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## Aldehyde/Olefin Cooxidations: Parallel Epoxidation Pathways and Concerted Decomposition of the Peroxyacyl-Olefin Adduct

Kevin R. Lassila\*, Francis J. Waller, Steven E. Werkheiser, and Amy L. Wressell

Corporate Science and Technology Center  
Air Products and Chemicals, Inc.  
Allentown, PA 18195

**Abstract.** Aldehyde-mediated olefin epoxidations appear to proceed by parallel peracid and radical addition pathways. For that portion of the reaction proceeding by radical addition, several lines of evidence favor an explanation in which the peroxyacyl-olefin adduct decomposes in a *concerted* manner to form alkyl radical, CO<sub>2</sub>, and epoxide.

Kaneda *et al* recently reported<sup>1</sup> that reaction of an olefin with oxygen produces epoxide in high yield under mild conditions (40 °C, 1 atm O<sub>2</sub>) when carried out in the presence of certain aldehydes. Cooxidations of this type have been widely reported<sup>2</sup> and appear to proceed by a mechanism related to aldehyde autooxidation. Kaneda *et al* suggest that the epoxidation occurs by way of a peracid formed by autooxidation of the aldehyde. This hypothesis is consistent with their observations of carboxylic acid coproducts, retention of the olefin stereochemistry in isovaleraldehyde-mediated epoxidations, and higher yields with electron-rich olefins. We undertook a closer examination of this work in connection with a program exploring the chemistry of dioxygen because we were intrigued by the mild reaction conditions and the absence of metal catalysts. A fundamental understanding of this chemistry has the potential to provide spinoffs to water treatment, chemical synthesis, polymerization, and other applications.

Preliminary experiments summarized in Table 1 agree with reported data<sup>1</sup> in that more highly substituted olefins are epoxidized more readily and excess aldehyde generally increases olefin conversions. The need for excess aldehyde is expected if the epoxidation proceeds by way of an intermediate peracid since the peracid could be intercepted by aldehyde to produce two equivalents of carboxylic acid.<sup>3</sup> The probable existence of this side reaction, and the fact that peracid epoxidations also produce acid, requires that the amount of acid formed be greater than or equal to the amount of epoxide formed if epoxidation occurs exclusively *via* the peracid. Epoxidations of diisobutylene mediated with one equivalent of either pivaldehyde or isobutyraldehyde, however, produce substantially more epoxide than acid, contradicting this analysis. These observations require the existence of a pathway which is alternative to that proceeding by way of the peracid.

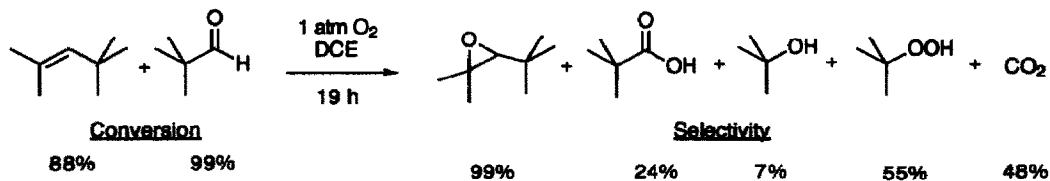
The literature appeared to indicate that the parallel path proceeds by addition of peroxyacyl radical to olefin followed by closure to epoxide and formation of a carboxyl radical.<sup>4</sup> Decarboxylation would produce CO<sub>2</sub> and an alkyl radical which would react with oxygen to produce, after hydrogen atom abstraction, the

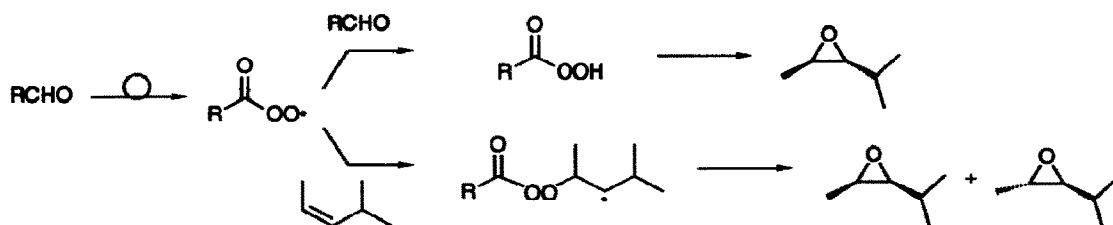
**Table 1.** Preliminary Experiments on Cooxidations of Aldehydes and Olefins.<sup>a</sup>

Aldehyde (mmol)	Olefin	t (h)	Olefin		Yield		
			Conversion	Epoxide	Acid	Hydroperoxide	Alcohol
Pivaldehyde (400)	1-Octene	8.5	40	23	32	40	10
		10.0	42	16	27	43	11
Pivaldehyde (80)	1-Octene	5.3	37	27	34	44	11
		4.0	38	30	38	46	11
Pivaldehyde (400)	Diisobutylene	7.5	100	110	32	48	15
Pivaldehyde (80)	Diisobutylene	6.5	90	94	37	58	5
Isobutyraldehyde (400)	1-Octene	9.0	47	36	68	---	---
Isobutyraldehyde (80)	1-Octene	7.0	27	28	37	---	---
		6.0	25	28	23	---	---
Isobutyraldehyde (400)	Diisobutylene	5.0	100	99	84	---	---
		7.5	100	99	86	---	---
Isobutyraldehyde (80)	Diisobutylene	9.0	87	87	30	---	---

<sup>a</sup>Reaction Conditions: Olefin (80 mmol), 1,2-dichloroethane (100 mL), decane (internal standard, 10 g), 40 °C, O<sub>2</sub> bubbled through solution continuously. Conversions and yields (molar, based on starting material leading to product) by internal standard GC. Reactions run to > 90% aldehyde conversion.

alkyl hydroperoxide observed in oxidations mediated with pivaldehyde.<sup>5</sup> In order to establish the existence of the parallel path in this case, an oxidation of diisobutylene mediated with pivaldehyde (1 eq) was performed, and the off-gas from the reaction was sparged through a 1 L graduated cylinder containing excess Ba(OH)<sub>2</sub>. In other respects, the reaction was performed as indicated in Table 1. The results summarized in Figure 1 suggest that addition of the peroxyacyl radical to the olefin is not only significant, but it may be the dominant pathway for epoxidation of diisobutylene.<sup>6</sup> The fact that the amounts of CO<sub>2</sub> and hydroperoxide are approximately equal can be rationalized by postulating that ring closure to epoxide results in the formation of a very unstable carboxyl radical which decarboxylates much more rapidly than it abstracts hydrogen atoms to form carboxylic acid. This explanation is also consistent with the observation that formation of carboxylic acid is not very efficient, possibly indicating that acid may be formed only as a byproduct of epoxidation with peracid. These results are readily explained by a rapid decomposition of the carboxyl radical, but they could equally well be explained by postulating that ring closure to epoxide, decarboxylation, and formation of alkyl radical occur concertedly.<sup>7</sup>

**Figure 1.** Product Distribution of Cooxidation of Diisobutylene (1 eq) and Pivaldehyde (1 eq).



**Figure 2.** Parallel Peracid and Addition Paths for Epoxidation.

In order to evaluate these competing explanations for formation of epoxide by the radical pathway, heats of formation were calculated for intermediates formed during addition of the peroxyacyl radical derived from pivaldehyde to 2-butene followed by epoxide formation. The calculations were performed using the MOPAC 93<sup>8</sup> AM1 restricted Hartree-Fock method using the keyword DOUBLET to minimize the radicals. All minimizations were done using the keyword PRECISE, which tightens the minimization criteria and improves final energies and geometries. The results show that addition of the peroxyacyl radical from pivaldehyde ( $\Delta H_f = -51.9$  kcal/mol) to *cis*-2-butene ( $\Delta H_f = -2.3$ ) to form the adduct ( $\Delta H_f = -62.0$ ) is about 8 kcal/mol exothermic, indicating addition is quite favorable. More interesting is that decomposition of this intermediate to carboxyl radical ( $\Delta H_f = -33.3$ ) and epoxide ( $\Delta H_f(cis) = -21.6$ ,  $\Delta H_f(trans) = -22.5$ ) is about 6 kcal/mol endothermic, *but concerted decomposition to t-butyl radical* ( $\Delta H_f = -2.8$ ),  $CO_2$  ( $\Delta H_f = -79.9$ ) and epoxide is over 100 kcal/mol exothermic. The calculations thus point toward a concerted decomposition of the peroxyacyl-olefin adduct to form alkyl radical,  $CO_2$ , and epoxide for that portion of the epoxidation proceeding by the radical addition route. This explanation is also intuitively appealing because formation of  $CO_2$  provides a means to overcome the strain associated with epoxide formation.

Results for epoxidations of *cis*-4-methyl-2-pentene with various aldehydes summarized in Table 2 support this explanation. The results can be interpreted on the basis of the mechanism in Figure 2. The peroxyacyl radical derived from the aldehyde can either abstract a hydrogen atom from aldehyde to produce peracid and eventually *cis*-epoxide, or it can add to olefin to produce epoxide with a randomized stereochemistry. The results showing enhanced *cis* selectivity with high aldehyde concentrations and with the sterically less-demanding isovaleraldehyde than with isobutyraldehyde are consistent with this explanation.

**Table 2.** Effect of Aldehyde and Stoichiometry on Oxidation of *cis*-4-Methyl-2-Pentene.

Aldehyde (mmol)	t (h)	Conversion		Yield		<i>cis:trans</i>
		Aldehyde	Olefin	Acid	Epoxide	
Pivaldehyde (80)	7	95	100	63	64	86:14
Isobutyraldehyde (80)	20	86	90	64	73	71:29
Isovaleraldehyde (80)	23	8	70	7	7	84:16
Pivaldehyde (400)	12	75	98	51	75	93:7
Isobutyraldehyde (400)	10	86	100	85	76	79:21
Isovaleraldehyde (400)	15	91	99	88	60	90:10

<sup>a</sup>Reaction Conditions: Olefin (80 mmol), 1,2-dichloroethane (100 mL), decane (internal standard, 10 g), 40 °C,  $O_2$  bubbled through solution continuously. Conversions and yields (molar, based on starting material leading to products) by internal standard GC.

For that portion of the reaction proceeding by addition, the epoxide stereochemistry will be determined by the lifetime of the peroxyacyl-olefin adduct [Figure 3]. If this intermediate were to decompose by formation of carboxyl radical, it would be expected that the lifetime would be independent of aldehyde structure. One would thus be led to predict that oxidations mediated with isobutyraldehyde would exhibit higher *cis* selectivities than those mediated with pivaldehyde because more of the reaction would proceed by way of the peracid route. This prediction clearly contradicts the experimental results. The observation of higher *cis* selectivity with pivaldehyde can be explained by postulating that decomposition of the peroxyacyl-olefin adduct occurs concertedly to produce epoxide, CO<sub>2</sub>, and alkyl radical. In this case, the additional stability associated with *t*-butyl relative to isopropyl radical would be reflected in the transition state for the decomposition, resulting in more rapid ring closure and higher *cis* selectivities.

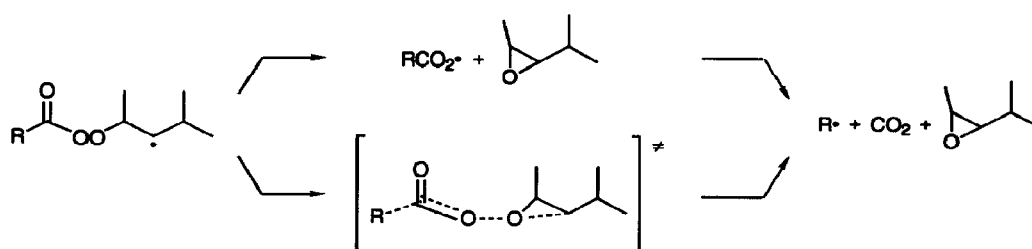


Figure 3. Decomposition Pathways for the Peroxyacyl-Olefin Adduct.

In conclusion, several lines of evidence support the hypothesis that aldehyde-mediated olefin epoxidations proceed by parallel peracid and radical addition pathways. Furthermore, for that portion of the reaction proceeding by radical addition, thermodynamic calculations and stereochemical results favor an explanation in which the peroxyacyl-olefin adduct decomposes in a concerted manner to form alkyl radical, CO<sub>2</sub>, and epoxide.

#### References and Notes

1. Kaneda, K.; Haruna, S.; Imanaka, T.; Hamamoto, M.; Nishiyama, Y.; Ishii, Y. *Tetrahedron Letters* **1992**, *33*, 6827-30.
2. For a review, see Filippova, T. V.; Blyumberg, E. A. *Russ. Chem. Rev.* **1982**, *51*, 582-591.
3. Mageli, O. L.; Sheppard, C. S. in *Organic Peroxides*, Volume 1; Daniel Swern, Ed.; Wiley-Interscience: New York, 1970; p. 62.
4. See, for example, a) Simmons, K.; Van Sickle, D. *J. Am. Chem. Soc.* **1973**, *95*, 7759-7763. b) Tsuchiya, F.; Ikawa, T. *Can. J. Chem.* **1969**, *47*, 3191-3197.
5. Hydroperoxides were not observed in oxidations mediated with isobutyraldehyde, possibly because of instability of isopropyl hydroperoxide under the GC conditions.
6. Qualitative experiments using isobutyraldehyde, 2-ethylhexanal, and isovaleraldehyde also showed evidence of CO<sub>2</sub> formation, suggesting that addition of peroxyacyl radical followed by ring closure and decarboxylation is occurring in all of these aldehyde-mediated oxidations.
7. Concerted decomposition alkyl radical and CO<sub>2</sub> has been observed in thermolysis of peresters: Bartlett, P. D.; Simons, D. M. *J. Am. Chem. Soc.* **1960**, *82*, 1753-1756..
8. Quanta: Version 3.3; Molecular Simulations, Inc; 200 Fifth Avenue, Waltham, MA 02154.

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