

CATALYZED EXCHANGE BETWEEN TRITIUM GAS AND ORGANIC MOLECULES IN SOLUTION

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The exchange reaction between gaseous tritium and organic molecules in solution is known to occur in the presence of platinum oxide (Adam's catalyst)^(1,2). Also, the isotopic exchange of bibenzyl and tritium has been examined, using VIIIth group metal oxide catalysts⁽³⁾. Palladous(II) oxide was found to be the most efficient catalyst in such a type of exchange performed *in situ*⁽²⁾. Recently, similar exchange reactions have been reported⁽⁴⁾ using Pt black, Pd black or PdO/BaSO₄ as catalyst.

We have compared the efficiency of the two catalysts PtO₂ and PdO to exchange hydrogen with tritium in compounds differing in their structure. These oxides were chosen for their exchange ability, as found in preliminary trials. The compounds were chosen for their importance in biological and pharmaceutical research.

The very mild experimental conditions such as ambient temperature and low tritium pressure prevented, in most of the cases, decomposition or reduction of sensitive double-bonds. The *in situ* procedure has been found to be effective in various solvents, including organic. Therefore, it is suitable for labelling organic compounds insoluble in aqueous solutions.

Instrumental and experimental details have been previously reported⁽²⁾. All the experiments were carried out in a volume of 0.3 ml solvent. The reaction was stopped after 3 Ci of tritium gas has reacted with the metal oxide.

Table I: Comparison of Tritium Labelling, Using PtO ₂ and PdO as Catalyst.				
TRITIATED COMPOUND	STRUCTURE	SOLVENT	SPECIFIC ACTIVITY*	
			PdO	PtO ₂
Abscisic Acid		Methanol	12,20	0.04
Ethylbenzilate		Methanol	0.04	0.00
Diethylamino ethylbenzilate. HCl		Methanol	0.29	0.29
Dimethylamino ethylbenzilate. HCl		Methanol	0.61	0.41
N-Methyl-4-piperidylbenzilate		Dioxane	1.83	1.87
Bibenzyl		Dioxane	4.90	1.80
Chlorpromazine. HCl		Methanol	1.43	0.94
Desipramine. HCl		Methanol	19.70	0.46
p-Hydroxyacetanilide		aq. NaOH 1N	0.32	0.00

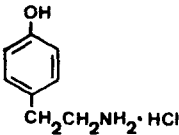
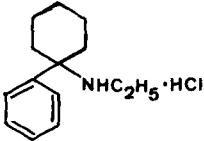
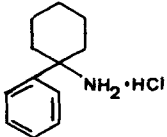
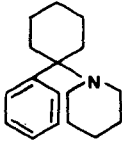
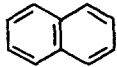
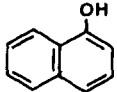
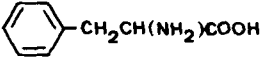
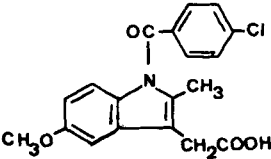
Table I: (continued)				
TRITIATED COMPOUND	STRUCTURE	SOLVENT	SPECIFIC ACTIVITY*	
			PdO	PtO ₂
Ci/mmol				
Tyramine. HCl		Methanol	0.45	0.50
Ethylphenacyclidine. HCl		Methanol	1.64	0.22
1-Phenylcyclohexylamine. HCl		Methanol	0.38	0.35
Phencyclidine. HCl		Methanol	3.77	0.09
Naphthalene		Dioxane	0.40	0.99
1-Naphthol		Methanol	0.50	0.09
L-Phenylalanine		Water	2.31	0.16
Indomethacin		Methanol	1.03	0.00

Table I: (continued)				
TRITIATED COMPOUND	STRUCTURE	SOLVENT	SPECIFIC ACTIVITY *	
			PdO	PtO ₂
Methicillin sodium		Methanol	1.05	0.02
Ouabain		Methanol	7.02	0.09
Scopolamine. HBr		Methanol	1.08	0.30
Atropine sulfate		Methanol	1.32	0.43
Valinomycin		Methanol	0.20	0.08
Pilocarpine. HCl		Methanol	11.06	0.06

* Specific activity of purified compound.

Experimental conditions:

0.1 mmol of compound dissolved in 0.3 ml solvent; 12.6 mg PdO or 12.2 mg PtO₂; 0.05 mmol (3 Ci) tritium consumed by activation of the catalyst; 100 mm Hg initial tritium pressure (7 Ci); reaction temp.: 25°C.

The chemical purity of the tritiated compounds was determined by UV, by GLC or by analytical TLC; the radiochemical purity was determined by scanning of the TLC plates (silica gel) developed in, at least, two different solvent systems. The radioactive impurities were removed by preparative TLC. The radioactivity was measured by liquid scintillation counting.

The specific activities obtained in our experiments are given in table I.

We have found that, generally, palladous oxide is the more active exchange agent of the two catalysts. This is particularly noted in molecules with hydrogen atoms in benzylic positions or in the α - position of a conjugated system and, to a lesser extent, in methyl and methylene groups bound to secondary and tertiary amines.

It is of interest to note that the yield of exchange is not affected when platinum oxide is used instead of platinum dioxide: after activation of the two oxides with tritium, about the same specific activity of labelled bibenzyl was obtained⁽⁵⁾. This result leads us to assume that the oxidation number of the metal is zero when it acts as catalyst in the hydrogen-tritium exchange.

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