A simplified model for catalyzed isobutane autoxidation: implications for the mechanism of catalysis by halogenated porphyrin complexes

Jay A. Labinger

Division of Chemistry and Chemical Engineering, California Institute of Technology, 139-74, Pasadena, CA 91125, USA

Received 18 October 1993; accepted 3 February 1994

A simple kinetic model shows that a radical-chain mechanism can account for the high activity and selectivity found for oxidation of isobutane to *t*-butanol catalyzed by highly halogenated metalloporphyrins.

Keywords: selective oxidation; metalloporphyrins; isobutane

Lyons and coworkers have reported that iron complexes of highly halogenated porphyrins, such as octabromotetra(pentafluorophenyl)porphyrin ($TFPPBr_8$), are active and selective catalysts for the oxidation of isobutane to *t*-butanol by molecular O_2. One possible mechanism that was considered involves abstraction of H· by an Fe^{IV}=O species, related (but not identical) to the accepted mechanism of alkane hydroxylation by cytochrome P450 [1]. Metal-catalyzed autoxidations are generally considered to proceed via radical-chain mechanisms, with the sole role of the catalyst being decomposition of alkyl hydroperoxides to produce more chain-carrying radicals [2]; however, such reactions rarely if ever produce the levels of activity and selectivity for alcohol formation seen here. Lyons and coworkers showed that the halogenated porphyrin complexes *are* exceptionally active catalysts for decomposition of *t*-BuOOH, and noted a possible connection to isobutane oxidation [3]. The key question is whether, given sufficient activity for peroxide decomposition, a radical-chain autoxidation mechanism *could* account for the isobutane oxidation results. We have constructed a kinetic model, simple enough to handle on a PC, that permits at least semiquantitative assessment of the potential contribution of peroxide decomposition to overall oxidation.

Previous models for isobutane oxidation have primarily aimed at reproducing global properties, such as overall rate and reaction order [4], and/or are too complex to solve easily by a PC-level program [5]. Furthermore, they do not include steps that are crucial to the catalyzed peroxide decomposition. The present

model starts with that of Allara et al. [5] and makes the following two simplifying assumptions:

(i) All reactions involving the *i*-butyl radical may be neglected. (No products deriving therefrom were reported in the catalyzed oxidation [1]; levels of such products in uncatalyzed autoxidation are typically no more than 1% [6].)

(ii) All reactions of R· with O_2 to give ROO· are much faster than any possible competing reaction. (This is consistent with rates in Allara's model; it is also supported by isotopic labeling experiments [7].)

With these assumptions, use of a simple expression for chain initiation, and the addition of eq. (5) which is important in peroxide decomposition, the model becomes:

$$RH \xrightarrow{k_i} R\cdot \xrightarrow{O_2,\text{fast}} ROO\cdot \qquad \text{(i)}$$

$$ROO\cdot + RH \xrightarrow{k_1} ROOH + R\cdot \xrightarrow{O_2,\text{fast}} ROO\cdot \qquad (1)$$

$$2ROO\cdot \xrightarrow{k_2} 2RO\cdot + O_2 \qquad (2)$$

$$2ROO\cdot \xrightarrow{k_3} ROOR + O_2 \qquad (3)$$

$$RO\cdot + RH \xrightarrow{k_4} ROH + R\cdot \xrightarrow{O_2,\text{fast}} ROO\cdot \qquad (4)$$

$$RO\cdot + ROOH \xrightarrow{k_5} ROH + ROO\cdot \qquad (5)$$

$$RO\cdot \xrightarrow{k_6} Me_2C{=}O + Me\cdot \xrightarrow{O_2,\text{fast}} MeOO\cdot . \qquad (6)$$

We make the further simplifying assumption that the only fate of the methylperoxy radical is the rapid [#1] termination reaction with ROO·, or

$$MeOO\cdot + ROO\cdot \xrightarrow{\text{fast}} ROH + CH_2O + O_2 . \qquad (6')$$

Assuming a homolytic or Haber–Weiss mechanism for catalyzed peroxide decomposition, with the oxidation of peroxide rate-limiting [2]:

$$ROOH + M^{III} \xrightarrow{k_c} ROO\cdot + H^+ + M^{II} \qquad (7)$$

$$ROOH + M^{II} \xrightarrow{\text{fast}} RO\cdot + OH^- + M^{III} . \qquad (7')$$

From the above set of reactions we get the following differential equations:

$$d[RH]/dt = -k_i[RH] - k_1[ROO\cdot][RH] - k_4[RO\cdot][RH] \qquad (8)$$

[#1] Disproportionation reactions of primary and secondary peroxy radicals are much faster than eqs. (2) and (3); see ref. [8].

$$d[ROOH]/dt = k_1[ROO\cdot][RH] - k_5[RO\cdot][ROOH] - 2k_c[M][ROOH] \quad (9)$$

$$d[ROH]/dt = k_4[RO\cdot][RH] + k_5[RO\cdot][ROOH] + k_6[RO\cdot] \quad (10)$$

$$d[ROOR]/dt = k_3[ROO\cdot]^2 \quad (11)$$

$$d[Me_2C{=}O]/dt = k_6[RO\cdot]\,. \quad (12)$$

Applying mass balance gives the following equation:

$$k_i[RH] - 2k_3[ROO\cdot]^2 + 2k_c[M][ROOH] - 2k_6[RO\cdot] = 0\,. \quad (13)$$

Rearranging:

$$[ROO\cdot]^2 = \{k_i[RH] + 2k_c[M][ROOH] - 2k_6[RO\cdot]\}/2k_3\,. \quad (14)$$

Steady-state in [RO·] further requires:

$$d[RO\cdot]/dt = 2k_2[ROO\cdot]^2 - k_4[RO\cdot][RH] - k_5[RO\cdot][ROOH] + k_c[M][ROOH] - k_6[RO\cdot] = 0\,. \quad (15)$$

Substituting the expression for $[ROO\cdot]^2$ from eq. (14) and rearranging gives:

$$[RO\cdot] = \frac{(k_2/k_3)k_i[RH] + (1 + 2k_2/k_3)k_c[M][ROOH]}{k_4[RH] + k_5[ROOH] + (1 + 2k_2/k_3)k_6}\,, \quad (16)$$

which in turn can be substituted into eq. (14) to give an expression for [ROO·].

We now have a set of differential equations which can be readily handled by a simple BASIC program for numerical integration: [RO·] and [ROO·] are calculated from eqs. (16) and (14), the set of rate constants, and the instantaneous concentrations of stable species; changes in concentrations of the latter for a given time interval are calculated from eqs. (8)–(12); and the process is iterated for any desired total reaction time.

Values for rate constants k_1–k_6 valid near room temperature were taken from the literature[#2]. Using the conditions for catalyzed decomposition ([M] = 1×10^{-5} M; [ROOH] = 1.8 M) the value of k_c was varied to fit the conversion. It proved necessary to use a value of k_6 ($8 \times 10^4\ s^{-1}$) significantly higher than the literature values (8×10^2 to $3 \times 10^3\ s^{-1}$) in order to get even close to the reported acetone yield. This could be accounted for by some degree of metal catalysis of eq. (6)

[#2] Two sources were used: refs. [4,9]. Some of the rate constants differ by as much as an order of magnitude between the two sources; average values were used. The ability of the model to reproduce selectivities accurately is sensitive to some of the constants, particularly k_1; unfortunately, it does not appear that a more reliable and self-consistent set of constants is available. The qualitative behavior of the model, however, does not change much as the constants are varied over the range of literature data. The calculated degree of conversion is insensitive to the value of k_i over a wide range, since eqs. (7) and (7′) now become by far the major source of radicals. A value of $k_i = 10^{-10}$ was used, based on extrapolations from high-temperature uncatalyzed autoxidation; this value predicts <0.2% conversion without catalyst at 25°.

Table 1
Comparison of experimental and calculated parameters for peroxide decomposition and isobutane oxidation

	Peroxide decomposition		Isobutane oxidation	
	experimental [a]	model [b]	experimental [c]	model [d]
conversion (%)	95	95	22	23
time (h)	1.9	1.9	71.5	71.5
ROH (%)	90	90	91.5	85
$Me_2C{=}O$ (%)	2	2	8.5	8.5
ROOH (%)	–	–	none	none
ROOR (%)	8	8	none	7

[a] Ref. [3].
[b] Parameters used: $[M] = 1 \times 10^{-5}$ M; $[ROOH]_0 = 1.8$ M; $k_2 = 500\ M^{-1}\ s^{-1}$; $k_3 = 100\ M^{-1}\ s^{-1}$; $k_5 = 6 \times 10^6\ M^{-1}\ s^{-1}$; $k_6 = 8 \times 10^4\ s^{-1}$; $k_c = 4.7\ M^{-1}\ s^{-1}$.
[c] Ref. [1d].
[d] Parameters used: $[M] = 1.6 \times 10^{-4}$ M; $[RH]_0 = 10$ M; $k_i = 10^{-10}\ s^{-1}$; $k_1 = 4 \times 10^{-3}\ M^{-1}\ s^{-1}$; $k_4 = 8 \times 10^4\ M^{-1}\ s^{-1}$; other k's as above.

[10]. The values of k_6 and k_c obtained by fitting to the peroxide decomposition data were added to the model, and the expected results for catalyzed oxidation ($[M] = 1.6 \times 10^{-4}$ M; $[RH] = 10$ M) were determined. The list of rate constants used, and the comparison of calculated and experimental conversions and selectivities, are given in table 1.

It is notable that addition of the peroxide decomposition steps to the autoxidation mechanism accurately predicts the observed reactivity for catalyzed oxidation. The selectivity agrees well for acetone make but predicts a significant yield of ROOR, which was not reported; however, this deviation is probably not surprising given the absence of highly reliable rate constants. The model thus suggests that the radical chain mechanism *is* sufficient to account for catalyzed oxidation, as a consequence of the remarkably high peroxide decomposition activity. In contrast, previously reported "active" peroxide decomposition catalysts [11], which do *not* also catalyze isobutane oxidation at low temperatures, are at least two orders of magnitude less active than $Fe(TFPPBr_8)$.

The model may also be used to predict the potential improvements for rate of isobutane oxidation by designing an even better peroxide decomposition catalyst. Within the family of iron porphyrins, peroxide decomposition rate correlates well with reduction potential [#3] [3], suggesting a more oxidizing complex could be a still better catalyst. The model predicts that the rate of isobutane oxidation should increase with k_c, but eventually will level off.

It should be emphasized that this is an incomplete model, and at best shows that the radical chain mechanism *can* account for the extraordinary low-tempera-

[#3] A linear plot of $\log k$ versus E_0 is obtained using either the observed decomposition rates [3] or the values of k_c that model those rates.

ture catalytic activity reported; it by no means rules out contributions from mechanisms such as those previously proposed [1]. However, the degree to which *both* activity and product selectivity are reproduced indicates that the radical chain mechanism may indeed be responsible for most, if not all, of the low-temperature isobutane oxidation.

Acknowledgement

I thank Harry Gray, Mark Grinstaff, Mike Hill, Jim Lyons and Paul Ellis for valuable discussions. This work was supported by the Department of Energy, Morgantown Energy Technology Center; the Gas Research Institute; and Sun Company, Inc.

References

[1] (a) P.E. Ellis and J.E. Lyons, Catal. Lett. 3 (1989) 389;
(b) P.E. Ellis and J.E. Lyons, Coord. Chem. Rev. 105 (1990) 181;
(c) J.E. Lyons and P.E. Ellis, Catal. Lett. 8 (1991) 45;
(d) J.E. Lyons, P.E. Ellis and V.A. Durante, in: *Structure–Activity and Selectivity Relationships in Heterogeneous Catalysis*, eds. R.K. Grasselli and A.W. Sleight (Elsevier, Amsterdam, 1991) p. 99.
[2] R.A. Sheldon and J.K. Kochi, *Metal-Catalyzed Oxidations of Organic Compounds* (Academic Press, New York, 1981).
[3] J.E. Lyons, P.E. Ellis, H.K. Myers and R.W. Wagner, J. Catal. 141 (1993) 311.
[4] P.S. Nangia and S.W. Benson, Int. J. Chem. Kinet. 12 (1980) 169.
[5] D.L. Allara, D. Edelson and K.C. Irwin, Int. J. Chem. Kinet. 4 (1972) 345.
[6] D.E. Winkler and G.W. Hearne, Ind. Eng. Chem. 41 (1949) 2597.
[7] J.A. Howard and S.B. Tong, Can. J. Chem. 57 (1979) 2755.
[8] R. Hiatt, T. Mill, K.C. Irwin and J.K. Castleman, J. Org. Chem. 33 (1968) 1428, and references therein.
[9] K.U. Ingold, in: *Free Radicals*, Vol. 1, ed. J.K. Kochi (Wiley, New York, 1973) pp. 37–66.
[10] R.A. Sheldon and J.K. Kochi, *Metal-Catalyzed Oxidations of Organic Compounds* (Academic Press, New York, 1991) p. 344.
[11] R. Hiatt, K.C. Irwin and C.W. Gould, J. Org. Chem. 33 (1968) 1430.