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THERMODYNAMIC AND KINETIC STUDY OF THE REACTION OF NITROSYLCHLORIDE WITH ALIPHATIC ALCOHOLS IN GLACIAL ACETIC ACID BY STOPPED-FLOW TECHNIQUE.

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The kinetics and equilibria for the reactions of nitrosylchloride with alcohols : $ROH + NOCl \rightleftarrows RONO + HCl$ have been studied spectrophotometrically (at 464 nm. where only NOCl absorbs) in glacial acetic acid at 20°C. The reactions are very fast and the rates and equilibria are sensitive to electronic effects and hyperconjugation and show little sensitivity to steric effects.

The equilibrium measurements were run on a Unicam SP800 spectrophotometer. The presence of a sharp isosbestic point and the fact that the same equilibrium position is reached, whether the initial reagents are NOCl+ROH, RONO+HCl+ROH or NOCl+HCl+ROH, show that in the present experimental conditions the equilibrium considered is the only process taking place. The ranges of initial concentrations were :

alcohol : 0,5 to 1,8 $M.l^{-1}$; HCl : 0 to 0,274 $M.l^{-1}$; NOCl : 0 to 0,18 $M.l^{-1}$; nitrite : 0 to 0,3 $M.l^{-1}$. (K(a), Table 1).

The kinetic experiments were run with a Durrum stopped-flow spectrophotometer. The initial concentrations were varied between 0,5 and 1,5 $M.l^{-1}$ for the alcohols and between 0,020 and 0,090 $M.l^{-1}$ for NOCl to observe a significant variation in absorbance.

The kinetic equation is :

$$V = \vec{k}_2[ROH].[NOCl] + \vec{k}_3[ROH]^2.[NOCl] - \overleftarrow{k}_2[RONO].[HCl] - \overleftarrow{k}_3[RONO].[HCl].[ROH]$$

but the constants k_3 are significant only for methanol ($\vec{k}_3 = 49\ s^{-1}M^{-2}l^2$) so that for all the other alcohols the kinetic equation is simplified to :

$$V = \vec{k}_2[ROH].[NOCl] - \overleftarrow{k}_2[RONO].[HCl] \qquad (\vec{k}_2,\ \text{Table 1})$$

In the second series of experiments the equilibrium constants were also determined by measuring the absorbance of a blank (A_0 : without ROH) and of the reaction mixture when the equilibrium was reached ($A_{éq}$) (K(b), Table 1).

The equilibrium constants vary slightly with the alcohol concentration but may be considered constant in the concentration range used except for methanol :

K at $C_{MeOH} = 1\ M.^{-1} = 3{,}45.10^{-2}$ and K (extrapolated at $C_{MeOH} = 0) = 2{,}4.10^{-2}$.

TABLE 1

EQUILIBRIUM CONSTANTS AND KINETIC CONSTANTS FOR REACTION :

$ROH + NOCl \rightleftharpoons RONO + HCl$

Solvent : glacial acetic acid ; temperature : 20°C.

N°	R-	$K.10^3$(a)	$K.10^3$(b)	$\overrightarrow{k}_2\ s^{-1}M^{-1}l$(b)	$\overleftarrow{k}_2\ s^{-1}M^{-1}l$(c)
1	n.butyl-	24 ±2	24 ±3	93 ±11	3300± 360
2	isobutyl-	20 ±3	20 ±1	73 ±4,5	3580± 750
3	sec-butyl-	13 ±2	12 ±2	19,5±1,1	1560± 350
4	tert-butyl-	2,3±0,4	2,4±0,5	7 ±0,8	3100± 950
5	2Cl-ethyl-	1,3±0,1	1,3±0,2	12,2±0,9	9200±1600
6	2 pentyl-	12 ±1,6	13 ±2	19,7±1,3	1600± 300
7	cyclohexyl-	-	10 ±1	30 ±2,6	3000± 600
8	cyclohexyl-methyl-	-	24 ±2	79 ±4,5	3200± 450
9	methyl-	-	24 ±1 (d)	80 ±5,7	2300± 350
10	4Cl-butyl-	5,8±0,6	5,7±0,8	42 ±8,5	7200±2200

(a) First series of measurements (equilibria only, UNICAM SP800)

(b) Second series of measurements (equilibria + kinetics, DURRUM stopped-flow)

(c) $\overleftarrow{k}_2 = K.\overrightarrow{k}_2$ except for n.butyl- derivative where the value is experimental

(d) Extrapolated at $C_{MeOH} = 0$.

In all cases the equilibrium is shifted towards the reactants. Since the reaction is exothermic the entropy has to decrease. This may be attributed to the fact that HCl is more solvated, being more polar than NOCl.

The kinetics of the reaction between butylnitrite and HCl have also been investigated. This reaction is so rapid that its rate can only be measured when the reactants are mixed in nearly stoechiometric concentrations. In these conditions the reaction is almost complete and the kinetic equation is :

$$V = \overleftarrow{k}_2[n.butONO].[HCl] \qquad \text{with } \overleftarrow{k}_2 = 3300 \pm 360\ s^{-1}M^{-1}l$$

This value of $\overleftarrow{k}_2$ is consistent with the equilibrium measurements since :

$$\frac{\overrightarrow{k}_2}{\overleftarrow{k}_2} = 2{,}9.10^{-2} \pm 0{,}6.10^{-2} \text{ and } K = 2{,}4.10^{-2} \pm 0{,}2.10^{-2}$$

The values of K and $\overrightarrow{k}_2$ have been correlated by TAFT-INGOLD equation :

$$\log K = - 2,36.\sigma^* + 0,17.E_s + 0,49.(N-3) - 1,26$$

with $r = 0,988$ and $\Delta\rho^* = 0,14$

$$\log \overrightarrow{k}_2 = - 1,40.\sigma^* + 0,05.E_s + 0,62.(N-3) + 2,41$$

with $r = 0,943$ and $\Delta\rho^* = 0,19$

The calculated equation for the reverse reaction is :

$$\log \overleftarrow{k}_2 = 0,96.\sigma^* - 0,12.E_s + 0,13.(N-3) + 3,67$$

and it is in fair agreement with the result obtained for n.butylnitrite since it gives for $\overleftarrow{k}_2$ a value of 2900 $s^{-1}M^{-1}l$.

The electron-donating substituents shift the equilibrium to the right by enhancing the basicity of the alcohol and stabilizing the nitrous ester.

The polar effects of the substituents on the equilibria is rather important : the ρ value is much greater than those observed for the acid-base equilibrium ($\rho = 1,4$) (2) and the esterification of alcohols ($\rho \approx 1$ since β esterification = 0,7 (3)). The -N=O group appears thus to be a much better electron withdrawer than the $R-\underset{|}{C}=O$ group. This is in agreement with the fact that cis-trans conformers are observed at room temperature in the nitrite series and not in the carboxylic esters.

The rate of the direct process is increased by electron-donating substituents which enhance the nucleophilicity of the alcohols.

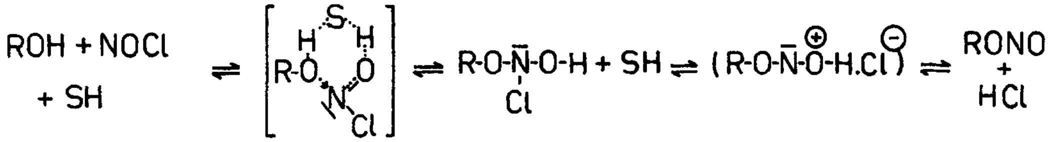
The ρ* values for the rates are about half of that observed for the equilibria. This suggests that the charge on the oxygen in the transition state has a value half way between that for the reactants and the products.

The influence of steric effect on the equilibrium is weak. This is probably due to enhanced solvation of alcohol when hindrance is poorer, the reactionnal site being then still inaccessible. The nucleophilicity of the alcohol is also diminished by solvation with acetic acid.

The hyperconjugation stabilizes probably the nitrous ester by enhancing the charge delocalization in the nitrite group.

The weak influence of steric effect on the reaction rate is explained by the small size of nitrosyl group. The hyperconjugation probably stabilizes the transition state where a positive charge appears on the oxygen.

We propose a mechanism in which the alcohol attacks the NOCl to form an adduct on the N=O double bond and the intermediate loses HCl giving the nitrite:



S-H is acetic acid or alcohol.

This mechanism analogous to the one proposed for the alcoholysis of acyl chlorides by Minato (4) fits well our results. It is difficult to decide which step is the rate determining one ; yet, we feel it is the formation of the intermediate. This mechanism explains the catalysis by a second molecule of alcohol. In the reverse reaction the first step has to occur in the ion pair to fit the observation that only a first order in HCl is observed while Allen (5) found a first plus a second order in HCl for the acid-hydrolysis of the nitrites.

The effect of the methanol concentration on the equilibrium constant is probably a solvent effect : the solvation by the alcohol reduces the activity of HCl. A hydrochloric acid-methanol complex, $CH_3OH.HCl$ has been described in the gaseous phase (6) and alcohol-acid association is much more stable for methanol than for other alcohols (7) in acetic acid.

These results have been useful to specify the conditions for realizing the demination of amides in organic solvents by an active nitrosating species produced from nitrous ester. As in aqueous solvents an acid catalysis is necessary (1). The kinetics of the reaction are however complicated by the protonation of the amides and associations in the solvent used (8).

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(1) In previous works (9) it was proposed that nitrites react with amides without catalysis. In the sequel it was observed that pure nitrites do not react. The values of the equilibrium constants reported in this paper are useful to understand that acid traces in the nitrite are able to catalyze the reaction chiefly if the nitrous ester is in great excess.

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