A similar analysis of the solvent effect on E_T for the well-characterized n → π^* transition of ethyl acetate in aqueous ethanol[11] shows a steady monotonic drift of E_T from 140.0 kcal/mole in water to 138.38 kcal/mole in $X_{H_2O} = 0.582$, although the ethyl acetate ground state goes through a clearly defined maximum at $X_{H_2O} = 0.85$ in this system.[3,4]

Although we consider the above type of analysis of solvent effects on transition energies to be formally correct, several factors complicate interpretation of the results. Firstly, the position of λ_{max} on the broad well-separated spectral curves for these large molecules in solution is not purely a function of transition energy, but also of transition probability. There can be no change in solvation entropy during a Franck–Condon transition so that the entropy of transfer of the excited state from one solvent to another will be the same as that for the ground state. However, change in solvation entropy of the ground state, due to a change in solvent composition, can alter the position of the most likely frequency for energy absorption among a continuum of closely related transitions under the band envelope. Second, there is no guarantee that a solvent effect on the excited state ($\delta_M\Delta\bar{H}_s^{Ex}$) does not reflect a distortion of its potential function rather than a raising or lowering of the entire Morse curve. This factor is a clean breakdown of the analogy to molecules in quasiequilibrium with transition states.

The aqueous *t*-butyl alcohol system was chosen for the present study because prior experience with enthalpy behavior in aqueous binaries suggested that an easily dissected spectral shift would occur in this system. There is every reason to believe[12] that other binary mixtures also will give characteristic solvent enthalpy effects while dissolving a much wider range of organic solutes than do the aqueous ones. A practical consequence of such research could be a greater control over photochemical processes. We are pursuing this approach.

(11) W. Closson unpublished results. We are grateful to Professor Closson for making these data available to us.

(12) D. R. McKelvey, unpublished results.

E. M. Arnett, D. Hufford, D. R. McKelvey
Department of Chemistry, University of Pittsburgh
and Mellon Institute, Pittsburgh, Pennsylvania 15213

Received March 29, 1966

Evidence against an Exclusive Zwitterion Intermediate in Ozonide Formation

Sir:

The mechanism of ozonolysis of the carbon–carbon double bond is usually interpreted as involving formation of an unstable primary ozonide followed by its decomposition into zwitterion and carbonyl fragments.[1] Recombination of these fragments is then thought to lead to the normal ozonide. We wish to report results which clearly demonstrate that ozonide cannot arise exclusively through the intermediacy of the Criegee zwitterion and a carbonyl fragment. Specifically, we have found that the *cis*:*trans* ratio in the two symmetrical ozonides produced upon ozonolysis of an unsymmetrical olefin *is dependent upon olefin geometry*.

Contrary to Criegee's proposal that recombination of the zwitterion and carbonyl fragments takes place without exchange in a solvent cage,[2] a number of recent reports have demonstrated that unsymmetrical olefins do, in fact, yield a mixture of both symmetrical and unsymmetrical ozonides[3–6] whose composition, at least in the pentene-2 system,[5] was dependent on the olefin concentration and the nature of the solvent. Furthermore, *cis–trans* isomeric ozonides have been observed in the ozonolysis of several olefins, including di-*t*-butylethylene,[7] 1,4-dibromo-2,3-dimethylbutene-2,[8] methyl oleate and elaidate,[4,9] methyl *p*-methoxycinnamate,[10] and a number of simple alkenes.[5,6,11]

The observation of isomeric *cis–trans* ozonides has provided the basis for an important new probe with which to study, in detail, the mechanism of ozonolysis; that is, it has now become possible to evaluate the effect of olefin geometry on the course of the reaction through the determination of *cis*:*trans* ozonide ratios. There are several reported examples in which there seems to be a definite dependence of the *cis*:*trans* ozonide ratio on olefin geometry.[6–8,10,11] Indeed, recent work in this laboratory indicates that such dependence is a general phenomenon and appears to be related to steric factors in the olefin. The results reported by Greenwood[12] on the relative stabilities of the molozonides from *cis*- and *trans*-olefin isomers are undoubtedly also intimately involved in this olefin–ozonide relationship.

The finding that ozonide configuration is influenced by the geometry of the parent olefin, of course, raises serious questions about the validity of the Criegee zwitterion–carbonyl combination as the ozonide-producing reaction since such a process would lead to the same *cis*:*trans* ozonide ratio for either the *cis*- or the *trans*-olefin. A more exacting test of the Criegee zwitterion mechanism, however, is provided by examining the effect of olefin geometry on the *cis*:*trans* ratios of *cross-ozonides* since, in these cases, an intramolecular stereoselective pathway[13] from the olefin–ozone adduct would be obviated.

We have determined the ratio of the cross-products, *cis*- (**1**) and *trans*-2,5-dimethylhexene-3 ozonide (**2**), produced in the ozonolysis of *cis*- (**3**) and *trans*-4-methylpentene-2 (**4**). On the basis of the Criegee zwitterion mechanism the *cis*:*trans* ratio of the cross-ozonides would, of course, be expected to remain invariant with olefin geometry. In fact, the diisopropyl ozonide (**1, 2**)[14] ratio obtained from *trans*-4-

(1) For a thorough discussion of the mechanism of ozonolysis, including the Criegee formulation, see P. S. Bailey, *Chem. Rev.*, **58**, 925 (1958).

(2) R. Criegee, *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.), **18**, 111 (1957).

(3) O. S. Privett and E. C. Nickell, *J. Am. Oil Chemists' Soc.*, **41**, 72 (1964).

(4) G. Riezebos, J. C. Grimmelikhuysen, and D. A. Van Dorp, *Rec. Trav. Chim.*, **82**, 1234 (1963).

(5) L. D. Loan, R. W. Murray, and P. R. Story, *J. Am. Chem. Soc.*, **87**, 737 (1965).

(6) O. Lorenz and C. R. Parks, *J. Org. Chem.*, **30**, 1976 (1965).

(7) G. Schröder, *Chem. Ber.*, **95**, 733 (1962).

(8) R. Criegee, S. S. Bath, and B. V. Bornhaupt, *ibid.*, **93**, 2891 (1960).

(9) O. S. Privett and E. C. Nickell, *J. Lipid Res.*, **4**, 208 (1963).

(10) P. Kolsaker, *Acta Chem. Scand.*, **19**, 223 (1965).

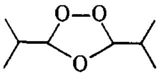
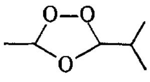
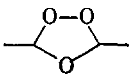
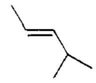
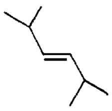
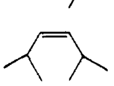
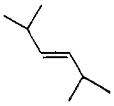
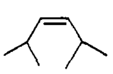
(11) F. L. Greenwood and B. J. Haske, *Tetrahedron Letters*, 631 (1965).

(12) F. L. Greenwood, *J. Org. Chem.*, **29**, 1321 (1964); **30**, 3108 (1965).

(13) This suggestion in very general terms has been offered to explain the observed stereochemical results for some *normal ozonides*.[5,6]

(14) Ozonolyses were carried out at *ca.* −70° and used 23.5 mmoles of olefin in 25 ml of pentane. Ozonolysis was continued to 75% of the

Table I. Summary of Ozonide *cis–trans* Ratios Observed

Olefins	 **1,2**	 **6**	 **5**
 4	50:50	48:52	38:62
 3	66:34	49:51	49:51
	53:47	. . .	. . .
	66:34	. . .	. . .
	$\xrightarrow{CH_3CHO}$ 56:44	47:53	. . .
	$\xrightarrow{CH_3CHO}$ 56:44	40:60	. . .

methylpentene-2 (**4**) was 50:50 (*c*:*t*) while that obtained from the *cis* olefin (**3**) was 66:34 (*c*:*t*). Likewise, the ratios in butene-2 ozonide (**5**), the other cross-ozonide, were 38:62 (*c*:*t*) from **4** and 49/51 from **3**[15] (Table I). These surprising results clearly indicate that *cross-ozonides are not produced exclusively by a Criegee zwitterion–carbonyl combination pathway* if, indeed, the Criegee zwitterion is involved at all.[16,17]

We have observed that the *cis*:*trans* ratio of methyl isopropyl ozonide (**6**) produced by ozonolysis of *cis*- and *trans*-diisopropylethylene in the presence of added acetaldehyde is also dependent upon olefin geometry, but that, in this case, the *cis*-olefin gives a *cis*:*trans* ozonide ratio less than 1, in sharp contrast to the previous example; the *trans*-olefin, on the other hand gives approximately the same *cis*:*trans* ratio.

To eliminate the possibility that ozonide formation may be reversible under any of the reaction conditions a control reaction was run whereby an ozonide of known *cis*:*trans* ratio was present during ozonolysis of another olefin and also in the presence of an added aldehyde. The *cis*:*trans* ratio of the recovered ozonide was unchanged.

The assignment of *cis* and *trans* structures to the ozonide geometric isomers was made on the basis of gpc, infrared, and nmr data as before.[5,18]

theoretical ozone required. In the aldehyde experiments, the same amount of olefin was used, but the solvent consisted of 23 ml of pentane and 2 ml of aldehyde. The ozonide analyses were made by gpc at 70° or lower using a 10-ft 10% cyanosilicone column. These conditions gave sufficient separation of the *cis–trans* isomers to permit separate integration. All ozonides gave correct C, H, and O analyses and had infrared and nmr spectra completely consistent with the assigned structures.

(15) Ozonide *cis*:*trans* ratios reported are the result of several integrations of the gpc peak area and have a maximum variation of ±0.5%. Control experiments demonstrated that the gpc conditions used do not affect the ozonide *cis*:*trans* ratios.

(16) We have observed the dependence of cross-ozonide *cis*:*trans* ratios on olefin geometry in several other cases as well.

(17) In the accompanying communication we consider some new proposals for the mechanism of ozonolysis.

(18) R. W. Murray, P. R. Story, and L. D. Loan, *J. Am. Chem. Soc.*, **87**, 3025 (1965).

R. W. Murray, R. D. Youssefyeh
Bell Telephone Laboratories, Inc.
Murray Hill, New Jersey

Paul R. Story
Department of Chemistry, The University of Georgia
Athens, Georgia 30601

Received April 9, 1966

The Ozonolysis Reaction. A Working Hypothesis

Sir:

Evidence has been presented in the preceding communication clearly demonstrating that the Criegee zwitterion cannot constitute the sole pathway to ozonide formation upon ozonolysis of the carbon–carbon double bond.[1] The factors influencing the ozonolysis reaction have not been at all well understood, and it now appears that the one unifying concept available, the Criegee zwitterion mechanism,[2] is, at best, somewhat limited and bears reexamination.

In the course of our investigations of the mechanism of this reaction, we have developed a working hypothesis, based on work in our own and in other laboratories, which we believe provides a cohesive framework for understanding the reaction of ozone and olefins.

In brief, it is our thesis that ozone and the double bond (**1**) first form a π complex, **2**, as previously suggested by Bailey,[3,4] regardless of the olefin structure. The fate of the π complex **2** is then determined principally by the steric requirements of the double bond substituents.[5]

***trans* and Sterically Unhindered *cis* Olefins.** There is good evidence[6,7] for the intermediacy of a molozonide in the ozonolysis of most *trans* olefins; reasonably unhindered *cis* olefins probably also lead to a molozonide (**3**). Consequently, we propose that the initial π complex, in these cases, collapses to the molozonide **3**.

Critical reexamination of the cleavage path usually depicted for molozonides[8,9] leads us to suggest an alternative pathway which can accommodate the finding that olefin geometry influences the structure of cross-ozonides.[1]

Using *trans*-4-methylpentene-2 (**1**) to illustrate, we contend that the most reasonable intermediate on heterolysis of the molozonide **3** is structure **4**.[10] This zwitterion (**4**) may, of course, cleave further to produce the Criegee zwitterion (**5**) and a carbonyl fragment. Recombination of these fragments may produce cross-ozonides, but ozonides whose geometry should be

(1) R. W. Murray, R. D. Youssefyeh, and P. R. Story, *J. Am. Chem. Soc.*, **88**, 3143 (1966).

(2) R. Criegee, *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.), **18**, 111 (1957).

(3) P. S. Bailey, *Chem. Ind.* (London), 1148 (1957).

(4) P. S. Bailey, *Chem. Rev.*, **58**, 925 (1958).

(5) We shall consider at this time only simple olefins containing no heteroatoms or other substituents which may introduce special electronic effects.

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

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

(8) R. Criegee in "Peroxide Reaction Mechanisms," J. O. Edwards, Ed., Interscience Publishers, Inc., New York, N. Y., 1962, p 32.

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

(10) This proposal is made on the grounds that a structure in which the positive charge can be delocalized over two oxygen atoms will be more stable than one involving a single positive oxygen.[8]