478. *The Reaction between Iodine and Silver Perchlorate.*

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Addition of iodine to silver perchlorate in ether at a low temperature produces a solution containing the complex $AgClO_4,IClO_4$ and precipitates silver iodide. On addition of silver perchlorate to an excess of iodine under the same conditions the same complex is produced, together with the compound $I(ClO_4)_3$. In ethanol at low temperature only iodine monoperchlorate, $IClO_4$, is produced, together with silver iodide.

THE reaction between iodine and silver perchlorate in non-aqueous solvents was first investigated by Gomberg.[1] For solutions in ether he reported the following stoicheiometry, $2AgClO_4 + I_2 = 2AgI + 2ClO_4$, with a total reaction time of 12 hours or more. His results have, however, been disputed.[2-4]

Birckenbach and Goubeau [2] used the same reaction for iodinating aromatic compounds. They suggested a primary reaction, $AgClO_4 + I_2 = AgI + IClO_4$, the iodine perchlorate then attacking the solvent. In ether, after 24 hours, all the iodine had been precipitated as silver iodide and the solution no longer oxidized potassium iodide. They suggested that attack on the ether had taken place, giving, first, ethyl 1-iodoethyl ether (I), then with silver perchlorate the perchlorato-ether (II), and finally with water the 1-hydroxy-ether (hemiacetal) (III):

$$IClO_4 + Et_2O \longrightarrow EtO{\cdot}CHMeI\ (I) + HClO_4$$

$$EtO{\cdot}CHMeI + AgClO_4 \longrightarrow EtO{\cdot}CHMe{\cdot}O{\cdot}ClO_3\ (II) + AgI$$

$$EtO{\cdot}CHMe{\cdot}O{\cdot}ClO_3 + H_2O \longrightarrow EtO{\cdot}CHMe{\cdot}OH\ (III) + HClO_4$$

This was supported by the power of the final solution to reduce silver salts, as hemiacetals are known to do.

For the original reaction in methanol and ethanol they found that the equivalence point, when further addition of iodine produced a permanent colour, depended on the temperature. They quoted the figures in Table 1.

TABLE 1.

Equivalence point in the reaction of iodine and silver perchlorate in ethanol, after Birckenbach and Goubeau.[2]

Temperature	20°	0°	−80°
Ratio, $2AgClO_4 : nI_2$	1·24	1·54	1·98

Haszeldine and Sharpe [4] showed that, shortly after iodine had been added to an ethereal solution of silver perchlorate, addition of potassium iodide solution would release as much iodine as had been added originally, which is consistent with:

$$I_2 + AgClO_4 = AgI + IClO_4$$

$$IClO_4 + KI = I_2 + KClO_4$$

But the oxidizing power decreased rapidly with time, and further silver iodide was precipitated. Finally, when no oxidizing power remained, a total of 2 moles of silver iodide had been formed for each mole of iodine $[I_2]$ added.

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[1] Gomberg, *J. Amer. Chem. Soc.*, 1923, **45**, 398.

[2] Birckenbach and Goubeau, *Ber.*, 1932, **65**, 395.

[3] Gomberg and Gamrath, *Trans. Faraday Soc.*, 1934, **30**, 24; Goodeve, *Trans. Faraday Soc.*, 1934, **30**, 30; Schmeisser, *Angew. Chem.*, 1953, **65**, 324.

[4] Haszeldine and Sharpe, *J.*, 1952, 993.

Carlsohn [5] studied the reaction in pyridine and in the presence of pyridine. He obtained iodine dipyridine perchlorate and silver iodide:

$$AgClO_4 + I_2 + 2Py = IPy_2ClO_4 + AgI \quad (Py = pyridine)$$

It is clear that previous workers have been handicapped by attack on the solvent. In an attempt to avoid this the present work was carried out at −85°.

The various solvents can be divided into three groups. In nitrobenzene, carbon disulphide and, from Gomberg's work,[1] cyclohexane and carbon tetrachloride no reaction occurs between iodine and silver perchlorate. Those in which reaction occurs but is followed by too rapid attack on the solvent for quantitative study are acetone, acetonitrile, and dimethylformamide, and, according to Gomberg, benzene, heptane, and chlorobenzene (he also found that bromobenzene, ethylene dichloride, and ethylene dibromide reacted with silver perchlorate). In ethanol, ether, and, according to Carlsohn,[5] pyridine, reaction occurs but is not immediately followed by attack on the solvent.

In these three solvents addition of potassium iodide solution immediately after reaction has occurred liberates an amount of iodine equal to that originally added. In the present work the equivalence point of the reaction has been investigated, conductometrically and visually, for ether and ethanol, and the amounts of silver iodide precipitated have been measured.

The end-points of the low-temperature titrations in ether and ethanol, and the amounts of silver iodide precipitated, are shown in Table 2. In ethanol, and in 1 : 9 ethanol–ether, conductometric titrations between silver perchlorate and iodine were unsuccessful as the change in conductivity was insufficient to permit an end-point to be detected.

TABLE 2.

End-points and amounts of silver iodide precipitated in the reaction of silver perchlorate with iodine (at −85°).

Order of addition	End-point, $2AgClO_4 : nI_2$ Conductometric	Visual	Silver iodide precipitated
		In ethanol	
Either	Impossible	$n = 2$	The amount is as expected for $AgClO_4 + I_2 = AgI + IClO_4$
		In ether	
I_2 to $AgClO_4$	$n = 1$ (Fig. 1)	$n = 1$	When $I_2 : AgClO_4$ is less than 2 : 1, the amount of silver iodide is as expected for $2AgClO_4 + I_2 = AgI + AgClO_4,IClO_4$; when the ratio is more than 2 : 1, the amount of precipitate is less than expected.
$AgClO_4$ to I_2	$n = 2{\cdot}32, 2{\cdot}84, 4{\cdot}28$ (Fig. 2)	Colour not discharged	At $3AgClO_4 : 2I_2$ the amount is more than is expected from the equation above; at $2AgClO_4 : I_2$ it is less.
		10% *Ethanol in ether*	
I_2 to $AgClO_4$	Impossible	$n = 1{\cdot}7$	Not measured.

In ethanol at −85° the results are consistent with the reaction

$$I_2 + AgClO_4 = AgI + IClO_4 \quad \text{. . . . .} \quad (1)$$

The visual end-point, the amount of silver iodide precipitated, and the amount of oxidizing power retained agree with the stoicheiometry of this equation. This appears to be the fundamental reaction in any solvent, but it can only take place in solvents which can co-ordinate with, or are sensitive to electrophilic attack by, the I^+ cation. Thus there is no reaction in nitrobenzene or carbon disulphide.

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[5] Carlsohn, "Über eine neue Klasse von Verbindungen des positiv einvertigen Iods," Verlag Hirsel, Leipzig, 1932.

The results in ethereal solution for the titration of iodine into silver perchlorate are explained by the formation of the complex $AgClO_4,IClO_4$. The reaction then becomes

$$2AgClO_4 + I_2 = AgI + AgClO_4,IClO_4$$

the conductometric and visual end-points occur at a 2 : 1 ratio of $AgClO_4 : I_2$. The amount of silver iodide precipitated at this point and the oxidizing power retained by the solution also agree with this stoicheiometry. Addition of further iodine merely decreases the amount of solid silver iodide present, the silver iodide dissolving in the iodine, presumably as AgI_3. Addition of ethanol to such a solution in ether produces a further precipitate of silver iodide, and provided that the solution has an $AgClO_4 : I_2$ ratio of less than 1 : 1, removes the colour, oxidizing power still being retained. The stoicheiometry has returned to that of equation (1). Addition of pyridine to the ethereal solution gives a precipitate of iodine dipyridine perchlorate. These experiments show that the $AgClO_4,IClO_4$ complex, once formed, is stable to iodine in ether though it is decomposed if the dielectric constant of the solution is increased or if strong co-ordinating agents are added. The $AgClO_4,IClO_4$ complex, though very much less stable, is similar, in formulation and presumably in structure, to the complex $CF_3{\cdot}CO_2Ag,CF_3{\cdot}CO_2I$ found by Haszeldine and Sharpe[4] in their study of the reaction between iodine and silver trifluoroacetate and to the complexes $R{\cdot}CO_2Ag,R{\cdot}CO_2I$ formed during the reactions of iodine with the silver salts of monocarboxylic acids.[6]

The results of Birckenbach and Goubeau[2] for ethanol can now be interpreted in terms of partial formation of the complex $AgClO_4,IClO_4$ at room temperature (equivalence point $2AgClO_4 : 1{\cdot}24I_2$). The gradual change in reaction ratio with temperature, coupled with the partial change in 1 : 9 ethanol–ether, indicates that the major cause is the change in dielectric constant of the solvent. (The dielectric constant of ether at $-85°$ is 7, of ethanol at $-80°$ is 45, and of ethanol at $+20°$ is 11.) Differences in co-ordinating power may also be partly responsible; certainly iodine perchlorate is co-ordinated by the solvents. Attempts to discover how many moles are co-ordinated per mole of iodine perchlorate by adding ethanol or ether to iodine and silver perchlorate in equivalent quantities in nitrobenzene were unsuccessful. Although reaction occurred, the amounts of ethanol and ether needed were much more than stoicheiometric, more than 100 moles per mole causing incomplete reaction. This contrasts with the addition of pyridine to the nitrobenzene solution, when reaction occurred with equivalent quantities:

$$I_2 + AgClO_4 + 2Py = IPy_2ClO_4 + AgI$$

When silver perchlorate is added slowly to iodine in ether the results obtained are markedly different. The colour becomes lemon-yellow and lighter, but is not discharged. (If the addition is rapid the colour can be discharged.) The conductometric end-points, though sharp, appear to be variable, depending on the concentrations and on the rate of addition of silver perchlorate. They do not correspond to any fixed stoicheiometry. Oxidizing power is still retained. These results can be explained as follows:

When addition of silver perchlorate starts, the iodine is in great excess, and the reaction (1) (above) first occurs. There will then be two competing reactions as more silver perchlorate is added:

$$AgClO_4 + IClO_4 = AgClO_4,IClO_4 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

and the original reaction (1). We have shown that in ether the complex $AgClO_4,IClO_4$ does not react with iodine. However, it may react with iodine perchlorate:

$$AgClO_4,IClO_4 + IClO_4 = AgI + I(ClO_4)_3 \quad . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

giving an overall stoicheiometry for the formation of iodine triperchlorate of:

$$3AgClO_4 + 2I_2 = 3AgI + I(ClO_4)_3$$

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[6] Simonini, *Monatsh.*, 1893, **14**, 81; Hershberg, *Helv. Chim. Acta*, 1934, **17**, 351; Prévost, "Atti X° congr. intern. chim.," 1939, Vol. III, p. 318; Wieland and Fischer, *Annalen*, 1926, **446**, 49.

As reaction proceeds, iodine is used up and reaction (2) predominates over reaction (1). The overall result will be formation of both iodine triperchlorate and the complex $AgClO_4,IClO_4$, the amounts of each depending on the exact conditions. The weight of silver iodide precipitated will depend on how much of each is formed. At a ratio $3AgClO : 2I_2$ the extreme possibilities are

$$3AgClO_4 + 2I_2 = 3AgI + I(ClO_4)_3$$

and

$$3AgClO_4 + 2I_2 = 1{\cdot}5AgI + 1{\cdot}5AgClO_4,IClO_4 + 0{\cdot}5I_2$$

In the latter case some of the silver iodide dissolves as tri-iodide. Two results were: $3AgClO_4$ gave $2{\cdot}0AgI$ and $2{\cdot}6AgI$. At a ratio $2AgClO_4 : I_2$ the extreme possibilities are

$$2AgClO_4 + I_2 = 1{\cdot}5AgI + 0{\cdot}5I(ClO_4)_3 + 0{\cdot}5AgClO_4$$

and

$$2AgClO_4 + I_2 = AgI + AgClO_4,IClO_4$$

In the former case some of the silver iodide redissolves in the silver perchlorate as Ag_2I^+,Ag_3I^{2+}.[7] One result was that $2AgClO_4$ gave $0{\cdot}59AgI$.

Anhydrous iodine triperchlorate had been reported as greenish-yellow,[8] and recently iodine trinitrate has been prepared and shown to be yellow.[9] This accounts for the colour of the solution. Reactions similar to (3) must occur in the formation of iodine tricarboxylates from complexes of the type $R{\cdot}CO_2Ag,R{\cdot}CO_2I$, where the overall reaction $3R{\cdot}CO_2Ag + 2I_2 = 3AgI + (R{\cdot}CO_2)_3I$ has been shown to occur under favourable conditions.[10]

EXPERIMENTAL

Materials.—These were purified by normal means, when necessary, and rigorously dried: silver salts by heating them under a vacuum over phosphorus pentoxide; ether over sodium; ethanol by passage down a column of a molecular sieve (B.D.H. Type 4A); nitrobenzene over barium oxide or a molecular sieve; acetone over calcium sulphate; other solvents over a molecular sieve. All solutions were made up, and as many as possible of the manipulations were carried out, in a dry box. All the conductometric and gravimetric work was carried out at −85° (acetone–carbon dioxide). Conductivities were measured with a Philips type 9500 conductivity bridge.

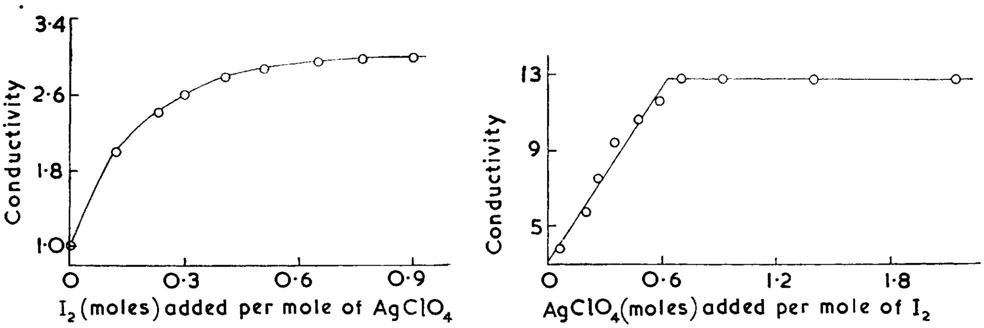

FIG. 1. FIG. 2.

Conductometric titration of (Fig. 1) iodine into silver perchlorate in ether, and (Fig. 2) silver perchlorate into iodine in ether (conductivity in arbitrary units).

Titration End-points.—Running iodine into silver perchlorate in ether did not give sharp end-points. The curves levelled off between $2AgClO_4 : 1{\cdot}0I_2$ and $2AgClO_4 : 1{\cdot}2I_2$, as shown if Fig. 1. Running silver perchlorate into iodine in ether gave much sharper end-points. Here,

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[7] Dallinga and Maekor, Proc. Internat. Conf. Co-ordination Chemistry, 1955, p. 276; Kratohvil and Težak, *ibid.*, p. 250; Lieser, *Z. anorg. Chem.*, 1957, **292**, 97; 1960, **304**, 296; 1960, **305**, 133.

[8] Fichter and Kappeler, *Z. anorg. Chem.*, 1915, **91**, 134.

[9] Schmeisser and Brändle, *Z. angew. Chem.*, 1957, **69**, 781.

[10] Oldham and Ubbelohde, *J.*, 1941, 368.

however, the position of the end-point was variable. A typical conductometric curve is shown in Fig. 2, and a series of results for these titrations recorded in Table 3.

TABLE 3.

End-points for titration of silver perchlorate into iodine in ether.

Mol. ratio at cond. end-point; n in $AgClO_4 : nI_2$	Ml. of $AgClO_4$ soln. added to 10 ml. of I_2 soln.	Original concn. (mg./10 ml.)		Mmoles at end-point	
		$AgClO_4$	I_2	$AgClO_4$	I_2
1·16	3·2	50·6	23·1	7·8	9·1
1·61	2·3	51·4	22·8	5·6	9·0
2·14	3·7	25·2	25·1	4·6	9·86

Oxidizing Power.—This was measured by adding the solution produced by mixing iodine and silver perchlorate to 10% aqueous potassium iodide and titrating the iodine with thiosulphate. In a typical experiment the total amount of iodine added was 0·0246 g. and estimation gave 0·025 g. It was very difficult to obtain repeatable results because loss of oxidizing power, accompanied by further precipitation of silver iodide, occurred rather rapidly (appreciably in 10 min.). This may have been partly due to local warming up of the solution when a second uncooled solution was run into it, even though this was done slowly. Similarly addition of ethanol often caused some loss of oxidizing power.

Precipitate Weights.—Some typical results are listed in Table 4.

TABLE 4.

Precipitate weights (in grams and, in parentheses, millimoles).

	I_2	$AgClO_4$	AgI
In ether			
Adding I_2 to $AgClO_4$	0·228 (0·90)	0·0369 (1·96)	0·0217 (0·92)
	0·0924 (0·37)	0·0514 (0·25)	0·0030 (0·013). and on addition of ethanol a further 0·0559 (0·24)
Adding $AgClO_4$ to I_2	0·0285 (0·11)	0·045 (0·22)	0·015 (0·065)
	0·0258 (0·102)	0·0316 (0·153)	0·0304 (0·0130)
	0·0188 (0·074)	0·0231 (0·113)	0·0130 (0·0721)
In ethanol			
Adding I_2 to $AgClO_4$	0·6949 (2·74)	0·2869 (1·38)	0·3108 (1·38)

The presence of iodine perchlorate in the ethereal solutions was confirmed by adding pyridine to them. This gave a precipitate shown to be iodine dipyridine perchlorate by its infrared absorption spectrum (measured on a Perkin–Elmer Infracord spectrophotometer) and by its giving iodine from potassium iodide solution. Though pure iodine dipyridine perchlorate is colourless, this sample was yellow because the pyridine caused co-precipitation of silver iodide.

The solubility of silver iodide in iodine was independently demonstrated by adding iodine to an excess of silver perchlorate in ether, filtering the mixture through sintered glass, and washing the precipitate with ether several times (the precipitate being kept continuously moist), and then washing it with a solution of iodine in ether. This gave a clear solution, which on addition of ethanol deposited silver iodide.

Visual End-points.—When iodine was added to silver perchlorate in ether, the first persistence of colour could be readily detected and occurred at a ratio of $2AgClO_4 : I_2$. On addition of silver perchlorate into iodine, if the total addition was performed in 5—10 min., the colour generally disappeared at about the ratio $2AgClO_4 : I_2$ (partly obscured by the precipitate formed). If the addition was carried out slowly, over about an hour, the colour persisted to at least the ratio $4AgClO_4 : I_2$. Attempts to study the absorption spectra of these yellow solutions failed, as they decomposed on warming to room temperature.

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