

## Pressure-dependence of the Pyrolysis of the Isopropoxyl Radical

By R. A. LIVERMORE and L. PHILLIPS

*(Explosives Research and Development Establishment, Ministry of Aviation, Waltham Abbey, Essex)*

PRESSURE-DEPENDENCE of the pyrolysis of the t-butoxyl radical was suggested by Hershenson and Benson<sup>1</sup> to account for the reported low frequency factors; they point out that this is in accord with

theory<sup>2</sup> since, when  $E/T$  is small, fall-off from unimolecular behaviour should occur at relatively high pressures. This was confirmed by Flowers, Batt, and Benson<sup>3</sup> in the pyrolysis of di-t-butyl

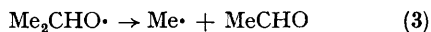
<sup>1</sup> H. Hershenson and S. W. Benson, *J. Chem. Phys.*, 1962, **37**, 1889.

<sup>2</sup> A. F. Trotman-Dickenson, 'Gas-Kinetics,' Butterworth, 1955, Ch. II.

<sup>3</sup> M. Flowers, L. Batt, and S. W. Benson, *J. Chem. Phys.*, 1962, **37**, 2662.

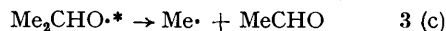
peroxide (DTBP)-HCl mixtures where the decomposition of the t-butoxy-radical was found to be in the transition region between 20 and 130 mm., but the scatter of results led to much uncertainty in the determination of kinetic parameters. Mulcahy and Williams<sup>4</sup> obtained similar results with the DTBP-phenol system. In neither case was the effect of added chemically-inert gases examined.

We are studying the pressure-dependence of the C-C decomposition of alkoxy radicals using alkyl nitrites and peroxides as radical sources. With isopropyl nitrite (IPN) Levy<sup>5</sup> and Ferguson and Phillips<sup>6</sup> showed that the main reactions at 170–200° and 35 mm. were



with<sup>6</sup>  $k_3 \approx 4.5 \times 10^{10} \exp(-16,000/RT)$  sec.<sup>-1</sup>, but the pressure-dependence of (3) was not studied. With IPN-nitric oxide mixtures, we find the relationship  $R(\text{Me}_2\text{CO})/(\text{MeCHO}\cdot[\text{NO}]) = k_2/k_3$  holds when  $[\text{NO}]$  is varied at constant  $[\text{IPN}]$ , but the ratio decreases with increasing  $[\text{IPN}]$  and constant  $[\text{NO}]$  over the range 20–230 mm. at 200°, and also decreases at constant  $[\text{IPN}]$  and  $[\text{NO}]$  when chemically-inert gases are added. Reaction (3) is therefore not in the first-order region.

Assuming a simple Hinshelwood-Lindemann mechanism



it follows that

$$R(\text{Me}_2\text{CO})/R(\text{MeCHO}\cdot[\text{NO}]) = k_2(1/k_\infty + 1/k_0[\text{M}])$$

where  $k_\infty$  and  $k_0$  are the limiting high- and low-pressure values of  $k_3$ . Our results at 180, 190, and 200° give good linear plots of the left-hand side against  $1/[\text{M}]$  where  $[\text{M}] = [\text{IPN}] = 20\text{--}230$  mm. ( $[\text{IPN}] = [\text{NO}]$ ). Taking the estimated values<sup>7</sup> of  $E_2 \approx 0$  kcal. mole<sup>-1</sup> and  $A_2 \approx 10^{10}$  cm.<sup>3</sup> sec.<sup>-1</sup>, we find  $E_\infty = 12.5$  and  $E_0 \approx 9.5$  kcal. mole<sup>-1</sup>, corresponding to seven effective oscillators on the Slater theory,<sup>8</sup> and  $A_\infty = 10^{9.6}$  sec.<sup>-1</sup> and  $A_0 \approx 10^{13.6}$  mole<sup>-1</sup> cm.<sup>3</sup> sec.<sup>-1</sup>. As with the acetyl radical,<sup>9</sup> the low value of  $A_\infty$  may be due to the reaction being non-adiabatic, since an excited electronic state must be involved.

We find the following efficiencies of added gases ( $\text{IPN} = 1.0$ ): argon 0.06, nitrogen 0.04, nitric oxide <0.1, carbon dioxide 0.4, ethane 0.7, propane 0.7, n-butane 0.7, neopentane 0.6. The added hydrocarbons are inert under our conditions because isopropyl alcohol yields show that reaction with isopropoxy radicals is negligible, and known rate constants<sup>10</sup> indicate that reaction with methyl radicals from (3) does not occur. All the above efficiencies appear to be normal except for carbon dioxide which is unusually high.

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<sup>4</sup> M. F. R. Mulcahy and D. J. Williams, *Austral. J. Chem.*, 1964, **17**, 1291.

<sup>5</sup> J. B. Levy, *Ind. Eng. Chem.*, 1956, **48**, 762.

<sup>6</sup> J. M. Ferguson and L. Phillips, *J. Chem. Soc.*, in the press.

<sup>7</sup> E. A. Arden, L. Phillips, and R. Shaw, *J. Chem. Soc.*, 1964, 5126.

<sup>8</sup> A. F. Trotman-Dickenson, *J. Chem. Soc.*, 1964, 63, 78.

<sup>9</sup> E. O'Neal and S. W. Benson, *J. Chem. Phys.*, 1962, **36**, 2196.

<sup>10</sup> A. F. Trotman-Dickenson, *loc. cit.*, p. 199.