The Atmospheric Fate of Isobutoxy Radicals

A contribution to subproject CMD

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Introduction

Under atmospheric conditions, long-chain alkoxy radicals can generally react via 3 reaction pathways:

(1) Reaction with O_2 (k_1, => aldehyde/ketone + HO_2),
(2) thermal decomposition (k_2, => aldehyde/ketone + alkyl/H),
(3) isomerisation (k_3, => hydroxyaldehyde/hydroxyketone).

The relative and, in particular, the absolute values of k_1, k_2, and k_3 are not well established. However, these values are necessary in order to evaluate the ozone formation potential of long-chain hydrocarbons.

In this work, the reactive behaviour of isobutoxy radicals has been studied in a temperature controlled 12 l reaction chamber from stainless steel (Fig. 1). Isobutoxy radicals are major intermediates in the atmospheric degradation of isobutane. Since a six-membered transition state is not possible for isobutoxy radicals, channel (3) is unimportant in this case and (2) competes with (1).

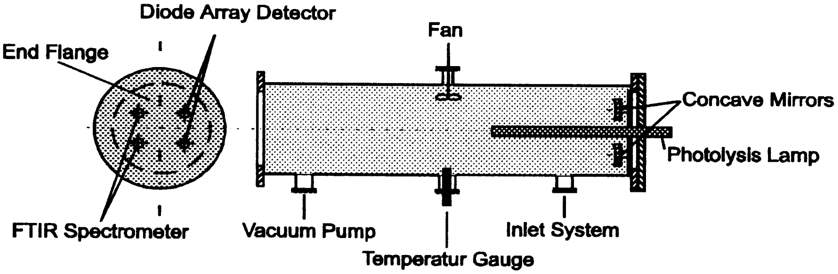

Fig. 1: Temperature controlled 12 L reaction chamber from stainless steel

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Method

Isobutoxy radicals were prepared by 3 methods:

I. Stationary photolysis of isobutyl iodide at 254 nm in the presence of O_2 and NO.

II. Stationary photolysis of isobutyl nitrite at 254 nm in the presence of O_2 and NO.

III. Stationary photolysis of isobutyl nitrite at 320–400 nm in the presence of O_2 and NO. In system I, alkoxy radicals are formed via the sequence:

$$i\text{-}C_3H_7CH_2 + O_2 + M \;=>\; i\text{-}C_3H_7CH_2O_2 + M \qquad (k_4) \qquad (4)$$

$$i\text{-}C_3H_7CH_2O_2 + NO \;=>\; i\text{-}C_3H_7CH_2O + NO_2 \qquad (k_5) \qquad (5),$$

whereas in systems II and III they are formed directly in the primary photolysis step. Due to the presence of an excess of NO, reactions of peroxy radicals with other peroxy radicals are unimportant in these systems. The products isobutyraldehyde and formaldehyde are a measure for the reaction of *i*-butoxy with O_2 and its thermal decomposition, respectively (see Fig. 2).

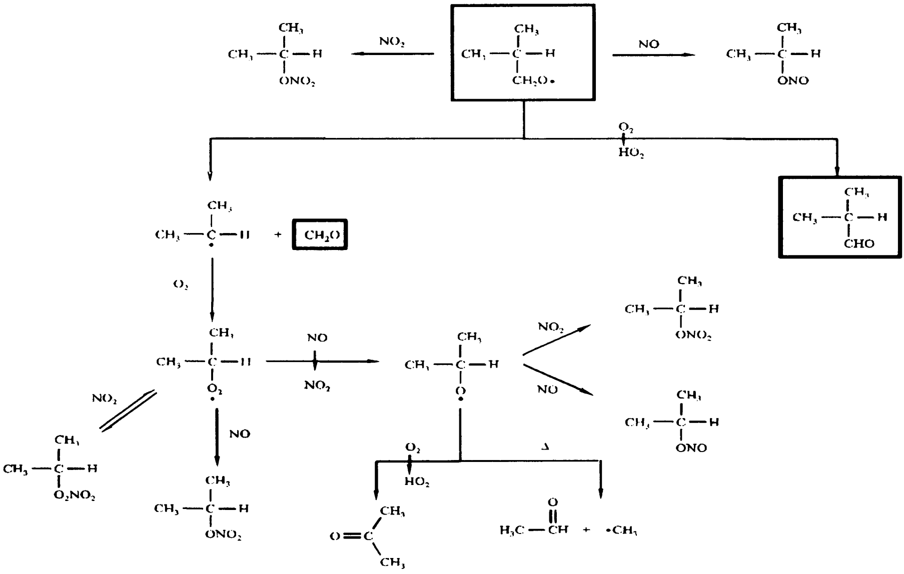

Fig. 2: Degradation mechanism of isobutoxy radicals in the presence of O_2 and NO_x

The ratio k_1/k_2 is determined from the yields of these stable products as measured *in situ* by IR absorption with an FT-IR spectrometer (optical pathlength = 2 m).

Results

At 298 K, the formaldehyde yield (which is indicative of the decomposition channel) is con-siderably larger in system III than in systems I and II (see Table 1).

Table 1: Reaction enthalpies and product yields for the generation of *i*-butoxy radicals from different precursors in the presence of 800 mbar O_2.

System	$\Delta H^0_{r,298}$ [kJ mol^{-1}]	$\Delta[CH_2O]/\Delta[i\text{-}C_3H_7CHO]$
(I) $i\text{-}C_4H_9OO + NO \Rightarrow i\text{-}C_4H_9O + NO_2$	50	0.32
(II) $i\text{-}C_4H_9ONO + h\nu(360\ \text{nm}) \Rightarrow i\text{-}C_4H_9O + NO$	160	0.54
(III) $i\text{-}C_4H_9ONO + h\nu(254\ \text{nm}) \Rightarrow i\text{-}C_4H_9O + NO$	299	10.6

$$i\text{-}C_4H_9O \leftrightarrow i\text{-}C_3H_7 + CH_2O, \quad \Delta H^0_{r,298} = +49\ \text{kJ mol}^{-1} \qquad (2,-2)$$

This result is most easily explained by the large excess energy of the $i\text{-}C_4H_9O$ radicals formed in the 254 nm photolysis of $i\text{-}C_4H_9ONO$: A considerable fraction of the excited $i\text{-}C_4H_9O$ radicals possibly decompose before thermal equilibrium is attained and competition with the O_2 reaction becomes effective. The relatively small decrease in the CH_2O yield when going from system II to system I, however, gives confidence that excited $i\text{-}C_4H_9O$ radicals play no role in system I. Recently, it was suggested that the majority of the CF_3CHFO radicals formed in the reaction of CF_3CHFO_2 with NO (which is exothermic by 71 kJ mol^{-1}) decompose spontaneously at atmospheric pressure (Møgelberg *et al.*, 1997).

The yields of *i*-butyraldehyde and formaldehyde in reaction system I were measured at 289, 298, and 310 K as a function of O_2 partial pressure. The ratios k_1/k_2 were calculated according to the relationship

$$k_1/k_2 \quad = \quad \Delta\,[i\text{-}C_3H_7CHO] \,/\, ([CH_2O]\,[O_2]).$$

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At O_2 partial pressures below 200 mbar, the yields of isobutyraldehyde were low, and the evaluation of the data was inaccurate. At O_2 partial pressures $\geq$ 200 mbar, the resulting values of k_1/k_2 were approximately constant. The results are summarised in Table 2.

Table 2: Kinetic results for the competition between reaction with O_2 and thermal decomposition of *i*-butoxy radicals

T [K]	k_1/k_2 [cm^3]	$k_1 [O_2] / k_2$ for 1 bar synth. air	$k_1 [O_2] / (k_1 [O_2]+k_2)$ * for 1 bar synth. air
289	2.3×10^{-19}	1.15	0.53
298	1.7×10^{-19}	0.83	0.45
310	0.92×10^{-19}	0.43	0.30

* = Δ [i-butyraldehyde] / (Δ [i-butyraldehyde] + Δ [formaldehyde])

The ratio, k_1/k_2 at 298 K, is lower by more than an order of magnitude as compared to previous experimental work (Hoffmann *et al.*, 1993) and in good agreement with a value estimated from a recent review by Atkinson (Atkinson, 1997) provided that the low value of the heat of formation of the *i*-propyl radical (79.5 kJ mol^{-1}) from the most recent JPL review (DeMore *et al.*, 1997) is used. Table 2 implies that, at standard atmospheric conditions, *i*-butoxy radicals react by addition of O_2 about half of the time, and thermal decomposition is another major reaction pathway leading to C_3H_7 and CH_2O. The thermal lifetime of *i*-butoxy radicals at 298 K and atmospheric pressure is in the order of 20 μs.

Conclusions

Isobutoxy radicals are thermally less stable than was suggested by earlier experimental work. Under ambient conditions, comparable yields of formaldehyde, *i*-propyl radicals and *i*-butyraldehyde are formed from isobutoxy radicals by thermal decomposition and reaction with O_2.

References

Atkinson, R.; *Int. J. Chem. Kinetics* **29** (1997) 99–111.

DeMore, W. B., S. P. Sander, D. M. Golden, R. F. Hampson, M. J. Kurylo, C. J. Howard, A. R. Ravishankara, C. E. Colb, and M. J. Molina, *Chemical Kinetics and Photochemical Data for Use in Stratospheric Modelling*, JPL Publication 97–4, Jet Propulsion Laboratory, California Institute of Technology, Pasadena 1997.

Hoffmann, A., V. Mörs and R. Zellner, *EUROTRAC Annual Report 1992, Part 8, LACTOZ*, EUROTRAC ISS, Garmisch-Partenkirchen 1993, pp. 212–221.

Møgelberg, T.E., J. Sehested, T.J. Wallington, O.J. Nielsen; *Int. J. Chem. Kinetics* **29** (1997) 209–218.