

The ionization potentials for  $\alpha$ -aminoalkyl radicals are the lowest observed for any organic or organometallic species.<sup>28</sup> Moreover, they decrease with increasing C- or N-alkylation. They are substantially lower than ionization potentials for simple alkyl radicals, which fall on the range 7–10 eV,<sup>28</sup> and are close to those for lithium (5.39 eV) and sodium (5.14 eV). The description of  $\alpha$ -aminoalkyl radicals as "organic metals"<sup>29</sup> seems to be entirely appropriate.

$\alpha$ -Aminoalkyl radicals are powerful reducing agents by virtue of their low ionization potentials. This has prompted the use of amines as sacrificial donors in photochemical reductions<sup>30</sup> because

(28) Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data, Suppl.* 1977, 6, 1.

(29) We thank Professor S. W. Benson for this suggestion.

(30) See, for example: DeLaire, P. J.; Lee, J. T.; Sprintschnik, H. W.; Abruna, H.; Meyer, T. J.; Whitten, D. J. *J. Am. Chem. Soc.* 1977, 99, 7094. Chandrasekaran, K.; Whitten, D. G. *Ibid.* 1980, 102, 5119.

the  $\alpha$ -aminoalkyl radicals thus formed generally carry out a second chemical reduction, effectively doubling the overall quantum yield.

To summarize,  $\alpha$ -aminoalkyl radicals have remarkably high stabilization energies and low ionization potentials. Stabilization energies increase and ionization potentials decrease with increasing C- or N-alkylation. These thermodynamic properties underlie many of the observed chemical properties of  $\alpha$ -aminoalkyl radicals and their parent amines.

**Registry No.** Me<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>, 110-18-9; Me<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>NHMe, 142-25-6; H<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>, 107-15-3; H<sub>2</sub>N(Me)CHCH(Me)NH<sub>2</sub>, 563-86-0; H<sub>2</sub>N(Me)<sub>2</sub>CC(Me)<sub>2</sub>NH<sub>2</sub>, 20485-44-3; Me<sub>2</sub>NCH<sub>2</sub>, 30208-47-0; MeNHCH<sub>2</sub>, 31277-24-4; H<sub>2</sub>NCH<sub>2</sub>, 10507-29-6; H<sub>2</sub>N(Me)CH<sub>2</sub>, 30208-36-7; H<sub>2</sub>N(Me)<sub>2</sub>C, 26374-12-9.

(31) A slightly higher value for AE(MeNCH<sub>2</sub><sup>+</sup>) from MeNCH<sub>2</sub>-CH<sub>2</sub>NMe, 8.30 eV, has been reported from photoionization experiments (Loguinov, Y.; Takhistov, V. V.; Vatlina, L. P. *Org. Mass Spectrom.* 1981, 16, 239).

## Mechanism of the Ozonolysis of Propene in the Liquid Phase

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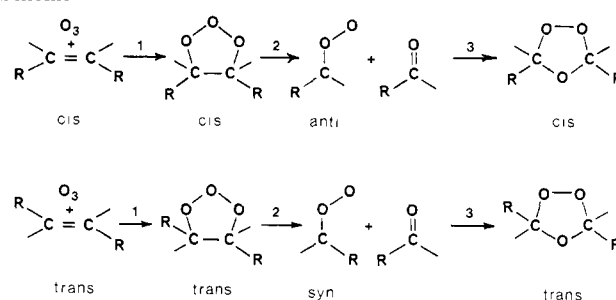
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**Abstract:** Propylene was ozonized in isobutane, chlorodifluoromethane, and methyl chloride solvents. Propylene ozonide, ethylene ozonide, and 2-butene ozonide (cis and trans isomers) were obtained in ratios of about 82:16:2. The amount of butene ozonide increased while that of ethylene ozonide usually decreased for reactions in the presence of added acetaldehyde. The cis-trans stereochemistry of the butene cross ozonide from propylene was studied at various conditions. Usually the cis isomer was preferentially formed, but addition of acetaldehyde could alter this. The cis-/trans-butene ozonide ratio was 67/33 when formed from cis- or trans-2-butene in CHClF<sub>2</sub> and 50/50 as a cross ozonide from trans-2-pentene. The kinetic secondary isotope effects upon ozonolysis of propene-2-d<sub>1</sub> ( $k_H/k_D = 0.88$  (6)) and propene-1-d<sub>1</sub> (0.88 (8)) were evaluated. These results are discussed with reference to the Criegee mechanism of ozonolysis.

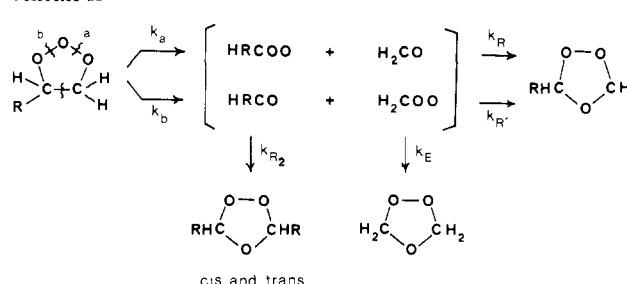
It has been documented that a cis(trans)-alkene upon ozonolysis usually yields more cis (trans) final ozonide.<sup>2-4</sup> One rationale for this, the three-step concerted Criegee mechanism, is outlined in Scheme I and applies to the predominant process for the cis- or trans-alkene.<sup>5</sup> The most comprehensive presentations of this model were first forwarded qualitatively and inferentially by reaction chemists.<sup>8,9</sup>

One difficulty encountered by this proposal arises with small alkenes such as 2-butene and 2-pentene. For these cases, more trans ozonide has been observed irrespective of the alkene configuration.<sup>8-11</sup> In a series of papers,<sup>12</sup> Cremer has suggested a

Scheme I



Scheme II



solution to this puzzle. Guided by energy calculations, he has argued that step 2 in Scheme I is endothermic or nearly thermally

(1) (a) University of Michigan. (b) Indian Institute of Technology, Madras.

(2) Murray, R. W. *Acc. Chem. Res.* 1968, 1, 313.

(3) Bailey, P. S. "Ozonation in Organic Chemistry"; Academic Press: New York, 1978; Vol. 1.

(4) Kuczkowski, R. L. "1,3-Dipolar Cycloaddition of Ozone and Carbonyl Oxides"; Padwa, A. W., Ed.; Wiley: New York, in press.

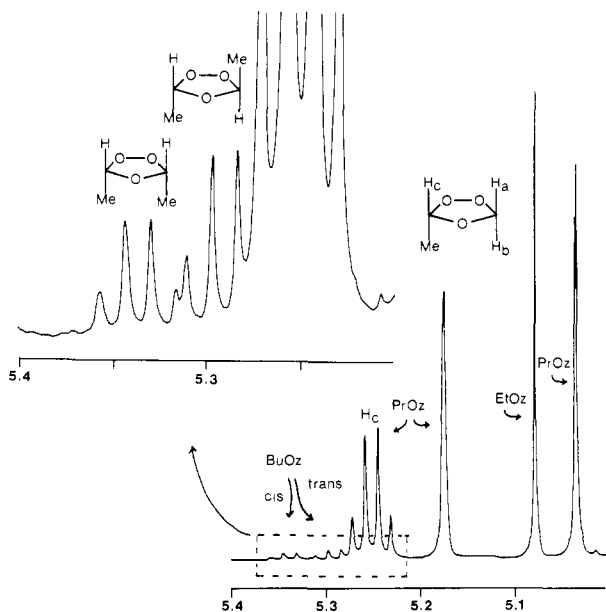
(5) This paper will not consider in detail any nonconcerted pathways such as those suggested as an alternative pathway to ozonide formation, at least in some circumstances.<sup>6,7</sup>

(6) (a) Murray, R. W.; Hagan, R. *J. Org. Chem.* 1971, 36, 1098. (b) Su, J.; Murray, R. W. *Ibid.* 1980, 45, 678. (c) Ramachandran, V.; Murray, R. W. *J. Am. Chem. Soc.* 1978, 100, 2197.

(7) Harding, L. B.; Goddard, W. A., III *J. Am. Chem. Soc.* 1978, 100, 7180.

(8) (a) Bauld, N. L.; Thompson, J. A.; Hudson, C. E.; Bailey, P. S. *J. Am. Chem. Soc.* 1968, 90, 1822. (b) Bailey, P. S.; Ferrell, T. M. *Ibid.* 1978, 100, 988.

(9) Lattimer, R. P.; Kuczkowski, R. L.; Gillies, C. W. *J. Am. Chem. Soc.* 1974, 96, 348.



**Figure 1.** 360-MHz proton NMR spectrum in the region  $\delta$  5.1–5.4 of a mixture of ethylene, propylene, and butene ozonides obtained from ozonolysis of propylene in isobutane at  $-95^\circ\text{C}$  in the presence of 1 M  $\text{CH}_3\text{CHO}$ .

neutral for small alkenes but becomes exothermic as the size of R increases. This implies a change from a late to an early transition state (Hammond postulate) as substituent bulk increases. A late transition state is influenced by product properties and leads to the more stable syn carbonyl oxide<sup>12a</sup> and subsequently to the trans final ozonide. An early transition state resembles reactants and produces syn or anti carbonyl oxide depending on the primary ozonide configuration. This is the case described in Scheme I, applicable when the substituents are large.

Cremer's calculations also suggest a late transition state for the primary ozonide decomposition from 1-alkenes.<sup>12c</sup> However, the  $\text{R}_2$  cross ozonides produced from a 1-alkene (Scheme II) do not correlate well with this proposal since more *cis*- $\text{R}_2$  ozonide has been obtained in the cases reported.<sup>9,13,14</sup> For example, from GC the *cis*/*trans* ratio of the butene ozonide from propylene was 81/19 in marked contrast to the typical ratio ( $\sim 35/65$ ) from ozonolysis of *cis* or *trans*-2-butene.<sup>9</sup>

Because the propylene results were at odds with the attractive rationale of Cremer, we have reinvestigated its cross ozonide stereochemistry. One goal was to redetermine the stereo results by a different technique. Proton NMR spectroscopy at 360 MHz was chosen since the high resolution made it possible to obtain good analytical data on the ozonide mixtures with minimum handling (see Figure 1). A related goal was to evaluate the cross ozonide stereochemistry for various conditions. It was also attractive to investigate  $\text{CH}_3\text{CD}=\text{CH}_2$  and  $\text{CH}_3\text{CH}=\text{CHD}$  to determine if they exhibit a kinetic secondary isotope effect appropriate for a concerted cycloaddition between ozone and propylene.

## Results and Discussion

**Propylene. Kinetic Secondary Isotope Effect (KSIE).** The first step in the Criegee mechanism (see Scheme I) is generally considered a concerted cycloaddition between ozone and alkene on the basis of a variety of stereochemical results, thermochemical calculations, and activation energy and kinetic measurements.<sup>3,4</sup> A method to confirm this employs secondary kinetic isotope effects.

**Table I.** Kinetic Secondary Isotope Effect ( $k_{\text{H}}/k_{\text{D}}$ ) for Propylene Consumption in Ozonolysis of  $\text{C}_3\text{H}_6/\text{C}_3\text{H}_5\text{D}$  Mixtures<sup>a</sup>

reaction	NMR		microwave	
	PR <sup>b</sup>	PrOz <sup>c</sup>	PR <sup>d</sup>	PR <sup>e</sup>
$\text{CH}_3\text{CH}=\text{CHD}$				
1	0.79	0.89	0.74	0.75
2	0.78	0.87	0.92	0.87
3	0.89	0.82	0.86	0.75
4	0.75	0.93	0.79	0.76
$k_{\text{H}}/k_{\text{D}} = 0.82 \pm 0.06$ (195 K)				
$\text{CH}_3\text{CD}=\text{CH}_2$				
5	0.81	0.83	0.92	0.66
6			0.75	0.72
7	0.80	0.86		0.89
8	0.71	0.90	0.97	0.86
$k_{\text{H}}/k_{\text{D}} = 0.82 \pm 0.08$ (195 K)				

<sup>a</sup> Reactions conducted in isobutane at  $-78^\circ\text{C}$  to 30% based on ozone. <sup>b</sup> NMR analysis of initial and recovered propylene (PR). <sup>c</sup> NMR analysis of initial propylene and recovered propylene ozonide (PrOz). <sup>d</sup> Microwave analysis of intensities of  $1_{01} \rightarrow 2_{02}$  rotational transitions of initial and recovered PR. <sup>e</sup> Microwave analysis of intensities of the  $1_{10} \rightarrow 2_{11}$  rotational transitions of initial and recovered PR.

**Table II.** Ozonide Yields from Propylene as Temperature, Solvent, and Concentration of Added Acetaldehyde Vary<sup>a</sup>

solvent	T, $^\circ\text{C}$	$\text{CH}_3\text{CHO}$ , M	yield <sup>b</sup>			total yield <sup>c</sup>
			PrOz	EtOz	BuOz	
isobutane	-78	0.0	80	18	2	
	-78	0.3	76	16	8	
	-95	0.3	84	11	5	66
	-95	1.0	81	11	8	60
$\text{CF}_2\text{ClH}$	-78	0.0	84	13	3	
	-78	1.0	79	11	10	60
	-116	0.0	82	16	2	
$\text{CH}_3\text{Cl}$	-116	1.0	81	13	6	56
	-78	0.0	79	19	2	60
	-78	1.0	72	21	7	60

<sup>a</sup> All reactions contained  $\sim 1$  M propylene and were run to 30–50% completion based on  $\text{O}_3$ . <sup>b</sup> Relative ozonide yield. PrOz = propylene ozonide; EtOz = ethylene ozonide; BuOz = *cis*- and *trans*-butene ozonides. Relative yields vary a few percent from run to run. <sup>c</sup> Percent ozonide yield based on input ozone.

An inverse effect ( $k_{\text{H}}/k_{\text{D}} < 1$ ) generally is exhibited by a transition state involving deformation of an  $\text{sp}^2$  carbon atom to  $\text{sp}^3$  hybridization. Therefore, to confirm that the transition state involves bond formation to both alkene carbon atoms, competitive experiments were conducted with mixtures of  $\text{C}_3\text{H}_6/\text{CH}_3\text{CD}=\text{CH}_2$  as well as  $\text{C}_3\text{H}_6/\text{CH}_3\text{CH}=\text{CHD}$ . The results are listed in Table I.

Three or four different estimates of  $k_{\text{H}}/k_{\text{D}}$  were made for each reaction run. This ratio is very sensitive to small changes in the relative amounts of  $\text{C}_3\text{H}_6$  and  $\text{C}_3\text{H}_5\text{D}$  leading to a range of estimates for  $k_{\text{H}}/k_{\text{D}}$ . Nevertheless, the data are certain enough to establish an inverse KSIE of similar magnitude for deuterium substitution at either carbon atom as expected for a concerted cycloaddition between ozone and propylene. The results are comparable to data from  $\text{C}_2\text{H}_4/\text{C}_2\text{D}_4$  in various solvents which gave  $k_{\text{H}}/k_{\text{D}} = 0.90$  (3) (per D, average value between  $-95$  and  $-136^\circ\text{C}$ ).<sup>15</sup> The larger KSIE for propylene may suggest greater rehybridization in the transition state. But, a firm interpretation is not warranted without some transition-state calculations to help probe the reaction process.

**Cross Ozonide Yields.** The ozonide yields from ozonolysis of propylene or a mixture of propylene and acetaldehyde are compared for various conditions in Table II. Addition of  $\text{CH}_3\text{CHO}$  decreases somewhat the relative amounts of propylene ozonide (PrOz) and ethylene ozonide (EtOz) and increases the butene

(10) Murray, R. W.; Youssefeyeh, R. D.; Story, D. R. *J. Am. Chem. Soc.* **1967**, *89*, 2429.

(11) Greenwood, F. L. *J. Am. Chem. Soc.* **1966**, *88*, 3146.

(12) (a) Cremer, D. *J. Am. Chem. Soc.* **1979**, *101*, 7199. (b) *Ibid.* **1981**, *103*, 3619. (c) *Ibid.* **1981**, *103*, 3627. (d) *Ibid.* **1981**, *103*, 3633. (e) *Angew. Chem.* **1981**, *93*, 934.

(13) Murray, R. W.; Williams, G. J. *J. Org. Chem.* **1969**, *34*, 1891.

(14) Vinyl fluoride is an exception. See ref 12d and: Mazur, U.; Lattimer, R. P.; Lopata, A.; Kuczkowski, R. L. *J. Org. Chem.* **1979**, *44*, 3181.

(15) Fong, G. D.; Kuczkowski, R. L. *J. Am. Chem. Soc.* **1980**, *102*, 4763.

Table III. Model Kinetic Calculations for Scheme II Applied to Propylene<sup>a</sup>

calcn	initial concentrations,				bimolecular rate constants				% yields		
	[A <sub>0</sub> ] CH <sub>3</sub> CHOO	[B <sub>0</sub> ] H <sub>2</sub> CO	[C <sub>0</sub> ] H <sub>2</sub> COO	[D <sub>0</sub> ] CH <sub>3</sub> CHO	[A][B] k <sub>R</sub>	[C][D] k <sub>R'</sub>	[B][C] k <sub>E</sub>	[A][D] k <sub>R<sub>2</sub></sub>	AB + CD PrOz	BC EtOz	AD BuOz
1	0.50	0.50	0.50	0.50	1	1	1	1	50.0	25.0	25.0
2	0.75	0.75	0.25	0.25	1	1	1	1	62.5	18.7	18.7
3	0.65	0.65	0.35	0.35	1	1	0.67	0.067	79.4	16.3	4.3
4	0.65	0.65	0.35	0.95	1	1	0.67	0.067	80.2	9.2	10.6
5	0.90	0.90	0.10	0.10	1	1	2	0.2	85.5	11.0	3.5
6	0.65	0.65	0.35	0.35	1	1	0.4	0.04	85.7	11.5	2.7
7	0.65	0.65	0.35	0.35	1	1	0.5	0.05	83.3	13.4	3.3
8	0.65	0.65	0.35	0.35	0.25	1	0.25	0.025	81.2	11.8	7.0

<sup>a</sup> Rate of formation: AB = k<sub>R</sub>[A][B], etc. The relative (%) yields were obtained by numerical summation of rate equations for small reaction increments until 90–100% of the maximum ozonide yield was reached. Only the relative values of concentration and rate constants are significant.

ozonides (*cis*-BuOz plus *trans*-BuOz). The amounts of EtOz plus BuOz range from 16 to 21% with considerable preference for EtOz. These cross ozonide yields are in contrast to ethylene<sup>15</sup> where they ranged from 3–4% in isobutane to 30–40% in CHClF<sub>2</sub> and CH<sub>3</sub>Cl. For ethylene in a nonpolar solvent, little ozonide formation (<10%) occurred outside the original solvent cage where primary ozonide fragmentation took place while in a polar solvent at least 80–90% was formed outside the original solvent cage.

These yield data can be interpreted via Scheme II by postulating preferential cleavage of the primary ozonide to CH<sub>3</sub>C-HOO and H<sub>2</sub>CO (k<sub>a</sub> > k<sub>b</sub>), extensive scrambling of the cleavage products even for low solvent polarity, and different recombination rates between cleavage products (e.g., k<sub>E</sub> > k<sub>R<sub>2</sub></sub>). The operation of such a model can be illustrated by kinetic calculations summarized in Table III. For these calculations, it is assumed that the decomposition step proceeded to completion before the recombination step commenced. Thus, the initial relative concentrations of CH<sub>3</sub>CHOO, H<sub>2</sub>COO, CH<sub>3</sub>CHO, and H<sub>2</sub>CO were fixed by the choice of k<sub>a</sub>, k<sub>b</sub>, and any added aldehyde. This was followed by stepwise numerical summation of the bimolecular recombination steps for various values of k<sub>R</sub>, k<sub>E</sub>, etc. up to 90–100% of the maximum possible ozonide yield. For equal cleavage pathways and recombination rate constants (statistical scrambling throughout), the amounts of PrOz, EtOz, and BuOz are in the ratio 50:25:25 (calculation 1). The amounts of cross ozonide can be decreased by unequal cleavage pathways (calculation 2; in effect, k<sub>a</sub> > k<sub>b</sub>) and/or by a solvent cage effect. However, the amounts of the two cross ozonides will remain equal. One way to introduce unequal cross ozonide yields that approximately correspond to experimental runs is by a combination of a preferential cleavage to CH<sub>3</sub>CHOO and H<sub>2</sub>CO along with different recombination rates as in calculation 3. The increase in the BuOz between calculations 3 and 4 upon increasing [CH<sub>3</sub>CHO] about 2.7 times also reasonably parallels the experimental results.

While this provides a reasonable model to rationalize the observed data, the rate constants are not highly sensitive to the ozonide yields. See, for example, calculation 5, where a 9:1 preference for CH<sub>3</sub>CHOO over H<sub>2</sub>COO is assumed or calculations 6–8 for other values of rate constants. Nevertheless, other indications can be found to also support this basic picture. For example, the 18% yield of EtOz in isobutane approaches the limiting value of 25% expected for statistical scrambling throughout (calculation 1). It singularly suggests that the solvent cage effect is considerably less important compared to ethylene. This is also implied by the similar cross ozonide yields observed in the two polar solvents.

The preferential cleavage to CH<sub>3</sub>CHOO and H<sub>2</sub>CO (k<sub>a</sub> > k<sub>b</sub>) is also consistent with literature data on propylene with formaldehyde and methanol as trapping agents. When H<sub>2</sub>CO is added in isobutane, the amount of BuOz apparently decreased and that of EtOz increased by several percent.<sup>16</sup> With methanol as a

Table IV. Percent *cis*-Butene Ozonide Obtained as a Cross Ozonide from Propylene<sup>a</sup>

T, °C	CHClF <sub>2</sub> solvent		<i>i</i> -C <sub>4</sub> H <sub>10</sub> solvent	
	without CH <sub>3</sub> CHO	with CH <sub>3</sub> CHO <sup>b</sup>	without CH <sub>3</sub> CHO	with CH <sub>3</sub> CHO <sup>b</sup>
−116	80 ± 2 (4) <sup>c</sup>	56 ± 10 (4)		
−95			68 ± 1 (2)	37 ± 8 (3)
−78	76 ± 1 (2)	49 ± 7 (4)	62 ± 5 (3)	50 ± 6 (4)
−45	79 ± 15 (2)	38 ± 2 (2)	44 ± 2 (2)	41 ± 2 (2)

<sup>a</sup> % *cis*-BuOz + % *trans*-BuOz = 100. <sup>b</sup> Data with [CH<sub>3</sub>CHO] = 0.25 and 1.0 M are averaged. See also Table V. <sup>c</sup> Number in parentheses indicates number of ozonolyses used to compute average.

Table V. Dependence of Percent *cis*-Butene Ozonide from Propylene on Acetaldehyde Concentration<sup>a</sup>

CH <sub>3</sub> CHO, M	solvent	
	CHClF <sub>2</sub>	<i>i</i> -C <sub>4</sub> H <sub>10</sub>
0	78 ± 6 (8) <sup>b</sup>	58 ± 11 (7)
0.25	55 ± 7 (7)	46 ± 1 (3)
1.0	46 ± 8 (6)	43 ± 10 (6)

<sup>a</sup> % *cis*-BuOz + % *trans*-BuOz = 100. <sup>b</sup> Data at various temperatures (Table IV) were averaged. The number in parenthesis is the number of data points used.

solvent to trap the carbonyl oxide, the CH<sub>3</sub>CHOO/H<sub>2</sub>COO cleavage proportions were estimated as 62/38.<sup>17</sup> Theoretical calculations also suggest that this is the preferred cleavage direction on the basis of estimates of Δ*H*<sup>o</sup>(0 K).<sup>12c</sup>

By extrapolation of the relative ozonide yield data to other alkenes, the negligible yields of R<sub>2</sub> cross ozonide (in the absence of added aldehyde) for heavier 1-alkenes should be explicable by a similar preferential cleavage to RHCOO (as also suggested in earlier work<sup>13,17</sup>) and recombination kinetics that disfavor R<sub>2</sub> cross ozonide formation.<sup>18</sup> Also, the solvent cage effect is apparently more important for large 1-alkenes.<sup>19</sup>

Perhaps the most striking result is the lesser importance of the solvent cage effect for propylene compared to ethylene in isobutane. Although it is difficult to estimate the amount of ozonide formation for propylene outside the original solvent cage, simple arguments place the limits between 40 and 100%. Thus the introduction of a CH<sub>3</sub> group markedly affects the recombination kinetics in the original solvent cage. One interpretation is that CH<sub>3</sub>CHOO is less reactive than H<sub>2</sub>COO. Energy estimates have emphasized that the methyl group stabilizes the carbonyl oxide and that its recombination with an aldehyde becomes less exothermic.<sup>12,20</sup>

(17) Fliszár, S.; Renard, J. *Can. J. Chem.* **1970**, *48*, 3002.

(18) Normal ozonide and ethylene ozonide in ~90/10 ratio have been observed from isobutylene and 1-butene in C<sub>2</sub>H<sub>5</sub>Cl, but no R<sub>2</sub> cross ozonide was reported. See: Vrbaski, T.; Cventanovic, R. J. *Can. J. Chem.* **1960**, *38*, 1063.

(19) Murray, R. W.; Williams, G. J. *J. Org. Chem.* **1969**, *34*, 1896.

(16) Gillies, C. W.; Lattimer, R. P.; Kuczkowski, R. L. *J. Am. Chem. Soc.* **1974**, *96*, 1536. In this study using GC, the yields of BuOz and EtOz were approximately 4% and 11–12%, respectively.

**Cross Ozonide Stereochemistry.** The previous section indicates that the low BuOz yields from propylene can be rationalized by a Criegee model incorporating various competitive reactions. Therefore, it is appropriate to also examine the stereochemistry of the BuOz yields in the context of this mechanism.

Tables IV and V list the percent *cis*-BuOz obtained from ozonolysis of propylene or propylene-acetaldehyde mixtures in two solvents. In the absence of added acetaldehyde, the *cis*-BuOz/*trans*-BuOz ratio favors *cis*-BuOz except at high temperatures in isobutane.<sup>21</sup> Acetaldehyde decreases this ratio and *trans*-BuOz becomes favored. At  $[\text{CH}_3\text{CHO}] = 1 \text{ M}$ , the ratio is close to that obtained from *cis*- or *trans*-2-butene ozonolyses ( $\sim 35/65$ ). In  $\text{CHClF}_2$  there is a temperature dependence when  $\text{CH}_3\text{CHO}$  is added, but none in its absence. In isobutene, a temperature dependence is observed in the absence of added  $\text{CH}_3\text{CHO}$ , while with  $\text{CH}_3\text{CHO}$  the temperature behavior seems more complex.

Many of the stereochemical trends in the presence of added aldehyde have precedents in other cross ozonide studies.<sup>13,22,23</sup> However, a compelling interpretation of how the concentration of added aldehyde affects the stereochemistry is not yet clear. Possibilities include the following: (1) a solvent effect (such as solvent polarity or nucleophilicity) altering transition states or the syn/anti carbonyl oxide ratio; (2) a more direct interaction of the aldehyde such as attack on the primary ozonide; (3) promotion by the added aldehyde of nonconcerted pathways having different stereochemical consequences.<sup>5,7</sup>

Regarding reaction temperature, some effects are apparent in Table IV, but they depend on the solvent and addition of  $\text{CH}_3\text{CHO}$ . The range of variation is similar to other examples employing a fast warm-up *post* reaction.<sup>24-26</sup> In general terms, temperature can affect stereochemistry by promoting syn-anti carbonyl oxide equilibrium or by influencing the kinetics in the primary ozonide decomposition or carbonyl oxide recombination steps. For propylene, syn-anti equilibrium after formation initially appears attractive, especially at  $-45^\circ\text{C}$  since three systems in Table IV give  $\sim 40\%$  *cis*-BuOz. This implies that the syn-anti free energy difference is nearly zero (or partial equilibrium is attained).<sup>27</sup>

In summary, the cross ozonide stereochemistry overall has resulted in complex data only partly rationalized by current Criegee models unless ad hoc "corrections" are applied. In one view, the preference for a *cis*/*trans* ratio  $>1$  at low temperatures and in simple solvents (without  $\text{CH}_3\text{CHO}$ ) fits the more empirically based arguments for 1-alkenes.<sup>8b,9</sup> These predict more *cis*-ozonide since the R substituent should prefer an equatorial position in the transition state of the 1-alkene primary ozonide. This leads to more anti carbonyl oxide and *cis* final ozonide (early transition state: primary ozonide stereochemistry controls the syn/anti ratio). This model can be extended to explain some of the temperature-dependent data as well as changes with solvent and added aldehyde (cf. above), but the arguments are not easily generalized and tend to be case by case.

As noted in the introduction, a *cis*/*trans* cross ozonide ratio  $>1$  is troublesome for Cremer's thermochemical-based rationale, which proposes syn carbonyl oxide production on the grounds that carbonyl oxide stability becomes a factor<sup>12</sup> (late transition state,

**Table VI.** Percent *cis*-Butene Ozonide Obtained as a Normal or Cross Ozonide at  $-78^\circ\text{C}^a$

alkene	$\text{CH}_3\text{CHO}$ , M	solvent		
		<i>i</i> -C <sub>4</sub> H <sub>10</sub>	$\text{CHClF}_2$	$\text{CH}_3\text{Cl}$
<i>cis</i> -2-butene	0	37	67	42
<i>cis</i> -2-butene	0.25		57	
<i>cis</i> -2-butene	1.0	34	49	
<i>trans</i> -2-butene	0	37	66	38
<i>trans</i> -2-pentene	0	35	50	
propylene	0	62	76	55
	1.0	50	49	33

<sup>a</sup> % *cis*-BuOz + % *trans*-BuOz = 100.

carbonyl oxide stability influences the syn/anti ratio). Nevertheless, this model can apply to the data at higher temperatures, higher added aldehyde concentrations, or other conditions where the *trans* isomer predominates. In other words, either the late or the early transition-state models can be useful starting points to discuss the stereochemistry for 1-alkenes, but they are oversimplifications in the face of the reaction diversity. Neither model seems successful enough for all conditions or free enough of intuitive assumptions to presently make it a clearly superior rationale.

It is perhaps not so surprising that the reaction diversity with conditions proves difficult to model when analyzed in terms of reaction energetics for competing processes.<sup>28</sup> The largest *cis*/*trans* cross ozonide ratios observed in this study (4/1) would imply activation energy differences of only about 0.4–0.6 kcal/mol in competing paths leading to *cis* vs. *trans* ozonides. Consequently, very modest energy changes will affect stereochemistry ratios, and it can understandably prove difficult to identify them in a general way. These energy differences are comparable to solvent interactions so that solvent-transition state effects may be a partial factor. Zero point vibrational energy differences for competing transition states could cloud interpretations for stereo ratios close to unity. From another perspective, the resolution may bear on how energy is localized and dissipated in bond breakage/formation processes and how the solvent cooperates at the intermolecular level. This would necessitate a closer examination of reaction-solvent coupling at the microscopic level than heretofore considered practical.

**2-Butene and 2-Pentene. Butene Ozonide Stereochemistry.** An illustration of the importance of the solvent on the stereochemistry was obtained from an unexpected result with 2-butene. Numerous previous ozonolyses of the *cis*- and *trans*-2-butene system have been reported, and the *cis*-/*trans*-butene ozonide stereochemistry has always favored the *trans* isomer regardless of the starting material.<sup>29</sup> Since propylene gave more *cis*-butene ozonide in  $\text{CHClF}_2$ , the 2-butene isomers were also ozonized in this solvent. The results are listed in Table VI and demonstrate that more *cis* isomer can be produced in this solvent. To test whether a simple correlation between ozonide stereochemistry and solvent polarity occurs, *trans*-2-butene was also ozonized in  $\text{CH}_3\text{Cl}$ , but the ozonide yields reverted in favor of the *trans* form (Table VI).

*trans*-BuOz is also favored in nearly all reported cases when BuOz is formed as a cross ozonide from various 2-pentenones and other unsymmetrical 2-alkenes.<sup>32</sup> This trend was also examined for *trans*-2-pentene in  $\text{CHClF}_2$ . The results (Table VI) indicated an increase in the amount of *cis*-BuOz compared to a solvent like isobutane, but the change is not as great as for 2-butene.

Extensive discussion of the 2-butene ozonolysis has preceded this work.<sup>8,9,12b-c,12e,34,35</sup> A rationalization of the preference for

(20)  $\Delta H^\circ(0 \text{ K}) = -61 \text{ kcal}$  for recombination of  $\text{H}_2\text{CO} + \text{H}_2\text{COO}$  and  $-54 \text{ kcal}$  for  $\text{CH}_3\text{CHOO}$ .<sup>12c</sup> These are too exothermic to be a factor in the comparative reactivities except as they parallel trends in early transition states.

(21) The ratio 68/32 in isobutane at  $-95^\circ\text{C}$  can be compared to 81/19 obtained from the partially resolved GC isomer peaks.<sup>9</sup>

(22) Murray, R. W.; Youssefyeh, R. D.; Williams, G. J. *Tetrahedron* **1968**, *24*, 4347.

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(27) The syn-anti energy difference favors syn- $\text{CH}_3\text{COO}$  by 2.5 kcal according to Cremer.<sup>12a</sup> This alone is too large since it would lead to *cis*-BuOz/*trans*-BuOz  $\ll 1$ . His calculations and others<sup>4</sup> predict high barriers for syn-anti interconversion. The possibility that solvent interactions might nullify the calculated predictions cannot be eliminated.

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(29) *cis*-BuOz/*trans*-BuOz varies from 29/71 to 45/55. See ref 8–11, 30, and 31.

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(31) Loan, L. D.; Murray, R. W.; Story, P. R. *J. Am. Chem. Soc.* **1965**, *87*, 737.

(32) *cis*-BuOz/*trans*-BuOz varies between 27/73 and 49/51. One run in  $\text{CH}_2\text{Cl}_2$  for *cis*-*i*-PrCH=CHCH<sub>3</sub> resulted in more *cis*-BuOz. See ref 8, 10, 11, and 33.

(33) Fliszár, S.; Carles, J. *Can. J. Chem.* **1969**, *47*, 3921.

*trans*-BuOz when obtained as a cross ozonide from unsymmetrical *cis*- and *trans*-alkenes has also been forwarded.<sup>8b,9</sup> Like the situation for 1-alkenes, these proposals are useful starting points for a stereochemical analysis. Nevertheless, the ozonolyses in  $\text{CHClF}_2$  are a reminder that the solvent environment may also play a role in determining the ozonide stereochemistry. The neglect of reaction-solvent coupling in present stereochemical Criegee models is a possible origin, at least in part, for some of the limitations that occur in their application.

### Experimental Section

$^1\text{H}$  NMR were obtained with a Bruker WM-360 spectrometer. Microwave spectra were recorded with a Hewlett-Packard 8460A spectrometer. Conventional vacuum-line techniques on a calibrated manifold were employed for most manipulations of reactants and products. A Welsbach Model T-408 ozonator was employed.

**Materials.** CP grade propylene (Matheson), *cis*-2-butene (Matheson), *trans*-2-butene (Matheson), *trans*-2-pentene (Aldrich), acetaldehyde (Matheson Coleman and Bell), and solvents (isobutane,  $\text{CHClF}_2$ , and  $\text{CH}_2\text{Cl}_2$ ) were normally dried by passage through cold traps. (*E*)-Propene-*l*- $d_1$  (67% enriched) was prepared in our lab,<sup>36</sup> and propene-2- $d_1$  (98% enriched) was purchased from Merck Co. Isotopic enrichments were checked by microwave spectroscopy.

**Ozonolysis Procedure.** Reactions were conducted with flow rates of 0.1–0.2 mmol of  $\text{O}_3$ /min by standard techniques.<sup>9,15,16</sup> The solutions were  $\sim 1.0$  M in alkene (usually 2 mmol of alkene in 20 mmol of solvent), and 0.6–1.0 mmol of ozone was used. All the input ozone was consumed in the reaction vessel. After reaction, a fast warm-up procedure was employed.<sup>6a</sup> The reaction mixture was then distilled through traps held at  $-78$  and  $-196$  °C. The ozonides were collected in the  $-78$  °C trap.

The total yields of ozonides were determined manometrically. They were around 60% from propylene, 35% from *cis*- or *trans*-2-butene, and less than 20% from *trans*-2-pentene.

**Relative Yields and *cis*-/*trans*-2-Butene Ozonide Stereochemistry.** Ozonolysis of propylene produces the normal and cross ozonides (Scheme II). The relative yields of these ozonides were analyzed by 360-MHz proton NMR. Figure 1 shows a part of the NMR spectrum of the ozonide mixture. Peak assignments were obvious from the relative integrations and the splittings. For *cis*- and *trans*-2-butene ozonides, a quartet arises from the methine hydrogen for each stereoisomer. The downfield quartet was assigned to the *cis* isomer,<sup>8,10,30,31</sup> consistent with the GC/microwave results, which unequivocally determined the stereochemistry.<sup>9</sup> Integration of these peaks and the other resonances in this

region gave the relative ozonide yields. Although the methyl groups in the *cis*- and *trans*-2-butene ozonide mixture also produce two doublets at  $\delta$  1.40, they were too overlapped to be used for quantitative measurements.  $^1\text{H}$  NMR (room temperature, in  $\text{CDCl}_3$ ): ethylene ozonide  $\delta$  5.082; propylene ozonide,  $\delta$  1.424 (d,  $J$  = 4.90 Hz, 3 H), 5.038 (d,  $J$  = 0.46 Hz, 1 H), 5.178 (s, br, 1 H), 5.256 (q, 1 H); *cis*-2-butene ozonide  $\delta$  1.404 (d,  $J$  = 4.98 Hz, 3 H), 5.335 (q, 1 H); *trans*-2-butene ozonide  $\delta$  1.402 (d,  $J$  = 4.88 Hz, 3 H), 5.290 (q, 1 H).

**KSIE of  $\text{CH}_3\text{CH}=\text{CH}_2/\text{CH}_3\text{CD}=\text{CH}_2$  and  $\text{CH}_3\text{CH}=\text{CH}_2/\text{CH}_3\text{CH}=\text{CHD}$ .** A mixture of approximately 50% propylene- $d_0$  and 50% propylene- $d_1$  was prepared on a vacuum line and a portion saved for later analysis. The mixture was ozonized to 30% in isobutane at  $-78$  °C followed by distillation through  $-78$ ,  $-116$ , and  $-196$  °C traps. Ozonide was collected at  $-78$  °C, solvent at  $-116$  °C, and unreacted propylene at  $-196$  °C. The recovered and initial propylene as well as the ozonides were analyzed by 360-MHz NMR in  $\text{CDCl}_3$  at room temperature.

Propylene gives a complex spectrum with multiplets centered at  $\delta$  1.71, 4.93, 5.02, and 5.82. The peak at  $\delta$  5.82 arises from the methine hydrogen since its multiplicity appeared to be 16 and its intensity decreased with propene-2- $d_1$ . The peak at 4.93 could be assigned to the H trans to  $\text{CH}_3$  from the intensity change with (*E*)-propene-*l*- $d_1$ . Multiplet regions were integrated and simple relationships were used to extract the  $d_0/d_1$  ratios. For example, with mixtures of propene- $d_0$  and -2- $d_1$ , the resonances at 5.82 arise from the  $d_0$  species while the multiplets at either 4.93 or 5.02 can be used to determine the  $d_0$  and 2- $d_1$  sum. For mixtures of propene- $d_0$  and (*E*)-propene-*l*- $d_1$ , the resonances at 4.93 arise from the  $d_1$  species while either of the other two multiplets downfield determine the  $d_0$  and  $d_1$  sum. The relative intensities of the  $1_{01} \rightarrow 2_{02}$  and  $1_{10} \rightarrow 2_{11}$  microwave transitions of the normal and both deuterated species of propylene were also used to determine the  $d_0/d_1$  ratios.<sup>36,37</sup> These transitions are split into partially resolved doublets due to methyl tunneling effects so the intensity ratios were evaluated by cutting and weighing. Base-line problems are accentuated by this procedure and contribute to some of the data scatter. The  $d_0/d_1$  NMR analysis of the propylene ozonide was carried out in a manner similar to that of propylene. These data were used in relationships previously discussed to determine  $k_H/k_D$ .<sup>15</sup>

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**Registry No.**  $\text{D}_2$ , 7782-39-0;  $\text{CH}_3\text{CHO}$ , 75-07-0; propylene, 115-07-1; *cis*-2-butene, 590-18-1; *trans*-2-butene, 624-64-6; *trans*-2-pentene, 646-04-8.

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## Chemistry of Singlet Oxygen. 43. Quenching by Conjugated Olefins

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**Abstract:** The interaction of singlet oxygen with the olefins 2,5-dimethyl-2,4-hexadiene (DMHD) and 1-methyl-2-phenylindene (MPI) leads to both reaction and quenching. Although the initial interaction with singlet oxygen is nearly independent of solvent and temperature, the relative amount of quenching depends on solvent in the case of DMHD and on both solvent and temperature in the case of MPI. The increased reaction rate for indenenes at lower temperatures is caused by a decrease in the fraction of the initial interaction which leads to quenching. A similar factor governs the increase in DMHD rates in going from aprotic to protic solvents.

The interaction of  $^1\text{O}_2$  with organic substrates has been studied extensively.<sup>1-3</sup> It is known that three major paths are available

to  $^1\text{O}_2$  in solution, as shown in Scheme I.<sup>4</sup>

Two of the three paths in Scheme I are dependent on the