Kurze Mitteilungen

Maximalumfang: 6 Schreibmaschinenseiten (alles inbegriffen). Bis zum 15. des Monats bei der Redaktion eingehende Manuskripte können günstigstenfalls am 15. des folgenden Monats veröffentlicht werden.

A New Class of Nucleosides. Synthesis, Reactivity and Biological Activity of Keto-Hexose Nucleosides*

Summary

Direct oxydation of sterically hindered hexosyl purines led to keto-hexosylpurines, important synthetic intermediates. The first unsaturated keto-nucleosides have also been obtained by acetylation of the corresponding keto-hexosyl purines. Most of the keto-hexosyl purines especially those deriving from 6-deoxyhexoses exhibit cell growth inhibitory activity whereas the parent nucleosides, before oxidation, are inactive.

Synthesis

Contrary to the synthesis of nucleosides containing hexuloses which has been realized since 1959[1], that of the first hexosulosyl purine has been reported only in 1970[2]. The use of fusion procedures to obtain keto-nucleosides was prooved to be inadequate in the case of hexosuloses because of the difficulties to acetylate keto-hexoses. β-elimination reactions occur indeed during the acetylation of these keto-hexoses leading to various unsaturated compounds[3]. This prompted us to investigate the possibility of employing an oxidizing system directly on a partially protected hexosyl purine.
The system DMSO/DCC–CF_3COOH/Pyridine previously used by Moffatt *et al.* to obtain pentosulosyl pyrimidines[4], permitted this oxidation with satisfactory yields. On the other hand the DMSO/Ac_2O system[5] prooved to be unsuitable since side-reactions occur preferentially leading to acetates[6] or to methyl thiomethylether-nucleosides[7, 8].

A—Use of the DMSO/DCC–CF_3COOH/Pyridine system

a) 7 (3′-O-Methyl-β-D-arabino-hexopyranosulosyl) theophylline (**1**)[2]. This keto-nucleoside which constitutes the first example of a keto-hexosyl purine, has been obtained by oxidation of 7 (4′,6′-O-benzylidene-3′-O-methyl-β-D-arabino-hexopyranosyl) theophylline (**2**) after modification of the procedure[2] and acid elimination of benzylidene group.

b) 7 (6′-Deoxy-β-L-lyxo-hexopyranosulosyl) theophylline (**3**)[6] [7 (2′-keto-β-L-fucopyranosyl) theophylline]. This is the first keto-deoxynucleoside which was synthetized in 1971[6] by direct oxidation of 7 (6′-deoxy 3′,4′-O-isopropylidene-β-L-galactopyranosyl) theophylline (**4**) and mild acid hydrolysis of the isopropylidene group.

c) 7 (6′-Deoxy-α-L-lyxo-hexopyranos-4′-ulosyl) theophylline (**5**)[8] [7 (4′-keto-α-L-rhamnopyranosyl) theophylline]. This 4′-keto-nucleoside constitutes a key indermediate of 4′-branched chain sugar-nucleosides. It has been obtained by oxidation of 7 (6′-deoxy-2′,3′-O-isopropylidene-α-L-mannopyranosyl) theophylline (**6**) and acid hydrolysis of the protected group. This oxidation was found to be much more rapid than those of the foregoing hexosyl purines.

d) 6-Chloro 9-(6′-deoxy-β-L-lyxo-hexopyranosulosyl) purine (**7**)[10] and 6-chloro 9-(6′-deoxy-α-L-lyxo-hexopyranos-4′-ulosyl) purine (**8**)[8] were obtained by oxidation of respectively 6-chloro-9 (6′-deoxy 3′,4′-O-isopropylidene-β-L-galactopyranosyl) purine and 6-chloro-9 (6′-deoxy-2′, 3′-O-isopropylidene-α-L-mannopyranosyl) purine and mild acid hydrolysis of protecting groups.

e) 7 (3′-O-Acetyl 4′,6′-dideoxy-β-L-glycero-hex-3-enopyranosulosyl) theophylline (**9**)[9] and 6-chloro 9-(3′-O-acetyl-4′, 6′-dideoxy-β-L-glycero-hex-3-enopyranosulosyl) purine (**10**)[10] constitute the first examples of unsa-

* Received September 17, 1974.

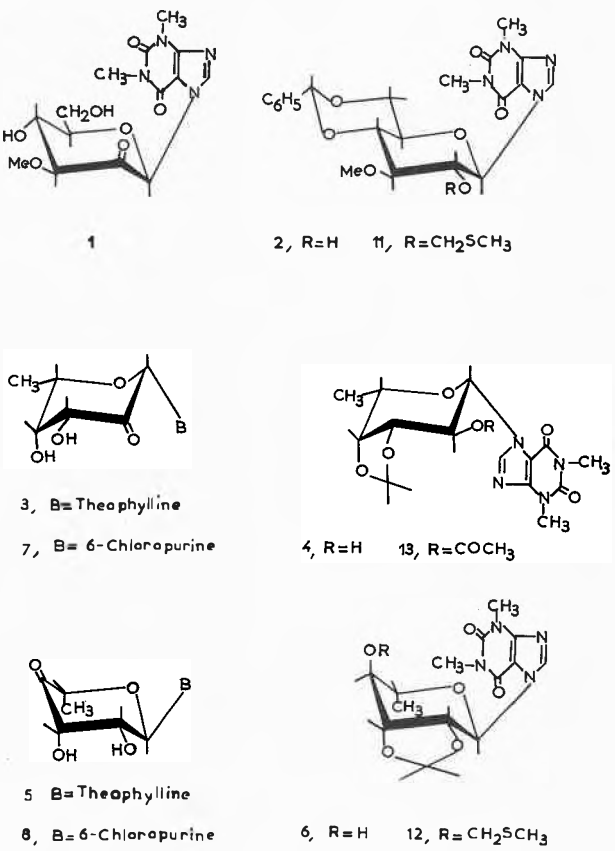

Fig. 1

turated keto-nucleosides. They have been obtained by acetylation of the corresponding keto-nucleosides (**3**) and (**7**) followed by β-elimination of an acetyl group.

B—Use of the DMSO/Ac_2O system

a) 7 (4′,6′-O-Benzylidene 3′-O-methyl 2′-O-methylthiomethyl-β-D-glucopyranosyl) theophylline (**11**)[7] and 7 (2′,3′-O-isopropylidene 4′-O-methylthiomethyl-α-L-rhamnopyranosyl) theophylline (**12**)[8], are the first isolated methylthiomethylether derivatives in the nucleoside field. They have been obtained pure only after sodium borohydride reduction of the mixtures containing keto-nucleosides[7].

b) 7 (2′-O-Acetyl 3′,4′-isopropylidene-β-L-fucopyranosyl) theophyline (**13**)[6] was rapidly formed in the DMSO/Ac_2O mixture and has been crystallized from ethanol.

Behavior in alkaline medium

In contrast to the pentosulosyl-pyrimidines which are instantaneously decomposed in alkaline medium[11], the hexosulosyl-purines are slowly degradated under the same conditions and very often with no concomitant glucosidic cleavage. The formation of intermediate compounds has been followed by spectrometric analysis and paper chromatography[12].

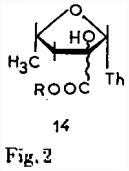

Fig. 2

It is of considerable interest to emphasize the isolation and characterization of the 7 (3′,6′-dideoxy 2′-C-carboxy-β-L-pentofuranosyl) theophylline intermediate (**14** compound formed during the degradation of 7 (3′,4′-O-isopropylidene 2′-keto-β-L-fucosyl) theophylline in methanolic sodium hydroxide. This branched-chain sugar nucleoside constitutes the first exemple of a "saccharinic" acid-nucleoside[12].

Acetylation; unsaturated keto-nucleosides

The first synthesis of unsaturated keto-nucleosides (**9**) and (**10**)[10,9] was accomplished by acetylation, with acetic anhydride in pyridine, of the recently described[6,10] keto-nucleosides, (**3**) and (**7**). This acetylation is followed by β-elimination of an acetyl group leading to the corresponding α, β-unsaturated keto-nucleosides.

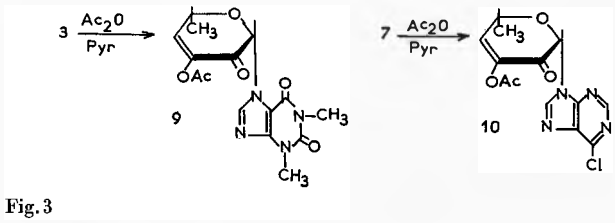

Fig. 3

These structures were assigned on the basis of the i.r. bands at 1440 cm^{-1} attributable to C=C, by the absence of signals for H-3′ in the n.m.r. spectra and the chemical shift of H-4′ (superimposed upon H-1′), characteristic of these conjugated molecules.

It is important to note finally that these nucleosidic enolones are key intermediates in a novel route to deoxynucleosides recently reported[13].

Stereospecific reduction

The metal hydride reduction of various saturated and unsaturated keto-nucleosides has been examined in some detail[13,14], since this provides additional novel routes to rare sugar nucleosides and deoxynucleosides.

Reduction of (**1**) and (**3**) in ethanol afforded the theophylline derivatives of, respectively, 3-methyl-β-D-mannose and 6-deoxy-α-L-talose which were isolated in high yield. These reductions appeared to be essentially stereospecific since no trace of the isomers were detected. The sterospecificity of the reduction from the less-hindered equatorial side of the carbonyl group parallels previous observations[15] with several hexopyranosulose derivatives.

Table I

		Configuration	Conformation	Biological activity 0,17 mg/ml	0,7 mg/ml
	7-Nucleosides				
Fucose	Fucosyl 7-theophylline	β-L	1C	O	O
	7 *(2'-keto* fucosyl) theophylline **(3)**	β-L	1C	++	+++
	7 *(2'-keto* fucosyl) theophylline unsaturated **(9)**	β-L	1C	+++	
	7 (4'-deoxy fucosyl) theophylline	β-L	1C	O	
Rhamnose	Rhamnosyl 7-theophylline	α-L	C1	O	O
	7 *(4'-keto* rhammosyl) theophylline **(5)**	α-L	C1	++	
	7 *(4'-keto* rhamnosyl) theophylline unsaturated	α-L	C1	+++	
3-Methyl Glucose	7 (4',6'-benzylidene 3'-methyl glycosyl) theophylline **(2)**	β-D	1C		+
	7 (2'-*keto* 3'-methyl glucosyl) theophylline **(1)**	β-D	1C		+
Branched-chain sugars	7 *(2'-C-nitromethyl* 3'-methyl glucosyl) theophylline	β-D	1C		+
	7 *(2'-C-nitromethyl* fucosyl) theophylline	β-L	1C		O
	7 (2'-C-carboxy fucosyl) theophylline **(14)**	β-L			±
	9-Nucleosides				
Fucose	6-chloro-9-(fucosyl) purine	β-L	1C	O	O
	6-chloro-9-(2'-*keto* fucosyl) purine **(7)**	β-L	1C	++	+++
	6-chloro-9-*(2'-keto* fucosyl) purine unsaturated **(10)**	β-L	1C	++++	
Branched-chain sugars	6-chloro-9-*(2'-C-nitromethylidene* fucosyl) purine	β-L	1C		++

In the case of the unsaturated structures **(9)** and **(10)** the sodium borohydride reduction in ethanol affords deoxynucleosides, the reaction appears to be more sterospecific than that of steroïdal enol-acetates[16], since none of the other isomers was detected. This stereospecificity may be explained by invoking nucleophilic addition to a conjugated system[13].

Nucleophilic additions

The addition of nitromethane to keto-nucleosides has been examined in order to obtain nucleosides of branched-chain nitromethyl and aminomethyl sugars[17, 18].

The direct addition of nitromethane in anhydrous methanol in the presence of sodium methoxide[17] to keto-nucleosides led respectively to the protected 2'-C-nitromethyl derivatives of 9-(β-D-lyxo-furanosyl) adenine and 7-(3'-O-methyl-β-D-hexopyranosyl) theophylline. In the case of 6-chloro-9-(3',4'-O-isopropylidene-β-L-fucosulosyl) purine, the condensation with nitromethane under the same conditions led to the corresponding 2'-C-nitromethylene derivative[18] formed by spontaneous dehydration of the nitromethyl intermediate in the reaction mixture. When the same compounds were treated with ethyl malonate and ammonium malonate, under the Doebner-Knowenagel reaction conditions, only a negligible yield of the expected branched chain sugar nucleosides was formed.

Biological activity

The discovery that 7 (2'-keto-β-L-"fucosyl") theophylline **(3)**, first synthetized keto-deoxyhexosyl purine, exhibits growth inhibitory activity against K.B. cancerous cells[19] created considerable interest in this new class of nucleosides.

Recent investigations to all keto-hexosyl purines actually konwn, confirmed that deoxynucleosides possessing a keto group in the sugar moiety inhibit K.B. cancerous cell growth whereas the parent nucleosides, before oxidation, are inactive under the same conditions[19].

From the overal results (Table I) it is clear that the 7- and 9-unsaturated keto-nucleosides **(9)** and **(10)** have the highest inhibitory activity and 9-keto-nucleosides **(7)** **(8)** **(10)** are more active than the 7-keto-nucleosides **(3)** **(5)** **(9)**. However this was the first time that the growth inhibitory activity of 7-(hexosyl) purines has been demonstrated[19]. This difference, between the activity of 7- and that of 9-keto-nucleosides, cannot be attributed to the conformation of the hexosyl-purines because either 7- or 9-(keto-hexosyl) purines studied possess both Cl and 1C conformations.

In examing the results obtained from the studies on the keto-nucleosides described, it appears that the carbonyl group plays an important role, whatever their mechanism of action. Thus, not only were compounds inactive before oxidation but those derived from reduction of the ketone (isomers or deoxynucleosides) did not inhibit cellular growth under the same condition.

K. Antonakis

Institut de Recherches Scientifiques sur le Cancer du C.N.R.S.,
94800 Villejuif (France)

References

1 W. Schroeder and H. Hoeksema, *J. Amer. Chem. Soc. 81* (1959) 1767.
2 K. Antonakis and F. Leclercq, *C. R. Acad. Sci. 272-C* (1970) 1197; *Bull. Soc. Chim. France 1971*, 2142.
3 F. W. Lechtenthaler and P. Heidel, *Angew. Chem. Internat. Ed. 8* (1969) 978; F. W. Lechtenthaler, *Meth. Carbohyd. Chem. 6* (1972) 348; T. Tsuchiya, K. Suo and S. Umezawa, *Bull. Chem. Soc. Japan 43* (1970) 531; G. M. Cree, D. W. Mackie and A. S. Perlin, *Can. J. Chem. 47* (1969) 511.
4 K. E. Pfitzner and J. G. Moffatt, *J. Amer. Chem. Soc. 85* (1963) 3027, *87* (1965) 5670.
5 J. D. Albright and L. Goldman, *J. Amer. Chem. Soc. 87* (1965) 4651.
6 K. Antonakis and M. J. Arvor, *C. R. Acad. Sci. 272-C* (1971) 1982; K. Antonakis, *Carbohyd. Res. 24* (1972) 229.
7 K. Antonakis and F. Leclercq, *Bull. Soc. Chim. France 1971*, 4309.
8 K. Antonakis and J. Herscovici, *C. R. Acad. Sci. 273-C* (1972) 2099; J. Herscovici and K. Antonakis, *J. Chem. Soc., Perkin I.* (1974) 979.
9 K. Antonakis and M. J. Arvor-Egron, *Carbohyd. Res. 27* (1973) 468.
10 K. Antonakis and M. Bessodes, *Carbohyd. Res. 30* (1973) 192.
11 A. F. Cook and J. G. Moffatt, *J. Amer. Chem. Soc. 89* (1967) 2697; U. Brodbeck and J. G. Moffatt, *J. Org. Chem. 35* (1970) 3552.
12 T. Halmos, J. Herscovici and K. Antonakis, *C. R. Acad. Sci. 279-C* (1974) 855.
13 K. Antonakis, *C. R. Acad. Sci. 275-C* (1972) 1101.
14 K. Antonakis, M. J. Arvor-Egron and F. Leclercq, *Carbohyd. Res. 25* (1972) 518.
15 P. M. Collins and W. G. Overend, *J. Chem. Soc. 1965*, 1912; K. Antonakis, *Bull. Soc. Chim. France 1969*, 122; G. J. F. Chittenden, *Carbohyd. Res. 15* (1970) 101.
16 B. Bellau and T. F. Gallagher, *J. Amer. Chem. Soc. 73* (1951) 4458.
17 A. Rosenthal, M. Sprinzl and D. A. Baker, *Tetrahedron Letters 48* (1970) 4233.
18 F. Leclercq, M. Bessodes, J. Jumelet and K. Antonakis, *J. Carbohyd. Nucleos. & Nucleot. 1* (1974) 349.
19 K. Antonakis and I. Chouroulinkov, *C. R. Acad. Sci. 273-D* (1971) 2661; *Biochem. Pharmacol. 23* (1974) 2095.

Radiometric Analysis of Hg (II), Ag (I), Cl (I) and SCN (I) Using a Solid Surface as an Analytical Reagent*

Summary

A rapid radioanalytical procedure for the determination of micro concentrations of Hg (II), Ag (I), Cl (I) and SCN (I) ions in an aqueous medium is presented. The displacement of radioactive silver ion from a fixed concentration of the solid silver tetraphenylborate in the presence of mercury ion and the isotopic exchange of the inactive silver with the radioactive silver in the solid surface form the basis for the analysis of Hg (II) and Ag (I) respectively. It has been observed experimentally that 4 μg/ml Hg (II) and 1 μg/ml Ag (I) can be quantitatively analysed without any elaborated experimental conditions.

The silver exchange reaction has been further used in the indirect radiometric analysis of Cl (I) and SCN (I) anions in solution. In this case inhibition of the isotopic exchange of a known concentration of inactive silver in the presence of an anion of interest is measured. The reactions are sensitive up to 1 μg/ml for both the anions studied.

Introduction

In some earlier publications it has been shown that micro analyses of many inorganic species can be conveniently performed using solid surfaces as analytical reagents[1–4]. These solid reagents in many a case offer selectivity and the desired sensitivity. Such reagents termed as "Englomerate salts" are now becoming somewhat popular because of their ready adaptability to automation, gas phase analysis and even in the field testing. In the present communication are described the analytical uses of the solid reagent silver tetraphenylborate tagged with the radioisotope Ag-110 m. This reagent is stable in an aqueous medium and is not affected by minor changes in the acidity of the system.

Determination of Hg (II) and Ag (I)

In the presence of mercury ions the radiosilver in the solid surface is quantitatively and rapidly exchanged by the displacement mechanism:

$$Hg^{2+} + 2\ {}^*Ag(B(C_6H_5)_4) \rightleftarrows Hg(B(C_6H_5)_4)_2 + 2\ {}^*Ag^+ \quad (1)$$

The release of the radioactivity in the aqueous phase thus becomes a direct measure of the mercury concentration in solution. The analytical data obtained under controlled experimental conditions show a linear correlation in 40 to 1000 μg/ml range when the exchange is performed under static condition. Under the dynamic column operation using only 200 mg of the solid supported on a filter paper of 2.5 cm diameter the sensitivity of the exchange is enhanced considerably and one actually observes a linear correlation in 40 to 80 μg/ml range (cf. figure Ia). The mercury exchange appears to be selective on this surface since the presence of other common cations and anions have no influence on the system. The quantitative measurements show that radio-

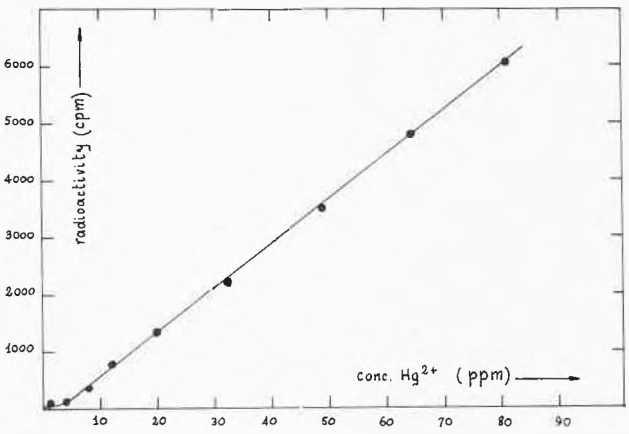

Fig. Ia. Analytical curve for Hg^{2+} determination

* Preliminary communication. Received December 12, 1974.

activity released in the presence of 20 μg/ml Hg^{2+} solution is no different from the radioactivity released by a similar solution containing up to 100 μg/ml of Cu^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, Tl^{+}, SO_4^{2-}, CH_3COO^- and NO_3^- ions. The only interfering ion was Ag^+ practically at any concentration. Likewise the halogens and other ions forming an insoluble compound with silver ion inhibit the release of radiosilver from the column and hence are serious interferences.

The interference of Ag^+ ion has been attributed to the isotopic exchange between the inactive silver and the radiosilver in the solid surface.

$$Ag^+ + {}^*Ag\,B(C_6H_5)_4 \rightleftarrows Ag\,B(C_6H_5)_4 + {}^*Ag^+ \qquad (2)$$

This is supported by the fact that there is a linear release of the radioactive silver when progressively increasing concentrations of inactive silver are passed over the fixed ($\sim$ 200 mg) column of the radioactive solid surface. The data in figure Ib show that the exchange gets saturated near about 15 μg/ml Ag^+ concentration. In any event a rapid radioanalytical method for inactive silver analysis is thus available.

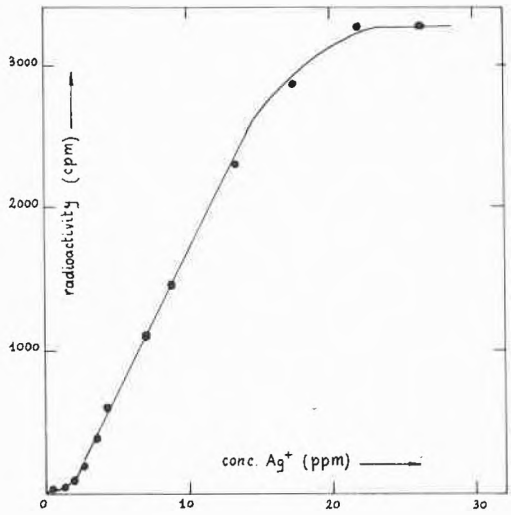

Fig. Ib. Analytical curve for Ag^+ determination

Determination of Cl (I) and SCN (I)

The silver isotopic exchange reaction has been further exploited in the indirect radiometric analysis of some anions. Under the similar experimental conditions one can actually show by calculation that anions such as Cl(I) and SCN(I) would form insoluble species with Ag(I) cation. If to a known amount of inactive silver ($\sim$15 μg/ml Ag^+ as seen above) micro amounts of the anion of interest are added the solution would become visibly turbid because of the precipitation reaction. Such a solution if passed over the solid surface column would naturally show a diminished radioactivity in the effluent

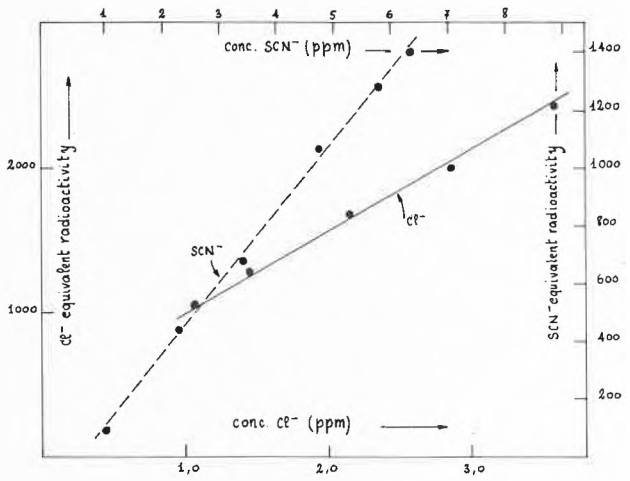

Fig. II. Analytical curves for Cl^- and SCN^- determination

phase. This decrease would be in direct proportion to the equivalence that exists between Ag(I) and the anion under investigation. On the other hand one can correlate this decrease in radioactivity to the concentration of the anion. When actually applied to the solutions of Cl(I) and SCN(I) anions it is found that a linear correlation exists for these anions in 1 to 6 μg/ml range as seen in figure II. This indirect radioanalytical approach is thus relatively simple and fairly sensitive for the analyses of these anions. No sample preparation is necessary and the turbid solutions are simply passed over the column which also functions as a filter for the suspended precipitates. In principle this method can be extended for the analysis of two anions simultaneously if one forms an insoluble compound in acidic medium while the other does so only in neutral condition. In such a case two independent evaluations in acidic and neutral conditions would furnish relative concentration of each species simply by subtraction of the radioactivity released in each case.

M. C. Mehra and W. Haerdi *

Département de chimie
Université de Moncton, Canada
Département de chimie minérale et analytique
Université de Genève, Suisse

References

1 M. C. Mehra and J. L. Lambert, *Microchem. J. 18* (1973) 226.
2 M. C. Mehra and P. O'Brien, *Microchem. J.*, under publication.
3 C. Bourque, Thesis, Université de Moncton, 1974.
4 J. L. Lambert and D. Manzo, *Anal. Chim. Acta 48* (1969) 185.

* Author to whom requests should be adressed: Département de chimie minérale et analytique, Université de Genève, quai de l'Ecole de Médecine 30, CH-1211 Genève 4.

Adsorption of Iodine and Halogen-containing Organic Molecules on Gold Studied by Photo-electron Spectra*

Summary

The relative proportion of undissociated organic molecules and of separate iodine adsorbed on gold surfaces is studied, using photo-electron signal intensities and chemical shifts.

Since the photo-electron spectra induced by 1253.6 (magnesium anti-cathode) or 1486.6 eV (aluminium) photons characterize the outermost 20 to 30 Å of solid samples, most metals show oxide, hydroxide, carbonate or other corrosion products. This is not true for gold, where the strong Au $4f_{7/2}$ with I* = 83.8 eV (relative to the Fermi level) frequently[1] is used for standardization. As a by-product of our study[2] of 600 compounds containing 77 elements, we found that 0.2 mm 99.99 percent gold foil (from Métaux Précieux, Geneva) which had been exposed to laboratory air shows distinct sharp iodine signals, presumably due to reaction with volatile organic iodine compounds produced in other rooms or buildings. Table 1 shows the I* values recorded by our Varian IEE-15 photo-electron spectrometer. The I values relative to *vacuo* can be found[2,3] by adding the difference (here typically 5.2 eV) between 290 eV and I* (C1*s*) of surface hydrocarbons. Alternatively[3,4] one may assume the work function of pure gold to be 5.3 eV and I (Au $4f_{7/2}$) = 89.1 eV, suggesting distances half an eV higher in Table 1.

It is striking that the (probably monomolecular) layer of iodine adsorbed on gold from iodine vapour survives both washing with acetone and the *vacuo* (10^{-6} torr) prevailing in the instrument for 20 hours. The same persistence is found using highly volatile methyl iodide and iodoform. One may ask the question whether the organic molecule is adsorbed *in toto*, or whether C—I bonds are broken, leaving the same product as I_2 forms. A related problem of adsorption of fluorine-substituted olefins on platinum was recently studied[5] using photo-electron spectra, and it was shown that vinyl fluoride dissociates by eliminating HF. In our case, it is possible to exploit the semi-quantitative results for 1486.6 eV photons[6,7] and the somewhat better reproducible (± 15 percent) values for 1253.6 eV photons (from the high-intensity source[8] used here) to investigate whether nitrogen- or fluorine-substituted iodobenzenes have the N1*s* or F1*s* intensities expected from the stoichiometry of the entire molecule. Fig. 1 shows that the iodine signals of tetraiodothiophene and 4-iodoaniline shows shoulders at higher I* amounting to about a-fifth and about a-third of the total iodine intensity. Correspondingly, the S2*p* and N1*s* signals have about 20 and 30 percent of the intensities expected. The dissociation of

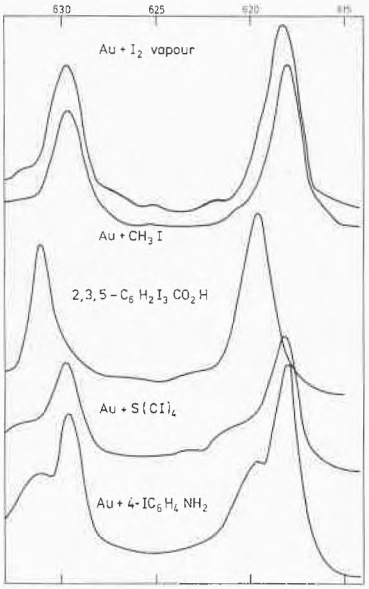

Fig. 1. I* values in eV measured in the iodine 3*d* region of five gold cylinders covered with adsorbed molecules

the iodine-containing molecules is almost complete in the cases of 2-iodoaniline, 3-iodonitrobenzene and 4-iodo-flurobenzene where 5 percent or less of N1*s* or F1*s* signals can be detected. This conclusion is corroborated by the chemical shift (of complicated origin[2,9]) where a (fairly thick layer) of tri-iodobenzoic acid exemplifies I* (I3*d*) about 2 eV higher than of the adsorbed Au—I, and representing the typical behaviour of iodine bound to carbon (as also known[2] from the dyestuff Bengal Rosa B). For comparison, it may be mentioned that solid gold(I) iodide (from Drijfhout, Amsterdam) after correction[2] for a charging effect $\hat{o}$ = 1.6 eV has I* (Au $4f$) increased 0.7 eV and I* (I3*d*) 1 eV relative to iodine adsorbed on gold. The organic compounds were high-quality products from Fluka, and showed no trace of iodine colouration with exception of a weak trace of purple tint in dissolved tetraiodothiophene. It does not seem plausible that the gold surface extracts iodine molecules dissolved as impurities in the samples selected. Catalytic reactions with air oxygen cannot be fully excluded. The acetone (solvent used) has no perceptible residue of distillation.

An instance of adsorption of an entire molecule on gold is 1,1,2,2-tetrabromoethane where the I* values recorded are 83.7 eV for Au $4f_{7/2}$, 69.1 eV for Br3*d*, 182.3 eV for Br $3p_{3/2}$ and 283.7 eV for C1*s*. The same spectrum is observed 2 hours later in the apparatus, and is rather different from the spectrum of gold corroded in bromine vapour, where the lower I* values are 83.5, 67.9, 181.3 and 283.5 eV, respectively.

* Received December 27, 1974.

Table 1. I* values in eV (relative to the spectrometer work function) of the strongest signals observed of gold, carbon and iodine

	Au $4f_{7/2}$	C 1*s*	I $3d_{5/2}$	I $3d_{3/2}$
Au + I_2 (exposed to vapour 5 minutes)	83.4	284.2	618.1	629.7
Au + I_2 (washed with acetone)	83.3	284.3	618.0	629.5
Au + CHI_3 (in acetone)	83.3	284.2	618.0	629.5
Au + CH_3I (liquid)	83.3	284.2	618.0	629.5
Au + C_6H_5I (liquid)	83.3	284.1	618.1	629.7
Au + 4-IC_6H_4F	83.6	284.4	618.4	629.9
Au + 3-$IC_6H_4NO_2$	83.5	284.6	618.4	629.9
Au + 2-$IC_6H_4NH_2$	83.4	284.1	618.0	629.5
Au + 4-$IC_6H_4NH_2$	83.3	284.2	618.1 (620.0)	629.6 (631.6)
Au + tetraiodothiophene	83.3	284.3	618.1 (621.0)	629.6 (632)
Au + 2,3,5-$I_3C_6H_2CO_2H$	83.2	283.9	619.7	631.2
AuI (solid)	85.6	284.6	620.9	632.5
AuI (corrected for charging)	84.0	–	619.3	630.9
AuI (after 15 hours)	86.0	284.7	621.1	632.6
AuI (≫, corrected for changing)	84.4	–	619.5	631.0

Acknowledgements. The Swiss National Science Foundation provided the grant for the photo-electron spectrometer.

Lucette Balsenc, Hervé Berthou and Christian K. Jørgensen

Département de Chimie minérale et analytique
Université de Genève
CH-1211 Geneva 4

References

1 G. Johansson, J. Hedman, A. Berndtsson, M. Klasson and R. Nilsson, *J. Electron Spectr. 2* (1973) 295.
2 C. K. Jørgensen and H. Berthou, *Mat. Fys. Medd. Dan. Vid. Selskab 38* (1972) No. 15.
3 C. K. Jørgensen and H. Berthou, *Chem. Physic. Letters*, in press.
4 S. Evans, *Chem. Physic. Letters 23* (1973) 134.
5 T. A. Clarke, I. D. Gay and R. Mason, *Chem. Comm.* (London) *1974*, 331.
6 C. D. Wagner, *Analyt. Chem. 44* (1972) 1050.
7 C. K. Jørgensen and H. Berthou, *Disc. Faraday Soc. 54* (1973) 269.
8 H. Berthou and C. K. Jørgensen, *Analyt. Chem. 47* (1975) in press.
9 C. K. Jørgensen, *Adv. Quantum Chem. 8* (1974) 137.