

not vitiate the view that *d*-orbitals may be involved in olefine co-ordination.

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² Anderson, *J. Chem. Soc.*, 971 (1934).

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Pyrolysis of 1,2 Dichlorethane

THE kinetics of the pyrolysis of 1,2 dichlorethane have recently been described by Barton and Howlett¹. Over the temperature-range 360°–480° C. they find that the reaction is first order and proceeds by a radical chain-mechanism in vessels coated with a carbonaceous film ($k = 10^{10.81} \exp -47,000/RT$). Strong evidence for the radical nature of the decomposition is provided by the powerful inhibiting effect of propylene. The maximally inhibited rate, which is independent of further increase in propylene concentration, is shown to be partially heterogeneous in character.

Almost simultaneously, Baldt and Cremer² have published an account of a similar investigation which led to different conclusions. They claim that the graph of $\log k$ against $1/T$ is sharply segmented corresponding to a heterogeneous reaction ($k = 10^{4.15} \exp -28,100/RT$) from 377° to 415° C., and from 415° to 442° C. to a unimolecular process ($k = 10^{16.70} \exp -64,500/RT$). (The graph does not, in fact, correspond to the data quoted in a table. Accepting the latter, the activation energy for the heterogeneous process becomes $\sim 25,500$ cal./gm. mol.)

This result does not, in fact, follow from the Arrhenius plot, for it is easily seen that neither of these two reaction-rates is negligible in comparison with the other at any point of the narrow temperature-range studied. Thus the operation of these two reactions would lead to a continuous curve for the Arrhenius plot, and furthermore the value of $\log k$ at 415° should be 0.3 units above the point of intersection of the limiting straight lines, because the observed velocity constant would be the sum of the two (equal) constants for the alternative reactions. (This assumes that reaction does not greatly disturb the equilibrium between normal and activated molecules.) However, the experimental points lie on excellent straight lines with a point actually at the intersection. This is difficult to interpret.

It is noteworthy that at 442° C. (where direct comparison is possible) the rate constant quoted by Baldt and Cremer is intermediate between the values given by Barton and Howlett for the normal and maximally inhibited reactions. Coupled with the fact that the pyrolysis is notoriously sensitive to trace contaminants³, this suggests that Baldt and Cremer may have been observing partially retarded decompositions. The latter give the impression that their rates are obtained for reactions in clean glass vessels, but it is most probable that they refer to product-fouled surfaces. Thus their rates are slower than those of Barton and Howlett, who report the accelerating effect of clean glass surfaces⁴.

The question of the nature of 1,2 dichlorethane decomposition is an important one. The fact that it proceeds by a radical mechanism, whereas 1,1 dichlorethane decomposes unimolecularly, is strong evidence for the predictions put forward correlating structure and mode of decomposition in chloro-hydrocarbon pyrolyses by Barton, Onyon and Howlett⁵. Experiment has so far verified these predictions⁶.

A significant difference between the two experimental techniques lies in the method of pressure measurement used to follow reactions. Barton and Howlett used an all-glass Bourdon gauge, whereas the other authors employed a heated mercury capillary manometer. Mercury is known to inhibit the analogous decomposition of ethyl bromide⁷, and would be expected to react with chlorine atoms under the experimental conditions, thus suppressing any tendency towards radical mechanisms.

I have therefore carried out further experiments in a new apparatus, using an all-glass pressure-measuring system to follow the reaction. In addition, a heated 1-mm. capillary tube containing mercury could be connected to the reactor, or isolated by a tap, so that decompositions in the presence or absence of mercury could be studied at will. General experimental procedure was as described previously¹.

In the absence of mercury, the new experiments have amply confirmed the results of Barton and Howlett for both clean and coated vessels. Furthermore, mercury vapour has been shown to inhibit the reaction. The runs were carried out using the mercury capillary heated to 120° C., at which the vapour pressure of mercury is approximately 0.8 mm. Actual determination of the rise in pressure on opening the evacuated reactor to the capillary gave a value of 0.5 mm. The results obtained in a coated vessel are summarized in the accompanying table.

Temp.	(CH ₂ Cl) ₂ alone			(CH ₂ Cl) ₂ + Hg	
	No. of runs	10 ⁴ × mean <i>k</i>	10 ⁴ <i>k</i> (B. and H.) (ref. 1)	No. of runs	10 ⁴ × mean <i>k</i>
435° C.	3	1.71	1.99	4	1.31
447° C.	9	3.53	3.46	7	2.55
459° C.	3	6.49	6.57	3	5.47

All rates are expressed in units sec.⁻¹.

The first day's experiments with a clean 'Pyrex' reactor gave a mean $k = 3.3 \times 10^{-2}$ sec.⁻¹ at 408° C., in good agreement with the dynamic results of Barton³.

The retardation of the homogeneous pyrolysis by traces of mercury vapour provides further evidence of the radical nature of the decomposition, and it must be concluded that the results of Baldt and Cremer refer to partially inhibited reactions.

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² Baldt, R., and Cremer, E., *Monatsh.*, **80**, 153 (1949).

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⁴ Compare Barton, D. H. R., and Onyon, P. F., *Trans. Farad. Soc.*, **45**, 725 (1949).

⁵ Barton, D. H. R., Onyon, P. F., and Howlett, K. E., *Trans. Farad. Soc.*, **45**, 733 (1949).

⁶ Private communication from Dr. D. H. R. Barton.

⁷ Fugassi, P., and Daniels, F., *J. Amer. Chem. Soc.*, **60**, 771 (1938).