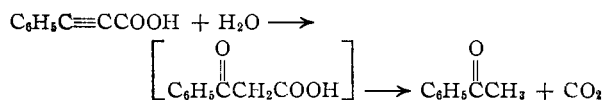## CATALYSIS OF THE HYDRATION OF ACETYLENIC COMPOUNDS BY RUTHENIUM(III) CHLORIDE

Sir:

We wish to report that ruthenium(III) chloride, in aqueous solution, is an effective catalyst for the hydration of acetylenic compounds. This catalytic activity has been demonstrated with acetylene itself as well as with several mono- and di-substituted acetylenes, all of which were found to undergo hydration under relatively mild, and apparently homogeneous, conditions. Recently we have reported[1] that ruthenium(III) chloride is also a homogeneous catalyst for certain hydrogenation reactions.

The ruthenium(III) chloride was prepared, as described earlier,[1] by the reduction of an aqueous solution of ruthenium(IV) chloride with hydrogen. In a typical experiment at 50°, acetylene, at atmospheric pressure, was taken up by a 5 M HCl solution containing 0.1 M Ru(III) and converted to acetaldehyde (along with a small amount of crotonaldehyde) at a rate of 2×10^{-3} mole/liter min. Methylacetylene and ethylacetylene were converted, under similar conditions, to acetone and methyl ethyl ketone, respectively. With phenylpropiolic acid the final products were, as expected, acetophenone and carbon dioxide. since the initial hydration product, a β-keto acid, is unstable with respect to decarboxylation

$$C_6H_5C\!\equiv\!CCOOH + H_2O \longrightarrow$$

$$\left[\begin{matrix} O \\ \| \\ C_6H_5CCH_2COOH \end{matrix} \right] \longrightarrow C_6H_5\overset{O}{\overset{\|}{C}}CH_3 + CO_2$$

In each of these cases the products are the same as obtained with the familiar mercuric salt catalysts.

The rate-law for the hydration of acetylene was found to be

$$-d[C_2H_2]/dt = k[C_2H_2][Ru(III)]$$

The rate constant, k, varied with the HCl concentration, as shown in Fig. 1, passing through a maximum at about 4 M HCl, and falling off very markedly at higher concentrations. This variation apparently reflects a dependence on the Cl^- concentration, since varying the HCl concentration from 1 to 6 M while keeping the Cl^- concentration constant at 6 M with LiCl was without effect on the rate. The most obvious interpretation of this Cl^- dependence is in terms of changes in the relative concentrations of the various Ru(III) chloro-complexes. Using the complex formation data of Fine,[2] it was found that while the rate could not be correlated with the concentration of any single complex, an excellent correlation, shown in Fig. 1, was obtained with the combined concentrations of $Ru(H_2O)_2Cl_4^-$ and $Ru(H_2O)\text{-}Cl_5^-$. This suggests that the observed catalytic activity is due predominantly to these species and, furthermore, that the decline in catalytic activity at high Cl^- concentrations is due to the formation of $RuCl_6{}^{3-}$, *i.e.*, to replacement of the last water molecule in the coördination shell of Ru^{3+}, by Cl^-. A reasonable inference from this is

(1) J. F. Harrod, S. Ciccone and J. Halpern, *Can. J. Chem.*, **39**, 1372 (1961).

(2) D. A. Fine, "Chloride Complexes of Ruthenium(III)," Ph.D. Dissertation, University of California, Berkeley, 1960.
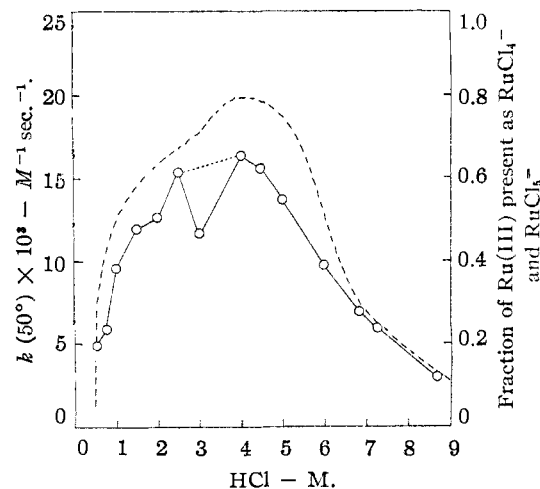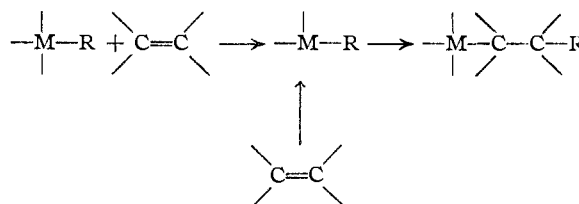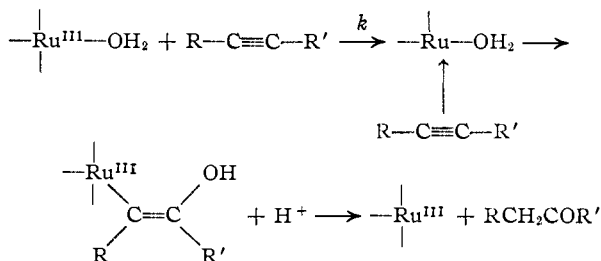
Fig. 1.—Dependence of the rate constant (—O—) and of the concentration of Ru(III) chloride complexes (- - - -) on the HCl concentration: $RuCl_4^-$ and $RuCl_5^-$ concentrations estimated from ref. 2, Fig. 8.

that the hydration reaction involves a *ligand water molecule.*

Many addition reactions of unsaturated (particularly olefinic) compounds, including hydrogenation,[3] hydroformylation[4] and polymerization,[5] have been reported recently which are catalyzed in solution by transition metal complexes. A common feature of the mechanisms which have been proposed[6] for a number of these reactions involves the formation of an intermediate π-complex which rearranges to add the metal ion and another ligand across the unsaturated bond

$$-\!\overset{|}{\underset{|}{M}}\!-\!R + \overset{|}{\underset{/}{C}}\!=\!\overset{/}{\underset{\backslash}{C}} \longrightarrow -\!\overset{|}{\underset{|}{M}}\!-\!R \longrightarrow -\!\overset{|}{\underset{|}{M}}\!-\!\overset{|}{\underset{/}{C}}\!-\!\overset{/}{\underset{\backslash}{C}}\!-\!R$$

$$\overset{\backslash}{\underset{/}{C}}\!=\!\overset{/}{\underset{\backslash}{C}}$$

(where R may be a hydrogen atom, a growing polymer chain, etc.), and then elimination of the addition compound. We believe a similar mechanism operates in the present case, *i.e.*

$$-\!\overset{|}{\underset{|}{Ru^{III}}}\!-\!OH_2 + R\!-\!C\!\equiv\!C\!-\!R' \overset{k}{\longrightarrow} -\!\overset{|}{Ru}\!-\!OH_2 \longrightarrow$$

$$R\!-\!C\!\equiv\!C\!-\!R'$$

$$-\!\overset{|}{\underset{|}{Ru^{III}}} \qquad \begin{matrix} \backslash \\ C \end{matrix}\!=\!\begin{matrix} OH \\ / \\ C \end{matrix} + H^+ \longrightarrow -\!\overset{|}{\underset{|}{Ru^{III}}} + RCH_2COR'$$

$$R \qquad R'$$

The observed kinetics and, in particular, the Cl^--dependence of the rate find a plausible inter-

(3) J. Halpern, J. F. Harrod and B. R. James, *J. Am. Chem. Soc.*, **83**, 753 (1961).

(4) D. S. Breslow and R. F. Heck, *Chem. and Ind.*, 467 (1960); *Proc. 2nd Intern. Cong. Catalysis*, Paris, 1960, Vol. 1, p. 671.

(5) W. L. Carrick, A. G. Chasar and J. J. Smith, *J. Am. Chem. Soc.*, **82**, 5319 (1960); F. J. Karol and W. L. Carrick, *ibid.*, **83**, 2654 (1961).

(6) See, for example, ref. 5; also *Chem. and Eng. News*, April 10, 1961, p. 43.

pretation in terms of this mechanism. Thus the requirement for a *ligand* water molecule in the mechanism can explain the decline in catalytic activity at high $[Cl^-]$, *i.e.*, on going to $RuCl_6^{3-}$. On the other hand, the decrease in catalytic activity at low Cl^- concentrations ($<2\ M$) presumably is associated with the predominance in this region of the lower (*i.e.*, neutral and cationic) chloro-complexes and is attributable to the substitution-inertness of these complexes since the proposed rate-determining formation of an Ru(III)-acetylene complex is essentially a substitutional reaction. This is consistent with Fine's[2] observation that the anionic chloro-complexes of Ru(III) are substitution-labile and equilibrate rapidly with their solution environment, while the lower cationic ones do so only very slowly.

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BIOSYNTHESIS IN THE AMARYLLIDACEAE. TYROSINE AND NORBELLADINE AS PRECURSORS OF HAEMANTHAMINE

Sir:

The incorporation of 2-C^{14}-tyrosine into lycorine,[1,2] norpluvine,[1] and galanthamine[2] by several plants of the *Amaryllidaceae* has been reported. It has been proposed[3] that these alkaloids are synthesized in the plant through the oxidative coupling of phenolic intermediates related to norbelladine (I) and experiments *in vivo* have shown the
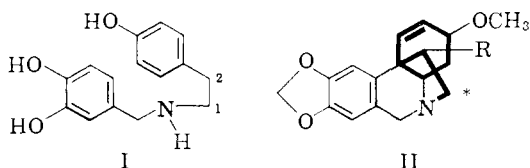
incorporation of activity from norbelladine and several of its partially methylated derivatives into galanthamine,[2] galanthine,[4] haemanthamine[4] lycorine,[5] and norpluviine.[5]

At present the position of the radioactive atom in the alkaloids derived from precursors labeled in the carbon skeleton has been determined by degradation only in the cases of lycorine derived from 2-C^{14}-tyrosine[1] and lycorine derived from 1-C^{14}-norbelladine[5] (I); these two precursors were fed separately to "Twink" double Narcissus plants. We now report the isolation and degradation of radioactive haemanthamine (II, R — OH) isolated from the same feeding experiments. The

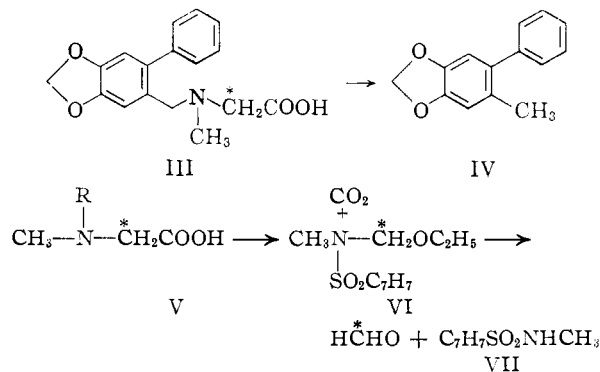(1) A. R. Battersby, R. Binks and W. C. Wildman, *Proc. Chem. Soc.*, 410 (1960).

(2) D. H. R. Barton and G. W. Kirby, *ibid.*, 392 (1960).

(3) D. H. R. Barton and T. Cohen in "Festschrift A. Stoll," Birkhäuser, Basel, 1957, p. 117.

(4) D. H. R. Barton, G. W. Kirby, J. B. Taylor and G. M. Thomas, *Proc. Chem. Soc.*, 254 (1961).

(5) A. R. Battersby, R. Binks, S. W. Breuer, H. M. Fales and W. C. Wildman, *ibid.*, 243 (1961).

cultivation of the bulbs and isolation of lycorine and norpluviine have been reported in our earlier work.[1,5] The alkaloidal fraction remaining after the isolation of lycorine and norpluviine was fractionated on alumina to give radioactive caranine and haemanthamine (II, R = OH) [0.079% and 0.078% incorporation, respectively, from tyrosine; 0.28% and 0.15% incorporation, respectively, from norbelladine]. The degradation of haemanth-

amine to the acid (III) and methanol has been reported earlier.[6] The methanol was converted into its 3,5-dinitrobenzoate. Hydrogenolysis of III afforded the oily biphenyl (IV) (*Anal*. Calcd. for $C_{14}H_{12}O_2$: C, 79.22; H, 5.70. Found: C, 79.05; H, 5.95) and sarcosine (V, R = H) which was isolated as the N-tosyl derivative (V, R = tosyl), m.p. 150–151°.[7] Kolbe electrolysis[8] of the latter afforded carbon dioxide (collected as barium carbonate) and N-ethoxymethyl-N-methyl-*p*-toluene-sulfonamide (VI), $n^{28}D$ 1.5125. (*Anal*. Calcd. for $C_{11}H_{17}NO_3S$: C, 54.29; H, 7.04; N, 5.76; N-CH_3, 6.18; OC_2H_5, 18.52. Found: C, 54.49; H, 7.13; N, 5.88; N-CH_3, 6.42; OC_2H_5, 17.75. Hydrolysis of VI in dilute ethanolic hydrochloric acid in the presence of excess dimedone reagent gave the formaldehyde derivative, m.p. 190–190.5°, and N-methyl-*p*-toluenesulfonamide (VII), m.p. 78–80°. The relative activities of compounds II–VII are listed in the table. Haemanthamine used in the tyrosine experiment had a specific

TABLE I

Compound	Tyrosine-fed	Norbelladine-fed
Haemanthamine (II, R = OH)	1.00^a	1.00
Oxohaemanthamine (II, R = O)	1.00	0.99
2-Methyl-4,5-methylenedioxy-biphenyl (IV)	<0.01	.01
Methyl 3,5-dinitrobenzoate	(.00)	.00
N-Tosylsarcosine (V, R = tosyl)	.98	.99
Barium carbonate	.00	$< .01$
N-Methyl-*p*-toluenesulfonamide (VII)	($< .01$)	.00
Formaldehyde dimethone	.92	.87

^{a} The two parenthetical figures were obtained by combustion of the samples to barium carbonate, counted as an infinitely thick disc. The rest were obtained by scintillation counting in toluene–(2,5-diphenyloxazole-1,4'-bis-2-(5-phenyloxazolyl)-benzene solution.

(6) H. M. Fales and W. C. Wildman, *J. Am. Chem. Soc.*, 82, 197 (1960).

(7) E. Fischer and M. Bergmann. *Ann.*, 398, 118 (1913).

(8) *Cf.* R. P. Linstead, B. R. S. Shepard and B. C. L. Weedon, *J. Chem. Soc.*, 2854 (1951).