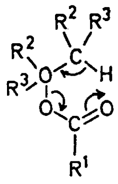
The Thermolysis of ^{18}O Labelled t-Butyl *NN*-Dimethyl Carbamate and its Possible Bearing on the Course of Thermal β-Elimination Reaction Mechanisms

By HAROLD KWART* and JOEL SLUTSKY
(*Department of Chemistry, University of Delaware, Newark, Delaware* 19711)

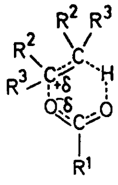
Summary The absence of randomisation of the oxygen label in the unreacted ^{18}O carbamate, after subjecting *NN*-dimethyl carbamate to thermolysis under non-catalytic conditions which effect *ca.* 60% β-elimination, is evidence against an ion-pair intermediate intervening in even the lowest activation gas-phase ester elimination processes; an unsymmetrical, concerted transition state of bond breaking and making is proposed.

THE rate-determining step in the thermal decomposition of carbamates is regarded[1] as the same as that observed in acetates, xanthates, and carbonates. The three possible mechanisms are (**1**), (**2**), and (**3**), where R^1 = alkyl, aryl, or $-NR^2R^3$; R^2 and R^3 = alkyl, aryl, or H.

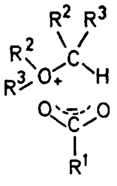
Recently, Smith, Voorhees, and Kelly[2] have reported on the pyrolysis of ethyl acetate enriched with ^{18}O at the ether oxygen. Their results suggest that mechanism (**3**) could not occur, or, if such an intimate ion pair were formed in the course of thermolysis, it is prevented from reversion to the ester, and mechanism (**2**) is favoured.[3] However, the very large rate differences between analogous ethyl and t-butyl esters,[4,5] are not reconcilable with differences in the extent of charge separation in (**2**). It is possible that ethyl esters thermolyse by mechanism (**2**) and t-butyl esters by mechanism (**3**), and that cases of intermediate activation energy correspond to a spectrum of transition states between (**2**) and (that of) (**3**).



(1)



(2)



(3)

To qualify as an ion-pair intermediate,[6] (**3**) must possess a lifetime greater than one free rotation, *i.e.* an ether oxygen ^{18}O enriched t-butyl carbamate must experience a measurable degree of randomisation of the label in the unreacted ester, when subjected to partial thermal decomposition. ^{18}O Labelled t-butyl carbamate in dilute toluene solution was passed into a Pyrex-tube flow system maintained at 325 °C with dry nitrogen as the carrier gas. The flow-rate was adjusted to obtain *ca.* 60% reaction. The rate of thermolysis was approximately equal to the rate determined in a kinetic flow system[7] using a gold coil reactor. The *ca.* 40% unreacted carbamate which survived thermolysis was collected in a cold trap, purified by distillation under reduced pressure, and submitted to mass spectral analysis.

TABLE

Distribution of ^{18}O in the unreacted t-butyl carbamate mass spectrometric determination

	% Relative abundance			
	$(Me_2NCO)^+$		$(Me_2NCO_2Bu^t)^+$	
	m/e 72	*m/e* 74	*m/e* 145	*m/e* 147
Non-enriched	100	0·69 ± 0·1	100	1·2 ± 0·7
^{18}O Enriched	100	0·78 ± 0·1	100	7·5 ± 0·7
^{18}O Enriched–thermolysed	100	0·53 ± 0·1	100	6·7 ± 0·7

The mass spectrum of the labelled t-butyl carbamate showed that no randomisation occurred during the course of measurement in the spectrometer. Since this spectrum did not possess an ion for the t-butoxy fragment, the actual analysis was carried out by measuring the relative abundance of *m/e* 72 and 74 ions which correspond to the $(Me_2NCO)^+$ ion, arising from cleavage alpha to the carbonyl.[8] An exact mass measurement confirmed the structure of *m/e* 72 as C_3H_6NO.

The results summarised in the Table clearly indicate that no equilibration of the oxygen had occurred in the thermolysis. If significant equilibration had taken place in thermolysis, the percent relative abundance of the *m/e* 74 would have been *ca.* 3·6 instead of the 0·5—0·7 actually found.

Thus, even though the t-butyl carbamate undergoes thermolytic elimination with an activation energy nearly 10 kcal smaller than ethyl carbamate, there is no evidence for intimate ion or radical pair formation in this process. Bond making and bond breaking in the cyclic transition state are experienced concertedly. The lowered activation energy of the t-butyl esters suggests that the transition structure is not fully symmetrical. That is to say, the double bond of the product may be more fully formed in the transition state of t-butyl esters than is the case of ethyl esters.

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