Mechanism of Electrophilic Substitution at a Saturated Carbon Atom. Part XI.¹ Bimolecular and Unimolecular Substitution of Mercury for Gold in Alkylgold Complexes

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Reactions in which gold, bound to methyl, ethyl, and 1-cyano-1-ethoxycarbonylpentyl groups in their triphenylphosphinegold(I) derivatives, is displaced therefrom by entering mercury from mercuric or alkylmercuric halides, acetates, or nitrates have been examined kinetically in dioxan, acetone, dimethylformamide, and dimethyl sulphoxide solvents. Most of the mercury-for-gold substitutions are second-order processes, and, where this is so, the effect on rate of changes of the anion in the mercurial, and also the kinetic effect of added salts, make clear that the bimolecular electrophilic mechanism of substitution, $S_{\rm E}2$, is under observation. However, the reactions in which gold from the cyano(ethoxycarbonyl)pentylgold complex is replaced by mercury in solvents containing dimethyl sulphoxide are kinetically of first order in the gold complex, and zeroth order in the mercurial. They illustrate the unimolecular electrophilic mechanism, $S_{\rm E}1$. In this mechanism all mercurials react at the same rate, which is the rate of formation of a carbanion by heterolysis of the carbon–gold bond. The reaction between mercuric bromide and one gold(III) complex, *viz*. trimethyl(triphenylphosphine)gold(III), has been examined. In dioxan and acetone as solvents, the gold is displaced from one methyl group only, to be replaced by mercury in an $S_{\rm E}2$ process.

Most of our knowledge of the mechanisms of electrophilic metal-for-metal substitution at saturated carbon derives from studies of the replacement of mercury. Other replaceable Group B metals, and also, as M. D. Johnson and others have shown, a number of transition metals, show parts of the same mechanistic pattern. The subject of electrophilic, metal-for-metal substitutions at saturated carbon is here extended in the field of Group B metals to the replacement of gold(I).

In contrast to mercury(II), which takes up two alkyl ligands with linear hybridisation, gold(I), because of its fewer valency electrons, needs first a donor ligand, but can then take up, presumably with linear hybridisation, a single alkyl ligand. The field of suitable donor ligands is restricted. They must be not only co-ordinative electron donors but also, it seems, conjugative electron acceptors, possibly in order to withdraw the 5*d* electron shell from around the new alkyl bond. Whatever the

¹ Part X, J. R. Coad and C. K. Ingold, J. Chem. Soc. (B), 1968, 1455.

detailed requirements may be, Coates and his co-workers observed that tertiary phosphines fulfil them.² We used triphenylphosphine as our donor ligand throughout this work. Our simple and substituted alkyl groups all carried the gold which was to be replaced in the form of the substituent \cdot AuPPh₃ in the gold(1) complexes, and \cdot AuMe₂PPh₃ in the single gold(11) complex studied.

We found that, whilst methyl- and ethyl-gold(I) derivatives of the above type could readily be prepared and employed in kinetic investigations, the analogous secondary and tertiary alkylgold(I) derivatives were insufficiently stable. The simplest asymmetric derivative, the s-butyl-gold(I) compound could be prepared, but even that could not be kept long enough for kinetic study. However, J. Lewis and his co-workers had shown that stable compounds with the same gold side-chain could be obtained from secondary alkyl structures furnished

² C. Calvin, G. E. Coates, and P. S. Dixon, *Chem. and Ind.*, 1959, 1628; G. E. Coates and C. Parkin, *J. Chem. Soc.*, 1962, 3220. with electronegative substituents, as in the diacetylmethyl group.³ We have examined the gold(I) compounds of this group, and the analogous cyano(ethoxycarbonyl)methyl group. They are conveniently stable, and Lewis's method of inducing stability is evidently a general one. We extended it to the production of stable gold(I) derivatives of substituted tertiary alkyl structures. We prepared the 1,1-diethoxycarbonylpentyl, and 1-cyano-1-ethoxycarbonylpentyl derivatives. They also are quite stable. We were particularly interested in asymmetric molecules, looking to the time when we shall want such for stereochemical purposes.

The gold compounds mentioned here are all described in the Experimental section, but only three gold(I) compounds, *viz.* methyl-, ethyl-, and 1-cyano-1-ethoxycarbonylpentyl-(triphenylphosphine)gold(I), MeAuPPh₃, EtAuPPh₃, and n-BuC(CN)(CO₂Et)AuPPh₃, and one gold(III) compound, trimethyl(triphenylphosphine)gold-(III), Me₃AuPPh₃, were chosen for our kinetic studies of gold replacement.

In this first investigation of electrophilic gold replacement, the substituting agents were mercuric salts HgX_2 , and methylmercuric salts MeHgX, with X = Cl, Br, I, OAc, or NO₃, in both series. We chose mercury electrophiles, because experience of mercury exchange had shown that, on varying the ionicity of the salts by changing their anions, we could learn something of the polarity of the substitution.

The solvents used were dioxan, dioxan-acetic acid, aqueous dioxan, acetone, dimethylformamide, dimethyl sulphoxide, and dimethyl sulphoxide-dioxan mixtures.

The stoicheiometry of the substitution by mercuric salts in gold(I) complexes can be represented by the equation

$$R-AuPPh_3 + HgX_2 \longrightarrow R-HgX + XAuPPh_3$$

provided that the initial gold complex is not in excess. If it is in excess, then this reaction is succeeded by a slower one between the initial gold compound and the first mercury product:

 $R-AuPPh_3 + RHgX \longrightarrow R-HgR + XAuPPh_3$

This reaction was studied separately with greater convenience by taking alkylmercuric salts as initial reactants. The stoicheiometry of substitution in the gold(III) complex is set down in section 7.

The progress of substitution was followed by two methods, called in Tables and elsewhere the 'direct' method (D) and the 'partition' method (P). The direct method involved measurement of the change of absorbance at 275—300 mµ in a solution reacting in the thermostatted cell-holder of a spectrophotometer. The 'partition' methods required the partitioning of aliquot portions of the reaction solution between carbon tetrachloride and aqueous potassium iodide. The unchanged mercuric salt was thus converted into tetraiodomercurate ion, the abundance of which was measured spectrally at 323 mµ. Where these two methods were checked against each other they agreed. The 'partition' method is not applicable to reactions of alkylmercuric salts, because such salts do not complex with halide ions in the conditions.

RESULTS AND DISCUSSION

1. The $S_{E}2$ Mechanism of Substitution of Mercury from Mercuric Salts for Gold in Methyl(triphenylphosphine)gold(I).—Our first kinetic studies were of the displacement of gold from methyl(triphenylphosphine)gold(I) by entering mercury provided as mercuric iodide, bromide, chloride, and acetate, in a number of solvents. The reactions of the three halides were examined in dioxan. The reaction of the acetate required the presence of some acetic acid in the solvent in order to avoid the precipitation of mercuric oxide. For this substitution we employed a solvent mixture of dioxan with acetic acid (19:1 v/v); and in order to obtain some assessment of the purely kinetic effect of the acetic acid, we applied the same solvent mixture to the reaction of mercuric bromide. In order to assess the kinetic effect of water as a co-solvent, we examined the reaction of mercuric bromide in mixtures (9:1 and 8:2 v/v) of dioxan with water. As to other solvents, we studied the reactions of mercuric bromide and mercuric chloride in acetone, and that of mercuric bromide in dimethylformamide.

In all these conditions the reactions were kinetically of second order, *i.e.* first order with respect to each reactant. This was shown by the course of the runs, which were all followed to at least 75% of complete reaction, and gave good second-order constants. Moreover, the rate-constants, thus determined for any one substituting agent, solvent, and temperature, remained the same over independent variations in the initial concentrations of the reactants, as shown in Table 1.

The reaction of mercuric bromide with the methylgold complex was briefly surveyed in one other solvent, viz. dimethyl sulphoxide. However, this attempt was foiled, because a reaction of measurable rate occurred between the mercuric salt and the solvent. It ran extensively for some hours at 25°, and was still going slowly after 1 day. It was marked by a change of u.v. absorption spectrum, and a strong increase in electrical conductance: apparently it was some form of ionisation. We measured the rate of reaction of methyl(triphenylphosphine)gold with solutions of mercuric bromide in dimethyl sulphoxide which had been ' matured ' at 24.7° for 24 hr., when the ion-forming process appeared to be nearing its equilibrium. The rates fell off with continuing time faster than required by a second-order law calculated on stoicheiometric concentrations of the We obtained initial second-order rate conreactants. stants which seemed approximately independent of the initial stoicheiometric concentrations of the reactants. but do not record them because they cannot have any simple significance, except to show that both the gold complex and the mercurial are involved in rate control.

The mean values of the rate constants in Table 1 are ³ D. Gibson, D. F. Johnson, J. Lewis, and C. Oldham, *Chem. and Ind.*, 1966, 342.

assembled in Table 2. One of the probes on which we have relied in the past in order to distinguish between $S_{\rm E}$ 2- and $S_{\rm E}$ i-type substitutions, which both require second-order kinetics, is that of the variation of sub $stitution {\it rate} with increasing ionicity of substituting agents$

TABLE 1

Rates of reaction of mercuric salts with methyl-(triphenylphosphine)gold(I)

			- ,0 ()	
Substi-				
tuting	[]	IeAuPPh_]	. [HøX.].	k.
agent	Method (1	0^{-4} mole/l	$(10^{-4} \text{ mole}/1)$	(sec -1 molo-11)
agent	method (1	io more/i.,	(10 mole/1.)	(sec mole - 1.)
In dioxa	an at 24.7°			
HgI.	D	1.00	1.0	156
Hol.	-	0.50	0.50	157
Hal	,,	0.50	0.50	140
LIGI2	,,	0.50	0.50	140
	,,	0.30	0.90	153
Hg12	,,	0.25	0.25	158
Hgl ₂	,,	0.10	0.10	167
HgI ₂	,,	0.20	1.00	144
HgI,	,,	0.50	0.25	170
HgI,		1.00	0.50	169
Hel		0.25	0.20	163
Høl		0.25	0.10	164
HaBr	p	0.25	0.95	1954
UaBr	1	0.50	0.50	100 -
IIgDi ₂	,,	0.50	0.00	130
HgDr ₂	,,	0.50	0.25	160
HgBr ₂	"	0.25	0.50	130
$HgBr_2$	D	1.00	1.00	167
$HgBr_2$,,	0.71	0.71	153
HgBr,	,,	0.20	0.50	157
HgBr.		0.50	0.20	138
HøBr.	,,	0.50	0.50	139
HaBr	,,	0.40	0.40	140 6
$\mathbf{U}_{\alpha}\mathbf{D}_{\alpha}$,,	0.90	0.49	159
IIgDI ₂	,,	0.30	0.42	100
HgBr ₂	,,	0.25	0.21	138
HgBr ₂	,,	0.50	0.33	139
HgBr ₂	,,	1.00	0.50	140
$HgBr_2$,,	0.33	0.50	141
HgBr,	,,	0.16	0.50	130
HğBr.		0.16	1.00	144
HøBr		0.71	1.00	136
HoCL	,,	1.00	1.00	72
Haci	,,	0.50	0.50	78
$U_{\alpha}C^{1}$,,	0.95	0.95	70
ngCl ₂	,,	0.20	0.20	12
HgCl ₂	,,	0.50	2.30	11
HgCl ₂		0.50	1.00	71
HgCl ₂	,,	0.50	0.25	80
HgCl ₂	,,	1.00	0.50	72
HgCl,	,,	0.10	0.50	70
HgCl		1.00	2.50	68
- 0 - 2				
In dioxa	n-acetic aci	id $(19:1 v)$	(v) at 24.7°	
HoBr	D	0.50	0.50	147
UgBr	D	0.95	0.25	149
$11gD1_2$,,	0.20	0.20	140
Hgbr ₂	.,,	0.30	0.20	109
HgBr ₂	,,	0.25	0.50	155
$Hg(OAc)_2$,,	0.020	0.020	ca. 3800
$Hg(OAc)_2$,,	0.020	0.020	ca. 4900
Hg(OAc) ₂	,,	0.020	0.020	ca. 4400
Hg(OAc).		0.025	0.025	ca. 5100
HglOAch		0.025	0.025	ca. 4500
Hg(OAc).		0.050	0.025	ca 4200
116(0110/2	,,	0 000	0 020	<i>tu</i> . 12 00
In dioxa	n-water (9	1 v/v at	24.7°	
U ~D.	D	0.50	0.50	440
Igdi_2	r	0.00	0.00	440
HgBr ₂	,,	0.25	0.25	400
HgBr ₂	,,	0.10	0.10	420
HgBr₂	,,	0.25	0.10	410
$HgBr_2$,,	0.10	0.25	430
		-		
In dioxa	n-water (4	: 1 v/v) at .	24·7°	
HgBr.	Р	0.30	0.30	770
HğBr.		0.10	0.10	780
HøBr-	,,	0.080	0.060	680
HoBr	,,	0.060	0.10	740
HaBr	,,	0.30	0.10	600
15012	,,	0.00	0.10	000

	TABLE 1 (0	Continued)	
Method	$[MeAuPPh_3]_0 (10^{-4} mole/l.)$	$[HgX_{2}]_{0}$ (10 ⁻⁴ mole/l.)	k_2 (sec. ⁻¹ mole ⁻¹ l.)
ne at 0.0°	0.005	0.005	1050

HgBr_2	\mathbf{P}	0.085	0.085	1370
$HgBr_2$,,	0.050	0.050	1250
HgBr ₂		0.085	0.035	1340
HgBr ₂		0.035	0.085	1300
HgCl,		0.10	0.10	1100
HgCl,		0.085	0.085	1170
HgCl,		0.050	0.050	1130
HgCl,		0.050	0.010	1060
HgCl ₂	,,	0.10	0.050	1140
In din	nethylforma	mide at 24.7	0	
HgBr,	\mathbf{P}	0.25	0.25	190
HgBr,		0.10	0.10	180
HgBr,		0.050	0.050	190
HgBr,		0.050	0.050	200
HgBr,		0.050	0.10	200
HgBr,		0.10	0.25	230
HgBr ₂	,,	0.10	0.050	190
	^a Details in	n Table 20.	^b Details in Tab	ole 19.

Substituting

agent

In acetone

giving a common cation.⁴ Along a series of electrophilic substituting agents, such as $HgHal_2 < Hg(OAc)_2 <$ $Hg(NO_3)_2$, the rate of an S_E2 process should rise sharply, and the rate of an $S_{\rm E}$ i process should fall sharply. As in relations between rate and structure generally, it is only the large changes of rate that have a clear significance: small changes, e.g. by a factor of two, can be created or distorted by many small but complicated kinetic effects. In the figures in Table 2, we have a clear answer to the mechanistic question: the much greater rate of substitution by mercuric acetate than by any of the mercuric halides points to the $S_{\rm E}2$ mechanism, and is definitely inconsistent with an $S_{\rm E}$ i process. The reaction of mercuric acetate was almost as fast as we could follow in the dioxan solvent used, which was the slowest of our solvents; and the small amount of acetic acid which had been added cannot be held responsible for this result, as is shown by the comparison experiment with mercuric bromide.

TABLE 2

Mean second-order rate constants (sec.⁻¹ mole.⁻¹ l.) of reactions of mercuric salts with methyl(triphenylphosphine)gold(1)

Solvents	HgI_2	$HgBr_2$	HgCl ₂	Hg(OAc) ₂
Dioxan ^a	159	144	74	
Dioxan-acetic acid $(19:1)^{a,c}$		155		~ 4500
Dioxan-water $(9:1)^{a,c}$		430		
Dioxan-water $(4:1)^{a,c}$		730		
Acetone ^b		1320	1120	
Dimethylformamide "		200		
α At 24.7°. δ	At 0.	0°. ° v	/v.	

In previous work,⁴ a second test for distinguishing between mechanisms $S_{\rm E}2$ and $S_{\rm E}i$ has been widely used

⁴ H. B. Charman, E. D. Hughes, and C. K. Ingold, J. Chem. Soc., 1959, 2530; H. B. Charman, E. D. Hughes, C. K. Ingold, and F. G. Thorpe, *ibid.*, 1961, 1121; E. D. Hughes, C. K. Ingold, F. G. Thorpe, and H. C. Volger, *ibid.*, p. 1133; E. D. Hughes, C. K. Ingold, F. G. Thorpe, H. C. Volger, and H. B. Charman, ibid., p. 1142.

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in cases in which a mercuric halide is the electrophilic substituting agent. This test consists in observing the kinetic effect of an added lithium halide, which will complex with the mercuric halide to give a trihalogenomercurate ion of very much reduced electrophilic strength. The effect will be to quench substitution by mechanism $S_E 2$. On the other hand, the complexing will provide a new halide ion to carry away the outgoing metal, and so will bring to prominence any tendency towards mechanism $S_E i$. Ordinary salt effects can occur, as a control on which one may examine the effect of added lithium perchlorate. The results of some experiments on these lines are given in Table 3.

TABLE 3

Effect of added lithium salts on the rate of reaction of mercuric bromide with methyl(triphenylphosphine)gold(I) (by the ' partition ' method throughout)

	[MeAuPPh ₃]	[HgBr,]0	[LiX]	k_{2}	k_2 Li
Lithium	(10-4	(10-4	(10-4	(sec1	(sec1
salt	mole/l.)	mole/l.)	mole/l.)	mole ⁻¹ l.)	mole ⁻¹ l.)
In dio	xan-water (9:	1 v/v) at 2	4·7°		
None	Mean from 7	Table 2	0.0	430	430
LiClO	0.10	0.10	0.65	420	420
LiClO ₄	0.10	0.10	3.25	440	440
LiBr	0.10	0.10	0.064	425	
LiBr	0.10	0.10	0.64	270 ª	
LiBr	0.10	0.10	6.4	150 ª	
In dio:	xan-water (4 :	1 v/v) at 2	4·7°		
None	Mean from 2	Table 2	0.0	730	730
LiClO ₄	0.10	0.10	0.287	730	730
LiClO	0.10	0.10	2.87	800	800
LiBr	0.10	0.10	0.178	720	
LiBr	0.10	0.10	1.78	450 °	
In ace	tone at 0.0°				
None	Mean from 7	Table 2	0.0	1320	1320
LiClO	0.050	0.050	0.090	1230	1220
LiClO	0.050	0.050	0.18	1420	1420
LiBr	0.085	0.085	0.016	1020	1240
LiBr	0.085	0.085	0.032	760 ª	1340
LiBr	0.085	0.085	0.048	460 a	1290
LiBr	0.10	0.10	0.11	0.7	0.0
LiBr	0.10	0.10	0.22	0.6	0.0
		 Initial 	rate.		

The Table shows that added lithium perchlorate has no significant effect on the rate of substitution in the gold complex by mercuric bromide in any of the solvents, but that added lithium bromide depresses the rate, moderately in the aqueous dioxan solvents, but strongly in solvent acetone. We assume that the equilibrium constant for complexing by lithium perchlorate is vanishingly small, whilst that for complexing with lithium bromide is moderate in the aqueous dioxan solvents, but large in the acetone solvent. If we also assume that bimolecular rate of electrophilic substitution by all mercurate anions are negligibly small in comparison with rates by molecular mercuric bromide, then rate equations covering kinetic effects of added salts can be written down without knowledge of the equilibrium constants for mercurate formation, provided that these constants are small enough or large enough. This is true in the conditions for which figures are given

in the last column of Table 3. For added lithium perchlorate the equation is:

$$\begin{aligned} \text{Rate} &= \\ & k_2^{\text{Li}}[\text{MeAuPPh}_3][\text{HgBr}_2] = k_2[\text{MeAuPPh}_3][\text{HgBr}_2] \end{aligned}$$

and for added lithium bromide in acetone, the equations are:

$$\begin{split} \text{Rate} &= k_2^{\text{Li}}[\text{MeAuPPh}_3]\{[\text{HgBr}_2] - [\text{LiBr}_2]\},\\ &\text{if } [\text{HgBr}_2] > [\text{LiBr}],\\ \text{rate} &= 0, \text{ in } \text{case } [\text{HgBr}_2] \leqslant [\text{LiBr}]. \end{split}$$

These equations define the $k_2^{\rm Li}$ constants illustrated in Table 3. They mean that the reaction of HgBr₂ is wholly quenched by conversion into HgBr₃⁻. This in turn means that the mechanism of substitution by HgBr₂ must be $S_{\rm E}2$, as already concluded. It also means that mechanism $S_{\rm E}i$ is not raised to perceptible importance by the replacement of the HgBr₂ by HgBr₃⁻.

The complementary character of the second test of mechanism will be clear. When rate rises with ionicity along a series $A < B < C < \ldots$, the conclusion that the mechanism is of $S_E 2$ type is compulsory for B, C, D, \ldots , but only permissive for A. In all cases in which the second test of mechanism has been applied to A, it is shown that A also belongs to the same family mechanism.

2. $S_{\rm E}2$ Substitutions by Mercuric Salts in Ethyl(triphenylphosphine)gold(1).—The reactions of mercuric salts with ethyl(triphenylphosphine)gold(1) were kinetically investigated by the methods used for methyl(triphenylphosphine)gold(1). As before, the reactions of mercuric iodide, bromide, and chloride were studied in pure dioxan, and of mercuric acetate in dioxan-acetic acid (19:1 v/v). The reactions, measured never over less than 75% of their stoicheiometric maxima, followed a second-order course. The second-order rate constants, obtained by the 'direct' and 'partition' methods for different initial concentrations of the reactants, are given in Table 4.

TABLE 4

Rates of reaction of mercuric salts ethyl(triphenylphosphine)gold(I)

Substi-				
tuting		[EtAuPPha]	$[HgX_2]_0$	k_{2}
agent	Method	(10 ⁻⁴ mole/l.)	$(10^{-4} \text{ mole/l.})$	(sec. ⁻¹ mole ⁻¹ l.)
In dio	xan at 24	• 7 °		
HgI,	D	0.375	0.375	690
HgI,	\mathbf{P}	0.10	0.10	710
HgI,	D	0.063	0.063	720
HgI_2	,,	0.25	0.125	690
HgI,	,,	0.125	0.25	700
HgBr ₂	,,	0.375	0.375	590
$HgBr_2$,,	0.125	0.125	630
$HgBr_2$	\mathbf{P}	0.10	0.10	600
$HgBr_2$	D	0.125	0.25	610
$HgBr_2$,,	0.25	0.125	630
HgCl ₂	,,	0.20	0.50	270
HgCl ₂	,,	0.25	0.25	240
HgCl ₂	\mathbf{P}	0.10	0.10	270
HgCl ₂	\mathbf{D}	0.63	0.25	260
HgCl ₂	,,	0.25	0.50	270

In dioxan-acetic acid (19:1 v/v) at $24 \cdot 7^{\circ}$ Hg(OAc)₂ Too fast to measure

>10,000

The average values of these rates are included in Table 6. They are all larger than the corresponding rates for the methyl gold complex—about 4 times larger where the measurements could be completed. This very close parallelism of rates of substitution in the methyl- and ethyl-gold complexes, especially with respect to variation with the anions of the mercuric salts, makes clear that the same mechanism is at work.

The comparison of rates shows already that, in these solvents at least, the common mechanism $S_{\rm E}2$ is facilitated by electron release towards that carbon atom which is the seat of substitution. In other words, the need for electrons to bind the incoming mercury electrophile determines the sign of the polar effect exhibited by the reaction in the dioxan solvents used.

3. $S_{E}2$ Substitutions by Mercuric Salts in 1-Cyano-1-ethoxycarbonylpentyl(triphenylphosphine)gold(1).— This gold complex is our example for the replacement of gold(I) bound to an electronegatively substituted alkyl group. The rates of its reactions with mercuric iodide, bromide, and chloride were measured in dioxan, as had been done for the methyl- and ethyl-gold complexes (sections 1 and 2). The rate of reaction of the electronegatively substituted alkyl gold complex with mercuric acetate could not be measured, as the rates for the methyl- and ethylgold complexes had been, in dioxan-acetic acid (19:1 v/v), because this amount of acid acidolysed the gold complex to give 1-cyano-1-ethoxycarbonylpentane (ethyl n-butylcyanoacetate) and (triphenylphosphine)gold(I) acetate. However, we found that one thousandth of the previous amount of acetic acid would here serve

TABLE 5

Rates of reaction of mercuric salts with 1-cyano-1-ethoxycarbonylpentyl(triphenylphosphine)gold(1) in dioxan at 24.7° (by the 'direct' method)

Substi-		$[HgX_2]_0$	k_2
tuting	$[BuC(CN)(CO_2Et)AuPPh_3]_{0}$	(10-4	(sec1
agent	(10 ⁻⁴ mole/l.)	mole/l.)	mole ⁻¹ l.)
HgI2	$2 \cdot 22$	$2 \cdot 22$	41
HgI,	0.244	0.244	44
HğI,	0.244	1.22	42
HğI,	0.61	0.205	44
HgBr,	1.00	1.00	42
HgBr,	0.20	0.20	45
HgBr,	0.70	1.75	46
HğBr,	1.00	0.25	49
HgBr,	0.71	1.03	44
HgCl,	1.25	1.25	23
HgCl,	0.20	0.50	22
HgCl,	0.25	0.25	20
HgCl,	0.75	0.25	25
HgCl ₂	0.20	1.25	21
Hg(OAc), ª	0.50	0.50	270
Hg(OAc) a	0.125	0.125	260
Hg(OAc), "	0.75	0.25	250
Hg(OAc),	0.25	0.75	240
$Hg(NO_3)_2$	Too fast to measure		$>\!5000$

^a The solvent contained 10⁻³M-acetic acid.

the purpose of averting the precipitation of mercuric oxide without causing perceptible acidolysis. We employed 10^{-3} M-acetic acid, *i.e.* 0.006 vol. %, and so, from the viewpoint, of kinetic solvent effects, the solvent for

the reaction was still essentially dioxan. With all the mercuric reagents, the reactions of the substituted alkylgold complex were slower than corresponding reactions of the methyl and ethyl complexes. The rate of the reaction of mercuric acetate with the cyano(ethoxycarbonyl)pentyl complex was now in the measurable range, and so we could attempt a further step along the series of increasing ionicities of mercuric substituting agents. We examined the reaction of mercuric nitrate with the cyano(ethoxycarbonyl)pentyl complex in dioxan. This reaction was too fast for measurement.

In all these measurements, the 'direct' method was employed, and all measurable runs were followed to 75%or better of their stoicheiometric extent. They were of second-order form, and their rate constants from runs at various initial concentrations are in Table 5.

As shown by the summary of rate constants in Table 6, the rates of the reactions of the cyano(ethoxycarbonyl)pentylgold complex rise strongly along the series HgHal₂, Hg(OAc)₂, Hg(NO₃)₂. This type of rate variation is expected, if the substitutions in the cyano-(ethoxycarbonyl)pentylgold complex are again $S_{\rm E}2$ processes. It certainly excludes the other electrophilic mechanism, which is consistent with the observed second-order kinetics, namely, mechanism $S_{\rm E}i$.

Table 6 compares mean second-order rate constants as observed in dioxan solvents for the methyl-, ethyl-, and cyano(ethoxycarbonyl)pentyl-gold complexes. Evidently, the rate constants for the cyano(ethoxycarbonyl)pentyl complex are substantially smaller than for the methyl and ethyl complexes. This is as expected from the already drawn conclusion (section 2) that the polarity of the $S_E 2$ mechanism in such solvents is determined by the demand for electrons at the site of substitution in order to bind the entering mercury before the gold can be released.

TABLE 6

Mean second-order rate constants (sec.⁻¹ mole.⁻¹ l.) for reactions of mercuric salts with simple and substituted alkylgold complexes in dioxan at 24.7°

	MeAuPPh ₃	EtAuPPh ₃	BuC(CN)(CO ₂ Et)AuPPh ₃
HgI,	159	700	43
HğBr ₂	144, 155 ª	610	45
HgCl ₂	74	250	22
Hg(OAc) ₂	4500 ª	>10,000 °	255 ^b
$Hg(NO_3)_2$			> 5000
a C 1		0.0	

 a Solvent contained 0.8M-acetic acid. b Solvent contained 0.001M-acetic acid.

4. $S_{\rm E}2$ Substitutions by Methylmercuric Salts in Methyl(triphenylphosphine)gold(1).— These reactions typify the second of the two steps of substitution which occur between mercuric salts and alkylgold(1) complexes, when the latter are in excess. We went over to the independent study of substitutions by methylmercuric salts for several reasons, one of which was that they are slower than corresponding reactions of mercuric salts. Another was that alkylmercuric halides are noncomplexing, thereby automatically excluding mechanism $S_{\rm E}i$. These halides are also believed to be less ionising

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than simple mercuric halides, and so it was to be hoped that the spontaneous ionising reaction of the latter in dimethyl sulphoxide, which made the kinetics of subsubstitution by mercuric halides in the methylgold complex so difficult to study in that solvent, would not be a difficulty with methylmercuric halides.

The reactions of methylmercuric salts with methyl-(triphenylphosphine)gold(I) were studied in two solvents, *viz.* dioxan-water (4:1 v/v), and dimethyl sulphoxide. The reactions were followed by the direct method over at least 75% of their stoicheiometric course. They were all of second-order kinetic form, even those in dimethyl sulphoxide. The rate constants derived from runs with different initial concentrations of the reactants are given in Table 7. Mean values are included in Table 11, section 5.

TABLE 7

Rates of reaction of methylmercuric salts with methyl-(triphenylphosphine)gold(I) (by the 'direct' method)

Substi-			
tuting	[MeAuPPh ₃] ₀	[MeHgX] ₀	k_2
agent	(10-4 mole/l.)	(10 ⁻⁴ mole/l.)	(sec. ⁻¹ mole ⁻¹ l.)
In dioxan	-water $(4:1 v/v)$	at 24.7°	
MeHgI	6.67	6.67	0.64
MeHgI	2.00	2.00	0.54
MeHgI	5.00	2.00	0.57
MeHgI	2.00	5.00	0.62
MeHgBr	5.00	5.00	0.41
MeHgBr	2.50	2.50	0.41
MeHgBr	1.00	1.00	0.43
MeHgBr	5.00	1.00	0.39
MeHgBr	1.00	5.00	0.42
MeHgCl	6.67	6.67	0.46
MeHgCl	2.00	2.00	0.50
MeHgCl	2.00	5.00	0.47
MeHgCl	5.00	2.00	0.45
MeHgOAc	5.00	5.00	5.7
MeHgOAc	3.00	3.00	$5 \cdot 2$
MeHgOAc	1.00	1.00	5.1
MeHgOAc	1.00	5.00	$5 \cdot 2$
MeHgOAc	5.00	1.00	4.7
MeHgNO.	0.25	0.25	ca. 7200
MeHgNO	0.125	0.125	ca. 9400
MeHgNO3	0.050	0.050	ca. 8800
In dimeth	vl sulphoxide at 3	24·7°	
MeHøI	6.67	6.67	2.7
MeHøl	5.00	5.00	$\bar{2}.8$
MeHgI	2.00	2.00	2.9
MeHøI	3.33	6.67	3.1
MeHgI	5.00	2.50	2.9
MeHgBr	6.67	6.67	1.12
MeHgBr	5.00	5.00	1.15
MeHøBr	3.33	3.33	1.20
MeHgBr	2.00	2.00	1.33
MeHgBr	4.00	1.00	1.07
MeHgBr	2.00	8.00	1.09
MeHgCl	6.67	6.67	0.75
MeHgCl	2.00	2.00	0.83
MeHgCl	3.33	8.33	0.72
MeHgCl	5.00	2.50	0.76
MeHgOAc	6.67	6.67	0.88
MeHgOAc	5.00	5.00	0.93
MeHgOAc	2.00	2.00	0.83
MeHgOAc	5.00	1.00	0.80
MeHgOAc	1.00	5.00	0.76
MeHgNO.	Verv fast	0.00	>4000

As far as comparison can be made, the rates of substitution by methylmercuric salts in the aqueous dioxan solvent are smaller by three orders of magnitude than the rates of substitution by corresponding mercuric salts. Except for an anomaly mentioned below, the rates of substitution by the methylmercuric salts in the methylgold complex are similar in the two solvents, and large increases of rate accompany changes of the salt along the series MeHgHal, MeHgOAc, MeHgNO₃. These increases are similar to those found in electrophilic substitutions by mercuric salts generally when the anions of those salts are similarly changed. The large increases are significant for mechanism, and again point to the operation of mechanism $S_{\rm E}2$.

The anomaly is that of the reaction of methylmercuric acetate in dimethyl sulphoxide. In that solvent only, its rate is no larger than those of the methylmercuric halides. The cause of this is suspected to be that two dimethyl sulphoxide molecules complete a four-coordinate shell stable enough to inhibit ionisation, not only of the halides, but also of the acetate, indeed, of all but the most strongly ionising of the salts. The measurements of electrical conductivity in Table 8 support that idea. The nitrate is essentially a 1 : 1 electrolyte, but the halides, and also the acetate, are essentially nonelectrolytes showing very small degrees of ionisation in equilibrium. We shall add detail to this picture in section 5.

 TABLE 8

 Electrical conductivities of methylmercuric salts in dimethyl sulphoxide at 25°

	-	
Compound	[Compound] (10 ⁻⁴ mole/l.)	Λ_m (ohm ⁻¹ cm. ²)
MeHgI	5.00	0 ∙30
MeHgBr	5.00	0.45
MeHgCl	5.00	0.33
MeHgOAc	5.00	0.25
MeHgNO ₃	5.00	62.9
Et ₄ NI	4.92	59.6

The kinetic effects of added lithium perchlorate and bromide, and of sodium acetate on the reaction of methylmercuric bromide with methyl(triphenylphosphine)gold(I) were briefly investigated in both the aqueous dioxan and the dimethyl sulphoxide solvents. The rate constants so obtained are in Table 9. All the salts seem to produce small increases in rate. We expect a positive salt effect because of the positive effect of polar co-solvents. Lithium bromide has a larger effect than either of the other salts, but still one small enough to be classified as a salt effect, rather than as a gross effect of complexing. Actually, we do not expect effects of the latter kind, because alkylmercuric halides show no obvious tendency to complex with halide ions.

5. S_{E2} Substitutions by Methylmercuric Salts in Ethyl(triphenylphosphine)gold(I).—We examined the kinetics of the reactions of methylmercuric salts with the ethylgold complex in one solvent only, viz. dimethyl sulphoxide. The experimental methods were exactly as for the methylgold complex, and again the runs were second-order. The rate constants of runs with different initial concentrations of reactants are in Table 10. Mean values are included in Table 11. The rates were

be found in Table 11. We suggested in section 4 that the reason the rate of attack by methylmercuric acetate on the methylgold complex is only of the order of magnitude of the rates of attack by the methylmercuric halides, and is not substantially larger, is that below a certain high threshold of ionicity which is attained only by the nitrate, two dimethyl sulphoxide molecules complete a

TABLE 11

Mean second-order rate constants (sec.⁻¹ mole⁻¹ l.) for reactions of methylmercuric salts with alkylgold complexes in " 80%" aqueous dioxan and in dimethyl sulphoxide at 24.7° (by the ' direct ' method)

	In ag. dioxan	In dimethyl sulphoxide		
	MeÂuPPh3	MeAuPPh ₃	EtAuPPh ₃	
MeHgI	0.59	$2 \cdot 9$	2.7	
MeHgBr	0.41	1.16	0.78	
MeHgCl	0.47	0.77	0.190	
MeHgOAc	$5 \cdot 2$	0.84	0.162	
MeHgNO ₃	~ 8500	$>\!4000$	~ 8000	

stereochemically well defined four-co-ordination shell, so 'freezing' covalent character. Of course, this applies equally to rates of attack on the ethylgold complex; and the hypothesis can take care of a number of details. The four-co-ordination will be looser and less stable when its tetrahedral stereochemistry is impaired by the presence of one large ligand. And so it is natural that rates, in either the methyl- or the ethyl-gold series of reactions with the covalent methylmercuric salts, should fall with progressive stiffening of the co-ordination shell, as the size of the variable ligand becomes reduced to a limit below which size is immaterial: $I > Br > Cl \sim OAc$. Again it seems natural that the ratios of the rates of attack by each of the covalent methylmercuric salts on the methyl- and ethyl-gold complexes should rise along the same series of variable ligands to the same limit: $I < Br < Cl \sim OAc$; for steric sheltering in the ethyl-gold bond, as compared with the methyl-gold bond, will surely be more important when the mercury is within a stiff co-ordination shell than when it is within a loose one.

6. Substitution of Mercury for Gold in 1-Cyano-1-ethoxycarbonylpentyl(triphenylphosphine)gold(I). The $S_{\rm E}$ Mechanism.—The reactions of 1-cyano-1-ethoxycarbonylpentyl(triphenylphosphine)gold(I) with methylmercuric chloride, and with the corresponding acetate, in solvent dimethyl sulphoxide at 25°, were found to be practically instantaneous. This surprising result was obtained again, with the same two methylmercuric salts, when the above gold complex was changed to diacetylmethyl(triphenylphosphine)gold(I). This very rapid replacement of gold through the agency of not particularly reactive mercurials thus seemed to be a property of electronegatively substituted alkylgold complexes.

In order to obtain an indication of whether the dimethyl sulphoxide solvent was an important factor in producing this phenomenon, we studied the reaction of 1-cyano-1-ethoxycarbonylpentyl(triphenylphosphine)-

TABLE 9

- Effects of added salts on the rate of reaction of methylmercuric bromide on methyl(triphenylphosphine)gold(I)
- Initially, $[MeAuPPh_3]_0 = [MeHgBr]_0 = 5.00 \times 10^{-4}M$ throughout. (Kinetics by the 'direct' method at 24.7° throughout.)

In dioxan–water $(4:1 v/v)$			In dime	ethyl sulph	loxide
	[Added	Ь		[Added	<i>b</i>
Added	(10-4	(\sec^{-1})	Added	(10^{-4})	(\sec^{n_2})
salt	mole/l.)	mole ⁻¹ l.)	salt	mole/l.)	mole ⁻¹ I.)
None	0.0	0.41	None	0.0	1.16
LiClO ₄	12.9	0.43	LiClO ₄	11.8	1.20
LiClO	21.5	0.47	LiBr	3.3	1.93
NaOAc	13.3	0.44	LiBr	6.7	$2 \cdot 3$
NaOAc	19.6	0.46	LiBr	13.3	3.4
LiBr	13.3	0.58	LiBr "	13.3	$3 \cdot 3$
LiBr	19.4	0.66			

^a Solvent contained 1% water.

similar to those for the methylgold complex, with minor though possibly significant differences as mentioned below. The rate of reaction of methylmercuric nitrate with the ethylgold complex was again very high, but just within the range of approximate measurement by the method used.

TABLE 10

Rates of reaction of methylmercuric salts with ethyl-(triphenylphosphine)gold(I). (In dimethyl sulphoxide at 24.7° by the ' direct ' method)

Substituting	[EtAuPPh ₃] ₀	[MeHgX] ₀	k_2
agent	(10^4 mole/l.)	(10^4 mole/l.)	(sec. ⁻¹ mole ⁻¹ l.)
MeHgI	6.67	6.67	$2 \cdot 6$
MeHgI	1.54	1.54	2.7
MeHgI	2.00	5.00	2.7
MeHgI	5.00	2.00	$2 \cdot 8$
MeHgBr	6.67	6.67	0.78
MeHgBr	2.00	2.00	0.76
MeHgBr	2.00	5.00	0.80
MeHgBr	5.00	2.00	0.78
MeHgCl	6.67	6.67	0.185
MeHgCl	1.00	1.00	0.186
MeHgCl	2.00	5.00	0.192
MeHgCl	5.00	2.00	0.198
MeHgOAc	8.00	8.00	0.126
MeHgOAc	4.80	4.80	0.163
MeHgOAc	4.80	1.60	0.160
MeHgOAc	2.40	6.40	0.169
MeHgNO ₃	0.250	0.250	ca. 7500
MeHgNO ₃	0.125	0.125	ca. 10,000
MeHgNO ₃	0.125	0.125	ca. 7500
MeHgNO ₃	0.125	0.125	ca. 8500
$MeHgNO_3$	0.063	0.063	ca. 9000
MeHgNO ₃	0.125	0.063	ca. 6000
MeHgNO ₃	0.063	0.125	ca. 6500

The gross features of these results are just as for the corresponding reactions of the methylgold complex. In the reactions of either complex, the one high rate applies to the one salt which is wholly ionic in the solvent, whilst low rates belong to all the other salts, all of which are essentially covalent in the solvent. Once again, the mechanism of substitution is shown by its connexion with ionicity to be $S_{\rm E}2$.

The minor differences between the rates given by the covalent methylmercuric salts in their reactions with the methylgold and with the ethylgold complex are not uninteresting. A comparison of mean rate constants will gold(1) with methylmercuric chloride in solvent dioxan. The reaction proceeded at a very moderate rate, pursuing the usual second-order kinetic course. The measured rate constants are given in Table 12.

TABLE 12

Second-order rate constants of the reaction of methylmercuric chloride with 1-cyano-1-ethoxycarbonylpentyl(triphenylphosphine)gold(I) in dioxan at 24.7° (by the 'direct' method)

$[BuC(CN)(CO_2Et)AuPPh_3]_0 $ (10 ⁻⁴ mole/l.)	[MeHgCl] ₀ (10 ⁻⁴ mole/l.)	k_2 (sec. ⁻¹ mole/l.)
4.00	4.00	16.0
$1 \cdot 25$ $0 \cdot 71$	$1.25 \\ 0.71$	$\begin{array}{c} 17.3 \\ 16.1 \end{array}$ 16.2
3.70	1.48	16.2
1.67	3.33	14·8 J

The very high rates in dimethyl sulphoxide are evidently due jointly to the presence of electronegative substituents in the gold complex and the use of that particular solvent. Now the unimolecular mechanism of electrophilic substitution has been established for the displacement of mercury from saturated carbon in two examples of mercury exchange. In one, the displacement was from *a*-ethoxycarbonylbenzylmercuric bromide,⁵ and in the other it was from p-nitrobenzylmercuric bromide.⁶ In both examples the alkyl group is electronegatively substituted, and in both the solvent was dimethyl sulphoxide: no other solvent has been found which will act similarly. It has been concluded 5,6 that dimethyl sulphoxide is of quite special value as a solvent for promoting the separation of a carbanion from mercury. The conditions in which the $S_{\rm E}$ mechanism of mercury exchange has been established are so similar to those now found to produce the very fast reactions of the gold complexes as to induce the suspicion that these reactions too have the $S_{\rm E}1$ mechanism, *i.e.* that the combination of polar and solvent effects which produces them does so by securing the separation of a carbanion from gold.

Our plan for trying to check this theory was to reduce the rates of the fast reactions by mixing increasing proportions of a 'slow' solvent, such as dioxan, with the ' fast ' solvent dimethyl sulphoxide, in the hope that the reductions of rate would lead into the region of measurable rates before it changed the mechanism, as it eventually must (cf. Table 12) to $S_{\rm E}2$. The first experiments of this kind were done on the reaction between 1-cyano-1-ethoxycarbonylpentyl(triphenylphosphine)gold(I) and methylmercuric chloride. In pure dimethyl sulphoxide this reaction is practically instantaneous, and in mixtures down to dimethyl sulphoxide-dioxan (1:2 v/v) it gave rates which were still much too high for measurement. But dimethyl sulphoxide-dioxan (1:9 v/v) gave rates which were high but measurable. The kinetic course of these reactions was not of second order; it was of first order in the gold complex and zeroth order in the mercurial. Only the first-order constant k_1 of the rate equation: rate = k_1 [gold complex] was steady throughout the run, and, as illustrated in Table 13, was constant as between runs started with different concentrations of reactants. We have indications that disturbances of finite kinetic order in mercurial affect the overall reaction at higher reactant concentrations than those illustrated.

From the kinetic equation it follows that the rate constant should remain the same when the mercuric

TABLE 13

First-order	rate	constants	for	the	reaction	of	1-cyano-
1-ethox	ycarl	onylpenty	l(trij	heny	ylphosphi	ne)g	old(I)
with va	rious	mercurials	in d	imet	hyl sulph	oxid	le-dioxan
(1:9v)	/v) at	24.7°					

Mer-	[BuC(CN)(CO ₂ Et)AuPPh ₃]	[RHgX]	k,
curial	(10 ⁻⁴ mole/l.)	$(10^{-4} \text{ mole/l.})$	$(10^{-3} \text{ sec.}^{-1})$
MeHgCl	1.00	1.00	7.6
MeHgCl	1.00	1.00	$8 \cdot 3$
MeHgCl	0.20	0.50	8.3
MeHgCl	0.20	0.50	7.4
MeHgCl	0.25	0.25	8.5
MeHgCl	0.25	0.25	7·5 ª
MeHgCl	0.25	0.25	8.8
MeHgCl	0.50	1.00	$7 \cdot 9$
MeHgCl	0.50	0.25	$8 \cdot 3$
MeHgCl	1.00	0.50	$7 \cdot 1$
MeHgCl	0.25	0.50	8.6
EtHgCl	1.00	1.00	8.1
EtHgCl	0.50	0.50	9.2
EtHgCl	0.25	0.25	8.7
EtHgCl	0.20	1.00	8.8
EtHgCl	0.50	0.25	8.4
MeHgBr	1.00	1.00	$8 \cdot 2$
MeHgBr	1.00	1.00	9.4
MeHgBr	0.20	0.50	9.0
MeHgBr	0.20	0.50	$9 \cdot 2$
MeHgOAc	1.00	1.00	$7 \cdot 5$
MeHgOAc	0.50	0.50	$8 \cdot 5$
			

^a Details in Table 21.

reagent is changed. We checked this conclusion by running the reaction of the gold complex, not only with methylmercuric chloride, but also with ethylmercuric chloride, methylmercuric bromide, and methylmercuric acetate, as substituting agents. As Table 13 shows, all the rates were the same. The mean first-order rate constants, taken over all the runs in the Table, is 0.0083 sec.⁻¹. This common rate is interpreted as the rate of heterolysis of the carbon-gold bond, *i.e.* it is the rate of formation of a carbanion, which is instantly trapped by any active electrophile that is available.

Although we did not check the point, we have no doubt that the reactions of the gold complex with inorganic mercuric salts would go in the same conditions with the same kinetics, and at the same common rate. When the experiments with mercuric salts were done, we had no evidence that mechanism $S_{\rm E}1$ was possible for organogold compounds, and none as to how it could be realised. We had found that dimethyl sulphoxide induces a slow change in inorganic mercuric salts, so interfering with the kinetic studies of their $S_{\rm E}2$ reactions.

⁶ V. A. Kalyavin, T. A. Smolina, and O. A. Reutov, *Doklady Akad. Nauk S.S.S.R.*, 1964, 156, 95; 157, 919.

⁵ O. A. Reutov, B. Praisner, I. P. Beletskaya, and V. I. Sokolov, *Izvest. Akad. Nauk S.S.S.R., Ser. khim.*, 1963, 970; E. D. Hughes, C. K. Ingold, and R. M. G. Roberts, *J. Chem. Soc.*, 1964, 3900.

But the slow change cannot disturb an S_E1 reaction, because the mercuric salts are irrelevant to its rate.

7. S_E2 Substitution by Mercuric Salts in Trimethyl-(triphenylphosphine)gold(III).--Mercuric salts react with this gold(III) complex to form a methylmercuric salt and a dimethyl(triphenylphosphine)gold(III) salt, according to the equation

$$Me_{3}AuPPh_{3} + HgX_{2} \longrightarrow MeHgX + Me_{2}AuPPh_{3}X$$

In our conditions the gold parted from only one of its methyl groups, even when a five-fold excess of mercuric salt was employed.

In the kinetic work on these reactions, the mercuric salts were mercuric bromide and mercuric acetate, and the solvents were dioxan, dioxan containing acetic acid or water or both, acetone, and dimethyl sulphoxide. In all but the last of these solvents, the runs had an uncomplicated second-order kinetic form as far as they were followed, never to less than 75% of their complete course. For the same solvent and temperature the secondorder rate constant of runs at various initial concentrations of the reactants were the same, as shown in Table 14.

TABLE 14

Rates of reaction of mercuric salts with trimethyl(triphenylphosphine)gold(III) (by the 'partition' method throughout) - 10701 - 7

Substituting agent	$[Me_{3}AuPPh_{3}]_{0}$ (10 ⁻⁴ mole/l.)	$[HgX_{2}]_{0}$ (10 ⁻⁴ mole/l.)	k_2 (sec. ⁻¹ mole ⁻¹ l.)
In dioxan	at 24.7°	((
HgBr.	1.00	1.00	135
HgBr	0.50	0.50	133
HgBr.	0.10	0.10	120
HgBr	1.00	0.25	138
HgBr	0.10	0.25	131
HgBr.	0.25	1.00	124
$HgBr_2$	0.25	0.10	127
In dioxan	-acetic acid (19 :	$1 v/v$ at 24.7°	
HgBr.	0.50	0.50	193
HgBr	0.10	0.10	182
HgBr	0.20	0.10	173
HgBr.	0.10	0.50	188
Hg(OAc).	0.10	0.10	ca. 9000
Hg(OAc).	0.060	0.060	ca. 9000
Hg(OAc),	0.020	0.020	ca. 9500
$Hg(OAc)_{2}$	0.040	0.060	ca. 10,000
In dioxan	-water $(4:1 v/v)$	at 24.7°	
HgBr.	0.20	0.20	1380
HgBr.	0.060	0.060	1430
HgBr.	0.060	0.10	1500
HyBr,	12:21	ው ዕያ	14291
In dioxan	-water-acetic aci	id (76:19:5 v/v	v) at 24·7°
Hg(OAc) ₂	Very fast		>10,000
In aceton	e at 0·0°		
HgBr,	0.10	0.10	2000
HgBr.	0.050	0.050	1900
HgBr.	0.040	0.040	2200
HğBr,	0.020	0.020	2000
HgBr ₂	0.010	0.010	2300
HgBr ₂	0.060	0.10	1700
HgBr.	0.10	0.040	1800

The most striking picture of these rates is their close similarity to the rates of attack of the mercuric salts on methyl(triphenylphosphine)gold(I), as reported in section 1. The mean rate constants, for like solvents and temperatures, of attack by the mercuric salts on the gold(I) and gold(III) complexes are brought together in Table 15. The reason for the similarity in rates is not understood, but its closeness alone would justify the conclusion that the mechanism of attack on both gold complexes is the same, *i.e.* that the reactions of the gold-(III) complex proceeded by mechanism $S_{\rm E}2$.

The above conclusion is supported on the internal evidence of the two tests that we usually apply to electrophilic aliphatic substitutions which display

TABLE 15

Comparison of mean second-order rate constants (sec.⁻¹ mole.⁻¹ l.) for reactions of mercuric salts with methyl-(triphenylphosphine)gold(1) and trimethyl(triphenylphosphine)gold(III) . .

	Triphenylphosphine complex		
Reagent and solvent	Methyl- gold(I)	Trimethyl- gold(III)	
Reactions of HgBr ₂ in			
Dioxan at 24.7°	144	130	
Dioxan-acetic acid $(19:1)$ at 24.7°	155	184	
Dioxan-water $(4:1)$ at 24.7°	730	1450	
Acetone at 0.0°	1320	2000	
Reactions of Hg(OAc) ₂ in			
Dioxan-acetic acid $(19:1)$ at 24.7°	$\sim \! 4500$	~9500	

second-order kinetics. First, the rate of attack on the gold(III) complex rises sharply from the reagent mercuric bromide to the more ionising mercuric acetate. This is what it should do under mechanism $S_{E}2$, but the opposite of what it should do under mechanism $S_{\rm E}$ i. Second, added lithium bromide quenches the reaction between mercuric bromide and the gold(III) complex. This again should happen under mechanism $S_{\rm E}2$, though the opposite should occur if mechanism $S_{\rm E}$ i were operative. As Table 16 shows, the quenching is practically quantitative in acetone, with the result that the rate, as modified by added lithium bromide, can be calculated from the equation given in section 1 for the rate constant k_2^{Li} .

TABLE 16

Effect of added lithium salts on the rate of reaction of mercuric bramide on trimethyl (triphenylphosphine)gold(III) in acetone at 0.0°

[Me ₃	$AuPPh_3]_0 = [Hg]$	$Br_2]_0 = 0.050 \times 10^{-10}$	0 ⁻⁴ mole/l.
	[LiX]	k_2	k2 11
LiX	(10 ⁻⁴ mole/l.)	(sec. ⁻¹ mole ⁻¹ l.)	(sec. ⁻¹ mole ⁻¹ l.)
	No salt (Table	15) 2000	2000
LiClO	0.073	1800	1800
LiClO	0.36	1800	1800
LiBr	0.0051	1800	2100
LiBr	0.0101	1700	2300
LiBr	0.020	1200 •	2100
LiBr	0.030	800 4	1800
LiBr	0.021	0.9	0.0
LiBr	0.101	0.4	0.0
	a T.	sitial rata	

The mechanism $S_{\rm E}2$ is thus confirmed. The effects of radical inhibitors, *viz.* of 2,6-di-t-butylphenol and of cyclohexene, were tried; but they had no effect.

Our kinetic study of the reaction of mercuric bromide with trimethyl(triphenylphosphine)gold(III) in dimethyl sulphoxide led to difficulties of the type encountered in the reactions of mercuric salts with methyl(triphenylphosphine)gold(I) in that solvent. We do not report those experiments, because they were not pressed to a firm conclusion, though we do not doubt that a main cause of complication was that mercuric bromide itself changes in the solvent at rates comparable to those of the reactions which occur with the gold complex.

EXPERIMENTAL

Materials.—Triphenylphosphinegold(I) chloride. Methods for the preparation of this and other gold(I) halides were developed from those used by Mann, Wells, and Purdie for analogous compounds.⁷ A solution of triphenylphosphine (14 g.) in acetone (100 ml.) was carefully added at 0° to a solution of chloroauric acid (51% Au; 10 g.) in acetone (50 ml.). After the mixture had been concentrated to about 50 ml., the precipitated triphenylphosphinegold(I) chloride was collected. Washed with a little acetone, it was pure enough for preparative use (yield 80%), m.p. 248—249° (from benzene-ligroin) (Found: C, 43.7; H, 3.1; Au, 39.6. Calc. for C₁₈H₁₅AuClP: C, 43.7; H, 3.0; Au, 39.8%), v_{max}. 331s and 323ms cm.⁻¹, λ_{max} . 269 and 275 mµ. Triphenylphosphinegold(I) bromide. The chloride just de-

Triphenylphosphinegold(1) bromide. The chloride just described (3 g.) and tetraethylammonium bromide (7.5 g.) in ethanol (75 ml.) were boiled for 2 hr. under reflux and cooled to 0°. The precipitate was collected and treated similarly with fresh tetraethylammonium bromide (7.5 g.) and ethanol (75 ml.). The precipitate of triphenylphosphinegold(1) bromide thus obtained had m.p. 250—251° (from benzene-ligroin) (yield 80%) (Found: C, 40.6; H, 3.0; Au, 36.2. Calc. for C₁₈H₁₅AuBrP: C, 40.2; H, 2.8; Au, 36.6%), γ_{max} 233s cm⁻¹, λ_{max} 269 and 275 mµ.

Triphenylphosphinegold(1) iodide. The chloride (1 g.) and tetra-n-butylammonium iodide (5 g.) in ethanol (30 ml.) were boiled under reflux for 2 hr. and cooled to 0°. The precipitate was collected, the treatment with tetrabutylammonium iodide was repeated, and the product, m.p. 234-235°, was purified as in the preceding example (yield 66%) (Found: C, 37.3; H, 2.6; Au, 33.8. Calc. for $C_{18}H_{15}AuIP: C, 36.9; H, 2.6; Au, 33.6\%), \lambda_{max}$ 269 and 275 mµ.

Methyl(triphenylphosphine)gold(I). Our preparations of this and the ethyl homologue were based on those of Coates and his coworkers.² The Grignard compound from methyl iodide (7.8 ml.) in ether (100 ml.) and a suspension of the gold(1) chloride (10 g.) in ether (50 ml.) were mixed at 0°. The mixture was stirred for 1 hr. and the reaction was completed by heating for 1 hr. under reflux. Excess of the Grignard compound was destroyed by 0.5% aqueous sulphuric acid, and the mixture was then filtered. The residue was extracted with benzene, and this extract was combined with the ether layer in the filtrate, washed with water, and concentrated under reduced pressure to about 200 ml. The pale brown concentrate was decolourised by charcoal, and colourless methyl(triphenylphosphine)gold(I) was then precipitated with pentane (500 ml.) at -10° m.p. 173-175° (from benzene-pentane) (yield 73%) (lit.,²

175°) (Found: C, 48·4; H, 3·6; Au, 41·1. Calc. for $C_{19}H_{18}AuP$: C, 48·1; H, 3·8; Au, 41·5%), ν_{max} 534s cm.⁻¹, λ_{max} 275 mµ.

Ethyl(triphenylphosphine)gold(I). A 0.33M-solution of ethyl-lithium in ether (40 ml.) was added to a suspension of triphenylphosphinegold(I) chloride (5 g.) in ether (75 ml.) at -10° . The mixture was stirred for 30 min., and then allowed to warm to room temperature. It was cooled to 0°, water (50 ml.) was added, and then ether (50 ml.) to dissolve the ethyl(triphenylphosphine)gold. The ether layer was dried, decolourised with charcoal, concentrated under reduced pressure to about 50 ml., and cooled to -10° with addition of ligroin to complete precipitation of the ethylgold complex, which had m.p. 150–152° (decomp.) (from ether-ligroin) (yield 73%) [lit.,² ca. 130° (decomp.)] (Found: C, 49.0; H, 3.9; Au, 40.6. Calc. for C₂₀H₂₀AuP: C, 49.2; H, 4.1; Au, 40.4%), ν_{max}. 533s cm.⁻¹, λ_{max}. 275 mμ.

s-Butyl(triphenylphosphine)gold(I). The filtered Grignard solution prepared from s-butyl bromide (2.7 ml.) and ether (50 ml.) was added slowly to a suspension of triphenylphosphinegold(1) chloride (2 g.) in ether (60 ml.). A pale yellow solution was obtained together with a small amount of a black precipitate of metallic gold. The solution was stirred for 30 min., and after treatment with $0{\cdot}5\%$ aqueous sulphuric acid, the ether layer was separated, dried, concentrated to about 10 ml. under reduced pressure and cooled to -70° with the addition of ligroin (40 ml.). The precipitated s-butylgold complex was washed with light petroleum, and was thus obtained as off-white crystals. When allowed to warm to room temperature, the crystals started to turn brown, and they were therefore analysed at once for gold content (yield 24%) (Found: Au, 38.7. $C_{22}H_{24}AuP$ requires Au, $38\cdot 2\%$). A sample kept at 0° turned brown overnight, and one kept at room temperature turned dark brown and sticky in 30 min.

Diacetylmethyl(triphenylphosphine)gold(I). Following work by Lewis and others,³ a suspension of triphenylphosphinegold(I) chloride (I g.) and thallous acetylacetonate (0.8 g.) in acetone (50 ml.) was shaken for 2 hr., the precipitated thallous chloride was filtered off, and the filtrate was evaporated to dryness. The white solid so obtained was extracted with acetone (25 ml.), ligroin was added (25 ml.), and most of the acetone was pumped off. When the concentrate was cooled to -70° , the diacetylmethylgold complex crystallised, and, after a further crystallisation from acetone-ligroin, had m.p. 164—165° (yield 70%) (Found: C, 49.5; H, 3.9; Au, 35.4. C₂₃H₂₂AuO₂P requires C, 49.5; H, 4.0; Au, 35.3%), v_{max}. 1660s, 1646s, and 533s cm.⁻¹, λ_{max} . 275 mµ. τ (CHCl₃) 2.3 (15H), 5.25 (1H, d), and 7.58 (6H).

Diethoxycarbonylmethyl(triphenylphosphine)gold(1). Triphenylphosphinegold(1) chloride (1 g.) was added to an ethanolic solution (25 ml.) of diethyl sodiomalonate [from ethyl malonate (0.38 ml.) and sodium (0.05 g.)], and the suspension was stirred for 2 hr. After removal of most of the ethanol with a rotary evaporator, the residue was extracted with benzene (100 ml.), the extract was evaporated to about 30 ml., and ligroin (50 ml.) was added. The precipitated complex was collected (yield 48%), m.p. 212° (decomp.) (from benzene-ligroin) (Found: C, 48.6; H, 4.2; Au, 31.8%), v_{max} . 1693s and 533ms cm.⁻¹, λ_{max} . 275 and 323 mµ. Cyano(ethoxycarbonyl)methyl(triphenylphosphine)gold(1).

⁷ F. G. Mann, A. F. Wells, and D. Purdie, *J. Chem. Soc.*, 1937, 1828.

This was prepared like the preceding compound, except for for the replacement of ethyl malonate by ethyl cyanoacetate (0·32 ml.), up to the stage of evaporation of the ethanol. The residue from this process was extracted with acetone (125 ml.). Ligroin (50 ml.) was then added, and the solution was concentrated to about 50 ml., and cooled to -70° . The colourless *crystals* which separated were crystallised from acetone–ligroin, and then had m.p. 253— 255° (decomp.) (yield 60%) (Found: C, 48·5; H, 4·0; Au, 34·6. C₂₃H₂₁AuNO₂P requires C, 48·3; H, 3·7; Au, 34·5%), ν_{max} 2170ms, 1660s, and 533s cm.⁻¹, τ (CHCl₃) 2·3 (15H), 5·57 (2H, q, CH₂), and 8·67 (3H, t, Me), λ_{max} 275 and 323 m μ .

1-Cyano-1-ethoxycarbonylpentyl(triphenylphosphine)gold(I). Ethyl n-butylcyanoacetate, prepared in the standard way from n-butyl iodide and ethyl cyanoacetate, had b.p. 130- $140^{\circ}/20-22$ mm. Sodium (0.22 g.) was dissolved in a mixture of ether (40 ml.) and ethanol (10 ml.), and ethyl n-butylcyanoacetate (2.7 ml.) was added. To the solution of the sodio-ester thus formed, a suspension of triphenylphosphinegold(I) chloride (3 g.) in ether (20 ml.) was added, and the mixture was stirred for 4 hr. The precipitated sodium chloride was filtered off and light petroleum (200 ml.; b.p. $60-80^{\circ}$) was added to the filtrate. The solution was pumped down under nitrogen to about 50 ml., and cooled to -70° . The precipitate was collected and washed with pentane. It separated from ether-ligroin in white microcrystals, m.p. 131-132° (yield 63%) [Found: C, 51.8; H, 4.8; Au, 31.6%; M (benzene), 630. $C_{27}H_{29}AuNO_2P$ requires C, 51.7; H, 4.7; Au, 31.4%; M, 627.5], v_{max.} 2200ms, 1700s, and 538s cm.⁻¹, $\lambda_{max.}$ 275 mµ, τ (acetone) 2·1 (15H), 5·67 (2H, q), and 8·6—9·1 (12H).

Trimethyl(triphenylphosphine)gold(III).² Bromoauric acid was first prepared from chloroauric acid (4.5 g.; 51% gold) and potassium bromide (12 g.), which were dissolved in a mixture of ether (50 ml.) and water (20 ml.). The mixture was shaken for 1 hr., the ether layer was separated, and the water layer was extracted with ether $(2 \times 20 \text{ ml.})$. The combined ether solution was dried with calcium chloride and then with a freshly activated molecular sieve. To this solution a 1.3M-ethereal solution (40 ml.) of methyl-lithium was added at -70° . The red colour of the bromoauric acid disappeared, and a white precipitate remained. A solution of triphenylphosphine (3.1 g.) in ether (20 ml.) was added, still at -70° , and the mixture was stirred for 30 min. at the same temperature. It was then allowed to warm to room temperature, and water was added (30 ml.). As some decomposition to metallic gold occurred, the mixture was quickly filtered, and the ether layer was separated, dried, and pumped down to about 50 ml. Hexane (150 ml.) was added, and the solution was concentrated by pumping, again to 50 ml., and was cooled to -70° . The crystals thus obtained had m.p. 119° (decomp.) (from hexane) (lit.² 120°) (Found: C, 50.0; H, 4.7; Au, 39.3. Calc. for C₂₁H₂₄AuP: C, 50·1; H, 4·8; Au, 39·1%), v_{max} , 531s and 514s cm.⁻¹.

Dimethyl(triphenylphosphine)gold(III) bromide. The trimethylgold(III) complex just described (0.1 g.) dissolved in ether (20 ml.) was treated with a solution (5.9 ml.) containing bromine (0.54 g.) in ether (100 ml.). When the solution was colourless, the solvent was removed in a rotatory evaporator, and the *product* was crystallised from acetone-hexane at -70° . It had m.p. 151° (decomp.) (yield 70%) (Found: C, 42·2; H, 3·7; Au, 33·9. $C_{20}H_{21}$ -AuBrP requires C, 42·2; H, 3·7; Au, 34·6%), ν_{max} 527s, 506s, and 230s cm.⁻¹. Addition of silver nitrate in aqueous acetone gave an immediate precipitate of silver bromide.

Other materials. Most of the mercuric or other salts required were already available. Dialkylmercurys were prepared by known methods.⁴ Alkylmercuric salts excepting the following one were prepared from the dialkylmercurys and mercuric salts. 1-Cyano-1-ethoxycarbonylpentylmercuric bromide was prepared by mercurating ethyl sodiobutylcyanoacetate in ether-ethanol with mercuric bromide (1 mol.). The product was a glass-like solid which could not be crystallised, v_{max} . 2225m and 1710s cm.⁻¹ (*cf.* ethyl butylcyanoacetate 2250m and 1750s cm.⁻¹). Acetone, dioxan, and dimethyl sulphoxide were purified by already described methods.⁸

Products.—In order to isolate the products, it was necessary to work with much larger concentrations than were used in the kinetic experiments. However, in the reactions of gold(I) compounds, the gold-containing product was always a triphenylphosphinegold(I) salt, and this could be identified through its u.v. absorption spectrum in the solution left at the end of a kinetic experiment, so confirming its identity with the gold salt isolated from the product of a completed reaction in more concentrated solution.

Products from organogold(I) compounds with mercuric salts. Solutions of the triphenylphosphinegold(I) compound (0.5— 1.0 g., 1 mol.) in the solvent (30 ml.) and of the mercuric salt (1 mol.) in the same solvent (30 ml.) were mixed, and after 1—2 hr. the solvent was removed under reduced pressure in a rotatory evaporator. The residue was extracted with methanol (3 × 10 ml.), from which the alkylmercuric salt was crystallised. It was identified by comparing its i.r. spectrum with that of an authentic specimen. The residue remaining from the methanol extraction was dissolved in benzene (25 ml.), and reprecipitated with light petroleum (75 ml.). This material was identified as the triphenylphosphinegold(I) salt by its i.r. spectrum.

This procedure had to be modified when the solvent was either dimethylformamide or dimethyl sulphoxide, because these solvents were not removed in the rotary evaporator easily enough wholly to avoid decomposition of the solutes. This difficulty was overcome by precipitating the products of reactions in either solvent (60 ml.) by addition of water (150 ml.).

When the gold-containing product was either triphenylphosphinegold(I) nitrate or acetate no authentic specimen was available with which to compare the i.r. spectrum. However, the spectra observed (acetate: ν_{max} . 1630s and 1310s; nitrate: 1380s and 826m cm.⁻¹) were consistent with these structures, and the gold-containing product from the reaction of methyl(triphenylphosphine)gold(I) with mercuric acetate in the solvent mixture dioxan-acetic acid (19:1) was confirmed as *triphenylphosphinegold*(I) acetate by elemental analysis (Found: C, 46.0; H, 3.4; Au, 38.1. C₂₀H₁₈AuO₂P requires C, 46.4; H, 2.9; Au, 38.0%).

The yields of separated products in general amounted to more than 75% of the requirements of equation (1)

 $RAuPPh_3 + HgX_2 \longrightarrow XAuPPh_3 + RHgX$ (1)

This stoicheiometry was confirmed by the final u.v. absorption spectra obtained in kinetic experiments by the 'direct' method, or the final concentration of mercuric salt measured in kinetic experiments by the 'partition' method. When

⁸ A. I. Vogel, 'A Text-book of Practical Organic Chemistry,' Longmans, London, 1959, pp. 171, 177; J. A. Keiner, Thesis, London, 1965.

the gold-containing reactant was initially in excess, observations by the 'direct' method indicated that the reaction (1) written above was being succeeded by a much slower reaction, presumably (2).

$$RAuPPh_3 + RHgX \longrightarrow XAuPPh_3 + R_2Hg$$
 (2)

Products from organogold(I) compounds with methylmercuric salts. A solution of the triphenylphosphinegold(I) compound (0.2-0.5 g., 1 mol.) in the solvent (20 ml.) was mixed with one of the methylmercuric salt (1 mol.) in the solvent (20 ml.), and the mixture was kept overnight. The method of separation of the products depended on the organogold(I) compound used.

When this was methyl- or ethyl-(triphenylphosphine)gold-(I) the expected mercury-containing product was dimethylmercury or ethylmethylmercury. Either compound was distilled from the solution under reduced pressure, trapped at the temperature of liquid nitrogen, dissolved in carbon tetrachloride, and identified by its ¹H n.m.r. spectrum [Me₂Hg: τ 9.7; MeEtHg: 8.7 (m, Et) and 9.7 (Me)]. The triphenylphosphinegold(I) salt was isolated by evaporation of the solvent, or by precipitation with water. It was identified by its i.r. spectrum.

When the organogold reactant was 1-cyano-1-ethoxycarbonylpentyl(triphenylphosphine)gold(I), the solvent was removed by means of a rotary evaporator, and the residue was extracted with carbon tetrachloride. The ¹H n.m.r. spectrum of the carbon tetrachloride solution [τ 5.67 (q, CH₃CH₂), 8.4—9.1 (CH₃CH₂ and CH₃[CH₂]₃), and 9.1 (CH₃Hg)] showed the presence of 1-cyano-1-ethoxycarbonylpentyl(methyl)mercury. The residue remaining from the extraction with carbon tetrachloride was dissolved in benzene (15 ml.), and the triphenylphosphinegold(I) salt was precipitated with light petroleum (50 ml.). It was identified by its i.r. spectrum. The yield of the gold salt was never less than 75% of the requirement of the equation:

Products from an organogold(III) compound with mercuric salts. The procedure for separating the products from the reactions of trimethyl(triphenylphosphine)gold(III) with mercuric salts was just that described for the reaction of organogold(I) compounds with mercuric salts. The product salts, those formed according to the equation:

$$Me_{3}AuPPh_{3} + HgX_{2} \longrightarrow Me_{2}AuPPh_{3}X + MeHgX$$

were identified by comparison of their i.r. spectra with those of authentic specimens. The yields exceeded 75% of the theoretical. With concentrations of about 10^{-4} M, and measurement of the amount of mercuric salt left at the end of the reaction by the 'partition' method, it was shown that only one methyl group was removed from the gold complex, even when a five-fold excess of mercuric salt was employed.

Kinetics.—The 'direct' method. This involved measurement of the absorbance $A = \log_{10}(I_0/I)$ of a length l (cm.) of reaction solution, as a function of time t (sec.). With extinction coefficients $\varepsilon_1 - \varepsilon_4$ (l. mole⁻¹ cm.⁻¹) and concentrations a, b, and x (mole/l.) defined according to the scheme:

$$\begin{array}{cccc} & \varepsilon_1 & \varepsilon_2 & \varepsilon_3 & \varepsilon_4 \\ \text{RAuPPh}_3 + \text{HgXY} \longrightarrow \text{XAuPPh}_3 + \text{RHgY} \\ (t = 0) & a & b & 0 & 0 \\ (t = t) & a - x & b - x & x & x \end{array}$$

and on the assumption that the Beer-Lambert law is obeyed by all solute species, the extent of reaction x at time t is given in terms measured absorbances, A_0 and A_t , by

$$x = (A_0 - A_t)/(\varepsilon_1 + \varepsilon_2 - \varepsilon_3 - \varepsilon_4)l$$

The wavelengths used depended on a and b, and on the nature of X and Y, and were in the region 275-300 m μ .

Solutions of the reactants and products were checked with respect to their conformity with the Beer-Lambert law, and then the extinction coefficients were determined (Table 17). When the extinction coefficient of a product

TABLE 17

Extinction c	oefficients (ε	in 1. mc	ole. ⁻¹ cm.	-1)	of reactants
and	products in	various	solvents	at	25°

	εat	275 mu	280 mu	290 mu	300 mu
In dioxan					
MeAuPPh,		3510	1690	256	32
EtAuPPh ₃		4180	3200	1750	620
BuC(CN)(ČO,Et)AuPPh ₂	3300	1270	175	72
AuPPh ₂ Í`	,	3500	1320	244	37
AuPPh, Br		2050	283	8	3
AuPPh ₃ Cl		1880	219	~ 0	0
AuPPh ₃ OAc		2200	352	18	0
HgI,		~ 5000	4520	2960	1640
HgBr,		89	52	29	10
Hg(OAc), a		24	11	6	0
Hg(NO ₃),		450	290		
MeHgI		145	78	18	2
MeHgBr		9	5	2	0
EtHgI		295	183	68	30
EtHgBr		12	8	4	2
Et₂Hg		~ 110	~ 60	~ 10	~1
HeCl Matt	CI MATTA		L-NO M	. II TAT	T. Cl

HgCl₂, MeHgCl, MeHgOAc, MeHgNO₃, Me₂Hg, EtHgCl, and EtHgOAc did not absorb at these wavelengths.

In dioxan-water $(4:1 v/v)$)			
MeAuPPh ₃	3320	1430	180	23
AuPPh ₃ I	3450	1250	170	35
AuPPh ₃ Br	2000	275	6	3
AuPPh ₃ Cl	2020	260	~ 0	0
AuPPh ₃ OAc	1980	300	~ 0	0
MeHgl	160	98	30	10
MeHgBr	41	27	11	4

MeHgCl, MeHgOAc, MeHgNO₃, and Me₂Hg did not absorb at these wavelengths.

In dimethyl sulphoxide

MeAuPPh3	3370	1750	226	~ 30
EtAuPPha	4240	3200	1470	614
BuC(CN)(CO ₂ Et)AuPPh ₃	3380	1480	130	~ 20
CHAc ₂ AuPPh ₃	4600	2800	1600	1100
AuPPh ₃ I	3380	1690	210	50
AuPPh ₃ Br	2180	780	32	0
AuPPh ₃ Cl	2030	600	18	0
AuPPh ₃ OAc	2440	830	50	0
MeHgl	280	172	84	63
MeHgBr	285	190	65	

MeHgCl, MeHgOAc, MeHgNO₃, and Me₂Hg did not absorb at these wavelengths.

In dimethyl sulphoxide-di	ioxan (1 :	9 v/v)	
BuC(CN)(CO2Et)AuPPh3	3300	1330	170
AuPPh ₃ Cl	2000	295	0
^a Solvent contai	ned ~ 10	- ³ м-acetic	acid.

could not be determined, for instance that of triphenylphosphinegold(I) nitrate, which was not isolated in the pure state, it was calculated from the absorbance at the cessation of chemical change, on the assumption that the reaction had then proceeded to stoicheiometric completion. When all the extinction coefficients were known, the final absorbance was used as a check that the reaction was indeed stoicheiometrically complete.

Figures 1, 2, and 3 show samples of the principal u.v. absorption spectra in dioxan on which we relied. The

FIGURE 1 U.v. absorption spectra of organogold(I) compounds and of alkylmercuric salts in dioxan (c 3·33 × 10⁻⁴M, l 1 cm.):
1, EtAuPPh₃; 2, MeAuPPh₃; 3, BuC(CN)(CO₂Et)AuPPh₃;
4, EtHgI; and 5, MeHgI

300

λ(mμ)

325

350

spectra in the other solvents used in the kinetic studies were very similar. The other methylmercuric and ethylmercuric salts involved in the kinetic runs, and also mercuric chloride, had negligible absorbances at the wavelengths of the Figures.

All u.v. spectral measurements were made with an SP 500 spectrophotometer. Kinetic runs by the 'direct' method were done in flasks from which samples were taken for spectrophotometric measurement, when the time of half-change was longer than 1 hr. Faster runs were done in a thermostatted spectrophotometer cell of path-length 4 cm.

 $0.5 - \frac{1}{275} \frac{1}{300} \frac{1}{325} \frac{1}{350}$ RE 2 U.y. absorption spectra of organogold(1) salts

FIGURE 2 U.v. absorption spectra of organogold(I) salts in dioxan ($c 3.33 \times 10^{-4}$ M, l 1 cm.): 1, AuPPh₃I; 2, AuPPh₃OAc; 3, AuPPh₃Br; and 4, AuPPh₃Cl

In either case reactants were brought to temperature before being mixed. The times at which readings of the faster runs were taken were recorded to 0.1 sec. by an English Numbering Machines counting unit; and this enabled timeintervals to be specified to within 1 sec.

The 'direct' method was inapplicable to reactions in certain solvents, notably acetone, because of interference by the absorption spectrum of the solvent.

The 'partition' method. The reactions were followed by adding samples (5 ml.) of the reaction solution to a mixture of carbon tetrachloride (20 ml.) and air-free aqueous 0.04M-potassium iodide (10 ml.). The absorbance at 323 mµ, due



FIGURE 3 U.v. absorption spectra of mercuric salts in dioxan (c $3\cdot33 \times 10^{-4}$ M, l 1 cm.): 1, HgI₂; 2, Hg(NO₃)₂; 3, HgBr₂; and 4, Hg(OAc)₂

essentially to tetraiodomercurate ion, measured the surviving mercuric salts HgX_2 . There was also a small absorbance due to the initial presence of RHgX. For each solvent, the absorbances measuring mercuric bromide and methylmercuric bromide were measured as functions of the concentrations of the salts, and, from the slopes of the straight-line graphs obtained, 'apparent' extinction coefficients (*i.e.* uncorrected for the dilution resulting from the treatment with potassium iodide solution) were calculated (Table 18).

When dioxan or aqueous dioxan was the solvent, it was difficult to avoid the formation of a small amount of iodine on adding the reaction sample to the quenching mixture. This contributed, as tri-iodide ion, to the absorbance. The needed correction for this was small, and was determined by utilising certain characteristics of the absorption spectra of HgI_4^{2-} and I_3^{-} . The absorbance of HgI_4^{2-} passes through a maximum at 323 mµ and is zero at 400 mµ. The absorbance of I_3^{-} is finite at both wave-lengths, but is 2.01 times as great at 323 mµ as at 400 mµ. Thus, by measuring the absorbance of each treated kinetic sample at both wave-lengths, one could make the connection.

The progress of reaction was computed from the formula given on p. 287, in which $\varepsilon_1 = \varepsilon_3 = 0$ and $\varepsilon_2 \gg \varepsilon_4$.

The 'partition' method was found to be satisfactory when the gold complexes were methyl(triphenylphosphine)-

2.0

1.5

1.0

0.5

0

2.0

1.5

1-C

275

gold(I), ethyl(triphenylphosphine)gold(I), and trimethyl-(triphenylphosphine)gold(III), but not when it was 1-cyano-1-ethoxycarbonylpentyl(triphenylphosphine)gold(I). With this reactant, readings by the ' partition ' method remained constant, although readings by the ' direct ' method showed that reaction was going on. Our hypothetical explanation

TABLE 18

Apparent (cf. text) extinction coefficients (l. mole.⁻¹ cm.⁻¹ at 323 mµ) of HgX₂ and MeHgX₂ after treatment with excess of KI

Solvent	HgX_2	MeHgX
Dioxan	6600	280
Dioxan-water $(9:1 v/v)$	6310	270
Dioxan-water $(4:1 v/v)$	6260	260
Dioxan-acetic acid $(19:1 v/v)$	6600	400
Acetone	7190	320
Dimethylformamide	5630	263
Dimethyl sulphoxide	5960	244

of this is that, in the presence of the electronegatively substituted alkyl group the formed mercurial is unstable, and loses its mercury by hydrolysis, to give eventually the tetraiodomercurate ion.

Rate constants. The mean rate constants of the kinetic runs are given in Tables 1, 3-7, 9, 10, 12-14, and 16. Each constant was derived from the run as a whole by arranging suitable straight line plots of functions of measured reaction concentrations against the time. The linearity of the plots formed part of the evidence of the kinetic form under observation, as also did the consistency of the constants at different initial concentrations of reactants. As illustrations of results by the 'direct' and ' partition' methods, their levels of accuracy, the two types of kinetic form, and the procedures of calculation, Tables 19-21 are given.

TABLE 19

Second-order reaction of methyl(triphenylphosphine)gold(I) with mercuric bromide in dioxan at 24.7°; 'direct' method (cf. Table 1)

a= Initial $[{\rm MeAuPPh_3}]=0.40\times 10^{-4}$ mole/l. b= Initial $[{\rm HgBr_2}]=0.40\times 10^{-4}$ mole/l.

Time	x	Reaction	1/(a - x)
(min.)	(10 ⁻⁴ mole/l.)	(%)	(10^{4} l./mole)
0.0	0.000	0.0	2.50
0.6	0.052	13.0	2.88
1.0	0.089	$22 \cdot 3$	3.21
1.5	0.132	33.0	3.74
$2 \cdot 0$	0.157	39.3	4.11
$3 \cdot 0$	0.201	50.3	5.02
4 ·0	0.231	57.8	5.92
5.0	0.255	63 ·8	6.90
6 ∙0	0.271	67.8	7.75
8.0	0.292	73.0	9.26
10.0	0.312	78.0	11.4
12.0	0.323	80.8	13.0
15.0	0.336	84.0	13.6
60.0	0.375	93.8	

For second-order reactions, the linear plot is of 1/(a - x) against t, in case a = b, the gradient being k_2 , or of $\log_{10}\{(a - x)/(b - x)\}$ against t, if $a \neq b$, the gradient being $k_2(a - b)/2.303$. For first-order reactions, the plot is of $\log_{19}(a - x)$ vs. t, with the gradient $-k_1/2.303$. The linear plots resulting from Tables 19–21 are not reproduced, but the figures are left ready for plotting.

Miscellaneous.—Infrared spectra were obtained by use of a Perkin-Elmer 337 recording spectrophotometer for the range 4000—400 cm.⁻¹ and a Grubb-Parsons DM2 instrument for the range 400—200 cm.⁻¹. Spectra were taken of

TABLE 20

Second-order reaction of methyl(triphenylphosphine)gold(I) with mercuric bromide in dioxan at 24.7°; ' partition ' method (cf. Table 1)

a = Initial	$[MeAuPPh_3] = 0.25$	imes 10 ⁻⁴	mole/l.	b = Initial
$[HgBr_2] = 0.2$	5×10^{-4} mole/l.			

x	Reaction	1(a - x)
(10 ⁻⁴ mole/l.)	(%)	(104 l./mole)
0.000	0.0	4.00
0.042	16.7	4.81
0.085	34.0	6.06
0.111	44.4	7.19
0.139	$55 \cdot 6$	9.01
0.123	61.2	10.3
0.169	67.6	12.3
0.186	74.4	15.6
0.249	99.6	
	$\begin{array}{c} x \\ (10^{-4} \text{ mole/l.}) \\ 0.000 \\ 0.042 \\ 0.085 \\ 0.111 \\ 0.139 \\ 0.153 \\ 0.169 \\ 0.186 \\ 0.249 \end{array}$	$\begin{array}{cccc} & & {\rm Reaction} \\ (10^{-4} {\rm mole}/{\rm l.}) & (\%) \\ 0{\cdot}000 & 0{\cdot}0 \\ 0{\cdot}042 & 16{\cdot}7 \\ 0{\cdot}085 & 34{\cdot}0 \\ 0{\cdot}111 & 44{\cdot}4 \\ 0{\cdot}139 & 55{\cdot}6 \\ 0{\cdot}153 & 61{\cdot}2 \\ 0{\cdot}169 & 67{\cdot}6 \\ 0{\cdot}186 & 74{\cdot}4 \\ 0{\cdot}249 & 99{\cdot}6 \end{array}$

TABLE 21

First-order reaction of 1-cyano-1-ethoxycarbonylpentyl-(triphenylphosphine)gold(1) with methylmercuric chloride in dimethyl sulphoxide-dioxan (1:9 v/v)at $24 \cdot 7^{\circ}$; 'direct' method (cf. Table 13)

a= Initial [BuC(CN)(CO_2Et)AuPPh_3] = 0.25 \times 10^-4 mole/l. b= Initial [MeHgCl] = 0.25 \times 10^-4 mole/l.

Time	x	Reaction	
(sec.)	(10 ⁻⁴ mole l.)	(%)	$6 + \log_{10} (a - x)$
0	0.000	0.0	1.40
17	0.018	$7 \cdot 2$	1.36
31	0.071	28.4	1.25
51	0.101	40.4	1.17
78	0.125	50.0	1.10
113	0.149	59.6	1.04
149	0.167	66.8	0.92
179	0.185	74.0	0.81
216	0.208	$83 \cdot 2$	0.62
250	0.215	86 ·0	0.54
310	0.226	90.4	0.38
1200	0.25	100	

Nujol mulls between potassium bromide plates in the range 4000-400 cm.⁻¹, and between polythene plates in the range 400-200 cm.⁻¹.

All accurate measurements of u.v. spectra were made with a Unicam SP 500 spectrophotometer, but scans of the range 250—400 m μ were obtained with a Unicam SP 800 recording spectrophotometer.

Proton magnetic resonance spectra were determined with a Perkin-Elmer R-60 spectrometer, thermostatted to $33 \cdot 4^{\circ}$. Tetramethylsilane was used as an internal standard.

Molecular weights were determined in benzene with the aid of a Mechrolab Model 301A vapour-phase osmometer. Benzil in benzene was used for calibration.

Conductivities were determined at concentration c mole/l., and at 25°, with a Wayne-Kerr Universal Bridge B 221, in a cell having platinum electrodes of about 1 cm.² area about 1 cm. apart. The readings, when multiplied by the determined cell constant, gave specific conductivities Kohm⁻¹ cm.⁻¹, and hence $\Lambda_m = 1000 K/c$ ohm⁻¹ cm.².

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