A Quantitative Investigation of the Ozonolysis Reaction. XI. On the Effects of Substituents in Directing the Ozone Cleavage of *trans*-1,2-Disubstituted Ethylenes

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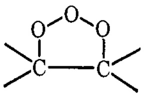
Abstract: The cleavage of the primary ozonides of a series of 1,2-disubstituted ethylenes $R_\alpha CH{=}CHR_\beta$ has been studied. The proportions of the two ways of cleavage to yield (a) $R_\alpha CHO + R_\beta C^+HOO^-$ and (b) $R_\alpha C^+HOO^- + R_\beta CHO$ obey the equation $\log [x/(1-x)] = [\Delta G_R{}^{\ddagger}(\alpha) - \Delta G_R{}^{\ddagger}(\beta)]/2.3RT$, where x is the proportion of cleavage following path a, and $\Delta\Delta G^{\ddagger} = -\Delta G_R{}^{\ddagger}(\alpha) + \Delta G_R{}^{\ddagger}(\beta)$, the Gibbs activation energy difference between transition states of paths a and b. This equation enables the proportion of cleavage (x) following path a to be calculated from a table of values for the group contributions $\Delta G_R{}^{\ddagger}$ ($\Delta G_R{}^{\ddagger}(\alpha)$ for R_α and $\Delta G_R{}^{\ddagger}(\beta)$ for R_β) which, in most cases, are constant for each group, irrespective of the substituent on the other ethylenic carbon atom. It is concluded that the zwitterion which is formed preferentially is the one whose environment is better able to stabilize the positive charge by increasing the electron density in the vicinity of the potential zwitterionic carbocation (in the transition state) *via* inductive and mesomeric effects. The relative efficiencies of the groups (indicated by their $\Delta G_R{}^{\ddagger}$ values) in stabilizing zwitterions are in the order $COCH_3$ (−0.34) > CH_3 (−0.28) > COOH (−0.18) > H (0.00) > OCH_3 (0.12) > CN (0.23) > CH_2OH (0.44) > CH_2I (0.59) > $OCOCH_3$ (0.68) > $COOCH_3$ (0.74) > CH_2Br (0.82) > CH_2Cl (0.95) > CH_2CN (1.07). For the phenyl group, however, no constant group contribution $\Delta G_R{}^{\ddagger}$ is observed.

The reaction of ozone on a carbon–carbon double bond in an inert solvent is believed to occur *via* an electrophilic[1] 1,3-dipolar cycloaddition[2] to give the very unstable 1,2,3-trioxolane intermediate (primary ozonide) I.



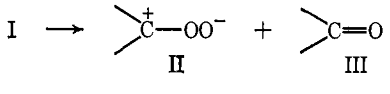
I

The great instability of the primary ozonides, even at low temperatures, prevented, until recently, their detection. However, Criegee and Schröder[3] and later Greenwood[4] reported evidence for the existence of the primary ozonides of some *trans*-alkenes, and some evidence has also been given[5] for the existence of *cis* primary ozonides at −130° in dichlorodifluoromethane solutions.

The 1,2,3-trioxolane structure of the primary ozonide of *trans*-di-*t*-butylethylene was confirmed by Bailey[6] from low-temperature nmr experiments (−110°), which indicate that both methine protons are equivalent. This five-membered ring structure is thus in agreement with the structure previously favored by Criegee.[7] Present evidence suggests that primary ozonides of *cis* olefins, like those of *trans* olefins, have a 1,2,3-trioxolane structure, although this has not been established to the extent that it has with *trans* olefins. The *cis* primary ozonides are reported to be even more unstable than the *trans* isomers[5] at temperatures as low as −110°.

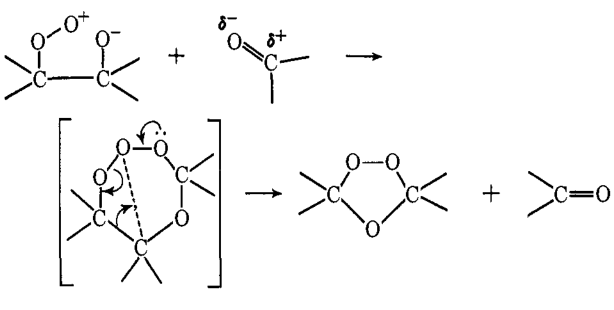
The fate of the primary ozonide in the ozonolysis mixture can be discussed in terms of two possible alternatives: (i) the very rapid cleavage of I to give a zwitterion II and a carbonyl compound III (Scheme I),

Scheme I



or (ii) the Murray–Story–Youssefyeh (MSY) mechanism,[8] which implies a reaction between the 1,2,3-trioxolane and an aldehyde molecule (Scheme II).

Scheme II



The first alternative is considered in the orginal Criegee mechanism,[9] for which considerable experimental support is given.[10] This mechanism, however, has been found inadequate to explain the experimental observations[8,11,12] that *cis* and *trans* olefins often do not

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(1) A. J. Whitworth, R. Ayoub, Y. Rousseau, and S. Fliszár, *J. Amer. Chem. Soc.*, **91**, 7128 (1969); D. G. Williamson and R. J. Cvetanović, *ibid.*, **90**, 3668 (1968); D. G. Williamson and R. J. Cvetanović, *ibid.*, **90**, 4248 (1968).

(2) R. Huisgen, *Angew. Chem. Intern. Ed. Engl.*, **2**, 565, 633 (1963).

(3) R. Criegee and G. Schröder, *Chem. Ber.*, **93**, 689 (1960).

(4) F. L. Greenwood, *J. Org. Chem.*, **29**, 1321 (1964).

(5) L. J. Durham and F. L. Greenwood, *Chem. Commun.*, 24 (1968); L. J. Durham and F. L. Greenwood, *J. Org. Chem.*, **33**, 1629 (1968).

(6) P. S. Bailey, J. A. Thompson, and B. A. Shoulders, *J. Amer. Chem. Soc.*, **88**, 4098 (1966).

(7) R. Criegee in "Peroxide Reaction Mechanisms," J. O. Edwards, Ed., Interscience Publishers, New York, N. Y., 1962, p 29.

(8) 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).

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

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

(11) E. Briner, E. Dallwigk, and M. Ricca, *Helv. Chim. Acta*, **41**, 1390 (1958); E. Briner and M. Ricca, *ibid.*, **41**, 2178 (1958); E. Briner

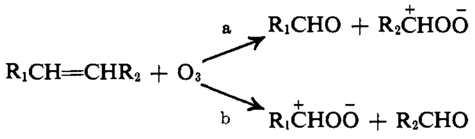
give the same proportions of ozonolysis products, *i.e.*, *cis*- and *trans*-ozonides, aldehydes, and peroxidic compounds. The observations[8,12] that the *cis–trans*-ozonide ratios for the normal ozonides,[13] as well as for the cross ozonides obtained from unsymmetrical olefins, in a number of cases depend on the olefin geometry induced several workers to offer refined mechanisms of ozonide formation. On the basis of conformational analyses of the 1,2,3-trioxolanes, Bailey[14] has expressed rules for the formation of *syn* and *anti* zwitterions from *cis* and *trans* primary ozonides, and for the formation of *cis*- and *trans*-ozonides from these isomeric zwitterions. These rules describe the stereochemical dependence of the ozonide *cis–trans* ratios on the olefin geometry. It was also considered[15] that the *syn* and *anti* zwitterions may be stabilized by adequate olefin (or solvent) molecules, and that this stabilization participates in directing the ozonide *cis–trans* distributions. In any event, the possible participation of *syn* and *anti* zwitterions in the formation of *cis*- and *trans*-ozonides does not alter, in essence, the nature of the first step of the reaction of the primary ozonide, *i.e.*, its unimolecular decomposition into zwitterion and carbonyl compound.

The MSY mechanism[8] depicted in Scheme II implies, on the contrary, a reaction between the primary ozonide and aldehyde.[16] This mechanism, which is considered by its authors to be complementary to the Criegee mechanism, is invoked to explain the stereospecific dependence of the ozonide *cis–trans* ratios on the olefin geometry. Owing to the extreme instability of the primary ozonides,[3–6] it is considered that even in those cases where the MSY mechanism could possibly contribute to the overall reactions such a participation should be negligible at sufficiently high temperatures, compared to the contribution of the unimolecular decomposition of the primary ozonide to give zwitterion and carbonyl compound.

The scope of the present work is to study the cleavage of the primary ozonides of unsymmetrical *trans*-1,2-disubstituted ethylenes. These reactions were studied at temperatures (0–25°) where the participation of any primary ozonide–aldehyde mechanism is unlikely. Assuming Criegee's mechanism, the two possible ways of cleavage of unsymmetrical olefins can be represented by Scheme III.

Earlier studies on the direction of cleavage of 1-substituted 1,2-dibenzoylethylenes,[18] indene,[19] styrene,[20,21] β-methylstyrene,[21] and 2-methylpropenylbenzene[21] indicated that in some cases the zwitterion having the better possibility of resonance stabilization is formed preferentially, and that the electron-donating power of the substituents may participate in favoring one path of cleavage.

Scheme III



$$R_1CH{=}CHR_2 + O_3 \xrightarrow{a} R_1CHO + R_2\overset{+}{C}HO\overset{-}{O}$$

$$R_1CH{=}CHR_2 + O_3 \xrightarrow{b} R_1\overset{+}{C}HO\overset{-}{O} + R_2CHO$$

These views were recently confirmed by studies on ring-substituted styrenes[22] and on a series of β-substituted styrenes bearing a substituent in the phenyl ring.[23] The results obtained led to the suggestion that the β substituent always influences the proportions of the two ways of cleavage in the same manner, irrespective of the α substituent. This conclusion, however, is based only on results for compounds with substituted phenyl groups in the α position and does not necessarily imply that this is the case when substituents, other than substituted phenyl groups, are found in the α position. The present study attempts to clarify this point for a series of substituents by the examination of the proportions of cleavage following the paths a and b, as depicted in Scheme III. The knowledge of the properties of a series of groups in distributing the two ways of cleavage will enable, in a number of cases, a simple *a priori* calculation of the proportions of cleavage in either direction.

However, only *trans*-1,2-disubstituted olefins are considered in this study, along with monosubstituted ethylenes, for the following reason. In the primary ozonides of *cis*-1,2-disubstituted ethylenes, the substituents are in axial,equatorial conformation. The groups are not expected to behave in an identical manner during the cleavage, when in axial or in equatorial conformation: according to Bauld and Bailey's analysis of the stereoselective cleavage of primary ozonides, an equatorial substituent is incorporated into a zwitterion moiety in preference to an axial substituent.[14] Hence a possible "conformational contribution" in distributing the paths of cleavage has to be considered for *cis* primary ozonides. In *trans* primary ozonides, on the contrary, the substituents are in axial,axial or in equatorial,equatorial conformations, depending upon the size of the substituents.[14] No conformational difference between the two substituents can thus participate in discriminating between the paths of cleavage. Consequently, the substituent effects can be studied in isolation, without any interference of conformational effects, only with *trans* olefins. The "conformational effects" which are observed with *cis* olefins will be discussed in a forthcoming paper.

Results

The reactions occurring in the ozonolysis of unsymmetrical olefins in an inert solvent are complex. In addition to the normal ozonide, the formation of

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and S. Fliszár, *Helv. Chim. Acta.*, 42, 1310 (1959); E. Briner and S. Fliszár, *ibid.*, **42**, 2063 (1959).

(12) G. Schröder, *Chem. Ber.*, **95**, 733 (1962); P. Kolsaker, *Acta Chem. Scand.*, **19**, 223 (1965); O. Lorenz and C. R. Parks, *J. Org. Chem.*, 30, 1976 (1965); F. L. Greenwood and B. J. Haske, *Tetrahedron Lett.*, 631 (1965); R. W. Murray, R. D. Youssefyeh, and P. R. Story, *J. Amer. Chem. Soc.*, 88, 3143 (1966); F. L. Greenwood, *ibid.*, 88, 3146 (1966).

(13) The term "normal ozonide" describes the ozonide corresponding to the olefin; the "cross-ozonides" are the two symmetrical ozonides that are obtained from unsymmetrical olefins.

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

(15) S. Fliszár and J. Carles, *Can. J. Chem.*, 47, 3921 (1969).

(16) Alternative primary ozonide–aldehyde mechanisms are discussed in ref 17.

(17) S. Fliszár and J. Carles, *J. Amer. Chem. Soc.*, **91**, 2637 (1969); S. Fliszár, J. Carles, and J. Renard, *ibid.*, **90**, 1364 (1968).

(18) P. S. Bailey, S. B. Mainthia, and C. J. Abshire, *ibid.*, **82**, 6136 (1960).

(19) S. Fliszár, Cz. Belzecki, and J. B. Chylińska, *Can. J. Chem.*, **45**, 221 (1967).

(20) S. Fliszár, *ibid.*, **44**, 2351 (1966).

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

(22) S. Fliszár and J. Renard, *Can. J. Chem.*, **45**, 533 (1967); S. Fliszár, *Tetrahedron Lett.*, 6083 (1966).

(23) S. Fliszár and M. Granger, *J. Amer. Chem. Soc.*, **91**, 3330 (1969).

Table I. Ozonolysis of 1.0 mmol of *trans*-4-Methyl-2-pentene in Ethyl Acetate–Methanol (3 *M*) at 25°

Active O, mg-atom	$CH_3CH(OCH_3)OOH$, mmol	i-$C_3H_7CH(OCH_3)OOH$, mmol	Hydroperoxides, total, mmol	% cleavage, path a		% cleavage, path b
				Method 1[a]	Method 2[b]	
0.250	0.172	0.074	0.246	69.0	70.0	29.6
0.335	0.240	0.086	0.326	71.6	73.6	26.0
0.420	0.300	0.126	0.426	71.4	70.4	30.0
0.430	0.310	0.120	0.430	72.0	72.1	28.0
0.495	0.350	0.138	0.488	70.8	71.7	28.0

[a] Method of calculation 1 (path a): mmol of $CH_3CH(OCH_3)OOH$/mg-atoms of active oxygen, as determined from iodometric analysis of the latter. [b] Method 2: mmol of $CH_3CH(OCH_3)OOH$/mmol of total hydroperoxide, as determined by polarography. The percentage of cleavage following path b is calculated from the amounts of i-$C_3H_7CH(OCH_3)OOH$ and active oxygen which are produced.

two cross ozonides, the production of peroxidic compounds from the zwitterions, and their reduction to carbonyl compounds with evolution of oxygen[24] have to be considered. The fact that the normal ozonide can be formed from the products (zwitterions and aldehydes) which are produced by both paths (a and b) makes it impossible for the proportions of the two ways of cleavage to be determined in a nonparticipating solvent.

In the presence of excess methanol (or ethanol), however, the zwitterions $R_1C^+HOO^-$ and $R_2C^+HOO^-$ are quantitatively trapped to give the corresponding alkoxy hydroperoxides $R_1CH(OR)OOH$ and $R_2CH(OR)OOH$. It has been verified in a number of cases[20,22,23] that 1 mol of olefin, when ozonized in the presence of alcohol, produces 1 mol of compounds containing active oxygen, as determined by iodometric titrations. It was also found that, in agreement with the stoichiometry indicated in Scheme III, a total of 1 mol of aldehyde is produced in the ozonolysis of a series of olefins when in the presence of methanol.[23] Kolsaker and Bailey[25] have shown that methoxy hydroperoxides react with aldehydes in Baeyer–Villiger fashion when the reaction mixtures are allowed to stand for several days at room temperature and when they are heated to reflux until the peroxide is decomposed. It is important, therefore, to analyze for aldehyde immediately on completion of the ozonolysis. However, control analyses performed 2 hr after the ozonolysis did not indicate any appreciable change in the aldehyde content. In order to confirm further that no reaction occurs between aldehyde and methoxy hydroperoxide under our experimental conditions, dimethyl fumarate was ozonized in methanol at room temperature, and an equivalent amount of benzaldehyde added. Analyses performed immediately, and 1 hr after the reaction, demonstrated unambiguously that no aldehyde reacted with the hydroperoxide.

Recent polarographic analyses of the reaction products obtained in the presence of methanol have enabled the individual methoxy hydroperoxides to be detected and their amounts in ozonolysis mixtures measured.[26] These experiments clearly demonstrate that a total of 1 mol of methoxy hydroperoxides is formed during the ozonolysis of 1 mol of olefin in the presence of methanol and they provide an independent determination of the proportions of the two ways of cleavage. These were found to be equal to those determined from the analysis of the aldehydes formed. A typical example of a polarographic determination of the methoxy hydroperoxides is given in Table I which refers to the ozonolysis of 10 ml of a 0.1 *M* solution of *trans*-4-methyl-2-pentene in ethyl acetate–methanol (3 *M*) at 25°.

The analytical methods used to determine the direction of cleavage depend on the nature of the olefin investigated and the properties of the compounds formed upon ozonolysis. In general, olefins can be readily determined by gas phase chromatography. In some cases, however, the amounts of olefin used can be determined more conveniently by the iodometric titration of the methoxy hydroperoxides produced. From the knowledge of the amounts of olefin used and of either one of the carbonyl compounds formed, the direction of cleavage which yields that particular carbonyl compound can be determined, the proportion of cleavage following the other path being complementary. In most of the cases the aldehydes were determined by vapor phase chromatography and/or infrared spectroscopy. In some cases, however, the direction of cleavage can be determined from nmr measurements of the proportions of the alkoxy hydroperoxides which are formed or, finally, by polarographic analysis of one or both methoxy hydroperoxides. Table II gives the results of determinations of the direction of cleavage obtained by different analytical methods.

The reproducibility of the experimental results is quite satisfactory. Typical examples are shown in Table III. It is seen that the results are not affected by the initial olefin concentration or the extent of the reaction.

In a previous study it was shown that for cinnamyl alcohol, styrene, *p*-chlorostyrene, and anethole, the proportions of cleavage are not influenced by changes of temperature of ozonolysis. For these olefins, however, the temperature interval explored was rather limited (0–35°). In some cases, the proportions of cleavage have now been studied in the temperature range −78° to room temperature. As indicated by the results in Table IV, no significant change of the proportions of cleavage occurs on varying the temperature of ozonolysis.

Further evidence on the significance of the factors that may contribute to the direction of cleavage has been obtained from the proportions of cleavage for the unsymmetrical olefins listed in Table V. The results indicated have been obtained from 7–12 independent experiments and are expressed with a confidence limit $\geqslant 95\%$.

Discussion

In order to identify the products formed *via* the two paths of cleavage a and b, the following conventions

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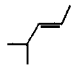
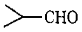
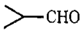
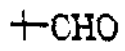
(24) S. Fliszár and J. B. Chylińska, *Can. J. Chem.*, **46**, 783 (1968).

(25) P. Kolsaker and P. S. Bailey, *Acta Chem. Scand.*, **21**, 537 (1967).

(26) J. Renard and S. Fliszár, *Can. J. Chem.*, **47**, 3333 (1969).

Table II. Comparison of Results Obtained by Different Methods

Olefin[a]	Carbonyl compd	% cleavage yielding the carbonyl compd, as determined by Vpc	Polarogr	Nmr	Ir
$p\text{-}ClC_6H_4CH{=}CH_2$	$p\text{-}ClC_6H_4CHO$	57 ± 1	57.7 ± 1		
$p\text{-}CH_3OC_6H_4CH{=}CHCH_3$	$p\text{-}CH_3OC_6H_4CHO$	68 ± 1	67.5 ± 1		
$Ph_2C{=}CH_2$	Ph_2CO		31 ± 1		33 ± 1
			71 ± 1		73 ± 4
			57 ± 1	55 ± 2	
			38 ± 1	39 ± 2	
$CH_2{=}CHCN$	HCHO	40 ± 1		40 ± 1	
$CH_3CH{=}CHCH_2OH$	CH_3CHO	23 ± 0.5		24 ± 2	
$CH_3CH{=}CHCH_2Cl$	CH_3CHO	11 ± 0.5		11 ± 1	
$CH_2{=}CHCH_2OH$	HCHO	33 ± 1		32 ± 1	

[a] *trans* configuration, unless specified otherwise.

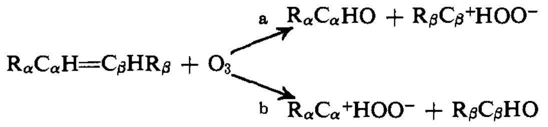
Table III. Ozonolyses of Olefin Solution (10 ml) in CCl_4–Methanol (1 *M*) at 0°

Olefin	Concn, *M*	Amt, mmol Olefin used	Aldehyde produced		% cleavage giving this aldehyde
$H_2C{=}CHCH_2OH$	0.13	0.146	0.0501	HCHO	34.3
		0.196	0.0609		31.1
		0.203	0.0642		31.6
		0.635	0.220		34.6
		1.019	0.341		33.5
	0.10	0.537	0.177		32.9
		0.690	0.216		31.3
				Mean	32.8
$CH_3CH{=}CHCH_2Cl$	0.10	0.298	0.0330	CH_3CHO	11.1
(*trans*)		0.314	0.0341		10.9
		0.320	0.0336		10.5
		0.381	0.0438		11.5
	0.15	0.562	0.0637		11.3
		0.823	0.0865		10.5
				Mean	11.0

Table IV. Proportions of Cleavage Observed at Different Temperatures

Olefin (*trans*)	Temp, °C	Solvent	% of cleavage giving the aldehyde	
$CH_3CH{=}CHCOOH$	−78	MeOH	44.3	CH_3CHO
	−20	MeOH	44.5	
	0	EtOH (1 *M*)–CCl_4	45.3	
$CH_2{=}CHCH_2OH$	−78	MeOH	32.5	HCHO
	−15	MeOH (1 *M*)–CCl_4	33.4	
	0	EtOH (1 *M*)–CCl_4	32.8	
	25	MeOH (1 *M*)–CCl_4	33.0	
$CH_2{=}CHCN$	−78	MeOH	39.2	HCHO
	0	MeOH (1 *M*)–CCl_4	40.0	
	20	MeOH	39.5	
$CH_3CH{=}CHCH_2OH$	−78	MeOH	22.7	CH_3CHO
	0	EtOH (1 *M*)–CCl_4	23.0	
	20	MeOH	23.0	
$CH_3CH{=}CHCH_2Cl$	−78	MeOH	10.5	CH_3CHO
	0	MeOH (1 *M*)–CCl_4	11.0	
	20	MeOH	11.0	

will be adopted. Let x be the proportion of cleavage following path a, with the rate constant k_a, and, consequently, $1 - x$ the proportion of cleavage following path b, with a rate constant k_b. With this convention *x always represents the proportion of cleavage producing the aldehyde on C_α.*



If both reactions are of the same order, which is reasonable to assume, it follows that

$$x/(1 - x) = k_a/k_b \quad (1)$$

Table V. Proportion of Cleavage (x) Yielding $R_\alpha CHO + R_\beta C^+HOO^-$ from *trans* Olefins $R_\alpha CH{=}CHR_\beta$

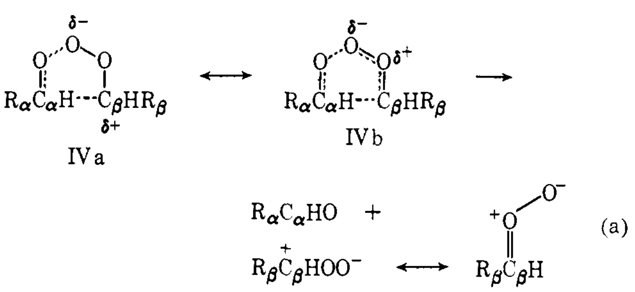
R_α	R_β	x Exptl	x Calcd
CH_3	$COCH_3$	0.53 ± 0.01	0.525
	COOH	0.45 ± 0.01	0.457
	H	0.38 ± 0.01	0.384
	CH_2OH	0.230 ± 0.005	0.229
	$COOCH_3$	0.150 ± 0.005	0.152
H	$COCH_3$	0.64 ± 0.01	0.640
	COOH	0.57 ± 0.01	0.575
	CH_2OH	0.33 ± 0.01	0.322
	$COOCH_3$	0.224 ± 0.004	0.223
COOH	$COOCH_3$	0.18 ± 0.01	0.175
CH_2OH	COOH	0.736 ± 0.005	0.740
	$COOCH_3$	0.38 ± 0.01	0.376
OCH_3	H	0.55 ± 0.01	*a*
CN	CH_3	0.70 ± 0.01	0.703
	H	0.60 ± 0.01	0.596
$OCOCH_3$	H	0.76 ± 0.005	*a*
CH_2I	H	0.73 ± 0.01	*a*
CH_2Br	CH_3	0.866 ± 0.005	0.865
	H	0.80 ± 0.01	0.800
	$COOCH_3$	0.536 ± 0.01	0.534
CH_2Cl	CH_3	0.89 ± 0.005	0.889
	H	0.83 ± 0.005	0.833
CH_2CN	H	0.852 ± 0.005	0.859
	C_6H_5	0.796 ± 0.008	0.794
	p-$CH_3C_6H_4$	0.84 ± 0.02	0.826

[a] Not calculated, because the parameter required for the calculation (*i.e.*, $\Delta G_R^\ddagger$ for R_α) has been obtained only from the olefin indicated.

As mentioned in earlier papers,[22,23] it can be deduced from the theory of Wynne-Jones and Eyring[27] that

$$\log k_a/k_b = -(\Delta G_a^\ddagger - \Delta G_b^\ddagger)/2.3RT \qquad (2)$$

where $\Delta G_a^\ddagger$ and $\Delta G_b^\ddagger$ represent the activation free energies accompanying the formation of transition states corresponding to the two ways of cleavage a and b, respectively. These transition states could approach structures IVa ↔ IVb corresponding to the cleavage following path a, and similar structures for path b.



However, probable structures of the transition states and of the product zwitterions are not of immediate importance in this discussion, as attention will be focused on the thermodynamic behavior and the kinetic implications of eq 2, the applicability of which is not related to any precise knowledge of the intermediates, provided only that two reaction paths exist. Here, any structure of the intermediates can only be considered as *a posteriori* possible interpretation in terms of organic chemistry of observed kinetic properties related to thermodynamic quantities.

From eq 1 and 2, and letting $\Delta\Delta G^\ddagger = \Delta G_a^\ddagger - \Delta G_b^\ddagger$, eq 3 is deduced. This theoretical equation has been compared with experimental observations and has been found to give satisfactory agreement on series of ring- and β-substituted styrenes.[22,23] In order to account for the substituents in the benzene ring, Hammett's relationships 4 and 5 were used,[28] from which

$$\log [x/(1 - x)] = -\Delta\Delta G^\ddagger/2.3RT \qquad (3)$$

$$\Delta G_a^\ddagger = \Delta G_{0a}^\ddagger - 2.3RT\rho_a\sigma \qquad (4)$$

$$\Delta G_b^\ddagger = \Delta G_{0b}^\ddagger - 2.3RT\rho_b\sigma \qquad (5)$$

$\Delta\Delta G^\ddagger$ can be deduced. Replacing the expression for $\Delta\Delta G^\ddagger$ in eq 3, eq 6 was deduced and found to agree with the experimental data obtained with olefins of structure $RC_6H_4C_\alpha H{=}C_\beta HR_\beta$.

$$\log [x/(1 - x)] = -\Delta\Delta G_0^\ddagger/2.3RT + (\rho_a - \rho_b)\sigma \qquad (6)$$

In eq 6 the substituent R in the phenyl ring is accounted for by the term $(\rho_a - \rho_b)\sigma$, and $\Delta\Delta G_0^\ddagger$ (= $\Delta G_{0a}^\ddagger - \Delta G_{0b}^\ddagger$) is the Gibbs energy difference between the assumed transition states corresponding to paths a and b for β-substituted styrenes which have no substituent in the aromatic ring (*i.e.*, $\sigma = 0$). The values of $\Delta\Delta G_0^\ddagger = -2.3RT \log [x/(1 - x)]$ (Table VI) there-

Table VI. Proportion of Cleavage (x) Yielding the Aromatic Aldehyde

R_β	x	$\Delta\Delta G_0^\ddagger$, kcal/mol, 25°	$\rho_a - \rho_b$
$COCH_3$	0.90 ± 0.02	−1.28	1.21
CH_3	0.82 ± 0.01	−0.90	1.24
COOH	0.61 ± 0.01	−0.24	1.38
C_6H_5	0.500	0.00	1.28
H	0.41 ± 0.01	0.23	1.25
CH_2OH	0.26 ± 0.01	0.61	1.24
$COOCH_3$	0.23 ± 0.01	0.74	1.20

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(27) W. F. K. Wynne-Jones and H. Eyring, *J. Chem. Phys.*, 3, 492 (1935).

(28) K. J. Laidler, "Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1965, p 248.

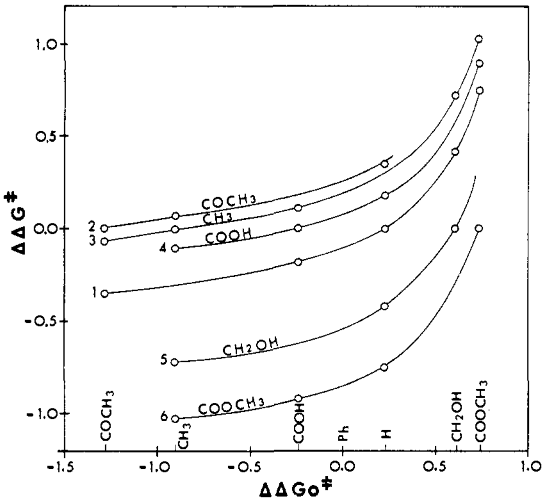

Figure 1. A comparison of the $\Delta\Delta G^{\ddagger}$ values (Table VII) *vs.* the $\Delta\Delta G_0^{\ddagger}$ values (Table VI): R_α = H (1), $COCH_3$ (2), CH_3 (3), COOH (4), CH_2OH (5), and $COOCH_3$ (6).

fore depend only on the substituent in the β position, *i.e.*, R_β; these $\Delta\Delta G_0^{\ddagger}$ values may be used for comparison of the electronic effects which can be attributed to the β substituent in a series of β-substituted styrenes.[23] It must be borne in mind that these $\Delta\Delta G_0^{\ddagger}$ values are expressed with reference to the phenyl group (*i.e.*, $\Delta\Delta G_0^{\ddagger} = 0$ for stilbene) and correspond to the replacement, in stilbene, of the phenyl group on C_β by R_β.

This scale of $\Delta\Delta G_0^{\ddagger}$ values based on $\Delta\Delta G_0^{\ddagger} = 0$ for a phenyl substituent in the R_β position is not sufficiently basic for its application to $\Delta\Delta G^{\ddagger}$ values obtained with other substituents in the molecule. A more suitable reference scale would permit the study of the effect of replacing a hydrogen atom of ethylene by a substituent group. Such a simplified reference scale is discussed below.

From eq 3, $\Delta\Delta G^{\ddagger}$ values can be calculated for olefins $R_\alpha C_\alpha H{=}C_\beta HR_\beta$ using the results in Table V. These $\Delta\Delta G^{\ddagger}$ values for those groups for which the $\Delta\Delta G_0^{\ddagger}$ values are known (Table VI) are given in Table VII.

Table VII. $\Delta\Delta G^{\ddagger}$ Values (kcal/mol, 25°) Calculated from Table V, Using Eq 3

R_β	R_α					
	$COCH_3$	CH_3	COOH	H	CH_2OH	$COOCH_3$
$COCH_3$	0.00	−0.07	*a*	−0.34	*a*	*a*
CH_3	0.07	0.00	−0.10	−0.28	−0.72	−1.03
COOH	*a*	0.10	0.00	−0.18	−0.62	−0.92
H	0.34	0.28	0.18	0.00	−0.44	−0.74
CH_2OH	*a*	0.72	0.62	0.44	0.00	−0.30
$COOCH_3$	*a*	1.03	0.92	0.74	0.30	0.00

[a] Not determined.

Curve 1 in Figure 1 represents the plot of the $\Delta\Delta G^{\ddagger}$ values calculated for the substituted ethylenes (R_α = H) *vs.* the $\Delta\Delta G_0^{\ddagger}$ values determined for the β-substituted styrenes. The fact that these quantities are not linearly related indicates that the influence exerted on the direction of cleavage by the phenyl group (or possibly the ethylenic H atom) is affected by the R_β group. For example, the replacement of the carboxyl group in the β position by H results in a change of $\Delta\Delta G_0^{\ddagger}$ (Table VI) of 0.47 kcal/mol. If the α substituent is not phenyl but H, the change of $\Delta\Delta G^{\ddagger}$ is 0.18 kcal/mol (Table VII).

Curves 2–6 (Figure 1) represent the plots of the $\Delta\Delta G^{\ddagger}$ values (Table VII) *vs.* the $\Delta\Delta G_0^{\ddagger}$ values for the ethylenes with an α substituent other than H. An examination of Figure 1 reveals that curves 1–6 are parallel. This means, for example, that curve 3 ($CH_3C_\alpha H{=}C_\beta HR_\beta$) can be obtained by adding 0.28 kcal/mol to each point of curve 1 ($HC_\alpha H{=}C_\beta HR_\beta$). This observation indicates that, except for the phenyl group, *the replacement of an ethylenic hydrogen atom by any group influences the proportions of the two possible ways of cleavage always in the same manner, irrespective of the substituent on the other ethylenic carbon atom.* This conclusion, which is drawn only from the substituents listed in Table VII, can also be recognized from an inspection of the $\Delta\Delta G^{\ddagger}$ values given in Table VII. It is seen that a change in the R_α group results in the same increment of the $\Delta\Delta G^{\ddagger}$ value, whatever the R_β substituent. For example, the replacement of $R_\alpha = CH_3$ by H is accompanied by a decrease in the $\Delta\Delta G^{\ddagger}$ value of 0.28 (±0.01) kcal/mol (25°) irrespective of the R_β substituent.

As a direct consequence of these observations, the quantity $\Delta\Delta G^{\ddagger}$ can be considered as consisting of two independent contributions, one from each substituent. A scale of $\Delta\Delta G^{\ddagger}$ values can be defined if $\Delta G_R^{\ddagger}$, the group contribution of group R, for R = H is 0, *viz.*, $\Delta G_{R=H}^{\ddagger} = 0$, *i.e.*

$$\Delta G_R^{\ddagger} = \Delta\Delta G^{\ddagger} \qquad (7)$$

for the olefins $H_2C_\alpha{=}C_\beta HR_\beta$. The $\Delta G_R^{\ddagger}$ function thus represents the contribution of a group which replaces a H atom in ethylene.

In order to distinguish the contributions of R_α and R_β, $\Delta G_R^{\ddagger}$ may be written $\Delta G_R^{\ddagger}(\alpha)$ for R_α, and $\Delta G_R^{\ddagger}(\beta)$ for R_β. Comparison with eq 3 gives eq 8 and 9

$$\log\,[x/(1-x)] = -\Delta G_R^{\ddagger}(\beta)/2.3RT \qquad (8)$$

for $H_2C_\alpha{=}C_\beta HR_\beta$

$$\log\,[x/(1-x)] = \Delta G_R^{\ddagger}(\alpha)/2.3RT \qquad (9)$$

for $R_\alpha C_\alpha H{=}C_\beta H_2$, x being the proportion of cleavage following path a, *i.e.*, yielding the aldehyde on C_α.

Because the effects of the substituents R_α and R_β are independent of each other, it follows that

$$-\Delta\Delta G^{\ddagger} = \Delta G_R^{\ddagger}(\alpha) - \Delta G_R^{\ddagger}(\beta) \qquad (10)$$

By comparison of eq 8–10 with eq 3, eq 11 is obtained. This equation enables the proportions of cleavage of α,β-disubstituted ethylenes to be calculated from the knowledge of the $\Delta G_R^{\ddagger}$ values that are associated with each R group.[29]

$$\log\,[x/(1-x)] = [\Delta G_R^{\ddagger}(\alpha) - \Delta G_R^{\ddagger}(\beta)]/2.3RT \qquad (11)$$

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(29) It is possible that the appropriate $\Delta G_R^{\ddagger}$ value corresponding to a given R group cannot be calculated from eq 7 because the proportions of cleavage of the corresponding olefin $H_2C{=}CHR$ cannot be determined. However, if the direction of cleavage (x) can be determined for an olefin $R_\alpha C_\alpha H{=}C_\beta HR_\beta$ for which $\Delta G_R^{\ddagger}$ is known for R_β, the unknown $\Delta G_R^{\ddagger}(\alpha)$ can be calculated from the equation

$$\Delta G_R^{\ddagger}(\alpha) = 2.3RT\log\,[x/(1-x)] + \Delta G_R^{\ddagger}(\beta) \qquad (11a)$$

which is obtained from eq 11. The $\Delta G_R^{\ddagger}(\alpha)$ value should be determined for at least two olefins, differing by their β substituent, in order to test whether the group (R_α) under consideration does not interfere with the R_β group.

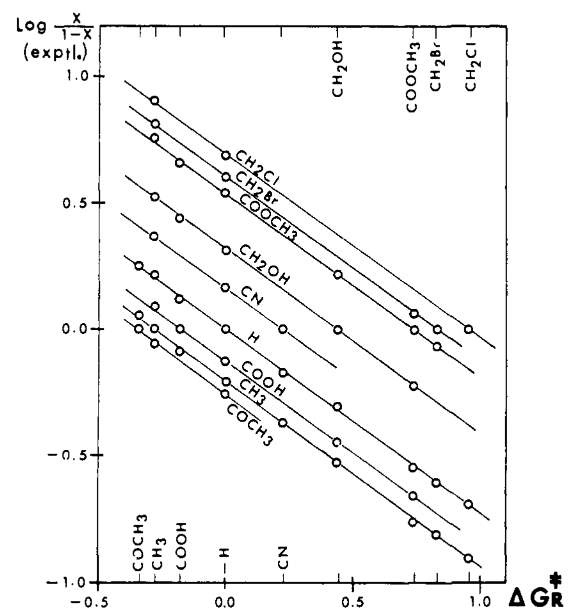


Figure 2. Experimental verification of eq 11: log $[x/(1-x)]$ *vs.* $\Delta G_{\mathrm{R}}^{\neq}$.

Table VIII gives the $\Delta G_{\mathrm{R}}^{\neq}$ values determined from eq 7 and 11, using the experimental results in Table V. Most of these values have been determined from $n \geq 2$ olefins (n = number of olefins).

Table VIII. Group Contributions $\Delta G_{\mathrm{R}}^{\neq}$ (kcal/mol, at 25°)

R	$\Delta G_{\mathrm{R}}^{\neq}$	n
$COCH_3$	−0.34	2
CH_3	−0.28	8
COOH	−0.18	4
H	0.00	8
OCH_3	0.12	1
CN	0.23	2
CH_2OH	0.44	4
CH_2I	0.59	1
$OCOCH_3$	0.68	1
$COOCH_3$	0.74	5
CH_2Br	0.82	3
CH_2Cl	0.95	2
CH_2CN	1.07	1[a]

[a] This value is confirmed by the results obtained with cinnamyl cyanide and *p*-methylcinnamyl cyanide, as explained in the text.

The experimental verification of eq 11 is described by Figure 2. The points in this figure are calculated from log $[x/(1-x)]$ inserting *experimental* values of x (Table V) at the $\Delta G_{\mathrm{R}}^{\neq}$ values given in Table VIII. The lines represent the *theoretical* log $[x/(1-x)]$ values, as calculated by means of eq 11. The excellent agreement which is observed fully confirms the applicability of eq 11 for the calculation of the directions of cleavage of *trans*-1,2-disubstituted ethylenes.

The agreement between calculated and experimental values is also apparent from a comparison (Table V) of the experimental x values with those calculated from eq 11 using the $\Delta G_{\mathrm{R}}^{\neq}$ values listed in Table VIII.

The consistency of the results presented facilitates discussion on the ability of different groups to stabilize the zwitterionic species. It is seen from eq 8 that x, *i.e.*, the proportion of $R_\beta C_\beta^+HOO^-$ production, increases as $\Delta G_{\mathrm{R}}^{\neq}$ decreases for the R_β group considered. Hence, the lower the $\Delta G_{\mathrm{R}}^{\neq}$ value for a group, the more this group favors the formation of the corresponding zwitterion. The groups in Table VIII are thus listed in decreasing order of stabilizing ability, the group which most favors the zwitterion formation being $COCH_3$.

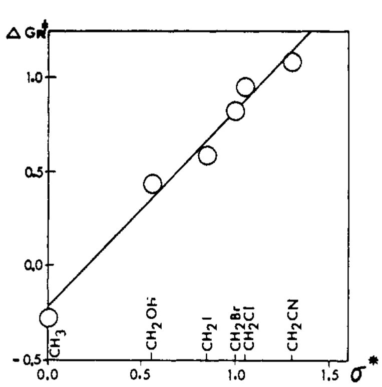
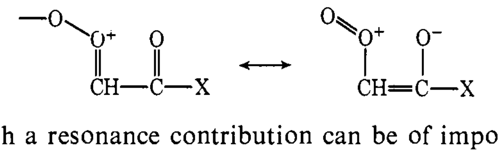


Figure 3. $\Delta G_{\mathrm{R}}^{\neq}$ values (Table VIII) *vs.* Taft's polar σ^* values.

The order exhibited by these groups is unusual in terms of classical organic chemistry in that electron-releasing and -attracting groups alternate in this sequence. The observations can, however, be explained in terms of inductive and resonance contributions of the groups to zwitterion stabilization.

The participation of inductive effects is illustrated by the order of decreasing stabilizing ability indicated by Table VIII for the groups $CH_3 > CH_2OH > CH_2I > CH_2Br > CH_2Cl > CH_2CN$. Figure 3 presents a comparison of the $\Delta G_{\mathrm{R}}^{\neq}$ values of these groups *vs.* Taft's[30] polar σ^* values. This sequence clearly indicates that electron-releasing groups favor the zwitterion formation on the carbon atom to which they are attached, whereas electron-withdrawing groups act in the opposite way. This conclusion, which is in agreement with previous findings,[18,21] is also confirmed by the observation that the electron-withdrawing groups OCH_3, $OCOCH_3$, and $COOCH_3$ do not favor zwitterion formation. In addition, the excellent agreement of eq 6 for olefins of the structure $RC_6H_4CH{=}CHR_\beta$, with $\rho_a - \rho_b = 1.24 \pm 0.04$, indicates that the zwitterion which is formed preferentially is the one whose environment is better able to stabilize the positive charge by increasing the electron density in the vicinity of the potential zwitterionic carbocation (in the transition state) *via* inductive and mesomeric effects.[22,23]

The behavior of the groups $COCH_3$ and COOH, which tend to stabilize zwitterions despite the fact that they are electron-withdrawing groups, has been explained by the possible participation of resonance stabilization.[23]



Such a resonance contribution can be of importance when X = CH_3, and to a somewhat smaller extent when X = H, because the methyl group in particular favors electron delocalization. For X = OCH_3, however, the participation of the mesomeric form of the ester

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

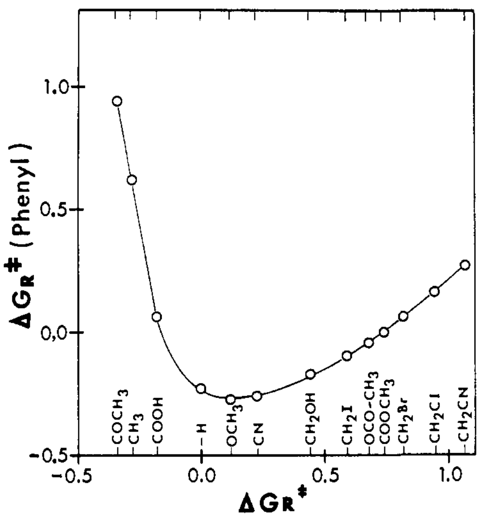
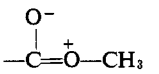


Figure 4. Dependence of $\Delta G_R{}^{\ddagger}$(phenyl) on R_β.

function reduces its ability to confer any stability by resonance. The ester group thus exerts its influence on the direction of cleavage mainly by its inductive effect.



$$-\overset{\overset{\displaystyle O^-}{|}}{C}=\overset{+}{O}-CH_3$$

The mode of participation of the phenyl ring in directing the proportions of cleavage appears to be quite different from that exhibited by the groups discussed above. A consideration of the results obtained with styrene[20,21] indicates that the phenyl ring appears to contribute to the zwitterion stabilization (or to the stabilization of the zwitterion when in its transition state) by some resonance effect. The relatively low value for the energy difference (0.23 kcal/mol, 25°) between the transition states which originate the paths of cleavage a and b, which is reflected by the observation that the most favored path is followed in a proportion of only 59%, is an indication of the relatively weak stability conferred by the benzene ring.

The contribution of the phenyl ring is, however, strongly dependent on the β substituent, as is seen from an inspection of the results obtained with β-substituted styrenes. The experimental group contribution for the benzene ring can be calculated by means of eq 11a.[29] For β-substituted styrenes, $2.3RT \log [x/(1-x)] = -\Delta\Delta G_0{}^{\ddagger}$ (eq 6, with $\sigma = 0$) and hence the group contribution $\Delta G_R{}^{\ddagger}$ for R = Ph can be calculated as follows, using the $\Delta\Delta G_0{}^{\ddagger}$ values listed in Table VI. For ex-

$$\Delta G_R{}^{\ddagger}(\text{phenyl}) = -\Delta\Delta G_0{}^{\ddagger} + \Delta G_R{}^{\ddagger}(\beta) \qquad (12)$$

ample, the group contribution $\Delta G_R{}^{\ddagger}$ for R = Ph is found to be −0.23 kcal/mol (25°) in styrene, because $\Delta G_R{}^{\ddagger}(\beta) = 0$ for R_β = H, but in β-methylstyrene the $\Delta G_R{}^{\ddagger}$ value for the phenyl group becomes 0.90 − 0.28 = 0.62 kcal/mol (25°). The $\Delta\Delta G_0{}^{\ddagger}$ values not listed in Table VI were calculated from Figure 1, as indicated below. Hence, unlike the other groups listed in Table VIII which exhibit a constant $\Delta G_R{}^{\ddagger}$ value irrespective of the substituent on the other ethylenic carbon atom, $\Delta G_R{}^{\ddagger}$ is variable for the phenyl group. The dependence of $\Delta G_R{}^{\ddagger}$(phenyl) on R_β is illustrated in Figure 4.

This figure indicates that the lowest $\Delta G_R{}^{\ddagger}$(phenyl) value is found for $R_\beta = OCH_3$ (−0.27). Thus in this case the phenyl group posseses its greatest ability to stabilize the potential zwitterionic carbocation in its transition state. For any other R_β substituent, $\Delta G_R{}^{\ddagger}$(phenyl) is higher and, consequently, the contribution of the phenyl group in stabilizing the zwitterion (in its transition state) is reduced. On the basis of the experimental observations it is thus concluded, for β-substituted styrenes ($R_\beta \neq OCH_3$), that any β substituent causes a significant perturbation in the phenyl ring lowering its efficiency toward the formation of the PhC^+HOO^- zwitterion.

Despite this, it is possible to calculate the direction of cleavage of an olefin $RC_6H_4CH{=}CHR_\beta$ from the knowledge of the direction of cleavage of an olefin $R_\alpha C_\alpha H{=}C_\beta HR_\beta$, provided that the $\Delta G_R{}^{\ddagger}$ value for R_α and Hammett's σ value for R are known. This is illustrated by the following calculation of x for cinnamyl cyanide and p-methylcinnamyl cyanide. The olefin $H_2C_\alpha{=}C_\beta HCH_2CN$ is found to yield 14.8% HCHO + $CH_2CNC_\beta{}^+HOO^-$, thus $x = 0.148\ (\pm 0.005)$. Hence (eq 7), $\Delta\Delta G^{\ddagger} = \Delta G_R{}^{\ddagger}(CH_2CN) = 1.07$ kcal/mol (25°). Figure 1, which is constructed from the data collected in Tables VI and VII, enables the $\Delta\Delta G_0{}^{\ddagger}$ value to be extrapolated from the curve of $\Delta\Delta G^{\ddagger}$ *vs.* $\Delta\Delta G_0{}^{\ddagger}$. This gives $\Delta\Delta G_0{}^{\ddagger} = 0.80$ kcal/mol for $\Delta\Delta G^{\ddagger} = 1.07$. Inserting this value for $\Delta\Delta G_0{}^{\ddagger}$ in eq 6 results for cinnamyl cyanide in $x = 0.206$ PhCHO (experimental $x = 0.204 \pm 0.008$). For p-methylcinnamyl cyanide, with $\rho_a - \rho_b = 1.24 \pm 0.04$ and $\sigma = -0.170$(p-methyl), it is calculated that $x = 0.174 \pm 0.005$(p-tolualdehyde). This calculated x value is in satisfactory agreement with the experimental value $x = 0.16 \pm 0.02$, determined for the p-methylcinnamyl cyanide.

The unusual behavior of the phenyl group illustrates the necessity with every new group that is investigated to check for the constancy of the corresponding $\Delta G_R{}^{\ddagger}$ value by means of eq 11a. However, any departure from eq 11 makes it possible to investigate the intimate properties of the groups concerned, as revealed by the perturbations caused by the overall structure of the olefin.

A final observation on the results reported in Table IV and similar results discussed previously[23] indicates that the proportions of the two ways of cleavage are invariant with temperature in the range explored. It follows from eq 3 that $\delta(\Delta\Delta G^{\ddagger}/T)/\delta T = 0$ and, consesequently, that $\Delta\Delta H^{\ddagger} = \Delta H_a{}^{\ddagger} - \Delta H_b{}^{\ddagger} = 0$, and thus eq 3 can be written as

$$\log [x/(1-x)] = \Delta\Delta S^{\ddagger}/2.3R \qquad (13)$$

where $\Delta\Delta S^{\ddagger}$ (= $\Delta S_a{}^{\ddagger} - \Delta S_b{}^{\ddagger}$) is the activation entropy difference between transition states corresponding to the paths of cleavage a and b. It appears, therefore, that the entropy factors, which may be related to the vibrational states of the transition states, primarily govern the direction of cleavage of the primary ozonides. It must be remembered, however, that the validity of eq 6 requires a constancy in the entropy terms, *or* their direct dependence on the enthalpy terms.[31] This suggests that any discussion of substituent effects should include both the entropy and enthalpy contributions, although the latter does not appear in eq 13.

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(31) *Cf.* H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).

Experimental Section

Ozonolysis Procedure. The technique of ozonolysis, using O_2–O_3 mixtures, together with the dosimetry of ozone, has been described previously.[32] The ozone output was varied between 0.07 and 0.2 mmol of O_3/min. The ozone used was limited to 50–80% of the theoretical amount, in order to prevent autoxidation of aldehydes to peracids. Unless otherwise specified, the solvent used was 1.0 *M* CH_3OH in CCl_4, and the initial concentration of olefin was 0.1 *M*.

The time required for the ozonolysis never exceeded 15 min. It can therefore be assumed that the amounts of aldehydes and hydroperoxides, which were measured immediately after completion of the ozonolysis, had not been affected by secondary reactions, such as a slow decomposition of the hydroperoxides or an autoxidation of the aldehydes.

The amounts of hydroperoxides were measured as indicated in a previous paper,[23] by a iodometric procedure similar to that described by Lohaus,[33] and/or by polarography.[26] The analyses made under these conditions were very reproducible, providing they were carried out shortly after completion of the ozonolysis; the values found for the hydroperoxides decreased by only a few per cent 1 hr after the ozonolysis.

The olefins were analyzed by gas chromatography or, as with acrylonitrile, acrylic acid, and methyl acrylate, by the morpholine method.[34]

The gas chromatographic analyses were performed using a 5750 F & M gas chromatograph, using a flame detector. Six-foot columns of 10% Carbowax 20M or of silicone rubber UCW98 were used. After the ozonization, the solvent loss due to evaporation during the ozonolysis was carefully compensated and 5-μl samples were injected in the gas chromatograph. The chromatograms were integrated by means of a planimeter and the area under the peak corresponding to the olefin which did not react and also to the aldehydes which were formed were compared to the areas under the peaks obtained under the same conditions using standard samples of the appropriate substances. The analyses were repeated a minimum of five times. For each substance seven to twelve experiments were carried out to determine the proportion of cleavage; two different oven temperatures were used with no effect on the results. Formaldehyde and acetaldehyde were analyzed as hemiacetals, using the Carbowax column, at room temperature. The observed yields of HCHO from $CH_2{=}CHCH_2OH$ were 32.8% in ethanol, and 33.1% in methanol. The HCHO observed in the methanolic ozonolysis of styrene amounts to 58.6% (with respect to the olefin), in excellent agreement with the value 59 ± 1%, as calculated from the infrared analysis of the benzaldehyde produced.[20,22] The gas chromatographic analysis of CH_3CHO produced in the methanolic ozonolysis of $CH_3CH{=}C(CH_3)COCH_3$ indicates a yield of 52.5 ± 0.5% CH_3CHO (with respect to the olefin used), in excellent agreement with the value of 53.1 ± 0.5%, as calculated from the production of butanedione. In a number of cases (Table II), the results obtained by gas chromatography were found equal to those obtained by other analytical methods.

Nmr Measurements. On completion of the ozonization, the solvent was evaporated and replaced by the minimum amount of CCl_4. The nmr spectra were recorded, with tetramethylsilane as internal reference, using a Jeolco C-60 H and a Jeolco 4 H-100 spectrometer. The following signals are suitable for the determination of the direction of cleavage:[26] methyl H (δ 1.3–1.4), methoxy H (3.35–3.50), and the signal at 4.5–4.8 of the methine proton(s). From the integrated values of these signals, the direction of cleavage can be calculated by solving the appropriate system of equations. For example, the methanolic ozonolysis of acrylonitrile yields a concentration x of $CH_2(OCH_3)OOH$ and a concentration y of $CNCH(OCH_3)OOH$. The integration (a) of the methoxy H at δ 3.5 is $a = 3x + 3y$. The methine protons are observed at 4.8, and their integration gives $b = 2x + y$. By solving the equations for x and y, the relative amounts of the methoxy hydroperoxides are deduced.

Materials. The olefins were obtained from K & K Laboratories Inc. and Aldrich Chemical Co. Inc., or prepared by standard methods reported in the literature. The *p*-methylcinnamyl cyanide was prepared following the method indicated by Oda, Kawabata, and Tanimoto,[35] by heating (5 hr at 100°) 40 g of triphenylphosphine, 19 g of tolualdehyde, 10 ml of acrylonitrile, and 2.5 ml of ethanol. After distillation (125° at 2.5 mm), the olefin was recrystallized twice in petroleum-ether, and had mp 54–55°, yield 20%. *Anal.* Calcd for $C_{11}H_{11}N$: C, 84.04; H, 7.05; N, 8.91. Found: C, 83.9; H, 7.1; N, 9.0. The analyses were made by Dr. C. Daesslé (Organic Microanalyses), Montreal.

Acknowledgment. The financial support given by the National Research Council of Canada is gratefully acknowledged.

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[32] S. Fliszár, D. Gravel, and E. Cavalieri, *Can. J. Chem.*, **44**, 67 (1966).

[33] G. Lohaus, *Ann. Chem.*, **583**, 4 (1953).

[34] F. E. Critchfield, G. L. Funk, and J. B. Johnson, *Anal. Chem.*, **28**, 76 (1956).

[35] R. Oda, T. Kawabata, and S. Tanimoto, *Tetrahedron Lett.*, 1653 (1964).