A Fast Reversible Equilibrium in the Reaction of Olefins with Mercuric Trifluoroacetate in Aprotic Solvents. Nature of the Addition Compounds

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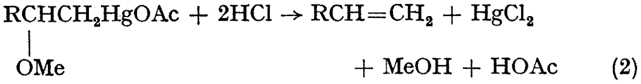
Summary In aprotic solvents such as tetrahydrofuran, olefins react rapidly and reversibly with mercuric trifluoroacetate to form addition compounds, in contrast to their behaviour with silver nitrate with which they form silver ion π-complexes.

THE reaction between an olefin and an appropriate mercuric salt is generally believed to involve a reversible reaction[1] (1).

$$\text{C=C} + HgX_2 \rightleftharpoons \text{X–C–C–HgX} \qquad (1)$$

However, the existence and position of such equilibria does not appear to have been demonstrated directly, possibly because such reactions are generally carried out in protic media and the direct participation of the solvent in such oxymercuration reactions causes them to be essentially complete. Consequently, the reversibility of the reaction is generally deduced from the fact that the olefins are readily regenerated from the oxymercurials by the addition of reagents which complex strongly with mercuric ion[2] (2).



$$\underset{\text{OMe}}{RCHCH_2HgOAc} + 2HCl \rightarrow RCH{=}CH_2 + HgCl_2 + MeOH + HOAc \qquad (2)$$

Mercuric trifluoroacetate, $(CF_3{\cdot}CO_2)_2Hg$, in contrast to other commonly used mercuric salts, is highly soluble in a wide variety of aprotic solvents[3] (moles per litre of solvent, 25°): dimethylformamide (4·4); tetrahydrofuran (THF) (4·3); diethyl ether (7·0); ethyl acetate (1·6); benzene (5·3). In such solutions olefins react rapidly with the reagent, but the reactions generally do not go to completion. For example, in a THF solution with initial concentrations of cyclohexene and $(CF_3{\cdot}CO_2)_2Hg$ of 0·50M, the reaction proceeded to an equilibrium containing 0·10M-cyclohexene (20% of the original concentration). The position of the equilibrium (3) could be established easily.

$$(CF_3{\cdot}CO_2)_2Hg + \text{C=C} \rightleftharpoons CF_3{\cdot}CO_2\text{–C–C–}HgO_2C{\cdot}CF_3 \qquad (3)$$

The effect of structure on the equilibrium constant (4) was examined.

$$\frac{[\text{Compound}]}{[(CF_3{\cdot}CO_2)_2Hg][\text{Olefin}]} = K \qquad (4)$$

At 25·0° equal volumes of 1·00M-solutions in THF of $(CF_3{\cdot}CO_2)_2Hg$ and the olefin (containing a small amount of n-heptane as an internal standard) were mixed to give solutions 0·50M in each reactant. At appropriate intervals, 1·00 ml. portions were removed and rapidly evaporated at 10—20 mm. and trapped at −78°. Portions were examined until successive samples gave constant olefin : n-heptane ratios (g.l.p.c. analysis). The reliability of the technique was shown by determining K for solutions containing cyclohexene and mercuric trifluoroacetate at both 0·50M and 1·00M: values of 37·5 and 37·8 l. mole^{-1} were obtained. The results are summarized in Table 1, together with data on the silver nitrate complexes.[4]

TABLE 1

Equilibrium constants for olefins and metal salts

Olefin	$K^a[Hg(O_2C{\cdot}CF_3)_2]$	$K^b[AgNO_3]$
Hex-1-ene	826	4·3
3,3-Dimethylbut-1-ene	91·5	2·2
Styrene	14	
2-Methylpent-1-ene	7·9	2·1
α-Methylstyrene	0·95	
cis-Hex-2-ene	2·2	0·8
trans-Hex-2-ene	9·2	3·1
1-Methylcyclohexene	4·4	0·5
Cyclopentene	3·4	7·3
Cyclohexene	38	3·6
cis-Cyclo-octene	3·3	14·4
Norbornene	500,000	62

[a] Present study, using 0·50M-solutions of the reactants in THF.

[b] Complex formation with silver nitrate in ethylene glycol at 40°.[4]

The reversibility of the reaction is further established by adding an equimolar quantity of norbornene to a cyclohexene–mercuric trifluoroacetate system at equilibrium. In 30 min. at 25° a quantitative liberation of cyclohexene was observed. It is evident from the two equilibrium constants that the formation of the norbornene complex will be strongly favoured.

The difference in the stability of the complexes formed by silver nitrate with hex-1-ene and 3,3-dimethylbut-1-ene is relatively small, but there is a much larger difference in the equilibria involving the mercury salt. Similarly, of the three cyclic olefins examined, cyclo-octene forms the most stable complex with silver nitrate, whereas it is cyclohexene which gives the most stable complex with $(CF_3{\cdot}CO_2)_2Hg$. These differences point to a major difference in the factors influencing the relative stabilities of the products in these two series. They suggest that these highly reversible derivatives of $(CF_3{\cdot}CO_2)_2Hg$ are not related to the silver ion π-complexes, but to the more stable oxymercuration products in which actual addition to the double bond (3) has been demonstrated.[1,5] We are currently examining the n.m.r. spectra to test this conclusion.

Irrespective of the final conclusions as to the structure, it is evident that these readily formed derivatives should be very helpful in separations and in synthetic work. The olefins can be readily regenerated from the complexes by addition of two moles of pyridine per mole of $(CF_3{\cdot}CO_2)_2Hg$. The reaction evidently proceeds through the formation of a stable co-ordination complex, $(CF_3{\cdot}CO_2)_2Hg,2py$, m.p. 187—188°. Consequently, these derivatives should be helpful for complementing the silver ion complexes to remove a more reactive olefin structure from less reactive structures, followed by mild regeneration with pyridine.

Most of our work was done with THF solutions. However, other solvents are applicable. The results of a study of the effect of solvents on the equilibrium involving cyclohexene are summarized in Table 2.

It therefore appears that the less basic the solvent, the more stable the derivative. In benzene the reaction is 96% complete, as compared to 80% in THF, and 40% in DMF (all for 0·5M-solutions). Consequently, it appears that benzene may be the solvent of choice for the conversion of the less reactive olefins. It is an ideal solvent in which to form the addition compounds for n.m.r. examination.

TABLE 2

The cyclohexene–mercuric trifluoroacetate equilibrium in various solvents

Solvents	$K^a(25°)$, l. mole^{-1}
Dimethylformamide	7·5
Tetrahydrofuran	38
THF + pentane (1 : 1 vol.)	180
THF + pentane (15 : 85 vol.)	500
Diethyl ether	200
Ethyl acetate	413
Benzene	1330

[a] The initial concentration of the two reactants was 0·50M.

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