Thermolyses of *NN*-Dimethylcarbamates and the Implications for Thermal β-Elimination Reaction Mechanisms

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Summary Ethyl *NN*-dimethylcarbamate, isopropyl *NN*-dimethylcarbamate, and t-butyl *NN*-dimethylcarbamate undergo β-elimination during gas-phase thermolysis; the influence of structure on rates and activation energies shows that the reactions which are unimolecular involve heterolytic rather than homolytic bond fission and support an unsymmetrical transition state.

RECENTLY the distribution of ^{18}O in unreacted ^{18}O enriched t-butyl *NN*-dimethylcarbamate which has been subjected to thermolysis in a flow system has been reported.[1] As there was no evidence for intimate ion or radical pair formation, an unsymmetrical concerted transition state was suggested. We had previously proposed that transition states for carbamates were probably represented by (**1**), (**2**), or (**3**), but were unable to exclude the possibility of a concerted mechanism involving homolytic bond fission.[2]

We now report that in a conventional static system ethyl *NN*-dimethylcarbamate (EDMC), isopropyl *NN*-dimethylcarbamate (PDMC) and t-butyl *NN*-dimethylcarbamate (BDMC) decompose in the gas-phase according to equation (1). For each carbamate the pressure-time data are

$$Me_2NCOOR \longrightarrow Me_2NH + CO_2 + \text{Alkene} \qquad (1)$$

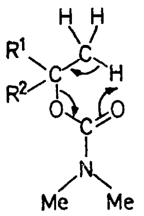
described by a first-order rate law to *ca.* 60—70% reaction. Variations of first-order rate constants with temperature over a 50—60° range are described by the equations (2), (3), and (4).

$$k = 10^{12.10}\exp(-44{,}340 \pm 400/RT)\mathrm{s}^{-1}\ \text{(EDMC)} \quad (2)$$

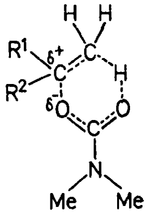
$$k = 10^{13.04}\exp(-43{,}310 \pm 400/RT)\mathrm{s}^{-1}\ \text{(PDMC)} \quad (3)$$

$$k = 10^{12.87}\exp(-37{,}740 \pm 400/RT)\mathrm{s}^{-1}\ \text{(BDMC)} \quad (4)$$

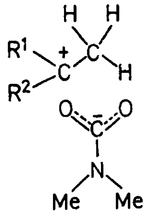
where activation energies are quoted in cal mol^{-1}. For each carbamate rate constants are not affected by a 5 to 8-fold variation in the initial pressure, nor by a change of 0·8—8·0 cm^{-1} in the surface to volume ratio of the reaction vessel. Addition of either cyclohexene or isobutene to reaction mixtures had no effect on rates and reactions appear to be molecular. In all cases rate constants calculated from pressure-time data measure rates of formation of amine and alkene. Extents of reaction calculated from rate constants are plotted against extents of reaction by alkene analysis in the Figure. The line drawn is that assuming a 1 : 1 correlation.



(1)



(2)



(3)

TABLE. *Relative rates of ester and carbamate thermolyses at* 400 °C

Compound	Ethyl	Isopropyl	t-Butyl
Formates[a]	1	20	720
Acetates[a]	1	26	1660
NN-Dimethylcarbamates ..	1	19	820

[a] Taken from ref. 3.

A comparison of the relative rates of thermolysis of carbamates, acetates, and formates is shown in the Table. The pattern of substituent effects shows that these carbamates undergo the same class of heterolytic thermal reactions as esters,[3] so that the homolytic mechanism may be ruled out. Thus only transition states (**1**) and (**2**) remain appropriate.

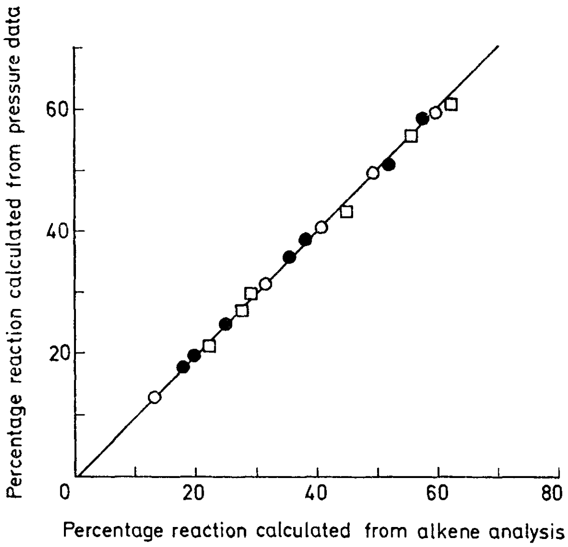


FIGURE. *Extent of reaction calculated from rate constants and from analytical data.* ○ *Ethylene from EDMC at* 340·5 °C, ● *propene from PDMC at* 399·6 °C, □ *isobutene from BDMC at* 240·1 °C.

Kwart and Slutsky[1] considered that the lowered activation energy of t-butyl esters suggests that the transition state is not fully symmetrical. The lowering of activation energies observed in the progression of structures from EDMC to BDMC supports this view. The entropies of activation, $\Delta S^{\ddagger}$ −6·77 (EDMC), −2·47 (PDMC), and −3·25 cal. deg^{-1} mol^{-1} (BDMC) are appropriate for such a transition state. The difference in $\Delta S^{\ddagger}$ between EDMC and PDMC contributes significantly to the relative rates at 673 °K. It may be that the transition states are different, and that for EDMC is less polar while those for PDMC and BDMC are as suggested by the activation energies.

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[1] H. Kwart and J. Slutsky, *J.C.S. Chem. Comm.*, 1972, 552.

[2] N. J. Daly and F. Ziolkowski, *Austral. J. Chem.*, 1971, **24**, 2541.

[3] A. Maccoll and P. J. Thomas, "Progress in Reaction Kinetics", vol. 4, Pergamon Press, London, 1967.