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EVIDENCE FOR AN ADDITION INTERMEDIATE IN THE HYDROLYSIS OF ALKYL NITRITES

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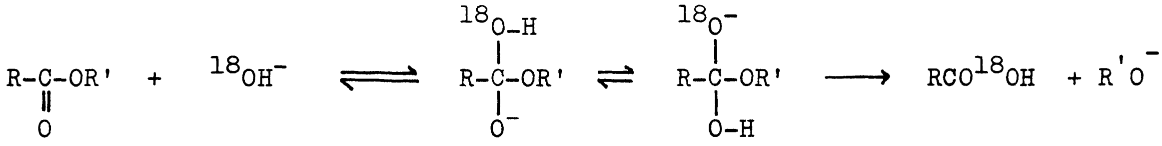
Formation of an addition intermediate in the hydrolysis of alkyl nitrites is suggested on the basis of the incorporation of the oxygen atom of water into the ester recovered.

The existence of a tetrahedral addition intermediate (I) or (I') in the hydrolysis of carboxylic esters and amides has been firmly established by kinetic evidence and by oxygen-18 incorporation into the ester recovered from the medium water.$^{1)}$



$$R\text{-}\underset{\underset{O}{\|}}{C}\text{-}OR' + {}^{18}OH^- \rightleftharpoons R\text{-}\overset{{}^{18}O\text{-}H}{\underset{O^-}{C}}\text{-}OR' \rightleftharpoons R\text{-}\overset{{}^{18}O^-}{\underset{O\text{-}H}{C}}\text{-}OR' \longrightarrow RCO^{18}OH + R'O^-$$

(I) (I')

The formation of similar addition intermediates in the hydrolysis of esters or amides other than carboxylic acid derivatives has not been verified except for alkyl hydrogen phosphates in acid conditions.$^{2)}$ On the contrary, for sulfuric esters,$^{3)}$ diarylphosphinic esters,$^{4)}$ aryl sulfonates,$^{5)}$ and arylsulfinamides$^{6)}$ no incorporation of the oxygen atom of the medium is reported, and the existence of such intermediate was denied in these cases.

During the hydrolysis of alkyl nitrite under both alkaline and acid conditions we have observed oxygen exchange into the ester recovered and the results will be described in this paper.

Kinetics of the hydrolysis of alkyl nitrites has been studied by Allen.$^{7)}$ The reaction followed a second order rate equation in the alkaline medium:

$$-d[RONO]/dt = k[RONO][OH^-]$$

Under the acid conditions, the rate is expressed by the following equation:

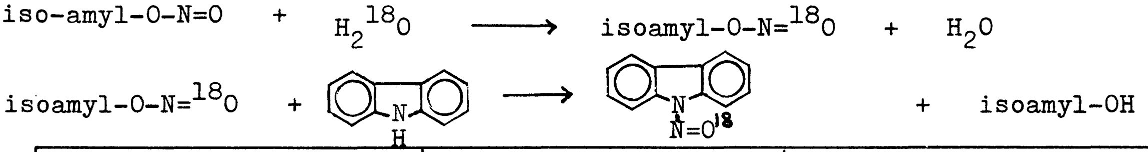
$$-d[RONO]/dt = k'[RONO][H^+]$$

The fact that the bond cleaved is not the C-O bond but the N-O bond is shown by use of the ^{18}O label technique and also by retention of the configuration of the alcohol obtained by the hydrolysis of optically active 1-methylheptyl nitrite.$^{7)}$ The reaction mechanism in the presence of an acid catalyst was written as follows:

$$RONO + H^+ \rightleftharpoons [RO{\cdot}NOH]^+$$
$$[RO{\cdot}NOH] + H_2O \rightleftharpoons ROH + [H_2NO_2]^+ \quad \text{----- rate determining step}$$
$$[H_2NO_2]^+ \rightleftharpoons HNO_2 + H^+$$

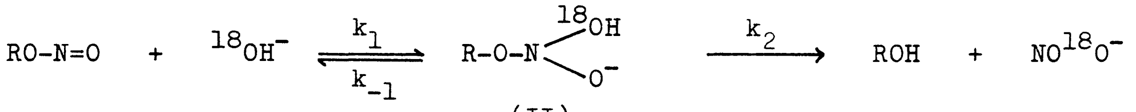
Allen did not consider the possibility of the formation of an addition intermediate.

When isoamyl nitrite was hydrolyzed in a dimethyl sulfoxide-$H_2{}^{18}O$ or dimethyl sulfoxide-$D_2{}^{18}O$ mixture in the presence of alkali (sodium hydroxide or tetramethylammonium hydroxide) at room temperature and the reaction was interupted halfway, the ester recovered was found to contain a significant amount of ^{18}O. When the hydrolysis was carried out in the presence of a catalytic amount of sulfuric acid in dioxane-$D_2{}^{18}O$ at room temperature, a larger percentage of ^{18}O was detected in the ester recovered. In order to determine the distribution of ^{18}O, the ester recovered was treated with carbazole in dioxane at room temperature for two days, giving N-nitrosocarbazole, which was found to contain about twice of the label. Therefore, Oxygen-18 entered into nitroso group of the ester during the hydrolysis.



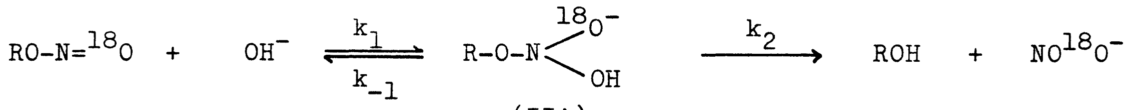
reaction conditions	$Me_4NOH/DMSO-H_2{}^{18}O$	H_2SO_4/dioxane-$D_2{}^{18}O$
	^{18}O excess atom percent$^{8)}$	
recovered ester	0.14 ± 0.03 %	0.40 ± 0.03 %
N-nitrosocarbazole	0.35 ± 0.04 %	0.70 ± 0.04 %
starting water	1.30 %	1.30 %

Above results may be explained by assuming the formation of an addition intermediate (II), which has a sufficient life time to allow the scrambling of the label.



$$\text{RO-N=O} + {}^{18}OH^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{R-O-N}\begin{matrix} {}^{18}OH \\ O^- \end{matrix} \xrightarrow{k_2} \text{ROH} + NO^{18}O^-$$

(II)



$$\text{RO-N=}{}^{18}O + OH^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{R-O-N}\begin{matrix} {}^{18}O^- \\ OH \end{matrix} \xrightarrow{k_2} \text{ROH} + NO^{18}O^-$$

(II')

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