in the C–F bonds of **1d**, *is not enough to cause the planar geometry to be as stable as the nonplanar geometry. Upon strengthening the resonance interaction with both the ring and the fluorines, a planar geometry is increasingly favored.* This effect is illustrated in the difluorocyclopropylcarbonium ion, **1e**, where the planar conformation is the most stable geometry. It is much more stable than any geometry with a significant out-of-plane deviation. This is in accord with Pauling's[24] expectation that the planar geometry is increasingly more stable relative to nonplanar geometry as the electronegativity difference between C and F decreases.

Acknowledgments. The authors wish to acknowledge the University of Alabama's Research Committee, Project 562, and the College Work-Study Program for support of this work. Mr. C. Henry Copeland is thanked for valuable assistance in the computer programming problems. Extensive computer time was provided by the University of Alabama Computer Center and NSF Improvement of Computer Center Grant No. GJ-212.

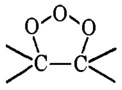
A Quantitative Investigation of the Ozonolysis Reaction. XV. Quantum Chemical Interpretation of the Substituent Effects on the Cleavage of 1,2,3-Trioxolanes[1a]

Sándor Fliszár,*[1b] J. Renard,[1b] and David Z. Simon[1c]

Contribution from the Department of Chemistry, University of Montreal, Montreal, Quebec, Canada, and Faculty of Pharmacy, University of Montreal, Montreal, Quebec, Canada. *Received January 28, 1971*

Abstract: Experimental distributions of the reaction paths of selected alkyl-substituted 1,2,3-trioxolanes to give (a) $R_1C^+HOO^- + R_2CHO$ or (b) $R_1CHO + R_2C^+HOO^-$ are compared with Mulliken overlap populations and with gross electron densities of the trioxolanes. In general, the preferential path of cleavage yields the zwitterion retaining the carbon atom having the highest C–O overlap in the trioxolane ring, and the cleavage appears to be initiated at the C–C bond. Both the EHMO and the CNDO/2 calculations indicate that the inductive effects, expressed in terms of net electron release by the substituents, are remarkably constant for the individual groups and correlate with Taft's polar σ^* constants. Both methods indicate the participation of an additional effect, by which the preferentially formed zwitterion is the one in which the environment is electron richer, and is, thus, favored by alkyl groups in the order $CH_3 > \ldots >$ *tert*-C_4H_9. A consideration of this effect, together with the inductive effect, enables the consistent discussion of the reactivity of primary ozonides.

According to Criegee's mechanism of ozonolysis,[2] which is well supported by considerable experimental evidence,[3] ozone adds onto carbon–carbon double bonds to give the very unstable intermediate 1,2,3-trioxolanes (primary ozonides) I.

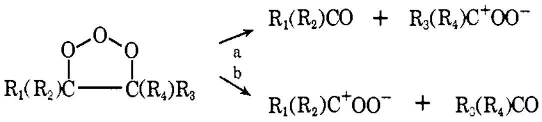


I

Evidence for the existence of the primary ozonides of some trans and cis alkenes has been given, and experimental findings confirm structure I.[4] However, owing to the extreme instability of the primary ozonides,[5] their conformational study is, at present, impossible with conventional experimental methods: quantum chemical LCAO–EHMO methods were used to gain information about the shape of selected alkyl-substituted primary ozonides.[6]

Their cleavage into zwitterion and carbonyl compound has been the object of recent detailed studies.[7-9] With unsymmetrical olefins $R_1(R_2)C{=}C(R_4)R_3$, two possible paths of cleavage are to be considered (Scheme I).

Scheme I



Because of the complexity of the reactions occurring in ozonolyses in inert solvents (*e.g.*, CCl_4, hexane),

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(1) (a) Paper presented at the Symposium on Cyclic Peroxides, Metrochem '71, San Juan, Puerto Rico, April 30, 1971. Abstracted in part from the Ph.D. Thesis of J. Renard, Université de Montréal, Montréal, Québec, Canada, 1969. (b) Department of Chemistry. (c) Faculty of Pharmacy.

(2) R. Criegee and G. Wenner, *Justus Liebigs Ann. Chem.*, **564**, 9 (1949); R. Criegee, *ibid.*, **583**, 1 (1953); R. Criegee, *Rec. Chem. Progr.*, **18**, 111 (1957).

(3) P. S. Bailey, *Chem. Rev.*, **58**, 926 (1958).

(4) (a) R. Criegee and G. Schröder, *Chem. Ber.*, **93**, 689 (1960); (b) F. L. Greenwood, *J. Org. Chem.*, **29**, 1321 (1964); 30, 3108 (1965); (c) P. S. Bailey, J. A. Thompson, and B. A. Shoulders, *J. Amer. Chem. Soc.*, **88**, 4098 (1966); (d) L. J. Durham and F. L. Greenwood, *Chem. Commun.*, 24 (1968); L. J. Durham and F. L. Greenwood, *J. Org. Chem.*, **33**, 1629 (1968).

(5) The "most stable" primary ozonide (that of *trans*-di-*tert*-butylethylene) decomposes in an explosive way when "heated" up to −60°.[4a] The cis primary ozonides are reported to be even more unstable than the trans isomers,[4d] at temperatures as low as −110°.

(6) J. Renard and S. Fliszár, *J. Amer. Chem. Soc.*, **92**, 2628 (1970).

(7) S. Fliszár and J. Renard, *Can. J. Chem.*, **45**, 533 (1967); S. Fliszár and M. Granger, *J. Amer. Chem. Soc.*, **91**, 3330 (1969).

(8) S. Fliszár and M. Granger, *ibid.*, **92**, 3361 (1970).

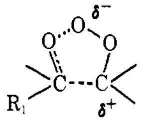
(9) S. Fliszár and J. Renard, *Can. J. Chem.*, **48**, 3002 (1970).

the reactions indicated in Scheme I are studied adequately in the presence of an alcohol ROH. In this case, the ozonolysis yields only four products which are well defined, *i.e.*, two carbonyl compounds and two alkoxy hydroperoxides, $R_1(R_2)C(OR)OOH$ and $R_3(R_4)C(OR)OOH$, the latter resulting from the attack of the alcohol ROH on the zwitterions. It has been shown, in all cases studied,[7-10] that in the presence of enough methanol (or ethanol) the zwitterions are *quantitatively* trapped to give the corresponding alkoxy hydroperoxides. Under adequate experimental conditions, the latter do not react further with the carbonyl compounds and they are, in general, sufficiently stable to make their analysis possible.

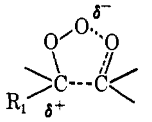
Detailed mass balances were thus made available, which indicated that the ozonolysis of 1 mole of olefin, in the presence of excess alcohol, results in the production of a total of 1 mole of the mixture of carbonyl compounds and of a total of 1 mole of the mixture of alkoxy hydroperoxides. This is in complete agreement with the stoichiometry anticipated in Scheme I. Hence, the formation of any additional compound, at least in an appreciable amount, by a path not indicated in this scheme can be excluded.[11]

On the basis of these studies, it became thus possible to discuss the substituent and, to a certain extent, the conformational effects in distributing the proportions of the two ways of cleavage. Linear free energy relationships were established[7-9] which describe accurately the distributions of the reaction products, depending on the olefin.

These studies may assist the organic chemist in his attempt to predict the course of ozonolysis reactions. However, beside the specific interest in ozone chemistry, a different, and more general, point of interest may deserve attention. The transition states corresponding to paths a and b, both of which yield zwitterionic carbocations, differ in the site of localization of the partial positive charge on one carbon atom in preference to the other in the 1,2,3-trioxolane ring. It is considered that the energies of the transition states are governed by the more or less efficient stabilization of the corresponding potential zwitterionic carbo cations by neighboring groups. Owing to the fact that the reactions depicted in Scheme I are, in general, extremely "clean," as indicated by the numerous mass balance determinations, it appears, thus, that the cleavage of appropriate series of primary ozonides is an excellent probe for studying the factors governing the stabilization of carbonium ions.



IIa (path a)



IIb (path b)

The advantages resulting from the possibility of studying a clean reaction are obvious. Several other fortunate circumstances, which have emerged from previous studies, contribute in making the cleavage of primary ozonides a sort of "school example" for the quantitative evaluation of substituent effects in favoring the formation of carbonium ions. The following points, which refer to the reactions indicated in Scheme I, have received experimental confirmation.

(i) The proportions of cleavage following paths a and b are independent of temperature, in the range −78° to room temperature.[8,9]

(ii) The distribution of paths a and b is independent of solvent.[9]

(iii) The decomposition of I obeys first-order kinetics.[12]

(iv) The cleavage of I is very exothermic.[13] According to Hammond's postulate,[14] the transition states are expected to possess structures close to that of the initial state (primary ozonide); there should be no regular tendency for the most stable products to be formed most rapidly in competitive reactions.

(v) Inhibition of either one of the two possible ways of cleavage by steric hindrance need not to be considered.[9] Steric effects which can be expected from the change in hybridization are the same for both reaction paths and are thus not likely to participate in distributing the proportions of cleavage.

(vi) The cleavage of the carbon–carbon bond precedes any oxygen–oxygen bond cleavage,[15a,b] thus initiating the concerted cleavage.

From a consideration of these points, it results that only substituent effects in directing the cleavage need be considered.[16] The effects which were found to participate in distributing the reaction paths are given below.

(i) The resonance stabilization which, in some cases, plays an important role,[7,8] as in the formation of the zwitterions $RC^{+}HOO^{-}$ with R = $COCH_3$ and COOH. The participation of the phenyl group has also been studied in some detail.[8] In the present study, resonance stabilization is not discussed further, although it may be invoked occasionally.

(ii) The inductive effects which play a predominant role in the cleavage of the primary ozonides of alkylmonosubstituted ethylenes.[9]

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[10] G. Klutsch, J. Grignon, J. Renard, and S. Fliszár, *Can. J. Chem.*, **48**, 1598 (1970).

[11] Olefins which undergo "abnormal ozonolysis"[3] are not considered in the present study.

[12] F. L. Greenwood and L. J. Durham, *J. Org. Chem.*, **34**, 3363 (1969).

[13] The heat of decomposition of the primary ozonide of *trans*-1,2-di-*tert*-butylethylene, as determined by calorimetric methods,[4a] is close to 40 kcal/mol.

[14] G. S. Hammond, *J. Amer. Chem. Soc.*, 77, 334 (1955).

[15] (a) From any cleavage initiated at an oxygen–oxygen bond, products other than methoxy hydroperoxide and carbonyl compound should be formed in the presence of methanol. This has never been found to occur in normal ozonolysis,[7-10] and mass balances based on the production of methoxy hydroperoxides and carbonyl compounds and on the consumption of olefin have been proved satisfactory in all cases investigated. The lower thermal stability of the 1,2,3-trioxolanes, as compared to their aliphatic O_3 analogs $R_3COOOCR_3$, is attributed to (i) the assistance to its decomposition from concerted cleavage of the central C–C bond, and (ii) the prevention of the normal skew conformation of the O–O–O chain by the constraint of the five-membered ring.[15b] (b) P. D. Bartlett and P. Günther, *J. Amer. Chem. Soc.*, **88**, 3288 (1966).

[16] There is no indication (*e.g.*, solvent or temperature effects[8,9]) that the presence of alcohol in the solvent contributes in distributing the pathways of cleavage. This is also illustrated by the cleavage of the primary ozonides of ring-substituted *trans*-stilbenes in the presence of methanol.[7b] If the product-determining step were the S_N2 attack of ROH on a trioxolane C atom, the preferential products should be p-$NO_2C_6H_4CH(OCH_3)OOH$ + PhCHO for the *p*-nitrostilbene, and $C_6H_5CH(OCH_3)OOH$ + p-$CH_3C_6H_4CHO$ for *p*-methyl-*trans*-stilbene. These expectations, on the ground of an S_N2 reaction, are contrary to the experiments, since only 9 (±2)% of the products expected with the former olefin and 39 (±2)% of the products indicated for the *p*-methyl *trans*-stilbene are produced. Hence, the cleavage must be completed or, at least, almost completed at the stage of the alkoxy hydroperoxide formation.

(iii) The relative "hyperconjugative stability" conferred by the substituents in the transition states. This term is used, with all the tacit reservations which may seem appropriate, in those cases where the formation of zwitterions is favored by substituents in the order $CH_3 > C_2H_5 > i\text{-}C_3H_7 > tert\text{-}C_4H_9$. This order of stabilizing ability prevails in the cleavage of the primary ozonides of trans and cis 1,2-disubstituted ethylenes.[9]

The scope of the present work is to compare quantum chemical information with the observed reactivities of the primary ozonides, as revealed by the experimental distributions of reaction paths. For convenience, the electrocyclic cleavage, the inductive effects, and the hyperconjugative stabilization are discussed in separate sections. Attention is focussed on the behavior of aliphatic substituents, such as the methyl, ethyl, *n*-propyl, isopropyl, and *tert*-butyl groups, for which effects other than resonance are important.

Experimental Section

Method of Calculation. The calculations were made with the aid of a CDC-6400 computer using the extended Hückel molecular orbital (EHMO) program developed by Hoffmann.[17] The reliability of this method for predicting the shape[18] and reactivity[19] of molecules has been the object of earlier discussions. The valence state ionization potentials are taken according to Pritchard and Skinner,[20] and Slater's exponential parameter μ according to Mulliken,[21] as indicated in ref 6. In the approximation $H_{ij} = 0.5K(H_{ii} + H_{jj})S_{ij}$, the Wolfsberg–Helmholtz proportionality coefficient K has been taken as 1.75.[17] Details about the interatomic distances and the conformations of the primary ozonides are indicated in a previous work.[6] Unless specified otherwise, the Mulliken overlap populations and the gross electron densities which are discussed are those of the most stable conformation of the primary ozonides. In selected cases, the gross electron densities were also calculated by a CNDO/2 method,[22] using the preferred conformation of the primary ozonides, as determined by Hoffmann's LCAO–EHMO method.

For the comparison with the quantum chemical information, the experimental results are expressed in terms of log $[x/(1 - x)]$, where x = the proportion of cleavage giving a specified zwitterion. As shown in earlier papers,[7] it can be deduced from the theory of Wynne-Jones and Eyring[23] that

$$\log [x/(1 - x)] = -(\Delta G_a^{\ddagger} - \Delta G_b^{\ddagger})/2.3RT = -\Delta\Delta G^{\ddagger}/2.3RT \quad (1)$$

where $\Delta G_a^{\ddagger}$ and $\Delta G_b^{\ddagger}$ represent the activation free energies accompanying the formation of transition states corresponding to paths a and b. This theoretical equation has been compared with experimental observations and has been found to give satisfactory results.[7,8] Equation 1 may also be expressed as follows[8]

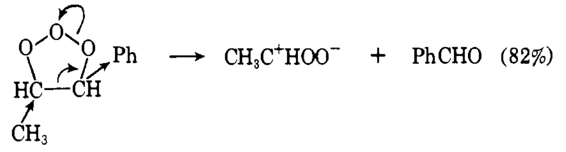
$$\log [x/(1 - x)] = \Delta\Delta S^{\ddagger}/2.3R \quad (2)$$

owing to the fact that the quantity $x/(1 - x)$ is independent of temperature, where $\Delta\Delta S^{\ddagger}$ ($= \Delta S_a^{\ddagger} - \Delta S_b^{\ddagger}$) is the activation entropy difference between transition states corresponding to paths a and b.

The quantity log $[x/(1 - x)]$ appears to be a suitable variable for expressing the experimental results because it is related to properties which depend directly on the substituents. More precisely, log $[x/(1 - x)]$ can be regarded as a convenient measure for the difference in the substituent effects which operate on the two carbon atoms of the trioxolane ring.

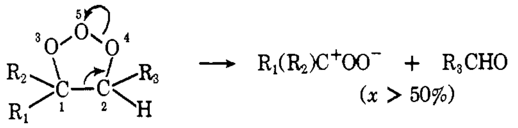
Results and Discussion

Electrocyclic Cleavage of Primary Ozonides. The electron circulation which is believed to occur in the cleavage of primary ozonides is usually represented as in the following example, which is typical for a codirectional electrocyclic cleavage.[7,24]



In order to study in what manner the organic chemist's description of the preferential way of cleavage is reflected by the quantum chemical information, the experimental results are, in the following, compared to the Mulliken overlap populations in the 1,2,3-trioxolane ring, calculated by means of Hoffmann's EHMO program. The atoms and the substituents are numbered as follows.

Scheme II



The experimental directions of cleavage are expressed in terms of log $[x/(1 - x)]$. The quantity x represents the proportion of cleavage which yields the zwitterion $R_1(R_2)C^+OO^-$, which, in every case, is the one formed in preference. Hence, in Table I, the results are ordered so as to reflect that the direction of cleavage indicated by the arrows is the preferential one, occurring thus in a proportion $x > 0.5$. The quantity Δn indicated in Table I is the difference in overlap population between C_1–O_3 and C_2–O_4.

From a consideration of the Δn values calculated for the monosubstituted ethylenes **1–5** it appears that, under the influence of the alkyl substituents, the difference in the Mulliken overlap populations between the C_1–O_3 and the C_2–O_4 bonds increases as the electron-releasing ability of the substituent increases. This is clearly indicated by the correlation between the Δn values and Taft's polar σ^* constants[25] of the substituents (Figure 1).

As indicated by their log $[x/(1 - x)]$ values, in alkyl-monosubstituted ethylenes the formation of the zwitterion $R_1C^+HOO^-$ is favored by R_1 in the order $CH_3 < C_2H_5 < i\text{-}C_3H_7 < tert\text{-}C_4H_9$, *i.e.*, in the inductive order. Hence, the preferential electrocyclic cleavage gains in importance as the C_2–O_4 overlap is poorer, as compared to the C_1–O_3 overlap (Figure 2).

The arrow representing the direction of the preferred cleavage of the C_1–C_2 bond is, in all cases, directed toward the C–O bond with the lowest overlap population. The comparison of the O_3–O_5 and O_4–O_5 overlap populations indicates that, in the process of completing the electrocyclic cleavage, the oxygen–oxygen bond

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(17) (a) R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.*, **36**, 2179, 3489 (1962); (b) R. Hoffmann and W. N. Lipscomb, *ibid.*, **37**, 2872 (1962); (c) R. Hoffmann, *ibid.*, **39**, 1397 (1963).

(18) L. C. Allen and J. D. Russel, *ibid.*, **46**, 1029 (1967); G. Blyholder and C. A. Coulson, *Theor. Chim. Acta*, **10**, 316 (1968).

(19) L. B. Kier, *Tetrahedron Lett.*, 1233, 1236 (1967); K. Fukui, H. Hao, and H. Fujimoto, *Bull. Chem. Soc. Jap.*, 40, 2787 (1967), and references therein; K. Fukui and H. Fujimoto, *ibid.*, 42, 348 (1969); A. G. Hopkinson, R. A. McClelland, K. Yates, and I. G. Csizmadia, *Theor. Chim. Acta*, **13**, 65 (1969).

(20) G. Pritchard and H. A. Skinner, *J. Inorg. Nucl. Chem.*, **24**, 937 (1962).

(21) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833, 1841, 2338, 2343 (1955).

(22) J. A. Pople, D. P. Santry, and G. A. Segal, *ibid.*, **43**, S129, S136 (1965).

(23) W. F. K. Wynne-Jones and H. Eyring, *ibid.*, **3**, 492 (1935).

(24) W. P. Keaveney, M. G. Berger, and J. J. Pappas, *J. Org. Chem.*, **32**, 1537 (1967).

(25) R. W. Taft, *J. Amer. Chem. Soc.*, **75**, 4231 (1953).

Table I. Mulliken Overlap Populations

	R_1	R_2	R_3	log [x/ (1 − x)]	C_1–C_2	C_1–O_3	C_2–O_4	O_3–O_5	O_4–O_5	$10^3\Delta n$
1	CH_3	H	H	0.212	0.7876	0.4732	0.4674	0.4066	0.4088	5.8
2	C_2H_5	H	H	0.231	0.7854	0.4748	0.4673	0.4043	0.4089	7.5
3	n-C_3H_7	H	H	0.176	0.7854	0.4748	0.4673	0.4041	0.4088	7.5
4	i-C_3H_7	H	H	0.250	0.7860	0.4757	0.4679	0.4033	0.4076	7.8
5	*tert*-C_4H_9	H	H	0.368	0.7880	0.4767	0.4649	0.4021	0.4079	11.8
6	CH_3	H	C_2H_5	0.105	0.8117	0.4726	0.4745	0.4057	0.4031	−1.9
7	CH_3	H	n-C_3H_7	0.176	0.8117	0.4726	0.4744	0.4056	0.4029	−1.8
8	CH_3	H	i-C_3H_7	0.389	0.8090	0.4745	0.4734	0.4060	0.4069	1.1
9	CH_3	H	*tert*-C_4H_9	0.865	0.8140	0.4771	0.4717	0.4021	0.4069	5.4
10	C_2H_5	H	i-C_3H_7	0.278	0.8076	0.4738	0.4734	0.4063	0.4068	0.4
11	C_2H_5	H	*tert*-C_4H_9	0.825	0.8125	0.4763	0.4717	0.4026	0.4067	4.6
12	H	CH_3	C_2H_5	0.035	0.8054	0.4759	0.4757	0.4057	0.4045	0.2
13	H	CH_3	n-C_3H_7	0.070	0.8054	0.4759	0.4755	0.4057	0.4042	0.4
14	H	CH_3	i-C_3H_7	0.122	0.8052	0.4746	0.4754	0.4074	0.4051	−0.8
15	H	*tert*-C_4H_9	CH_3	0.213	0.7837	0.4672	0.4631	0.3557	0.2636	4.1
16	H	*tert*-C_4H_9	C_2H_5	0.235	0.7923	0.4657	0.4691	−0.0575	−0.0946	−3.4
17	CH_3	CH_3	CH_3	0.525	0.8330	0.4816	0.4744	0.4037	0.4058	7.2
18	CH_3	CH_3	C_2H_5	0.630	0.8316	0.4817	0.4736	0.4036	0.4064	8.1
19	CH_3	CH_3	i-C_3H_7	1.5	0.8314	0.4817	0.4744	0.4041	0.4051	7.3
20	CH_3	CH_3	*tert*-C_4H_9	∞	0.8147	0.4802	0.4696	−0.1012	−0.1040	10.6
21	CH_3	C_2H_5	CH_3	0.908	0.8312	0.4826	0.4741	0.4019	0.4058	8.5
22	C_2H_5	CH_3	CH_3	0.689	0.8331	0.4810	0.4756	0.4049	0.4064	5.4
23	$(CH_2)_5$		H	1.5	0.7967	0.4788	0.4597	0.4039	0.4070	19.1
24	$(CH_2)_5$		CH_3	1.06	0.8205	0.4783	0.4688	0.4030	0.4044	9.5

having the highest overlap in the initial state, *i.e.*, O_4–O_5, is consistently cleaved in preference to O_3–O_5. The correlation between the familiar schematic representation of the preferential electrocyclic cleavage and the Mulliken overlap population analysis of the primary ozonide ring is, hence, as shown in Scheme III (L = low, H = high overlap population).

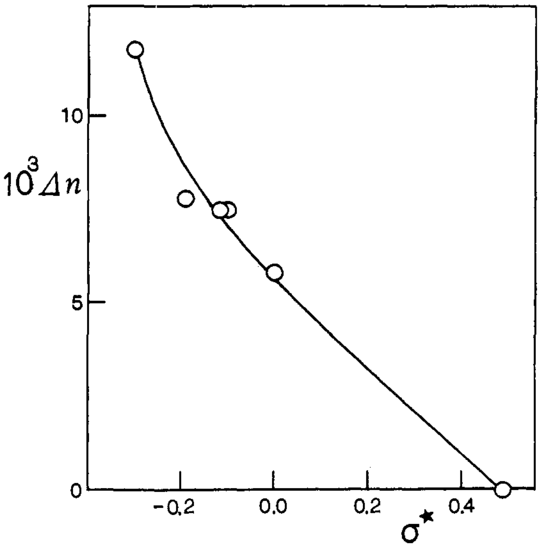
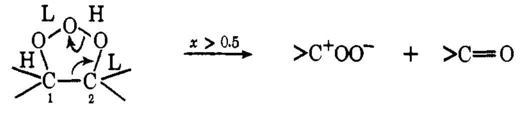


Figure 1. Correlation between Δn and Taft's polar σ^* constants. The primary ozonide of ethylene, being symmetrical, has necessarily the same Mulliken overlap population on both C–O bonds, hence $\Delta n = 0$.

Scheme III



A similar correlation between the log [x/(1 − x)] and the Δn values is also observed for the trans 1,2-disubstituted ethylenes **6–11** (Figure 2). With these olefins, however, the ability of the substituents in favoring the formation of the corresponding zwitterions increases in the order: *tert*-C_4H_9 < i-C_3H_7 < C_2H_5 < CH_3, *i.e.*, in the hyperconjugative order.[9] This is indicated (Table I) by the increase of the proportion (x) of $CH_3C^+HOO^-$ zwitterion which is formed as R_2 is changed from ethyl to *tert*-butyl, and by the comparison of the log [x/(1 − x)] values for **10–11** with those of **8** and **9**. In this respect, the trans 1,2-disubstituted ethylenes contrast markedly from the monosubstituted ethylenes, since for the latter the substituents favor the formation of the corresponding zwitterions in the inductive order.

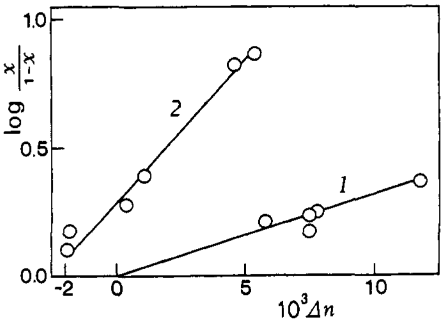
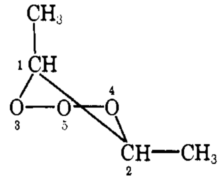


Figure 2. Log [x/(1 − x)] *vs.* difference in overlap population Δn for monosubstituted (1) and trans 1,2-disubstituted primary ozonides (2). For the symmetrical ethylene primary ozonide the cleavage is necessarily 50% each way, hence log [x/(1 − x)] = 0 for Δn = 0.

This observation explains the fact that for *trans*-2-pentene (**6**) and *trans*-2-hexene (**7**) positive log [x/(1 − x)] values are observed although their corresponding Δn values are negative. The experimental log [x/(1 − x)] values reflect both the inductive and the hyperconjugative ability of the substituents. The predominance of the hyperconjugative over the inductive effect results in a substantial increase of the log $[x/(1 - x)]$ value; indeed, for **6–11**, all these values would be negative under the influence of the inductive effects alone. Hence, it may be considered that the predominance of the hyperconjugative over the inductive effect explains the positive log $[x/(1 - x)]$ values observed for **6** and **7** in the region of negative Δn values.

These two cases (**6** and **7**) are the only major exceptions to the rule depicted in Scheme III. This is indicated by the positive Δn values which result from the calculation of the primary ozonides **1–5**, **8–13**, and **17–24**. The primary ozonides **15**, **16**, and **20** are not to be considered in the discussion of this rule, although **15** and **20** obey it. Their conformational analysis,[6] as well as the experiment, indicates that for cis primary ozonides with a *tert*-butyl group no "stable" conformation exists: once the ozone is added onto the carbon–carbon double bond, there is a continuous evolution toward cleavage. Hence, no "most stable" conformation can be calculated for **15**, **16**, and **20**, to be used for the evaluation of this rule. Because of the similarity of the steric interactions between the substituents in *cis*-4-methyl-2-pentene primary ozonide (**14**) with those of its ill-behaved *tert*-butyl analog (**15**), the significance of $\Delta n = -0.8$ for **14** may be questioned: a distortion[26] of the ring, during the cleavage, from 25 to 27.5° would cause Δn to change from -0.8 to $+0.8$.

It is concluded that, in general, the rule of cleavage in terms of Mulliken overlap populations reflects satisfactorily the preferential electrocyclic cleavage described in Scheme III. Despite the crudeness of the model, this rule provides a useful means for predicting the preferential course of cleavage. This is illustrated by the following example: the cleavage of *cis*-2-butene primary ozonide.



C_1—O_3 0.4757

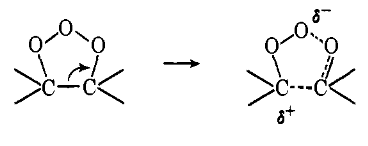
C_2—O_4 0.4729

O_3—O_5 0.4051

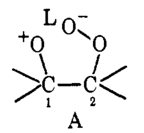
O_4—O_5 0.4069

The positive Δn value (2.8×10^{-3}) indicates that the axial methyl group is incorporated into the zwitterion moiety in preference to the equatorial methyl group. A consideration of the magnitude of this Δn value, in comparison with the Δn values calculated for *cis*-2-pentene (**12**) and *cis*-2-hexene (**13**), also indicates that the disymmetry in the cleavage is important. From a rough extrapolation, using the Δn values for **12** and **13**, approximately 76% of the cleavage would appear to occur with the retention of the axial methyl group in the zwitterion.[27] The only justification for presenting this extrapolation is that it happens to agree surprisingly well with the value (78%) previously determined.[30]

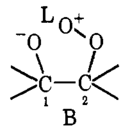
There is one more important point which can be discussed in terms of the present results. The correlation between the overlap populations and the experimental log $[x/(1 - x)]$ values, as represented in Scheme III, implies that the stronger O_4–O_5 bond in the initial state is cleaved in preference to the weaker one, O_3–O_5. This would be contrary to accepted views, if the cleavage were assumed to begin with the rupture of an oxygen–oxygen bond. In the present description of the cleavage, however, it is assumed that the cleavage is initiated at the carbon–carbon bond,[15] which would cause, during the cleavage, a redistribution of the electrons in the transition state, possibly weakening the O_4–O_5 bond.



If, on the contrary, it is assumed that the cleavage of the primary ozonide ring begins with the rupture of an oxygen–oxygen bond,[31] the bond to be cleaved would be the weakest one (L), to give A or B.



A



B

Neither one of these two forms is in agreement with the experimental fact that the preferred zwitterion is $>C_1{}^+OO^-$, even if imaginative arrow pushing were able to explain the next step to give $>C_1{=}O$ + $>C_2{}^+OO^-$.[33] It is concluded that a consideration of the Mulliken overlap populations is consistent with Criegee's mechanism of ozonolysis, initiated by the C–C bond cleavage, whereas a consideration of any cleavage initiated at the weakest O–O bond is contradictory to the experimental direction of cleavage.

The Inductive Effect. In the following, gross electron densities are used for determining in what manner Hoffmann's EHMO and the CNDO/2 methods of calculation reproduce the electron-releasing ability of the alkyl groups. Taft's polar σ^* constants are used for comparison, since these quantities are derived from observed chemical reactivities. Before discussing the primary ozonides, the simple example of hydrocarbons is considered.

The gross electron densities which were calculated by Hoffmann[17c] for a series of hydrocarbons are indicated in Table II.

All these hydrocarbons have the structure RCH_3. The *net charge* for each R group, indicated by $\delta(R)$, is calculated from the gross electron densities reported in

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[26] This distortion is defined by the dihedral angle between the planes $C_1C_2O_5$ and $C_1C_2O_3$ (or $C_1C_2O_4$).

[27] This seems to be in violation with the Bailey–Bauld 2nd rule.[28] It must be remembered, however, that these authors explicitly stated that this rule holds only for ethylenes with sufficiently large substituents. In fact, also in the case of *cis*-2-pentene a slight preference in favoring the incorporation of the axial methyl group into the zwitterion moiety has been detected.[9] It also results from the Bailey–Bauld stereochemical analysis of the cleavage of cis primary ozonides that axial substituents favor the production of syn zwitterions which react with aldehydes to give in preference trans ozonides. Hence, in the case of *cis*-2-butene primary ozonide, the high proportion of zwitterion retaining the axial methyl group is expected to result in the production of significantly more *trans*-2-butene ozonide than cis ozonide. This is indeed observed:[29] 61% of *trans*- and 39% of *cis*-2-butene ozonide are produced in the ozonolysis of *cis*-2-butene in pentane solution, at −70°.

[28] N. L. Bauld, J. A. Thompson, C. E. Hudson, and P. S. Bailey, *J. Amer. Chem. Soc.*, **90**, 1822 (1968).

[29] R. W. Murray, R. D. Youssefyeh, and P. R. Story, *ibid.*, **88**, 3143 (1966).

[30] M. Granger and S. Fliszár, in preparation.

[31] Such a cleavage is considered in the Murray–Story–Youssefyeh mechanism of ozonolysis.[32]

[32] P. R. Story, R. W. Murray, and R. D. Youssefyeh, *J. Amer. Chem. Soc.*, **88**, 3144 (1966); R. W. Murray, R. D. Youssefyeh, and P. R. Story, *ibid.*, **89**, 2429 (1967).

[33] The formation of zwitterion and carbonyl compound is a must, in order to account for the mass balances.

Table II. Gross Electron Densities for Selected Hydrocarbons[a,b]

Hydrocarbon	R	C-1	C-2	H-1	H-2	$10^3\delta(R)$
$CH_3\overset{2}{C}H_2\overset{1}{C}H_3$	C_2H_5	4.373	4.185		0.895	12
$CH_3CH_2\overset{2}{C}H_2\overset{1}{C}H_3$	n-C_3H_7	4.372	4.202	0.880		12
$(CH_3)_2\overset{2}{C}H\overset{1}{C}H_3$	i-C_3H_7	4.388	4.019	0.879	0.908	23
$(CH_3)_3\overset{2}{C}\overset{1}{C}H_3$	*tert*-C_4H_9	4.403	3.863	0.877		35

[a] See ref 17c. [b] H-1 is attached to C-1, H-2 to C-2.

Table III. Net Partial Charges δ of the Substituents in the Primary Ozonides of Monosubstituted Ethylenes

		$10^3\delta(R)$		$10^3\delta(H)^a$		
	R_1	EHMO	CNDO/2	H_{ax}^{gem}	H_{ax}	H_{eq}
1	CH_3	+3.5	+19.5	−9.8	−3.9	+6.2
2	C_2H_5	+20.6	+28.9	−10.2	−4.5	+5.8
3	n-C_3H_7	+19.4	+34.2	−10.7	−5.1	+5.4
4	i-C_3H_7	+33.4	+36.3	−10.0	−4.5	+6.0
5	*tert*-C_4H_9	+48.0	+42.5	−14.2	+0.3	+5.8

[a] Calculated by the CNDO/2 method.

this table. The positive $\delta(R)$ values represent the loss of electrons by R toward the methyl group and can, hence, be considered as a measure of the inductive ability of R. In isobutane, for example, $\delta(R) = +23 \times 10^{-3}$ means that the i-C_3H_7 group has released 23×10^{-3} electron to the methyl group. For R = CH_3, it is $\delta(R) = 0$ because both methyl groups are equivalent in ethane.

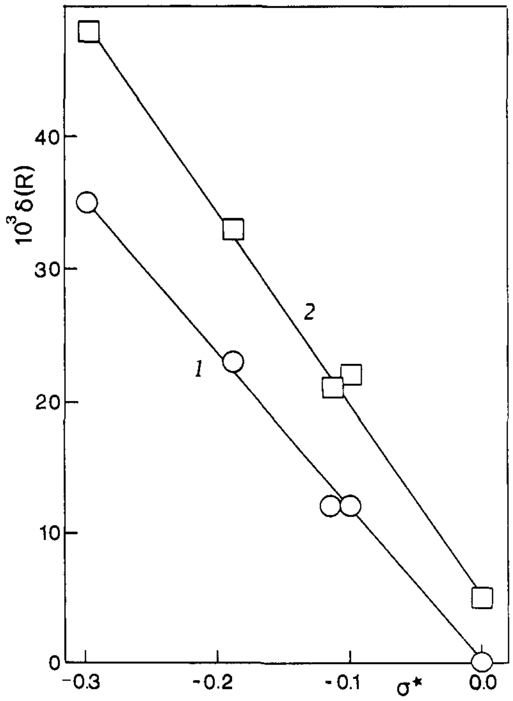

Figure 3. Net (EHMO) electron release $\delta(R)$ by the substituents in hydrocarbons (1) and in primary ozonides (2) *vs.* Taft's σ^* constants.

A comparison of these $\delta(R)$ values with Taft's σ^* constants (Figure 3) indicates that Hoffmann's EHMO calculation reproduces correctly the inductive effect, this, although the charge separations which are calculated by this program are admittedly likely to be overemphasized.

A similar correlation between the $\delta(R)$ and Taft's σ^* values is also observed for the substituents in the primary ozonides. The net partial charges of the substituents in monosubstituted primary ozonides are indicated in Table III.

The proportion of retention of the substituent R_1 into the zwitterion moiety increases in the Taft order[9] $CH_3 < \ldots <$ *tert*-C_4H_9; hence, the correlation between the $\log[x/(1-x)]$ values (Table I) and the $\delta(R)$ values is evident. It is noted, incidentally, that the experimental result for the n-C_3H_7 group correlates better with the EHMO than with the CNDO/2 value for $\delta(R)$, but this indication is probably not significative. It is interesting to observe that, of the two H atoms attached to C-2, the equatorial one appears to be a better electron donor than the axial one. In the following, this observation is found to apply to any alkyl group and appears to be a significant conformational effect, capable of explaining some experimental facts. In the primary ozonides of monosubstituted ethylenes, however, no such conformational effect can be observed for the alkyl substituents, since they are all in preferential equatorial position.[6]

The difference between axial and equatorial substituents is revealed, both by the EHMO and the CNDO/2 methods, by the $\delta(R)$ values which are calculated for the trans and cis 1,2-disubstituted ethylenes (Tables IV and V).

The equatorial substituents in trans and cis primary ozonides exhibit practically constant $\delta(R)$ values, which are very similar to those calculated for monosubstituted primary ozonides. Their "average" $\delta(R)$ values are reported in Table VI.

The EHMO calculations indicate that the $\delta(R)$ values for the axial substituents are very similar in trans and cis primary ozonides. Whether the axial methyl and ethyl groups are really electron withdrawing with respect to the 1,2,3-trioxolane ring is an open question. In any case, it appears clearly that any substituent is a better electron donor when in equatorial than when in axial position. From the average $\delta(R)$ values which are summarized in Table VI, it appears that $\delta_{ax} \approx \delta_{eq} - 28$ (10^{-3} electron-unit). A similar behavior has been pointed out for the hydrogen atoms

Table IV. Net Partial Charges δ ($\times$ 10^3) on the Substituents in the Primary Ozonides of Trans-1,2-Disubstituted Ethylenes

	R_1	R_2	Conform[a]	EHMO		CNDO/2	
				$\delta(R_1)$	$\delta(R_2)$	$\delta(R_1)$	$\delta(R_2)$
	CH_3	CH_3	e,e	+5.5	+5.5	+17.3	+17.3
6	CH_3	C_2H_5	e,e	+5.0	+22.8	+16.8	+26.5
7	CH_3	*n*-C_3H_7	e,e	+5.0	+21.6	+16.2	+32.1
	CH_3	CH_3	a,a	−21.0	−21.0	+7.4	+7.4
8	CH_3	*i*-C_3H_7	a,a	−21.8	+3.2	+6.1	+22.7
9	CH_3	*tert*-C_4H_9	a,a	−20.7	+20.7	+5.2	+28.8
	C_2H_5	C_2H_5	e,e	+22.3	+22.3	+26.0	+26.0
	C_2H_5	C_2H_5	a,a	−7.7	−7.7	+14.6	+14.6
10	C_2H_5	*i*-C_3H_7	a,a	−7.5	+2.9	+14.6	+21.5
	i-C_3H_7	*i*-C_3H_7	a,a	+6.0	+6.0	+23.4	+23.4
	tert-C_4H_9	*tert*-C_4H_9	a,a	+21.8	+21.8	+27.0	+27.0
11	C_2H_5	*tert*-C_4H_9	a,a	−7.6	+21.3	+13.8	+27.3

[a] The conformational analysis[6] indicated that the a,a and the e,e conformations of 2-butene and 3-hexene are equally stable.

Table V. Net Partial Charges δ ($\times$ 10^3) on the Substituents in the Primary Ozonides of Cis 1,2-Disubstituted Ethylenes

	R_{ax}	R_{eq}	EHMO		CNDO/2			
			$\delta(R_{ax})$	$\delta(R_{eq})$	$\delta(R_{ax})$	$\delta(R_{eq})$	$\delta(H_{ax})$	$\delta(H_{eq})$
	CH_3	CH_3	−21	+6	+10.3	+16.3	−16.8	−2.8
	C_2H_5	C_2H_5	−8	+23	+17.8	+24.5	−17.9	−3.2
12	CH_3	C_2H_5	−19	+24	+12.5	+24.0	−12.7	−3.4
13	CH_3	*n*-C_3H_7	−19	+23	+11.8	+29.6	−13.1	−3.8
14[a]	*i*-C_3H_7	CH_3	−11	+24	+28.5	+13.9	−13.1	−2.1

[a] Note the exceptional δ values for compound **14**, whose particular behavior has been pointed out in the discussion of the electrocyclic cleavage.

Table VI. Net Partial Charges δ ($\times$ 10^3) on the Alkyl Substituents

R	EHMO		CNDO/2		
	eq	ax	eq	ax, trans	ax, cis
CH_3	5	−21	17	6	11
C_2H_5	22	−7	26	14	18
n-C_3H_7	21		32		
i-C_3H_7	33	4	36	23	29
tert-C_4H_9	48	21	43	29	

Table VII.[a] Direction of Cleavage (x) of the Primary Ozonides of Selected Trans and Cis Ethylenes $R_1CH{=}CHR_2$

R_1	R_2	Proportion of $CH_3C^+HOO^-$ formed from Trans	Cis
CH_3	C_2H_5	0.56 ± 0.02	0.52 ± 0.02
CH_3	*n*-C_3H_7	0.60 ± 0.03	0.54 ± 0.02
CH_3	*i*-C_3H_7	0.71 ± 0.01	0.57 ± 0.01
CH_3	*tert*-C_4H_9	0.88 ± 0.01	0.38 ± 0.01

[a] Results extracted from ref 9. No "stable" primary ozonide corresponds to *cis*-4,4-dimethyl-2-pentene.[6]

in monosubstituted ethylenes and is also found for the H atoms in cis primary ozonides (Table V).

The CNDO/2 calculations, contrasting with the EHMO results, indicate that all the axial substituents release electrons toward the trioxolane ring ($\delta > 0$), slightly better in the cis than in the trans isomeric primary ozonides. The approximate relations, which are revealed by the summary given in Table VI, between the axial and the equatorial $\delta(R)$ values are: $\delta_{ax} \approx \delta_{eq} - 12.5$ (trans) and $\delta_{ax} \approx \delta_{eq} - 7$ (cis).

For the discussion of the reactivity of the primary ozonides, only the most significant of the present results is retained, *i.e.*, $\delta_{eq} > \delta_{ax}$, on which both methods of calculation agree.

This result bears some resemblance with the second rule in the Bailey–Bauld analysis[28] of the conformational effects which participate in directing the cleavage of cis primary ozonides. This rule, which states that "in cis primary ozonides an equatorial substituent is incorporated into a zwitterion moiety in preference to an axial substituent," has been verified in a number of cases,[9] for sufficiently large substituents. It now appears that the Bailey–Bauld second rule reflects the "inductive contribution," $\delta_{eq} > \delta_{ax}$. The difficulty of generalization can be attributed to the fact that the cleavage is not determined solely by the inductive effects.

The result that $\delta_{eq} > \delta_{ax}$ is not unexpected. It might be considered that an electromeric effect would result from an overlap between, and general delocalization of, the π components of the molecular orbitals. These π components are perpendicular to the plane of the σ components of any of the atoms in question. Thus, an electromeric effect into C-1 and C-2 and subsequently into the O_3 bridge of a "relatively planar" molecule, such as the 1,2,3-trioxolane, would be dependent upon the relative positions in space of the contributing groups. The O_3 bridge, of course, would be expected to direct its π components toward the axial position. Thus, substitutions on C-1 and C-2 in the axial position would be expected to show little electromeric effect upon the cycle, since its π components are nearly orthogonal to the main π network of the ring. The equatorial position, however, would be expected to show a maximal delocalization of the π components.

The results indicating that $\delta_{eq} > \delta_{ax}$ are consistent with the experimental distributions of cleavage of the cis and trans isomeric primary ozonides of 2-pentene and 2-hexene (Table VII).

Table VIII. Gross Electron Populations, Calculated by Means of Hoffmann's EHMO Program

Compd	C-1	C-2	O-3	O-4	C(R-1)	C(R-2)	H-1	H-2
1	3.4309	3.5906	6.6041	6.5971	4.3430	0.8865	0.9184	0.9000[a]
2	3.4483	3.5894	6.6046	6.5970	4.1771	0.8866	0.9166	0.8999[a]
3	3.4467	3.5895	6.6048	6.5971	4.1943	0.8866	0.9166	0.8999[a]
4	3.4627	3.5940	6.5977	6.6041	4.0215	0.8803	0.9144	0.8986[a]
5	3.4727	3.6274	6.5976	6.6039	3.8683	0.8730	0.9135	0.8778[a]
6	3.4454	3.4642	6.6049	6.6056	4.3504	4.1839	0.9142	0.9125
7	3.4455	3.4625	6.6050	6.6058	4.3504	4.2010	0.9142	0.9125
8	3.4416	3.4790	6.5916	6.5891	4.3682	4.0454	0.8996	0.8981
9	3.4727	3.4891	6.5949	6.5899	4.3669	3.8959	0.8713	0.8971
10	3.4597	3.4780	6.5898	6.5893	4.2030	4.0456	0.8982	0.8982
11	3.4972	3.4881	6.5929	6.5901	4.2017	3.8960	0.8700	0.8972
12	3.4396	3.4597	6.6091	6.6112	4.4003	4.2011	0.8999	0.9119
13	3.4397	3.4581	6.6091	6.6115	4.4003	4.2181	0.8998	0.9119
14	3.4346	3.4786	6.6094	6.6082	4.3814	4.0552	0.9145	0.8950

[a] Axial H atom on C-2. The ring atom numbering is indicated in Scheme II. For compounds **1** to **5**, the atom R-2 is the equatorial H attached to C-2; for the other compounds, C(R-2) is the C atom of R attached to C-2. C(R-1) is the C atom of R attached to C-1.

For both isomers it appears that the inductive effects of the substituents cancel each other to a certain extent, leaving thus the "hyperconjugative stabilization" to be the predominant factor in distributing the reaction paths. For the trans isomers, it is irrelevant whether both substituents are in axial or in equatorial position, since the change from equatorial to axial position is accompanied, for all substituents, by the same decrease in inductive effect.

In the *cis*-2-pentene and *cis*-2-hexene primary ozonides, however, the methyl group loses some of its inductive effect because of its axial position, whereas the ethyl, or the *n*-propyl, group is in equatorial position. Hence, the mutual partial cancellation of inductive effects is expected to be somewhat reduced in these cis primary ozonides, with respect to their trans isomers. This is confirmed by the lower $CH_3C^+HOO^-$ zwitterion production in the cis case, as compared to trans.

For the primary ozonide of *cis*-4-methyl-2-pentene no definite simple interpretation can be offered. In this primary ozonide the isopropyl group is found to be in preferred axial conformation. Hence, the production of $CH_3C^+HOO^-$ should be higher in the cis than in the trans case, because of the loss of opposing inductive effect contributed by the isopropyl group. On the other hand, however, the negative value of Δn which was discussed above should tend to reduce the formation of the $CH_3C^+HOO^-$ zwitterion.

The Hyperconjugative Stabilization of Zwitterionic Carbonium Ions. It is attempted, in the following, to correlate (i) the hyperconjugative effects revealed by the experimental proportions of cleavage of primary ozonides to (ii) the gross electron distributions in these molecules. The primary ozonides of trans and cis 1,2-disubstituted ethylenes are considered in the first place, because the results (Table VII) clearly indicate that the formation of zwitterions RC^+HOO^- is favored by the substituents R in the order $CH_3 > C_2H_5 > i\text{-}C_3H_7 > tert\text{-}C_4H_9$.

Little comparison with "accepted views" on hyperconjugation is presented, since organic chemists seem to disagree on what hyperconjugation really is. The Baker–Nathan effect[34] has been discussed in detail in terms of C–C or C–H hyperconjugation and, by Schubert, *et al.*,[35] in terms of steric hindrance in the solvolysis. Dewar[36] considers that "there is in any case no reason for believing that hyperconjugation could account for the Baker–Nathan effect even if it were significant." The common interpretation of the Baker–Nathan effect[37,38] in terms of net electron release in the order $CH_3 > \ldots > tert\text{-}C_4H_9$ and the conclusion[39] that "hyperconjugation of C–H bonds provides the most consistent and satisfactory explanation" have been seriously questioned.[35,40,41] Hoffmann[42] has also pointed out the weakness of the usual argument that electron donation toward a positive site is the effect that explains the relative stabilities to carbonium ions.

In the present discussion of the hyperconjugative effect, only the electron distributions in the *initial* 1,2,3-trioxolanes are considered. Hence, no speculative hyperconjugative philosophy is developed, which would distort the familiar concept that "electroneutrality is a good thing" in the sense that *during* the cleavage an electron source next to a positive site should release electrons to it and that, in the final analysis, the best way of stabilizing a positive site is to get rid of it as much as possible. The point of view which is adopted may be named "fatalistic": basically, the electron distributions are those which correspond to the minimum total electronic energy of the molecule, even if this implies building up important negative charges next to positive sites. It is then pointless to argue that it might be better to have an electron release toward the positive site in order to satisfy the picture of electroneutrality. In the 1,2,3-trioxolanes, positive sites are more or less developed on both carbon atoms (Tables VIII and IX), under the influence of the substituents to which they are attached. Hence, it may

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(41) W. M. Schubert and R. Minton, *J. Amer. Chem. Soc.*, 82, 6188 (1960).

(42) R. Hoffmann, *J. Chem. Phys.*, 40, 2480 (1964).

Table IX. Gross Electron Populations, Calculated by Means of Pople's CNDO/2 Method

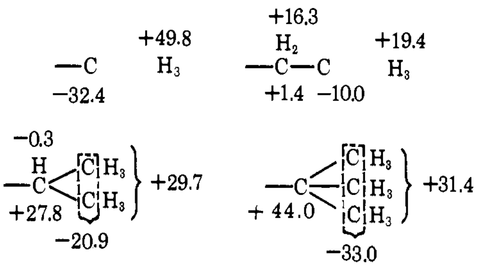
Compound	C-1	C-2	O-3	O-4	C(R-1)	C(R-2)	H-1	H-2
1	3.8441	3.8676	6.1317	6.1283	4.0315	0.9938	1.0098	1.0039[a]
2	3.8483	3.8698	6.1327	6.1285	3.9978	0.9942	1.0102	1.0045[a]
3	3.8515	3.8693	6.1331	6.1289	4.0015	0.9946	1.0107	1.0051[a]
4	3.8509	3.8697	6.1357	6.1296	3.9722	0.9940	1.0100	1.0045[a]
5	3.8518	3.8745	6.1366	6.1295	3.9560	0.9942	1.0142	0.9997[a]
6	3.8473	3.8493	6.1368	6.1377	4.0326	3.9991	1.0136	1.0134
7	3.8469	3.8525	6.1372	6.1380	4.0326	4.0027	1.0141	1.0138
8	3.8476	3.8523	6.1332	6.1341	4.0373	3.9779	1.0070	1.0111
9	3.8531	3.8533	6.1344	6.1367	4.0367	3.9627	1.0014	1.0108
10	3.8516	3.8544	6.1338	6.1339	4.0045	3.9779	1.0068	1.0118
11	3.8572	3.8554	6.1350	6.1365	4.0100	3.9627	1.0011	1.0116
12	3.8506	3.8512	6.1401	6.1379	4.0361	4.0006	1.0034	1.0127
13	3.8503	3.8543	6.1404	6.1382	4.0361	4.0042	1.0038	1.0131
14	3.8455	3.8548	6.1350	6.1419	4.0311	3.9759	1.0177	1.0022
$R_1 = R_2 = CH_3$ e,e	3.8452	3.8452	6.1367	6.1367	4.0327	4.0327	1.0131	1.0131
$R_1 = R_2 = CH_3$ a,a	3.8472	3.8472	6.1355	6.1355	4.0380	4.0380	1.0044	1.0044
$R_1 = R_2 = C_2H_5$ e,e	3.8514	3.8514	6.1378	6.1378	3.9990	3.9990	1.0139	1.0139
$R_1 = R_2 = C_2H_5$ a,a	3.8533	3.8533	6.1359	6.1359	4.0051	4.0051	1.0049	1.0049
$R_1 = R_2 =$ *i*-C_3H_7 a,a	3.8526	3.8526	6.1332	6.1332	3.9770	3.9770	1.0146	1.0146
$R_1 = R_2 =$ *tert*-C_4H_9 a,a	3.8603	3.8603	6.1380	6.1380	3.9621	3.9621	1.0057	1.0057
$R_1 = R_2 = CH_3$ a,e	3.8475[a]	3.8445	6.1378	6.1346	4.0349[a]	4.0313	1.0028	1.0168[a]
$R_1 = R_2 = C_2H_5$ a,e	3.8536[a]	3.8507	6.1384	6.1353	4.0031[a]	3.9991	1.0032	1.0179[a]

[a] Indicates axial position. The ring atom numbering is indicated in Scheme II. Definitions as in Table VIII. The compounds indicated by $R_1 = R_2 =$ alkyl refer to the primary ozonides of ethylenes $R_1CH{=}CHR_2$.

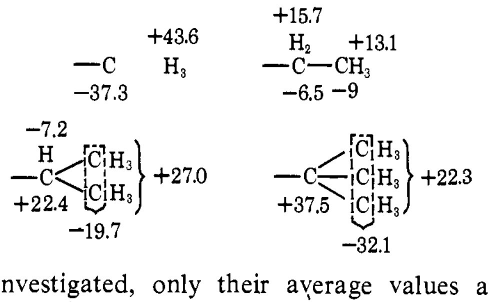
be justified to discuss the factors governing the stabilization of positive sites in this static situation.

To begin with, it appears interesting to consider the gross electron distributions in the alkyl substituents, as calculated by the CNDO/2 method (Schemes IV and V). Because of the similarity of these values in all cases investigated, only their average values are reported.[43] The net charges are expressed in 10^{-3} electron unit.

Scheme IV. Equatorial Substituents



Scheme V. Axial Substituents



For convenience, the carbon atoms which are attached to the trioxolane ring are identified by the subscript i, and the atoms attached to C_i by the subscript j.

Inspection of the net charges represented in Schemes IV and V indicates that the positive charge carried by C_i is greater as the total negative charge carried by the C_j's is increased. Conversely, positive charges neighboring C_i deplete the positive charge on C_i; this is well illustrated by the charge distributions on the methyl groups, where the C_i carry important negative charges.

The parallelism of the present results with Hoffmann's calculations[42] on the carbonium ions is self-explanatory. It also should be noted that, according to Hoffmann's results,[42] the energy gain in the stabilization of the carbo cations in the rehybridization $R_{tetr}^{+} \rightarrow R_{trig}^{+}$ is accompanied by the elaboration of a more positive charge on the carbonium ion. The fact that in the series of primary to tertiary carbonium ions the tertiary one, in which the central C atom carries the largest positive charge, is the most stable ion may suggest that stability and charge of carbonium ions are associated with the total negative charge carried by the neighbors. For the alkyl groups, as for the carbonium ions, this may be expressed as follows, in familiar terms: a positive site is favored in a situation in which it is best "inbedded" in a negative surrounding (and conversely for a negative site).

In quantitative terms, this concept may be represented by an equation relating the net charge q_{C_i} on C_i to the total net charge $\Sigma q_{C_j} + \Sigma q_{H_j}/k$ of the neighboring atoms. The factor k is introduced to account for the fact that an equal net charge on a carbon or on a hydrogen atom is likely not to have the same effect in favoring a site q_{C_i}. Different curves can be drawn, depending upon the choice of k. For $k = 2.4$, the charge q_{C_i} is linearly related to $\Sigma q_{C_j} + \Sigma q_{H_j}/2.4$ (Figure 4), but whether this choice of k is meaningful is an open question.[44]

When the same concept is used for discussing the effects of the alkyl substituents in favoring zwitterionic carbonium ions in the transition state, it appears that, because of its highly negative q_{C_i} value, the methyl

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[43] The relative constancy of the charges on the j atoms is of the same order as that observed for the C_i atoms.

[44] Similar results are obtained when the trioxolane C atom is included in the calculation of Σq_{C_j} because its positive charge is nearly constant for each individual substituent (*e.g.*, $+150 \pm 2 \times 10^{-3}$ electron when attached to an equatorial ethyl group) and depends little on the nature or position of the substituent (Table IX).

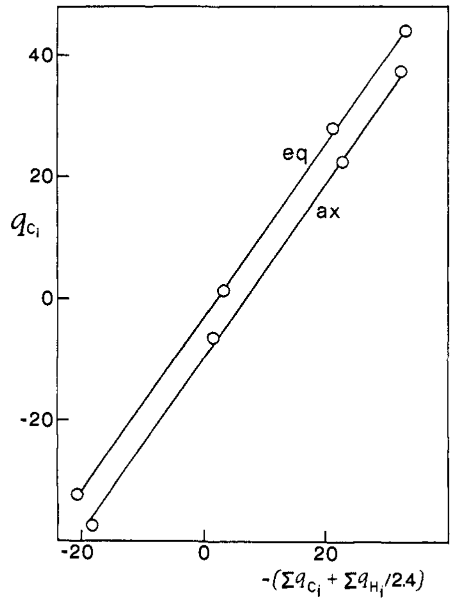

Figure 4. Net charge q_{C_i} on C_i *vs.* total net charge on the neighboring C and H atoms (CNDO/2).

group should promote the formation of the corresponding zwitterion better than the ethyl, isopropyl, or *tert*-butyl groups, in that order. Furthermore, since q_{C_i} is more negative (or less positive) in axial than in equatorial substituents, the axial position is expected to favor the formation of the corresponding zwitterion. This is, indeed, indicated by the cleavage of *cis*-2-butene primary ozonide, where the axial methyl group is incorporated into the zwitterion moiety in preference to the equatorial methyl group.[30]

When the concept "that a positive site is best favored by electron-richer neighboring atoms" is applied to the primary ozonide ring, it is considered that the difference in stabilization of the charges on C-1 and C-2 is contributing to the distribution of the reaction paths. The sums Q_1 and Q_2 of the charges on the atoms neighboring C-1 and C-2 are

$$Q_1 = q_{C_i}' + q_{C_2} + q_O' + q_H'/k \quad \text{(for C-1)} \qquad (3)$$

$$Q_2 = q_{C_i}'' + q_{C_1} + q_O'' + q_H''/k \quad \text{(for C-2)} \qquad (4)$$

For the comparison with the experimental expression for the difference in substituent effects, it appears reasonable to compare the quantity $\Delta Q = Q_1 - Q_2$ to the log $[x/(1 - x)]$ values. As indicated by the results (Tables VIII and IX), the charges on the oxygen atoms attached to C-1 and C-2 are very similar; hence,

$$\Delta Q \approx q_{C_i}' - q_{C_i}'' + q_{C_2} - q_{C_1} + (q_H' - q_H'')/k \qquad (5)$$

The comparison of the log $[x/(1 - x)]$ with the ΔQ values calculated from the CNDO/2 results (Table IX), using $k = 2.4$, is presented in Figure 5. Because of the small contribution of the term $(q_H' - q_H'')/k$, the actual choice of the numerical value for k has little importance.

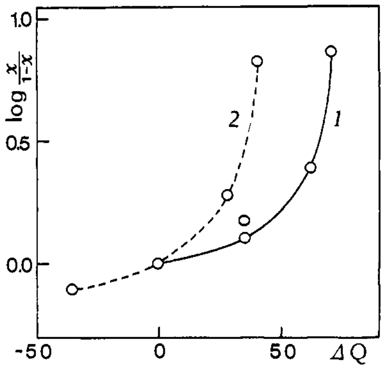

Figure 5. Log $[x/(1 - x)]$ *vs.* ΔQ for the trans primary ozonides derived from $CH_3CH{=}CHR$ (1) and from $C_2H_5CH{=}CHR$ (2). In both curves, the points are (from left to right) in the order R = CH_3, C_2H_5, *i*-C_3H_7, *tert*-C_4H_9. The point which falls outside curve 1 is for R = *n*-C_3H_7.

The curves obtained for the primary ozonides derived from the trans olefins $CH_3CH{=}CHR$ (1) and from the trans olefins $C_2H_5CH{=}CHR$ (2) are superimposable.[45] Their general shape is satisfactory, because ΔQ is necessarily finite, whereas log $[x/(1 - x)]$ tends to infinity for $x \rightarrow 1$. Incidentally, the corresponding curves which are obtained by inserting the EHMO results (Table VIII) in eq 5 are very similar to those presented in Figure 5, based on CNDO/2 results.

Curve 1 clearly indicates that x, *i.e.*, the proportion of $CH_3C^+HOO^-$ formation, increases as R is changed from methyl to ethyl, to isopropyl, or to *tert*-butyl; hence, that the methyl group is the best and *tert*-butyl the worst substituent for promoting the formation of the corresponding zwitterion. Similar conclusions can also be drawn from an inspection of curve 2. The proportions of cleavage of the primary ozonides with R = *tert*-C_4H_9 (**9** and **11**) indicate that the $C_2H_5C^+HOO^-$ formation is, at a significantly lower ΔQ value, similar to that of $CH_3C^+HOO^-$ formation. This is so, although, from a consideration of its ΔQ value *only*, a much lower log $[x/(1 - x)]$ value than the actual one would be expected in the case of ethyl. It must be considered, however, that the inductive effect promotes the formation of the ethyl over that of the methyl zwitterion. Hence, the similarity of the log $[x/(1 - x)]$ values for **9** and **11** indicates that in the case of ethyl the loss in "ΔQ effect" is almost compensated by the gain in inductive effect. In the final analysis, the difference in inductive effects between the ethyl and the methyl groups explains why distinct curves are obtained for the two series of compounds described in Figure 5.

It is clear that the experimental log $[x/(1 - x)]$ values reflect the contributions of both the "hyperconjugative" and the inductive effects and that, consequently, any "complete" equation for calculating x should contain terms expressing these two contributions. It is felt, however, that there is little merit in constructing such an equation using, *e.g.*, ΔQ and δ(R) values; on the contrary, it is more interesting to separate these effects and to study them individually.

In the present discussion, the observed order exhibited by the alkyl groups in favoring the formation of zwitterions (*i.e.*, $CH_3 > \ldots > tert\text{-}C_4H_9$) has been referred to as "hyperconjugative order." Hyperconjugation as such, however, has not been discussed. Basically, the observed distributions of reaction paths have been compared to effects related to, and interpreted

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[45] Similar trends are observed with the cis primary ozonides. Their study, however, is complicated by the fact that only the primary ozonides of *cis*-2-pentene and -2-hexene are comparable because they both have the methyl group in axial position, whereas in the *cis*-4-methyl-2-pentene primary ozonide the methyl group is equatorial.

in terms of, conditions accompanying the formation of carbonium ions. In essence, it has been considered that, whatever the interpretation derived from this observation, it is equivalent to saying that a zwitterionic carbo cation is favored in a situation where the neighboring atoms are electron richer or to say that zwitterions are favored by alkyl groups in the hyperconjugative order. The extension of these views to other reactivity problems in which alkyl groups operate in the hyperconjugative order is tempting, but should not be considered on the basis of ozonolysis results alone, since other phenomena, such as steric hindrance in solvolysis, may participate in determining the order of reactivity.

In the study of the 1,2,3-trioxolanes, however, the present approach has the merit of offering an interpretation of a particularity which is observed in the cleavage of monosubstituted primary ozonides. The plot (Figure 6) of the log $[x/(1 - x)]$ values *vs.* Taft's polar σ^* constants indicates that the proportion (x) of RC^+HOO^- zwitterion formation increases in the inductive order. For R = *tert*-C_4H_9, *i*-C_3H_7, *n*-C_3H_7, C_2H_5, CH_3, and H, the slope is approximately -0.43. The alkyl groups are placed in reversed orders when their "hyperconjugative" stabilization abilities are compared to their inductive effects. In the *tert*-butyl group, for example, when compared to methyl, the gain in inductive effect is attenuated by the loss in hyperconjugative stabilizing ability. This mutual partial compensation of the effects may thus explain the relatively low value of the Taft slope.

One would then expect that if the hyperconjugative and the inductive effects of the substituents were to act in the same direction, that is, negatively, then a destabilization effect would be shown upon the carbonium ion because of the withdrawal of negative charge from the substituent C atom. This, of course, would be demonstrated by a steeper slope of the log $[x/(1 - x)]$ *vs.* Taft's σ^* plot. Furthermore, if these substituents were of a type of which the withdrawal effects were predictable, then some interpretation could be evinced from the results of the cleavage. Thus, if the groups are of the type CH_2X (where X is a halogen), the electronegativity of the group increases in the same order as the electronegativity of the halogen [$\sigma^* = 0.85$ (CH_2I), 1.00 (CH_2Br), 1.05 (CH_2Cl)], and the negative charge on the carbon atom of the group decreases in the same order. The result of this decrease in negative charge should tend to destabilize the carbonium ion, also in the same order. Experimental results show that this is indeed the case. The value of the slope of the Taft plot shows an abrupt change (Figure 6) from the value -0.43 to a value of -1.2 where the substituent is CH_2X.

Conclusions

A consideration of Mulliken overlap populations in the 1,2,3-trioxolane ring indicates that, in most cases, the preferential path of cleavage yields the zwitterion retaining the carbon atom having the highest C–O overlap in the primary ozonide. The results are consistent with a cleavage initiated at the C–C bond, but would lead to serious difficulties if it were postulated that the cleavage was initiated by the rupture of an oxygen–oxygen bond.

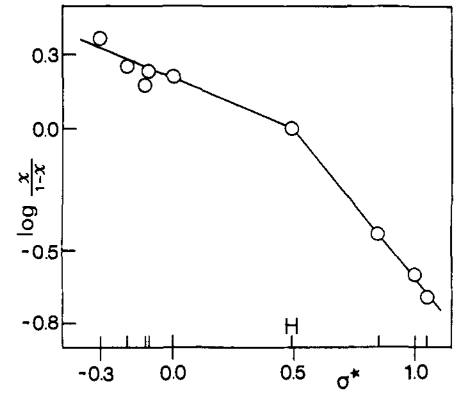

Figure 6. Comparison of the log $[x/(1 - x)]$ values for monosubstituted primary ozonides with Taft's polar σ^* constants. The values for the halogenated compounds are extracted from ref 8.

Both the EHMO and the CNDO/2 calculations indicate that the inductive effects, expressed in terms of net electron release $\delta(R)$ by the substituents, are remarkably constant for each equatorial group, regardless of the other substituents in the molecule, and regardless of whether the zwitterion formation is favored in the inductive order (as for the monosubstituted primary ozonides) or in the hyperconjugative order (as for the trans and cis 1,2-disubstituted primary ozonides). The $\delta(R)$ values correlate with Taft's polar σ^* constants. Similar conclusions also hold for the axial substituents, which, however, exhibit a somewhat reduced inductive effect, in terms of $\delta(R)$, as compared to their equatorial analogs. Hence, as far as inductive effects are concerned, the formation of zwitterions is favored by equatorial rather than by axial substitution. This difference between axial and equatorial substituents is capable of explaining why the mutual partial cancellation of the inductive effects contributed by the two substituents is somewhat reduced in cis primary ozonides, with respect to their trans isomers.

A consideration of the charge distributions in the substituents indicates that a positive site is the best favored as its immediate surroundings are the most negative. The use of this approach for the trioxolane C atoms indicates that the zwitterion which is formed preferentially is the one whose environment is electron richer, and that the alkyl groups promote the formation of the carbonium ion in the order $CH_3 > \ldots >$ *tert*-C_4H_9, somewhat better when in axial than in equatorial position. This is indicated both by the CNDO/2 and EHMO calculations of electron populations. This effect is predominant in the cleavage of trans and cis 1,2-disubstituted primary ozonides because of the mutual partial cancellation of the inductive effects, but also appears to play an important role in the cleavage of monosubstituted primary ozonides.

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