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HOMOGENEOUS HYDROGENATION IN THE PRESENCE OF SULPHUR COMPOUNDS

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Tris(triphenylphosphine)chlororhodium, $(Ph_3P)_3RhCl$, was first described as an efficient homogeneous hydrogenation catalyst by Wilkinson,[1] and we have shown previously[2,3] that this catalyst has useful applications in synthetic organic chemistry. A serious disadvantage of heterogeneous catalysts is their susceptibility to poisoning, particularly by traces of sulphides and thiols, and in continuation of our studies we have briefly examined the possibility of using the above catalyst in the presence of sulphur compounds.

(a) In the Presence of Thiophenol

In the presence of thiophenol the rate of hydrogenation of octene-1 and of dehydrolinalool is reduced by the addition of a $2\frac{1}{2}$ molar sulphide:catalyst ratio, but hydrogenation still proceeds at a useable rate. The ergosterol result below shows that this effect is common to olefins of different substitution types. Thiophenol in trace amounts has no marked effect. Addition of a large excess of thiophenol (42 mole excess) causes severe inhibition and the effect may be due to an equilibrium between the normal catalyst species and a catalyst-thiol complex, only the uncomplexed species causing hydrogenation. The results are summarized in Table 1.

TABLE 1

Substance reduced (100 mg. catalyst)	Thiophenol added (mg.)	Hydrogen absorbed (ml.)	Time (mins.)
Octene-1	0	70	60
(400 mg.)	30	19	60
		29	120
Dehydrolinalool	0	80 (1 mole)	13
(500 mg.)	30	80	90
	500	3	60
		5	150

Hydrogenation of ergosterol (500 mg.) with the catalyst (100 mg.) in benzene

(30 ml.) containing thiophenol (30 mg.) for 24 hours gave 18% reduction from the ultraviolet absorption at $\lambda_{max.}$ 283 mμ (ethanol). In the absence of thiophenol, reaction in benzene took ~ 6 hours.

(b) In the Presence of Sulphides

In contrast, sulphides do not affect the activity of the catalyst. Thus ergosterol (500 mg.) was hydrogenated for five hours using 100 mg. catalyst in benzene:ethanol (20 ml.) containing phenyl propyl sulphide (100 mg.). Ultraviolet spectroscopy showed the recrystallized product (413 mg.) to contain only 0.25% of ergosterol.

Allyl phenyl sulphide (500 mg.) was hydrogenated in two hours [100 mg. catalyst in benzene (20 ml.)] to phenyl n-propyl sulphide in 93% yield after distillation.

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References

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