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Cyclic voltammetry of heterocyclic Au(I) and Au(III) carbene complexes

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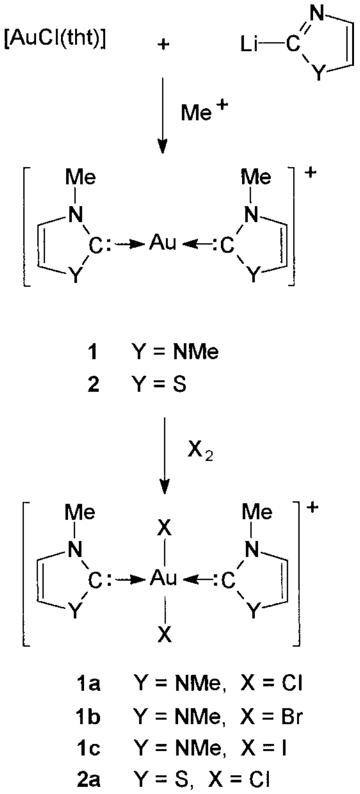
Abstract

Imidazolinylidene and thiazolinylidene complexes of gold in acetonitrile have been investigated by cyclic voltammetry. No Au(II) intermediate was observed during the redox reactions and Au(III) compounds form only by oxidative addition of halogens. © 1998 Elsevier Science S.A.

Keywords: Acetonitrile; Carbene; Cyclic voltammetry

1. Introduction

In contrast to four and six coordinated compounds such as [Au(I)(dppe)$_2$]PF$_6$ [1], [Au(II)([9]aneS$_3$)$_2$][BF$_4$]$_2$ ([9]aneS$_3$ = 1,4,7-trithiacyclononane) [2,3] and [Au(III)(1,2-S$_2$C$_6$H$_4$)$_2$][Bu$_4$N] [4], relatively few investigations involving the electron-transfer properties of linear organogold complexes have been undertaken [5–7]. In this paper, the cyclic voltammetry of cationic organogold bis(imidazolinylidene) and bis(thiazolinylidene) compounds (i.e., azolyl-derived carbene complexes) are reported. Although this type of carbene complex has recently received increased attention [8–12] especially with the advent of Arduengo-type free carbenes [13–15], the electrochemistry of only imidazolinylidene complexes of the type L(CO)$_3$M{CNMeCH=CHNMe}$_2$ (M = W, Mo; L = CO, PPh$_3$, PEt$_3$, CN-*c*-C$_6$H$_{11}$, pyridine) [16,17] has been examined. The homoleptic, heterocyclic carbene compounds of Au(I) used in this investigation were prepared earlier via our simple transmetallation-alkylation approach. Subsequent oxidative addition with halogens yielded the corresponding Au(III) complexes (Scheme 1) [18]. Since Au(II) is a rare oxidation state [19], we were particularly interested to determine whether such an intermediate could be detected during



Scheme 1.

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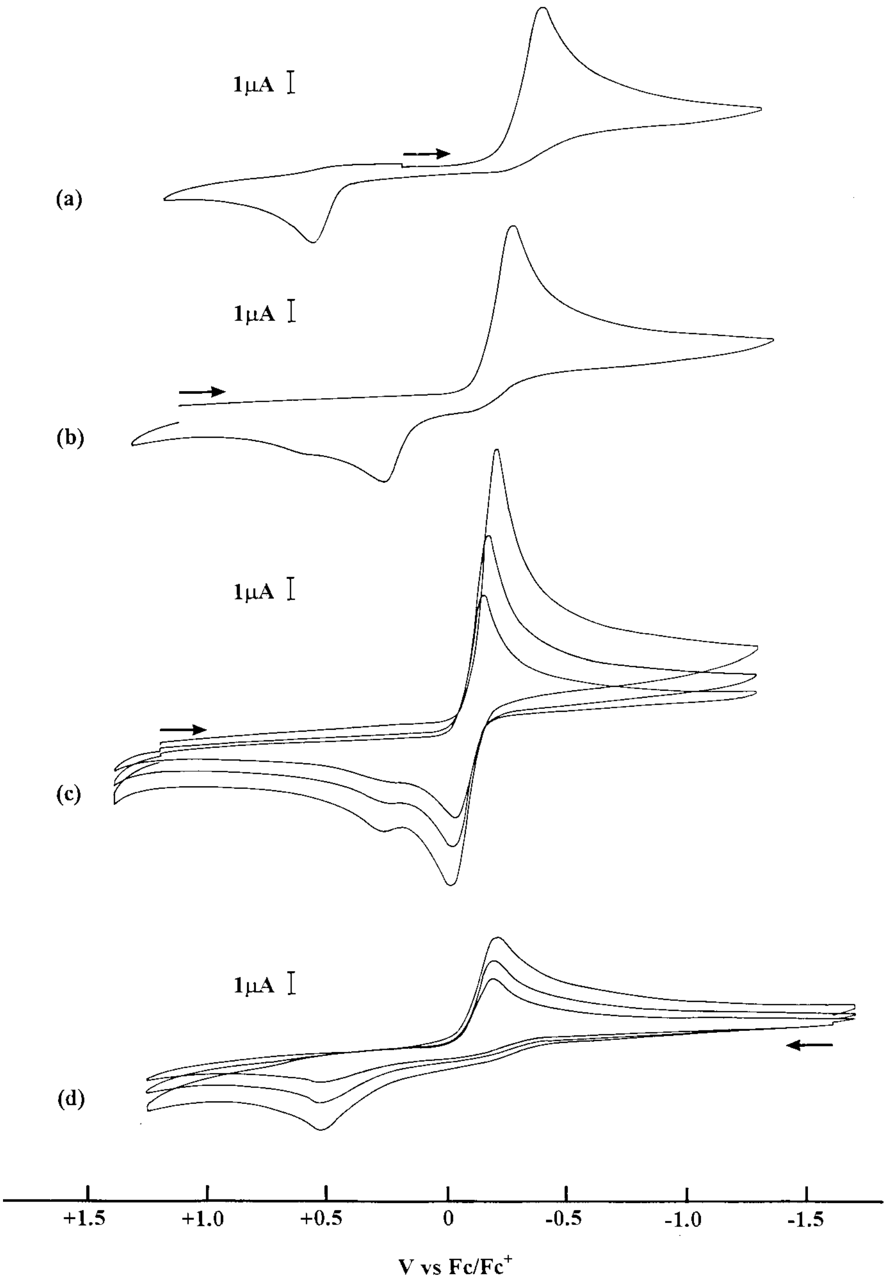

Fig. 1. Cyclic voltammograms in CH_3CN/0.1 M TBAP at 298 K of (a)$[Au\{CNMeCH{=}CHNMe\}_2Cl_2]CF_3SO_3$ **1a** at 100 mV/s; (b)$[Au\{CNMeCH{=}CHNMe\}_2Br_2]CF_3SO_3$ **1b** at 100 Mv/s; (c)$[Au\{CNMeCH{=}CHNMe\}_2I_2]CF_3SO_3$ **1c** at 50, 100 and 200 Mv/s; (d)$[Au\{CNMeCH{=}CHS\}_2Cl_2]CF_3SO_3$ **2a** at 50, 100 and 200 Mv/s.

the redox reactions. The electrochemistry of gold could be of pharmaceutical relevance.[1]

2. Results and discussion

The experiments were performed in an inert atmosphere. The solvent system was acetonitrile and tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte. Redox potentials were measured at a platinum working electrode since mercury electrodes are of limited use for studies on gold compounds due to transmetallation reactions that occur between metallic mercury and the gold complexes [19].

Cyclic voltammograms of solutions of the Au(III) imidazolinylidene compounds **1a**, **b**, **c** and the thiazolinylidene complex **2a** (Scheme 1) are displayed in Fig. 1. Each of these voltammograms exhibits one reduction wave with peak potentials at -0.38, -0.26, -0.17 and -0.20 V {vs. Fc/Fc^+ (Fc = ferrocene) in MeCN, 0.1 M TBAP}, respectively. One oxidation wave was exhibited in the carbene(chloro) complexes (**1a**,

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[1] See Ref. [1].

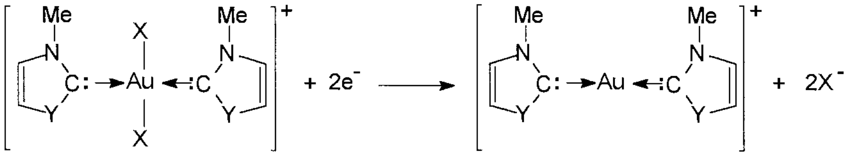
Table 1
Electrochemical data[a] of heterocyclic gold carbene complexes

Complex	X	E_{pc} (V) $[Au(III)/Au(I)]$	E_{pa} (V) $[X^-/0.5X_2^0]$	E_{pa} (V) $[X_3^-/1.5X_2^0]$
1a	Cl	-0.38	0.57	–
1b	Br	-0.26	0.27	0.59
1c	I	-0.17	0.03	0.26
2a	Cl	-0.20	0.53	–

[a] From cyclic voltammetry in $CH_3CN/0.1$ M TBAP. Potentials in V vs. $Fc^{+/0}$; scan rate 100 Mv/s. E_{pc} = cathodic peak potential. E_{pa} = anodic peak potential.

$E_{pa} = 0.57$ V; **2a**, $E_{pa} = 0.53$ V), whereas the iodo- and bromo-analogues each exhibited two oxidation waves (**1b**, $E_{pa} = 0.27$ and 0.59 V; **1c**, $E_{pa} = 0.03$ and 0.26 V). See Table 1 for electrochemical data of heterocyclic gold carbene complexes.

We interpret the cathodic currents shown in Fig. 1 in terms of reduction of the four-coordinated square-planar Au(III) carbene complexes **1a–c** and **2a** to their two-coordinated linear Au(I) counterparts complexes **1** and **2** (Eq. 1). The differences in the reduction potentials of the three halo compounds are insignificant. The reduction reaction (Eq. 1) is a two-electron process, established with coulometry indicating the uptake of 1.84 electrons per gold atom for complex **1a**. An electrochemical study of $[Au(I)(dppe)_2]PF_6$ [1] previously also indicated that a two-electron transfer couples the stable redox pair $[Au(I)(dppe)_2]^+/[Au(III)(dppe)_2]^{3+}$. No Au(II) intermediate could be detected by us within the time window of the applied method. This is not surprising, however, as this oxidation state of gold is mostly stabilised in dinuclear compounds, by coordination to nitrogen or sulfur [2,3,20]. We do not, however, completely exclude the existence of a Au(II) intermediate, as it could react extremely fast.



(1)

The anodic potential in the cyclic voltammograms in Fig. 1 closely resemble those obtained for the respective halide ions in the ammonium salts $[Et_3(CH_2Ph)N]Cl$, $[Bu_4N]Br$ and $[Bu_4N]I$ (Fig. 2), suggesting that they are due to halide rather than gold oxidation. In addition, the Au(III) imidazolinylidene complex **1a** does not exhibit an oxidation wave when an anodic scan is obtained first (Fig. 3a), indicating that the anodic peak in Fig. 1a is due to chloride ions formed during the reduction of the Au(III) imidazolinylidene complex.

The cyclic voltammograms of the (chloro)imidazolinylidene and -thiazolinylidene complexes **1a** and **2a**, therefore, exhibit single peak anodic waves (Fig. 1a and 1d) corresponding to the simple oxidation of the chloride ion (Eq. 2). The more complicated waves of the bromo and iodo counterpart complexes **1b** and **1c**, therefore, can be ascribed to a two-step oxidation of these halide ions in acetonitrile (Eqs. 3 and 4). Similar assignments were made from voltammetric studies of the oxidation of iodide [21,22] and bromide [23] ions in acetonitrile by Popov and Geske. Our results are also corroborated by a study on the redox behaviour of di(cyano)di(halo)aurate(III) complexes in acetonitrile [24]. The authors obtained similar results to ours, but interpret them differently by postulating the existence of relatively stable intermediates (albeit unknown) for the bromide and iodide derivatives. Since such an intermediate would have to contain Au(II), a far less common oxidation state of gold [20], it is likely that the two-oxidation waves in the cyclic voltammogram of $Au(III)Br_2(CN)_2$ are not due to an intermediate, but to a similar two-step oxidation of Br^- to Br_2 in acetonitrile (Eqs. 3 and 4).

$$2Cl^- \longrightarrow Cl_2 + 2e^- \tag{2}$$

$$3X^- \longrightarrow X_3^- + 2e^- \tag{3}$$

$$2X_3^- \longrightarrow 3X_2 + 2e^- \tag{4}$$

The oxidative addition reactions in Scheme 1 proceeded almost quantitatively, yet cyclic voltammograms of the Au(I) imidazolinylidene complex **1** (Fig. 3b) and the thiazolinylidene compound **2** showed no oxidation or reduction waves over a potential range from $+1.5$ V to -2.4 V (vs. Fc/Fc^+), thus confirming older comparable work where no oxidation of $[Au(I)(CH_3CN)_2]ClO_4$ in acetonitrile [25] occurs on anodic scans up to $+2.8$ V vs. SCE (saturated calomel electrode) [5,6]. As demonstrated in Fig. 3c, cyclic voltammetry of the carbene(chloro) Au(I) complex **1** in the presence of the salt $[Et_3PhCH_2N]Cl$ shows that a cathodic wave is only visible after scanning through the oxidation wave corresponding to (Eq. 2). We thus conclude that the Au(III)

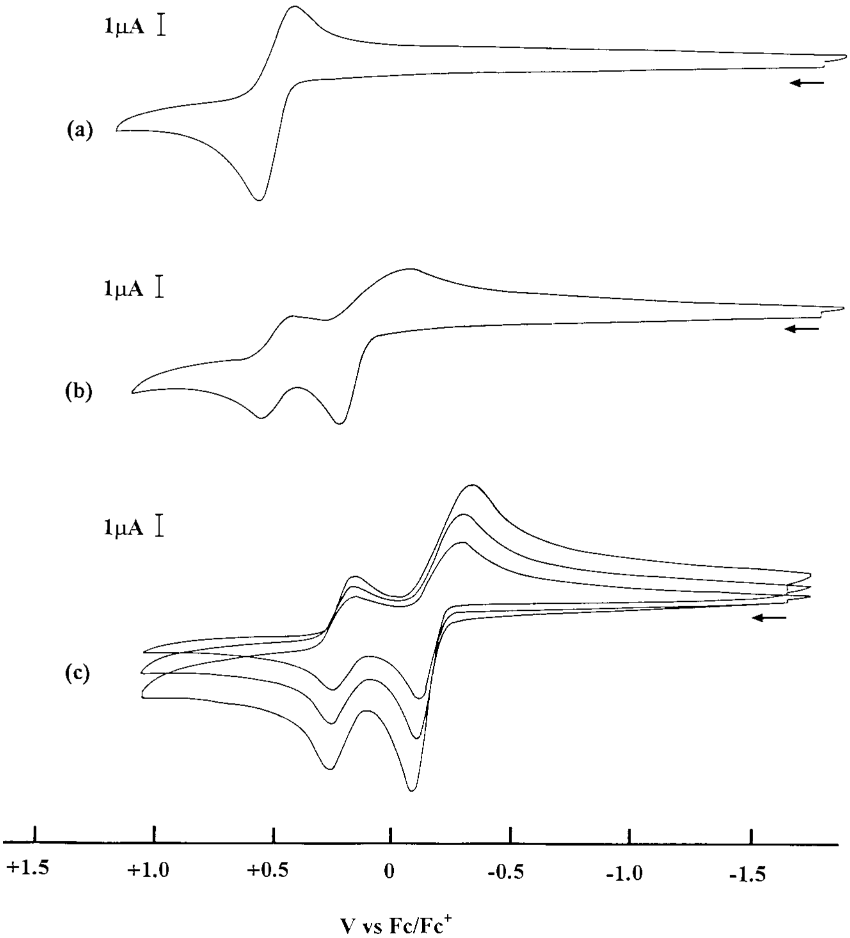


Fig. 2. Cyclic voltammograms in $CH_3CN/0.1$ M TBAP at 298 K of (a) $[Et_3(CH_2Ph)N]^+Cl^-$ at 100 Mv/s; (b) $[NBu_4]^+Br^-$ at 100 Mv/s; (c)$[NBu_4]^+I^-$ at 50, 100 and 200 Mv/s.

carbene complex **1a** was obtained by chemical oxidative addition of the electrochemically generated halogen to **1**. It is therefore obvious why a cathodic wave representing the reduction of Cl_2 to Cl^- is absent from the cyclic voltammogram (the generated Cl_2 is consumed in an oxidative addition to **1**). Since, no evidence of a solvated species $[Au\{CNMeCH{=}CHY\}_2(MeCN)_2]^{3+}$ (Y = NMe, S) was found within the potential window of the applied method, it is very likely that the X^--ligands are necessary to stabilise the Au(III)-centres in **1a**, **b**, **c** and **2a**. Since the reduction reaction involves both a change in the coordination number and geometry, it results in an 'inner sphere' change, in contrast to an 'outer sphere' mechanism that has been proposed for the redox couple $[Au(I)(dppe)_2]^+/[Au(III)(dppe)_2]^{3+}$ [26–29].

Table 2 lists electrochemical data of $[NEt_3CH_2C_6H_5]Cl$, $[NBu_4]Br$ and $[NBu_4]I$.

3. Conclusion

Our electrochemical investigation of Au(I) and Au(III) bis(carbene) complexes confirmed the efficiency of nucleophilic Lappert-type carbene ligands in stabilising different oxidation states of metals, as highlighted in a recently published report about the advantages of imidazolinylidene-coordinated Heck-catalysts [9]. Unlike the ligands in some (phosphine)Au(I) complexes

Table 2
Electrochemical data[a] of $[NEt_3CH_2C_6H_5]Cl$, $[NBu_4]Br$ and $[NBu_4]I$

Complex	E_{pa} (V) $[X^-/0.5X_2^0]$	E_{pc} (V) $[X^-/0.5X_2^0]$	E_{pa} (V) $[X_3^-/1.5\ X_2^0]$	E_{pc} (V) $[X_3^-/1.5X_2^0]$
$[NEt_3CH_2Ph]^+Cl^-$	0.58	0.43	–	–
$[NBu_4]^+Br^-$	0.19	−0.07	0.51	0.39
$[NBu_4]^+I^-$	−0.13	−0.29	0.23	0.15

[a] From cyclic voltammetry in $CH_3CN/0.1$ M TBAP. Potentials in V vs $Fc^{+/0}$; scan rate 100 Mv/s. E_{pc} = cathodic peak potential. E_{pa} = anodic peak potential.

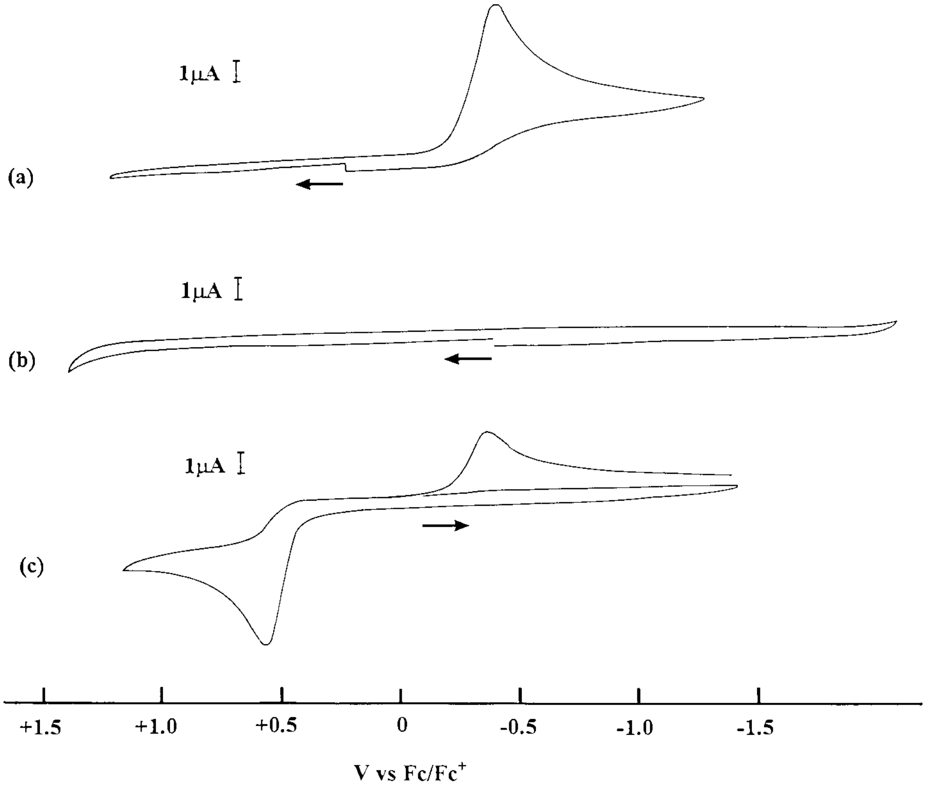


Fig. 3. Cyclic voltammograms in CH_3CN/0.1 M TBAP at 298 K of (a)[Au{CNMeCH=CHNMe}$_2$Cl$_2$]CF$_3$SO$_3$ **1a** at 100 Mv/s (first: anodic scan); (b)[Au{CNMeCH=CHNMe}$_2$]CF$_3$SO$_3$ **1** at 100 Mv/s; (c)[Au{CNMeCH=CHNMe}$_2$]CF$_3$SO$_3$ **1** in presence of 0.2 M [Et$_3$PhCH$_2$)N]$^+$Cl$^-$ at 100 Mv/s (after scanning the oxidation potential of ($Cl^- - e^- \rightarrow 0.5Cl_2^0$) the reduction of **1a** becomes observable).

[30], the carbene ligands do not dissociate from the metal upon oxidation to Au(III).

No evidence for a Au(II) intermediate was found for the overall two-electron reduction. The oxidation of Au(I) azolyl-derived bis(carbene) complexes and other linear two-coordinated Au(I) compounds depends on the presence of a generated free halogen in solution. In recent research, the role of free halogen in the oxidation of gold(I) compounds [6,30] and of gold(0) [3,5] has been discussed but, apart from the work of Pesic and Sergent [31], has not been seriously examined. Pesic and Sergent studied the dissolution of gold with bromine and concluded that an electrochemical/chemical mechanism is involved where $AuBr^-$ is produced electrochemically and $AuBr_4^-$ chemically. Since no solvated species like [Au(III){CNMeCH=CHNMe}$_2$(MeCN)$_2$]$^{3+}$ were detected in the present study, the X^--ligands seem to play an essential role in stabilising the positively charged Au(III)-centre which shows great affinity for halide ions [1,5,30].

4. Experimental

4.1. Electrochemical procedures

Current rotating disc electrode (RDE) and cyclic voltammetry were employed. A PAR 175 universal programmer, a PAR 173 potentiostat fitted with a PAR 176 current follower and connected to a HP 7045A X-Y recorder, were used for the RDE and cyclic voltammetric measurements. All measurements were carried out under an argon atmosphere in acetonitrile. The solvent was purified by refluxing over P_2O_5, followed by at least two fractional distillations through a 1 m glass-helices vacuum-jacketed column. The supporting electrolyte for all solvents was Bu_4NClO_4 (TBAP) present in 0.1 M concentration; the salt was purified by repeated crystallisations from ethanol/water mixtures and dried at 80°C and 10^{-2} mmHg. The purity of the solvent was checked by running a blank voltammogram before each measurement. Compound concentrations were 0.001 ± 0.0001 M.

All the experiments employed a conventional three-electrode configuration, with a platinum spiral wire auxiliary electrode and a reference electrode comprising a AgCl-coated Ag wire both dipped in a 0.1 M solution of Bu_4NClO_4 in acetonitrile and separated from the electrolyte solution by a fine frit. All potentials are quoted relative to the [ferrocene]$^{+/0}$ couple [32]. Ferrocene was usually added to the solution under investigation at the end of each experiment as an internal standard to check the stability of the reference electrode. In cases where this was not possible, e.g. when oxidation waves from the sample interfered with that of the [ferrocene]$^{+/0}$ couple, ferrocene was run immediately before or after the experiment under identical conditions. No compensation for IR drop losses was made. The working electrode was a platinum disc electrode (0.013 cm^2) which was rotated at 500 rpm for the voltammograms. Its surface was polished with 2–6 μm diamond paste until no scratches were observed at tenfold magnification. Before being inserted into the solution the electrode was rinsed with acetone and distilled water and dried in a warm dry air stream. Measurements were made at 25 ± 2°C, temperature control being achieved by careful operation of an airconditioning unit in a closed laboratory.

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