Table II. Calculated Orbital Energies of 1, 3, and 4

compd	−ε(ZDO)	−ε(MINDO/3)
1	(7.14 (n))	7.81 (a_2, π)
	7.39 (π)	8.01 (b_1, n_-)
	8.17 (π)	8.54 (b_2, π)
	8.57 (π)	8.75 (a_2, π)
	(9.34 (n))	8.88 (a_1, n_+)
	9.60 (π)	9.73 (b_2, π)
3	7.42 (π)	7.83 (π)
	8.09 (π)	8.43 (π)
	8.63 (n)	8.86 (π)
	9.41 (π)	9.03 (n)
	9.88 (π)	9.76 (π)
4	7.62 (π)	7.71 (π)
	8.41 (π)	8.43 (π)
	8.92 (π)	8.92 (π)
	9.78 (π)	9.72 (π)
	11.36 (π)	9.86 (π)

and for the amino group −10.6 eV.[6] Assuming a rotation of 40° around the CN bond in 3 and 0° in 4, we obtain the values shown in Table II. The agreement between experiment and ZDO calculation is fairly good. Our assignment given in Table I is based on the ZDO results.

b. Semiempirical Calculations. To derive the orbital sequence in 1, 3, and 4 by semiempirical methods we have used the MINDO/3 model.[7] For 4 we minimized all geometrical parameters with respect to the heat of formation. In the case of 1 and 3 the distances and angles for the fluorene skeleton were minimized as for 4 while for the dimethylamino groups in 1 and for the dimethylamino group in 3 we assumed a rotation of 90° and 40° out of the π-plane, respectively. The energy levels obtained are listed in Table II.

In the case of 3 and 4 the agreement between the results of the ZDO calculations and of the semiempirical calculations is good. For 1, however, the large split between the two lone-pair combinations, n_+ and n_-, as predicted by the ZDO model is not reproduced satisfactorily by the MINDO/3 method. The energies of the π-orbitals on the other hand are predicted by MINDO/3 close to those obtained by the ZDO model. We ascribe this discrepancy due to our assumed geometry of the dimethylamino groups.

Experimental Section

Compounds 3 and 4 were prepared according to the literature.[8] The synthesis of 1 has been reported recently.[1]

The PE spectra of the pure samples were recorded on a Perkin-Elmer PS 18 and a Leybold Heraeus UPG 200 photoelectron spectrometer equipped with a He(I) light source. The spectra were recorded at 73 °C (1), 58 °C (3), and 105 °C (4). The calibration has been carried out with Ar and Xe. A resolution of ±0.04 eV was achieved for the single bands and of ±0.1 eV for the shoulders.

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Registry No. 1, 86943-85-3; 3, 92013-89-3; 4, 7083-63-8.

Supplementary Material Available: A listing of the calculated or assumed geometrical parameters for 1, 3, and 4 (2 pages). Ordering information is given on any current masthead page.

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High-Field Rapid Injection NMR: Observation of Unstable Primary Ozonide Intermediates[1]

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A "rapid injection" NMR system is described for use on a 360-MHz superconducting spectrometer. The major advantages of the high-field system over our original system are increased sensitivity, resolution, and rapidity. The technique was used to study the ozonolysis of tetramethylethylene and (briefly) *cis*-but-2-ene, particularly the decomposition of the corresponding primary ozonides 2 and 4, with half-lives of 0.74 and 0.06 s, respectively, at −92 °C. It was found that the decomposition of 2 in CD_2Cl_2 (a) had $\Delta H^{\ddagger} = 39$ kJ/mol and $\Delta S^{\ddagger} = 28$ J/(mol K), (b) was unaffected by the presence of TCNE, but (c) was acid-catalyzed. The effects of substituents, solvent, and acid catalysts on the decomposition of primary ozonides are discussed.

Introduction

We have recently described the rapid injection NMR (RINMR) technique for the observation (at 60 MHz), of short-lived organic intermediates.[2] As a kinetic application we have measured the hydrolysis rates of very reactive methylating agents.[3] The RINMR method involves injection of a small volume (typically 10–15 μL) of a premagnetized reagent solution into a standard volume (300 μL) of a substrate solution already spinning in the NMR probe. The computer acquisition system is automatically triggered by the injection. The advantages of this con-

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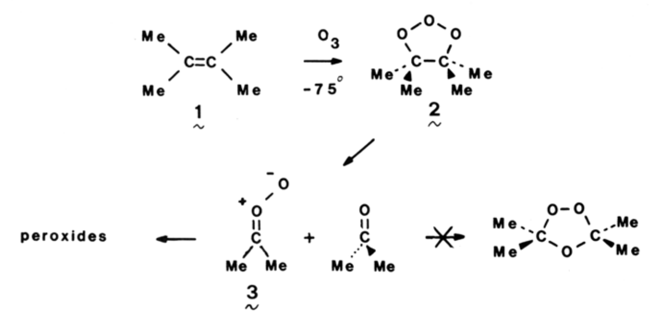
Scheme I



ceptually simple system over conventional stopped-flow[4] and continuous-flow[5] NMR techniques have been discussed.[2]

A further advantage of our simple approach is that extension to use with a high-field superconducting spectrometer is feasible. We now describe the construction of a RINMR system for a Bruker WH 360 spectrometer. Differing aspects of the system's performance at low temperature are illustrated by a study of the reaction between tetramethylethylene and ozone under a variety of conditions. The formation of carbonyl oxides as intermediates during the ozonolysis of olefins has been well established by a variety of experiments,[6,7] however attempts to detect and characterize them directly have so far been unsuccessful. An example of this class of compound that should be well suited for observation is acetone oxide **3**, formed by the ozonolysis of tetramethylethylene Scheme I. The initial attack of ozone to form the primary ozonide **2** is extremely rapid ($k_2 = 2 \times 10^5$ M^{-1} s^{-1} at 25 °C),[8] and furthermore the normal ozonide product is not formed,[9] presumably because acetone is not sufficiently reactive to trap **3** efficiently. We felt that this reaction sequence, and specifically the decomposition of **2** by a 1,3-dipolar cycloreversion reaction, could be fruitfully studied at low temperature by use of RINMR.

Experimental Section

Description of Apparatus. The solution to be injected is held in a Hamilton Gas Tight 1750 syringe A attached via a Kel F coupling to an injection capillary B (Wilmad Glass Company no. 800). The end of the capillary is fitted with a Kel F sheath perforated with three pores of diameter 0.3 mm (central), 0.2 mm, and 0.2 mm (lateral); this end piece is much less delicate and easier to machine than the glass sphere in our original system. The syringe is bedded in an Aluminium housing C, and its piston is attached via a brass clasp and Berylco rod D to a brass pneumatically driven piston E (Festo) operating at 800 kPa pressure. The course of the piston is set by a micrometer screw F calibrated in units corresponding to injections of 1 μL. Activation of E triggers the computer activation sequence by cutting a beam to a photoelectric cell G. Rotation of the sample is controlled by adjustment of the vent aperture H. The injection insert passes through a cylindrical brass block I, whose function is primarily shock absorption, and is supported by a screw J which allows height adjustment. The block I is supported above the magnet housing on a platform K. The horizontal planarity and centering of the platform are adjusted by screws at the ball socket on top of each of three supporting legs. (Alternatively the support block can be placed directly on the magnet housing if a Teflon disk 1 cm thick is provided as insulation.)

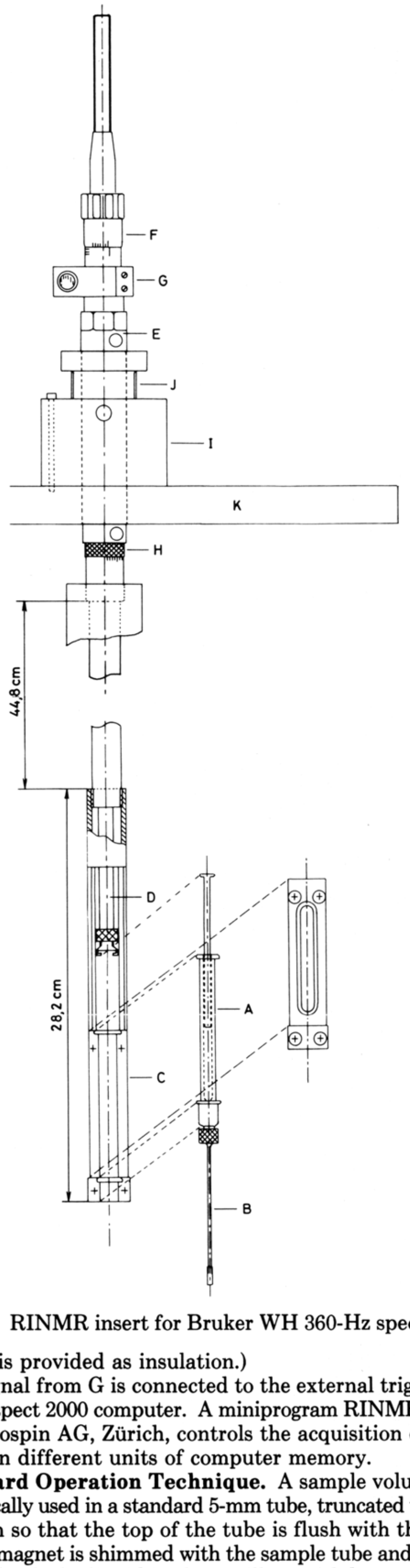


Figure 1. RINMR insert for Bruker WH 360-Hz spectrometer.

The signal from G is connected to the external trigger of the Bruker Aspect 2000 computer. A miniprogram RINMR supplied by Spectrospin AG, Zürich, controls the acquisition of a series of FIDs on different units of computer memory.

Standard Operation Technique. A sample volume of 300 μL is typically used in a standard 5-mm tube, truncated to a length of 11.0 cm so that the top of the tube is flush with the spinner top. The magnet is shimmed with the sample tube and the insert installed (with the liquid in the capillary withdrawn slightly to prevent diffusion). The spinning rate is adjusted at this time. The insert is then withdrawn, the capillary tip dried, and the liquid pushed down to completely fill the capillary. It is most important that there be no air bubble in the capillary tip as the field homogeneity is critically sensitive to the injection of bubbles. The volume to be injected is selected, and the computer acquisition sequence is activated, before the insert is replaced in the magnet. Injection should be carried out as soon as possible after insertion to reduce the risk of diffusion. The high sample spinning rate that we use with the WH 360 promotes diffusion out of the central

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pore of the capillary end, on the other hand, the close proximity of the pores limits this effect. After 10 s at a rotation rate of 17 s^{-1}, 1.8 μL had diffused, after an interval of 20 s this increased to 4 μL. In low temperature experiments one cannot preequilibrate the temperature in the capillary before introduction into the sample, as the cooling of the insert leads to contraction of the liquid in the syringe. The insert must be lowered as rapidly as possible and a (slight) uncertainty in the reaction temperature must be tolerated. Each low temperature was measured by using a CH_3OH sample, as the RINMR insert was found to substantially modify the relation between the real temperature and that indicated by the Bruker temperature controller.

Ozonolysis of Tetramethylethylene. Ozone solutions were prepared in acetone-d_6 and dichloromethane-d_2 by bubbling for 15 min a stream of ozone (3.5% in oxygen), previously dried by passage through two gas traps at −78 °C, through the solvents at −100 °C. These solutions initially contained 20–30 mM ozone, measured by adding an excess of tetramethylethylene and then comparing its NMR signal to a $CHCl_3$ standard, but this concentration diminished to 10 mM during storage at −95 °C for 3 h. The ozone solution, 300 μL, was transferred to a NMR tube, dried, and cooled to −95 °C under argon via a syringe previously dried and cooled to −80 °C. The tube was rapidly wiped off and placed in the cooled spectrometer probe. When another reagent, e.g., TCNE, was used, it was introduced in solution into the NMR tube before cooling and addition of the requisite quantity of ozone solution. Under standard conditions 10 μL of a solution of **1**, 150 mM, was injected into a solution 20 mM in ozone (300 μL) to give a final concentration of 4.8 mM.

For kinetic runs the concentrations of the various species were estimated by enlarging the peaks and weighing their cut outs. We recommend this admittedly tedious procedure in cases where the reactant peaks partially overlap with product peaks, particularly toward the end of a reaction. For experiments in CD_2Cl_2 the concentration of the product acetone was also measured and used to express the concentration of **2** as a fraction of the total. In each kinetic experiment the data were collected from at least three injections and for each injection normally 16 spectra were stored.

No attempt was made to identify all of the complex peroxide products[9] of the ozonolysis without added reagents. Acetone oxide dimer could be identified in the product mixture ($\simeq$15% yield) by comparison of the NMR spectrum with that of the authentic product (mp 130.5–131.5 °C), ^{1}H 1.37 (s, Me ax), 1.78 (s, Me eq at −90°), prepared according to Criegee.[9] The addition of TCNE (3.48×10^{-2} M) increased the yield of acetone by 80% (NMR estimation) whereas the peroxide product peaks at δ 1.40–1.63 disappeared into the baseline noise. The ozonolysis of **1** (142 mg, 1.68 mmol) in the presence of acetic acid (101 mg, 1.68 mmol) in CD_2Cl_2 at −80 °C by the conventional passage of ozone gas, led to acetone and only one other product (NMR estimation), presumed to be 2-hydroperoxy-2-propyl acetate (**5**): ^{1}H 1.64 (s, 6 H), 2.06 (s, 3 H), 11.30 (s, 1 H); ^{13}C 21.22 (q, ^1J = 130 Hz), 21.46 (q, ^1J = 129 Hz), 108 (bs), 170 (q, ^2J = 6.4 Hz).

Attempts to isolate this product at room temperature by washing with dilute $NaHCO_3$ and water, drying ($MgSO_4$), evaporating, and recrystallizing at −20 °C from methanol led to acetone oxide trimer (3,3,6,6,9,9-hexamethyl-1,2,4,5,7,8-hexaoxacyclononane): 87 mg, 69%; mp 95–96 °C (lit.[9] 90–93 °C); IR (CCl_4) 3010 m, 2955 m, 1465 m, 1380 s, 1358 s, 1232 m, 1200 s, 1180 s, 940 m, 880 s; ^{1}H NMR 1.46 (s); MS 117 (4), 101 (3), 75 (35), 59 (56), 58 (100), 57 (36).

The intermediate formed from **2** in the presence of trifluoroacetic acid, presumably 2-hydroperoxy-2-propyl trifluoroacetate (**6**), ^{1}H 1.80 (CH_3, the OH proton was indistinguishable from the excess acid proton), could not be isolated as it decomposed rapidly to acetone oxide dimer (3,3,6,6-tetramethyl-1,2,4,5-tetroxane) even at −80 °C.

Results and Discussion

Scope and Limitations of the Method. The operating principle of the RINMR method at 60 MHz has been fully discussed already,[2] and a description of the high-field insert is given in the Experimental Section. The following are the improvements in performance due to use of both a more powerful magnet and increased computer capacity.

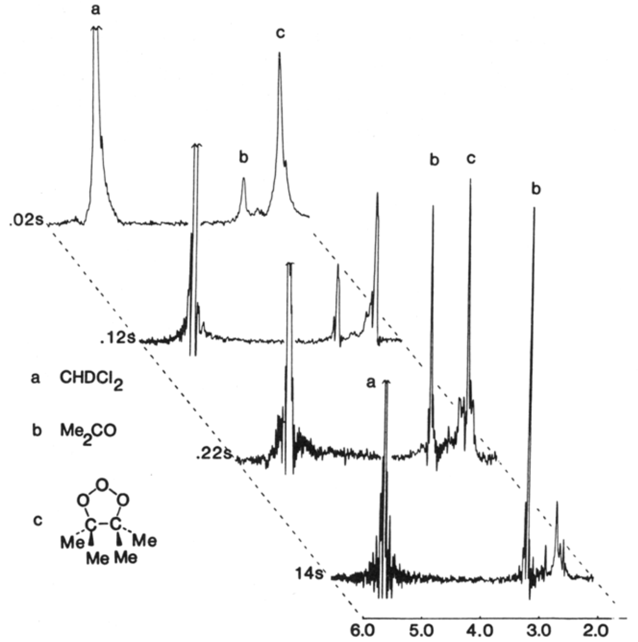

Figure 2. Spectra showing the decomposition of **2** at −85 °C in CD_2Cl_2.

Rapidity. We find that a delay of 40 ms, in addition to the computer deadtime of 15 ms, is necessary to allow complete equilibration of an injected sample in the first spectrum. However the final concentration is established to the extent of 95% after an imposed delay of 20 ms. In kinetic experiments a 20–40 ms delay is imposed and zero time is taken as the time of the first pulse, and not the time of injection. On the other hand where qualitative observation of a very reactive species is important, the sample may be pulsed during the mixing process, an example is given in Figure 2. The acquisition time used in most of the experiments described here was 72 ms, corresponding to the use of 2K data points for each FID (free induction decay) with a sweep width of 14 000 Hz. A further 20 ms interval is imposed by the program for changing the starting address. Consequently the normal pulse repetition interval was 92 ms, in some experiments intervals of 56 and 37 ms were used with a concomitant decrease in digital resolution.

Resolution. The best resolution that can be achieved with the injection assembly inserted is 0.7 Hz. Perturbation of the magnetic field homogeneity, due to the turbulence of injection, results in peak broadening to a line width of 2 Hz in the first spectrum (40 ms delay) when two identical solvents are mixed. The peaks narrow to the limiting digital resolution within 750 ms (see Figure 2). For fast acquisition conditions (72 ms), the digital resolution is 14 Hz per data point, so chemical shift differentiation is much improved over the low field system, although vicinal coupling is unobservable. We stress however the importance of being able to improve the digital resolution at will, if, after an intermediate has been observed, one can modify the reaction conditions to prolong its lifetime and hence permit a more detailed examination.

Sensitivity. Under optimum conditions with a pulse length of 6.6 μs (90°) a methyl singlet can be readily detected in a single pulse at a concentration level of 100 μM at 25 °C (signal to noise = 5:1).

The Ozonolysis of Tetramethylethylene (1). Tetramethylethylene was injected into a solution of ozone in dichloromethane-d_2 at −85 °C. Figure 2 portrays the evolution of the reaction. In the first spectrum the FID was acquired with minimum delay, and so the field homoge-

Table I. Decomposition Rates of 4,4,5,5-Tetramethyl-1,2,3-trioxolane (2) and *cis*-4,5-Dimethyl-1,2,3-trioxolane (4)

no.	solvent	T, °C	reagent	rate constant, s^{-1}	no. pts	$t^{1/2}$, s
2[a]	CD_2Cl_2	-80.8		4.6 ± 0.4[b]	11	0.15
		-87.0		1.78 ± 0.08	22	0.34
		-92.6		0.74 ± 0.03	25	0.94
		-96.8		0.39 ± 0.01	25	1.79
		-101.8		0.217 ± 0.004	25	3.19
	CD_3COCD_3	-91.5		0.29 ± 0.01	24	2.36
	CD_2Cl_2			0.94 ± 0.03	16	0.74
	CD_3COCD_3	-90.5		0.26 ± 0.01	45	2.66
			TCNE[c]	0.23 ± 0.01	33	3.01
	CD_2Cl_2	-89.4		1.30 ± 0.06	12	0.53
			CH_3CO_2H[d]	*e*	8	0.30[f]
			CF_3CO_2H[g]	*e*	8	0.26[f]
			CF_3CO_2H[h]	*e*	2	0.08[f]
4[i]		-91.5		*j*	2	0.02
		-96.0		*j*	4	0.06
		-100		*j*	8	0.33

[a] Concentration = 4.83×10^{-3} M. [b] The error quoted is one standard deviation. [c] Concentration = 4×10^{-2} M. [d] Concentration = 3.48×10^{-2} M. [e] See text. [f] First half-life. [g] Concentration = 1.5×10^{-2} M. [h] Concentration = 5.6×10^{-2} M. [i] Concentration = 6.45×10^{-3} M. [j] Not determined exactly.

neity was reduced by the turbulence of mixing. In the subsequent spectra there is a regular improvement in resolution. Only a trace of starting material δ 1.66 is visible even initially. Of the two readily discernible peaks, the minor one at δ 2.20 corresponds to acetone (at -85 °C), and the major peak at δ 1.36 is assigned to the primary ozonide (PO) **2**. This latter peak disappears with time, as the peaks of acetone and the complex mixture of peroxide products (δ 1.40–1.63) increase. No peak was observed that could be assigned to the carbonyl oxide **3**, and such was the case for all the subsequent experiments. However the ease of observation of **2** allows considerable scope for experimentation on its reactivity. The rate constants for the decomposition of **2** under a variety of reaction conditions are given in Table I.

For comparison the ozonolysis of *cis*-2-butene was briefly studied between -90 and -100 °C. At -90 °C no starting olefin could be observed in the initial spectrum (delay 25 ms), however the corresponding PO, 4,5-dimethyl-1,2,3-trioxolane **4**, was readily visible at δ 1.30 (CH_3), 4.97 (CH) (lit.[11] 4.52 in CF_2Cl_2) as a transient intermediate. The final products were the ozonides, *cis*- and *trans*-3,5-dimethyl-1,2,4-trioxolanes, unidentified peroxide products, acetaldehyde, and acetic acid. The acid was probably formed through oxidation of the aldehyde by a peroxy intermediate, as a control experiment showed that oxidation of acetaldehyde by ozone was slow.

Substituent Effects on the Stability of 1,2,3-Trioxolanes. Primary ozonides derived from trans-disubstituted olefins are well-established species. Not only have they been studied at low temperature by NMR[10,11] and by IR in the solid state[12] and in solution,[13] but one example, *trans*-4,5-di-*tert*-butyl-1,2,3-trioxolane has been crystallized at -78 °C.[14] On the other hand, early trapping experiments by Criegee[14] and Greenwood[15] showed that the primary ozonides of cis-disubstituted olefins are much less stable, and their instability is increased by increasing steric bulk of their substituents. Consequently they have been observed only by NMR spectroscopy at temperatures inferior to -130 °C[11] and by IR below -100 °C (solid phase)[12] and at -175 °C (solution).[13] One very unique report has however recently claimed the formation of both cis- and trans-disubstituted PO's from either *cis*-1,4-dichlorobut-2-ene or the trans isomer, and furthermore that both PO's survive for up to three days in methanol at room temperature.[16]

Several primary ozonides derived from olefins with terminal methylene groups,[12,13,17–19] or from tetrasubstituted olefins,[20,21] have been observed or characterized. In particular 4,4,5,5-tetramethyl-1,2,3-trioxolane **2** has been observed by IR spectroscopy (solid state) and found to decompose at -90 °C.

It is apparent from liquid-phase IR experiments, that the enthalpy of activation for the decomposition of trans-disubstituted PO's is systematically increased by an increase in the substituents' steric bulk.[13] Likewise it was shown directly that *cis*-4,5-diisopropyl-1,2,3-trioxolane is much less stable than the trans isomer.

It could be anticipated that tetrasubstituted PO's be doubly destabilized by cis-related substituent interactions. However we find that under the same conditions the PO of *cis*-butene (**4**) is approximately ten times less stable than **2** (at -96 °C $t^{1/2}(\mathbf{4}) \simeq 200$ ms, $t^{1/2}(\mathbf{2}) = 1.77$ s; at -101 °C $t^{1/2}(\mathbf{4}) \simeq 300$ ms, $t^{1/2}(\mathbf{2}) = 3.15$ s in CD_2Cl_2). Therefore the introduction of two trans-related substituents confers sufficient (kinetic) stability to overcome the increased steric compression due to the cis-related substituents.

This result is best interpreted in terms of the Bauld–Bailey theory of primary ozonide decomposition, where the ozonide conformation in which decomposition occurs is a half chair with well-defined axial and equatorial substituents.[22] A critical feature of this theory is that during the 1,3-dipolar cycloreversion there is rotation around each of the carbon oxygen bonds, so that cis-related ligands can

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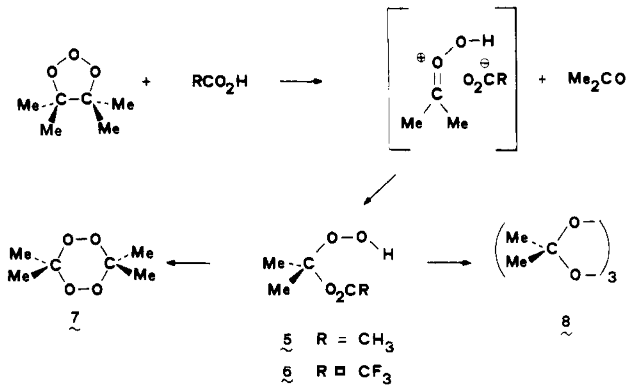
separate, whereas one of two trans-related ligands will inevitably be compressed. For disubstituted primary ozonides the compression will be between an alkyl group and a hydrogen atom, in the case of 2 the compression will be between two methyl groups, and thus will result in a greater activation free enthalpy. In the alternative scheme of Kuczkowski,[23] the cleavage of the primary ozonide is considered to occur from an exaggerated envelope conformation. Although the stereochemical course of the reaction is elegently rationalized, the influence of substituents on the stability of the PO is less predictable. A recent series of detailed ab initio calculations[24-26] indicate that the interaction between the methyl substituents in 4 are minor, and that steric compression of substituents affects the PO stability only for bulky alkyl groups in a cis relationship. Such an analysis does not accomodate our result that 2 is stabilized relative to 4; nor can it account for the effect of bulky trans substituents on the enthalpy of activation for the PO scission.[13]

Solvent Effects on the Stability of 1,2,3-Trioxolanes. The decomposition of *trans*-4,5-diisopropyl-1,2,3-trioxolane is more rapid in CS_2 than in pentane.[13] It is reasonable to interpret such an acceleration in a polar or polarizable solvent in terms of increased stability of a transition state which leads to two mutually repulsive dipoles.[13] However as an apparent contradiction, the decomposition of 2 at −91.5 °C is three times less rapid in acetone than in dichloromethane. To our minds the difference is too small to merit speculations as to its origin. We do note in passing that (a) according to Cremer's calculations,[25] the dipole moments of PO's are large (around 4.0 D) (b) the transition state for PO decomposition is not necessarily "product like",[26] and of course (c) that the concerted nature of a cycloreversion does not necessarily imply that all bonds are broken or formed to the same extent in the transition state.[27] Hence the dipolar character in the transition state need not be more developed than in the starting PO, and consequently the dependence of rate on solvent polarity may be slight.

The following activation parameters for the decomposition of 2 in CD_2Cl_2 were derived from the data in Table I, $\Delta H^\ddagger = 39 \pm 2$ kJ/mol, $\Delta S^\ddagger = -28 \pm 10$ J deg^{-1} mol^{-1} (Ea = 40 kJ/mol K), $A = 3.3 \times 10^{11}$ s^{-1}). The Arrhenius activation energy (Ea) is identical with that for the decomposition of *trans*-4,5-diisopropyl-1,2,3-trioxolane in CS_2, despite the fact that 2 is much less stable (by a factor of 10^3 at −91 °C). Hence the reactivity difference is governed by the entropy term. Although the entropy of activation for the decomposition of 2 is less negative than those reported for other PO's,[13,28,29] the negative value still reveals extensive solvent organization in the transition state. Neglect of this effect led Cremer[25] and Benson[30] to discount the previously reported Arrhenius A values as too low for unimolecular reactions and to increase the estimated Ea value to 48–56 kJ/mol for the decomposition of *trans*-4,5-diethyl-1,2,3-trioxolane. Solvent orientation is apparently very pronounced in the decomposition of the PO of 1-hexene.[29] However, for a series of trans-disubstituted PO's, the phenomenon becomes less important as the bulk of the substituents increases.[13] Consistent with this trend it would appear that solvent proximity to the reaction center, and solvent reorganization are less pronounced for the reaction of a tetrasubstituted PO such as 2, resulting in a less negative value of $\Delta S^\ddagger$. A direct comparison is however hazardous, as the increased polarity of CD_2Cl_2 relative to CS_2 could lead to less extensive solvent orientation.

Scheme II



Decomposition of 2 in the Presence of TCNE. Important evidence for the existence of carbonyl oxides as intermediates is supplied by trapping experiments with tetracyanoethylene (TCNE). Criegee demonstrated that the ozonolysis of 1 in the presence of TCNE led cleanly to 2 equiv of acetone and 1 equiv of tetracyanoethylene oxide.[31] It appears reasonable but has not until now been proven, that the reactive oxidizing species is the carbonyl oxide and not the PO 2. We have been able to show (Table I) that in the presence of an eight-fold excess of TCNE (in acetone-d_6 for solubility reasons) the decomposition rate of 2 is unaffected (within 95% probability limits). Under these reaction conditions the yield of peroxide products was reduced by 80% (estimated by NMR integration). Hence we confirm that as TCNE does not react with 2, it must be oxidized by another species formed from 2, most probably the carbonyl oxide 3.

Reaction of 2 with Carboxylic Acids. Several ozonolysis of 1 were carried out in the presence of acetic and trifluoroacetic acids, in the hope of sufficiently stabilizing the carbonyl oxide by protonation to permit its observation.[32] Unfortunately no signals that could be associated with the conjugate acid of 3 could be observed. On the other hand new products whose spectra were compatible with structures 5 and 6 were formed (Scheme II). Although α-acetoxy hydroperoxides have occasionally been isolated from ozonolyses of olefins in acetic acid,[33] both 5 and 6 underwent further decomposition under the reaction conditions. 6 reacted almost as rapidly as it was formed to yield acetone oxide dimer 7, which further decomposed to unidentified products at a rate dependent on the acid concentration. 5 was observed to be formed cleanly, as its decomposition was much less rapid than that of 6, and its ^{13}C NMR spectrum could be measured at low temperature. This difference in stability presumably arises from an easier displacement of trifluoroacetate by the hydroxyperoxy group in a nucleophilic substitution reac-

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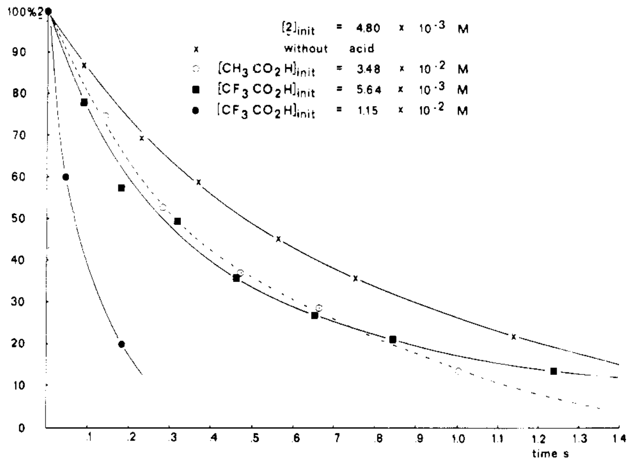

Figure 3. Dependence of the rate of decomposition of **2** on the presence of carboxylic acids in CD_2Cl_2 at −89.5 °C.

tion. Attempts to isolate **5** led only to acetone oxide trimer **8**.

The decomposition of **2** at −89.4 °C is acid-catalyzed as illustrated in Figure 3. The data were analyzed by nonlinear regression using eq 1 for parallel first- and second-order reactions,[34] where a and b are the initial concentrations of PO and acid, respectively, x is the concentration of the product (determined by integration), k_1 is the rate constant for first-order decomposition, and k_2 is the rate constant for the second-order reaction.

$$\frac{1}{(k_1/k_2) + b + a} \ln \frac{a}{(k_1/k_2) + b} \frac{(k_1/k_2) + b - x}{a - x} = k_2 t \tag{1}$$

This treatment yields values for the ratio k_2/k_1, which when combined with the independently determined value of k_1 gives for acetic acid $k_2 = 29 \pm 5\ M^{-1}\ s^{-1}$, and for trifluoroacetic acid $k_2 = 370 \pm 60\ M^{-1}\ s^{-1}$. The resultant values are necessarily crude given the method employed but clearly indicate the difference in catalytic efficiency of the two acids.

Scheme II illustrates the sequence of reactions involved. We have no indication as to whether the ring scission is preceded by protonation, or whether it is concerted with proton transfer within a hydrogen bonded complex. The acid catalysis may be accounted for in several ways. As there is now general agreement that a zwitterionic form such as **3**, with a formal negative charge on the terminal oxygen, best describes *substituted* carbonyl oxides in *solution*,[35] the basicity of **3** should be greater than that of **2**.

Hence the cleavage reaction will be more exothermic for the protonated substrate, with a consequent decrease in the activation energy. We do not know the basicity of **3** relative to acetate ion in dichloromethane, and so cannot comment on whether or not the overall transformation from **2** to protonated **3** is exoergonic.

The conversion of **2** into **3** and acetone is the reverse of a type II or type III 1,3-dipolar cycloaddition in Sustman's classification.[36] Such cycloadditions are accelerated by electron-withdrawing groups, which lower the energy of the LUMO, i.e., increase the electron affinity in *the dipole*. Protonation of a carbonyl oxide, to yield a positively charged species, should also increase its electron affinity. Hence the transition state stabilization could be a frontier orbital controlled, i.e., purely kinetic, phenomenon. As there is no indication to what extent the transition state is "reactant like" or "product like", the importance of this effect is difficult to assess but could be amenable to theoretical investigation.

In conclusion we find that the decomposition of the tetrasubstituted PO **2** is (a) less rapid at −100 °C than that of the cis-disubstituted PO **4**, (b) occurs at a 3-fold lower rate in acetone than in dichloromethane at −89 °C, (c) has activation parameters in CD_2Cl_2 more in line with predictions than those previously reported for other PO's, due to a less negative entropy of activation, (d) is not affected by TCNE which scavanges the product carbonyl oxide, and (e) is acid-catalyzed. Observations c and e are consistent with extensive charge separation in the transition state. Observation b may also be consistent with this situation as the entropy of activation is heavily influenced by the solvent, and cannot be neglected in assessing the effects of solvent polarity. There obviously remains an extensive area of investigation for ozonolysis chemists. We hope that the RINMR method will be of use in further explorations, as it allows use of a greater range of solvents, provides more definitive spectral characterization of intermediates and products than IR, and most importantly allows the study of species *10³–10⁶* times more reactive than those previously studied kinetically.

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Registry No. **2**, 14582-05-9; **4**, 15981-73-4; $(CH_3)_2C{=}C(CH_3)_2$, 563-79-1; *cis*-$CH_3CH{=}CHCH_3$, 590-18-1.

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