Rate Study on the Ozonolysis of Acetylenes

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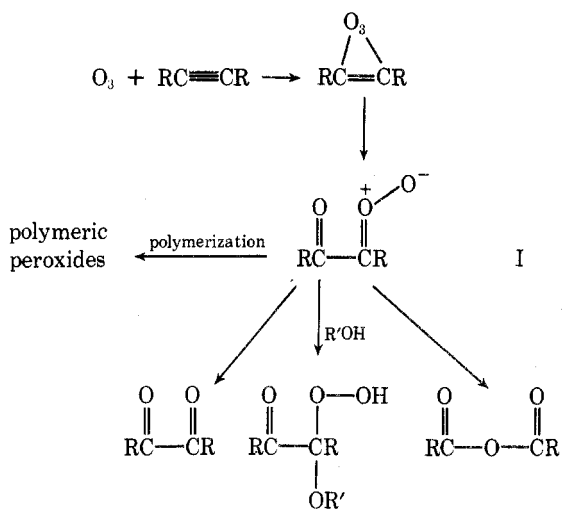
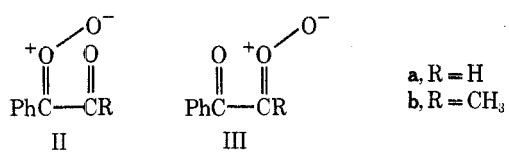
A kinetic study on the reaction of ozone with a series of propargyl compounds has been performed. Absolute rate data are included for the reaction of propargyl chloride in CCl_4 and propargyl acetate in a series of solvents of differing polarity. The absolute rate constants are relatively insensitive to solvent polarity. A relative rate study of several propargyl compounds in methylene dichloride has been made. The rates correlate well with the corresponding Taft substituent constant. From the linearity of the correlation and low ρ value, as well as the insensitivity of the reaction rate to solvent polarity, it is concluded that the initially formed species is a symmetrical nonpolar addition compound, most likely the five-membered ring cycloaddition product.

Compared to the number of mechanistic studies on the ozonolysis of alkenes, relatively little work has been done on the mechanism of the reaction of ozone and alkynes.[1] According to the Criegee–Lederer mechanism,[2] some initially formed species rearranges to an acylcarbonyl oxide, I, which can then react by any of several pathways, as shown below. The production of anhydrides and α-dicarbonyl

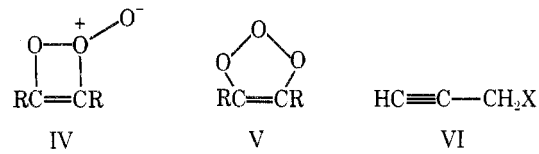


compounds is well known[1] and in addition to Criegee and Lederer, Bailey and coworkers[3] have identified the alkoxyhydroperoxide adducts in the ozonolysis of the two unsymmetrical alkynes, phenylacetylene and 1-phenylpropyne, in alcohol solution and found that of the two possible acrylcarbonyl oxides produced in either case (II, III) the



one with the carbonyl oxide adjacent to the benzene ring, II, was preferred by about 2:1. DeMore and Lin,[4] working at low temperatures in liquid CO_2, have recently directly observed by ir a thermally unstable intermediate in the ozonolysis of propyne and 1- and 2-butyne which they have identified as an acylcarbonyl oxide.

At present the nature of the precursor(s) to the acylcarbonyl oxide still remains in doubt. By analogy with either of the two currently cited mechanisms for the ozonolysis of alkenes, either IV[5a,b] or V[6] could be possible. In addition the observations of ozone–olefin π complexes[7,8] at low temperatures may imply a π complex precursor to either IV or V. In an effort to try to distinguish between either IV or V as an intermediate in the ozonolysis of acetylenes we undertook a kinetic study on a series of unsymmetrically substituted acetylenes of the type VI.



Experimental Section

Relative Rate Studies. An ozone–oxygen mixture produced by silent electric discharge in an oxygen stream was passed (at about 10^{-4} mol O_3/min) into a solution in methylene chloride (spectral grade) of the two compounds under study (0.1–0.01 *M* in each compound) and an unreactive internal standard (either dodecane or hexadecane, also 0.1–0.01 *M*) kept at 0° by immersion in an ice–water bath. The reaction was allowed to proceed to beyond 50% consumption of the more reactive component. Analyses of the remaining alkyne concentrations were performed on a P. E. 900 GPC using the flame ionization mode with either a 6-ft Carbowax 20M column or a 12-ft 1,2,3-tris(2-cyanoethoxy)propane column. The GPC response of the alkynes to that of standards was shown to be linear with their relative concentrations.

Propargyl alcohol, propargyl chloride, and propargyl bromide were all obtained commercially (Aldrich). Propargyl acetate was prepared from the alcohol, bp 122–125° (lit.[9] bp 124–125°). The *N,N*-dimethylpropargylamine was prepared from propargyl bromide and dimethylamine, bp 77–78° (lit.[10] bp 79–81°). The 1-decyne was prepared from 1,2-dibromodecane by dehydrohalogenation, bp 24–26° (0.5 mm).[11] The solvents used were spectral quality (Aldrich and Fisher).

Kinetic Studies. The apparatus used for the kinetic studies was an Aminco-Morrow stopped-flow apparatus whose amplifier output was fed into a Tektronix type 531A oscilloscope. The oscilloscope trace was photographed and the data analyzed. The light source was a Beckman DU monochromator and the photomultiplier tube had a type S-5 spectral response, uv transmitting glass, and maximum response at 340 nm.

The half-lives for ozone decay in the various solvents used in the study, in the apparatus, were >15 min.

The general procedure for a run involved first standardizing the instrument at the wavelength chosen (usually 290 nm) with a given solvent so that 1-V output was 10% transmittance. The reactant cylinders were then filled with the alkyne solution and the ozone solution. The reactant cylinders are made of Kel F, which is relatively inert to ozone. After several flushings the system was ready for use. To initiate reaction the drive plungers were forced down and the two reactant components mixed in the mixing chamber and flowed through the observation cell (made of Teflon with quartz windows oriented so the observation path length is 10 mm) and filled a storage cylinder forcing up the stopping plunger. The stopping plunger was forced against a trigger causing the flow to stop and triggering the oscilloscope. The two reactants reacted in the observation cell and the oscilloscope displayed the disappearance of the absorbing reactant (O_3) as a function of time, which was recorded by the camera. The time it took the solutions to go from the mixing chamber to the observation cell was about 4 msec.

For each concentration of acetylene at least three runs were made. The data were treated by a least-squares analysis and the resulting pseudo-first-order rate constants averaged.

Table I
Relative Rates of Reaction with Ozone and Taft σ^* Constants

Substituent, X	Relative rate[a]	σ^*
Cl	1	1.05
Br	1.3	1.00
O_2CCH_3	1.7	0.89
OH	5.5	0.55
$N(CH_3)_2$	8.5	0.22
$(CH_2)_6CH_3$	16.6	(−0.13)[b]

[a] Rate relative to propargyl chloride. [b] Estimated to be equal to that for n-C_4H_9.[9]

Table II
Products from Ozonolysis

Compd	Registry no.	Solvent	Products (after treatment with H_2O)
$HC{\equiv}CCH_2Cl$	624-65-7	CCl_4	HCO_2H, $ClCH_2CO_2H$
$HC{\equiv}CCH_2Br$	106-96-7	CCl_4	HCO_2H, $BrCH_2CO_2H$
$HC{\equiv}CCH_2O_2CCH_3$	627-09-8	$CHCl_3$	HCO_2H, $CH_3CO_2CH_2CO_2H$
$HC{\equiv}CCH_2OH$	107-19-7	CH_2Cl_2	$HCO_2CH_2CO_2H$, + some HCO_2H and $HOCH_2CO_2H$
$HC{\equiv}CCH_2N(CH_3)_2$	7223-38-3	CH_2Cl_2	HCO_2H, $(CH_3)_2NH^+CH_2CO_2^-$
$HC{\equiv}C(CH_2)_7CH_3$	764-93-2	$CHCl_3$	HCO_2H, $CH_3(CH_2)_7CO_2H$

Product Studies. An ozone–oxygen mixture was passed (about 10^{-3} mol O_3/min) into 10 ml of a 1 M solution of the alkyne in the indicated solvent (spectral grade) at 0° until a stoichiometric amount of O_3 had been added. An ir and uv of the product solutions was then taken. The solvent was removed under reduced pressure and the residue was treated with a few drops of H_2O or D_2O and taken up in D_2O or deuterioacetone, and the NMR was determined. For 1-decyne NaOD–D_2O was used as solvent. The products were identified either by comparison with genuine samples or from the spectrum itself.

Results

In a simple competition between two compounds A and B for O_3 the ratio of their rates of reaction, k_A and k_B, is given by

$$\frac{k_A}{k_B} = \frac{\log A_f/A_i}{\log B_f/B_i}$$

where A_i and B_i are initial concentrations and A_f and B_f are the final concentrations of A and B, respectively, if the reaction is first order in A and B.

Listed in Table I are the compounds studied and their rates of reaction relative to propargyl chloride in methylene chloride. Also listed are the Taft substituents constants, σ^*, for each of the substituents.[12,13] The σ^* constant for the n-heptyl group was estimated to be approximately equal to that for the n-butyl group.

In Table II are listed the products of ozonolysis of each of the compounds after aqueous work-up. A combination of ir and NMR was used to identify the products listed. Also from the lack of any significant absorption above 400 nm in the uv spectra of the product solutions it is concluded that in each case there was less than 0.1% of an α diketone produced. From the ir spectra of the product solutions before aqueous work-up it is apparent that there is an anhydride

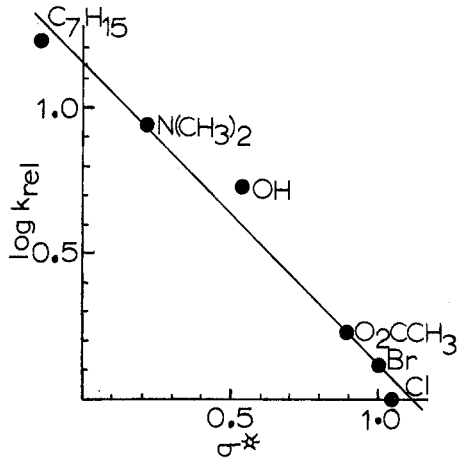


Figure 1. Plot of log k_{rel} vs. Taft substituent constant, σ^*, for the reaction of ozone and various propargyl compounds of the type $HCCCH_2X$.

present as well as some carboxylic acid (possibly from adventitious water). The principal product from ozonolysis of propargyl alcohol listed is a formic acid ester and probably arises from attack of the alcohol OH group (of the starting acetylene or product hydroxy anhydride) on the initially formed anhydride product.

A plot of log k_{rel} vs. the Taft constant is given in Figure 1. The least-squares line is described by the equation

$$\log k_{rel} = (-1.02 \pm 0.2)\sigma^* + (1.15 \pm 0.1)$$

and has a linear correlation coefficient of 0.986.

In addition to the relative rate study a kinetic study was performed on propargyl chloride in CCl_4 and propargyl acetate in a series of acetic acid–water mixtures and methyl acetate. The reactions were monitored using stopped-flow techniques by following the disappearance of ozone in the uv. The ozone concentrations varied from 10^{-3} to 10^{-4} M with the concentration of alkyne between 0.5 and 0.01 M. Under the conditions employed the alkyne was always in vast excess and its concentration varied little over the course of the reaction.

In Figures 2 and 3 are plotted the negative logarithm of the absorbance of the ozone vs. time for varying concentrations of propargyl chloride in CCl_4 and propargyl acetate in 100% acetic acid, respectively, at 24 ± 1°. The disappearance of ozone is first order for >4 half-lives. In Figure 4 is a plot of the logarithm of the pseudo-first-order rate constants vs. the logarithm of the concentration of the alkyne substrate for the two aforementioned compounds under the specified conditions. From the slopes of the lines the order of reaction for propargyl chloride is 1.1 ± 0.1 and for propargyl acetate 0.93 ± 0.06, both of which are within reasonable agreement of 1.0. In Table III are listed the second-order rate constants for reaction of the two compounds with ozone in various solvents.

Discussion

From the product studies it is apparent that for these propargyl compounds the course of the reactions seems to proceed almost exclusively through formation of the anhydride.

The reaction appears to be clearly first order in both ozone and acetylene, implying either that ozone and the acetylene are involved in a rate-determining encounter, or in some prior equilibrium, perhaps involving a π complex.

From the data in Table III it is apparent that the rate of reaction is virtually insensitive to the polar or hydrogen-bonding nature of the solvent. On comparing the rate con-

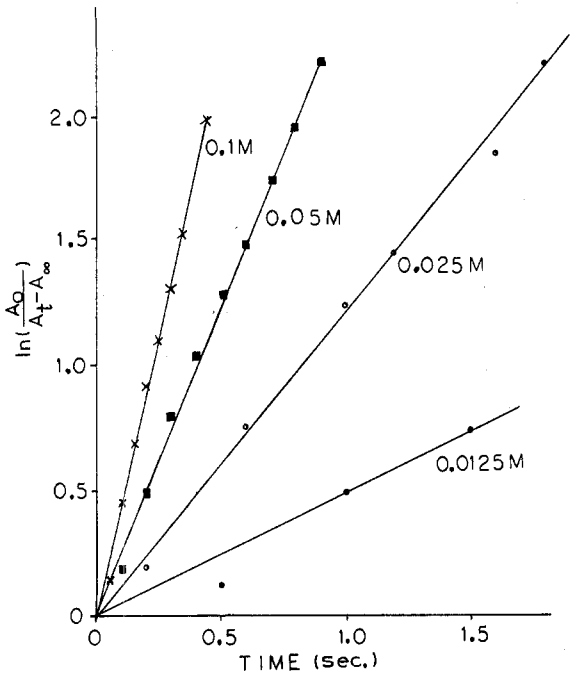


Figure 2. Plot of ln $A_0/(A_t - A_\infty)$ where A_0 is the initial absorbance, A_t is the absorbance at time t, and A_∞ is the absorbance at long reaction time vs. time for the reaction of ozone and propargyl chloride at various propargyl chloride concentrations under pseudo-first-order conditions, in CCl_4 at 24 ± 1° monitored at 290 nm.

Table III
Rate Constant for Reactions with Ozone at 24 ± 1°

Compd	k, M^{-1} sec^{-1}	Solvent
$HC{\equiv}CCH_2Cl$	52 ± 12	CCl_4
$HC{\equiv}CCH_2O_2CCH_3$	74 ● 7	CH_3CO_2H
$HC{\equiv}CCH_2O_2CCH_3$	168 ± 3	75:25 CH_3CO_2H–H_2O
$HC{\equiv}CCH_2O_2CCH_3$	270 ± 47	50:50 CH_3CO_2H–H_2O
$HC{\equiv}CCH_2O_2CCH_3$	264 ± 18	25:75 CH_3CO_2H–H_2O
$HC{\equiv}CCH_2O_2CCH_3$	218 ± 8	H_2O
$HC{\equiv}CCH_2O_2CCH_3$	104 ± 40	$CH_3CO_2CH_3$

stant for ozonolysis of propargyl acetate in pure acetic acid with its rate constant for reaction in the various acetic acid–water mixtures one finds a variation by at most a factor of 3. Comparison of the rate constant for this same substrate in methyl acetate and acetic acid shows again no significant variation. This insensitivity of the rate constant to solvent polarity and the hydrogen-bonding nature of the solvent would indicate that the intermediate formed in any rate-determining step is unlikely to be polar or able to accept hydrogen bonds from the solvent, characteristics one would expect for an intermediate such as IV. For the situation in which there is a prior equilibrium it is possible for these to be mutually compensating effects. This latter explanation seems unlikely, however, since the π complex usually invoked in such a prior equilibrium is not likely to be very polar. Some polarity for such a species might explain the slight sensitivity to solvent polarity observed.

The relative rates of ozonolysis are linearly correlated with the Taft substituent constant. The implication of such a correlation is that either there is no significant steric and/or resonance effect or they are of a compensatory nature. Most likely because of the linear arrangement of atoms about the triple bond in VI the substituent is held rigidly away from the approaching ozone molecule, minimizing steric factors. The presence of the methylene group would

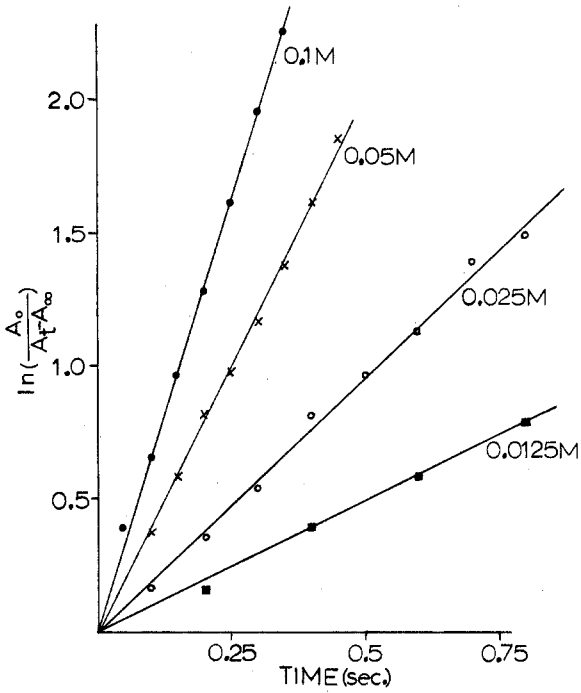


Figure 3. Plot of ln $A_0/(A_t - A_\infty)$ where A_0 is the initial absorbance, A_t is the absorbance at time t, and A_∞ is the absorbance at long reaction time vs. time for the reaction of ozone and propargyl acetate at various propargyl acetate concentrations under pseudo-first-order conditions, in CH_3CO_2H at 24 ± 1° monitored at 290 nm.

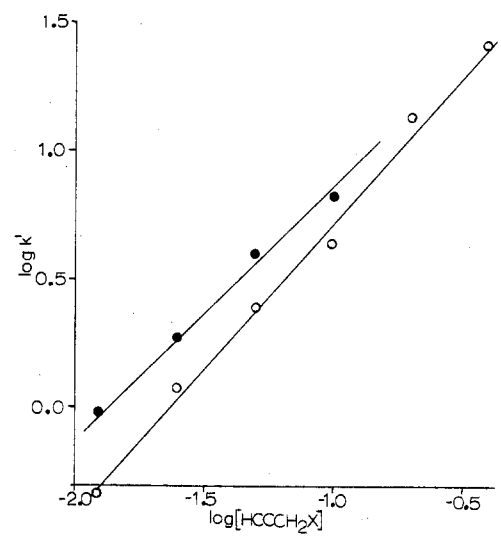


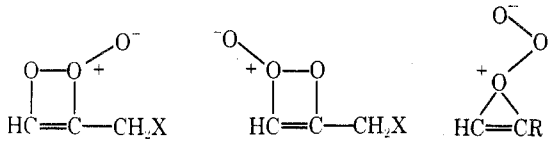
Figure 4. Plot of the log of the pseudo-first-order rate constant vs. log of the alkyne concentration for X = Cl (○) and for X = O_2CCH_3 (●) in CCl_4 and CH_3CO_2H, respectively, at 24 ± 1°.

prevent any resonance effect of the substituent from interfering. The predominant effect is therefore inductive.

The comparatively low slope (−1.02 ± 0.2) implies only a minimal sensitivity of the reaction to the polar nature of the substituent,[12] a characteristic of 1,3-dipolar cycloadditions.[14] The negative slope corresponds to increased rates for more inductively electron-donating substituents in line with and confirming the electrophilic nature of ozone.[15]

The low slope, or ρ value, as well as the good linear correlation of the relative rates is hard to understand in terms of the four-membered ring, Staudinger molozonide as an initially formed species. In the ozonolysis of unsymmetrical alkynes of the type VI, there are two conceivable orientations of a four-membered ring intermediate, VIIa and VIIb.

If the initially formed species were exclusively VIIb,



VIIa VIIb VIII

where the positive oxygen was three atoms away from the CH_2X group, the relative insensitivity of the reaction to varying inductive effects and the good linear correlation would not be unreasonable. However, it is unreasonable to expect that VIIb could possibly be the exclusive intermediate over the range of substituents used in this study and in light of the strongly supported intermediacy of the two possible acylcarbonyl oxides in Bailey's study.[3] The two acylcarbonyl oxides, II and III, could only arise from two four-membered ring precursors which differ in addition orientation, as in VIIa and VIIb. If varying proportions of VIIa and VIIb were formed, depending on the substituent, it would be highly unlikely that a linear correlation would exist; instead, as one went to more electron-donating substituents, VIIa would be favored, resulting in marked curvature up as one went to decreasing σ^* values, something that is not observed.

The initial rate-determining formation of a symmetrical π complex, or of a symmetrical three-membered ring of the type VIII, cannot be ruled out. However, the relative insensitivity of the rate of reaction to changing substituents and changing solvent polarity does tend to make it less likely that charge is developed in the transition state.

The above supports the intermediacy of a symmetrical intermediate of the type V whose cleavage could then be affected by the substitution pattern but whose formation would be only slightly affected by inductive and solvent effects, since no charge is developed.

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Registry No.—Ozone, 10028-15-6.

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Reaction of Diaminomaleonitrile with Acetaldehyde

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The reaction of diaminomaleonitrile with acetaldehyde in an aqueous buffer at pH 6.8 proceeds rapidly at 5° and leads to the formation of a product which results from the condensation of three molecules of acetaldehyde and one molecule of diaminomaleonitrile with the elimination of one molecule of water. The properties of the compound are consistent with a heterotricyclic ring system.

Diaminomaleonitrile,[1] a tetramer of hydrogen cyanide, has been implicated as an intermediate in the prebiotic synthesis of purines.[2] It has also been shown to be a very useful intermediate in the preparation of a variety of heterocyclic compounds containing from five to seven members in the rings.[3]

Except for the investigations concerned with chemical evolution, the synthetic procedures utilizing diaminomaleonitrile have largely employed nonaqueous solvents. This report deals with the reaction of diaminomaleonitrile with acetaldehyde in an aqueous buffer. The reaction proceeds rapidly under very mild conditions (pH 6.8, 5°) leading to an unexpected and unusual product. This is identified as a heterotricyclic system (structure **3**) resulting from the condensation of three molecules of acetaldehyde with one molecule of diaminomaleonitrile.

Results and Discussion

The crystalline product obtained from the reaction of diaminomaleonitrile with acetaldehyde was initially assumed to be a dihydroimidazole derivative (structure **1**, Scheme I). However, the proton magnetic resonance spectrum (Figure 1) revealed that three molecules of acetaldehyde had been incorporated into the product and that all three of the incorporated CH_3CH groups were in different chemical environments. That the three CH_3CH groups were each incorporated intact was shown by a spin-decoupling experiment in which the upfield methyl signals (integrating for nine protons) were irradiated, causing a collapse of the quartets in the δ 4–6 region of the spectrum. (The quartets integrated for three protons in a ratio of 1:1:1.) Addition of a small amount of D_2O to the Me_2SO-d_6 solution resulted in a disappearance of the two exchangeable NH signals at δ 7.96 and 8.22, each integrating for one proton. All of the incorporated acetaldehyde molecules were covalently bound because heating overnight at 100° under constant oil pump vacuum caused no significant loss of weight or change in the ir spectrum.

The low-resolution electron impact mass spectrum of the product is found in Figure 2. It can be seen that the spectrum is complex. In view of the fact that the product analyzed satisfactorily for $C_{10}H_{14}N_4O_2$ (mol wt 222) it is evident that the molecular ion is not sufficiently stable to appear in the low-resolution mass spectrum. However, a high-