

Thiophen and Furan as Metal Catalyst Poisons. Novel Methods for the Specific and General Labelling of These Compounds with Isotopic Hydrogen†

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THIOPHEN and furan are well-known poisons in the metal-catalyzed hydrogenation of aromatic compounds, particularly if active platinum is used as catalyst. With pre-reduced platinum, thiophen and furan also exchange very slowly with isotopic water¹ (Table, furan). In both hydrogenation² and exchange,¹ the poisoning has been attributed to the influence of the hetero-atom in the adsorption process presumably as species (I) or even elemental

conditions where the metal catalyst is not poisoned. In addition to the implications in fundamental catalysis, these results are important in general deuterium and tritium labelling since both compounds can be easily tagged in one step whereas this is difficult, particularly for furan, by alternate methods. Further, with certain catalysts, useful specificity of isotope may be incorporated (Table).

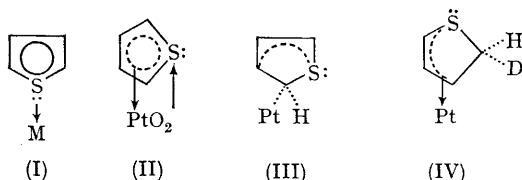
The catalyst for this work is predominantly

TABLE

Catalytic deuteration of thiophen and furan‡

Compound exchanged	Catalyst activation	Compound for catalyst preparation	Atom (% D)	Orientation		Deuterium distribution				
				(2-)+(5-) (α -)	(3-)+(4-) (β -)	d ₀	d ₁	d ₂	d ₃	d ₄
Thiophen	NaBH ₄	PtO ₂ , xH ₂ O	1.0			96.7	2.8	0.4	0.1	
Thiophen	Self-activation	RuO ₂ , H ₂ O	5.6	0.25	0.00	78.3	16.4	4.0	1.1	0.2
Thiophen		IrO ₂ , 2H ₂ O	6.0	0.16	0.08	85.7	5.9	4.8	2.1	6.5
Thiophen		PtO ₂ , xH ₂ O	19.5	0.64	0.14	55.3	20.3	17.3	4.8	2.3
Thiophen		NiCl ₂	4.1	0.16	0.00	86.4	11.6	1.4	0.5	0.1
Thiophen		HCl	39.4	1.05	0.53	12.9	36.2	34.3	13.5	3.1
Furan	NaBH ₄	PtO ₂ , xH ₂ O	1.0			95.9	3.8	0.3		
Furan	Self-activation	RuO ₂ , H ₂ O	7.6	0.22	0.01	82.4	8.6	6.1	1.8	1.1
Furan		IrO ₂ , 2H ₂ O	23.3	0.74	0.19	47.6	23.3	19.5	17.5	2.1
Furan		PtO ₂ , xH ₂ O	7.7	0.30	0.01	76.3	17.9	4.8	0.9	0.1
Furan		NiCl ₂	19.4	0.77	0.01	40.9	40.7	18.0	0.3	0.1

‡ Statistical equilibrium for all exchanges $D_{\infty} = 50.0\%$. Reagents used were thiophen, furan, 5×10^{-2} moles; D₂O, 10×10^{-2} moles; catalyst equivalent to 100 mg. metal. All reactions carried out without shaking at 130° for 48 hr.



sulphur as a consequence of species (I), followed by C-S bond rupture.

We now report the exchange of both thiophen and furan (Table) with isotopic water under

“self-activated” PtO₂,³ some of the other self-activated Group VIII transition-metal oxides and chlorides also being valuable (Table). Self-activation is *in situ* reduction of the inorganic oxide by the organic compound yielding a layer of active platinum atoms in a support of platinum oxide.⁴ Exchange then occurs on this “self-activated” catalyst presumably by the established mechanisms.⁵ Since thiophen and furan only exchange appreciably on “self-activated” platinum, a plausible mechanism for the process involves initial adsorption as species (II),⁶ the

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back-donation effect (or repulsion) of the oxygen in the platinum oxide being sufficient to tilt the molecule such that the sulphur atom no longer touches the catalyst surface and thus prevents poisoning. In the subsequent exchange, the sulphur atom is still repelled from the "self-activated" surface by the oxygen in the bulk PtO_2 ; however, a compensation effect appears to occur since the alpha positions exchange more readily than the beta. Thus the lone pair on the sulphur, whilst not strong enough to inhibit exchange, accentuates the formation of species (III) or (IV), the proposed transition states for the dissociative and associative π -complex substitution mechanisms.^{5,7}

In terms of labelling potential, self-activated PtO_2 is the most efficient for general exchange in thiophen, whereas $\text{IrO}_2 \cdot 2\text{H}_2\text{O}$ is the equivalent for furan. Under acid conditions, the relative rates of exchange at 25° with 57% sulphuric acid⁸ in thiophen at H(2) and H(3) were 1045 for deuterium and 911 for tritium. With dilute HCl in the present work at 130°, the ratio was 4 at the two positions for deuterium. With furan, however, polymerization with dilute acid was extensive and the best general labelling method was with self-activated $\text{IrO}_2 \cdot 2\text{H}_2\text{O}$. In the case of furan, with NiCl_2 , complete specificity of deuteration in the α -positions was observed.

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