793. *Solvolysis of Unsaturated Sulphides Assisted by Silver Ion.*

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Certain alkenyl alkyl sulphides have been found to undergo solvolysis at 25° in aqueous-ethanolic silver nitrate to give the corresponding isomeric alkenols, a double salt $AgSR,AgNO_3$, and nitric acid. The effects of the structure of the alkyl and alkenyl groups, ionic strength, and concentration of silver ions on the rate, and the observation of allylic rearrangement accompanying solvolysis, suggest that reaction proceeds by way of a sulphide complex containing two atoms of silver which is solvolysed by mechanism S_N1. The apparent requirement of two silver ions co-ordinating to the sulphide-sulphur atom in order to produce a solvolytically reactive intermediate is contrasted with co-ordination of a single proton to oxygen or nitrogen centres in acid-catalysed reactions, and receives a tentative interpretation.

HEAVY-METAL cations that have marked affinities for sulphur can promote fission of bonds between bivalent sulphur groupings (RS·) and a wide variety of electrophilic centres (X). Tarbell and Harnish [1] have noted fission, assisted by silver or mercuric ions, of many organic sulphur compounds RSX, where X is trityl, t-butyl, α-methylbenzyl, benzyl, or a group $R'S{\cdot}CH_2{\cdot}CH_2{\cdot}$, $R'{\cdot}SO_2CH_2{\cdot}CH_2{\cdot}$, $HO_2C{\cdot}CH_2{\cdot}$, EtO·C(:NPh)·, R'·NH·CO·, $(R'S)_2CH{\cdot}$, or R'N:C(NHR')·, R' being an unspecified group. Saville [2,3] has illustrated further examples where X = O:N· or RO·PR(:O)· and the metal ions are Hg^{2+} or Ag^+, respectively.

It has been suggested [1-3] that the above cleavages involve prior complex formation between the sulphide (RSX) sulphur atom and the heavy-metal centre (cf. stable sulphide complexes [4,5]) to afford a quasi-sulphonium entity (I), in which RMS^+ (M = metal) may

$$\mathrm{X{-}\overset{\cdot\cdot}{\underset{\cdot\cdot}{S}}{-}R + M^+ \rightleftharpoons X{-}\overset{+}{S}MR\ (I)} \qquad \text{(i)}$$

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[1] Tarbell and Harnish, *Chem. Rev.*, 1951, **49**, 1.

[2] Saville, *Analyst*, 1958, **83** 670.

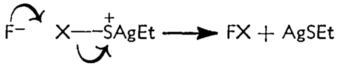
[3] Saville, *J.*, 1961, 4624.

[4] Ahrland, Chatt, Davies, and Williams, *J.*, 1958, 264.

[5] Coates, *J.*, 1951, 2003 (concerning Group VI donor atoms and silver iodide).

be regarded as a potential leaving groups from X, just as in acid-catalysed reactions of oxygen and nitrogen compounds oxonium and ammonium entities are the assumed intermediates. The fate of species (I) will then be determined by factors such as the nature of X and of the solvent and by the nucleophils available in the system.

Using fluoride ion as a nucleophil which does not form a complex with silver ion, the author[3] has shown that bimolecular substitution of the complex (I) [$R = Et, M^+ = Ag^+, X = EtO{\cdot}PEt({:}O){\cdot}$] takes place readily in water:



$$F^- \; X{-}\overset{+}{S}AgEt \longrightarrow FX + AgSEt \qquad \text{(ii)}$$

It seems probable that in the other examples,[1] where X is a carbonyl- or imidoyl-carbon centre, bimolecular substitutions of the corresponding complexes (I) by solvent or available nucleophils will be important. However, where X can exist as a stable carbonium ion the complex (I) can possibly decompose by a S_N1 unimolecular mechanism:

$$X{-}\overset{+}{S}MR \xrightleftharpoons{\text{Slow}} RSM + X^+ \xrightarrow{\text{Fast}} \text{Products}$$

This mechanism is supported by the observation[6] that optically active (α-methylbenzylthio)acetic acid is cleaved by aqueous mercuric chloride (*i.e.*, M^+ probably ^+HgCl; $R = HO_2C{\cdot}CH_2{\cdot}$, $X = {\cdot}CHPhMe$ in XSR) to racemised α-methylbenzyl alcohol, consistently with the intermediate formation of α-methylbenzyl cations (cf. ref. 7).

With the recent availability of a wide range of unsaturated sulphides[8-10] we can now make more informative studies of these metal-ion-assisted cleavage reactions. The present paper deals mainly with the silver ion-assisted solvolysis of alkyl 1,3-dimethylbut-2-enyl sulphides and related compounds in 75% (v/v) aqueous ethanol.

Preliminary work[9] indicated that sulphides containing the 1,3-dimethylbut-2-enyl group undergo quantitative decomposition in an excess of 0·5N-silver nitrate in 75% (v/v) aqueous ethanol during a few hours at room temperature:

$$CMe_2{:}CH{\cdot}CHMe{\cdot}SR + 2AgNO_3 \xrightarrow{H_2O} CMe_2{:}CH{\cdot}CHMe{\cdot}OH \text{ and } CHMe{:}CH{\cdot}CMe_2{\cdot}OH + AgSR,AgNO_3 + HNO_3 \qquad \text{(iii)}$$

where R is a simple alkyl group. This conclusion was based on isolation of the appropriate quantity of the silver double salt, liberation of the theoretical quantity of nitric acid, and formation of the corresponding methylpentenols demonstrated qualitatively by gas-liquid chromatography. The kinetics of such decompositions have now been studied by titration of the liberated acid after addition of pyridine and water to the systems to quench reaction (silver ions co-ordinated to pyridine do not promote sulphide solvolyses). The kinetics of the decomposition are overall of the third order, first order in sulphide concentration and second order in silver-ion concentration at constant ionic strength. The third-order equation

$$k_3t = \frac{2{\cdot}303}{(b - 2a)^2}\log_{10}\frac{a(b - 2x)}{b(a - x)} - \frac{2x}{b(b - 2a)(b - 2x)}$$

(where a and b are initial sulphide and silver-ion concentrations and x is the concentration of acid at time t) was therefore used to correlate results at lower silver-ion concentrations where b was comparable with a. At higher silver levels, first-order kinetics for sulphide decomposition became appropriate. Thus, for comparative purposes, it is convenient to express reactivities in terms of the first-order rate constants, k_1, which are computed either

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[6] Holmberg, *Arkiv Kemi, Min., Geol.*, 1940, **14**, *A*, No. 2; *Chem. Abs.*, 1941, **35**, 4364.
[7] Böhme, *Ber.*, 1938, **71**, 2372.
[8] Saville, *J.*, in the press.
[9] Evans, Higgins, Saville, and Watson, *J.*, in the press.
[10] Cain, Evans, and Lee, *J.*, 1962, 1694.

in the usual way or through the relation $k_1 = k_3b^2$. The results (Table 1) show that methyl substitution in the leaving group increases reactivity only moderately, *i.e.*, about ten times in the sequence R = Me ⟶ Bu^t, although this sensitivity is somewhat dependent on the silver-ion concentration's being considered. Changes in the constitution of the alkenyl group, particularly with regard to methyl substitution at the point of sulphur attachment, markedly affect reactivity (Table 2). Sulphide (VI) reacted almost immeasurably fast and the relative rate given is a conservative estimate.

TABLE 1.

First-order rate constants (k_1) for solvolysis of alkyl 1,3-dimethylbut-2-enyl sulphides in 75% (v/v) aqueous-ethanolic solutions of silver nitrate and sodium nitrate ($[Ag^+]_0 + [Na^+]_0 = 0{\cdot}5$ g.-ion l.$^{-1}$) at 25°. [Sulphide]0 = 0·033M.*

	$10^4 k_1$ (sec.$^{-1}$) for R in $Me_2C{:}CH{\cdot}CHMe{\cdot}SR$ =			
$[Ag^+]0$	Me	Et	Pr^i	Bu^t
0·10	0·160	0·617	1·18	2·13
0·20	0·606	2·67	4·21	6·81
0·30	1·39	5·11	8·30	14·5
0·40	2·01	8·87	13·4	20·9
0·50	2·83	12·7	17·5	26·3

* Suffix " 0 " refers to initial concentrations.

TABLE 2.

Relative rates of solvolysis of some alkenyl isopropyl sulphides in 0·20M-silver nitrate in 75% (v/v) aqueous ethanol at 25°.

Compound (R = Pr^i)	Relative rate	Compound (R = Pr^i)	Relative rate
II $CHEt{:}CMe{\cdot}CH_2{\cdot}SR$	1	V $CHMe{:}CH{\cdot}CMe_2{\cdot}SR$	$2{\cdot}3 \times 10^5$
III $CMe_2{:}CH{\cdot}CH_2{\cdot}SR$	10	VI $CMe_2{:}CH{\cdot}CMe_2{\cdot}SR$	$\not< 2{\cdot}2 \times 10^7$
IV $CMe_2{:}CH{\cdot}CHMe{\cdot}SR$	$1{\cdot}1 \times 10^4$		

These results are consistent with an S_N1 mechanism for alkenyl–sulphur fission with relative rates rather dependent on the opportunities for hyperconjugation within corresponding alkenyl-carbonium ions. They are inconsistent with any overall mechanism in which transfer of silver ions from solvent to the sulphide becomes rate-determining unless the ability of sulphur to co-ordinate with silver ions is, in some unexpected way, affected by the structure of the alkenyl group.

Pertinent also to the concept that an S_N1 process is operative is the fact that compound (V) (Table 2), although decomposing rapidly at first under the stated conditions, begins to become apparently less reactive after about two decomposition half-lives. The unsolvolysed sulphide isolable after this time contains only 13% of (V) and 87% of the iso-allylic counterpart (IV).

Allylic rearrangement during solvolysis is a powerful argument in favour of mechanism S_N1, and in the present case is conveniently explained by postulating that the carbonium ion $Me_2C{=\!=}\overset{+}{C}H{=\!=}CHMe$ exists in intimate contact with an alkyl sulphide entity and that this assembly can either be dismuted by solvent nucleophils or collapse giving controlled proportions of the iso-allylic sulphides (V) and (IV).

It is now of interest to consider how the rates found for alkyl 1,3-dimethylbut-2-enyl sulphides provide information regarding the formation of complexes between silver ions and the sulphide molecules which would be suitably reactive in solvolysis by the inferred S_N1 mechanism. The following results bear on this question: (i) The reactions take place exclusively in homogeneous solution. Thus, addition of the virtually insoluble double salt $AgSR,AgNO_3$ (reaction products from solvolysis) has no noticeable effect on the rates or kinetic form of sulphide decomposition, contrasting with the marked heterogeneous catalysis by silver halides in the solvolysis of alkyl halides in silver nitrate solutions.[11]

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[11] Hughes, Ingold, and Masterman, *J.*, 1937, 1236, and refs. therein.

(ii) The effect of addition of sodium nitrate on the rates of solvolysis of the isopropyl derivative in 0·1M-silver nitrate is to increase k_1, but not in a linear manner: these results (Table 3) are correlated satisfactorily by a plot of $\log_{10}k_1$ against μ (slope = +1·12)

TABLE 3.

Effect of variation of ionic strength (sodium nitrate additions) on rate of solvolysis of 1,3-dimethylbut-2-enyl isopropyl sulphide at 25°. $[\text{Ag}^+]_0 = 0{\cdot}1$.

μ	0·1	0·2	0·3	0·4	0·5
10^4k_1 (sec.$^{-1}$)	0·489	0·667	0·939	1·10	1·18

and are appropriate for a reaction involving interaction of two uni-positively charged entities. (iii) Small additions of nitric acid (up to 0·05M) do not affect the rates. (iv) Appreciable complex formation between silver ions and the alkenyl sulphides is indicated by the ability of aqueous silver nitrate (or perchlorate) to extract these sulphides fairly efficiently from heptane, but it was outside the scope of this work to extend it to the determination of equilibrium constants for stepwise argentation (*i.e.*, co-ordination with silver ions) of the general kind:

$$\begin{tikzcd}
 & & {[(\text{RSR}')_2\text{Ag}]^+} \arrow[r, shift left, "\text{RSR}'"] & {[(\text{RSR}')_3\text{Ag}]^+, \text{ etc.}} \arrow[l, shift left] & \\
\text{RSR}' + \text{Ag}^+ \arrow[r, shift left] & \underset{\text{(VII)}}{[\text{RSR}'{\cdot}\text{Ag}]^+} \arrow[l, shift left] \arrow[ur, shift left, "\text{RSR}'"] \arrow[dr, shift left, "\text{Ag}^+"] & & & \text{. . . . (v)} \\
 & & {[\text{RSR}'{\cdot}2\text{Ag}]^{2+}} \arrow[ul, shift left] \arrow[r, shift left, "\text{Ag}^+"] & {[\text{RSR}'{\cdot}3\text{Ag}]^{3+}, \text{ etc.}} \arrow[l, shift left] &
\end{tikzcd}$$

Evidence for equilibria defined by the upper branch of scheme (v) has been obtained, for soluble aromatic sulphide ligands, by Ahrland, Chatt, Davies, and Williams [4] who, however, did not discuss possible equilibria involving the co-ordination of more than one silver ion with a single sulphide ligand. Presumably the experimental techniques used by these workers would be unable to detect complex formation of the latter kind.

That complexes in which more than one silver ion is co-ordinated to the sulphur atom of organic sulphides are important in the description of the present solvolyses is deduced by considering qualitatively the variation of rate with silver-ion concentration given in Table 1. If one supposes that a monoargentated complex (VII) (*i.e.*, a complex containing one silver atom) is the reactive entity in solvolysis, *i.e.*:

$$\text{Ag}^+ + \text{RSR}' \xrightleftharpoons{\text{Fast}} \underset{\text{(VII)}}{[\text{RSR}'{\cdot}\text{Ag}]^+} \xrightarrow[\text{H}_2\text{O}]{\text{Slow}} \text{ROH} + \text{R}'\text{SAg} + \text{H}^+ \text{ (by S}_\text{N}\text{1)}$$

then the rate of solvolysis could vary with the first power of $[\text{Ag}^+]$. For a highly advanced degree of argentation some fractional-power dependence on $[\text{Ag}^+]$ would obtain, but in no circumstance could rates be proportional to a higher than the first power of $[\text{Ag}^+]$. Table 1 shows the observed rates to be proportional to about the square of $[\text{Ag}^+]$ at low $[\text{Ag}^+]$ though the exponent falls at higher silver levels.

Such a result is qualitatively in accordance with a mechanism * such as:

$$\text{Ag}^+ + \text{RSR}' \rightleftharpoons [\text{RSR}'{\cdot}\text{Ag}]^+ \xrightarrow{k'} \text{Products}$$

$$[\text{RSR}'{\cdot}\text{Ag}]^+ + \text{Ag}^+ \rightleftharpoons [\text{RSR}'{\cdot}2\text{Ag}]^{2+} \xrightarrow{k''} \text{Products}$$

where k' and k'' are first-order constants for decomposition of the appropriate complexes,

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* Although it is possible to show that according to this mechanism the observed first-order constants are related to $[\text{Ag}^+]$ by the equation

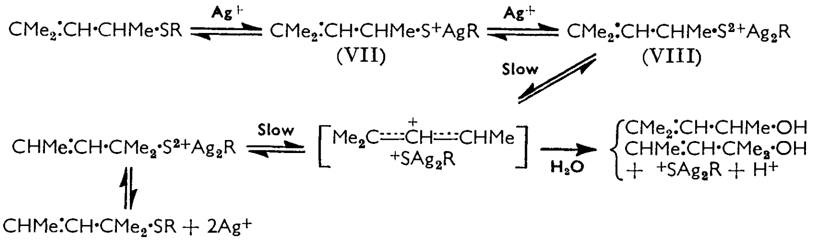
$$k_1 = \{k'K_1[\text{Ag}^+] + k''K_1K_2[\text{Ag}^+]^2\}/\{1 + K_1[\text{Ag}^+] + K_1K_2[\text{Ag}^+]^2\},$$

where K_1 and K_2 are the respective equilibrium constants for mono- and bis-argentation, very accurate data would be required to demonstrate or disprove such a relation convincingly.

and the important condition that $k''[\mathrm{RSR'}\cdot 2\mathrm{Ag}]^{2+} \gg k'[\mathrm{RSR'}\cdot\mathrm{Ag}]^{+}$ which may be derived on the basis of rates given in Table 1.*

However, whatever the intimate details, one cannot escape the conclusion that at least two silver ions are involved in forming the complex responsible for the observed solvolysis. This view is also consistent with the effect of ionic strength on rate (Table 3), if the co-ordination of one positive entity (Ag^+) to another positive entity ($[\mathrm{Ag}\cdot\mathrm{RSR'}]^+$) is a necessary process in formation of a reactive intermediate.

It is believed therefore that the kinetically important processes describing silver ion-assisted solvolysis of the alkenyl sulphides are as in the annexed scheme. Implicit



in this is the suggestion that two silver ions are bound to sulphur in species (VIII). Recent results indicate that silver ions can enter into " poly-argentation " equilibria with single polarisable ligands, *e.g.*, entities such as $\mathrm{Ag_3S^+}$, $\mathrm{AgC{\vdots}CAg,6AgNO_3}$, $\mathrm{Ag_2{}^+I}$, $\mathrm{Ag_3{}^{2+}I}$ have been recognised by a variety of methods.[12] It is now necessary to find a compelling explanation as to why a bis-argentated complex (VIII) rather than a mono-argentated complex (VII) is the intermediate which undergoes solvolysis, whereas in processes catalysed by hydrogen ions it is generally understood that only one proton need be attached to a donor centre (*e.g.*, in esters, ethers, and amides) to produce heterolytically reactive 'onium intermediates.

We suggest that the degree of charge transfer in forming a silver–sulphur bond is small, and hence when one silver ion co-ordinates with a sulphide molecule the sulphur atom carries only a small positive charge. The mono-argentated complex (VII) would then not be especially reactive in solvolysis since the positive charge on sulphur is not abnormally high. By virtue of the relatively undiminished $3p$-electron availability on the sulphur atom of the mono-argentated complex the latter can now reasonably co-ordinate with another silver ion to produce a bis-argentated complex in which the sulphur atom is sufficiently positive to attract the bonding pair of R'–S and lead to a solvolytically reactive intermediate.

If little overall charge transfer occurs in forming a silver–sulphur bond one may be tempted to infer that the bonding involves important d_π-contributions. However, Nyholm[13] does not subscribe to this interpretation and has called attention to the non-existence of stable silver carbonyls, a fact which seems at variance with the participation of silver in strong d_π-bonds. Some other explanation of the obvious strength and low polarity of silver–sulphur bonds therefore seems necessary for satisfactory interpretation of our kinetic results.

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* As a Referee has kindly pointed out, the dependence of rate on silver-ion concentration is also consistent with the possibility that co-ordination of the second silver ion to the sulphide sulphur atom is rate-determining. This situation could obtain in special cases if the decomposition of the bis-argentated complex were very fast compared with the rate of its formation from mono-argentated complex and silver ions. Here, then, is a qualification to be considered with respect to the steps marked " slow " in our mechanistic scheme.

[12] Reuter and Hardel, *Angew. Chem.*, 1960, **72**, 138; Osterlöf, *Acta Cryst.*, 1954, **7**, 637; Leden and Parck, *Acta Chem. Scand.*, 1956, **10**, 535.

[13] Nyholm, personal communication; *Proc. Chem. Soc.*, 1961, 273 (especially p. 284).

EXPERIMENTAL

Materials.—1,3-Dimethylbut-2-enyl ethyl, isopropyl, and t-butyl sulphide have been previously described.[8] The *methyl derivative* was made by methylating the sodium derivative of 4-methylpent-3-ene-2-thiol [8] in ethanol with methyl iodide or, better, methyl toluene-*p*-sulphonate; it had b. p. 53—54°/18 mm., n_D^{20} 1·4778 (Found: C, 64·5; H, 10·6; S, 24·4. $C_7H_{14}S$ requires C, 64·6; H, 10·8; S, 24·6%). 1,1-*Dimethylbut-2-enyl isopropyl sulphide* (97% isomer pure) was prepared by reaction of 1,3-dimethylbut-2-enyl isopropyl disulphide [14] and triphenylphosphine; [15] it had b. p. 62—62·5°/16 mm., n_D^{20} 1·4692 (Found: C, 68·5; H, 11·2; S, 20·3. $C_9H_{18}S$ requires C, 68·4; H, 11·4; S, 20·2%). Other sulphides were available by new general methods.[8-10]

Ethanol, pyridine, and inorganic materials were of " AnalaR " standard.

Reaction of 1,3-*Dimethylbut-2-enyl Isopropyl Sulphide with an Excess of Silver Nitrate.*—To silver nitrate (0·3 mole) in 75% aqueous ethanol (300 ml.) was added the sulphide (0·1 mole), and the mixture was set aside (with occasional shaking) for 6 hr. at room temperature, during which white crystals were deposited. The latter (34·8 g.) were removed, washed with water, dried, and shown to be *disilver isopropyl sulphide nitrate* (0·0986 mole) (Found: C, 10·2; H, 2·2. $AgSC_3H_7,AgNO_3$ requires C, 10·2; H, 2·0%) (it gave propane-2-thiol on dissolution in aqueous sodium cyanide). The initial filtrate and washings were combined, extracted with light petroleum (b. p. 30—40°) (2 × 100 ml.), and titrated with N-sodium hydroxide after addition of pyridine (30 ml.) and phenolphthalein. The alkali consumption (98·9 ml.) represents 98·9% formation of acid, as required by equation (iii). The petroleum extract was distilled through an efficient column; it left a residue (8·4 g.) which was largely a mixture of 4- and 2-methylpent-3-en-2-ol (as shown by qualitative gas–liquid chromatography) with only traces of unchanged sulphide.

Reactions of Other Alkyl 1,3-*Dimethylbut-2-enyl Sulphides with Silver Nitrate.*—These were carried out similarly to the above example but on a smaller scale. In these cases only the total acid production was measured; it was quantitative except in the case of the t-butyl derivative where 1·06 moles of nitric acid appeared per mole of sulphide taken; the high value is due to a silver-ion-assisted solvolysis of the silver butyl sulphide, giving silver sulphide as shown by a blackening of the initially white precipitate. No such complication arose for the methyl and ethyl sulphide which gave white precipitates of the appropriate disilver alkyl sulphide nitrate.

Kinetics of Sulphide Decompositions in 75% *Aqueous-ethanolic* (*v*/*v*) *Solutions of Silver Ions.*—Large volumes of stock solutions of silver nitrate (0·6M) and sodium nitrate (0·6M) in 70% (v/v) aqueous–ethanol were prepared and combined to give various silver concentrations of requisite ionic strength (0·6). By mixing these solutions (25 ml.) with 0·2M-ethanolic sulphide (5 ml.) one obtained, assuming zero volume change on mixing, an initial ionic strength of 0·5, and defined initial sulphide and silver concentrations. These operations were performed in a thermostat-bath at 25°. After suitable times the flasks were removed and solvolyses quenched by addition of 50% (v/v) aqueous pyridine (30 ml.). The nitric acid formed in the given reaction times was then determined by titration with 0·05N-sodium hydroxide (phenolphthalein). Concentrations were calculated and introduced into the appropriate kinetic equations to obtain rate constants.

Other kinetic features were similarly studied after suitable pre-mixing of the initial reactants.

Allylic Rearrangement During Solvolysis of 1,1-*Dimethylbut-2-enyl Isopropyl Sulphide.*—To 75% aqueous-ethanolic 0·2M-silver nitrate–0·3M-sodium nitrate (250 ml.) at 25° was added the above sulphide (0·01 mole, 1·48 g.). After 3 min. (~2 decomposition half-lives) ice–water was added to slow the reaction, the mixture was rapidly filtered, and the filtrate immediately extracted twice with light petroleum (2 × 150 ml.). Removal of the solvent gave a residue (1 g.) which gave peaks due to alcohols and sulphides on gas–liquid chromatograms. Removal of the alcoholic materials from this residue by conventional chromatography on alumina (petroleum elution) gave a new residue (0·28 g.), almost entirely a sulphide mixture, which contained 1,1- (13%) and 1,3-dimethylbut-2-enyl isopropyl sulphide (87%).

Extraction Studies on Sulphide Complexes with Silver Ions.—(i) 0·5M-Ethyl t-butyl sulphide

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[14] Saville, *Proc. Chem. Soc.*, 1962, 18.

[15] Cf. Moore and Trego, *Tetrahedron*, 1962, **18**, 205.

in n-heptane (also 0·2M in n-undecane as internal standard) was shaken with equal volumes of (*a*) aqueous 0·5M-silver perchlorate, and (*b*) aqueous 0·5M-silver nitrate, and the residual sulphide concentration in the organic phase was determined by quantitative gas–liquid chromatography. After treatment (*a*), the sulphide concentration had fallen to 0·06M and after treatment (*b*) it was 0·095M. The degree of extraction was not much affected by adding water (3 volumes) to the silver solutions used above. An excess of ammonia drove back sulphide almost completely from the aqueous into the organic phase. No evidence for reciprocal extraction of silver ions into the organic phase was found on shaking the organic extract with aqueous potassium iodide; hence it may be assumed that entities of the form $\mathrm{Ag(Bu^tSEt)_n{}^+ClO_4{}^-}$ are removed almost exclusively into the aqueous phase. The low solubility of ethyl t-butyl sulphide in water, when considered together with the rather efficient extractions, leaves little doubt that the association constants for complex formation are large.

(ii) Evidence that silver ions also form complexes with alkyl 1,3-dimethylbut-2-enyl sulphides was obtained by shaking 0·1M-solutions of sulphides in heptane (40 ml.) rapidly with aqueous 0·1M-silver nitrate (25 ml.) and quickly removing the aqueous phase before solvolysis could significantly disturb the partition equilibria. Aliquot parts (10 ml.) of the aqueous extract were then added to 0·5M-silver nitrate in 75% aqueous ethanol (30 ml.), and the mixtures were left overnight so that extracted sulphide underwent complete solvolysis.

Measurements of the acid liberated then gave the concentrations of sulphides in the initial aqueous silver nitrate extracts. In this way, one $\mathrm{Ag^+}$ in the aqueous phase was found to be associated with 0·46, 0·35, 0·27, and 0·22 mol. of 1,3-dimethylbut-2-enyl methyl, ethyl, isopropyl, and t-butyl sulphide, respectively. No interpretation of this order of extraction efficiency can be advanced on the above evidence, which merely demonstrates formation of water-soluble sulphide–silver ion complexes.

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