Oxidation of Carbon Monoxide by t-Butoxy-radicals

By E. A. Lissi* and J. C. Scaiano

(Laboratorio Central de Quimica, Universidad Tecnica del Estado, Santiago, Chile)

and A. E. Villa

(Facultad de Ciencias, Universidad de Chile)

Summary The study of the pyrolysis of di-t-butyl peroxide in the presence of carbon monoxide allows an evaluation of the rate constant for the oxidation of carbon monoxide by t-butoxy-radicals.
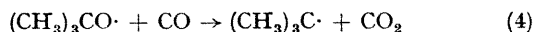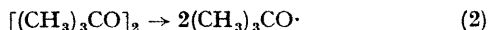
It has been reported[1] that carbon monoxide is not oxidized by t-butoxy-radicals at 150 °C and an upper limit for the rate constant of this reaction at such temperature was put at 3×10^6 cm^3 s^{-1} mol^{-1}. Evidence has also been presented[2] which indicates that reaction (1) is fast even at

$$HO\cdot + CO \rightarrow CO_2 + H\cdot \qquad (1)$$
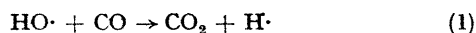
room temperature. As this type of reaction can be of importance in air pollution studies, the oxidation of carbon monoxide by t-butoxy-radicals was studied.

Di-t-butyl peroxide was employed as the radical source. Reaction products were analysed by standard g.l.c. techniques. Acetone, ethane, and carbon dioxide were found to be the only major products.

The data obtained support the simple mechanism in equations (2)—(5) for this system.

$$[(CH_3)_3CO]_2 \rightarrow 2(CH_3)_3CO\cdot \qquad (2)$$

$$(CH_3)_3CO\cdot (+M) \rightarrow CH_3COCH_3 + CH_3\cdot (+M) \qquad (3)$$

$$(CH_3)_3CO\cdot + CO \rightarrow (CH_3)_3C\cdot + CO_2 \qquad (4)$$

$$2\,CH_3\cdot \rightarrow C_2H_6 \qquad (5)$$

Assuming that no other radical reactions within the system produce or consume carbon dioxide or acetone, equation (6) can be derived. As reaction (3) is in the

$$k_4 = k_3 \times [CO_2]/[\text{Acetone}] \times [CO] \qquad (6)$$

fall-off region, the values of k_3 were obtained from previous results[3] by a simple Lindemann's mechanism assuming a carbon monoxide efficiency of 0.1.[4]

Ten runs were carried out under different experimental conditions at 136 °C. Partial pressures of carbon monoxide were varied from 60 to 305 Torr, of di-butyl peroxide from 2.4 to 5 Torr, and reaction times by a factor of three. In every case good agreement between experimental data and equation (6) was obtained. An average value of $(2.3 \pm 0.8)\ 10^5$ cm^3 mol^{-1} s^{-1} was obtained for k_4.

Least-square treatment of the experimental data arranged as an Arrhenius plot in the temperature range 371—421 K gives the following values.

$$\log A = 10.0 \pm 1.8\ \text{cm}^3\,\text{mol}^{-1}\,\text{s}^{-1}$$
$$E_4 = 10.4 \pm 3.4\ \text{kcal mol}^{-1}\,(43.5 \pm 14.3\ \text{kJ mol}^{-1})$$

High errors in the Arrhenius parameters are the result of the small temperature range available (at lower temperatures [acetone] becomes negligible and at higher temperatures secondary reactions become significant), the experimental errors involved in the analyses of minor amounts of carbon dioxide in the presence of large quantities of carbon monoxide, and of the uncertainty introduced by the estimation of k_3. Nevertheless, in spite of the relatively high errors of these parameters it can be concluded that the energy of activation of reaction (4) is much higher than that reported[2] for reaction (1). Further, it must be noted that the present results cannot be rationalized by the following mechanism [equations (7) and (8)] since it has been shown[5]

$$RO\cdot + CO \xrightarrow{\text{fast}} ROCO\cdot \qquad (7)$$

$$ROCO\cdot \xrightarrow{\text{slow}} R\cdot + CO_2 \qquad (8)$$
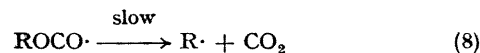
that ROCO· radicals decompose almost quantitatively into R· and CO$_2$. Finally, the values found in the present work are similar to those found in the methoxy–carbon monoxide system at room temperature[6] and are in agreement with the upper limit proposed by Porter and Benson.[1]

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