A Quantitative Investigation of the Ozonolysis Reaction. VII.[1] Ozonolyses of Phenylethylenes in the Presence of Oxygen-18-Labeled Benzaldehyde[2]

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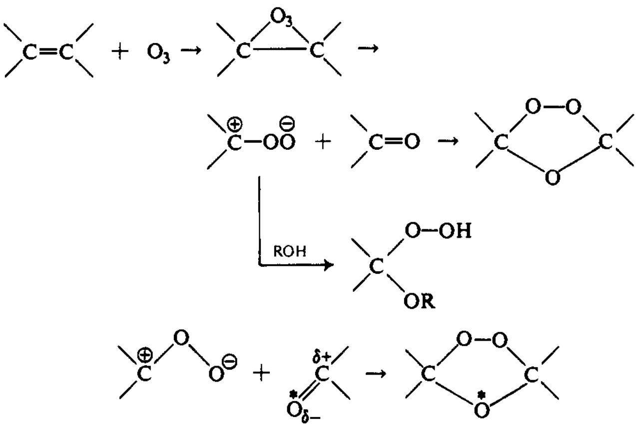
Abstract: The ozonization of *cis-* and *trans*-stilbenes, styrene, *trans*-β-methylstyrene, and triphenylethylene in the presence of ^{18}O-labeled benzaldehyde reveals that the incorporation of the ^{18}O takes place exclusively in the ether oxygen of the ozonides formed. The stilbene ozonide *cis/trans* distributions obtained from these olefins depend on the geometry of the olefin used. The presence of excess benzaldehyde does not affect the *cis/trans* distributions, and it is therefore unlikely that an initial ozonide–aldehyde reaction is involved. A refined Criegee mechanism is consistent with the observations of the labeling experiments and the stereospecificity of the *cis-* and *trans*-ozonides formation.

The mechanism of the ozonolysis reaction has been the subject of recent discussion.[3-5] The Criegee mechanism,[6] outlined in Scheme I, has received considerable experimental support.[7] This includes (i) the reaction of the zwitterion with those solvents which participate in the ozonolysis, forming hydroperoxides, or the reaction with added aldehyde to form an ozonide other than that of the original olefin, and (ii) the formation of cross ozonides from unsymmetrical olefins.[8]

Scheme I

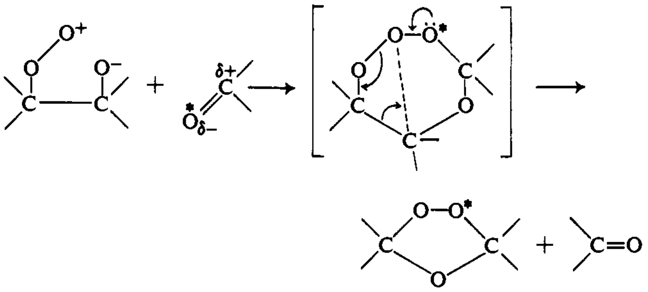


However the observations[9] that *cis* and *trans* isomers of 1-arylpropenes do not form the same proportions of the products (ozonides, aldehydes, and peroxides), and that the *cis-* and *trans*-olefins frequently give different *cis-/trans*-ozonide ratios,[3b,8d,10] cannot be explained by the original Criegee mechanism. More recent observations by Murray, Story, *et al.*,[3b,10e] on the stereospecific dependence of the *cis-/trans*-ozonide ratios, for both normal and cross ozonides, on the geometry of the olefin also indicated the need for a more sophisticated theory than that shown by Scheme I. Bailey[5] has attempted to accommodate these observations within the Criegee mechanism by interpreting the stereospecific orientation of the ozonolysis in terms of *syn* and *anti* zwitterions. Criegee[11] has suggested previously that *syn* and *anti* zwitterions may exist.

A different explanation by Murray, Story, and Youssefyeh[3] for the observed stereospecificity of the *cis-/trans*-ozonide distributions is represented by Scheme II, which is a simplified description of the key step of their theory, *i.e.*, the attack of an aldehyde molecule on an initial ozonide (1,2,3-trioxolane). The mechanism represented by Scheme II is considered by Murray, *et al.*,[3] to be competing with Criegee's mechanism, which is retained as "a possible contributing pathway."

These two approaches therefore differ essentially on the formation of the zwitterion as an intermediate in the ozonization.

Scheme II



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[1] Part VI: S. Fliszár and J. B. Chylińska, *Can. J. Chem.*, **46**, 783 (1968).

[2] Presented in part at the 51st Annual Meeting of the Chemical Institute of Canada, Vancouver, B. C., Canada, June 1968.

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

[4] S. Fliszár, J. Carles, and J. Renard, *ibid.*, **90**, 1364 (1968).

[5] N. L. Bauld, J. A. Thompson, C. E. Hudson, and P. S. Bailey, *ibid.*, **90**, 1822 (1968).

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

[7] P. S. Bailey, *Chem. Rev.*, **58**, 925 (1958).

[8] (a) G. Riezebos, J. C. Grimmelikhuysen, and D. A. Van Dorp, *Rec. Trav. Chim.*, **82**, 1234 (1963); (b) O. S. Privett and E. C. Nickell, *J. Am. Oil Chemist's Soc.*, **41**, 72 (1964); (c) L. D. Loan, R. W. Murray, and P. R. Story, *J. Am. Chem. Soc.*, **87**, 737 (1965); (d) O. Lorenz and C. R. Parks, *J. Org. Chem.*, **30**, 1976 (1965).

[9] E. Briner, E. Dallwigk, and M. Ricca, *Helv. Chim. Acta*, **41**, 1390 (1958); E. Briner and M. Ricca, *ibid.*, **41**, 2178 (1958); E. Briner and S. Fliszár, *ibid.*, **42**, 1310 (1959); E. Briner and S. Fliszár, *ibid.*, **42**, 2063 (1959).

[10] (a) R. Criegee, S. S. Bath, and B. von Bornhaupt, *Chem. Ber.*, **93**, 2891 (1960); (b) G. Schröder, *ibid.*, **95**, 733 (1962); (c) P. Kolsaker, *Acta Chem. Scand.*, **19**, 223 (1965); (d) F. L. Greenwood and B. J. Haske, *Tetrahedron Letters*, 631 (1965); (e) R. W. Murray, R. D. Youssefyeh, and P. R. Story, *J. Am. Chem. Soc.*, **88**, 3143 (1966); (f) F. L. Greenwood, *ibid.*, **88**, 3146 (1966).

[11] R. Criegee in "Peroxide Reaction Mechanisms," J. O. Edwards, Ed., Interscience Publishers, Inc., New York, N. Y., 1962, p 29.

The alternative mechanisms (Schemes I and II) can be discussed in terms of the fate of the oxygen of the added aldehyde molecule. This atom can be labeled ^{18}O and its subsequent interaction followed ($O^* = {}^{18}O$). The Criegee mechanism considers that the ^{18}O from the added aldehyde will be incorporated exclusively in the ether oxygen of the ozonide resulting from the aldehyde–zwitterion reaction. However the mechanism represented by Scheme II, which has been studied for aliphatic olefins and which the authors claim to apply mainly to *trans*-disubstituted and relatively unhindered *cis*-disubstituted olefins,[3,10e] involves the ^{18}O incorporation into one of the peroxidic oxygens of the ozonide.

Murray, Story, *et al.*,[12] have recently supported their mechanism by the ozonolysis of *trans*-diisopropylethylene in the presence of acetaldehyde-^{18}O in which they located the ^{18}O in the peroxidic oxygen position using a $LiAlH_4$ reduction technique. In a previous communication,[4] the present authors reported, on the basis of mass spectral evidence, that the ozonolysis of *cis*- and *trans*-stilbenes in the presence of benzaldehyde-^{18}O leads to a major incorporation of ^{18}O in the ether oxygen of the *cis*- and *trans*-ozonides.

This present communication is concerned with the ozonization, in the presence of benzaldehyde-^{18}O, of *cis*- and *trans*-stilbenes, styrene, *trans*-β-methylstyrene, and triphenylethylene, with particular reference to the position of incorporation of the ^{18}O atom within the ozonides produced.

As it is well known that the lowering of the temperature retards the decomposition of the initial ozonides, which will thus favor an initial ozonide–aldehyde mechanism, wherever possible experiments have been performed at −78°. This was the case with *cis*-stilbene, styrene, and *trans*-β-methylstyrene and with the stilbene ozonide obtained from styrene. Unfortunately, the low solubility of *trans*-stilbene and triphenylethylene at −78° prevented the ozonolysis of these olefins at this temperature.

Results

The *cis*- and *trans*-Stilbene Ozonides. *cis*-Stilbene solutions (0.1 *M* in pentane) were ozonized in the presence of 0.1 *M* $PhCH^{18}O$ (9.8% ^{18}O) at −78 and 25° with 70–90% of the theoretical amount of ozone. *trans*-Stilbene was studied in a similar way at −20 and 25°. The following ozonides were isolated (after evaporation of most of the solvent) by fractional crystallization and purified by recrystallization in CH_3OH. (i) Ozonide, mp 74° (lit.[13] mp 74°), is a 1:1 mixture of the *cis*- and *trans*-ozonides, as shown by the two nmr signals (in CCl_4) at τ 3.79 and 3.83 (methine protons) and by infrared spectroscopy (bands in CCl_4 at 914 and 952 cm^{-1}). Nmr measurements made with *cis–trans* mixtures in known proportions, prepared from the pure isomers, confirm the reliability of the method used. (ii) Ozonide, mp 82°, gives only the nmr signal at τ 3.79, and the two infrared bands at 914 and 952 cm^{-1}. (iii) Ozonide, mp 94°, also observed by Criegee,[13] shows the nmr signal at τ 3.83 and the infrared band at 914 cm^{-1}.

By comparison with similar systems[3b,10c,14] it seems reasonable to assign the *trans*-ozonide configuration to the higher melting compound (τ 3.83) and the *cis* configuration to the compound of mp 82° (τ 3.79).[15]

These isolation experiments were performed on solutions possessing ozonide *cis*/*trans* ratios of 60.5/39.5 in pentane at 25°, for the ozonization of *cis*-stilbene, and of 59/41 for the ozonization of the *trans*-olefin at the same temperature in pentane. At the lower temperatures these *cis*/*trans* ratios are practically unaltered. Although the *cis*-ozonide was always found to be in excess, the *trans* isomer was isolated in some cases because its lower solubility in pentane and in methanol made the isolation possible. The solubilities reported by Griesbaum[15] are, for CH_3OH, 0.95 g/100 ml for the *trans*-ozonide and 1.79 g/100 ml for the *cis* isomer, at room temperature. The isolation experiments are, however, difficult to reproduce, particularly in the presence of excess benzaldehyde. For this reason we failed to isolate the compounds of mp 82 and 94° in all of the labeling experiments (Table I) although, in other cases, all the three ozonides were isolated, both from *cis*- and *trans*-olefins.

It is considered that the tentative assignments of the stilbene ozonide configurations presented here are to be expected from the general properties exhibited by *trans* isomers, which have, in general, higher melting points, lower solubilities, larger R_f values in chromatography than *cis* isomers. With reference to *all* these physical properties and the nmr evidence, our assignments correspond to those proposed by Kolsaker[10c] for the *cis*- and *trans*-ozonides of methyl *p*-methoxycinnamate. In the absence of any contradictory evidence, the present assignments appear to be reasonable. The results presented here indicate a lower τ value (methine protons) for the *cis*-ozonide than for the *trans* isomer. Similar results are observed for the corresponding methine protons of the *trans*- (τ 4.38) and *cis*-ozonides (τ 4.33) of methyl *p*-methoxycinnamate. The nmr results can be interpreted[14] by considering that in the *trans*-ozonide the methine protons lie *above* the planes of the phenyl groups and thus long-range shielding by the benzene ring will be favored. In the *cis*-ozonide, however, each proton is more remote from the phenyl groups. Consequently the shielding of the protons will be less than in the *trans* isomer and a lower τ value will be expected for the *cis* isomer.

Furthermore it should be noted that, utilizing the present assignments, the observed ozonide *cis*/*trans* ratio obtained from the ozonolysis of *cis*-stilbene (Table V) is significantly higher (63.6/36.4) than the ozonide *cis*/*trans* ratio obtained from *trans*-stilbene (59.7/40.3). The results reported by Kolsaker[10c] are similar. The ozonide *cis*/*trans* ratio obtained by the ozonolysis of *cis*-

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(12) P. R. Story, C. E. Bishop, J. R. Burgess, R. W. Murray, and R. D. Youssefyeh, *J. Am. Chem. Soc.*, **90**, 1907 (1968).

(13) R. Criegee, A. Kerckov, and H. Zinke, *Chem. Ber.*, **88**, 1878 (1955).

(14) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, Inc., New York, N. Y., 1959, p 126.

(15) K. Griesbaum (Ph.D. Thesis, Karlsruhe, 1960) has described the *cis*-stilbene ozonide (mp 90–92°) and the *trans* isomer (mp 100–102°), which were obtained pure after many recrystallizations, and found, in $CDCl_3$, τ 3.82 (*trans*-ozonide) and τ 3.78 (*cis* isomer). However, from Griesbaum's results, the isomer with the lower melting point was tentatively assigned the *trans* configuration on the basis of dipole moment measurements. This isomer had a dipole moment of 1.44 D, which was smaller than the value of 1.55 D for the higher melting point isomer. Our measurements indicate a dipole moment of 1.55 ± 0.01 D for the isomer of mp 82°, and further work is in progress to clarify this point.

Table I. ^{18}O-Labeling of Stilbene Ozonides

Olefin	Temp ozonolysis, °C	Ozonide mp, °C	% ^{18}O at fragments m/e 196	m/e 122	m/e 106
cis-Stilbene	−78	74	5.0 ± 0.3	4.5 ± 0.1	0.86 ± 0.06
		94	5.9 ± 0.5	4.2 ± 0.1	1.15 ± 0.05
	25	74	7.4 ± 0.3	5.7 ± 0.1	1.85 ± 0.05
trans-Stilbene	25	74	6.6 ± 0.2	5.4 ± 0.1	1.16 ± 0.08
		82	5.0 ± 0.4	4.2 ± 0.1	0.56 ± 0.05
	−20	82	5.1 ± 0.35	4.9 ± 0.1	0.67 ± 0.04
Styrene[a]	20	74	34.8 ± 0.2	29.4 ± 0.1	5.7 ± 0.1
		74	34.6 ± 0.1	28.2 ± 0.7	6.1 ± 0.1
	−78	74	34.3 ± 0.1	28.0 ± 0.1	6.1 ± 0.1

[a] In CCl_4 solution.

methyl *p*-methoxycinnamate is higher (55/45) than the *cis*/*trans* ratio obtained from the *trans*-olefin (47/53). The observation that the *cis*/*trans* ratio is higher when a *cis*-olefin is ozonized, when compared to the *cis*/*trans* ratio obtained from the corresponding *trans*-olefin, is also in agreement with the very numerous observations made with olefins which show a stereospecifical dependence of the ozonide *cis*/*trans* ratio on olefin geometry.[3b,8b,10]

The stilbene ozonide, obtained as a cross ozonide during the ozonization of styrene in the presence of $PhCH^{18}O$ (as described in the next section), has mp 74° and is shown to be identical with the ozonide of the same melting point obtained from the *cis*- and *trans*-stilbenes.

The mass spectra[16] of the products of mp 74, 82, and 94° are practically identical; two possible fragmentation patterns (a and b) of the ozonide ring yielding *m*/*e* 122 and 106 are considered, as well as the fragmentation (c) yielding *m*/*e* 196.

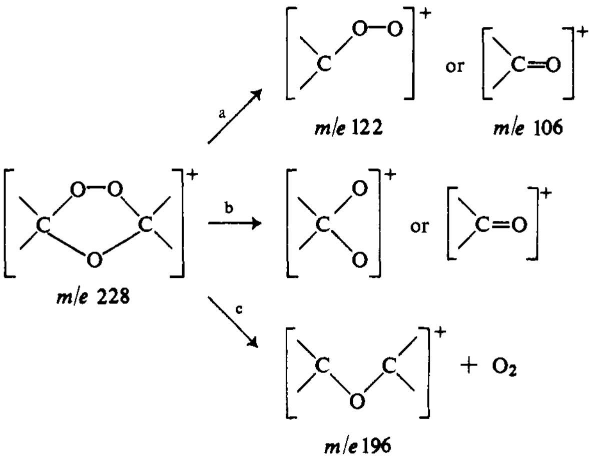


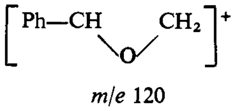
Table I shows the percentage of the molecules which have M + 2 (due to the replacement of ^{16}O by ^{18}O) in the *m*/*e* 196, 122, and 106 fragments. Whatever the mode of fragmentation (a or b), the sum of the incorporations of ^{18}O in the *m*/*e* 122 and 106 fragments represents the total labeling of the ozonide ring. This sum can be greater than or equal to the labeling of the ether oxygen. If the total labeling in the *m*/*e* 122 and 106 fragments exceeds that of *m*/*e* 196, then ^{18}O incorporation in the peroxidic oxygens takes place, whereas equal labeling in the *m*/*e* 122 and 106 fragments and in the *m*/*e* 196 fragment means that all the ^{18}O is found in the ether oxygen.

These results show that the total per cent labeling in the *m*/*e* 122, and 106 fragments does not (within experimental error) exceed significantly the labeling in the *m*/*e* 196 fragment. We conclude therefore that the ozonolysis of both *cis*- and *trans*-stilbenes under our experimental conditions leads to a major incorporation of ^{18}O in the ether oxygen. The same conclusion can be drawn for the stilbene ozonide formed, as cross ozonide, in the ozonolysis of styrene.

The Ozonization of Styrene. As previously shown,[17] if the Criegee mechanism is assumed, the styrene initial ozonide, in CCl_4 solution, cleaves to give 59 ± 1% PhC^+HOO^- + HCHO and, hence, 41 ± 1% HC^+HOO^- + PhCHO. Thus, in the presence of $PhCH^{18}O$, it is expected that the labeled stilbene ozonide will be obtained in good yield, beside the "normal" styrene ozonide.

Styrene solutions (0.2 *M* in pentane or CCl_4) were ozonized in the presence of 0.2 *M* $PhCH^{18}O$ (44.6% ^{18}O) with 70–90% of the theoretical amount of ozone. The styrene ozonide and the stilbene ozonide (mp 74°) were isolated and examined by mass spectrometry.

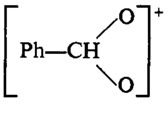
The styrene ozonide was found to possess an intense molecular ion (*m*/*e* 152), from which the total incorporation of ^{18}O in the ozonide can be calculated. Unfortunately the fragment ion



m/*e* 120

is not of quantitative value since the corresponding labeled fragment (*m*/*e* 122) cannot be distinguished from the fragment ions

$[Ph{-}CH{-}OO]^+$ or



m/*e* 122

either or both of which are abundant fragment ions from the nonlabeled styrene ozonide.

The fragment ion *m*/*e* 119, which corresponds to the *m*/*e* 120 fragment less one hydrogen is, however, readily observed, as is the corresponding fragment ion for the labeled compound. Table II shows the percentage of

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(16) A detailed study on the mass spectrometry of ozonides is presented by J. Castonguay, M. Bertrand, J. Carles, S. Fliszár, and Y. Rousseau, *Can. J. Chem.* **47**, 919 (1969).

(17) S. Fliszár, *ibid.*, **44**, 2351 (1966); S. Fliszár, and J. Renard, *ibid.*, **45**, 533 (1967).

ions which have M + 2 (due to the replacement of ^{16}O by ^{18}O) in the molecular ion *m/e* 152 and in the fragment *m/e* 119. Equal labeling implies that all the ^{18}O is found in the ether oxygen of the ozonide.

Ozonization of *trans*-β-Methylstyrene. The ozonide of *trans*-β-methylstyrene was obtained from the ozonization of 0.2 *M* solutions in CCl_4 at 20° or pentane at 20 and −78° in the presence of $PhCH^{18}O$ (44.6% ^{18}O). The nmr spectra of this ozonide indicated an approximate 1:1 mixture, which could not be separated by the techniques used.

It has been found[18] that the ozonolysis of *trans*-β-methylstyrene in CCl_4 solution yields, on the assumption of the Criegee mechanism, 82 ± 1% of $CH_3C^+HOO^-$ + PhCHO and, accordingly, 18 ± 1% of PhC^+HOO^- + CH_3CHO. This direction of cleavage explains the small yields of stilbene ozonide also produced in these labeling experiments and revealed by the nmr spectra. These yields of stilbene ozonide were too small to permit isolation and purification.

The mass spectral analysis of the *trans*-β-methylstyrene ozonide reveals the molecular ion (*m/e* 166) as well as the fragment *m/e* 134, due to loss of O_2 from the ozonide molecule (fragmentation pattern a), and the fragment ion *m/e* 133, due to loss of one hydrogen from *m/e* 134. This latter fragment is similar, from the standpoint of hydrogen loss, to that of *m/e* 119 which is observed in the mass spectra of the styrene ozonide. The results given in Table III show clearly that the ^{18}O incorporation in the fragments *m/e* 134 and 133 is the same. Equal incorporation in the fragments *m/e* 134, 133 and in the molecular ion *m/e* 166 reveals that the ^{18}O is found in the ether oxygen of the ozonide.

Further possible fragmentation patterns of the ozonide in the mass spectrometer can be considered. Patterns b and c yield *m/e* 60 and 106, and d and e yield *m/e* 122 and 44.

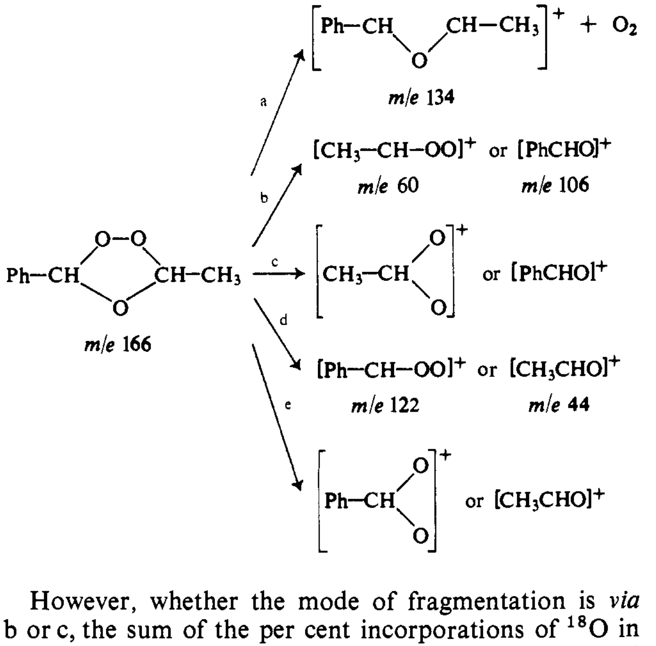

Table II. Ozonization of Styrene

Solvent	Temp ozonolysis, °C	% ^{18}O at fragments *m/e* 152	*m/e* 119
CCl_4	20	15.3 ± 0.2	15.7 ± 0.2
Pentane	20	16.5	16.1
	−78	12.5	12.7

Table III. Ozonization of *trans*-β-Methylstyrene

Ion *m/e*	CCl_4, 20°	Pentane, 20°	Pentane, −78°
166	30.4 ± 0.8	27.1 ± 0.4	22.2 ± 0.2
134	28.3 ± 0.8	26.3 ± 0.4	21.8 ± 0.3
133	29.5 ± 0.6	27.1 ± 0.4	22.4 ± 0.2
122	24.5 ± 0.1	23.0 ± 0.1	18.5 ± 0.1
106	5.8 ± 0.3	5.2 ± 0.3	4.3 ± 0.3
60	26.6 ± 1.2	23.4 ± 1.2	18.7 ± 1.2
44	4.5 ± 0.4	4.3 ± 0.2	4.0 ± 0.3

Table IV. Ozonization of Triphenylethylene

Ion *m/e*	CCl_4, 20°	Pentane, 20°
272	33.0 ± 1.0	31.8 ± 0.5
271	31.0 ± 1.0	32.4 ± 0.7
198	19.3 ± 0.8	17.7 ± 0.8
182	3.5 ± 0.2	3.8 ± 0.2
122	27.6 ± 0.2	28.6 ± 0.2
106	10.8 ± 0.4	12.6 ± 0.4

However, whether the mode of fragmentation is *via* b or c, the sum of the per cent incorporations of ^{18}O in the *m/e* 60 and 106 fragments represents the total labeling in the ozonide ring. This is confirmed by the comparison of this sum with the percentage labeling found in the *m/e* 166 molecular ion. Similarly, a consideration of the possible fragmentation patterns d and e indicates that the sum of the incorporations of ^{18}O in the *m/e* 122 and 44 fragments represents the total labeling in the ozonide ring.

Table III shows the percentage of the fragments which have M + 2 (due to the replacement of ^{16}O by ^{18}O). These results clearly indicate that, within experimental error, the labeling takes place in the ether oxygen of the ozonide, irrespective of the temperature of the ozonolysis.

The Ozonization of Triphenylethylene. The cleavage, in CCl_4 solution, of the initial ozonide of triphenylethylene into carbonyl compounds and zwitterions yields,[18] on the basis of Criegee's mechanism, 71 ± 1% of $Ph_2C^+OO^-$ + PhCHO and, hence, 29 ± 1% of Ph_2CO + PhC^+HOO^-. The main product of ozonolysis of this olefin in the presence of added benzaldehyde is thus the "normal" triphenylethylene ozonide. However, smaller amounts of stilbene ozonide have been isolated but have not been studied further, since these small amounts are difficult to purify.

The triphenylethylene (0.2 *M*) in CCl_4 and in pentane was ozonized at 20° in the presence of 0.2 *M* $PhCH^{18}O$ (44.6% ^{18}O). Attempts to ozonize this olefin at lower temperatures failed because solubility of this olefin in cold pentane is too low.

Mass spectral analysis indicated the fragmentation patterns outlined below. No molecular ion of triphenylethylene ozonide was observed.

In addition to the fragments *m/e* 272, 198, 106, 182, and 122, the fragment ion *m/e* 271 was observed. This corresponds to the *m/e* 272 fragment ion, less one hydrogen, which is confirmed by the calculation that the

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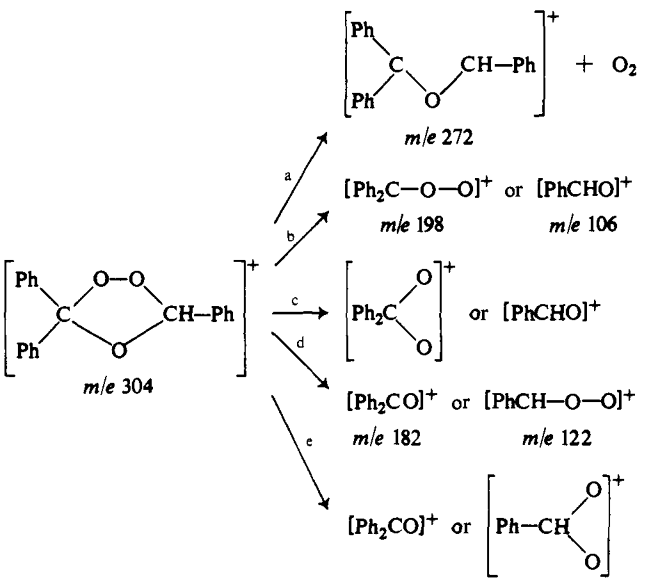
(18) S. Fliszár and M. Granger, to be published shortly.



same ^{18}O incorporation occurs in the m/e 272 and 271 fragments. This incorporation represents the labeling of the ether oxygen of the ozonide, which can be compared with the total labeling of the ozonide, as calculated from the fragmentation patterns b–e. Table IV gives the percentage of the fragments having M + 2, arising from the replacement of ^{16}O by ^{18}O.

Whatever the mode of fragmentation (b or c), the sum of the incorporations in *m/e* 198 and 106 represents the total labeling of the ozonide. Similarly, with fragmentation patterns d or e, the sum of the incorporations in *m/e* 182 and 122 also represents the total labeling of the ozonide. For the sample prepared in CCl_4, a total labeling of 30.1% (b, c) and 31.1% (d, e) was obtained in this way. This compares favorably with the incorporation of 31–33% found in the ether oxygen of the ozonide. For the ozonide prepared in pentane solution, one finds a total labeling of 30.3% (b, c) and of 32.4% (d, e), which is in good agreement with the values found for the ether oxygen, *i.e.*, 31.8–32.4%. Thus, in no case does the total labeling exceed that corresponding to the ether oxygen, which therefore can be considered to contain all the ^{18}O of the ozonide.

Discussion

The results presented above provide good evidence that the olefins which have been examined incorporate the ^{18}O exclusively in the ether oxygen when ozonization takes place in the presence of ^{18}O-labeled aldehyde. This is observed with all the olefins ozonized at room temperature and also with styrene, *trans*-β-methylstyrene and with the stilbene ozonide resulting, as cross ozonide, from ozonization of styrene, at low temperatures. The latter observation is of particular interest, remembering that at low temperatures the slower decomposition of the initial ozonides would favor the initial ozonide–aldehyde mechanism. The absence of ^{18}O in the peroxidic oxygens of the ozonides indicates that the reaction Scheme II is inadequate even under these conditions of low temperature, at least for the olefin studied in this paper.

Although the incorporation of ^{18}O corresponds to that shown in Scheme I, the original Criegee mechanism cannot be applied to those cases in which the stereospecific dependence of the *cis-/trans*-ozonide ratio on the geometry of the original olefin is observed. This stereospecificity is observed in the change in the *cis-/trans*-stilbene ozonide ratios when these ozonides are obtained from different olefins (Table V). These results are in agreement with the stereospecifical dependence observed for a number of alpiphatic olefins.[3,5,10e]

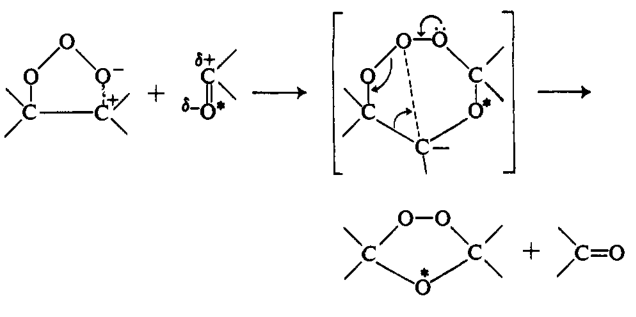
Table V. Stilbene Ozonide *cis/trans* Ratios Observed in CCl_4 at 20°

Olefin ozonized	Stilbene ozonide *cis/trans* ratio
cis-Stilbene	63.6/36.4
trans-Stilbene	59.7/40.3
Triphenylethylene	65.0/35.0
Styrene	58.9/41.1
trans-β-Methylstyrene	58.1/41.9

Since Scheme II, which has been used to explain this dependence,[3] has been shown not to be applicable and the original Criegee mechanism[6] is inadequate, further mechanisms must be considered.

An alternative initial ozonide–aldehyde interaction may be proposed (Scheme III). This mechanism agrees with the presented results, as does mechanism I, in that the labeled ^{18}O is finally situated in the ether oxygen of the ozonide.

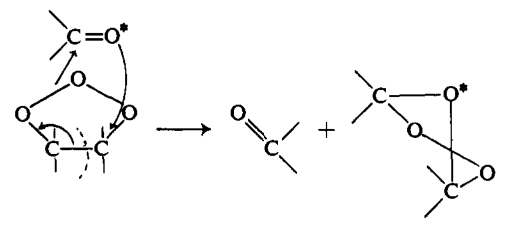
Scheme III



The mechanisms outlined in Schemes II and III differ by the mode of attack of the aldehyde on the molozonide, but, since the seven-membered ring intermediate is the same in each case, they are equally flexible in their attempt to explain the facts observed by Murray, *et al.*,[3,10e] concerning the *cis-* and *trans*-ozonide distributions.

A fourth mechanism, suggested by Criegee,[19] also involves an initial ozonide–aldehyde interaction (Scheme IV).

Scheme IV



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(19) R. Criegee, private communication.

Table VI. Proportions of *cis*-Stilbene Ozonide, Obtained at 20° in CCl_4

Olefin	% *cis*-Stilbene ozonide	
	Without added PhCHO	0.15 *M* PhCHO added
cis-Stilbene	63.6 ± 0.8	63.8 ± 0.8
trans-Stilbene	59.7 ± 0.4	59.6 ± 0.7
Triphenylethylene	65.0 ± 0.8	65.0 ± 0.7
Styrene	58.9 ± 0.5	59.0 ± 0.7

This initial ozonide–aldehyde displacement mechanism is considered to be concerted rather than to involve cleavage of the initial ozonide into aldehyde and zwitterion followed by combination of the latter with the foreign aldehyde. This reaction scheme agrees with the results of the labeling experiments and can also explain the observed dependence of the ozonolysis path on the olefin geometry.

However, the reactions represented by Schemes III and IV, both of which are initiated by an initial ozonide–aldehyde reaction, imply that the presence of added aldehyde will influence the *cis-/trans*-ozonide distributions, since an initial ozonide–aldehyde interaction would then be favored. The results shown in Table VI indicate that the addition of excess benzaldehyde does not influence the *cis-/trans*-stilbene ozonide distributions and it may be concluded on this basis that both mechanisms III and IV are unlikely to occur, although significant differences are observed in the *cis/trans* ratios.

Further evidence that Schemes II–IV, which involve an initial ozonide–aldehyde mechanism, play no part in directing the *cis-/trans*-ozonide distributions is indicated by the observation that the stereospecific dependence of these distributions on the olefin geometry is observed even as high as 20°, at which temperature extremely rapid decomposition of the initial ozonide is expected to occur.

It appears probable, therefore, that Scheme I—the Criegee mechanism—is the only one consistent with the present results. However, the important observations by Murray, *et al.*,[3b,10e] on the stereospecific dependence of the ozonide *cis/trans* distribution cannot be overlooked. Their observations may be explained in terms of a refined Criegee mechanism which invokes the formation of *syn* and *anti* zwitterions during the cleavage of the initial ozonide. The possible existence of *syn* and *anti* zwitterions was originally suggested by Criegee[11] and this concept was recently developed by Bailey[5] to explain the stereospecificity of ozonide formation. The stereospecific effects observed are consistent with such a mechanism involving the stereoselective decomposition of *cis*- and *trans*-initial ozonides to isomeric *syn* and *anti* zwitterions and the stereoselective recombination of these with aldehydes to give final ozonides.[5] Further work is in progress by the authors to obtain additional information on the involvement of the *syn* and *anti* zwitterions in ozonolysis.[20]

It must be stressed that in the present work only aromatic olefins have been studied. The present study does not necessarily imply that our conclusions would also be true for the aliphatic olefins. Aliphatic initial ozonides may be longer lived than the aromatic initial ozonides (at very low temperature) and, therefore, in favorable cases, it may be possible to observe some form of initial ozonide–aldehyde mechanism when aliphatic olefins are used.

Experimental Section

Ozonolysis Procedure. The technique of ozonolysis, using O_2–O_3 mixtures, together with the dosimetry of ozone, has been described previously.[21] The ozone output was varied between 0.07 and 0.2 mmol of O_3/min.

Nonlabeled Ozonides. Styrene ozonide and stilbene ozonide (mp 74°) were prepared and purified according to the method of Criegee, *et al.*[13] The preparation and description of the ozonides of triphenylethylene and β-methylstyrene have been reported elsewhere.[16]

^{18}O-Labeled Ozonides. The labeled ozonides were obtained by ozonizing 25 ml of 0.2 *M* solution of olefin in either CCl_4 or pentane in the presence of 0.2 *M* $PhCH^{18}O$ at the appropriate temperatures indicated in the text. The ozone was limited to 80% of the theoretical amount, in order to prevent formation of peracids (namely perbenzoic acid) due to the autoxidation of aldehydes, which is enhanced by ozone when no olefin is present to prevent this autoxidation.

The isolation of the ozonides was performed using a column (Baker silica gel) chromatograpic work-up procedure. The first fraction collected (CCl_4 fraction) contained some unreacted olefin. The ozonides were collected using a 1:1 hexane–benzene mixture and were purified by repeating the chromatographic procedure. In the case of styrene, triphenylethylene and β-methylstyrene, the stilbene ozonide, which is obtained as the cross ozonide, was collected in the hexane–benzene fraction prior to the "normal" ozonide of the particular olefin used. The stilbene ozonides, and the triphenylethylene ozonide, were further purified by crystallization from hot methanol.

The *cis*- and *trans*-stilbene ozonides have been obtained, as described in the text, by fractional crystallization. These isolation experiments, which are difficult to reproduce, have also been described by Griesbaum.[15]

Mass Spectral Analysis. The spectra were recorded using a single focussing Hitachi RMU-6D mass spectrometer, with a direct introduction system MG 158. The vapor pressures of the compounds examined are sufficiently high, so that no external heat on the sample holder was required. The ionization chamber was maintained between 150 and 170°, and the ionizing electrons were accelerated by a 70-V potential.

Measurements of the *cis-/trans*-Ozonide Ratios. For each experiment, 5 mmol of olefin, dissolved in 25 ml of CCl_4, was maintained at 20 ± 0.1° until temperature equilibration was attained. In the five to seven runs made for each olefin the amounts of ozone used were varied between 30 and 80% of the theoretical amount. The experiments, in which benzaldehyde was added, were performed under identical conditions, using an aldehyde concentration of 0.15 *M*. On completion of the ozonization, the solvent was evaporated and replaced by the minimum amount of CCl_4, and the nmr spectra recorded using tetramethylsilane as internal reference.

The stilbene ozonide *cis/trans* distributions (Tables V and VI) were, with one exception, calculated from nmr spectra recorded using a Varian A-60 and a JEOLCO C-60 H spectrometer. In the case of the ozonolysis of the *trans*-β-methylstyrene a JEOLCO 4 H-100 spectrometer was used. The higher resolution of this spectrometer enables the signal associated with *cis*- and *trans*-stilbene ozonides (τ 3.79 and 3.83) to be easily distinguished from those associated with the *cis*-β-methylstyrene ozonide (τ 4.00) and its *trans* isomer (τ 4.04). On the 100-cps scale the signals for the *cis*-stilbene ozonide (τ 3.79) and the *trans* isomer (τ 3.83) can be integrated separately. Measurements made with known proportions of *cis/trans* mixtures, which were prepared from the pure isomers, confirmed the reliability of the method used. Control experiments showed that the unreacted olefin, the aldehydes, and the peroxides, in addition to the "normal" ozonides which were

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[20] The stabilization of *syn* and *anti* zwitterions, at room temperature, by olefin or solvent molecules are discussed in a forthcoming paper.

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

produced during the ozonolysis of unsymmetrical olefins, did not interfere with the measurements. It was found that the *cis/trans* distributions did not depend on the extent of the reaction. The given proportions (Tables V and VI) were calculated from five to seven independent experiments in each case and they are expressed with a 95% confidence limit.

Acknowledgment. The authors express their gratitude to Professor Y. Rousseau and to Mr. M. Bertrand and J. Castonguay for their analysis of the mass spectra. The financial support given by the National Research Council of Canada is gratefully acknowledged.

Kinetics and Mechanism of the Osmium Tetroxide Catalyzed Oxidation of Acetone and Ethyl Methyl Ketone by Alkaline Hexacyanoferrate(III) Ion[1]

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Abstract: The studies in the kinetics of the osmium tetroxide catalyzed oxidation of acetone and ethyl methyl ketone by aqueous alkaline potassium hexacyanoferrate(III) were made at four temperatures to investigate the way osmium tetroxide participates as catalyst in the oxidation of ketones. The data suggest that the oxidation of these ketones proceeds *via* the formation of an activated complex between the enolate and osmium tetroxide which rapidly decomposes followed by a fast reaction between the reduced osmium species and ferricyanide. The product study has made it possible to give the intermediates and the reactions which occur.

Catalysis of oxidation by hexacyanoferrate(III) ion has been observed with a number of metal salts.[2] Recently, osmium tetroxide has been used as catalyst in analytical procedures with hexacyanoferrate(III) ion.[3] Solymosi[4] has studied a number of oxidations with alkaline hexacyanoferrate(III) ion in presence of osmium tetroxide from an analytical viewpoint. Krishna and Singh[5] were the first to examine kinetic features of this problem, and accordingly, they have studied the osmium tetroxide catalyzed oxidation of methanol and ethanol by hexacyanoferrate(III) ion in aqueous alkaline medium. The study was quite limited and could not account for much except a guidance in this field. Recently an attempt was made by us in the oxidation of mandelate ion,[6] and it has been concluded that there is formation of a mandelate–osmium complex through the hydroxyl group which decomposes with hydroxide ion giving an osmium(VI) species which in turn is rapidly oxidized by hexacyanoferrate(III) ion. However, the exact role of the osmium tetroxide in the oxidation of ketones has not yet been shown, and the present study has been made to obtain definite information concerning the possible participation of osmium tetroxide in the oxidation of methyl ketones by aqueous alkaline hexacyanoferrate(III) ion. Accordingly, the kinetic investigations were carried out with acetone and ethyl methyl ketone at four temperatures. The details of the results are presented.

Results and Discussion

The hexacyanoferrate(III) ion oxidation of these ketones has already been studied by the previous workers in alkaline medium in the absence of osmium tetroxide[7,8] catalyst, so here an attempt has been made to study the reactions in such a condition where there is no appreciable oxidation without the catalyst osmium tetroxide. The details of the kinetic data for the rate of osmium tetroxide catalyzed oxidation of acetone and ethyl methyl ketone are presented in Tables I–VI. The kinetic measurements were carried out in aqueous alkaline buffer solution obtained by carbonate and bicarbonate ions.

The standard zero-order rate constants (k_s) presented in these tables are the average ones obtained from a particular run and are given in terms of the concentration of hexacyanoferrate(II) ion obtained per minute.

The exact nature of the reaction is shown in Figures 1 and 2. Figure 1 shows a typical zero-order plot for the rate of oxidation of acetone and Figure 2 shows the same for the rate of oxidation of ethyl methyl ketone. It is obvious from these plots that the reaction velocity remains constant even up to 98% of the reaction. However, in the case of ethyl methyl ketone, some deviations occur from the above view when the concentration of hexacyanoferrate(III) ion or the catalyst is increased. The zero-order velocity constants begin to increase after some 65–70% of reaction. From these data it has been concluded that this increase in zero-order rate constant values might be due to further oxidation of some intermediate whose rate might appear after a certain interval of time at higher concentrations of hexacyanoferrate(III) ion or the catalyst osmium tetroxide. Table IA and B

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(1) Part of the work assigned for the Ph.D. degree of V. N. Singh, University of Allahabad, 1968.

(2) L. Rosenthaler, *Chem. Zentr.*, **56**, 441 (1932).

(3) N. Suseela, *Z. Anal. Chem.*, **145**, 175 (1955).

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