The conversion of $Re_2Cl_5(dppm)_2$ to $Re_2Cl_6(dppm)_2$ affords an unprecedented example of a one-electron oxidation of the Re_2^{5+} core (bond order 3.5) to Re_2^{6+} in which the metal–metal bond order is reduced rather than increased.

An important question that arises is why does $Re_2Cl_6(dppm)_2$ assume this chlorine-bridged structure rather than one in which all the Re–Cl bonds are terminal and the Re–Re bond is of order 4 (i.e., a $\sigma^2\pi^4\delta^2$ electronic configuration)? It is already known from the structure determination on $Re_2Cl_5(dppm)_2$[6] that the Re–Cl bond that occupies one of the coaxial positions on the metal atoms is a very long one and, hence, a weak one. Furthermore, ligand–ligand repulsions cause a quite dramatic contraction of the Cl–Re–Cl and P–Re–P angles (of the $ReCl_2P_2$ units) so that these coaxial sites are sterically congested. This may lead to an inherent instability of a structure in which a second axial Re–Cl bond has to be formed; consequently, the di-μ-chloro-bridged structure, in which all Re–Cl bonds are reasonably strong, results. Even though this structural change results in a decrease in the Re–Re bond order (from 4 to 2), this is more than compensated for (in a thermodynamic sense) by the formation of stronger Re–Cl bonds.

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Supplementary Material Available: Structure factor tables, tables of anisotropic thermal vibration parameters, complete lists of bond lengths and angles, and details of crystallographic work for all three structures (56 pages). Ordering information is given on any current masthead page.

Mechanism of the Ozonolysis of Ethylene–Acetaldehyde Mixtures

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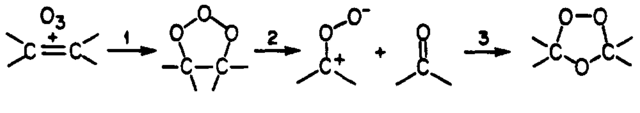
Abstract: Ethylene-*1,1*-d_2 was ozonized in the presence of acetaldehyde. The yields of ethylene ozonide-d_0, -d_2, and -d_4 and propylene ozonide-d_0 and -d_2 were determined by proton NMR, microwave spectroscopy, and manometric measurements. The ratio of propylene ozonide-d_0/propylene ozonide-d_2 decreased as the concentration of acetaldehyde increased. This indicates that an inverse kinetic secondary isotope effect is associated with the recombination reactions of the carbonyl oxide (Criegee intermediate). A kinetic model was employed to describe the Criegee reaction mechanism and to estimate the final product ratios. This model resulted in quantitative estimates of the KSIE for the carbonyl oxide, the relative dipolarophilicity of formaldehyde and acetaldehyde, and the cage effect upon primary ozonide decomposition. The inverse KSIE for the carbonyl oxide and formaldehyde in their recombination reaction is consistent with a concerted process.

The three step Criegee mechanism describes the formation of ozonides in solution.[1] This proposal (Scheme I) receives broad acceptance even though direct observation of the Criegee intermediate (**2**) is still lacking. In order to rationalize stereochemical results with substituted ethylenes, it has been postulated that the three reaction steps are a concerted cycloaddition, cycloreversion, and cycloaddition, respectively.[2] This leads to syn or anti isomerism in **2** followed by stereoselective recombination with the carbonyl compound in step 3. The evidence that step 1 is concerted is reasonably conclusive.[1,3,4] However, for steps 2 and 3, the evidence is more indirect and inferential since it is based on the observed stereochemistry in the final ozonide[2] (**3**) and on analysis of thermochemical[3] and ab initio reaction energetics.[5] Furthermore, some puzzling stereochemical results, solvent effects, and ozonide yields have resulted in suggestions that steps 2 and 3 may be nonconcerted at least for some conditions.[6]

Scheme I



1 2 3

One potential probe of concertedness in these steps employs deuterium kinetic secondary isotope effects (KSIE). An inverse KSIE ($k_H/k_D \approx 0.80$–0.95 at 25 °C) has been observed for a number of cycloaddition reactions where the carbons transform from sp^2 to sp^3 hybridization in the transition state.[7] Cycloaddition or reversion reactions which are nonconcerted and which

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Table I. Analysis of Products from Ozonolysis of 96% CH_2CD_2, 4% C_2H_3D, and CH_3OH in $CHClF_2$ at −78 °C

run	NMR intensity[a] CH_3	NMR intensity[a] CH_2OO, $CHDOO$[c] or CH_2O, $CHDO$[d]	$\frac{CH_2OO + CHDOO}{CH_2OO + CHDOO + CD_2OO}$	$\frac{CH_2O + CHDO}{CH_2O + CHDO + CD_2O}$	$\frac{CH_2OO^b}{CH_2OO + CD_2OO}$
			Species 1, 2, 3[e]		
1	3.000	1.006	0.503		0.493
2	3.000	1.000	0.500		0.490
3	3.000	1.058	0.529		0.519
			Species 4, 5, 6[e]		
1	3.000	1.052		0.526	0.484
2	3.000	1.030		0.515	0.495
3	3.000	0.980		0.490	0.520
					av 0.500 (15)

[a] ^1H, arbitrary units after integration. [b] Equivalent to $k_{a'}/(k_a + k_{a'})$ for 100% CH_2CD_2. Derived from columns 4 and 5 based on 4% CH_2CHD. [c] For species 1-3. [d] For species 4-6. [e] 1 = CH_3OCH_2OOH, 2 = $CH_3OCHDOOH$, 3 = CH_3OCD_2OOH, 4 = CH_3OCH_2OH, 5 = $CH_3OCHDOH$, 6 = CH_3OCD_2OH.

presumably lead to little rehybridization in the transition state at one of the carbon atoms or reactions such as styrene polymerization which develop a radical center at carbon have a normal or nearly normal KSIE ($k_H/k_D \approx 0.97$–1.20).[7d,8] Nevertheless, some apparently concerted reactions do not result in the expected inverse KSIE.[9] This indicates, along with the complex vibrational origin of the phenomena, that KSIE results must be used conditionally until they can be more fully supported by transition-state calculations or additional data.[10]

Recently, an inverse KSIE has been established for the carbon atom in formaldehyde in step 3.[7a] This result was based on data from ozonolysis of CHD=CHD in the presence of CH_2O/CD_2O. A preliminary communication[11] has reported that an inverse KSIE also can be associated with the carbonyl oxide (CH_2OO/CD_2OO) in step 3. These combined data argue that the cycloaddition between CH_2OO and CH_2O occurs with significant deformation about both nominally sp^2 carbon atoms in the transition state and is consistent with a concerted reaction. This paper elaborates on the analysis and kinetic calculations employed in the communication and extends the analysis to other conditions and products of the reaction.

An indirect approach had to be employed in order to investigate a KSIE for CH_2OO/CD_2OO since the carbonyl oxide is too reactive to follow by any spectroscopic methods. We decided to ozonize $CH_2{=}CD_2$ in the presence of CH_3CHO, which traps the carbonyl oxides. In order to interpret the results, a network of reactions involving the carbonyl oxides and their KSIEs had to be considered. They are illustrated in Scheme II.

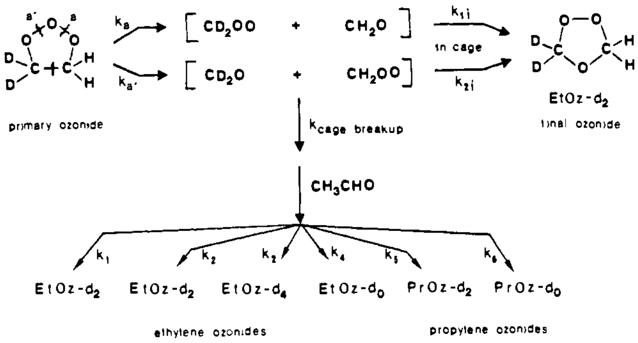
A computer program was written to model the unimolecular and bimolecular processes and to estimate final product ratios for comparison with the experimental results. This fitting was accomplished by trial and error through a systematic variation of input assumptions.

Results and Discussion

Ethylene-*1,1-d*$_2$. A strategy to evaluate a KSIE for the simplest carbonyl oxide, H_2COO/D_2COO, requires careful consideration of the alkene for ozonolysis, the reaction conditions, and the method of data analysis. The alkene chosen was $CH_2{=}CD_2$. Besides being an obvious source of H_2COO and D_2COO, this alkene minimizes complications from KSIEs associated with step 1 and step 2 of the Criegee mechanism.

Since the addition of ozone to ethylene is a concerted reaction,[1,3,4] the KSIE associated with the first step will not be a significant factor provided that the isotopic purity of the CH_2CD_2 sample is high. Analysis of the available material indicated that it contained only CH_2CD_2 and C_2H_3D in the proportions 0.958 (5)/0.042 (5). This was determined by microwave spectroscopy after oxidation of the ethylene to ethylene oxide. The C_2H_3D impurity leads to a small difference in the amounts of CH_2OO and CD_2OO produced during the reaction, which affects the amounts of deuteration in the propylene and ethylene ozonides. It is possible to estimate corrections for this contribution (~1%), and so results are reported on the basis of 100% CH_2CD_2 in subsequent tables unless otherwise noted.

Scheme II



CH_2CD_2–CH_3OH Ozonolyses. Ozonolysis reactions in the presence of methanol have been widely used to determine the direction of cleavage of unsymmetrical primary ozonides.[1] It has been argued that methanol quantitatively traps the carbonyl oxides to produce methoxymethyl hydroperoxides as opposed to a reaction between methanol and the primary ozonide.[1,12] This technique was employed to determine if a KSIE occurs upon decomposition of $\overline{CH_2OOOCD_2}$, leading to a preference for CH_2OO or CD_2OO.

Ozonolysis of CH_2CD_2–CH_3OH mixtures in $CHClF_2$ gave the expected products CH_3OCH_2OOH and CH_3OCD_2OOH as evidenced by the proton NMR spectrum.[13] CH_3OCH_2OH and CH_3OCD_2OH[13c] were also observed, indicative of a reaction between formaldehyde and methanol; trace amounts of acid may have catalyzed this reaction. These species were utilized to determine the CH_2OO/CD_2OO cleavage ratio. The data are presented in Table I. The average of six analyses corrected for 4% CH_2CHD in the mixture resulted in a value for this ratio of 0.500 (15). Therefore a KSIE in step 2 which might favor k_a or $k_{a'}$ is not readily evident.

Ethylene and Propylene Ozonide Yields. The ozonolyses of CH_2CD_2–CH_3CHO mixtures were run at −116 °C in $CHClF_2$. This temperature enhances any KSIE but is not low enough for formation of primary ozonide crystals. The solvent polarity assists

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Table II. Relative Yields and Deuterium Content of Ethylene Ozonide and Propylene Ozonide from Ozonolysis of CH_2CD_2-Acetaldehyde Mixtures, Experimental[a] and Calculated Values[b]

$[CH_3CHO]_0$, M	anal[c]	PrOz[d]/(PrOz + EtOz)	PrOz-d_0/(PrOz-d_0 + PrOz-d_2)	EtOz-d_0/(EtOz-d_0 + EtOz-d_2)	EtOz-d_4/(EtOz-d_0 + EtOz-d_2)
			Experimental		
0.1	NMR (3)	11.0 ± 0.5	51.6 ± 0.5[e]	28.1 ± 1.2	26.6 ± 2.2
	MW (1)			26.5 ± 2.2	
0.25	NMR (3)	15.5 ± 3.0	49.7 ± 0.7	24.5 ± 0.5	
0.5	NMR (3)	18.0 ± 2.0	48.0 ± 1.0		
	MW (1)			26.4 ± 2.1	29.4 ± 2.1
1.0	NMR (3)	24.2 ± 5.0	46.3 ± 0.5	22.9 ± 1.1	
3.0	NMR (4)	40.0 ± 10.0	42.5 ± 1.5	21.3 ± 1.5	
	MW (1)			20.9 ± 2.2	23.4 ± 2.0
			Calculated		
0.1		5.8	51.3	27.6	30.5
0.25		11.4	48.9	26.3	30.7
0.5		18.4	47.4	25.0	30.5
1.0		28.1	46.6	23.3	29.5
3.0		48.1	46.6	19.8	25.2

[a] $[CH_2CD_2] \approx 2$ M. $O_3/CH_2CD_2 \approx 0.35$, $T = -116$ °C, $CHClF_2$ solvent. Yield ratios multiplied by 100. [b] Calculated by using network in Scheme II and relative rate constants discussed in text. [c] Proton NMR or microwave relative intensity measurements. The number in parentheses is the number of reactions analyzed to compute the average. [d] PrOz = PrOz-d_0 + PrOz-d_2; EtOz = EtOz-d_0 + EtOz-d_4. [e] A reevaluation of the 0.1 M data has led to a lower value (−1.1%) than previously reported.[11]

the breakup of the initial solvent cage containing the carbonyl oxide and encourages its competitive reaction with the available aldehydes.[7a] The amounts of ethylene and propylene ozonides which are produced as well as their relative deuterium content are the experimental data from which any KSIE must be extracted.

Column 3 of Table II illustrates the dependence of the relative amounts of PrOz and EtOz on acetaldehyde concentration $[CH_3CHO]_0$. As expected, the ratio PrOz/(PrOz + EtOz) increases with added acetaldehyde. These ratios were determined from analysis of the proton NMR spectra of the ozonide mixture after separation from the solvent. Since the nominal singlet from EtOz arises from the d_0, d_2, and d_4 species, its intensity was normalized for two hydrogens per EtOz. This approximation introduces no substantive error since the amounts of EtOz-d_0 and -d_4 were close to equal (see below). The total yields of EtOz and PrOz based on input O_3 were also determined for several reactions and varied between 70 and 85%.

The relative amounts of PrOz-d_0 and PrOz-d_2 are also given in column 4 of Table II. The ratio PrOz-d_0/(PrOz-d_0 + PrOz-d_2) was determined by proton NMR and shows a systematic variation. In the absence of a KSIE for the carbonyl oxide, the relative amounts of CH_2OO–CD_2OO available for reaction with CH_3CHO should be constant, and no variation in the d_2 content of PrOz should result. On the other hand, a variation can be rationalized by an inverse KSIE for reactions of the carbonyl oxide with H_2CO and CH_3CHO. As the $[CH_3CHO]_0$ is changed, the various competitions for H_2COO and D_2COO alter their relative amounts, which would affect the yields of PrOz-d_0 and -d_2. This aspect will be explored more quantitatively in the next section.

The amounts of EtOz-d_0, -d_2, and -d_4 should also show a variation since they are coupled to the propylene ozonide yields through the carbonyl oxides. Their relative amounts are given in the last two columns of Table II. The ratio EtOz-d_0/(EtOz-d_0 + EtOz-d_2) could be estimated by proton NMR since a small deuterium isotope shift led to partial resolution of their nominal singlet resonances.[14] Microwave spectroscopy was also employed to estimate relative amounts of the three species. While the results are not very precise, they do indicate certain trends. The ratio EtOz-d_0/(EtOz-d_0 + EtOz-d_2) decreases with $[CH_3CHO]_0$ and there is an indication that the amount of EtOz-d_4 is about 15% larger than EtOz-d_0 when $[CH_3CHO]_0 \geq 0.5$ M. An intuitive interpretation of such trends is difficult without a more systematic analysis using Scheme II. This will be explored next.

Kinetic Scheme. In order to confirm that an inverse KSIE for the carbonyl oxide was the origin of the trends in column 4 of Table II and to estimate its value, a computer algorithm was developed to describe Scheme II. Input to the calculation included the initial concentrations of the primary ozonide and CH_3CHO and relative values for the rate constants. A multiplicative relationship was employed to identify a characteristic reactivity for H_2COO, H_2CO, CH_3CHO, and the deuterated species. Thus, $k_{1i} = k_1 = k_{CD_2OO}k_{CH_2O}$, etc. In this way, KSIEs and the dipolarophilicity difference between CH_3CHO and CH_2O could be separated.[16] The ozonide yields were then numerically calculated as the concentrations slowly changed for each iteration (typically ≤0.1%) until the carbonyl oxides were depleted. The algorithm contained several nested loops so that a systematic variation for many possible combinations of acetaldehyde concentrations and rate constants could be explored. More details on the calculation and assumptions are given in the Experimental Section and in the supplementary material.

The calculated results listed in Table II were selected as a typical example which reflected the correct qualitative variation in all the yield ratios (columns 3–6) and the kind of quantitative agreement that could be obtained in the best cases. From examination of this result and other credible calculations of similar quality, the data were deemed consistent with the following rate constant assumptions. (1) $k_{CH_2OO}/k_{CD_2OO} = 0.75 \pm 0.10$ in reactions with formaldehyde and 0.65 ± 0.10 for reactions with acetaldehyde.[17] These inverse KSIEs were necessary to reproduce the variation of the d_2 content in PrOz (column 4). The absence of a KSIE led to no variation in the d_2 content while a normal isotope effect gave the wrong slope. (2) The KSIE for H_2CO/D_2CO was 0.75 ± 0.10. This is nominally identical with the value previously reported for the recombination of H_2CO/D_2CO with the carbonyl oxide[7a] (0.80 (2) at −116 °C in CF_2BrH). (3) The relative reactivities (dipolarophilicities) of H_2CO and CH_3CHO were 5 (1):1. This is compatible with a previous analysis which

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(14) Upfield chemical shifts in the range of 10^{-2}–10^{-3} ppm due to deuterium in proton spectra are well documented for data obtained with high-field instruments.[15]

(15) Batiz-Hernandez, H.; Bernheim, R. A. *Prog. Nucl. Magn. Reson. Spectrosc.* **1967**, *3*, 63.

(16) This approximation divides a reaction into separate free energy components. Thus, $\Delta G^{\ddagger}_{k_1} = \Delta G^{\ddagger}(CD_2OO) + \Delta G^{\ddagger}(CH_2O)$. Furthermore, $\Delta\Delta G^{\ddagger}_{k_4-k_1} = \Delta G^{\ddagger}(CH_2OO) - \Delta G^{\ddagger}(CD_2OO) = -RT \ln (k_H/k_D)$. It will be less useful when vibrational coupling in the transition state diminishes the transferability of energy components between reactions.

(17) In this paper, although all experimental KSIEs involve double deuterium substitution at carbon, the KSIE ratios discussed quantitatively will always refer to a per deuterium basis at the reaction temperature of −116 °C. The conversion is $(k_{CH_2O}/k_{CD_2O})_{perD_2}{}^{1/2} = (k_{CH_2O}/k_{CD_2O})_{perD}$. It was felt that this would facilitate comparison with literature data. This approximation has a similar basis to that discussed in the previous footnote. The cumulative behavior of KSIEs upon successive deuteration appears to hold well for many systems. For Example: Shiner, F. J., Jr.; Murr, B. L.; Heinemann, G. *J. Am. Chem. Soc.* **1963**, *85*, 2413.

found that a 10-fold higher reactivity with $H_2CO + H_2COO$ compared to $CH_3CHO + CH_3CHOO$ could account for the high EtOz and low butene cross ozonide yields upon ozonolysis of propene.[4] Assuming a multiplicative relationship, this implies that H_2COO is about twice as reactive relative to CH_3CHOO. (4) The amount of EtOz formed in the initial solvent cage relative to total EtOz plus PrOz formed after breakup of this cage (out of cage) was 15 ± 5%. This also agrees with the amounts of EtOz-d_0, -d_2, and -d_4 from C_2H_4–C_2D_4 mixtures[7a] based on a similar ratio for the in cage vs. out of cage ozonide production.[18]

The kinetic calculations provide respectable agreement with much of the ozonide yield data and relative deuterium content in the products. The implication is that the Criegee network in Scheme II can accommodate the general trends in the distribution of reaction products with changes in $[CH_3CHO]_0$. Nevertheless, the reaction is a complex process and not all reaction details could be fit over the full range of conditions, indicating some limitations in the model and/or the experimental data. The most glaring and perplexing failures are the underestimation of the overall yields of PrOz at $[CH_3CHO]_0 \leq 0.5$ M and overestimation of the PrOz-d_2 at $[CH_3CHO]_0 = 3$ M.

Obviously, the neglect in Scheme II of about 20% of the products (uncharacterized residues) is a deficiency of the model. The presumption is that they are formed with KSIEs and reaction rates that do not greatly perturb relative concentrations and yield predictions. Scheme II might also include a cage equilibrium process. Absence of this equilibrium probably is not a serious deficiency if the breakup of the initial cage is fast compared to reestablishing a cage containing reaction partners. The calculations also presumed that the cleavage of the primary ozonide produced a 50/50 mixture of CH_2OO/CD_2OO. It was noted that better agreement with the calculated values of PrOz-d_0/(PrOz-d_0 + PrOz-d_2) for high acetaldehyde concentrations could be obtained by lowering the ratio of CH_2OO/CD_2OO. In fact, a cleavage ratio of 48/52 could lead to close agreement at $[CH_3CHO]_0 = 3$ M. However, the calculated values of PrOz-d_0/(PrOz-d_0 + PrOz-d_2) at the other concentrations of CH_3CHO also were about 3% lower and much less acceptable. It would be possible to alter the algorithm to explore some of these complications. However, at this stage it does not seem rewarding to add further assumptions and complexity to the scheme. Already, seven rate constant assumptions are employed to fit six reaction observations,[19] and questions of uniqueness can be raised.

In summary, the present evidence for the inverse KSIE for the carbonyl oxide appears compelling. This is principally indicated by the variation of the PrOz deuterium content with $[CH_3CHO]_0$. (A qualitative interpretation for this variation, apart from model calculations, has been given elsewhere.)[11] Along with the inverse KSIE for formaldehyde,[7a] this evidence argues that both carbon atoms are appreciably perturbed in the transition state in step 3 of the Criegee mechanism, as expected for a concerted reaction. Of course, this is one of the simplest ozonolysis reactions, and extrapolation of such an inference to more complex alkenes where yield anomalies, etc., are known is tenuous. The possibility that step 3 could occur with an inverse KSIE at both carbon atoms and still be nonconcerted can also not be completely ruled out given what little is known about reaction properties of the elusive carbonyl oxide. On this matter, exploration of the magnitude of the KSIEs based on transition-state calculations would be helpful.

Experimental Section

^1H NMR data were obtained with a Brüker 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. Ethylene-*1,1*-d_2 (98 atom % D) was purchased from Merck Co. Acetaldehyde (MCB) and $CHClF_2$(F22, Pennwalt) were dried by passage through cold traps. Methanol (MCB) was dried by adding small amounts of magnesium several hours before use. CP grade $ClC_6H_4CO_3H$ (Aldrich) and 1,4-dioxane (MCB) were used.

General Ozonolysis Procedure. Reactants were mixed in the gas phase before condensation into a reaction vessel. Reactions were conducted with flow rates of 0.1–0.2 mmol of O_3/min using standard techniques.[7a] After reaction, a fast warm-up procedure was employed.[3a] The reaction mixture was then vacuum-distilled through traps held at −78 °C and −196 °C. This separated the ozonide products and most of the acetaldehyde from the solvent and unreacted ethylene.

Deuterium Enrichment in $CH_2{=}CD_2$. $CH_2{=}CD_2$ (1.2 mmol) was oxidized by 1.2 mmol of chloroperoxybenzoic acid in 2 mL of dioxane to produce ethylene oxide (ETO),[20] which was analyzed by microwave spectroscopy.[21,22] The major impurity was found to be ETO-d_1. The relative intensities of the $2_{12} \rightarrow 2_{21}$, $3_{03} \rightarrow 3_{12}$, $3_{21} \rightarrow 3_{30}$, and $5_{23} \rightarrow 5_{32}$ rotational transitions were compared, and ETO-d_1 = 4.2 (5)%, ETO-*1,1*-d_2 = 95.8 (5)% were determined. The amounts of d_0 and the other deuterated species were negligible (≤0.5%).

The effect of 4.2% C_2H_3D in the analysis of the deuteration in ethylene and propylene ozonides can be taken into account by model calculations that neglect KSIEs in the production and reactions of CH_2OO and CD_2OO. An observed ratio for PrOz-d_0/PrOz-d_2 = 40/60 would upon correction to a 100% CH_2CD_2 basis become respectively 38.8/61.2; similarly 50/50 (obsd) = 49.0/51.0 (cor) and 60/40 (obsd) = 59.2/40.8 (cor).

$CH_2{=}CD_2/CH_3OH$ Ozonolysis. Experiments were done with 0.6–0.9 mmol of $CH_2{=}CD_2$, 4.5 mmol of dry methanol, 14.0–19.0 mmol of solvent ($CHClF_2$), and 0.3 mmol of ozone. The reaction temperature was −78 °C since a lower temperature would freeze methanol. This reaction produced methoxymethyl hydroperoxide and formaldehyde hemiacetal (CH_3OCH_2OH), which were isolated in a −78 °C trap after vacuum distillation. The identification of these products was from their proton NMR spectra.[13] ^1H NMR (room temperature in $CDCl_3$, reference $CHCl_3$(7.247 ppm)): CH_3OCH_2OOH δ 3.429 (s, 3 H), 4.887 (s, 2 H), CH_3OCH_2OH δ 3.371(s, 3 H), 4.671(s, 2 H). The hydroxyl proton resonances were usually broadened and not observed. The CH_3OCH_2OH assignment was confirmed by adding small amounts of HCl to a methanol and formalin solution.[23]

Relative amounts of the normal and deuterated compounds were calculated by comparing the intensity of the methyl and the methylene group (Table I). For example, with the mixture of CH_3OCH_2OOH and CH_3OCD_2OOH, the resonance at 4.89 ppm arises only from the normal species while both species contribute to the peak at 3.43 ppm. Actually, $CH_3OCHDOOH$, from the C_2H_3D impurity, also contributes to these peaks, and this is noted in columns 4 and 5 of Table I. Its contributions are subtracted to arrive at column 6.

Ozonolysis of $CH_2{=}CD_2$ with CH_3CHO. Typical runs employed 2 mmol of $CH_2{=}CD_2$, 0.1–3.0 mmol of acetaldehyde, 15–20 mmol of $CHClF_2$,[24] and 0.6–0.8 mmol of ozone at −116 °C. The final ozonides (Scheme II) were collected at −78 °C and analyzed by proton NMR and microwave spectroscopy. The assignments of the NMR spectra of the undeuterated ozonides are discussed elsewhere.[7b] The proton spectra around δ 5 of the deuterated species are (room temperature in $CDCl_3$) ethylene ozonide-*1,1*-d_2 (EtOz-d_2) δ 5.079 (s, 2 H, 0.0026 ppm upfield from EtOz-d_0), propylene ozonide-*1,1*-d_2(PrOz-d_2) δ 5.254 (q, 1 H, 0.0023 ppm upfield from PrOz-d_0). The relative amounts of PrOz-d_0 and -d_2 were determined by comparison of the methine (5.26 ppm) and methylene (5.178 ppm) peaks since the former arises from both species while the latter arises from PrOz-d_0 only. EtOz-d_0 and EtOz-d_2 were determined from the peaks at δ 5.082 (4 H) and 5.079 (2 H) by using resolution enhancement techniques which reduced the valley to between 5 and 25% of the full peak intensities.

The determination of the species ratios was usually repeated on subsequent days. The results are therefore averages from the several measurements on three or four reaction runs, and the uncertainty encompasses the measurement range. In order to test the reliability of the NMR method, two ozonolyses of mixtures of $CH_3CD{=}CH_2$ and C_3H_6 at −78 °C in isobutane were analyzed by NMR and MW spectroscopy.

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[18] For this reaction mixture the model included the known KSIE in the first step.[7a] It was not very sensitive to the KSIE in the third step and assumed no KSIE in the second step. An essentially exact match to the experimental data was obtained for 16.8% in-cage ozonide formation.

[19] The seven assumptions are essentially the rate of primary ozonide decomposition and cleavage direction, three KSIE ratios, the cage breakup rate, and the aldehyde dipolarophilicity ratio. The reaction observations are the methanol trapping yields and the yields of five ozonides. The predicted yields depend only weakly on the rate of primary ozonide decomposition.

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[24] The solvent was inadvertently labeled $CHCl_2F$ in the preliminary report.[11]

One reaction gave 60.0/40.0 for PrOz-d_0–/PrOz-d_1 by NMR and 60.4/39.6 from microwave (MW) transitions. The second reaction gave 46.3/53.7 by NMR and 46.2/53.8 by MW. Five MW transitions[2c] were used; the precision of the MW and NMR ratios were similar.

MW spectroscopy was employed to determine the relative amounts of EtOz-d_0, -d_2, and -d_4. The intensities of five microwave transitions ($10_{6,4} \rightarrow 10_{7,3}$ and $13_{11,3} \rightarrow 13_{12,2}$ for EtOz-d_0; $13_{9,4} \rightarrow 13_{10,3}$ and $14_{10,4} \rightarrow 14_{11,3}$ for EtOz-d_2; $13_{8,5} \rightarrow 13_{9,4}$ for EtOz-d_4) were used following procedures previously worked out.[7a] Because of the spectral complexity and the slow decomposition of EtOz in the MW cell, the uncertainties cannot be further reduced without considerable effort.

Overall yields were determined by manometric methods. In order to remove most of the acetaldehyde from the ozonides, the mixture was distilled from a −78 °C trap for ~1 h. The NMR indicated that the acetaldehyde was reduced to about 5% or less. Some ozonide may also have been lost during the long distillation, but their overall yields still ranged from 70% to 85%. No systematic differences were evident between runs at low and high acetaldehyde concentrations.

One of the parameters difficult to evaluate precisely is the actual acetaldehyde concentration during the ozonolysis. The initial amount added to the reaction was determined by a pressure measurement assuming only the monomer in the gas phase.[25] However, trimer formation is favored at the reaction temperature if the data for liquid CH_3CHO can be extrapolated to these conditions.[25] Nevertheless, it appears that the rate of trimer formation may be slow since the acetaldehyde exhibits monomer behavior under reaction conditions and incorporates extensively into the ozonide. Until this ambiguity can be better resolved, the reported acetaldehyde concentrations are considered upper limits and ignore any trimerization. In terms of the kinetic analysis, this implies that the dipolarophilicity of the CH_3CHO may be underestimated.

Computer Analysis. The algorithm for Scheme II used Euler's[26] method to approximate the solutions to the differential equations. It was written in Fortran-77 for a PDP-11/23 system. A calculation of yields for a single set of assumptions typically took 2 min. Some iterations, such as testing various combinations of KSIEs, consisted of several hundred calculations. A flow diagram and listing of the program as well as some additional calculations and examples of rate constants are available as supplementary material.

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Supplementary Material Available: Nine examples of rate constant assumptions (Table 1S) and calculated yields (Table 2S) and flow diagram and listing for the Fortran program, called KINET, predicting the product yields (15 pages). Ordering information is given on any current masthead page.

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Perchlorate Esters. 7.[1] Solvolysis of 2-Adamantyl Perchlorate: Rate and Product Studies

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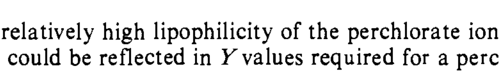
Abstract: The solvolysis of 2-adamantyl perchlorate proceeds at a convenient rate at temperatures close to ambient in a wide variety of pure and aqueous organic solvents. The nucleofugality of the perchlorate ion in S_N1 reactions is shown to be several orders of magnitude higher than for more conventional leaving groups, such as *p*-toluenesulfonate or bromide. Entropies of activation in pure organic solvents and in 80% ethanol are unusually high. Grunwald-Winstein plots are markedly curved, with deviations being especially marked for aqueous-acetone and aqueous-2,2,2-trifluoroethanol mixtures. A scale of Y_{OClO_3} values is developed and compared with scales for a variety of other leaving groups. In aqueous ethanol there is a preference for product formation by interaction with water molecules by a factor of ca. 1.7, essentially independent of solvent composition (96–50% ethanol) and temperature.

It has recently been reported that both methyl perchlorate[2] and 2-adamantyl perchlorate[3] can exhibit maxima in Grunwald–Winstein plots (eq 1) of log k against Y. In eq 1, k and k_0

$$\log (k/k_0) = mY \qquad (1)$$

represent the specific rates of solvolysis in the solvent under consideration and in the standard solvent (80% ethanol), Y represents the solvent ionizing power of the solvent under consideration, and m represents the sensitivity of the substrate to changes in solvent ionizing power.

The observation of a shallow maximum and an almost constant specific rate of solvolysis over the full range of composition of methanol–acetone mixtures for 2-adamantyl perchlorate[3] parallels the results of Luton and Whiting[4] for the solvolysis of 1-adamantyl picrate in methanol-tetramethylene sulfone mixtures. The perchlorate ion has a lipophilicity lower than picrate ion but higher than more familiar nucleofuges, such as *p*-toluenesulfonate (tosylate), bromide, and chloride ions, and one aim of the present investigation is to see, for several organic and aqueous organic systems, to what extent S_N1 solvolysis of perchlorate esters, such as 2-adamantyl (eq 2), shows unusual effects which can be related



(2)

to the relatively high lipophilicity of the perchlorate ion. Such effects could be reflected in Y values required for a perchlorate

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