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Note

Temperature variation of the mechanism of thermal decomposition of dioxygencarbonyl chloro-bis (triphenylphosphine) iridium (I)

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A recent publication[1] on the thermal deoxygenation of solid dioxygencarbonylchloro-bis(triphenylphosphine)iridium(I) showed that two reaction mechanisms were operative in the temperature range 379–425 K. These were a nucleation and growth process in the range 379–397 K and a phase boundary controlled process between 405–425 K. These processes had activation energies of 232 kJ mol^{-1} and 180 kJ mol^{-1}, respectively, and it was suggested that the change in mechanism was to be expected, since a high activation energy process should give way to a lower energy process as the temperature is raised.

Further work at even higher temperatures has shown that there is a further change in the mechanisms of the reaction to a process of even lower activation energy.

The preparation of starting material and all experimental details were as previously described[1], and samples were heated in a flow of nitrogen at temperatures

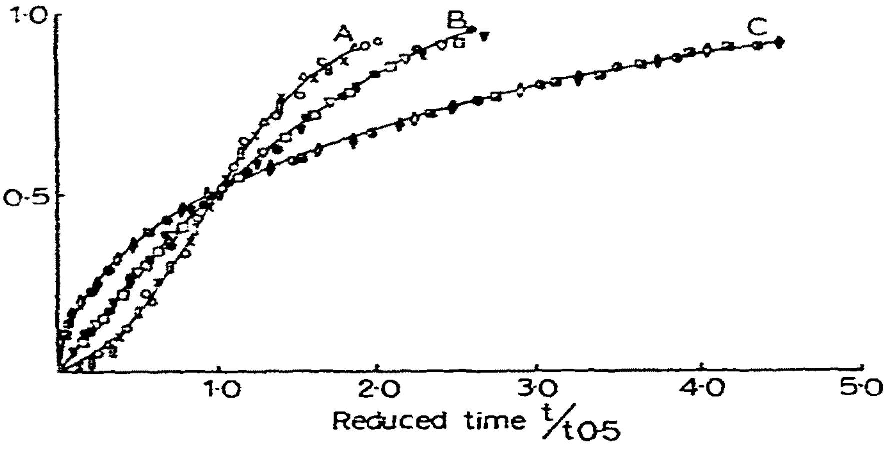

Fig. 1. Comparison of experimental and theoretical reduced time ($t/t_{0.5}$) curves.
Curve A: $(-\ln(1-\alpha)^{1/2} = kt$; × 379 K; ○ 385 K; ▯ 390 K; △ 347 K.
Curve B: $1-(1-\alpha)^{1/2} = kt$; ▽ 405 K; □ 413 K; ▼ 417 K; ● 422 K.
Curve C: $(1-\alpha)\ln(1-\alpha)+\alpha = kt$; ◇ 428 K; ◆ 433 K; ◑ 437 K; ◪ 443 K.

between 426 and 443 K. The weight loss vs. time curves were again treated by the method of reduced time plots[2] to decide on the best fit between experimental and calculated behaviour.

The best fit between experimental and calculated reduced time plots was in terms of the equation

$$(1-\alpha)\ln(1-\alpha)+\alpha = kt,$$

where α = proportion decomposed and t = time, i.e., the equation corresponding to diffusion in a disc. The fit obtained is shown in the Fig. 1, which also includes a comparison with the lower temperature behaviour. Rate constants were calculated using the equation, and an Arrhenius plot gave an activation energy and a frequency factor. The values for these are given in Table 1 and again compared with the lower temperature values. It can be seen that again increasing temperature leads to a process of lower activation energy.

TABLE 1

ARRHENIUS PARAMETERS

Temp. range (K)	*Reaction mechanism*	*Best fit equation*	*Activation energy (kJ mol⁻¹)*	*Frequency factor (sec⁻¹)*
379–397	nucleation	$-\ln(1-\alpha)^{1/2} = kt$	232	$10^{21.4}$
405–425	phase boundary	$1-(1-\alpha)^{1/2} = kt$	180	$10^{14.2}$
426–443	diffusion	$(1-\alpha)\ln(1-\alpha)+\alpha = kt$	84	10^{8}

The formal geometry of each process is the same throughout, i.e., two-dimensional, which suggests that the plate morphology of the starting material has a powerful effect on the kinetics of decomposition.

REFERENCES

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