mg, 625 μmol) using MSC (330 mg, 1.50 mmol) in dry pyridine (5 ml). The reaction was stopped after 4 hr by cooling and adding water (5 ml). Work-up by paper chromatography (solvent E) gave the fully protected tetranucleotide **21**, 7500 OD$_{280}$, 36%.

d-CEpTpC^{An}pA^{Bz}pG^{iB} (22). Treatment of the preceding compound (1000 OD$_{280}$, 18.5 μmol) with α-chymotrypsin (4.0 mg, enzyme-substrate ratio 10.8 units/μmol) in phosphate buffer, pH 7.5 (40 ml), at 37° for 24 hr gave the partially protected tetranucleotide d-CEpTpC^{An}pA^{Bz}pG^{iB} (**22**), 615 OD$_{280}$, 82%, isolated by paper chromatography in solvent E.

d-pTpC^{An}pA^{Bz}pG^{iB}. d-CEpTpC^{An}pA^{Bz}pG^{iB} (**22**, 50 OD$_{280}$) was hydrolyzed with 1 *N* sodium hydroxide solution (0.5 ml) for 10 min to give d-pTpC^{An}pA^{Bz}pG^{iB}, and isolated by chromatography in solvent D, R_f 0.19.

d-pTpCpApG. Treatment of d-pTpC^{An}pA^{Bz}pG^{iB} with concentrated ammonia for 2 days gave the tetranucleotide d-pTpCpApG, R_f 0.23, solvent B (R_f 0.20, solvent F). The tetranucleotide was characterized by degradation with snake venom phosphodiesterase to give the mononucleotides in the ratio d-pT-d-pC-d-pA-d-pG, 1.00:1.01:1.01:0.96. Further characterization was by removal of the terminal phosphate to give d-TpCpApG (R_f 0.45, solvent B) followed by degradation with spleen phosphodiesterase to give d-Tp-d-Cp-d-Ap-d-G, 1.00:1.10:1.05:1.08.

Registry No.—**1a**, 23706-27-6; **1b**, 37731-23-0; **1c**, 37731-24-1; **1d**, 37731-25-2; **2a**, 37731-26-3; **2b**, 37731-27-4; **2c**, 37731-28-5; **3a**, 37731-29-6; **3b**, 37731-30-9; **3c**, 37731-31-0; **5**, 37731-32-1; **6**, 37731-33-2; **7**, 37731-34-3; **8**, 37731-35-4; **9**, 37731-36-5; **10**, 37731-37-6; **11**, 37731-38-7; **12**, 37731-39-8; **13**, 37731-40-1; **14**, 37731-41-2; **15**, 37731-42-3; **16**, 37731-43-4; **17**, 37731-44-5; **18**, 37731-45-6; **19**, 37731-46-7; **20**, 37731-47-8; **21**, 37818-77-2; **22**, 37731-48-9; D-(+)-DCM, 17332-01-3; D-(+)-DCM (acid chloride), 37731-49-0; PDA, 37731-50-3; PDA (acid chloride) 37731-51-4; DHC, 501-52-0; DHC (acid chloride), 645-45-4; DHC (anhydride), 15781-96-1; d-pC^{An}, 32909-08-3; d-pC, 1032-65-1; d-pA^{Bz}, 4546-64-9; d-pA, 653-63-4; d-pT, 365-07-1; d-pG^{iB}, 32909-09-4; d-pG, 902-04-5; d-CEpA^{Bz}, 37740-89-9; d-CEpC^{An}, 37740-90-2; d-pTpC^{An}, 37731-45-6; pTpC, 2147-10-6; d-pTpC^{An}-pA^{Bz}, 37740-92-4; d-pTpCpA, 37740-93-5; d-pTpC^{An}-pA^{Bz}pG^{iB}, 37740-94-6; d-pTpCpApG, 37740-95-7.

Acknowledgment.—This work was supported by the National Institute of Medical Sciences, National Institutes of Health, Bethesda, Md. (Contract No. PH-67-1157). Valuable discussions with Drs. O. M. Friedman, D. Söll, J. B. Hendrickson, N. A. Starkovsky, and J. Hachmann are gratefully acknowledged. The technical assistance of Mrs. C. J. Crosscup and Mr. P. B. Szabady is appreciated.

Intermediates in the Ozonation of Simple Alkynes

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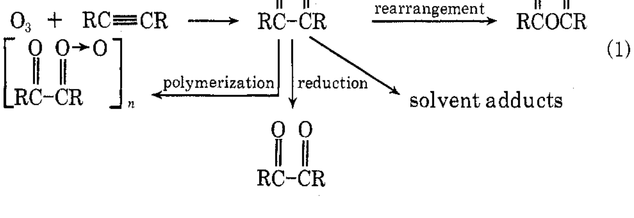
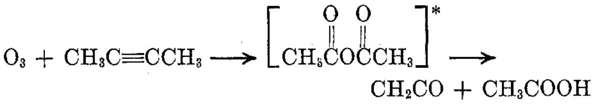
The reactions of O_3 with $HC{\equiv}CH$, $CH_3C{\equiv}CH$, $CH_3C{\equiv}CCH_3$, and $C_2H_5C{\equiv}CH$ have been studied in liquid CO_2 at −45°. The initial products were observed by *in situ* infrared spectroscopy, and subsequent changes occurring upon warm-up or flash vaporization of the mixture were followed by ir or gc analysis. The principal new spectral feature for all alkynes except acetylene was a strong carbonyl absorption near 1740 cm^{-1}, and all alkynes gave relatively weak absorption bands in the carbonyl region which are attributed to the corresponding acid anhydrides. The 1740-cm^{-1} band was shown to be an unstable precursor of the acid anhydrides and other products. The overall mechanism, the identity of the precursor, and factors influencing the final product distribution are discussed.

Relatively little is known about the detailed mechanism of alkyne ozonation. According to the Criegee–Lederer mechanism,[1] an acylcarbonyl oxide is produced which may react in a variety of ways.



(1)

Anhydride formation, first proposed by Paillard and Wieland[2] to explain product ratios in the ozonation of heptyne-1, has been observed only in the ozonation of diphenylacetylene.[3] For the gas-phase ozonation of simple alkynes, it has been suggested[4] that products corresponding to fission of the triple bond arise from the decomposition of an excited anhydride intermediate. For example, ketene and acetic acid produced by the gas-phase ozonation of dimethylacetylene can be explained as follows.



$$O_3 + CH_3C{\equiv}CCH_3 \longrightarrow \left[CH_3\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}CH_3\right]^* \longrightarrow CH_2CO + CH_3COOH \quad (2)$$

According to this interpretation, the excited anhydride is short-lived and decomposes completely at 1-atm pressure. However, at higher pressures or in the condensed phase the excited intermediate should be collisionally stabilized. The present work was carried out in an effort to isolate the anhydride intermediate, and to provide additional information on the anhydride precursor. The alkynes studied include acetylene, methylacetylene, dimethylacetylene, and ethylacetylene.

Apparatus and Methods

The experiments involved ozonation of the alkynes in liquid CO_2 at about −45° with *in situ* ir analysis of the products. The reaction cell (Figure 1) was a vac-

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[1] R. Criegee and M. Lederer, *Justus Liebigs Ann. Chem.*, **583**, 29 (1953).

[2] H. Paillard and C. Wieland, *Helv. Chim. Acta*, **21**, 1356 (1938).

[3] E. Dallwigk, H. Paillard, and E. Briner, *ibid.*, **35**, 1377 (1952).

[4] W. B. DeMore, *Int. J. Chem. Kinet. III*, 161 (1971).

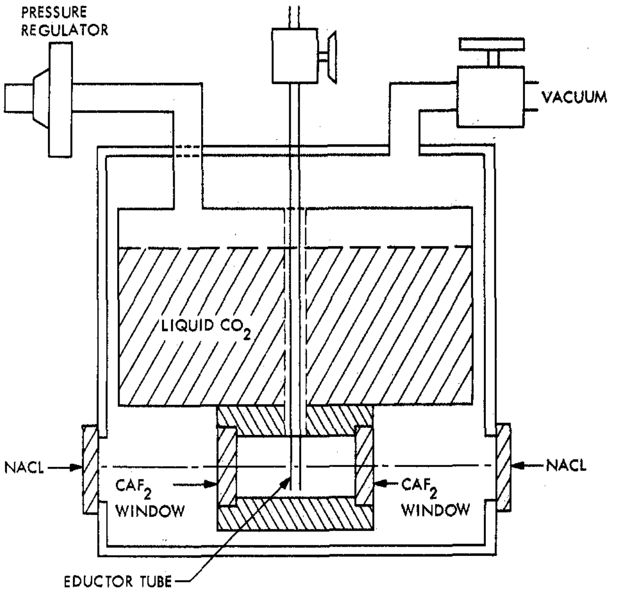

Figure 1.—Reaction cell for ozonation studies in liquid CO_2 solvent.

uum-jacketed, stainless steel cell fitted with CaF_2 windows. The cell was cooled by liquid CO_2 (separate from the reaction cell) held at about 120 psi. The ir spectra of the liquid mixtures were taken on a Model 421 Perkin-Elmer spectrometer. The combined transmission of liquid CO_2 (1 or 3 cm) and the CaF_2 windows gave good spectral observations in the carbonyl region and CH stretching region, the former being more useful for product analysis. Whenever possible product identifications were based on ir spectra of synthetic mixtures.

In addition to the *in situ* analysis, the final product distribution following warm-up of the mixture was examined in several ways. In one method, the CO_2 solution was rapidly vaporized through an eductor tube (Figure 1) into a 40-m long-path ir cell, or else into a 5-l. bulb. In the latter case the CO_2 was then separated by pumping the mixture through a U tube at −78°, followed by analysis of the trapped products in a conventional ir cell or by gc. The gc columns were Porapak Q (3 or 8 ft) operated at 140°. In some experiments the CO_2 was pumped away from the low-temperature cell, and the residual products were allowed to warm up in the cell and later collected for analysis.

Product yields were based on the initial ozone concentration, which was determined by uv spectrometry before addition of the alkyne. We used extinction coefficients for O_3 dissolved in other inert low-temperature solvents.[5] The yields of products following vaporization into the long-path ir cell were determined by calibration of the ir band strengths *vs.* pressure for authentic samples. The carbon monoxide yield in the liquid phase was determined by sampling the gaseous mixture above the liquid and calibrating the chromatographic peak height (8-ft molecular sieve, 40°) against standard mixtures of CO dissolved in the liquid CO_2.

The initial O_3 concentrations were usually about 5×10^{-3} *M*, and either equimolar or excess concentrations of alkyne were subsequently added.

Results

The principal new feature upon ozonation of all the alkynes except acetylene was a strong absorption band at 1740 cm^{-1} in the liquid-phase spectrum. This band is almost certainly a carbonyl absorption. It can be distinguished in several ways from the carbonyl bands of possible products such as anhydrides, α-dicarbonyls, acids (monomeric or dimeric), or other known products. As will be shown later, this band is due to a precursor of the anhydride.

In addition to the 1740-cm^{-1} band, relatively weak carbonyl absorption bands appeared in every case, including acetylene, which we identify (see below) as the carbonyl bands of the corresponding acid anhydrides

Figure 2a shows the spectral changes occurring in the carbonyl region for the ozonation of dimethylacetylene. The anhydride bands were identified by comparison with the spectrum of an authentic sample. Unfortunately, the biacetyl band is not clearly resolved from that of the intermediate, and therefore its presence in the original product mixture is uncertain. Figure 2b shows the slow thermal rearrangement of the intermediate to give anhydride and biacetyl. When the mixture is allowed to warm to room temperature (first pumping off the CO_2) and is then redissolved in liquid CO_2, the spectrum shows strong anhydride and biacetyl bands (Figure 2c). Vaporization of the product mixture through the eductor tube into the long-path ir cell gives the spectrum shown in Figure 2d. In addition to acetic anhydride and biacetyl, ketene and acetic acid are present. The product yields, while approximate, account for a substantial portion of the ozone. It should be noted that the weak anhydride bands present in the original reaction mixture, before vaporization, are much too weak to account for the amount of anhydride present after vaporization. This proves that anhydride formation occurs during the vaporization process. Figure 3 shows a chromatographic analysis of the products following vaporization into a 5-l. bulb.

The behavior of methylacetylene was similar to that of dimethylacetylene. The initial product spectrum in liquid CO_2 (Figure 4a) shows relatively weak formic–acetic anhydride bands and a strong band due to the unstable intermediate. The anhydride bands are similar to those reported by Stevens and Van Es[6] for formic–acetic anhydride in $CHCl_3$ solution. Vaporization into the long-path ir cell gave strong bands due to the anhydride and methylglyoxal (Figure 4b). No ketene was formed, which is consistent with the fact that the gas-phase reaction[4] does not give that product.

The initial product spectrum for ethylacetylene (Figure 5) was similar to that of methylacetylene. The two features at 1775 and 1795 cm^{-1} are believed to be due to formic–propionic anhydride, based on their similarity to the formic–acetic anhydride bands.[7] On standing, these bands increased in intensity and the 1740-cm^{-1} band decreased. However, in contrast to the previous cases, vaporization of the mixture into the long-path ir cell did not produce strong anhydride absorption in the gas-phase spectrum. (As previously discussed, the small amount of anhydride corresponding to the bands in Figure 5 would not produce appreciable

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(5) W. B. DeMore and O. Raper, *J. Phys. Chem.*, **68**, 412 (1964).

(6) W. Stevens and A. Van Es, *Recl. Trav. Chim. Pays-Bas*, **83**, 863 (1964).

(7) R. Schijf and W. Stevens, *ibid.*, **85**, 627 (1966).

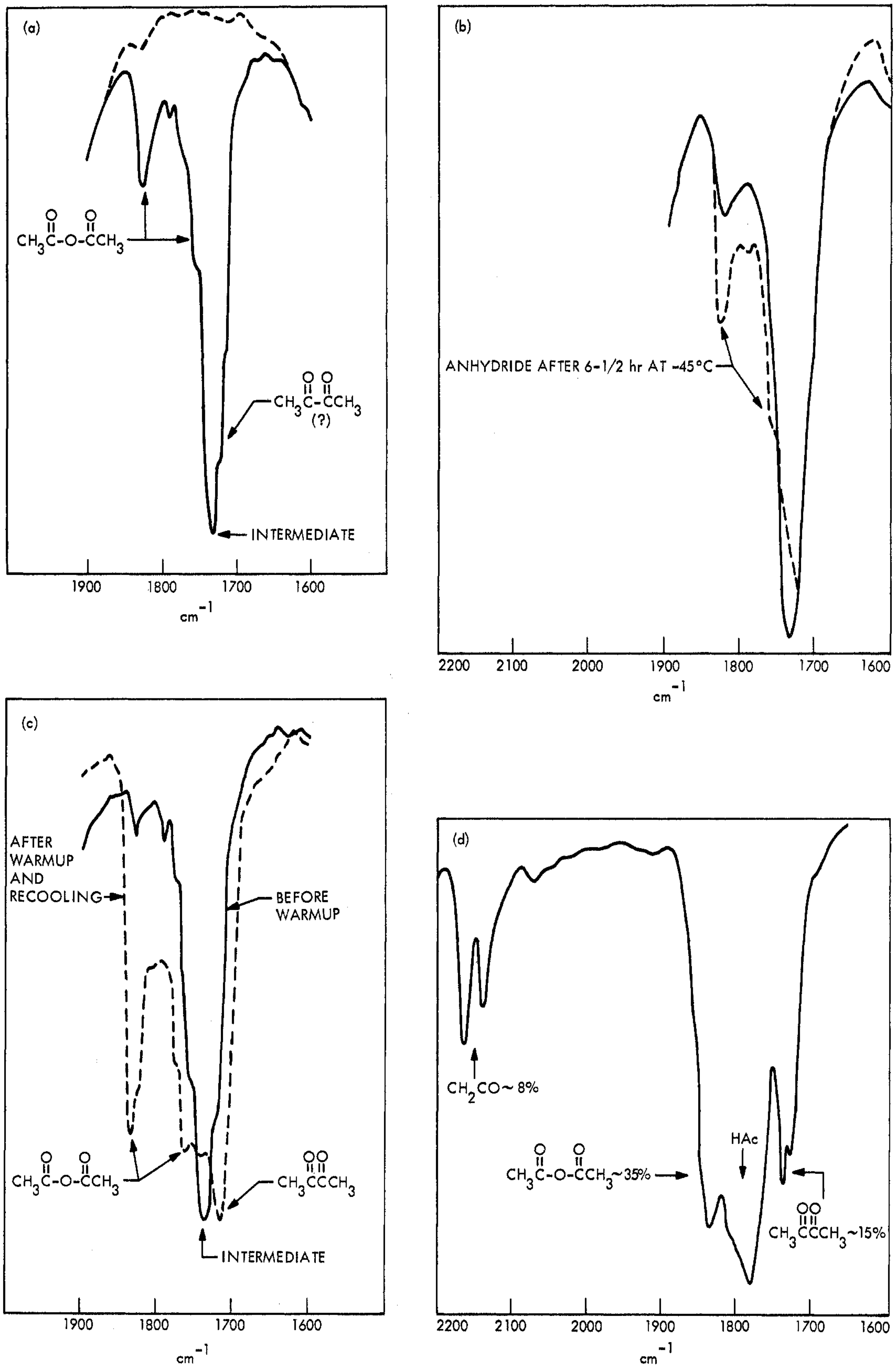


Figure 2.—Ozonation of $CH_3C{\equiv}CCH_3$ in liquid CO_2. (a) Dotted line is trace before reaction; solid line after reaction. (b) Dotted line shows spectral change after 6.5 hr at −45°. (c) Spectral changes after warm-up to room temperature followed by recooling. (d) Spectrum taken in long-path ir cell after flash vaporization of a mixture such as that of a.

absorption in the gas-phase spectrum.) No α-dicarbonyl was produced, although this product is formed when the ozonation of ethylacetylene is carried out in the gas phase. The only observable product appeared to be propionic acid.

Acetylene was the only alkyne studied which failed to give the 1740-cm^{-1} band. The strong carbonyl bands produced (Figure 6) are those of formic acid, probably in monomeric and dimeric forms. The weak band of 1810 cm^{-1} is believed to be due to formic anhydride,

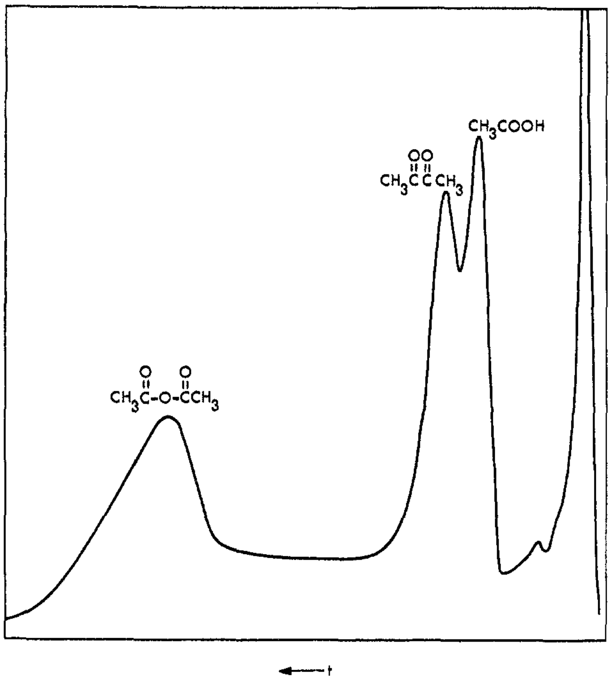


Figure 3.—Gas chromatographic analysis of $CH_3C{\equiv}CCH_3$ + O_3 reaction products after vaporization into a 5-l. bulb and separation of CO_2. Column was 3 ft Porapak Q at 140°.

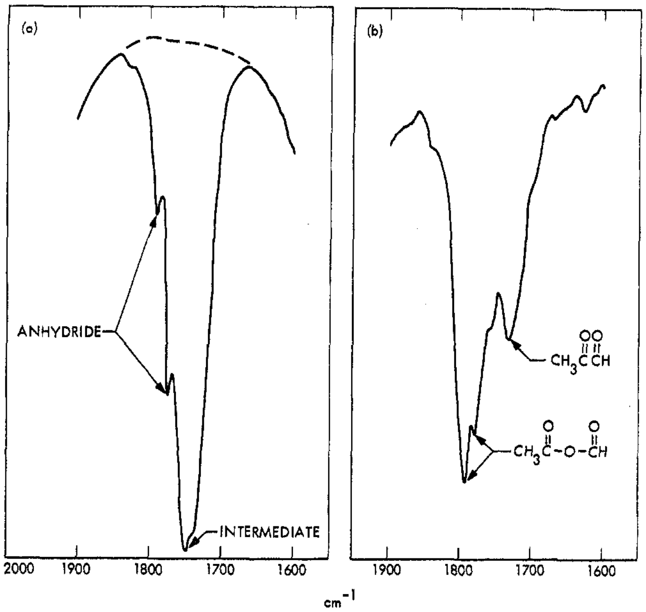


Figure 4.—Ozonation of $CH_3C{\equiv}CH$ in liquid CO_2. (a) Dotted line, before reaction; solid line, after reaction. (b) After vaporization into long-path ir cell.

although this identification is based only on the fact that the wavelength is approximately correct for a symmetric anhydride. By stoichiometry, CO should also be produced in yield equal to that of formic acid. Table I shows that such is the case, and that substantial amounts of CO are also formed in the ozonation of methyl- and ethylacetylene. Vaporization of the acetylene product mixture into the long-path ir cell gave only formic acid bands, with no more than a trace of glyoxal.

Table I

Carbon Monoxide Yields for Ozonation of Alkynes in Liquid CO_2 at −45°

Registry no.	Alkyne	Yield, %
74-86-2	$HC{\equiv}CH$	91 ± 18
74-99-7	$CH_3C{\equiv}CH$	36 ± 7
107-00-6	$CH_3CH_2C{\equiv}CH$	12 ± 3
503-17-3	$CH_3C{\equiv}CCH_3$	3 ± 1

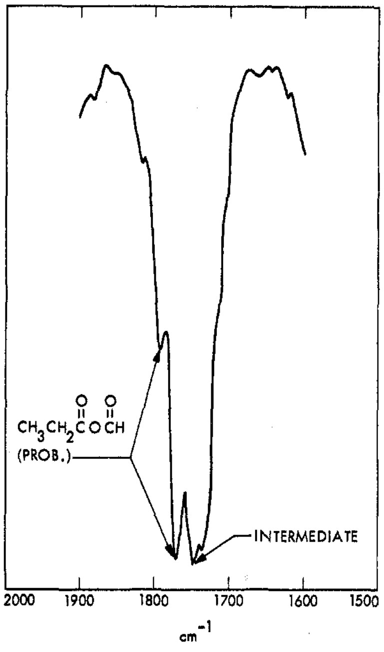
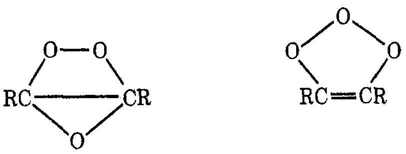


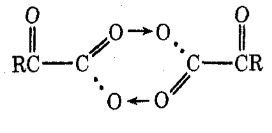
Figure 5.—Ozonation of $C_2H_5C{\equiv}CH$ in liquid CO_2.

Discussion

The Anhydride Precursor.—At this time it is not possible to specify the structure of the unstable intermediate responsible for the 1740-cm^{-1} band. The evident presence of a carbonyl bond tends to rule out "ozonide" structures shown below.

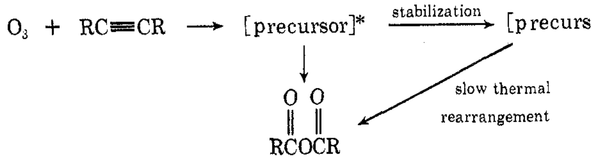


One possibility is that the presursor is the dimer (or higher polymeric form) of the acylcarbonyl oxide.



If so, the tendency of the intermediate to react in a manner characteristic of the monomer suggests that the polymerization is reversible.

Anhydride Formation.—Formation of small amounts of anhydride in the initial product mixture, before vaporization, indicates that not all of the precursor is stabilized before some rearrangement occurs (eq 3).

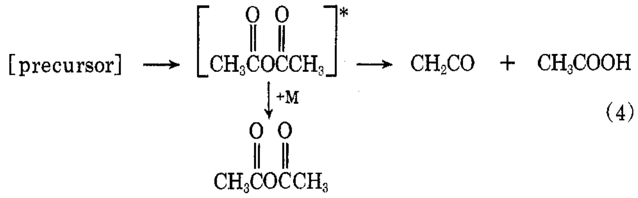


(3)

After thermalization at −45°, rearrangement to the anhydride is slow.

For acetylene, essentially none of the precursor could be stabilized, showing that either the precursor itself or the formic anhydride decomposes largely to HCOOH and CO before thermalization. Once equilibrated at −45°, the formic anhydride is evidently stable, assuming that our identification of the 1810-cm^{-1} band (Figure 6) is correct. Some decomposition also occurs in the cases of methyl- and ethylacetylene, as shown by the small amounts of CO present.

Absence of ketene in the liquid CO_2 in the dimethylacetylene experiments shows that the type of decomposition represented by eq 2 does not occur in the liquid. However, rearrangement of the precursor following vaporization releases sufficient energy to decompose part of the acetic anhydride (eq 4). When the ozonation



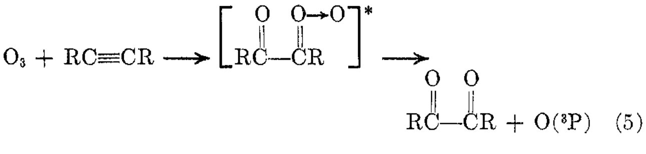
$$[\text{precursor}] \longrightarrow \left[\mathrm{CH_3\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}CH_3}\right]^* \longrightarrow \mathrm{CH_2CO} + \mathrm{CH_3COOH} \qquad (4)$$

$$\left[\mathrm{CH_3\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}CH_3}\right]^* \xrightarrow{+\mathrm{M}} \mathrm{CH_3\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}CH_3}$$

takes place in the gas phase at 1 atm, all the reaction exothermicity appears in the anhydride, and dissociation is complete. We have, in fact, carried out a few gas-phase experiments at high pressures (several hundred psi of CO_2) in which acetic anhydride was isolated as a product of the ozonation of dimethylacetylene. This shows that anhydride formation is not unique to the liquid-phase experiments.

The liquid-vaporization technique may serve as a useful synthetic method for mixed anhydrides such as formic–acetic anhydride.

Formation of α-Dicarbonyls.—More than one path may contribute to production of α-dicarbonyls, particularly when both liquid- and gas-phase reactions are considered. A probable mechanism in the gas phase is eq 5. The exact importance of reaction 5 cannot be



$$\mathrm{O_3 + RC{\equiv}CR} \longrightarrow \left[\mathrm{R\overset{O}{\overset{\|}{C}}{-}\overset{O\rightarrow O}{\overset{\|}{C}}R}\right]^* \longrightarrow \mathrm{R\overset{O}{\overset{\|}{C}}{-}\overset{O}{\overset{\|}{C}}R} + \mathrm{O(^3P)} \qquad (5)$$

assessed because of the possible contribution of surface reactions to α-dicarbonyl formation.[4] This reaction is considerably exothermic (87 kcal/mol for the biacetyl case) and would be expected to dominate the gas-phase mechanism were it not for the fact that it is spin forbidden. This either lowers the preexponential factor or else requires that the α-dicarbonyl be formed in an excited triplet state.

Reaction 5 is interesting in that it regenerates atomic oxygen. Occurrence of this reaction in air-pollution chemistry would have the novel effect of destruction of hydrocarbon with no attendant loss of ozone, since the ozone would be regenerated.

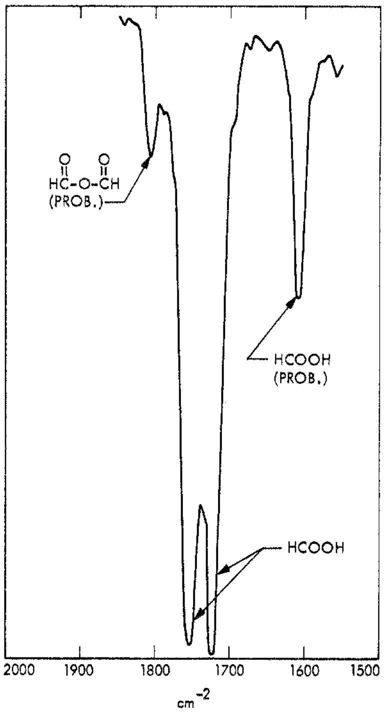
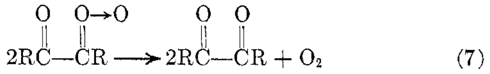


Figure 6.—Ozonation of HC≡CH in liquid CO_2.

$$\mathrm{O(^3P) + O_2 + M \longrightarrow O_3 + M} \qquad (6)$$

For the thermalized acylcarbonyl oxide, reaction 5 is undoubtedly much slower, possibly endothermic. This serves to explain why the yields of α-dicarbonyls were lower (or zero) in the liquid-vaporization experiments than in the gas-phase experiments. Some product may be formed by a disproportionation reaction of the thermalized precursor.



$$\mathrm{2R\overset{O}{\overset{\|}{C}}{-}\overset{O\rightarrow O}{\overset{\|}{C}}R} \longrightarrow \mathrm{2R\overset{O}{\overset{\|}{C}}{-}\overset{O}{\overset{\|}{C}}R + O_2} \qquad (7)$$

Briner and Wunenburger[8] obtained an 81% yield of glyoxal by ozonation of acetylene in CH_2Cl_2 at Dry Ice temperature, in contrast to our yield of zero for that product. This emphasizes the strong dependence of the reaction course on experimental conditions. A possible explanation of the different results is that under their experimental conditions some stabilization of the intermediate acylcarbonyl oxide was accomplished, with subsequent glyoxal formation by reaction 7.

Acknowledgment.—This paper presents the results of one phase of research carried out at the Jet Propulsion Laboratory, California Institute of Technology, under Contract No. NAS7-100 sponsored by the National Aeronautics and Space Administration.

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(8) E. Briner and R. Wunenburger, *Helv. Chim. Acta*, **12**, 786 (1929).