TRITIUM INCORPORATION INTO SOLVENTS UNDER THE CONDITIONS OF CATALYTIC DEHALOGENATION

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SUMMARY

Incorporation of tritium into selected polar solvents was studied in the presence of bases and buffering substances. Tritium gas was used as a tritium source and the reaction was catalyzed by PdO, Pd/BaSO$_4$, Raney nickel.

Key Words: Tritium gas, heterogeneous catalysts, incorporation into solvents.

INTRODUCTION

Incorporation of tritium into solvents under the action of heterogeneous catalysts is a side-reaction during catalytic hydrogenation and dehalogenation of organic compounds by tritium gas. The radioactivity losses occurring with less polar solvents have already been investigated[1]. The present study aims at extending the data to solvents, bases and catalysts used most frequently in catalytic dehalogenation. Experimental conditions were adjusted so that the data obtained could be without any modification applied to the practical preparations of tritiated compounds. We studied the incorporation of tritium into dimethylacetamide, ethyl acetate, methanol and water in combinations with bases /sodium acetate, ammonia, potassium hydroxide, triethylamine/ and buffering salts

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/ammonium carbonate, sodium tetraborate, phosphates/. The catalysts used included Pd/$BaSO_4$, PdO, Raney nickel.

EXPERIMENTAL

a/ Experimental procedure,sample collection and measurements were performed as described earlier[1]. The volume of solvents or mixtures was 1 ml. The pressure in the tritiation apparatus was kept in all cases at 600 Torr; during the first 30 min of experiment a slight pressure drop was observed caused by the sorption of $^3H_2$ on the catalyst. The volume of gaseous tritium above the reaction mixture was about 2.2 ml.

b/ Experiments were performed with gaseous tritium that had 30-35%, 45-50%, 95-100% of the carrier-free radioactivity. The specific radioactivity of the gas was measured and monitored using an ionization chamber.

c/ The solvents and bases under study were carefully purified and dried; their purity was checked by GLC. All aqueous solutions were prepared from doubly-distilled water.

d/ The amount of Pd/$BaSO_4$ /10%/ was 20 mg per experiment, that of PdO was 5 mg per experiment. The latter compound was reduced with hydrogen in dioxan, the solvent and the evolved water were removed by lyophilization and a mixture of solvent and base was added in an inert atmosphere. Raney nickel /activity W4/ was prepared[2] freshly before each experiment from 20 mg alloy. Before it was used in methanol solutions, the substance was washed with 5 x 0.5 ml absolute methanol.

RESULTS AND DISCUSSION

The values of incorporation of $^3H_2$ into the solvent-base mixture at different time intervals are summarized in Tables I and II.

TABLE I

Catalyst	50 % $^3H_2$	Incorporation (mCi)			A	B
	Solvent - Base	1 h	2 h	3 h	(mCi)	(mCi/h)
Pd/$BaSO_4$	H_2O - KOH 0.25 M	92	100	116	79	12
	H_2O - NH_4OH 0.5 M	124	126	133	119	4
	MeOH-KOH 0.25 M	68	79	110	44	21
	MeOH-Et_3N 0.15 M	48	59	77	32	15
	MeOH	93	120	140	71	23
PdO	H_2O-KOH 0.25 M	308	380	447	239	69
	H_2O-NH_4OH 0.5 M	346	435	544	244	99
	MeOH-KOH 0.25 M	320	415	447	267	63
	MeOH-Et_3N 0.15 M	366	511	725	175	180
Raney nickel	H_2O-KOH 0.25 M	84	140	208	20	62
	H_2O-NH_4OH 0.5 M	37	66	100	5	31
	MeOH-KOH 0.25 M	670	950	1060	503	195
	MeOH-Et_3N 0.15 M	852	1237	1637	430	402
	MeOH-MeONa 0.25 M	701	1111	1381	384	340

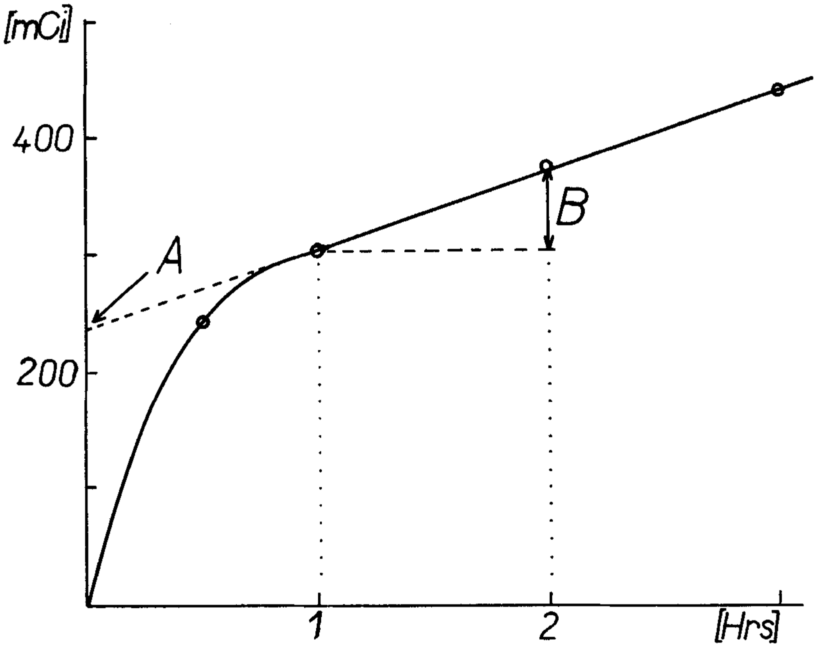
As with the previous results[1] the resulting dependence became about linear after approximately 1 h /cf. Figure/.

Extrapolation of this linear segment to the zero time - value A - corresponds approximately to the radioactivity of water reduced rapidly from the catalyst[1]. The value of A fluctuates considerably depending on the amount and type of catalyst and is thus unsuitable for assessing the actual exchange into the solvent. The value B, i.e. the slope of the linear segment, corresponds to the incorporation of radioactivity in 1 h and includes generally the sum of actual exchange reaction into the solvent /E/ and the radioactivity of water reduced at later stages /slowly/ from the catalyst /R/; hence B = E + R. The actual value of E and R, as well as A, may be determined in some solvents /e.g., ethyl acetate, dimethylacetamide/ by trapping the tritiated water after the experiment in a molecular sieve 3A.

Pd/$BaSO_4$: The values of B for this catalyst are very low in almost all experiments. In dimethylacetamide, ethyl acetate and the mixture dimethylacetamide-sodium acetate $B \simeq R$, since treatment with 3A molecular sieve reduced the solvent radioactivity to zero. Comparison of the values of B in these solvents /Table II/ with the data for Pd/$BaSO_4$ /Table I/ implies that neither aqueous nor methanolic solutions of bases exchange tritium, i.e. B = R. Exceptions include ethyl acetate and dimethylacetamide in a mixture with triethylamine. As indicated by the high values of radioactivity in the mixture after the molecular sieve treatment, an actual exchange reaction takes place in these mixtures. In addition, high values of A attest to an extensive reduction of water from the catalyst. It was necessary to ascertain whether triethylamine does not contain reducing impurities which could increase spuriously both A and B. For this reason, an experiment was performed in which a mixture of ethyl acetate + triethylamine + $^3H_2$ was stirred for 90 min and then another portion of the ethyl acetate-triethylamine mixture was

TABLE II

Pd/BaSO$_4$, 100% $^3H_2$	Incorporation (mCi)			After Sieve 3 A	A (mCi)	B (mCi/h)
Solvent - Base	1 h	2 h	3 h			
DMAA	303	365	420	15	246	59
DMAA-AcONa 0.15 M	260	308	332	31	228	36
DMAA-Et$_3$N 0.15 M	756	905	982	130	655	113
AcOEt	253	273	293	39	233	20
AcOEt-Et$_3$N 0.15 M	767	796	840	134	728	36



Incorporation of $^3H_2$ into H_2O-KOH (0.25 M), PdO, 50% $^3H_2$.

injected into the reaction vessel. No change was observed in the linear part of the incorporation curve.

PdO: The values of $\underline{A}$ and $\underline{B}$ are higher as compared with $Pd/BaSO_4$. According to the results obtained with nonpolar solvents[3], this increase is probably due to water reduced from the catalyst, i.e. $\underline{B} = \underline{R}$.

Raney Ni: A considerable amount of hydrogen bound to the catalyst /remaining there from the preparation of the catalyst/ dilutes markedly the gaseous tritium during the experiment. The course and equilibrium of pertinent reaction are very difficult to assess. The very low values of $\underline{A}$ in aqueous bases and the low value of $\underline{B}$ imply that no reduction of water from Raney Ni takes place. Consequently, in all mixtures under study, $\underline{B} = \underline{E}$. In contrast to aqueous bases, the values of $\underline{B}$ in methanolic bases are markedly higher. This points to a considerable exchange of tritium into methanol. The dilution of the gaseous tritium with the hydrogen from the catalyst and the solvent causes a bend on the linear dependence of incorporation and, hence, a high value of $\underline{A}$ in methanolic bases.

Aqueous buffers - $Pd/BaSO_4$: According to the literature[4] the exchange into water depends strongly on pH. A quantitative comparison of tritium incorporation into water was carried out in buffered solutions of pH 5.0 - 9.2 /Table III/. The pH dependence of $\underline{B}$ may be readily studied in phosphate buffers in which a pH change from 9.1 to 5.0 markedly /about twice/ increases the value of $\underline{B}$. A comparison of experiments 2 and 5 and experiments 1, 7 and 8 /the data are to be normalized in view of the unequal radioactivity of the gaseous tritium/ shows that $\underline{B}$ depends also on the type of buffering substance. It is thus probable that the buffer or its hydrolytic products directly participate in the exchange reaction.

TABLE III.

Exp. No.	Buffer	Buffer Conc. (M)	pH	Incorporation (mCi)			A (mCi)	B (mCi/h)
				1 h	2 h	3 h		
1	Na_2HPO_4	0.07	9.15	193	275	367	104	87
2	Na_2HPO_4 + KH_2PO_4	0.07	7	247	370	502	118	127
3	Na_2HPO_4 + KH_2PO_4	0.07	5	385	550	715	220	165
4	Na_2HPO_4 + KH_2PO_4	0.01	5	340	542	720	154	190
5	$(NH_4)_2CO_3$	0.1	7.8	132	181	212	95	40
6	$(NH_4)_2CO_3$	0.1	7.8	187	263	309	131	61
7	$Na_2B_4O_7$	0.1	9.25	145	152	165	134	10
8	$Na_2B_4O_7$	0.01	9.20	187	228	248	160	31

Experiments 1-5: 30-35% $^3H_2$, Experiments 6-8: 40-45% $^3H_2$

The dissociation constants of acids formed by hydrolysis or specific exchange properties of the buffers may affect the extent of the monitored exchange reaction into water. Comparison of experiments 3 and 4, as well as 7 and 8 indicates that the concentration of the buffer exerts only a slight influence on the values of B.

Conclusion:

Elimination of considerable losses of radioactivity into solvent-base mixtures during catalytic dehalogenation may be achieved by using aqueous and methanolic solutions of bases /KOH, ammonia, triethylamine/, with Pd/$BaSO_4$ or PdO as catalysts. With halogens of low reactivity, which necessitate the use of Raney Ni, the most suitable medium is aqueous KOH or NH_4OH. The radioactivity losses in aqueous buffers are lower when ammonium carbonate or sodium tetraborate are used.

The effect of bases and buffers on the catalytic activity of catalysts is the subject of further study.

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