[CONTRIBUTION FROM THE RICHARDSON CHEMISTRY LABORATORIES, TULANE UNIVERSITY]

THE PYROLYSIS OF SOME IMIDOESTER HYDROCHLORIDES

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Imidoester hydrochlorides are widely employed as intermediates in the preparation of orthoesters:

I. RCN + ROH + HCl \rightarrow RC(OR)=NH₂Cl

II. $RC(OR) = NH_2Cl + 2 ROH \rightarrow RC(OR)_3 + NH_4Cl$

Yields of orthoester are good if unsubstituted straight chain nitriles and alcohols are employed in the preparation of the salts. When the nitrile used has one or more substitutions in the *alpha* position or two in the *beta* position the quantity of orthoester obtained may be very low with an amide or a normal ester being obtained in considerable quantity (1).

III. $RC(OR) \longrightarrow NH_2Cl \xrightarrow{ROH} RCONH_2 + RCl$ IV. $RC(OR) \longrightarrow NH_2Cl + 2 ROH \xrightarrow{heat} RCOOR + ROR + NH_4Cl$

Steinkopf (2) has shown that imidoester salts are not even obtained when the following nitriles are treated with hydrogen chloride and methanol:

Cl₂CHCN; Cl₂CCN; Br₃CCN; CH₂(NO₂)CN; Cl₂(NO₂)CCN

These nitriles are converted completely to the corresponding amides.

Pinner (3) first showed that dry imidoester hydrochlorides decompose, when heated, into amides and organic halides (equation III without the alcohol). Hartigan and Cloke (4) have determined for this type of decomposition a "mean temperature of pyrolysis" for a considerable number of imido- and thioimidoester hydrochlorides. In the authors' laboratory it was noted (5), during an investigation of the properties of some benzyl imidoester hydrochlorides, that benzyl- β -chloroimidopropionate hydrochloride decomposed completely into β chloropropionamide and benzyl chloride when it stood for a few days at room temperature.

The purpose of the present work is to gain information about the influence variations in R— have on the ease of pyrolysis of the imidoester hydrochlorides.

The imidoester salts were heated, without a solvent, in a constant temperature bath for varying periods of time. The amount of decomposition was determined in each case and it was noted that fair first order constants were obtained for the reaction. Making use of this observation, half-life periods were calcu-

lated by means of the formula $t_{i} = \frac{0.693}{k}$. A few decomposition reactions were

then run for each salt and an approximate experimental half-life period was obtained. The figures given in Table I represent half-life values calculated from the data obtained when the reactions were 49-51% complete. Due to the complex nature of the systems under investigation, it was not practical to make measurements over a wide reaction range.

The extent of decomposition was determined as follows: the sample was removed from the bath and mixed with water to decompose the remaining imidoester hydrochloride:

 $RC(OR) = NH_2Cl + HOH \rightarrow RCOOR + NH_4Cl$

No.	R-	R'ª	$t_{1/2}$ in minutes at °C.				
			50.3	60.0	65.3	70.3	_
1	CH3-	C ₆ H ₅ CH ₂	465	110	50		
2	CH3-	m-NO ₂ C ₆ H ₄ CH ₂			1253	605	
3	CH3-	$p-\mathrm{NO}_2\mathrm{C}_5\mathrm{H}_4\mathrm{CH}_2$	i	1200	585		
4	C ₆ H ₅	$C_{6}H_{5}CH_{2}$	261		24		
5	C ₆ H ₅ —	$m - NO_2C_6H_4CH_2$	530	120			
6	C₅H₅—	$p-\mathrm{NO}_2\mathrm{C}_6\mathrm{H}_4\mathrm{CH}_2-b$		780			
7	$ClCH_2CH_2$ —	C ₆ H ₅ CH ₂	390	85	42		
8	$ClCH_2CH_2$ —	$m-\mathrm{NO}_{2}\mathrm{C}_{6}\mathrm{H}_{4}\mathrm{CH}_{2}-$	825	136			
9	$ClCH_2CH_2$ —	$p-\mathrm{NO}_2\mathrm{C}_6\mathrm{H}_4\mathrm{CH}_2$ b	1200				
10	C_6H_5	C_2H_5 —				2653	
11	ClCH ₂ CH ₂ —	C ₆ H ₆ ─				29 hours (r dec.)	10

TABLE I	
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DECOMPOSITION OF IMIDOESTER HYDROCHLORIDES, RC(OR')=NH2Cl

 a R'— = o-NO₂C₆H₄CH₂—; this group was not included because of unusual difficulties encountered in efforts to prepare the pure salts. b These compounds gave very erratic analytical results and for this reason are reported only at temperatures where reproducible figures were obtained.

Formaldehyde solution was added to combine with the ammonia and to liberate hydrogen chloride. The hydrochloric acid was then titrated with standard base. This method gave excellent results when it was used with the pure imidoester salts and with mixtures of salt, ester, and benzyl halide.

Each decomposition mixture was examined and shown to contain only imidoester hydrochloride, amide, and organic halide.

DISCUSSION

In a pyrolytic study on the solid state the results are not as simple (by comparison) to interpret as solution data in view of complicating factors such as crystal structure, two phase systems, etc. Therefore a reaction mechanism is not offered for the decomposition reaction. However if it is assumed, as suggested by McElvain (1), that the thermal decomposition of these salts involves an intramolecular attack of the halogen of an undissociated ion pair on the carbon of the alkoxy group, then the methyl group as R— in the formula RC(OR')NH₂Cl (Table I, compounds 1, 2, 3) should, and does, show a stabilizing effect over a group such as the phenyl of compounds 4, 5, and 6 or the chloroethyl group of compounds 7, 8, and 9. The nitrobenzyl group also should, and does, produce a higher degree of stability when it is in the R' position than the unsubstituted benzyl. Although the data confirm this prediction, it is not possible to estimate the relative stabilizing effects of a *meta* nitro or a *para* nitro group when these two groups only are being considered. A consideration of compounds 5 and 6 shows the nitro derivatives with a reversed order of relative stability over that noted for compounds 2 and 3. When R— is the chloroethyl group, as in compounds 8 and 9, the relative order of effect of the nitrobenzyl groups is the same as when R— is phenyl.

Compound 10 illustrates the relatively high degree of stability achieved when R'— is an unsubstituted alkyl group like ethyl. In a recent kinetic study, McElvain (1) has indicated this stabilizing effect of alkyl groups, particularly when R'— is other than methyl. In view of this stability it is not surprising to find that in the preparation of orthoesters the amide decomposition reaction is an insignificant factor when both R— and R'— are unsubstituted alkyl groups.

Compound 11 shows the extraordinary stability of the salt when R'— is phenyl. This result is in line with the fact that no one has reported the isolation of chlorobenzene from the decomposition of a phenyl-substituted imidoester hydrochloride.

EXPERIMENTAL

The *imidoester hydrochlorides* used were prepared in this Laboratory and have been previously reported (5).

Individually and accurately weighed samples (approximately 0.2 g.) were placed in small, ordinary weighing bottles and these bottles were used as reaction flasks. The cap of each bottle was wired on and the bottle was placed in a thermostatically controlled oilbath, the temperature of which was regulated to within $\pm 0.03^{\circ}$. After a definite time interval the bottle was removed from the bath, immediately opened, and its contents mixed with distilled water so as to hydrolyze the imidoester salt remaining. Then 10 ml. of 20% neutral formaldehyde solution was added to free hydrogen chloride from the ammonium chloride. The hydrochloric acid formed was titrated with 0.02 N NaOH using phenolphthalein as the indicator. From the data obtained the degree of decomposition of each salt was calculated.

Because of the hygroscopic nature of many of the salts, the compounds were handled, at all times, in the absence of atmospheric moisture.

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SUMMARY

A number of dry imidoester hydrochlorides $[RC(OR')=NH_2Cl]$ were heated at constant temperatures to bring about their decomposition into amides and organic chlorides. Approximate half-life values were obtained for each salt and the values were compared to show how variations in R— and R'— effected the rate at which the imidoester salts decomposed.

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