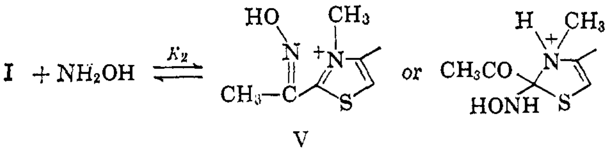
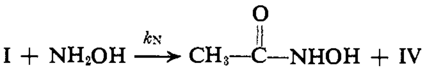
acyl carbonyl carbon, as in simple ester hydrolysis, is supported by the fact that if the acyl carbonyl were greatly susceptible to nucleophilic attack then the basic species of the buffers (particularly imidazole and Tris) would be anticipated to be nucleophiles as in the case of *p*-nitrophenyl acetate.[6,7] That hydration of the ketone could not be rate determining is also supported by the lack of effect of the buffer anions as general bases since ketone hydration is known to be quite susceptible to general base catalysis (for a compilation of references see ref 9). Carbonyl compounds whose hydrolysis follow the scheme of (1) are the electron-deficient ketones[8,9] in whose class I most logically falls.

In hydroxylamine buffers at constant pH the rate of disappearance of I from solution decreases with increase in concentration of NH_2OH (but is independent of NH_3^+-OH), reaching a constant minimum value. A reaction scheme in accord with this result is that of


(5)

V

$$I + OH^- \xrightarrow{k_{OH}} CH_3COO^- + IV$$



$$I + NH_2OH \xrightarrow{k_N} CH_3-\overset{O}{\overset{\|}{C}}-NHOH + IV$$

for which

$$\frac{-d[I]}{dt} = \left[\frac{k_{OH}[OH^-] + k_N[NH_2OH]}{1 + K_2[NH_2OH]}\right][T] \qquad (6)$$

where [T] = [I] + [II] + [V] (*i.e.*, the amount of [I] added to the solution at t_0). From the best fit of (6) to the experimental data (1620 IBM computer) the value of k_N = 1.117 l. mole^{-1} min^{-1} and K_2 = 100 mole^{-1}. A comparison of determined values of k_{obsd} (pH 6.04) for the disappearance of I in the presence of hydroxylamine to the values of k_{obsd} calculated from (6) are provided in Table I. Evidence for the ability of hydroxylamine to react at the 2 position of 2-acylthiazolium compounds has been found in biochemical studies.[10]

Table I. Comparison of Calculated (Eq 6) and Determined Values of the Pseudo-First-Order Rate Constants for the Disappearance of I[a]

	$k_{obsd} \times 10^2$, min^{-1}	
N_T, *M*	Calcd	Found
0.00	8.80	8.90
0.01	6.24	6.22
0.02	4.96	5.03
0.03	4.19	4.19
0.04	3.68	3.70
0.05	3.31	3.36
0.06	3.04	2.98
0.07	2.82	2.90
0.08	2.65	2.60
0.09	2.51	2.44
0.10	2.40	2.33

[a] As a function of N_T = (NH_2OH + NH_3^+OH) concentration (pH 6.04; μ = 1.0 with KCl, solvent water; T = 30°).

The reactions 5 are again those anticipated of an electron-deficient ketone. The ability of NH_2OH to act as a nucleophile toward the carbonyl carbon of I to yield a hydroxamate and an oxime or addition compound to the thiazole ring compared to the inability of the similarly basic imidazole to act as a nucleophile may be easily rationalized on the basis that bases exhibiting the α effect[11] are better nucleophiles than anticipated from their pK_a' values and provide kinetically more favorable and thermodynamically more stable derivatives (as V).[12] It should be concluded that the "high energy" 2-acetylthiamine shares with the also biologically important thioesters[13] the formation of kinetically important tetrahedral intermediates. This feature must be taken into account in the formulation of enzymic mechanisms for acyl transfer reactions involving 2-acetylthiamine. Further work on the mechanism of reactions of I is in progress.

Acknowledgment. This work was supported by the National Science Foundation.

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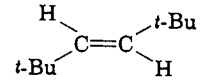
Structure of the Initial Ozone–Olefin Adduct

Sir:

Evidence that initial ozonides (ozone–olefin adducts)[1] actually exist has recently been obtained by Criegee and Schröder[2] and Greenwood[3] for certain *trans* olefins. There has been no proof offered, however, as to whether the structures of these substances are of type IV or V.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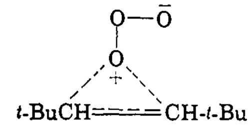
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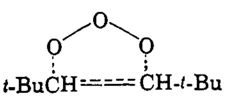
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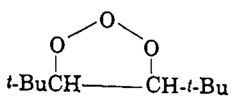
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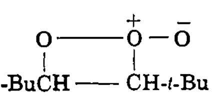
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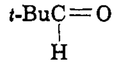
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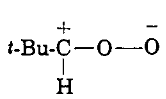
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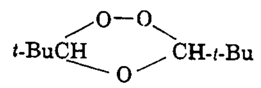
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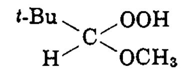
IX

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Table I. Nmr Studies of the Ozonation of *trans*-1,2-Di-*t*-butylethylene, etc.[a]

Spectra taken	Solvent	τ values: *t*-Butyl protons	τ values: Methine protons
Cold ozonation solution (initial ozonide of I)	Freon 11	9.03	5.80
Cold ozonation solution (initial ozonide of I)	Acetone-d_6	9.01	5.33
Ozonation solution at RT[c] (decomposition products)	Freon 11	8.95[b]	0.59
Ozonation solution at RT (decomposition products)	Acetone-d_6	9.09, 8.95	5.25, 0.54
Trimethylacetaldehyde (VI)	Freon 11	8.95	0.59
Trimethylacetaldehyde (VI)	Acetone-d_6	8.95	0.54
cis true ozonide (VIII)	Freon 11	9.03	5.24
cis true ozonide (VIII)	Acetone-d_6	9.03	5.10
trans true ozonide (VIII)	Freon 11	9.03	5.29
trans true ozonide (VIII)	Acetone-d_6	9.03	5.19
Starting olefin (I)	Freon 11	9.01	4.66
Starting olefin (I)	Acetone-d_6	9.01	4.60

[a] All solutions were approximately 1%; all τ values are measured in parts per million. [b] In addition, minor bands in the vicinity of τ 8.8–9.1 were observed. [c] RT, room temperature.

The other suggested structure, π complex II, does not appear likely for these initial ozonides, which actually have been observed and reduced to glycols.[2–4]

We have established structure type IV for the initial ozonide of *trans*-1,2-di-*t*-butylethylene (I) by means of the the same low-temperature nmr technique used to prove the structure of the transannular ozonide of 9,10-dimethylanthracene.[5] The ozonation was carried out in Freon 11 ($CFCl_3$) at −110° and in acetone-d_6 at −95°. In each case the nmr spectrum, determined on a Varian DP-60 spectrophotometer, consisted of two singlet peaks, one for the *t*-butyl protons and one for the methine protons, in the expected ratio of 9:1, respectively. As the temperature was allowed to rise above the ozonolysis temperature, no change in spectra in either solvent occurred until about −60°. At this temperature, the bands for the initial ozonide disappeared and new major bands characteristic of the decomposition products appeared. The τ values for the cold ozonation solutions containing the initial ozonide, the same solutions at room temperature containing the decomposition products, the *cis* and *trans* true ozonides (VIII),[6] trimethylacetaldehyde (VI), and the *trans* olefin (I), in both Freon 11 and acetone-d_6, are shown in Table I.

Evidence that the bands in the cold ozonation solutions were of the initial ozonide was obtained by treating the cold Freon 11 reaction mixture with cold methanol. This gave methoxy hydroperoxide IX in good yield.[2] The fact that the spectrum of the initial ozonide has only two bands shows that all *t*-butyl protons are equivalent and both methine protons are equivalent. This could only be true with structure type IV, since the unsymmetrical nature of V should give rise to a more complex spectrum.

The unusually large shift to lower field for the methine protons of the initial ozonide (*cf.* the other substances in Table I) in going from the less polar Freon 11 to the more polar acetone-d_6 may be more than a simple solvent effect. It could indicate that in the more polar solvent the initial ozonide has some double bond character.[7] The possibility that the structure of the initial ozonide may vary between the two extremes of complex III (or even II) and compound IV, depending on the polarity of the solvent and other factors, is under investigation.

The decomposition products (Table I) of the initial ozonide in acetone-d_6 were trimethylacetaldehyde (confirmed by addition of VI to the reaction mixture) and, presumably, polymers of zwitterion VII in equal amounts, which is within expectations based on the Criegee mechanism.[1,8] The decomposition product of the initial ozonide in Freon 11 (Table I) appeared to be largely trimethylacetaldehyde. Only small peaks for the polymers of VII were observed, due, apparently, to the low solubility of these substances in Freon 11.

Ozonation of *cis*-1,2-di-*t*-butylethylene in Freon 11 under the same conditions used for the *trans* olefin gave no evidence for an initial ozonide. Even at −110°, only bands for a mixture of the true ozonides (VIII) were observed, as identified by addition of a known mixture of the true ozonides.[6,10] This corroborates the earlier observations of Criegee and Schröder.[2] Either the *cis* isomer does not go through an initial ozonide intermediate or else the initial ozonide is too unstable to be observed even at −110°.[4,11]

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(4) A π complex is not eliminated, however, as a fleeting precursor to the initial ozonide or as an entity which in the case of certain *cis* or hindered olefins may collapse directly to products.

(5) R. E. Erickson, P. S. Bailey, and J. C. Davis, Jr., *Tetrahedron*, **18**, 388 (1962).

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

(7) We are grateful to one of the referees for emphasizing the possible importance of this shift.

(8) Additions of a known mixture of the true ozonides (VIII)[6] to the reaction mixture confirmed that no appreciable amounts of these were produced. The fate of moieties VI and VII depends greatly on the solvent. Schröder[2,6,9] also found that in many solvents *trans*-1,2-di-*t*-butylethylene produced aldehyde VI and polymers of VII to the exclusion of ozonides VIII. This was not generally true for the *cis* isomer.

(9) G. Schröder, Ph.D. Dissertation, Karlsruhe Technische Hochschule, 1959.

(10) The ratio of *cis* to *trans* ozonide, using Schröder's configurational assignments, in the pentane solution of the ozonides[6] was verified as 7:3. The ratio in the Freon ozonolysis mixture was shown to be 6:4.

(11) *Cf.* F. L. Greenwood and B. J. Haske, *Tetrahedron Letters*, 631 (1965); F. L. Greenwood, *J. Org. Chem.*, **30**, 3108 (1965).

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