

Theoretical Analysis of the Stereoselectivity in the Ozonolysis of Olefins. Evidence for a Modified Criegee Mechanism

Robert Ponec and Gleb Yuzhakov

Institute for Chemical Processes Fundamentals, Czech Academy of Sciences, Prague 6, Suchbát 2, 16502 Czech Republic

Yehuda Haas* and Uri Samuni

Department of Physical Chemistry and the Farkas Center for Light-Induced Processes, The Hebrew University of Jerusalem, Jerusalem, Israel

Received November 15, 1996[©]

The Criegee mechanism of the ozonolysis of *cis* and *trans* symmetric alkenes of the type RCH=CHR is investigated by semiempirical AM1 calculations. The observed stereoselectivity trends are qualitatively explained in terms of the original Criegee mechanism. However, it is shown that in order to elucidate some subtle stereochemical effects as well as to account for the vain attempts to detect the carbonyloxy intermediate, a modification is required. This is done by adopting a proposal made by Cremer et al. (*Chem. Phys. Lett.* **1991**, 187, 491) for the specific case of ethylene and applying it to all systems. The carbonyl oxide and aldehyde formed upon dissociation of the primary ozonide are not separated but form a strongly bound complex that subsequently transforms to the secondary ozonide.

Introduction

The mechanism of ozonolysis of olefins is of continuing interest because of the importance of this reaction in synthesis¹ and in atmospheric chemistry.^{2,3} The mechanism, introduced by Criegee^{4,5} to explain the ozonolysis reaction (Figure 1), stood the test of time in a remarkable way: two proposed intermediates, the primary and secondary ozonides (POZ and SOZ, respectively), were isolated and completely characterized. However, in spite of considerable efforts, the species intermediate between them was never observed in practice. It was speculated to consist of a pair of molecules, one being the carbonyl oxide (abbreviated CO) RHC(O), the other a carbonyl compound RH'CO. This pair will henceforth be called the Criegee intermediate (CI). Carbonyl oxides were observed separately in other systems and reasonably well characterized.^{6,7} Nonetheless, all efforts to obtain direct spectroscopic evidence for its involvement in the ozonolysis reaction itself were unsuccessful. Only indirect proofs of the presence of CO are available. In hydroxylic solvents, the formation of hydroperoxides was explained as due to a reaction between a CO and an alcohol;^{1,7} in nonpolar solvents, CO's were trapped by activated alkenes.⁸

A remarkable mechanistic feature of olefin ozonolysis is the unique stereospecificity: in general, for bulky substituents, the *cis* (*trans*) alkenes are found to yield primarily *cis* (*trans*) SOZ's. For instance, with R = *t*-Bu,

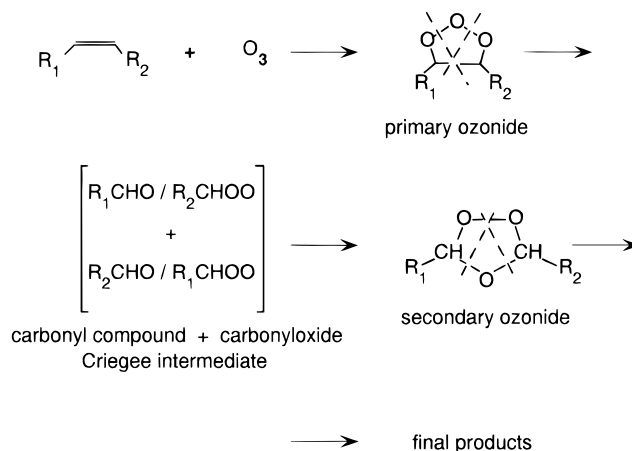


Figure 1. Criegee mechanism.

the *cis* alkene yields a *cis/trans* ratio of 7:3, while the *trans* isomer leads to a *cis/trans* ratio of 3:7 in the SOZ.⁹ For a small substituent, such as methyl, *both cis* and *trans* alkenes lead predominantly to the *trans* SOZ. Such findings have been rationalized by some heuristic models. Bauld,¹⁰ Bailey,⁹ and Kuczkowski¹¹ formulated simple rules governing the factors responsible for the observed stereospecificity. The Bauld–Bailey (BB) concept was based on the least motion principle: the product's stereochemistry is primarily determined by the system undergoing the least motion possible from the reactant's initial conformation. At the time of Bailey's formulation of the revised BB mechanism, the structure of the POZ was not known, and a CC half-chair conformation was assumed. This is now known to be erroneous, in view of microwave studies, definitely proving that it is an O-envelope half-chair (Figure 2). Bailey also assumed that

[©] Abstract published in *Advance ACS Abstracts*, April 1, 1997.

(1) (a) Bailey, P. S. *Ozonation in Organic Chemistry*; Academic Press: New York, 1978 (Vol. 1); 1982 (Vol. 2). (b) Zvilichovsky, G.; Zvilichovsky, B. In *Supplement E: The chemistry of hydroxyl, ether and peroxide groups*; Patai, S., Ed.; John Wiley & Sons Ltd.: New York, 1993; Vol. 2, pp 687–784.

(2) Demerjian, P. L.; Karr, J. A.; Calvert, J. G. *Adv. Environ. Sci. Technol.* **1974**, 4, 1–262.

(3) Grosjean, D. *Environ. Sci. Technol.* **1990**, 24, 1428–1432.

(4) Criegee, R. *Rec. Chem. Proc.* **1957**, 18, 111–120.

(5) Criegee, R. *Angew. Chem.* **1975**, 87, 765–771.

(6) Sander, W. *Angew. Chem., Int. Ed. Engl.* **1990**, 29, 344–354.

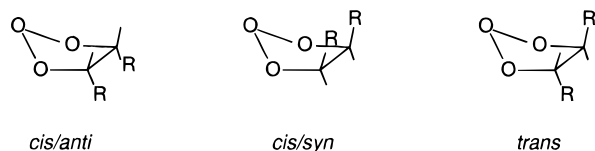
(7) Bunelle, W. H. *Chem. Rev.* **1991**, 91, 335–362.

(8) Keul, H.; Choi, H. S.; Kuczkowski, R. L. *J. Org. Chem.* **1985**, 50, 3365–3371.

(9) Bailey, P. S.; Ferrell, T. M. *J. Am. Chem. Soc.* **1978**, 100, 899–905.

(10) Bauld, N. L.; Thompson, J. A.; Hudson, C. E.; Bailey, P. S. *J. Am. Chem. Soc.* **1968**, 90, 1822–1830.

(11) Kuczkowski, R. L. In *1,3 Dipolar Cycloaddition Chemistry*; Padwa, A., Ed.; Wiley-Interscience: New York, 1984; Vol. 2, pp 197–276.

**Figure 2.**

several conformers may be in equilibrium and that it is not necessarily the thermodynamically most stable one that determines the final conformation. This contention was assumed to explain the unequal ratios obtained at different temperatures and/or different warming rates.

In recent years, considerable effort has been invested in quantum chemical (QC) theories aimed at elucidating the ozonolysis process.^{12–19} A straightforward way appears to be the calculation of the heats of formation of the various stable intermediated and transition states involved. This turns out to be a nontrivial task, particularly because of the difficulty to correctly describe ozone and the CO.^{6,15,19} The inclusion of electron correlation is absolutely required to make *ab initio* calculation reliable. For the larger members of the series, this makes the computation prohibitively expensive; therefore, *ab initio* calculations either dealt only with some individual steps and not with the whole reaction sequence^{17–19} or did partial rather than complete geometry optimization.^{14,15,17} The only comprehensive QC study of the Criegee mechanism to date appears to be a semiempirical one;¹⁶ that study did not consider specifically the stereochemical aspects of the reaction, nor the repeated failure to detect the CO.

In this study we discuss the application of the AM1 semiempirical method to the elucidation of these aspects. Dewar's study,¹⁶ which did not explicitly consider the stereochemical aspects of the Criegee mechanism, is complemented by an analogous systematic investigation of the ozonolysis of symmetric substituted alkenes of the type RCH=CHR, with R ranging from methyl to *tert*-butyl. It is shown that the reaction is expected to lead to stereospecific final products and that their preferred conformation is determined by the combined effect of the individual steps; the most decisive parameter is the activation energy. *However, incorporation of a modification to the Criegee mechanism due to Cremer¹⁸ is required in order to account for the experimental data.* This modification (supported by *ab initio* calculations) involves the formation of a complex between the CO and the aldehyde (both formed from the POZ splitting). This complex, held together by dipole–dipole interaction, is more stable than the separated pair and will be referred to as the dipole complex (DC).

Summary of Previous Work

(1) Formation of Primary Ozonides. The first step in the reaction, formation of the primary ozonide, can be

(12) Cremer, D. *J. Am. Chem. Soc.* **1981**, *103*, 3619–3626.

(13) Hiberty, P. C.; Devidal, J. P. *Tetrahedron* **1978**, *35*, 1015–1017.

(14) Hiberty, P. C. *J. Am. Chem. Soc.* **1976**, *98*, 6088–6092.

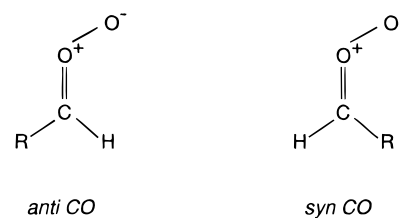
(15) Harding, L. B.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1978**, *100*, 7180–7188.

(16) Dewar, M. J. S.; Hwang, J. C.; Kuhn, D. R. *J. Am. Chem. Soc.* **1991**, *113*, 735–741.

(17) Cremer, D. *J. Am. Chem. Soc.* **1981**, *103*, 3627–3633.

(18) Cremer, D.; Kraka, E.; McKee, M. L.; Radhakrishnan, T. P. *Chem. Phys. Lett.* **1991**, *187*, 491–493.

(19) Cremer, D.; Gauss, J.; Kraka, E.; Stanton, J. F.; Bartlett, R. *Chem. Phys. Lett.* **1993**, *209*, 547–556.

**Figure 3.** Syn and anti forms of the carbonyl oxide.

classified as a symmetry-allowed ($4_s + 2_s$) cycloaddition of ozone to alkene. As such, and in keeping with the Woodward Hoffmann²⁰ rules, the reaction is expected to be stereospecific. Thus, *cis* and *trans* alkenes should lead to the formation of *cis* and *trans* POZ, respectively. These ozonides are rather unstable, and although detected by NMR,²¹ IR in low-temperature matrices,^{22–25} and microwave,²⁶ their steric conformations have not been experimentally determined. The structure of some simple POZ's is known,^{26,27} revealing an O-envelope form with C_s symmetry for the ethene POZ. For substituted alkenes, this implies the existence of two isomeric conformations for primary ozonides derived from *cis* alkenes (*syn* and *anti*), while for ozonides derived from the *trans* alkene, only one POZ conformer is possible as seen from Figure 2.

(2) Splitting of the Primary Ozonides. The second step in Criegee's mechanism involves the splitting of the POZ to the Criegee intermediate (a carbonyl oxide–aldehyde pair). The CO's can be formed in either a *syn* or an *anti* form (Figure 3) and were considered as having a decisive role in determining the overall stereochemical pathway of the reaction. Bauld¹⁰ and Kuczowski and co-workers^{11,27} predicted that *syn* CO's will be preferentially formed from POZ's derived from *trans* alkenes (particularly with bulky substituents) while *anti* CO's are expected to be derived from *cis* alkenes. These predictions are valid assuming a high barrier for *syn*–*anti* isomerization exists, a proposition supported by *ab initio* calculations.¹⁵

(3) Formation of the Secondary Ozonides. The last step of the reaction is calculated to be very exothermic (~50 kcal/mol for ethylene).^{15,16} Dewar¹⁶ calculated a low barrier for this step (1.5–5 kcal/mol), indicating an early reactant-like transition state. This step is an allowed retrocycloaddition of the CO and the aldehyde, which is expected to be stereospecific. However, in spite of the fact that this implies that the CO configuration will determine the overall stereoselectivity, no detailed account for the experimentally observed trends in the SOZ conformations is yet available.

(20) Hoffmann, R.; Woodward, R. B. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 781–853.

(21) Durham, L. J.; Greenwood, F. L. *J. Org. Chem.* **1968**, *33*, 1629–1632.

(22) Kohlmler, Ch. K.; Andrews, L. *J. Am. Chem. Soc.* **1981**, *103*, 2578–2583.

(23) Andrews, L.; Kohlmler, Ch. K. *J. Phys. Chem.* **1982**, *86*, 4548–4557.

(24) Hull, L. A.; Hisatsune, I. C.; Heicklen, J. *J. Am. Chem. Soc.* **1972**, *94*, 4856–4864.

(25) Samuni, U.; Fraenkel, R.; Haas, Y.; Fajar, R.; Pola, J. *J. Am. Chem. Soc.* **1996**, *118*, 3687–3693.

(26) Gillies, J. Z.; Gillies, C. W.; Suenram, R. D.; Lovas, F. J. *J. Am. Chem. Soc.* **1988**, *110*, 7991–7999.

(27) Kuczowski, R. L. *Chem. Soc. Rev.* **1992**, *21*, 79–83.

Table 1. AM1-Calculated Heats of Formation (in kcal/mol) of Species Participating in the First Step of the Criegee Mechanism of Ozonolysis^a

R in RCH=CHR	alkene/POZ ^b configuration	$\Delta H_f^{\text{alkene}}$	ΔH_f^{TS}	ΔH_f^{POZ}	E_a
H		16.5	65.7	5.6	11.4
Me	cis/syn	-2.2	51.1	-3.7	15.5
	cis/anti	-2.2	51.0	-3.2	15.4
	trans	-3.3	50.5	-4.7	16.0
Et	cis/syn	-16.6	38.1	-16.3	16.9
	cis/anti	-16.6	38.0	-15.8	16.8
	trans	-15.7	39.1	-16.4	17.0
<i>i</i> -Pr	cis/syn	-23.8	34.8	-22.0	20.8
	cis/anti	-23.8	35.1	-19.0	21.1
	trans	-25.1	31.1	-24.4	18.4
<i>t</i> -Bu	cis/syn	-19.0	37.6	-14.1	18.8
	cis/anti	-19.0	37.9	-13.8	19.1
	trans	-28.8	27.6	-29.0	18.6

^a $E_a = \Delta H_f^{\text{TS}} - (\Delta H_f^{\text{alkene}} + \Delta H_f^{\text{ozone}})$, where $\Delta H_f^{\text{ozone}} = 37.8$ kcal/mol. ^b Cis or trans refer to the alkene stereochemistry. Syn or anti refer to the POZ stereochemistry relative to the plane of the O-C-C-O ring and the peroxidic oxygen. See Figure 2.

Computational Results

In this work we used the AM1 method²⁸ as implemented in the MOPAC²⁹ and SPARTAN³⁰ packages, making it possible to directly compare the results with Dewar's work.¹⁶ In all cases, intermediates were checked to be true minima, and transition states to be true saddle points, by computing the Hessian matrix.

(1) Formation of the Primary Ozonides. The different conformations of the POZ's shown in Figure 2 were found to be stable species for all compounds studied in this work. Their heats of formation are reported in Table 1 along with those of the transition states leading to them (ΔH_f^{TS}). The calculation verified that all transition states were true saddle points, and the table lists also the derived activation barriers ($E_a = \Delta H_f^{\text{TS}} - (\Delta H_f^{\text{ozone}} + \Delta H_f^{\text{alkene}})$). The table clearly shows that the POZ's derived from trans alkenes are systematically more stable than those arising from cis alkenes. The absolute value of (ΔH_f^{POZ}) is seen to increase as the substituents become more bulky. Direct comparison with experiment is not possible, since experimental heats of formation are not known, but the trends agree with the NMR data of ref 21. Only minor differences are calculated between the activation barriers for formation of POZ from cis or trans alkenes and between formation of cis/anti and cis/syn POZ's from cis alkene.

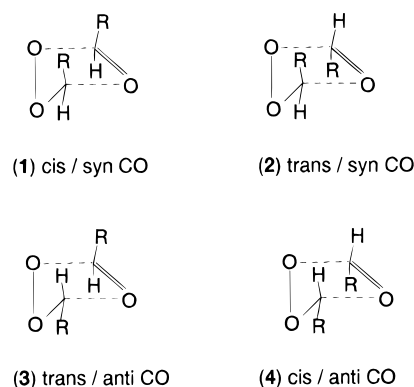
It is noted that all the structures of the stable POZ's obtained in these calculations are similar to each other, being of the O-envelope type; they are also quite close to the microwave determined structure of the parent 1,2,3-trioxolane (POZ derived from ethylene²⁶).

(2) Splitting of the Primary Ozonides. Table 2 reports the calculated heats of formation of the species involved in the second step of the Criegee mechanism (i.e. the CO and the aldehyde) as well as the transition states leading to them. It is found that the syn CO's are generally more stable than the anti ones, in agreement with Cremer's ab initio results.³¹ The activation energies for anti formation are uniformly smaller than those leading to the syn form, for reactions of cis alkenes. The

Table 2. AM1-Calculated Heats of Formation (in kcal/mol) of Species Participating in the Second Step of the Criegee Mechanism of Ozonolysis

R in RCH=CHR	POZ/CO ^a configuration	ΔH_f^{TS}	$\Delta H_f^{\text{CO+aldehyde}}$	E_a^b
H		25.1	-0.8	19.5
Me	cis/syn	15.7	-22.8	19.4
	cis/anti	14.2	-20.6	17.4
	trans/syn	13.7	-22.8	18.4
	trans/anti	13.0	-20.6	17.7
		3.3	-36.3	19.6
Et	cis/syn	3.3	-36.3	19.6
	cis/anti	1.4	-34.8	17.2
	trans/syn	2.9	-36.3	19.3
<i>i</i> -Pr	trans/anti	1.5	-34.8	17.9
	cis/syn	-1.6	-44.2	20.4
	cis/anti	-4.6	-43.0	14.4
<i>t</i> -Bu	trans/syn	-1.7	-44.2	22.7
	trans/anti	-5.7	-43.0	18.7
	cis/syn	3.8	-49.6	17.9
	cis/anti	-1.6	-48.2	12.2
	trans/syn	-9.1	-49.6	19.9
	trans/anti	-9.0	-48.2	20.0

^a The syn or anti refer to the stereochemistry of the carbonyl oxide, relative to its double bond. See Figure 3. Note that syn (anti) POZ can lead only to syn (anti) CO. ^b $E_a = \Delta H_f^{\text{TS}} - \Delta H_f^{\text{POZ}}$, see Table 1 for the calculated ΔH_f^{POZ} values.

**Figure 4.** Possible isomers of the Criegee intermediate.

prediction is therefore that anti CO's will be preferentially formed, in complete agreement with the empirical rules.^{10,11} The case of trans alkenes is different—the experimental preferential formation of syn CO's does not follow from the calculated activation barriers. Nonetheless, it is noted that the anti isomer formation preference decreases as the substituent becomes bulkier and practically disappears for *t*-Bu. We shall return to this result in the discussion of the overall reaction pattern.

(3) Formation of the Secondary Ozonides. Figure 4 shows all possible steric combinations of CO-aldehyde pairs; these structures are important since they are assumed to eventually determine the structure of the final product, SOZ. The calculated heats of formation of the transition states and the activation barriers for the different species are collected in Table 3. The activation barriers are seen to be smaller than for the previous steps; those leading to the anti isomer being significantly smaller than those involving the syn form.

Discussion

Following Criegee,⁵ Bauld-Bailey,^{9,10} and Kuczkowski,¹¹ it is assumed that the final stereochemistry of the products is determined by the combination of the different steps in the Criegee mechanism. In contrast with them, it is argued that the second step does not result in

(28) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. P.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902–3909.

(29) Stewart, J. J. P. MOPAC6, QCPE 455, Indiana University, Bloomington, IN, 1983.

(30) Spartan 4.0, Wavefunction, Inc., Irvine, CA 92715.

(31) Cremer, D. *J. Am. Chem. Soc.* **1979**, *101*, 7199–7205.

Table 3. Calculated Values of the Activation Barriers (in kcal/mol) for the Last Step of the Criegee Mechanism

R in RCH=CHR	type of TS ^{a,b}	$\Delta H^{\ddagger S}$	E_a^c
H		-3.1	barrierless
Me	1, cis/syn	-17.8	5.0
	2, trans/syn	-17.6	5.2
	3, trans/anti	-19.7	0.9
	4, cis/anti	-19.3	1.3
Et	1, cis/syn	-30.8	5.5
	2, trans/syn	-30.4	5.9
	3, trans/anti	-32.8	2.0
	4, cis/anti	-31.4	3.4
<i>i</i> -Pr	1, cis/syn	-38.5	5.7
	2, trans/syn	-38.7	5.5
	3, trans/anti	-40.9	2.1
	4, cis/anti	-40.7	2.3
<i>t</i> -Bu	1, cis/syn	-38.2	11.4
	2, trans/syn	-39.6	10.0
	3, trans/anti	-44.6	3.6
	4 cis/anti	-44.6	3.6

^a TS is the transition state for the formation of SOZ from the pair CO + aldehyde. ^b The stereochemical labeling is presented in Figure 4 and marked a, b, c, and d. The cis and trans are relative to the O-C-O-C plane formed by the approaching carbonyl oxide and aldehyde. The syn and anti refer to the stereochemistry of the carbonyl oxide. Note that the stereochemistry of the TS determines the stereochemistry of the resultant SOZ, trans (cis) TS leading to trans (cis) SOZ. ^c $E_a = \Delta H_f^{\ddagger S} - (\Delta H_f^{\text{CO}} + \Delta H_f^{\text{aldehyde}})$.

a separated CO-aldehyde pair but rather in a bound complex¹⁸ (the DC), whose formation is of crucial importance for the understanding of the overall reaction pattern.

(1) The Need To Modify Criegee's Mechanism. In the present calculations we emphasized the heats of formation of the different species and the activation barriers for their formation. In order to make comparisons with experiment, several assumptions were made. The main one is that the reaction follows the pattern outlined in Figure 1 and that each of the intermediates is allowed to form and relax to its potential well before the next step begins. In view of the extreme exothermicity of the reaction, this is not necessarily the case. Both the POZ and the CO are formed with a large amount of excess energy, sufficient to overcome the energy barrier for the subsequent step. Nevertheless, it is assumed that the fact that a potential well exists affects the reaction rate and that the reaction will tend to follow the path with the least energetic hindrance, as predicted by statistical theories of unimolecular reactions. The AM1 method cannot be expected to yield accurate reaction barriers. One may therefore wonder whether small differences (2–5 kcal/mol) between barriers of competing reactions are significant. Comparison with available experimental data indicates that, irrespective of possible systematic shifts in the absolute values, the relative values of heats of formation within a series of structurally related compounds are reproduced correctly. This was the case for the data reported in Tables 1–3. Further support for the trends revealed in the present calculations is the fact that the results agree well with sophisticated ab initio calculations, when available. For instance, the calculated stabilization energies of the dipole complex (DC) relative to its separated constituents were found to be in good agreement with ab initio calculations performed by Cremer¹⁸ and by others.³² They are of the order of 3–5 kcal/mol, large enough to

exist as stable entities in low-temperature rare-gas matrices and perhaps in the gas phase. They may not be able to survive the attack of alcohols or aldehydes in fluid solvents, accounting for the trapping of carbonyl oxides in this environment. It is therefore concluded that these species are needed to account for finer details of the ozonation reaction, and their inclusion in the mechanism is required. As shown below, some other aspects of the reaction, *vis*, the variation of the cis/trans ratio of SOZ, may also be better explained. A schematic energy reaction profile for the complete reaction, including the DC, is shown in Figure 5 (using *cis*-dimethylethylene as example).

(2) The POZ–SOZ Transformation. The final picture that emerges from the present calculation assumes that the various barriers along the reaction coordinate are important in determining the product distribution, even in the presence of a large energy excess. Ab initio calculations³² show that POZ dissociation begins by the stretching of an O–O bond. Direct formation of the SOZ by a concerted stretching and rotation of the O–O and O–C bonds was excluded by the calculation. When the O–O bond attains a critical length, the C–C bond begins to stretch, and the CO + aldehyde pair begins to form. As the two fragments start moving apart, a strong attraction builds up between the oppositely charged newly formed dipoles, creating a torque that flips one of them over with respect to the other and forms the DC adduct, which stabilizes at a C–O separation of about 2.4 Å (MP2/6-31G* level). This separation is much smaller than expected for a van der Waals adduct, but considerably larger than the C–O bonds of either POZ or SOZ. Thus, the separated carbonyl oxide and carbonyl compound are never formed in this reaction, explaining the fact that they could not be observed.

The rotation of the aldehyde with respect to the CO can take place in the plane of the heavy atoms, or in a plane perpendicular to it. In the former case the steric structure will be maintained, while in the latter it will be inverted. The former alternative appears to be the actual one, since experimentally it is found that the stereochemistry is maintained. The activation barriers reported in Table 3 are relevant, since the formation of the DC appears to involve a small energetic barrier. Thus, it is expected that anti CO's will react more rapidly than the syn ones and that the SOZ's will be primarily formed from them.

(3) The Role of the DC in the Final Step. As can be seen from Tables 2 and 3, for ethylene, the AM1 calculated heat of formation for the separated aldehyde and CO is higher than that of the transition state to the formation of ethylene SOZ (–0.8 and –3.1 kcal/mol respectively), implying a barrierless reaction. Introduction of the DC complex amends this unlikely result, predicting a stabilization of 4.3 kcal/mol and an activation energy of 2.0 kcal/mol for the formation of ethylene SOZ from the dipole complex (see Table 4). It is important to note that these findings shed light on a mismatch of AM1 and ab initio calculated results, for the decomposition of ethylene POZ, that has troubled Dewar et al.¹⁶ The problem encountered by them was that AM1 predicted this step to be strongly exothermic where as ab initio calculations predicted it to be endothermic. In light of our results it is now obvious that this apparent discrepancy arose because in fact Dewar calculated the heat of formation of a dipole complex rather than the sum of the heats of formation of the isolated aldehyde and CO. His

(32) S. Zilberg, private communication.

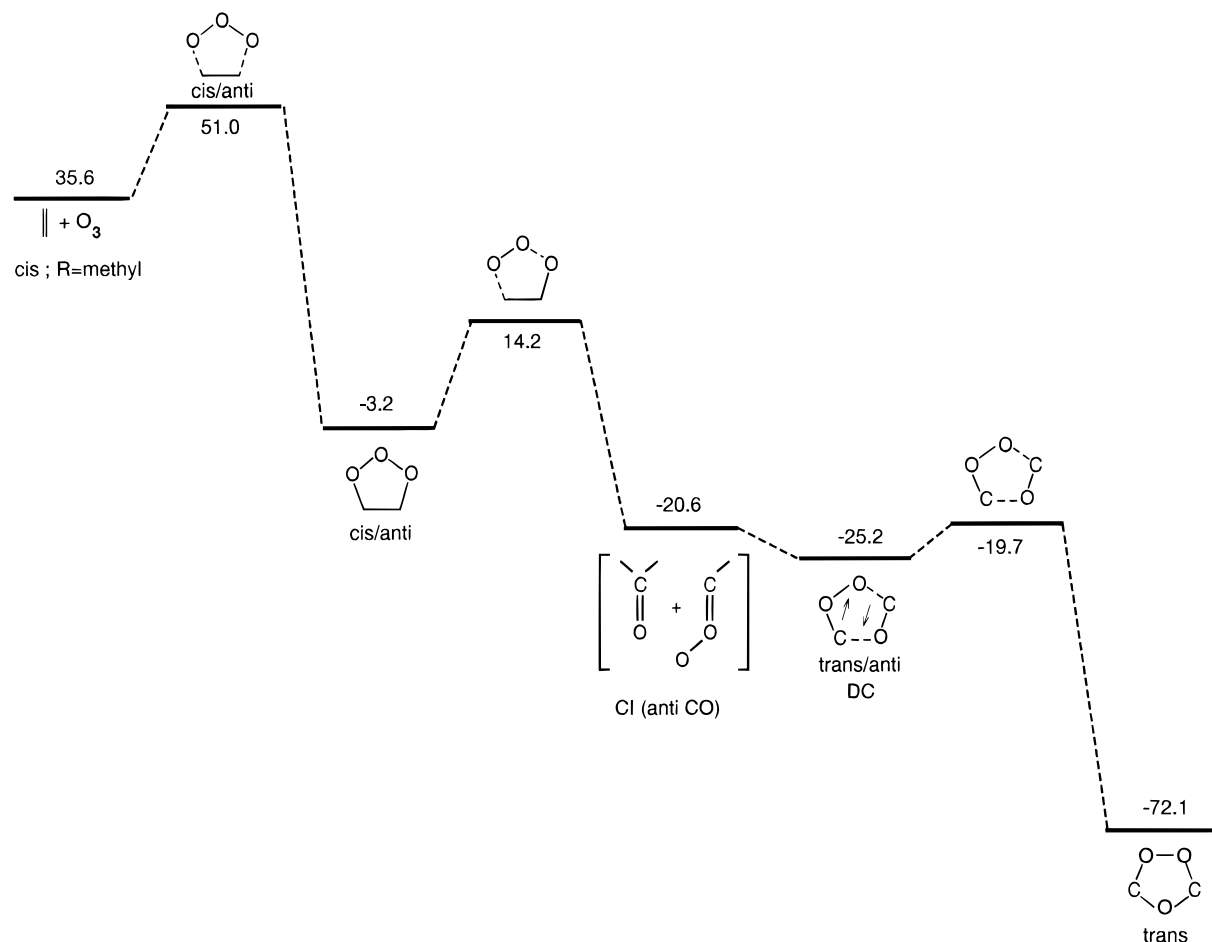


Figure 5. AM1-calculated energy profile for *cis*-dimethylethylene + ozone reaction, including the dipole complex (DC). The heats of formations (kcal/mol) for all intermediates and transition states are given.

Table 4. AM1-Calculated Values of DC Complexes Stabilization Energies and Corrected Activation Barriers (in kcal/mol) for the Formation of Secondary Ozonides

R in RCH=CHR	dipole complex configuration ^a	$\Delta E_{\text{stabil}}^b$	E_a (uncorrected) ^c	E_a (corrected) ^d
H		4.3	barrierless	2.0
Me	cis/anti	5.4	1.3	6.7
	trans/anti	4.6	0.9	5.5
<i>t</i> -Bu	cis/anti	3.1	3.6	6.7
	trans/anti	4.0	3.6	7.6

^a The term anti refers to the CO component of the DC complex. Cis or trans are with respect to the O-C-O-C plane of the DC complex. Note that the stereochemistry of the DC determines the stereochemistry of the resultant SOZ, trans (cis) DC leading to trans (cis) SOZ. ^b $\Delta E_{\text{stabil}} = (\Delta H_f^{\text{CO}} + \Delta H_f^{\text{aldehyde}}) - \Delta H_f^{\text{DC}}$. ^c Value from Table 3. ^d E_a (corrected) = $\Delta H_f^{\text{TS}} - \Delta H_f^{\text{DC}}$.

value of -5.1 kcal/mol is exactly the value we calculated for the dipole complex, whereas our value for the heat of formation for isolated aldehyde and isolated CO is -0.8 kcal/mol.

In order to discuss the effect of the substituent's size let us consider the methyl and *tert*-butyl groups. As Table 2 shows, the anti CO's are more likely to be formed in the case of methyl substitution from cis POZ, while in the case of trans POZ the barriers for syn and anti formation are comparable. According to Table 3 the barrier to trans formation is slightly lower than for cis, so that the former is expected to dominate, as observed experimentally.

With the bulky *t*-Bu group, Table 2 predicts that the anti CO will be preferentially formed, especially from cis

alkenes. In the last step, the activation barriers for the formation of cis and trans SOZ are the same (Table 3), so that one expects equal amounts of these species. In practice, the cis isomer dominates.

This discrepancy is removed when the DC is introduced. Its stabilization energy effectively increases the barrier for SOZ formation, *but not equally*. Table 4 lists the calculated corrected barriers (taking into account the DC formation) for both Me and *t*-Bu substitution. It is seen that this correction acts in the right direction: in addition to enhancing the preferential formation of trans SOZ for R = Me, it also introduces the correct difference in the activation barriers for R = *t*-Bu.

It is concluded that the present work succeeds in qualitatively accounting for the observed stereochemistry of some ozonolysis reactions. Several unsolved problems do remain, however. According to Table 1, the activation barriers *increase* as the substituent becomes bigger—in contrast with experiment.³³ The subtle changes reported for other symmetrically substituted alkenes⁹ are mostly, but not completely, accounted for. These trends appear to be beyond the power of the present calculation and suggest the need for a large-scale ab initio calculation that explicitly considers electron correlation.

Summary

Semiempirical calculations show that the observed rather complex stereochemistry of the ozonation reaction

can be explained in terms of a slightly modified Criegee mechanism. The calculated barriers for the different steps are the main factor determining the final conformation of the SOZ. Differences between alternative routes are sometimes rather small, indicating possible dynamic effects which may account for different product ratios when experimental parameters such as heating rates are varied.

Acknowledgment. This work was supported by the Grant Agency of the Czech Republic (Grant No. 203/

95/0650) and under Grant No. HRN-554-G-00-2078-00, US-Israel Cooperative Research Program, Human Capacity Development, Bureau for Global Programs, Field Support and Research, USAID. R.P. gratefully acknowledges the support of the CDR/AID program during his stay in Jerusalem, where part of the calculations were performed. The Farkas Center for Light Induced Processes is supported by Minerva mbH, Munich.

JO9621377