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LETTERS TO THE EDITORS

Deuteration of Pyridine and the Azines with Heavy Water and Transition Metal Catalysts Prepared by Self-Activation, Hydrogen, and Borohydride Reduction*

Previous publications in this series involving exchange reactions between organic compounds and heavy water have shown that the method used for catalyst reduction and activation is important in determining the final properties of the catalyst (*1*). Four methods of activation are currently in use with the transition metals, namely, exposure to hydrogen at various temperatures (*1*), sodium borohydride reduction (*2, 3*), self-activation (*4, 5*), and radiation-induced self-activation (*6*). For the last two techniques experiments have been essentially confined to platinum whereas with hydrogen and sodium borohydride activation, exchange reactions have been extended to include other Group VIII transition metals (*2, 7*).

In terms of fundamental catalysis, specifically π-complex chemisorption (*8–12*), the deuteration of heterocyclic compounds such as pyridine and the azines is important since in these systems there exists the possibility of an additional nitrogen electron-lone-pair interaction of the flatly adsorbed π-complexed molecule with the catalyst surface (*9*), with a possible subsequent effect on the exchange properties, particularly the orientation effect (*13*). Pyridine also exchanges with heavy water less readily than benzene, especially in the presence of hydrogen-activated platinum (*14*); however, this heterocyclic compound eventually reaches equilibrium within 48 hr at 130°C. By contrast, during self-activation on platinum oxide, pyridine exhibits poor exchange even after 48 hr at 130°C, although this deuterium rate may be increased by either UV or gamma radiation (*6*).

The present paper reports the preliminary results of exchange reactions between pyridine and the azines with heavy water in the presence of transition metals (Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, Pt) prepared by either self-activation, hydrogen, or sodium borohydride reduction of the water-soluble chlorides or insoluble metal oxides. In a typical experiment, sodium borohydride (400 mg) was added slowly to a suspension of the oxide (100 mg) in water (50 ml), hydrolysis of the excess borohydride completed by warming to 70°C, the reduced catalysts washed free from excess salts with water, and the water decanted. The reagents (pyridine, 4.0×10^{-2} moles, and D_2O, 10.0×10^{-2} moles) were then added, and the reaction vessels vacuum sealed and heated at 130°C for 2 days without shaking. For the metallic salts, the chlorides (containing the equivalent of 100 mg of metal) were dissolved in water (50 ml) prior to activation. Analyses were performed by low voltage mass spectrometry on a Metropolitan Vickers MS-2G instrument.

A significant feature of the results (Tables 1 and 2) is that, in general, sodium borohydride activation produces catalysts which are more active for pyridine exchange than catalysts prepared by either hydrogen reduction or self-activation, thus confirming a trend reported for benzene and ethyl benzene (*2*). With the possible exception of platinum, iron, and ruthenium, reduction of the soluble chlorides with $NaBH_4$ yields catalysts which are more

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TABLE 1
DEUTERATION OF PYRIDINE WITH CATALYSTS PREPARED BY $NaBH_4$ REDUCTION[a]

Metal	Oxide	Atom % D[a]	Chloride	Atom % D[a]
Fe	Fe_2O_3	0.30	$FeCl_3$	0.30
Co	Co_2O_3	1.8	$CoCl_2$	16.6
Ni	NiO	0.30	$NiCl_2$	20.1
Ru	$RuO_2{\cdot}H_2O$	26.0	$RuCl_3$	25.5
Rh	Rh_2O_3	26.8	$RhCl_3$	32.8
Pd	PdO	17.8	K_2PdCl_4	35.5
Os	OsO_4	7.6	—	—
Ir	$IrO_2{\cdot}2H_2O$	0.60	$(NH_4)_2IrCl_6$	2.7
Pt	$PtO_2{\cdot}H_2O$	43.2	H_2PtCl_6	27.4

[a] Reactions performed at 130°C for 48 hr; equilibrium $D = 50.0\%$.

reactive than the corresponding oxides in pyridine exchange (Table 1). Of importance in Table 1 is the outstanding reactivity of cobalt, nickel, and palladium chlorides and osmium tetroxide, cobalt being especially significant since the maximum deuteration obtained in benzene and ethyl benzene under equivalent conditions with this catalyst was 0.10 and 0.06% D, respectively.

In Table 2, the results show that hydrogen reduction of the oxides at room temperature yields more efficient catalysts than reduction of the soluble salts, while reduction of chloroplatinic acid produces a better catalyst for pyridine exchange than reduction of the corresponding ammonium salt. Further, self-activation of platinum oxide with pyridine is more efficient than with chloroplatinic acid, although in both systems the extent of deuteration is very small even after a long period of time.

The important result in the exchange of the diazines (Table 3) is the increased toxicity towards benzene deuteration exhibited by all three compounds when compared with pyridine. The toxicity of pyridine has already been reported (*14*) and has been utilized for the selective deuteration of the side-chain hydrogens in ethyl benzene on supported palladium catalysts (*15*); thus the present observation of the reactivity of the diazines should be of value in this work. Pyrazine is the most reactive of the diazines both with and without benzene, whereas *S*-triazine readily decomposes even at 60°C under the present catalytic conditions.

In conclusion, from the results in Table 3, it is obvious that the catalytic technique is attractive for the preparative labeling of pyridine and the diazines with deuterium or tritium (*17*) and is to be recommended because of the limitations of radiation-

TABLE 2
DEUTERATION OF PYRIDINE WITH CATALYSTS PREPARED BY SELF-ACTIVATION AND HYDROGEN REDUCTION

Method of activation	Metal	Oxide[a]	Atom % D	Chloride[b]	Atom % D
Hydrogen reduction	Fe	F_2O_3	0.40	—	—
	Co	Co_2O_3	0.20	—	—
	Ni	NiO	0.30	—	—
	Ru	$RuO_2{\cdot}H_2O$	19.9	—	—
	Rh	Rh_2O_3	26.7	$RhCl_3$	26.7
	Pd	PdO	36.6	K_2PdCl_4	10.1
	Os	OsO_4	0.60	—	—
	Ir	$IrO_2{\cdot}2H_2O$	0.50	—	—
	Pt	$PtO_2{\cdot}H_2O$	47.8	H_2PtCl_6	7.2
				$(NH_4)_2PtCl_6$	0.80
Self-activation	Pt[c]	$PtO_2{\cdot}H_2O$	1.5	H_2PtCl_6	0.80

[a] For direct comparison, all hydrogen reductions were performed at room temperature; however, the reactivity of this series changed slightly when higher reduction temperatures were used (*16*).

[b] The chlorides of Fe, Co, Ni, Ru, and Ir did not readily reduce with hydrogen at room temperature; thus insignificant deuteration of the corresponding pyridines was observed.

[c] Platinum was the only catalyst, either chloride or oxide, examined for self-activation with pyridine.

TABLE 3
Exchange of Pyridine and the Azines on Platinum[a]

Series	Reaction mixture	Quantity (moles × 10^2)	Atom % D
1	Pyridine	4.0	40.0[b]
	Benzene	3.33	15.9[b]
	D_2O	10.0	
2	Pyridazine	4.0	29.4
	D_2O	20.0	
3	Pyrimidine	4.0	25.3
	D_2O	20.0	
4	Pyrazine	4.0	45.2
	D_2O	20.0	
5	Pyridazine	4.0	—
	Benzene	6.67	0.20
	D_2O	20.0	
6	Pyrimidine	4.0	23.1
	Benzene	6.67	0.30
	D_2O	20.0	
7	Pyrazine	4.0	44.1
	Benzene	6.67	0.70
	D_2O	20.0	
8	*S*-triazine	4.0	*S*-triazine decomposed to an insoluble product
	Benzene	2.0	
	D_2O	6.0	

[a] Reactions performed at 130°C for 48 hours with 100 mg PtO_2 pre-reduced with hydrogen at room temperature.

[b] Equivalent data (14) for pyridine (2.0×10^{-2} moles), benzene (2.0×10^{-2} moles) and D_2O (11.0×10^{-2} moles) after 69 hours at 150°C was:—Pyridine (50 ± 2 atom % D, benzene (27.8 ± 0.3 atom % D).

induced methods (*18*). It is also significant that platinum remains the most active of the transition metal catalysts for this work and thus further validates the choice of this element in the development of the π-complex mechanism for catalytic tritiation (3).

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G. E. Calf
J. L. Garnett

School of Chemistry
The University of New South Wales
Kensington, N.S.W., Australia
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