\pm 6\%$.

As support of equation 2, a good linear dependence is observed when k_{obs} values are plotted against silver nitrate concentrations (10) (Table 1, footnote d). The values of k_c obtained for 5-methylthiophene-2-sulphonyl chloride are

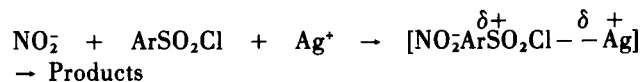
reproducible when either potassium nitrate or sodium perchlorate are used to keep the ionic strength constant (experiments 1-8, $k_c = 0.0263$ and 0.0258 , respectively) but the value is slightly higher when the ionic strength changes during the reaction ($k_c = 0.0388$). A strange feature displayed by the data reported in Table 1 is that the k_{obs} for the catalysed route is lower than that for the uncatalysed hydrolysis when the concentration of silver nitrate is less than that of sulphonyl chloride. We do not understand this behavior. Such a discrepancy could be ascribed to experimental errors, but repetition of some experiments several times always gave the same outcome.

A tentative explanation, which might be supported by the salt effects reported in Table 1 (experiments 17-20, 24-26, 30-32, 37-43), would call for a negative salt effect by silver nitrate at very low concentrations. Such an effect would be balanced and overwhelmed at higher concentrations by a silver ion positive catalytic effect.

A Hammett plot of the catalytic constants, k_c , is curved and very similar to that observed for the uncatalysed hydrolysis except for the 5-nitro derivative. A similar trend is observed for alkylation reactions of benzenesulphonyl chlorides with benzene and toluene in the presence of aluminum chloride in which incipient sulphonylium ions are involved (11) (Figure 1). These findings support the previous interpretation that the uncatalysed hydrolysis of thiophenesulphonyl chlorides proceeds with a transition state involving a partial sulphonylium character (S_N1 -like) except for the nitro derivatives (1). For such compounds the transition state has no sulphonylium character and the mechanism is shifted toward an S_N type (12). In fact for the 5-nitro compound we were not able to observe an appreciable increase in the observed hydrolysis rate by silver nitrate at high concentration of catalyst (ratio silver nitrate/arylsulphonyl chloride 18:1), indicating that the bond S-Cl is very little stretched.

ii) Catalysis by Silver Nitrite.

In a previous report (13) we have shown that the nitrite anion is able to catalyse nucleophilically the hydrolysis of thiophenesulphonyl chlorides. It turns out that the silver nitrite would be expected to be at the same time a nucleophilic and electrophilic catalyst, due to the simultaneous participation in the transition state of both nitrite and silver ions. In such a case we might write the overall process in this way:



$$k_{obs} = k'_c [\text{AgNO}_2]_0^2 \alpha^2 f^2 \quad (3)$$

where $[\text{AgNO}_2]_0$ is the stoichiometric concentration of silver nitrite, α is the degree of dissociation of silver nitrite

Table 2

Rate Constants k_{obs} and k for the Reaction of Substituted Thiophene-2-sulphonyl Chlorides with Silver Nitrite in Water at 25° and Degree of Dissociation α

Substituent	[ArSO ₂ Cl]10 ³ , M	[AgNO ₂]10 ² , M	α (a)	$\alpha^2 c^{10^5}$	$k_{obs} 10^3$, s ⁻¹	k l ² m ⁻² s ⁻²
5-CH ₃	0.409	0.382	0.833	1.01	1.44	0.423
	0.458	0.588	0.776	2.08	1.59	
	0.458	1.35	0.646	7.61	3.27	
	0.458	2.13	0.567	14.6	4.96	
H	0.413	0.923	0.708	4.27	0.652	0.202
	0.413	1.30	0.651	7.16	0.932	
	0.413	1.64	0.612	10.1	1.44	
	0.413	1.98	0.580	13.2	1.75	
	0.413	2.27	0.556	15.9	2.12	
5-Cl	0.387	0.375	0.835	0.980	0.253	0.110
	0.401	0.924	0.708	4.28	0.455	
	0.371	1.02	0.692	4.98	0.493	
	0.371	1.31	0.650	7.27	0.694	
5-NO ₂	0.413	0.908	0.711	4.17	0.526	0.0845
	0.413	1.29	0.653	7.10	0.702	
	0.413	1.65	0.611	10.2	0.864	
	0.413	2.06	0.573	13.9	1.05	

(a) Values obtained from the dissociation constant at 25° in water $k = 10^{-14}$ (16).

and f is the mean ionic activity coefficient.

Alternatively, if we postulate that the rate-determining step may be taken as the reaction between silver nitrite ion pairs with sulphonyl chloride, equation 3 becomes:

$$k_{obs} = k[AgNO_2]_i(1-\alpha) \quad (4)$$

Since $K_A = (1-\alpha)/\alpha^2[AgNO_2]_i f^2$, where K_A is the association constant for the silver nitrite equilibrium, equation 4 reduces to:

$$k_{obs} = k K_A [AgNO_2]_i^2 \alpha^2 f^2 \quad (5)$$

which is equivalent to equation 3.

A further possibility is to write the previous process as:



This would give an equivalent kinetic expression.

Considering also the uncatalysed route we have:

$$k_{obs} = \text{intercept} + k K_A [AgNO_2]_i^2 \alpha^2 f^2 \quad (6)$$

Experimental data support equation 6. There is a good linear correlation between k_{obs} values and $\alpha^2 [AgNO_2]_i^2$ rather than $\alpha [AgNO_2]_i$ (Figure 2) (14). Equation 4 has the advantage that allows the calculation of catalytic rate con-

stants regardless of the knowledge of f . Catalytic rate constants obtained from equation 4 are reported in Table 2 (15).

A Hammett plot of these values is curved, with a trend similar to that obtained for silver nitrate catalysis and, once again, supports the sulphonylium character of the transition state in the catalysed hydrolysis of sulphonyl chlorides.

This brief note of comment is in order concerning the role played by the nitrite anion. This anion is involved in the transition state and consequently the reaction rate is increased when a nitrite salt is added to the silver nitrite (Table 3) showing a different behavior from that displayed by the nitrate anion. As far as the substituent effects are considered, we observed that electron-donating groups slow the reaction rate in the sulphonyl chloride hydrolysis catalysed by only sodium nitrite (positive ρ value) (1), but they have an accelerating effect in the hydrolysis catalysed by silver nitrite (negative ρ) (Figure 3). These two facts might be rationalized in terms of a different timing between bond-making and bond-breaking. In the transition state for the hydrolysis catalysed by sodium nitrite the making of the sulphur-nucleophile bond is advanced with respect to the breaking of the sulphur-chloride bond while in the hydrolysis catalysed by silver nitrite the sulphur-chloride bond is considerably stretched when the sulphur nucleophile bond is starting to be made (Scheme 1).

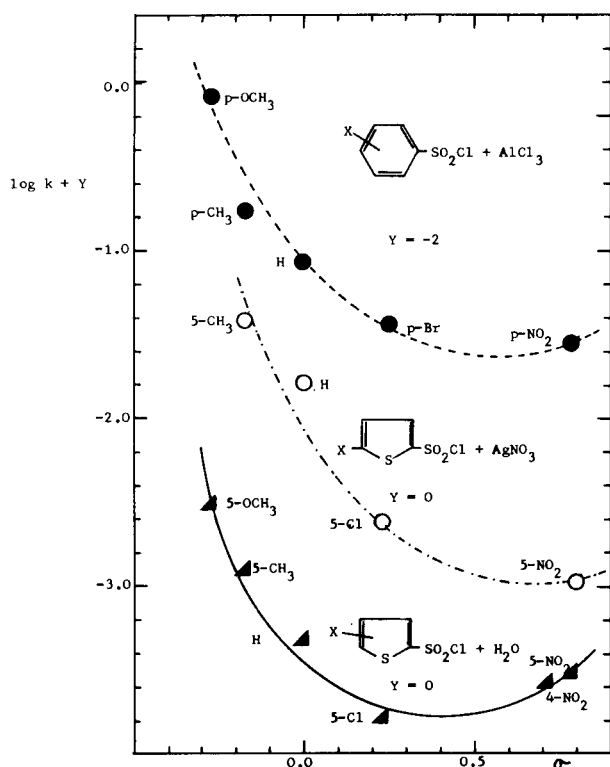
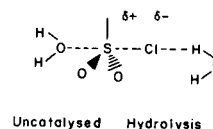


Figure 1. Hammett plots for the reactions of: 1) Sulfonylation by $X-C_6H_4SO_2Cl$ of benzene and toluene in the presence of aluminum chloride ($k = \text{reactivity ratio } k_{\text{toluene}}:k_{\text{benzene}}$) (11); 2) Thiophenesulphonyl chlorides catalysed by silver nitrate ($k = k_c = k_2$); 3) Uncatalysed hydrolysis of thiophenesulphonyl chlorides ($k = k_{\text{obs}}$) (1).

Assuming that similar Hammett plot trends observed for thiophenesulphonyl chlorides uncatalysed and catalysed hydrolysis reactions would mean comparable transition states, we could advance the hypothesis of an electrophilic "catalysis" by hydrogen bonding for uncatalysed hydrolysis. On this basis a probable transition state structure (which resembles that for silver nitrite catalysis) would be as follows:



with a molecule of water assisting electrophilically the sulphur-chloride stretching (bond-breaking) and another one attacking the sulphur reaction center nucleophilically (bond-making).

Substituent effects are intelligible on the basis of the above observations. A strong electron-withdrawing substituent in the aromatic moiety, as the 5-nitro group, contrasts the sulphur-chloride stretching but favours nucleophilic attack. Opposite behavior will be displayed by an electron-repelling derivative. The whole picture could be interpreted in terms of an S_N2 type mechanism which can be shifted toward an S_N1 or $S_A N$ process depending on the ring substituent, other factors being equal, as we suggested in a previous work (1,2).

EXPERIMENTAL

Materials

Thiophene-2-sulphonyl chlorides were obtained following the procedures described (17). Reagent grade inorganic sodium salts were used. Silver nitrate (RPE-ACS, Carlo Erba) was dried for several hours at 120° . Silver nitrite was prepared by mixing two saturated aqueous solutions of silver nitrate and sodium nitrite at room temperature and filtering the precipitate. The product obtained was carefully recrystallized from water, the temperature not being allowed to rise above 60° and

Scheme 1



Table 3

Effect of Added Sodium Nitrite on k_{obs} Values for the Reaction of 5-Methylthiophene-2-sulphonyl Chloride with Silver Nitrite in Water at 25°

$[ArSO_2Cl]10^2, M$	$[AgNO_2]10^2, M$	α	$[NaNO_2]10^2, M$	$[NO_2]_{\text{free}}10^2, M$	$k_{\text{obs}}10^3, s^{-1}$
0.0409	0.382	0.833	0.00	0.318	1.44
0.0409	0.382	0.431	4.48	4.65	2.13
0.0409	0.382	0.321	10.0	10.2	3.16
0.0409	0.382	0.277	14.6	14.7	3.95
0.0409	0.382	0.235	21.6	21.7	4.29
0.0409	0.382	0.207	29.0	29.1	6.32
0.0409	0.382	0.185	37.5	37.6	6.60
0.0409	0.382	0.169	45.6	45.7	8.83

(a) $[NO_2]_{\text{free}} = [NaNO_2] + [NO_2]$ from silver nitrite dissociation.

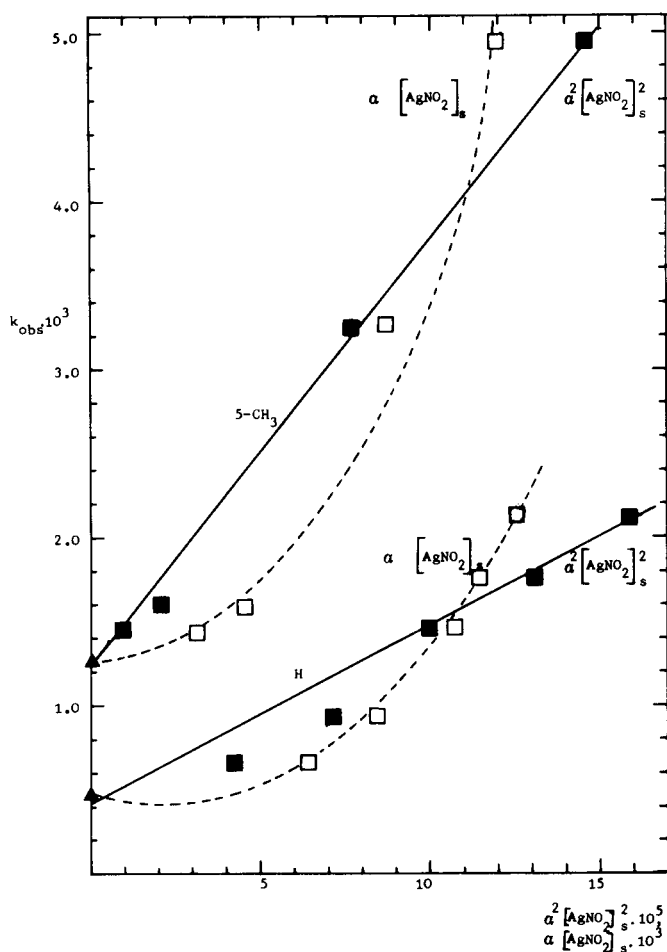


Figure 2. k_{obs} values for hydrolysis of thiophene-2-sulphonyl chlorides catalysed by silver nitrite against $\alpha[AgNO_2]_s$ and $\alpha^2[AgNO_2]_s^2$, respectively.

crystallization being carried out in the dark. The yellow needles were filtered, washed with water, and allowed to dry under vacuum in the dark. Mercuric bromide (RPE-ACS, Carlo Erba) was used without further purification.

Kinetic Procedure.

Rate measurements were carried out with a digital pH meter, Amel model 333, equipped with a motorized burette, Amel 233 by continuous titration of the acid product (2 equivalents per equivalent of acid chloride consumed) with standardized aqueous sodium hydroxide as previously reported (13, 18-20). The addition of the titrant was made using a suitable rate to keep the reaction mixture pH constant. However previous measurements (1) showed that the hydrolysis rates of sulphonyl chlorides are pH-independent in the range of pH 3-9. Pseudo-first order kinetics were followed until 50% of conversion; k_{obs} values were calculated by conventional plots of $\log(a-x)$ against time. In a typical run, 95 ml of solution of the chosen salt was placed in the reaction vessel and adjusted to the desired pH. The reaction was started by adding 5 ml of a sulphonyl chloride acetone solution (about 1 ml of acetone; final concentration of sulphonyl chloride about $10^{-3}M$).

Acknowledgement.

We thank C.N.R. (Rome) for financial support.

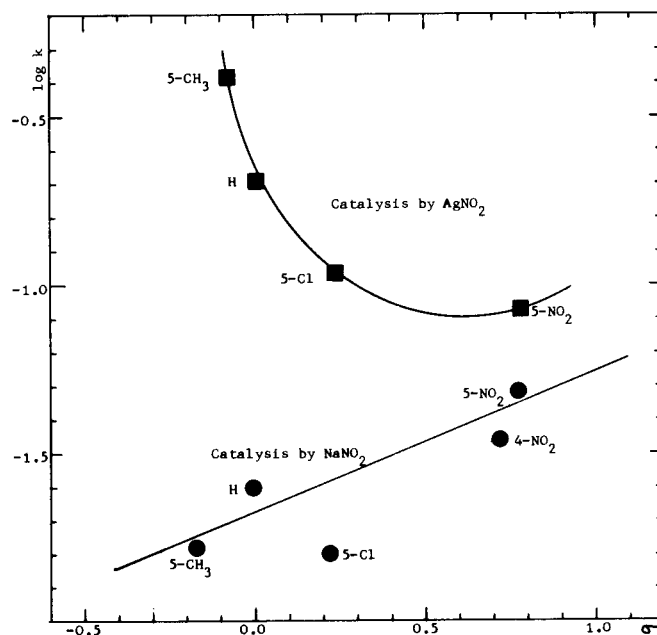


Figure 3. Hammett plots for hydrolysis of substituted thiophene-2-sulphonyl chlorides catalysed by silver nitrite ($k = k_1$) and by sodium nitrite ($k = k_2$) (1).

REFERENCES AND NOTES

- (1) For Part 1, see A. Arcoria, F. P. Ballistreri, G. Musumarra and G. A. Tomaselli, *J. Chem. Soc., Perkin Trans II*, 221 (1981).
- (2) For Part 2, see F. P. Ballistreri, A. Cantone, E. Maccarone, G. A. Tomaselli and M. Tripolone, *ibid.*, 438 (1981).
- (3) N. Kornblum, R. A. Smiley, R. K. Blackwood and D. C. Iffland, *J. Am. Chem. Soc.*, **77**, 6269 (1955).
- (4) G. S. Hammond, M. F. Hawthorne, J. H. Waters and B. M. Graybill, *ibid.*, **82**, 704 (1960).
- (5) For simplicity sake the many water molecules electrostatically associated with t.s. structures are not shown.
- (6) The K_A association constant for silver nitrate is $10^{-0.2}$ in water at 25° for an anionic strength of ca. 0 and $10^{-0.34}$ at $I = 2M$ (7). Using these K_A values one can calculate the range of α values reported above for the concentrations of silver nitrate used in our experiments.
- (7) R. M. Smith and A. E. Martell, "Critical Stability Constants", Vol. 4, "Inorganic Complexes", Plenum Press, New York and London, 1976, p. 47.
- (8) Mercuric ion should be able to act as an electrophilic metal ion similar to silver ion.
- (9) Hydrolysis of Thiophene-2-sulphonyl chloride in the presence of silver chloride (molar ratio with respect to substrate 1:1) gave $k_{obs} = 0.000479$.
- (10) A plot of $\log(k_{obs} - \text{intercept})$ against $\log [AgNO_3]$ afforded a unitary slope.
- (11) G. A. Olah, S. Kobayashi and J. Nishimura, *J. Am. Chem. Soc.*, **95**, 564 (1973).
- (12) A two step addition-elimination leading to a metastable intermediate along the reaction coordinate (1).
- (13) A. Arcoria, F. P. Ballistreri and G. A. Tomaselli, *Tetrahedron*, **34**, 2545 (1978).
- (14) Plotting $\log(k_{obs} - \text{intercept})$ against $\log \alpha [AgNO_3]$ gives the following values (substituent, slope, correlation coefficient): 5-methyl, 2.4, 0.996; 5-H, 2.3, 0.997; 5-chloro, 1.7, 0.995; 5-nitro, 2.0, 0.999.

(15) Calculation of catalytic rate constants, k , by equation 6, after correction for K_A and α values, gave the same outcome, indicating that f values are close to unity in the range of silver nitrite concentrations used.

(16) J. Tummavouri and P. Lume, *Suomen. Kem.*, **B45**, 21 (1972).

(17) E. Maccarone, G. Musumarra and G. A. Tomaselli, *Ann. Chim. (Rome)*, **63**, 861 (1973).

(18) A. Arcoria, E. Maccarone, G. Musumarra and G. A. Tomaselli, *J. Org. Chem.*, **32**, 2457 (1973); *Idem., ibid.*, **39**, 1689 (1974); *Idem., ibid.*, **39**, 3595 (1974).

(19) E. Maccarone, G. Musumarra and G. A. Tomaselli, *J. Chem. Soc., Perkin Trans II*, 906 (1976).

(20) A. Arcoria, V. Librando, E. Maccarone, G. Musumarra and G. A. Tomaselli, *Tetrahedron*, **33**, 105 (1977).