

## Formation of Carbon Monoxide in the Pyrolysis of *N*-Alkylchloroacetamides

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It has been shown<sup>1</sup> that an increase in acid strength enhances the thermal elimination of olefins from carboxylic esters. Since a common mechanism has been postulated for this reaction and for the thermal elimination of olefins from *N*-alkylacetamides,<sup>2</sup> the effect of acid strength on the pyrolytic behaviour of the amides is of interest. Although the amides are appreciably more resistant to thermal degradation than the corresponding esters, few kinetic data for pyrolysis of simple amides have appeared in the literature. We have

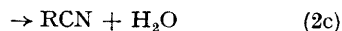
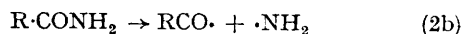
found that an increase in acid strength introduces a second major mode of decomposition in the *N*-alkylacetamides at temperatures at which olefin elimination was expected to predominate.

The *N*-*t*-butyl-amides of acetic, mono-, di-, and tri-chloroacetic acids were prepared and purified by standard methods;<sup>3</sup> all gave satisfactory elemental analyses. Pyrolyses were carried out in a static system at 354°C with a Pyrex reaction vessel seasoned with the decomposition products of allyl bromide and the amides. Reaction products

were distilled at  $-196^\circ$  and  $-98^\circ$  (methanol slush) and analysed by mass spectrometry and gas-liquid chromatography.

In the case of *N*-*t*-butylacetamide, isobutene was the only significant gaseous product, as had been found previously.<sup>4</sup> Pyrolysis of the chlorinated analogues gave, in addition to isobutene, a large amount of material volatile at  $-196^\circ$ ; mass spectrometric analysis showed this to be predominantly CO, with methane present in small amounts. Thus 2-chloro-*N*-*t*-butylacetamide gave a non-condensable product fraction containing 94 mole % CO and the comparable fraction from the pyrolysis of 2,2-dichloro-*N*-*t*-butylacetamide analysed at 99 mole % CO. The formation of CO and isobutene were shown to be kinetically of the first order: the experimental rate constants for CO formation are given in the Table.

either the chloroacetyl radical or the nitrile:—



Our results suggest that with increasing  $\alpha$ -substitution there is increasing competition between (1a—1b) and (2a—2c) as the main mode of decomposition of starting material. The quantitative yield of isobutene and the negligible amount of CO formed in the pyrolysis of *N*-*t*-butylacetamide point to (2a) and (2c) as the main reactions involved; it has been shown<sup>6</sup> that (2b) is negligible for acetamide below  $740^\circ$ . Analysis showed that water and MeCN were the only liquid products formed in the pyrolysis. For  $\text{R} = \text{CH}_2\text{Cl}$ , the yield of CO suggests that (1a) and (1b) are more important in the decomposition than in the previous case,

TABLE Production of CO from *N*-alkylchloroacetamides at  $354^\circ$

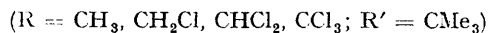
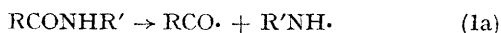
Compound R-CONH·CMe <sub>3</sub>	$10^5 k(\text{CO}) \text{ sec.}^{-1}$		Packed vessel <sup>b</sup> No Inhibitor	$\frac{k(\text{olefin})}{k(\text{CO})}$
	Unpacked vessel No inhibitor	Inhibitor <sup>a</sup>		
R = CH <sub>3</sub>	0·01	0·01	0·01	37 <sup>c</sup>
CH <sub>2</sub> Cl	0·28	0·20	0·31	2
CHCl <sub>2</sub>	5·30	4·00	4·8	1
CCl <sub>3</sub>	2·80	7·2	2·1	—

<sup>a</sup> Cyclohexene

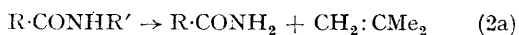
<sup>b</sup> Surface to volume ratio *ca.* 5.

<sup>c</sup> Values in this column refer to pyrolyses in unpacked vessels in the absence of inhibitor.

Fission of the amide at the carbonyl–nitrogen bond, followed by decomposition of the chloroacetyl radical, can account for the observed production of CO:—



However, it has been demonstrated<sup>5</sup> that *t*-butylamine is stable at the temperature of our experiments; the formation of isobutene cannot be explained in terms of the above reaction sequence. An alternative mechanism requires elimination of isobutene as the initial step, presumably by a process analogous to that for olefin elimination from the carboxylic esters:—



(II)

Subsequent decomposition of amide (II) can yield

although the formation of *t*-butylamine required by (1a) has not been confirmed unambiguously. The importance of (2a) and (2c) in the decomposition is indicated by the observed value of  $k(\text{olefin})/k(\text{CO})$  and the presence of water in the liquid products. The formation of  $\text{CH}_2\text{Cl-CN}$  has not been confirmed.

For  $\text{R} = \text{CHCl}_2$  and  $\text{R} = \text{CCl}_3$  unresolved analytical difficulties make discussion of the experimental results premature. It should be noted however, that the value of  $k(\text{olefin})/k(\text{CO})$  for the 2,2-dichloroacetamide is compatible with the proposed mechanism. The 2,2,2-trichloroacetamide seems to be a special case; pyrolysis in the absence of inhibitor gave CO as a product, but no isobutene. Pyrolysis in the presence of inhibitor gave isobutene as a product, and in addition the formation of CO was enhanced relative to the uninhibited decomposition. Reactions similar to those proposed by Mukaiyama<sup>7</sup> may be responsible for these results, although the ionic mechanism suggested does not seem credible under our experimental conditions.

The observed linear relationship between  $\log k(\text{CO})$  and the  $\text{p}K_{\text{actd}}$  for the cyclohexene-inhibited pyrolyses of these *N*-alkylchloroacetamides suggests that the experimental results can be interpreted in terms of the inductive effects of

the halogens.<sup>1,8</sup> A detailed study of the inhibited pyrolysis of the chloro-*N*-*t*-butylacetamides is currently in progress.

(Received, November 14th, Com. 892.)

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<sup>4</sup> A. Maccoll and R. T. B. Rye, unpublished results.

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<sup>7</sup> T. Mukaiyama, M. Tokizawa, and H. Tokei, *J. Org. Chem.*, 1962, **27**, 803.

<sup>8</sup> A. T. Blades, *Canad. J. Chem.*, 1954, **32**, 366; G. G. Smith, F. D. Bagley, and R. Taylor, *J. Amer. Chem. Soc.*, 1951, **73**, 875.