Table II. Comparison of Principal Directions of the g Tensors and Certain Directions in the Undamaged Crystals[a]

	vector	direction cosines			angle between vectors, deg
		a	b	c	
A	g_1	0.6866	−0.5187	0.5094	6.4
	$\perp$[b]	0.6054	−0.5906	0.5335	
	g_2	0.6210	0.7828	−0.0400	12.2
	$N_{(1)}$–Ni	0.5977	0.7832	0.1711	
	g_3	−0.3780	0.3438	0.8596	9.0
	$N_{(2)}$–Ni	−0.4588	0.2093	0.8635	
	$O_{(8)}$–Ni	0.6512	−0.3637	0.6660	
B	g_1	0.9462	0	−0.3236	12.6
	$\perp$[b]	0.9958	0	−0.1042	
	g_2	0.3236	0	0.9462	12.6
	bisector$_1$	0.1042	0	0.9958	
	g_3	0	1	0	0.0
	bisector$_2$	0	1	0	
	$O_{(1)}$–Ni	0.8699	−0.1051	−0.4820	

[a] Crystallographic data and atom labels taken from ref 15 and 16. [b] Unit vector perpendicular to the Ni–N plane.

B, the metal cation lies at the center of a square-planar arrangement of nitrogen atoms but is not bound to the perchlorate anions.[15,16] These are disposed at angles of 15.3° (A) and 23.6° (B) from the direction perpendicular to the NiN_4 plane (Figure 2) and in one case (A) make weak hydrogen bonds with ring nitrogens of the complex cation. There is some suggestion in our results, however, that Ni(III) formation is accompanied by a lattice rearrangement in which incipient bonding is established between the metal cation and the perchlorate anions.

The directions adopted by the unique $g_{\parallel}$ principal values, i.e., the directions of the d_{z^2} orbitals, provide evidence for a change in coordination (Table II). Dealing firstly with the trans ion (A), we note that $g_{\parallel}$ lies only 6° from the perpendicular to the nickel–nitrogen plane. Furthermore, the other two principal values lie approximately 10° from Ni–N directions. In the case of the cis ion (B), $g_{\parallel}$ lies 13° from the perpendicular to the nickel–nitrogen plane, and the larger of the remaining principal values lies along b, a bisector of a N–Ni–N angle. Thus, for both Ni(III) species the unpaired electron occupies a d_{z^2} orbital which lies only a few degrees off the anticipated direction, i.e., perpendicular to the $Ni–N_4$ plane of the undamaged crystal. Crystalline forces determine the directions of the large g values in B, whereas intramolecular forces are determinant in the case of isomer A.

Futher examination of the crystal structures[15,16] reveals a most interesting fact (Figure 2). In both A and B, $g_{\parallel}$ lies in a plane perpendicular to the NiN_4 plane which contains the shortest Ni–O distances. In each instance, $g_{\parallel}$ falls approximately midway between the perpendicular to the plane and the Ni–O vector (Figure 2). One is tempted to conclude that the d_{z^2} orbitals of the Ni(III) species are directed toward the ClO_4^- anions in order to achieve the preferred[21] octahedral coordination of the tervalent cation. This could conceivably be achieved by a concerted rotational motion (in opposite directions) of the perchlorate anions and the cation, leading to a new z axis for the ion, midway between Ni(II)–$OClO_3$ and the original z axis of the square-planar complex ion.

Conclusion

Spectroscopically detectable amounts of Ni(III) tetraazamacrocycle complexes are generated in the solid state by ^{60}Co γ irradiation of the corresponding Ni(II) species. The single unpaired electron in these d^7 ions is principally located in a Ni($3d_{z^2}$) atomic orbital which is directed a few degrees away from the perpendicular to the NiN_4 plane of the undamaged lattice. The proximity of the new z axis to Ni–$OClO_3$ directions suggests that Ni(III) formation is accompanied by a lattice rearrangment which results in incipient octahedral coordination of the nickel cation.

Registry No. A (Ni^{II}), 15392-95-7; A (Ni^{III}), 83602-86-2; B (Ni^{II}), 15308-64-2; B (Ni^{III}), 83572-90-1.

Mechanism of Ozonolysis of Acetylenes: Evidence for a Free-Radical Pathway for the Decomposition of Intermediates

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Abstract: Dimethylacetylene was ozonized at −78 °C and then warmed in the presence of spin traps. Acetoxyl and acetyl spin adducts are observed, indicating that radical reactions are, at least in part, involved in product formation. The temperature profile for spin adduct appearance suggests that the two spin adducts come from different precursors; on the basis of analogies with literature data, we suggest that the acetoxyl adduct comes from compound **5** and the acetyl adduct from compound **3**. We suggest that the acetoxyl radical in our system is too unstable to be scavengable by spin traps before it decarboxylates; therefore, we propose that **5** reacts with spin traps in a molecule-assisted decomposition process to give the acetoxyl adduct without involving free acetoxyl radicals. Spin adducts are observed even at −70 °C, and it is suggested that these adducts also result from an assisted decomposition of some type. Two possible mechanisms are suggested for this interaction, an electron transfer and a 1,3 dipolar addition. Some preliminary experiments on diphenylacetylene also are reported.

Mechanistic studies of the ozonolysis of acetylenes,[1] unlike the ozonolysis of olefins,[2] have been very limited. The reaction, as in the case of olefins, is believed to proceed via the intermediacy of the carbonyl oxide **2** as shown in Scheme I. All of the products (α-dicarbonyls, acid anhydrides, and polyperoxides) are believed to arise by the rearrangement or reactions of **2**.[1-10] On the basis

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

(2) For a comprehensive review on this subject, see: Bailey, P. S. "Ozonation in Organic Chemistry"; Academic Press: New York, 1978; Vol. 1, 1982; Vol. 2.

(3) Criegee, R.; Lederer, M. *Liebigs Ann. Chem.* **1953**, *20*, 583.

(4) Bailey, P. S.; Chang, Y.; Kwie, W. W. L. *J. Org. Chem.* **1962**, *27*, 1198.

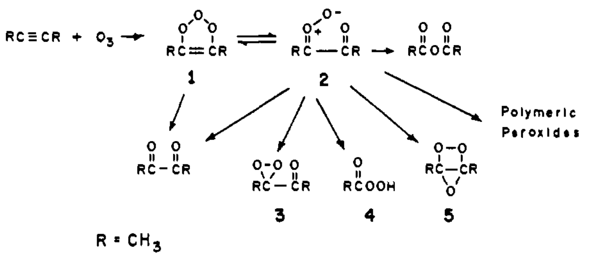
(5) DeMore, W. M.; Lin, C. *J. Org. Chem.* **1973**, *38*, 985.

(6) Yang, N. C.; Libman, J. *J. Org. Chem.* **1974**, *39*, 1782.

(7) Keay, R. E.; Hamilton, G. A. *J. Am. Chem. Soc.* **1976**, *98*, 6578.

0002-7863/82/1504-7563$01.25/0

Scheme I



of their ability to epoxidize olefins, Keay and Hamilton[7] identified three specie (**1**, **3**, and **4**, Scheme I) as major intermediates or products formed from **2** during the ozonolysis of dimethylacetylene (DMA). Species **3** was suggested to arise from the rearrangement of **1** (perhaps via **2**), but no mechanism for the formation of peroxyacetic acid, **4**, has been suggested. In addition to the above products, ketene and carbon monoxide have been identified as products of ozonolysis of DMA,[5] but the mechanism of their formation is unknown. Jenkins and Mendenhall[8] have shown that the ozonolysis of di-*tert*-butylacetylene in aprotic solvents yields isobutane, isobutene, carbon dioxide, and carbon monoxide and suggested that these products arise from the fragmentation of polymeric peroxides. Recently, Ando et al.[11] have reported evidence for **5**, which they prepared from the photosensitized reaction of singlet oxygen and 2-diazo-3-butanone; they suggest that **5** arises from rearrangement of **2** and that **5** decomposes to acetic anhydride and biacetyl at about −50 °C. This is the temperature where Keay and Hamilton[7] suggest that **1** is unstable; however, it seems more likely that **1** has a stability analogous to a typical trioxolane, and that the oxygen-transfer intermediate tentatively identified as **1** by Keay and Hamilton actually is **5**, as suggested by Ando et al.[11]

In this paper we present a study of the reactions of intermediates produced in the DMA–ozone system with nitrone and nitroso spin traps in aprotic solvents. Our aim was to probe the possible involvement of radicals in these reactions.

Experimental Section

The spin traps α-phenyl-*N*-*tert*-butylnitrone, PBN, and dimethylpyrroline *N*-oxide, DMPO, were purchased from Eastman Kodak and Aldrich, respectively. The PBN was recrystallized from hexane/chloroform before use. The dichloromethane solvent was washed with acid and distilled from calcium hydride. The dimethylacetylene and diphenylacetylene were from P&B Chemicals and Aldrich, respectively.

Solutions of DMA in dichloromethane (0.2–0.5 M) were ozonated at −78 °C with a precooled ozone–oxygen stream for sufficient time to ozonate about 30% of the alkyne. The reaction mixture was then flushed with cooled nitrogen, and a precooled solution of the required spin trap was added so as to make a final spin trap solution of 0.1 M. The sample was then deoxygenated with nitrogen again and ESR spectra were recorded as the samples were allowed to warm. Varying the concentration of DMA and ozone 10-fold had no effect on the nature of radicals spin trapped. Spectra were run with either a Varian E-109A or IBM 100D ESR spectrometer with Aspect 2000 computer and variable-temperature controller.

Results

When DMA–ozone reaction mixtures are treated with spin trap[12,13] solutions at −70 °C and the ESR spectrum recorded, signals begin to appear and the intensities of the signals grow as the temperature is raised. With α-phenyl-*N*-*tert*-butylnitrone (PBN), the spectrum initially obtained is shown in Figure 1A. On the basis of hyperfine coupling constants ($a^N = 13.4$ and $a^H = 1.4$ G), we assign this spectrum to the acetoxyl adduct adduct of PBN (however, see discussion below).[14-16] As the temperature of the reaction mixture is raised the spectrum begins to change at about −45 °C. The spectrum obtained at −30 ° is shown in Figure 1B; the major species at this temperature has hyperfine coupling constants ($a^N = 14.2$ and $a^H = 3.4$ G) consistent with the acetyl radical spin adduct of PBN.[16] In addition to the acetyl and acetoxyl adducts, a triplet ($a^N = 8.0$ G) signal due to benzoyl-*tert*-butyl nitroxide (PBNOx) is visible in the −30 °C spectrum shown in Figure 1B.[14]

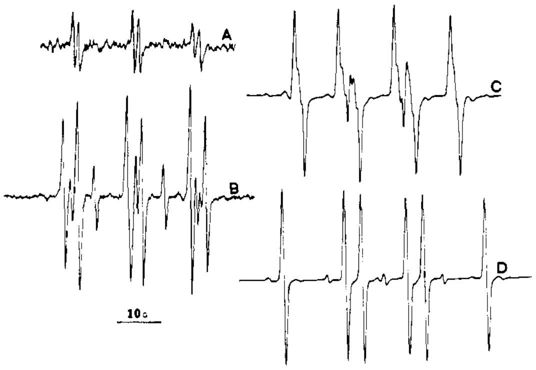


Figure 1. ESR spectra recorded in the DMA/ozone system. The DMA was ozonized at −78 °C and purged with nitrogen, spin trap was added, and the mixture was purged with nitrogen again. (A) The spectrum recorded at −70 °C in the presence of PBN showing the acetoxyl adduct. (B) The spectrum recorded after warming the previous sample A to −30 °C showing a mixture of the acetoxyl and acetyl adducts along with PBNOx. In addition, there is some evidence in the right-hand group of peaks for a third spin adduct of PBN that could be due to alkoxyl radicals. (C) The spectrum recorded at −70 °C in the presence of DMPO showing mainly the acetoxyl adduct, together with much weaker, unassigned absorptions. (D) The spectrum recorded after warming the previous sample C to −30 °C showing the acetyl adduct as the major identified species; the weaker signals have not been assigned.

Treatment of the DMA–ozone reaction mixture at −70 °C with 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) resulted in the spectrum shown in Figure 1C. We assign this spectrum ($a^N = 12.5$, $a^H = 10.0$, and $a^H = 0.9$ G) to the acetoxyl adduct of DMPO on the basis of following observations: (1) The ESR parameters are very similar to those reported for the benzoyloxyl radical spin adduct of DMPO.[17] (2) The photolysis of lead tetraacetate in the presence of DMPO at −70 °C gives a spectrum that is very similar to the complex spectrum shown in Figure 1C but with an additional weak signal due to 5,5-dimethyl-2-oxopyrrolinyl-*N*-oxy (DMPOx).

At the temperature is raised the spectrum shown in Figure 1C begins to change at about −45 °C; the spectrum obtained at −30 °C is shown in Figure 1D. The major signal ($a^N = 14.0$ and $a^H = 17.7$ G) is due to the acetyl radical spin adduct of DMPO.[17] In addition, an unidentified spin adduct with a three-line spectrum ($a^N = 13.0$ G) is present at low concentration.[18]

Further confirmation of the production of acetyl radicals in this system is obtained from the decomposition of the DMA–ozone mixture in the presence 2-methyl-2-nitrosopropane, where a three-line spectrum ($a^N = 7.7$ G) due to acetyl-*tert*-butyl nitroxide[19] is produced even at −70 °C.

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[8] Jenkins, J. A.; Mendenhall, G. D. *J. Org. Chem.* **1981**, *46*, 3997.

[9] Miller, D. J.; Nemo, T. E.; Hull, L. A. *J. Org. Chem.* **1975**, *40*, 2675.

[10] Jackson, S.; Hull, L. A. *J. Org. Chem.* **1976**, *41*, 3340.

[11] Ando, W.; Miyazaki, H.; Ito, K.; Auchi, D. *Tetrahedron Lett.* **1982**, 555.

[12] Janzen, E. G., *Acc. Chem. Res.* **1971**, *4*, 31.

[13] Janzen, E. G. In "Free Radicals in Biology"; Pryor, W. A., Ed.; Academic Press: New York, 1980; Vol. IV, Chapter 4.

[14] Janzen, E. G.; Blackburn, B. J. *J. Am. Chem. Soc.* **1969**, *91*, 4481.

[15] Forrester, A. R., Hepburn, S. P. *J. Chem. Soc.* **1971**, *77*, 2463.

[16] Janzen, E. G.; Lopp, I. G.; Morgan, T. V. *J. Phys. Chem.* **1973**, *77*, 139.

[17] Janzen, E. G.; Liu, J. P. *J. Magn. Reson.* **1973**, *9*, 510.

[18] The acetoxyl adduct of DMPO prepared from $Pb(OAc)_4$ at −70 °C is unstable on warming. At about the same temperature where the acetoxyl adduct begins to disappear, an unidentified nitroxide with a three-line spectrum and $a^N = 13.0$ G begins to appear.

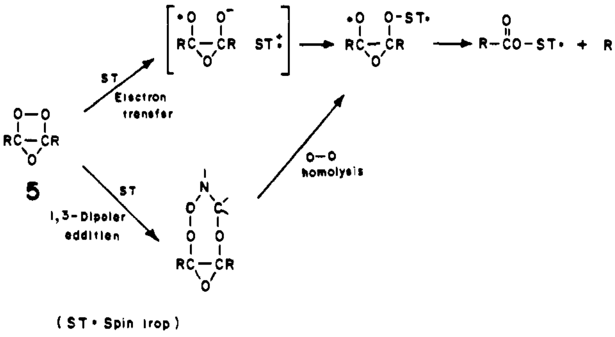
[19] Mackor, A.; Wajer, Th. A. J. W.; DeBoer, Th. J. *Tetrahedron* **1968**, *24*, 1623.

The temperature dependence of these signals was probed in the following manner: (1) If the reaction mixture is first warmed to 20 °C, cooled back to −78 °C, and then treated with the spin trap, no signals are observed. This indicates that intermediates formed during the ozonolysis are responsible for spin adduct formation and final products (or polymeric peroxides) are not. (2) If the reaction mixture is first warmed to −45 °C and then recooled to −78 °C and spin trap added, both the acetoxyl and acetyl adducts are detected. However, if the solution is warmed to −30 °C and then recooled to −78 °C and the spin trap added, only the acetyl adduct is observed. This indicates the acetyl and acetoxyl adducts come from different precursors and that the precursor of the acetoxyl spin adduct decomposes at temperatures in the range −45 to −30 °C whereas the precursor for the acetyl adduct decomposes between −30 °C and room temperature. (3) When methanol is present during ozonolysis, no spin adducts are observed; however, on warming to room temperature, a strong alkoxyl adduct signal is observed with DMPO. If methanol is added at −78 °C after ozonolysis but before the addition of spin trap, there is only a small effect, and both acetoxyl and acetyl adducts are observed. Since the presence of methanol during ozonation inhibits the formation of acetyl and acetoxyl spin adducts, the intermediates that give radicals probably are formed from **2**. Moreover, the fact that the addition of methanol after ozonation has relatively little effect on radical production strongly suggests that **1** and **2** rearrange at −78 °C to compounds that are the precursors of the radicals we spin trap. The precursors are unstable, however, since raising the temperature of the reaction mixture to 20 °C destroys them.

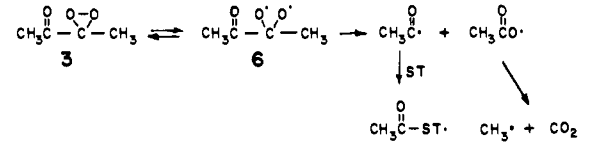
Discussion

We suggest that intermediates **3** and **5** are the most likely precursors of the spin adducts we observe. It is most reasonable to identify the precursor of the acetoxyl adduct as **5** since Ando et al.[11] have shown this compound begins to decompose at −50 °C. (See point 2 above.) Compound **3** appears to be the most likely precursor of the acetyl adduct (see below), since Keay and Hamilton[7] have tentatively identified this compound as being unstable above −15 °C.

Scheme II



Scheme III



Despite our detection of acetoxyl spin adducts, we suggest that acetoxyl radicals are too unstable to exist in free solution long enough to be spin trapped in our system.[14,15,20] The best data on the rate of decarboxylation of acetoxyl radical are those of Braun[21] that give $k = 1.6 \times 10^9$ s^{-1} at 60 °C and $E = 6.6$ kcal/mol,[22] giving an extrapolated rate constant for decarboxylation at −78 °C of 1.3×10^6 s^{-1}. If the rate constant for spin trapping the acetoxyl radical by PBN is assumed to equal that for the more stable (and readily spin trappable) benzoyloxyl radical,[23] then one obtains $k = 4 \times 10^5$ M^{-1} s^{-1} at 40 °C for the reaction of acetoxyl radicals with PBN. If the activation energy is taken as 5.5 kcal/mol for this reaction,[24] then k for spin trapping acetoxyl at −78 °C is estimated to be 7×10^2 M^{-1} s^{-1}. The conclusion from this analysis is that in a solution that is 0.1 M in PBN, the ratio of the rate of decarboxylation to the rate of spin trapping of the acetoxyl radical by PBN is 10^4. Although these data are quite soft, it appears that free acetoxyl radicals decarboxylate faster than they are spin trapped by PBN even at −78 °C. Thus, either acetoxyl radicals should not be spin trapped at all or, at very least, the data suggest that the signal from spin trapping the methyl radical also should be observed when free acetoxyl radicals are spin trapped.

We obtain a spectrum virtually identical with that shown in Figure 1A upon photolysis of lead tetraacetate in the presence of PBN at −78° C; this spectrum has been assigned to the acetoxyl adduct of PBN.[14,15] Janzen and Liu[17] tentatively ascribed the spin adduct obtained from the reaction of lead tetracetate with DMPO at room temperature to the acetoxyl radical spin adduct. We find, however, that when DMPO and $Pb(OAc)_4$ are mixed at room temperature, only DMPOx, an oxidation product of DMPO, is produced. This oxidation can be minimized if the solutions are precooled to −70 °C before mixing. On photolysis with a low-pressure mercury lamp at −70 °C, $Pb(OAc)_4$ and DMPO give a spin adduct spectrum similar to Figure 1C. This adduct is not stable and decomposes upon warming to a species with a three-line spectrum.[18] In contrast, low-temperature photolysis of acetyl peroxide in the presence of DMPO only gives the spectrum of the methyl adduct, except at high concentrations of the spin trap (near 0.5 M) where both the methyl and acetoxyl adducts are formed.

To rationalize the acetoxyl spin adducts we observe in the ozone/DMA system in the absence of strong methyl radical spin adducts, we hypothesize that spin traps react with compound **5** to give an acetoxyl spin adduct without going through free acetoxyl radicals. There are a number of mechanisms by which spin traps could induce the decomposition of unstable intermediates; two possible mechanisms for the induced decomposition of **5** are shown in Scheme II; one is an electron transfer[25,26] and the other a 1,3 dipolar addition.[27] Although Scheme II shows acetyl radicals being produced, we do not observe the acetyl adduct of either

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[20] (a) Pryor, W. A. "Free Radicals"; McGraw-Hill: New York, 1966; pp 87–91. (b) In a system where acetoxyl radicals were generated by oxidation of acetate ions, Bard et al.[20d] observed only the methyl adduct of PBN. However, Skell and May[20c] have reported a system where acetoxyl radicals appear to have sufficient lifetime outside of the cage to abstract hydrogen. They have rationalized this in terms of two types of acetoxyl radicals, σ and π forms; they believe the π radical is the stable species that they observe. Recently, Dewar et al.[20e] have done calculations that indicate that the reactive σ radical is actually the more thermodynamically stable species. Although we cannot rule out the possibility that we are trapping some type of acetoxyl radical in our system, at present we prefer to interpret the spin trapping results presented here in terms of molecular processes, particularly since we see no evidence for methyl radical adducts. (c) Skell, P. S.; May, D. D. *J. Am. Chem. Soc.* **1981**, *103*, 967. (d) Kraeutler, D.; Jaeger, C. D.; Bard, A. J. *Ibid.* **1978**, *100*, 4903. (e) Dewar, M. J. S.; Pakiari, A. H.; Pierini, A. B. *Ibid.* **1982**, *104*, 3242.

[21] Braun, W., Rajbenbach, L., Eirich, F. R. *J. Phys. Chem.* **1962**, *66*, 1591

[22] (a) These data give log $A = 13.5$, a value too low[22b] by 10^1–10^3. This implies the activation energy also may be too low; if it is, our estimate of the rate of decarboxylation at −78 °C is too large and the ratio of decarboxylation to spin trapping is even less favorable than is calculated here. (b) Benson, S. W. "Thermochemical Kinetics", 2nd ed.; Wiley: New York, 1976; pp 97–98.

[23] Janzen, E. G.; Evans, C. A.; Nishi, Y. *J. Am. Chem. Soc.* **1972**, *94*, 8236.

[24] (a) The value of the rate constant for spin trapping the benzoyloxyl radical 40 °C (4×10^5 M^{-1} s^{-1})[23] is only slighlty different from the rate constant for spin trapping primary alkyl radicals (1.3×10^5 M^{-1} s^{-1}) at 40 °C;[24b] the activation energy for spin trapping the alkyl radials has been determined to be 5.6 kcal/mol. With the assumption that the preexponential factor does not depend on the nature of the radical being trapped, these data allow us to estimate the activation energy for trapping the benzoyloxyl radicals to be 5.5 kcal/mol. This value was then used to extrapolate the rate constant for trapping acetoxyl radicals to −78 °C. (b) Schmid, P.; Ingold, K. U. *J. Am. Chem. Soc.* **1978**, *100*, 2493.

[25] Church, D. F.; Pryor, W. A. *J. Org. Chem.* **1980**, *45*, 2866.

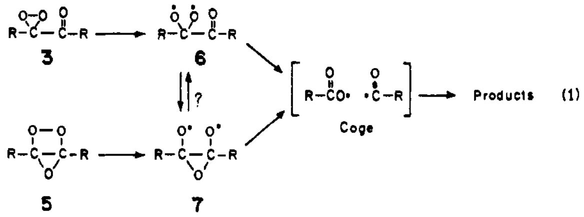
[26] Koo, J.; Schuster, G. B. *J. Am. Chem. Soc.* **1978**, *100*, 4496.

[27] Houk, K. N. *Acc. Chem. Res.* **1975**, *8*, 361.

DMPO and PBN below −45 °C. We suggest this is a reflection of the fact that both PBN and DMPO tend to trap carbon-centered radicals less readily than they trap oxy radicals, so that an observable yield of the acetoxyl adduct is produced via Scheme II where the acetyl adduct cannot be observed.[28,29] Above −45 °C we do observe acetyl spin adducts; we propose these adducts result from spin trapping free acetyl radicals produced from the homolysis of **3** as shown in Scheme III.

With all three spin traps, spin adducts are observed even at −70 °C. Since both **3** and **5** are stable at −70 °C, the appearance of nitroxide radicals at this temperature must be the result of the direct reaction of reactive species (such as **3** and **5**) with the spin trap.[30] With PBN and DMPO, acetoxyl spin adducts are formed, as discussed above. With NtB, the acetyl adduct is observed at −70 °C.[31]

Although acetoxyl radicals cannot exist outside a solvent cage and cannot be spin trapped, they do exist inside the cage.[20a] Thus, cage recombination of radicals from either **3** or **5** could give acetic anhydride, and combination of acetyl radicals in free solution could give biacetyl, both major products of these reactions as shown in eq 1. The proposal that acetic anhydride is formed from an intermediate like **3** is supported by the infrared studies of the ozonolysis of DMA by DeMore,[5] since the intermediate leading to the anhydride was shown to contain a carbonyl group. The recombination of benzoyl radicals has been suggested to be the source of benzil in the ozonolysis of 1,2-dibenzoylethylene.[32] The reaction of acetyl radicals with oxygen would yield acetyl peroxyl radicals that could then abstract hydrogen atoms to give peroxyacetic acid. The yield of this product can be as high as 25–30%,[7] supporting the suggestion that free radical reactions play a significant role in the ozonolysis of DMA.



(1)

Additional evidence for a radical pathway in the ozone–DMA reaction is the production of carbon monoxide and carbon dioxide. Carbon monoxide would result from the decarbonylation of acetyl radicals; similarly carbon dioxide would result from the decarboxylation of caged acetoxyl radicals. The decarboxylation of acyloxyl radicals and decarbonylation of acyl radicals yield alkyl radicals, the disproportionation of which can account for the isobutane and isobutene produced in the ozonolysis of di-*tert*-butylacetylene.[8]

Diphenylacetylene (DPA)–ozone reaction mixtures also were briefly examined by the spin-trapping technique. Previous studies[10] of the ozonolysis of DPA indicate that the intermediates formed in this system are different from the intermediates formed in the case of DMA. On warming DPA–ozone mixtures in the presence of PBN or DMPO, spin adducts due to benzoyloxyl and benzoyl radicals are produced; however, both radicals are spin trapped above −50° C, unlike the case of DMA. Clearly the DPA–ozone system is somewhat similar to the DMA system, but in this case all of the intermediates may be more stable. In particular, the benzoyloxyl radical is known to exist outside the cage,[33] and it probably can be spin trapped.

In conclusion, we suggest that radical reactions play a role in the ozonation of acetylenic compounds, although their quantitative contribution cannot be assessed by the present study.

Acknowledgment. This work was supported by grants from the National Science Foundation and the National Institutes of Health (HL-16029). We acknowledge helpful comments on this manuscript by Professors Phillip S. Bailey, Robert W. Murray, and Cheves Walling. We also acknowledge assistance from Drs. Donald G. Prier and Norio Ohto.

Registry No. DMA, 503-17-3; DPA, 501-65-5; PBN, 3376-24-7; DMPO, 3317-61-1.

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[28] Spin trapping is a very inefficient process,[29] and different radicals react with a given spin trap at very different rates.[24b]

[29] Merritt, M. V.; Johnson, R. A. *J. Am. Chem. Soc.* **1977**, *99*, 3713.

[30] We have assumed, in analogy with typical trioxolanes,[2] that the 1,2,3-trioxolene entirely rearranges to **3** and **5** at −78 °C and therefore that spin adduct formation at −78 °C cannot be explained by a molecular reaction between the spin trap and the 1,2,3-trixoxolene.

[31] A nitroso compound like NtB might not be as likely to undergo an electron transfer reaction as are nitrones such as PBN and DMPO. However, it seems clear that some type of induced decomposition of **5** by NtB must be involved in the production of radicals at −70 °C. The acetyl radicals thus produced would be trapped very efficiently by NtB. While an acetoxyl adduct of NtB might also be formed initially, this adduct may not be stable enough to be observed; nitroxides of this type have never been reported.

[32] Bailey, P. S.; Bath, S. S. *J. Am. Chem. Soc.* **1957**, *79*, 3120.

[33] Pryor, W. A. "Free Radicals"; McGraw-Hill: New York, 1966; pp 91–92.