Acylation. Part XXXV.[1] The Silver Ion-catalysed n-Butaminolysis of *S*-Ethyl Thiobenzoate in Aqueous Solutions

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Silver ions catalyse the n-butaminolysis of *S*-ethyl thiobenzoate in aqueous solution. The catalysed reaction involves the ester and the 1:1- and 2:1-complexes, (I) and (II) respectively, of n-butylamine with Ag^+. The rate equation is: $-d[\text{Ester}]/dt = \{k_1[(\text{I})] + k_2[(\text{II})]\}[\text{Ester}]$. At 26 °C the complex (I) is about twice as reactive as complex (II). A path *via* reaction of the ester with free silver ions and free butylamine makes a negligible contribution to the velocity. The mechanism probably involves a cyclic transition state in which the metal ion holds the ester and amine in close juxtaposition.

THE aminolysis of *O*-esters, $R^1CO{\cdot}OR^2$, is not catalysed by metal ions unless the substituent R^1 (or possibly R^2) contains a group which will co-ordinate with the metal.[2] However, this pre-condition does not apply for *S*-esters, $R^1CO{\cdot}SR^2$, whose aminolyses have been shown[3,4] (qualitatively) to be subject to catalysis by various metal ions. The silver ion is one of the most effective. Since the kinetics and mechanisms of these reactions have not been studied in any detail we report here on the n-butaminolysis of *S*-ethyl thiobenzoate catalysed by silver ions. Strictly, these reactions of thiol esters should be termed silver promoted,[2] since the overall process is (1); the silver mercaptan precipitates in aqueous solvents.

$$R^1COSR^2 + Ag^+(H_2O)_2 + R^3NH_2 \longrightarrow R^1CO{\cdot}NHR^3 + R^2SAg + H_3O^+ + H_2O \quad (1)$$

EXPERIMENTAL

Materials.—The sources and purities of the reagents were as previously described.[1] Deoxygenated distilled water was used in making up all solutions.

Kinetic Arrangements.—Owing to the relative insolubility of *S*-ethyl thiobenzoate, reaction mixtures were made up in a 3% (v/v) ethanol–water solvent. All runs were conducted in n-butylamine–perchloric acid buffers at 26 °C and at a constant ionic strength of 0·3M. Sodium perchlorate was used as the inert electrolyte. A volumetric flask containing a given mixture of n-butylamine, perchloric acid, and silver and sodium perchlorates in water was brought to 26 °C and the aminolysis was initiated by the addition of an aliquot portion of a stock solution of the ester in ethanol. Portions of the reaction mixture were withdrawn after appropriate intervals, centrifuged rapidly for 3—4 min, and the supernatant liquid examined spectroscopically at 280 nm where the ester and amide have very different absorptions.[5] The initial ester concentration was *ca.* 10^{-4}M and the n-butylamine and silver ion were always kept in at least a 10-fold excess of ester to promote simple kinetic behaviour. The observed loss of ester was, in fact, an accurately first-order process over at least two half-lives. Our values of k_{obs} under various concentration conditions are in the Table. They were reproducible to within ±4%. The pH of a portion of the reaction mixture was determined at the start and at the end (>10 half-lives) of every run. In no case did the pH alter by >0·05 unit during a run.

The pH values and the total silver ion and butylamine concentrations used, considered in conjunction with the magnitude of the k_{obs} values, show that the concomitant spontaneous and silver ion-promoted hydrolysis[4] and spontaneous butaminolysis[5] of *S*-ethyl thiobenzoate made

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[1] Part XXXIV, D. P. N. Satchell and I. I. Secemski, *J. Chem. Soc.* (*B*), 1970, 1306.

[2] M. L. Bender, in Advances in Chemistry Series No. 37, *Amer. Chem. Soc.*, Washington, 1963; S. Kyrtopoulos and D. P. N. Satchell, unpublished data.

[3] R. Schwyzer, *Helv. Chim. Acta*, 1953, **36**, 414; R. Schwyzer and C. Hürlimann, *ibid.*, 1954, **37**, 155.

[4] T. C. Bruice and S. J. Benkovic, 'Bioorganic Mechanisms,' Benjamin Inc., New York, 1966, vol. 1, ch. 3.

[5] B. Boopsingh and D. P. N. Satchell, to be published.

a mostly negligible contribution to the rate of removal of ester in the present investigation.

Reaction Products.—The effective quantitative formation of n-butyl benzamide under the kinetic conditions was demonstrated spectroscopically, as in our study of the spontaneous butaminolysis.[5] The low solubility of the ester makes preparative scale experiments under concentration conditions which simulate those of the kinetic runs inconvenient. A preparative experiment * using a 10% ethanol–water mixture led to, besides the amide, a sample of the precipitated silver-thiol product. Analysis showed it to be essentially EtSAg.

RESULTS AND DISCUSSION

$$\mathrm{PhCO{\cdot}SEt + Ag^+(H_2O)_2 + BuNH_2 \longrightarrow PhCONHBu + AgSEt + H_3O^+ + H_2O} \quad (2)$$

$$\mathrm{BuNH_2 + Ag^+(H_2O)_2 \rightleftharpoons \underset{(I)}{BuNH_2Ag^+OH_2} + H_2O} \quad (3)$$

$$\mathrm{BuNH_2 + (I) \rightleftharpoons \underset{(II)}{(BuNH_2)_2Ag^+} + H_2O} \quad (4)$$

The overall reaction is (2). n-Butylamine is known[6] to lead to both 1 : 1- and 2 : 1-complexes with the silver ion in aqueous solution, equations (3)—(4). The corresponding equilibrium constants[6] are $2{\cdot}7 \times 10^3$ l mol^{-1} and $11{\cdot}2 \times 10^3$ l mol^{-1} respectively at 25°. The Table gives the results of two series of experiments: (*a*) using a fixed total amine concentration and various total silver concentrations; (*b*) using a fixed total silver concentration and various total amine concentrations. For each reaction mixture the fraction of the Ag^+ existing in the form of each of the complexes (I) and (II) is given in the Table. For series (*a*) the silver ion is mostly present in deficit compared with the available free amine and, except at the highest silver concentrations, the silver exists largely in the form of complex (II). Under these circumstances k_{obs} can be seen to be proportional to [(II)] [equation (5)]. Our average value for $k_2 = 3{\cdot}4$ l mol^{-1} min^{-1}. At the highest silver concentrations not all the silver is complexed by the amine and both complexes (I) and (II) co-exist in comparable amounts. Here the rate is seen to begin to level off (and will fall at sufficiently low pH). Equation (6) with $k_1 = 7{\cdot}5$ l mol^{-1} min^{-1} reproduces all the experimental results reasonably well.

n-Butaminolysis of *S*-ethyl thiobenzoate in 3% v/v ethanol–water at 26° promoted by silver ions

$[\mathrm{Ester}]_{\mathrm{initial}} \simeq 10^{-4}$ M, k_{obs} = observed first-order rate constant (min^{-1}); k_{calc} from equation (6); $BuNH_2$—$HClO_4$ buffers; pK_a for n-$BuNH_2$ taken as 10·77; ionic strength = 0·30 M

(*a*) Constant buffer concentration ($[BuNH_2]_{total}$ = 0·10M)

pH	$10^3[Ag^+]_{total}$	$10^3[(I)]$	$10^3[(II)]$	10^3k_{obs}	10^3k_{calc}
9·85	1·00	~0	~1·00	3·60	3·4
9·62	1·75	~0	~1·75	6·01	6·0
9·60	2·50	~0	~2·50	8·03	8·5
9·40	3·75	0·07	3·68	12·9	12·8
9·03	5·00	0·25	4·70	17·0	16·9
8·45	7·50	1·05	5·65	26·9	26·8
8·42	8·75	1·20	6·65	30·0	31·5
8·16	10·00	2·00	4·40	31·0	30·0
8·00	11·20	2·25	3·60	30·2	29·2

(*b*) Constant silver concentration ($[Ag^+]_{total} = 2{\cdot}5 \times 10^{-3}$M)

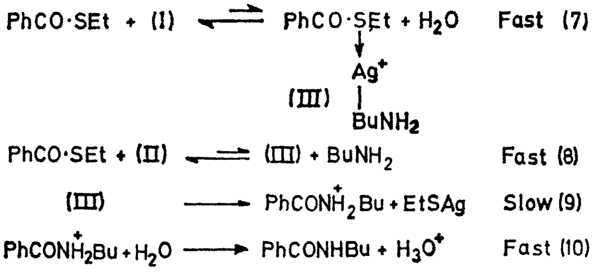
pH	$10^2[BuNH_2]_{total}$	$10^3[(I)]$	$10^3[(II)]$	10^3k_{obs}	10^3k_{calc}
8·70	0·25	0·15	0·05	1·01	1·0
8·72	0·50	0·27	0·13	2·30	2·4
8·75	1·00	0·40	0·60	4·61	5·0
8·78	1·50	0·46	0·85	6·88	6·6
8·80	2·50	0·43	1·40	8·10	8·2
9·17	5·00	0·15	2·28	8·19	8·8
9·45	10·00	~0	~2·50	8·12	8·5
9·45	15·00	~0	~2·50	9·00	8·5
9·50	20·00	~0	~2·50	9·25	8·5
9·50	25·00	~0	~2·50	9·56	8·5

For series (*b*) complexes (I) and (II) co-exist in comparable amounts at the lower butylamine concentrations, and here equation (6) again accounts satisfactorily for the observed variation in k_{obs}. At the highest amine concentrations effectively all the silver is in the form of complex (II) and, on the basis of equation (6), the value of k_{obs} should become constant. This is approximately true. The slight, but real, further increase in k_{obs} in this region, where there exists much free butylamine, can only be due in part (≲30%) to the spontaneous aminolysis of the ester.[5] The remainder is unlikely to be due to a catalysed reaction between the ester, free butylamine, and free silver owing to the extremely small concentration of the latter in this concentration region. The origin of this effect is not understood, but the principal reactions leading to the aminolysis clearly involve complexes (I) and (II), the former having roughly twice the reactivity of the latter.

$$-d[\mathrm{Ester}]/dt = k_2[(\mathrm{II})][\mathrm{Ester}] = k_{obs}[\mathrm{Ester}] \quad (5)$$

$$-d[\mathrm{Ester}]/dt = \{k_1[(\mathrm{I})] + k_2[(\mathrm{II})]\}[\mathrm{Ester}] = k_{obs}[\mathrm{Ester}] \quad (6)$$

Since silver ions do not facilitate the aminolyses of simple *O*-esters it is very probable that their efficacy with thiol esters lies in their great affinity for sulphur. The rapid pre-equilibrium scheme (7)—(10) must, however,



$$\mathrm{PhCO{\cdot}SEt + (I) \rightleftharpoons \underset{(III)\ \ \downarrow Ag^+ - BuNH_2}{PhCO{\cdot}SEt} + H_2O} \qquad \text{Fast (7)}$$

$$\mathrm{PhCO{\cdot}SEt + (II) \rightleftharpoons (III) + BuNH_2} \qquad \text{Fast (8)}$$

$$\mathrm{(III) \longrightarrow PhCO\overset{+}{N}H_2Bu + EtSAg} \qquad \text{Slow (9)}$$

$$\mathrm{PhCO\overset{+}{N}H_2Bu + H_2O \longrightarrow PhCONHBu + H_3O^+} \qquad \text{Fast (10)}$$

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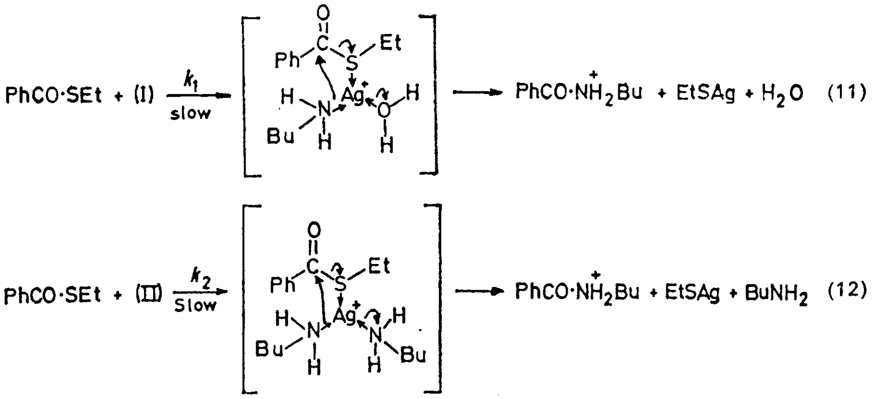
* Performed by Mr. S Kyrtopoulos.

[6] J. Bjerrum, *Chem. Rev.*, 1950, **46**, 381.

be rejected for two reasons. First, the presence of the equilibrium (8) would mean that, at high butylamine concentrations, when all the silver was present as complex (II), further increase in butylamine concentration would be expected to lead to a decrease in rate. This is not observed [series (*b*)]. Secondly, two-coordinate silver is rectilinear [7] and this makes the intramolecular step (9) unattractive on steric grounds. We conceive the reaction as proceeding *via* the synchronous steps (11) and (12), each followed by (10). The transition states for (11) and (12) are likely [7] to involve approximately trigonal arrangements about the silver atom and this will permit the indicated synchronous transfer of electrons. If the polarisation of the ester C–S bond by the silver complex is the dominant factor in determining *k*, it is reasonable to expect complex (I) to be more effective than complex (II), as found.



It appears very unlikely that these silver-promoted reactions proceed *via* carbonyl-addition intermediates of the conventional type. Our suggested mechanism is in line with earlier proposals [3,8,9] in which the essential function of the metal ion is to help to tie two reactants together in close juxtaposition and so effectively to convert an inter- to an intra-molecular substitution.

[2/537 *Received, 7th March,* 1972]

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[7] R. B. Heslop and P. L. Robinson, ' Inorganic Chemistry,' Elsevier Publishing Co., Amsterdam, 1960.

[8] J. I. Hoppé and J. E. Prue, *J. Chem. Soc.*, 1957, 1775.

[9] P. J. Briggs, D. P. N. Satchell, and G. F. White, *J. Chem. Soc.* (*B*), 1970, 1008.