THE TRITIUM INCORPORATION INTO THE SOLVENTS UNDER CONDITIONS OF CATALYTIC HYDROGENATION

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SUMMARY

The incorporation of tritium gas into dioxan, tetrahydrofuran, ethyl acetate, dimethylformamide, dimethylacetamide, dimethylsulfoxide and acetic acid anhydride was studied in the presence of heterogeneous catalysts PdO (Adams), PtO_2 *(Adams),* $Pd/BaSO_4$ *(10%). For the solvents and catalysts investigated the following dependencies were observed:*

1) *Wilzbach reaction of the solvents takes only a negligible part in the total incorporation into the solvents.*
2) *The traces of exchanging impurities in solvents caused much higher incorporation.*
3) *In the case of non exchanging solvents, practically all the radioactivity incorporated is bound on tritium water.*

The most effective method with respect to the attainment of high specific activity during the tritiation of organic compounds is undoubtedly the hydrogenation of double bonds or catalytic dehalogenation with carrier-free tritium. Literature gives various information proving that in both cases an appreciable incorporation of tritium into the solvent takes place, even when work is done with solvents lacking the so-called labile hydrogens, as for example dioxane, tetrahydrofuran, ethyl acetate etc. From the above mentioned reasons we studied factors affecting the losts of radioactivity into the solvents used.

Apparatus and material

a) For the measurement and for all operations with tritium gas we used an apparatus developed in our laboratory which enables the work under constant pressure of tritium, close to atmospheric pressure /1/. The reaction vessel provided with a magnetic stirrer was fitted with a tube with a silicon seal. The total volume of solvents used was 1 g. The solvent samples were taken via seal (approximately 10 mg) with a microsyringe. The samples were weighed in glass bubbles and measured by liquid scintillation method. The total pressure (tritium pressure and pressure of solvent vapour) in every experiment was approximately 600 Torr.

b) We used tritium gas imported from USSR in ampoules, which was purified and stored in the form of uranium tritide. The specific activity of this tritium was measured in a ionisation chamber developed in our laboratory. The contents of tritium in the imported gas were in the 75-85% range.

c) For our study we used common solvents recommended for tritiation. The solvents were carefully purified and dried by chemical means which are used for preparation of pure or extra pure solvents. The control of purity was carried our by gas chromatography.

d) PtO_2 (Adams) and PdO (Adams)' as well as $Pd/BaSO_4$ were used as catalysts. Pd/C requires special conditions for its preparation and storage, which would only complicate the work and therefore it was not employed. PdO and PtO_2 were reduced with hydrogen immediately before use and the solvent with traces of humidity was submitted to lyophilisation. The catalyst was used for the study of the exchanges after the addition of fresh solvent in inert atmosphere.

Results

The inseparable part of hydrogenation reaction is the interaction between the solvent and the tritium gas, i.e. Wilzbach reaction. We found that for ethyl acetate, dioxan, tetrahydrofuran and acetic acid anhydride the exchanges caused by Wilzbach reaction are of the order of tens of mCi, i.e. negligible in comparison with the exchanges taking place in the presence of catalyst. Linear course of the incorporation versus time plot, in the directions towards the origin, shows that the contribution to the activity caused by the solubility of tritium in the solvent is negligible.

The greatest attention was devoted to the incorporation into solvents under the influence of catalysts. Fig.1a shows the incorporation of tritium into ethyl acetate. After two to three hours a distinct slowing down of the incorporation takes place and the dependence on time assumes a linear character. An analogous dependence is obtained for all solvents investigated. The ethyl acetate used is very pure, see Fig.1b.

The purity of the solvents greatly affects the degree of incorporation. In Fig.2 this effect is documented for dioxan.

The dioxan used, 1,2,3, corresponds approximately to the following qualities: pure grade, analytical grade, for spectral measurements. For dioxan 2 almost total radioactivity is bound in impurities (Fig.3a). Perfectly pure dioxan does not contain exchangeable hydrogens under the conditions used.

In experiments with very pure solvents it was found that the

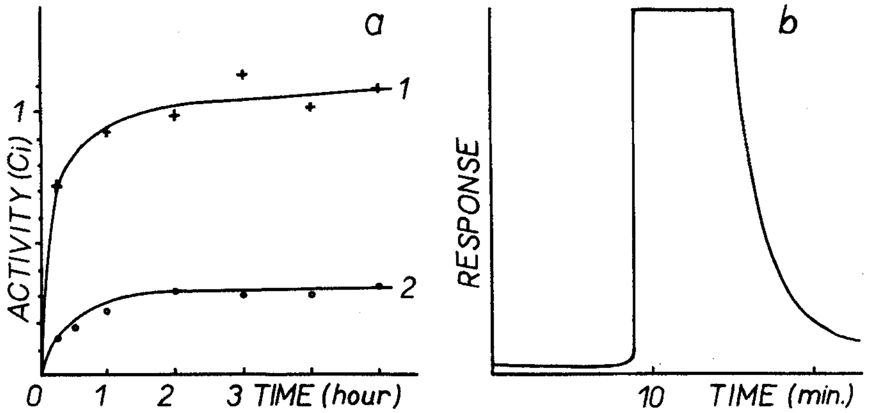


Fig.1. a) The dependence of incorporation of tritium into very pure ethyl acetate on time.
Catalyst: 1...PtO_2, 20 mg; 2...$Pd/BaSO_4$(10%), 20 mg. 80% T_2
b) Gas chromatogram of ethyl acetate used.

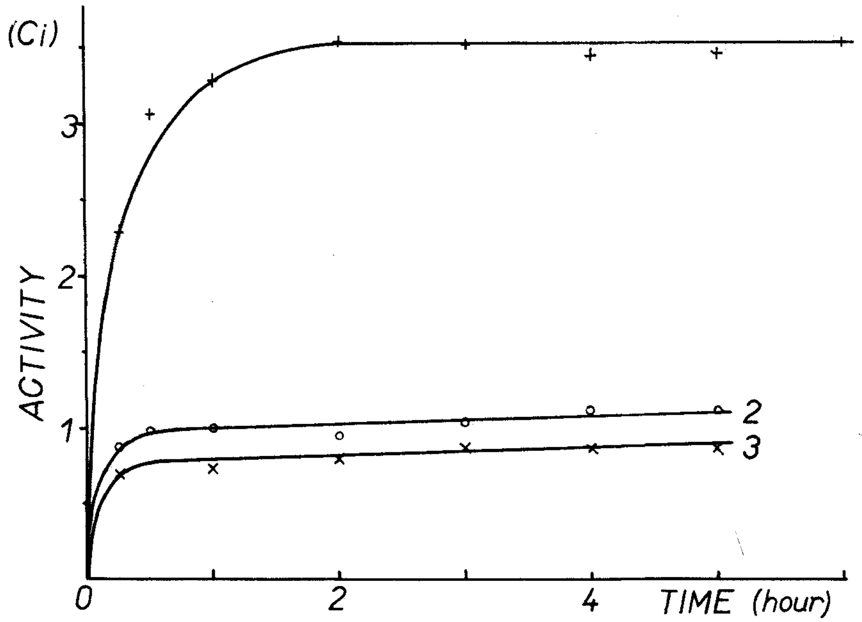


Fig.2. The dependence of incorporation of tritium into dioxan 1, 2 and 3 on time. Catalyst PtO_2, 20 mg, 80% T_2.

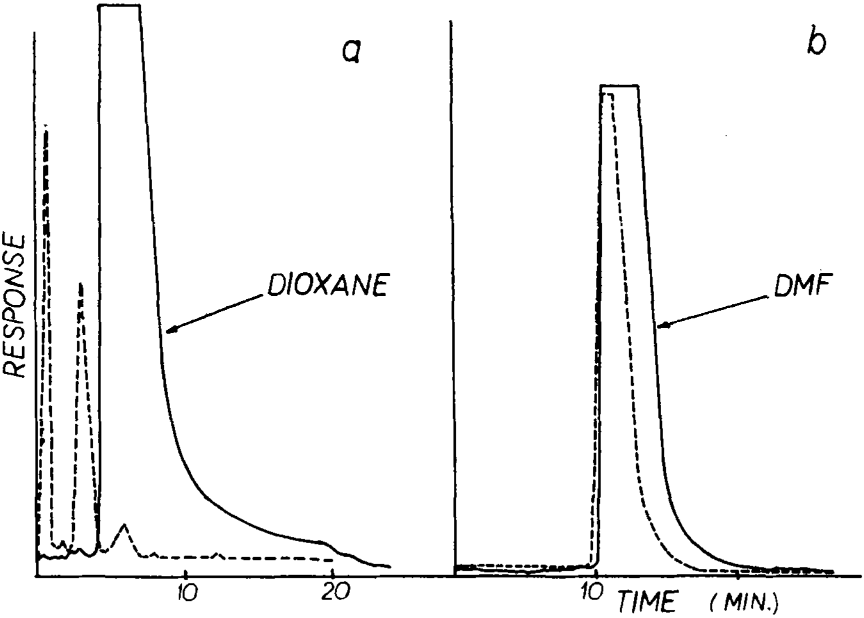


Fig.3. The distribution of the radioactivity: a) in the components of dioxan 2. Reaction time 5 hours. Gas chromatogram, 15% DEGS on Chromosorb W, 45°C. b) in very pure dimethyl formamide. Reaction time 4 hours. Gas chromatogram, Porapak Q, 197°C.

larger part of the incorporated radioactivity is in the form of tritium water. This water may be eliminated quantitatively by allowing the solvent to stand over a molecular sieve. The results of the incorporation of solvents (after five hours) and the decreases in radioactivity after standing over a molecular sieve are shown in Table 1.

Table 1

Tritium contents in used gas	Solvent	Catalyst			
		Pd/$BaSO_4$(10%),20mg		PtO_2,20mg	
		before sieve /mCi/	after sieve 3A /mCi/	before sieve /mCi/	after sieve 3A /mCi/
75-80%	dioxan	400	39	900	13
	tetrahydrofuran	420	38	1050	195
	ethyl acetate	300	34	1050	108
45-50%	dimethylformamide	770	390	-	-
	dimethylacetamide	240	7	970	27
	dimethylsulphoxide	470	20	-	-
	acetic acid anhydride	670	580$^+$	-	-

$^+$ after standing with molecular sieve 5A the radioactivity decreases do 353 mCi

The rapid drop in radioactivity to the values of tens of mCi in dioxan, tetrahydrofuran, ethyl acetate, dimethylacetamide and dimethyl sulphoxide indicates that the mentioned solvents do not contain exchangeable hydrogens under the given reaction conditions. A somewhat higher residual radioactivity (after sieve 3 A) in the case of tetrahydrofuran and ethyl acetate when platinum catalyst is used may be explained by the reaction of these solvents with a very active catalyst, under formation of traces of by-products. In the case of dimethyl sulphoxide the consumption of tritium was observed during the whole experiment. Evidently a slow reduction of this solvent occurs under formation of tritiated water as is also shown by a higher incorporated radioactivity (see Table 1), for example in comparison with dimethylacetamide. During the reductions of the C-C double bonds in dimethylsulphoxide, a rapid poisoning of the catalyst has been observed.

In dimethylformamide and acetic anhydride the incorporation of tritium increases distinctly even after two hours (Fig.4).

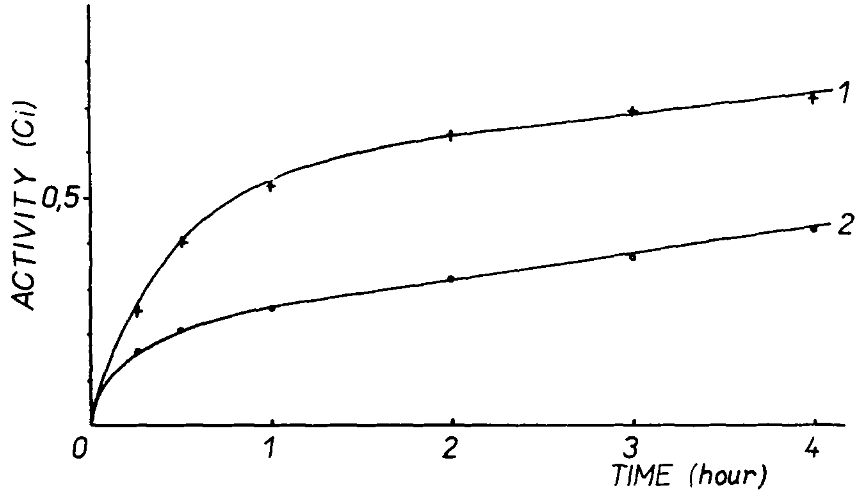
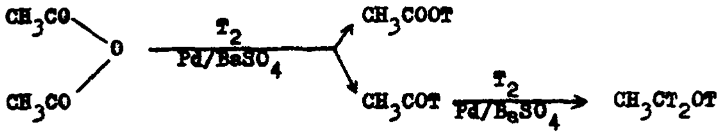


Fig.4. The dependence of incorporation of tritium into very pure acetic acid anhydride (1) and dimethylformamide (2) on time. Catalyst Pd/BaSO$_4$ (10%), 20 mg. 43% T_2.

In the case of dimethylformamide an exchange of the formyl group for hydrogen evidently occurs (Fig.3b). In the case of acetic anhydride the catalyst enhances hydrogenolysis. This is proved by the drop in pressure in the apparatus during the whole experiment. The course of the hydrogenolysis and the subsequent reduction is described by Musso and Figge /2/. For tritium the reaction scheme may be construed as follows:



From the reaction tritiated acetic acid and tritiated ethanol result. Acetic acid is formed both by the hydrogenolysis and by the reaction of acetic anhydride with tritiated water (tritium water is formed by the reaction of gaseous tritium with the catalyst - see below). For this reason the drop in radioactivity after sieve 3 A is very slight. From the calculation of the theoretical course of the reduction a value approximately about 250 mCi follows in the ethanol formed. The radioactivity of the

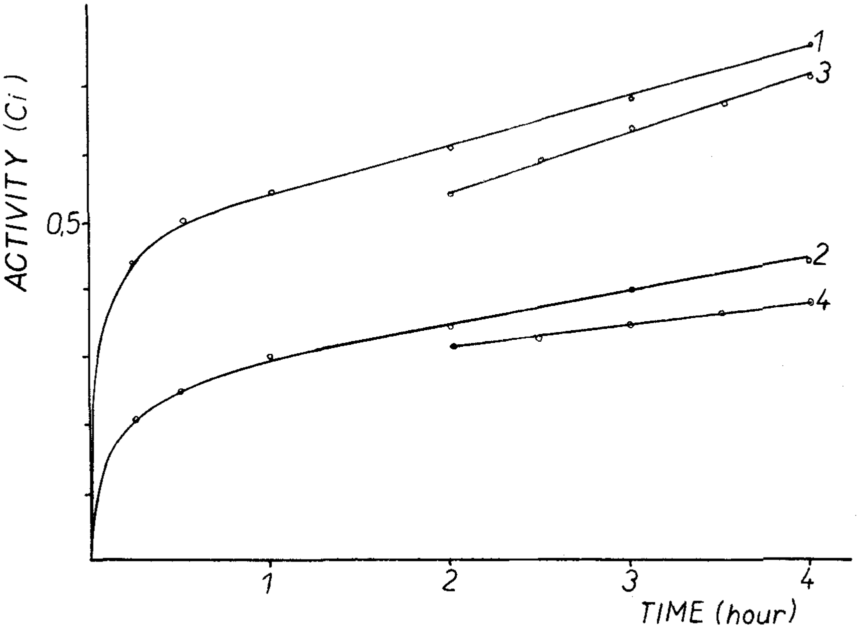


Fig.5. The dependence of incorporation of tritium into dioxan 3 on time. Catalyst: Pd/$BaSO_4$(10%), 1...40 mg, 2...20 mg; 70% T_2. PdO, 3...12,3 mg (0.1 mM), 4...6.15 mg (0.05 mM); 40% T_2.

reaction mixture did indeed decrease to this extent after the addition of the molecular sieve 5 A (it sorbs ethanol).

In order to explain the formation of tritium water in the course of the experiments we determined the effect of the amount of catalyst on the magnitude of the incorporation into the solvents (Fig.5). It is clear that in very pure solvents which do not exchange hydrogens, the catalyst is responsible for the majority of the incorporated radioactivity. So far it is not known in which form the traces of oxygen bound to the catalyst remain.

References

/1/ Hanuš J. and Vereš K. - This Journal 7: 425 (1971).

/2/ Musso H. and Figge K. - Chem.Ber.95: 1844 (1962).