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SHORT COMMUNICATION

A nuclear magnetic resonance study on the olefin oxidation in acid solution of mercuric nitrate

Oxidation of olefins in the solution of metal ions such as palladium(II)[1], mercury(II)[2,3], thallium(III)[4] or lead(IV)[5] is well known. As for palladium(II), the conversion of a stable π complex of the olefin into an unstable σ-complex was proposed to be the rate-determining step in the reaction sequence[6]. As far as mercury(II), thallium(III) or lead(IV) solutions are concerned, oxymetallated σ complexes have been postulated as the reaction intermediates.

NMR spectra during the oxidative decomposition of (2-hydroxypropyl)mercury(II) complex

When an aqueous solution of (2-hydroxypropyl)mercury(II) complex was maintained at 50°, with NMR spectra taken in sequence, a gradual decrease of the peak intensity due to this complex was observed in comparison with the external tetramethylsilane reference. There was observed a corresponding growth of a singlet peak due to acetone, which gas-chromatography showed to be the sole reaction product.

A rate constant first order with regard to the complex concentration could be determined from the gradual peak decrease of the complex by the following equation, as there is always an unchangeable peak of the external tetramethylsilane in each spectrum.

$$\ln[X/X_0] = -kt \tag{1}$$

In this equation X is the concentration of the complex at time t and X_0 is that of $t = 0$. Another rate constant is obtained from the gradual peak increase of acetone by:

$$\ln[1-(Y/X_0)] = -k't \tag{2}$$

as far as the relationship of $X+Y=X_0$ is recognized, where Y is the concentration of acetone at time t. On the same assumption, the reaction kinetics should obey the equation,

$$\ln[X/(X+Y)] = -k''t \tag{3}$$

without the intermediary of the external tetramethylsilane.

The rate constants, k, k' and k'' were determined to be 1.52×10^{-2}, 1.51×10^{-2} and 1.52×10^{-2} min^{-1}, respectively, for the homogeneous aqueous solution, made up of 2 N nitric acid, 2 M mercuric nitrate and 0.5 M sodium nitrate, with 0.69 M of propene dissolved at room temperature. The relationship of $X+Y=X_0$ was ascertained to hold for all data within the Gaussian dispersion $\sigma = 0.109$. The obedience to the same kinetic equation and the coincidence among the rate constants assures that (2-hydroxypropyl)mercury(II) complex has changed into acetone.

By use of a static reactor with a manometric device, together with gas-chromatographic analysis, the amounts of propene and acetone evolved into the gas phase during the reaction were verified to be negligible in comparison with those of (2-hydroxypropyl)mercury(II) complex and acetone dissolved in the liquid phase. The rate of dissolution of propene into the aqueous mercuric solution was too rapid to follow. At the final stage of the reaction, the solution became brown, a droplet of metallic mercury being precipitated. In the static reactor, the oxidation product of propene by the nitric acid solution of mercuric nitrate (2 *M*) was only acetone, although acrolein was reported to be the main product when diluted mercuric salts were used in acid solution[3].

The three unbranched butene isomers were oxidized to methyl/ethyl ketone more rapidly than was propene, whereas isobutene was hydrated to tert-butanol in the same solution.

NMR spectra of hydroxymercurated olefin complexes

The characteristics of the NMR spectra of hydroxymercurated ethylene were the same in the nitric acid solution of mercuric nitrate as in a basic aqueous solution[7], except that the magnitudes of $J(^{199}\text{Hg–H})$ in the present work were 270 cps for the α-protons and 229 cps for the β, whereas 217.5 cps and 159 cps, respectively, were reported for the basic solution[8]. These deviations may be due to the anion effect on

TABLE 1

THE CHEMICAL SHIFTS AND THE PROTON–PROTON SPIN COUPLING CONSTANTS OF HYDROXYMERCURATED OLEFINS

Olefin	*Hydroxymercurated olefin*	*Chemical shift (ppm)*[a]					*Coupling constant (cps)*		
		α^b	β	β'	γ	δ	$\alpha\beta$	$\alpha\beta'$	$\beta\gamma$
Ethylene	$HOCH_2CH_2Hg^+$	7.63	6.07				7.8[c]		
Propene	$CH_3CH(OH)CH_2Hg^+$	7.66	5.79		8.79		5.9		5.9
1-Butene	$CH_3CH_2CH(OH)CH_2Hg^+$	7.66	6.08		8.60	9.14	5.9		5.9
trans-2-Butene	*erythro*-$CH_3CH(OH)CH(CH_3)Hg^+$	6.93	6.13	8.70	8.81		5.4	7.6	6.0
cis-2-Butene	*threo*-$CH_3CH(OH)CH(CH_3)Hg^+$	6.99	6.14	8.62	8.81		4.0	7.6	6.0
Isobutene	$(CH_3)_2C(OH)CH_2Hg^+$	7.52			8.61				

[a] Acetone (τ 7.83 ppm) is used as the internal reference. [b] Designation of α, β, etc. is made from the mercurated carbon, β' being used for the branching protons. [c] Obtained as $(J_{AX}+J_{AX'})/2$.

TABLE 2

THE PROTON–MERCURY SPIN COUPLING CONSTANTS OF HYDROXYMERCURATED OLEFINS

Olefin	*Hydroxymercurated olefin*	*Coupling constant (cps)*					
		Hg–H$_\alpha$		*Hg–H*$_\beta$		*Hg–H*$_\gamma$	
		60 *Mc*[a]	100 *Mc*[b]	60 *Mc*[a]	100 *Mc*[b]	60 *Mc*[a]	100 *Mc*[b]
Ethylene	$HOCH_2CH_2Hg^+$	271	269	228	231		
Propene	$CH_3CH(OH)CH_2Hg^+$	261	259	?[c]	?[c]	0	0
Isobutene	$(CH_3)_2C(OH)CH_2Hg^+$	256	255			23	23

[a] NMR measurements are made at 60 Mc. [b] NMR measurements are made at 100 Mc. [c] Presence of ^{199}Hg satellites is questionable.

the ^{199}Hg–H coupling, which was recognized among organomercury(II) complexes[9]. Recently Kreevoy and Schaefer[10] showed that these values of $J(^{199}\text{Hg–H})$ are due to free rotation along the C–C single bond of this complex.

Hydroxymercurated *trans*-2-butene and *cis*-2-butene gave NMR spectra which differed from each other. Although no ^{199}Hg–H satellites were detected for these complexes, the simple $(2n+1)$ splitting pattern observed for hydroxymercurated *cis*-2-butene and the magnitude of $J(\text{H–H})_{\text{vic}}$ 5.4 cps for hydroxymercurated *trans*-2-butene can only be interpreted without contradiction by the free rotational model as well as for hydroxymercurated ethylene, because the J_{vic} value of hydroxymercurated olefin in the rigid trans conformation is 10 cps or so[11].

Hydroxymercurated isobutene gave two singlets accompanied by ^{199}Hg satellites. The observed magnitude of $J(^{199}\text{Hg–H})$ 23 cps is almost equal to $J(^{199}\text{Hg–H})$ $21 \sim 22$ cps of methoxymercurated isobutene[12,13], which suggests that substitution of a hydroxy group for a methoxy group has little influence, whereas the substituent effect on the long range ^{199}Hg–H coupling of alkyl groups is large[12].

No change in NMR characteristics of hydroxymercurated propene was observed between room temperature and 50°. Neither physically dissolved propene nor a π-complexed species was found under the conditions investigated. It is to be noted that the intensities of the ^{199}Hg–H satellites were less than those expected from the natural abundance of ^{199}Hg, although hydroxymercurated ethylene and isobutene gave proper intensities corresponding to it.

The chemical shifts and the proton–proton spin coupling constants of these complexes are tabulated in Table 1 and the proton–mercury spin coupling constants in Table 2.

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